

Waste Characterisation; Pitfalls to Pit Voids

David Allen and Catherine Galli

MBS Environmental, 4 Cook Street, West Perth, WA, 6005

Abstract

Reliable waste characterisation data is a prerequisite for effective rehabilitation of Waste Rock Stockpiles, Tailings Storage Facilities and other areas disturbed by mining activities. History has shown that many preliminary waste characterisation assessments in Australia and overseas using traditional acid-base accounting procedures are inaccurate more often than not; usually by grossly under-estimating or over-estimating potential for Acid and Metalliferous Drainage (AMD). Others do not consider potential contamination by neutral or alkaline mine drainage, which can result in offsite impacts just as severe as AMD.

A holistic approach is required to generate accurate and appropriate characterisation data for both waste and rehabilitation materials. In addition to traditional geochemical assessment methods, use of petrology, mineralogy, soil physics, plant nutrition and soil biology all have roles to play, with their relative contributions dependent on the geological and hydrological setting of the project.

This paper provides examples in which traditional geochemical assessment techniques provide an inadequate or, in some cases, erroneous indication of potential for contamination of the environment.

Introduction

History provides countless examples of environmental problems caused by mining. The main culprit is attributed to acidic drainage produced by many mines, particularly those extracting coal and base metals. The potential for acidic drainage to form from mining has been recognised since at least 1556 and was recorded as early as 1698 in Pennsylvanian coal mines. Impacts from acid mine drainage can be both visually spectacular and environmentally destructive. Less obvious are the effects of contaminants released into the environment under both neutral and alkaline conditions. Contaminants such as arsenic, selenium, fluoride and thallium are toxic to aquatic organisms, the loss of which can have major detrimental effects on whole ecosystems.

With very few exceptions, almost all rock types are unstable when exposed to elements of the atmosphere. Reactivity varies considerably, ranging from minutes in the case of evaporites to millions of years for inert minerals such as quartz and zircon.

Chemical degradation of rocks and minerals is mainly caused by the presence of three simple molecules in the earth's atmosphere and lithosphere:

- **Oxygen:** Molecular oxygen is a very powerful oxidising agent. If it was not for replenishment of atmospheric oxygen by photosynthesis in plants, it would not exist on Earth. Chemically, oxygen is almost as reactive as chlorine.
- **Water:** Water is a powerful solvent and can dissolve most chloride, nitrate and sulphate minerals, as well as some carbonate, phosphate and silicate minerals. It is also chemically reactive, an example being its role in the oxidation of pyrite (FeS_2) as shown by Equation 1. Oxidation of one tonne of pyrite consumes 525 litres of water (and produces the equivalent of 1.63 tonnes of concentrated sulphuric acid).
- **Carbon dioxide:** Carbon dioxide produces a weak acid when dissolved in water. The pH of rainwater is typically 5 to 5.5. The main effect of the high dilution of hydrogen ions in rainwater is on the reaction rate and not so much the final reaction products. Reactions that take place with mineral acids such as hydrochloric acid within minutes in the laboratory may take hundreds to thousands of years with rainwater. Such timeframes are still relevant to creation of stable, non-polluting landforms stipulated by our regulators and expected by stakeholders.



Regulatory Requirements and Guideline Materials for WA

The consequences of contamination by mining activities are broadly covered by Section 84 of the *Mining Act 1978* and Section 50 of the *Environmental Protection Act 1986*, as reproduced below:

84. Conditions for prevention or reduction of injury to land

- (1) *On granting of a mining lease, or at any subsequent time, the Minister may impose on the lessee reasonable conditions for the purpose of preventing or reducing, or making good, injury to the natural surface of the land in respect of which the lease is sought or was granted, or injury to anything on the natural surface of that land or consequential damage to any other land.*

50. Discharge of waste in circumstances in which it is likely to cause pollution

- (2) *A person who causes or allows waste to be placed in any position from which the waste-*
- (a) could reasonably be expected to gain access to any portion of the environment; and*
 - (b) would in so gaining access be likely to result in pollution,*
- Commits an offence.*

The Department of Mines and Petroleum (DMP) provides general, but not prescriptive, guidance material for characterisation of waste rock, tailings and soil for inclusion in Mining Proposals. Section 4.3.2 of the document "Mining Proposals in Western Australia (DMP 2006) states:

It is essential that the potential of acid mine drainage (AMD), otherwise known as acid rock drainage (ARD), be determined and, if significant, management strategies put in place to deal with potentially acid forming (PAF) material in waste rock dumps and tailings storages.

To deal with AMD issues, the mining proposal should include:

- *A summary of the characterisation of the mining wastes and tailings including chemical and physical characteristics such as sodicity, salinity and dispersive potential.*
- *An assessment of the potential for sulphide oxidation leading to acid generation including specific AMD chemical analyses (pH, Total Sulphur, Net Acid Producing Potential (NAPP), Net Acid Generation (NAG), Acid Neutralising Capacity (ANC), multi-element composition and mineralogy of mine waste and tailings samples.*
- *The full waste characterisation report must be included as an appendix in the mining proposal with details on the methodologies used for the above determinations.*
- *A map showing the intended final locations of PAF material.*
- *If significant PAF material is present, then a PAF material management plan (including remediation techniques) and monitoring program) should be provided.*

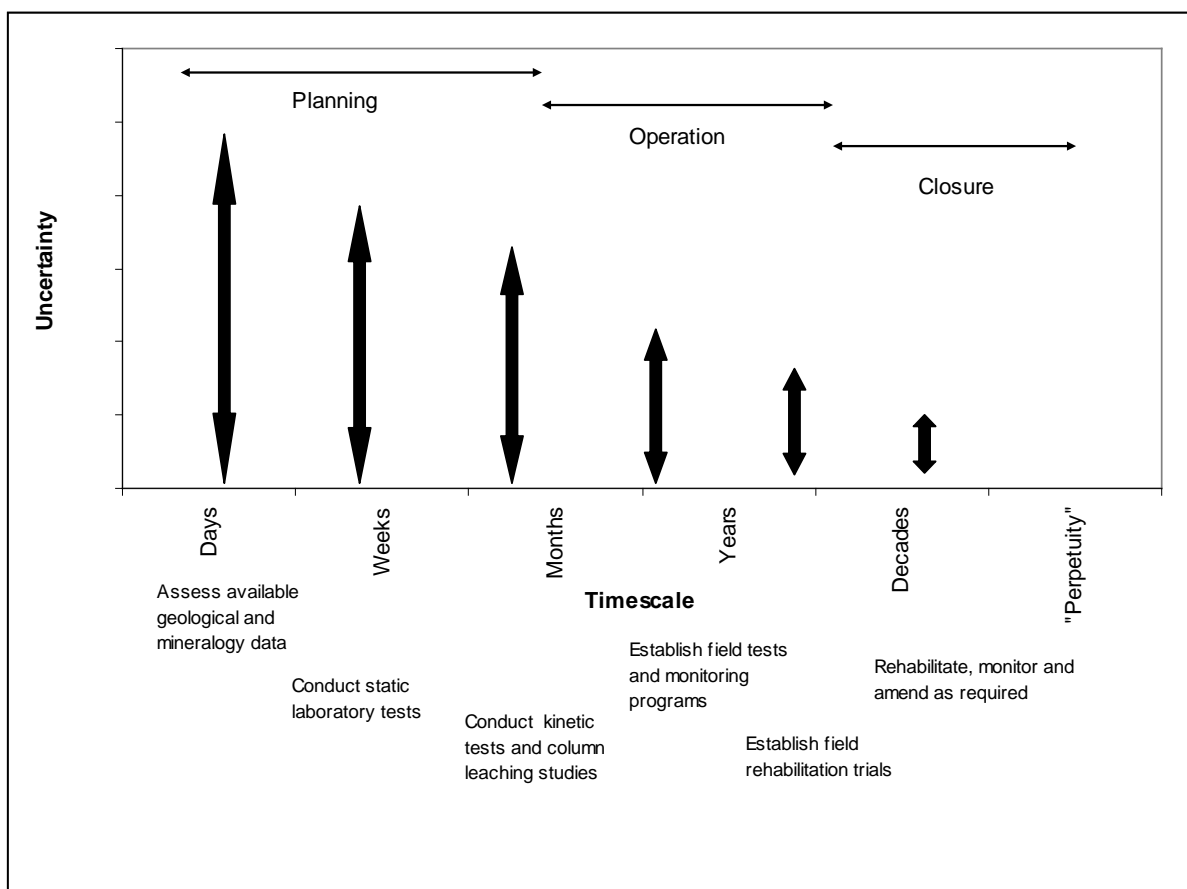
Waste Characterisation Process

MBS Environmental has adopted what it believes is generally accepted as World's Best Practice for waste characterisation. AMD assessment procedures generally follow those recommended by the

International Network for Acid Prevention (INAP) as documented in an on-line publication referred to as the Global Acid Rock Drainage Guide (GARD). GARD recommends a staged approach to AMD characterisation and management, which has been adopted in principle by MBS Environment for general waste characterisation.

Irrespective of which of the many laboratory and field test procedures are adopted for waste characterisation, there will always be an element of uncertainty. By using a well planned and implemented approach to waste characterisation, the level of uncertainty at mine closure can be reduced to very low levels by closure, as illustrated in Figure 1.

Figure 1: Schematic Illustration of a Geochemical Waste Characterisation Program



AMD Assessment Procedures

Laboratory methods for predicting potential for AMD by basic acid-base accounting procedures are well documented and will only be briefly summarised in this paper. Their key steps are outlined below:

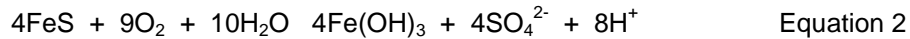
- Use a statistically valid and geologically appropriate sampling strategy to provide the necessary samples. Most of these samples for new mining project will be provided by drill core materials. Fresh material is ideal, but often not available. Archived material is suitable, provided it has been protected from exposure to the atmosphere. Pulp samples from laboratory assay work may be satisfactory if stored correctly.
- Measure total sulphur content in each sample. Combustimetric methods, e.g. LECO® instruments, usually provide accurate results to a reporting limit of 0.01%, which is considered adequate.
- Measure 'sulphate' sulphur using appropriate acid or alkali digestion procedures. Minerals containing sulphate sulphur are generally fully oxidised and therefore not capable of generating additional acidity.
- Calculate 'Total Oxidisable Sulphur' (TOS) by subtracting 'sulphate sulphur from total sulphur.
- Calculate Maximum Potential Acidity (MPA) by multiplying TOS (%) by 30.6. MPA is expressed in units of kilograms H₂SO₄ per tonne.
- Measure Acid Neutralising Capacity (ANC) by an approved method. The original Sobek (1978) method and variations thereof are widely used in Australia. ANC is also expressed in units of kilograms H₂SO₄ per tonne.
- Calculate Net Acid Producing Potential (NAPP) by subtracting ANC from MPA. Potentially Acid Forming (PAF) materials are indicated by positive NAPP values, while Non Acid Forming (NAF) materials are indicated by negative NAPP values.

Validity of MPA Estimation

Estimation of MPA from TOS assumes that all of the oxidisable sulphur will be oxidised to sulphuric acid (H₂SO₄) as the sole oxidation product. However, many sulphide minerals can be fully oxidised without forming any acidic products at all. These include sphalerite (ZnS), galena (PbS) and molybdenite (MoS₂). With few exceptions, sulphide minerals capable of generating acidity contain iron. Most important is pyrite (FeS₂), which is a common accessory mineral in mineralised rock. Others include marcasite (FeS₂), pyrrhotite (Fe_(1-x)S) and arsenopyrite (FeAsS).

A relatively simple test to verify the assumption that all of the TOS is acid generating is the Net Acid Generation (NAG) test, which uses hydrogen peroxide on a finely ground laboratory sample to ensure that oxidation is complete. The acidity produced is measured and NAG calculated and reported with units of kilograms H₂SO₄ per tonne. If the dominant sulphides are iron sulphides and not other base metal sulphides, NAG values will be very close to NAPP values.

Recent investigations conducted on tailings and waste rock from nickel ore mined in Western Australia has indicated anomalous behaviour. Pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$, or 'FeS' for simplicity) is the dominant iron sulphide mineral in ultramafic host rock for nickel ore. Under strongly oxidising conditions, pyrrhotite oxidises to sulphuric acid according to Equation 2.




Comparison of Equation 2 with Equation 1 shows that pyrrhotite and pyrite are expected to produce identical amounts of sulphuric acid based on sulphur content (every 32 kilograms of sulphide-sulphur can produce 98 kilograms of sulphuric acid). This can be verified in the laboratory, where NAG and NAPP values for rocks containing identical amounts of sulphide-sulphur provided by either pyrrhotite or pyrite are almost identical.

However, the availability of oxygen deep within a waste rock stockpile or a Tailings Storage Facility (TSF) is usually very much lower than that provided by hydrogen peroxide under laboratory conditions. Under conditions of reduced oxygen availability (or redox potential), pyrrhotite can be oxidised to several different sulphur containing oxidation products including pyrite, elemental sulphur (S), thiosulphate ($\text{S}_2\text{O}_3^{2-}$), polythionate ions ($\text{S}_n\text{O}_6^{2-}$; dithionate if $n = 2$) and sulphate. Depending on the nature of the sulphur oxidation product or the iron reaction product (ferrous iron, Fe^{2+} , under reducing conditions; ferrihydrite or ferric hydroxide ($\text{Fe}(\text{OH})_3$) under oxidising conditions), the pyrrhotite oxidation reaction may be either acid producing, neutral or even acid consuming (produces alkali). A summary of the acid generation (or consumption) upon oxidation of pyrrhotite to different reaction products is presented in Table 1.

An investigation was undertaken to determine the potential of tailings from a nickel mine in the north of Western Australia to produce acidic seepage. According to laboratory testing, fresh tailings were found to have a high content of pyrrhotite and were classified as highly PAF based on results from standard acid-base accounting procedures. When samples of tailings collected at different depths of an operational TSF at the same project were analysed, the major reaction product of the sulphide component were found to be elemental sulphur, with smaller amounts of pyrite, sulphate, thiosulphate and polythionate ions. The dominance of elemental sulphur indicated the redox conditions of tailings below the surface of the TSF were reducing and therefore the oxidation reaction was predicted to generate alkali and not acid. Monitoring of pH in porewater of these tailings over three years indicated moderately alkaline conditions, with a mean pH of 9.31.

Table 1: Amount of Acid Produced by the Oxidation of Pyrrhotite as Determined by the Nature of the Iron and Sulphur Reaction Products

Sulphur oxidation product(s)	Number of moles of acidity (H ⁺) produced per mole of sulphur			Increasing Oxygen Availability 
	O ₂ :FeS ratio	Fe ²⁺ product	Fe(OH) ₃ product	
H ₂ S	Nil	2 moles consumed	None	
Pyrite + S	0.25	1 mole consumed	1 mole produced	
Elemental S	0.5	2 moles consumed	None	
Sulphite	1.5	Nil	2 moles produced	
Dithionate	1.75	1 mole consumed	1 mole produced	
Sulphate	2.0	Nil	2 moles produced	

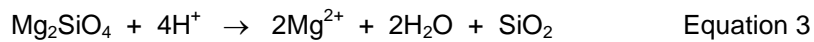
Validity of ANC Measurements

As for sulphide minerals, the reactivity, and therefore effectiveness of these minerals to neutralise any acidity, can vary widely. Most carbonate minerals, especially calcite (CaCO₃) and dolomite (CaMg(CO₃)₂) are highly reactive towards soluble acidity. Although generally more abundant in waste rock, silicate and aluminosilicate minerals also react with strong acid, but at very much slower rates than carbonate minerals. Therefore, the overall effectiveness of waste rock to neutralise acidity depends on the measurement technique. Methods for ANC determinations that involve relatively mild conditions (dilute acids, minimal heat) dissolve most of the reactive carbonate minerals and very little of the less reactive minerals, while other methods using stronger acids and prolonged heating (including the Sobek method) dissolve increasing amounts of the less reactive minerals. This can result in significant over-estimates of the 'true' acid neutralising capacity and therefore under-estimate potential for acid generation.

Analysis of tailings and waste rock from the nickel mine discussed in the previous Section for ANC by three laboratories produced a very wide range of ANC values, depending on the method used. Mineralogical analysis of samples of these materials indicated small amounts of calcite, but relatively high concentrations of silicate minerals including olivine, an iron-magnesium silicate with the generalised formula (Mg,Fe)SiO₄.

The ratio of magnesium and iron varies between the two end members of the solid state solution series; forsterite (Mg-end member) and fayalite (Fe-end member). Compositions of olivine are commonly expressed as molar percentages of forsterite (Fo) and fayalite (Fa) (e.g., Fo₇₀Fa₃₀).

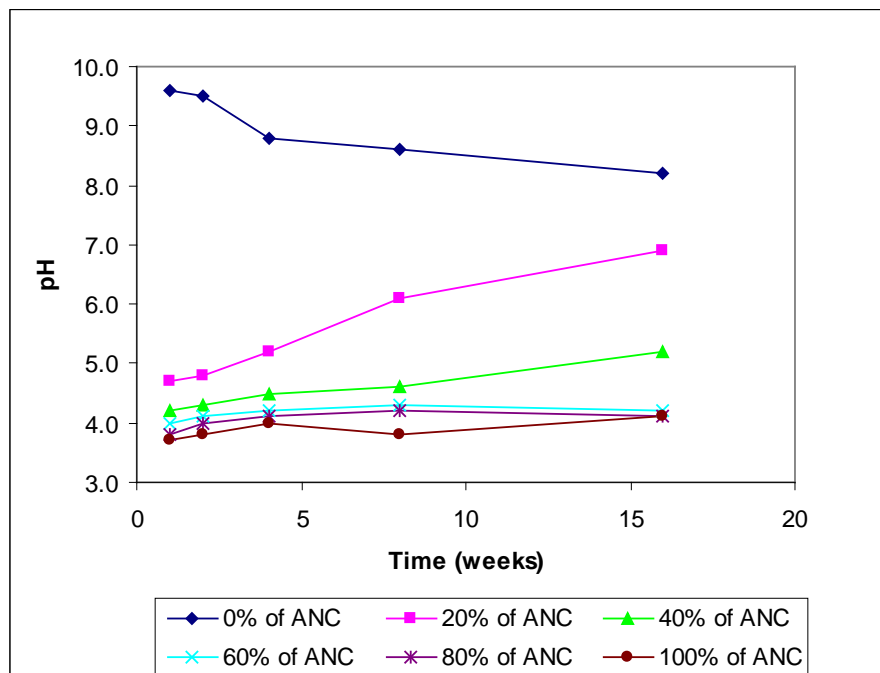
Forsterite has a high potential ANC, which can be described by the chemical equation for its congruent dissolution (Equation 3):



The variation in ANC results provided by different laboratories was attributed to differences in methodology, especially the strength of acid and temperature, on the amount of acid consumed by reaction with olivine. As the ANC of the olivine component was critical for classification of waste rock as either NAF or PAF (low ANC = PAF, high ANC = NAF), it was important to determine the effectiveness of olivine in neutralising acidity under conditions likely to be encountered in a waste rock stockpile or in a TSF.

An experiment was set up to monitor changes in pH over time following addition of different amounts of acid (expressed as a percentage of the measured ANC of the material) to sample of waste rock. Results for this experiment are presented in Chart 1. The observed pH values demonstrate that the olivine component conveys some neutralising capacity to acidity generated by oxidation of sulphides in the waste rock, but less than that indicated by the measured ANC.

Chart 1: pH Reaction Curves for Olivine-Rich Waste Rock



Evidence for the contribution of olivine in samples of coarse and fine waste rock, and tailings, to the acid neutralisation process is demonstrated by the release of magnesium and silicon into solution, as shown by Chart 2 and Chart 3, respectively. Magnesium dissolved from olivine in both coarse and

waste rock increased linearly with the amount of acid. Less magnesium was dissolved from the tailings, which contain less olivine than this particular waste rock type.

Chart 2: Magnesium Concentrations in Solution after 16 Weeks

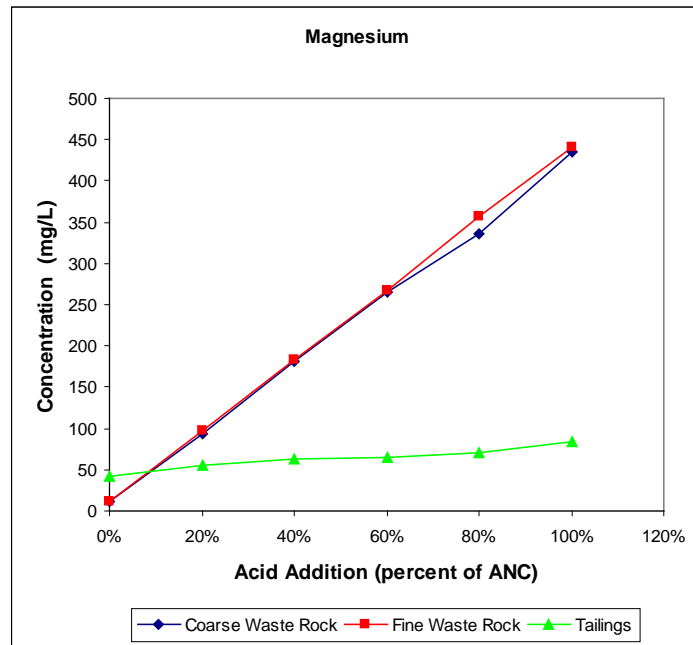
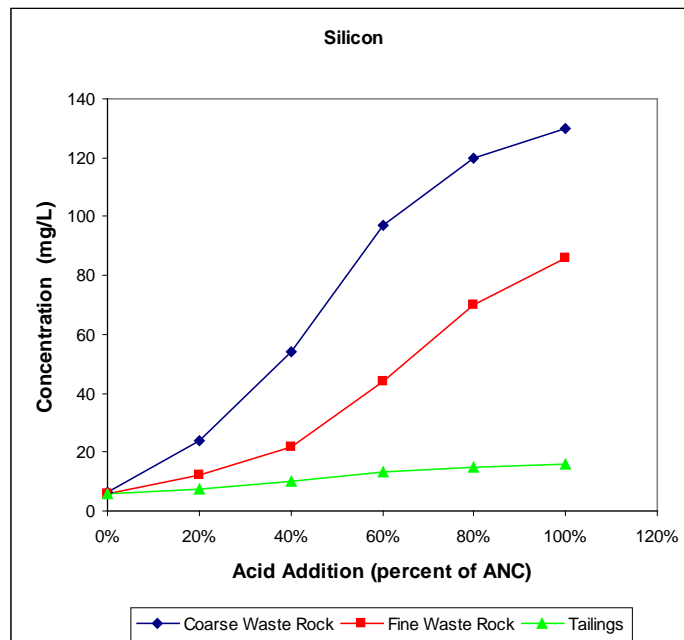


Chart 3: Silicon Concentrations in Solution after 16 Weeks

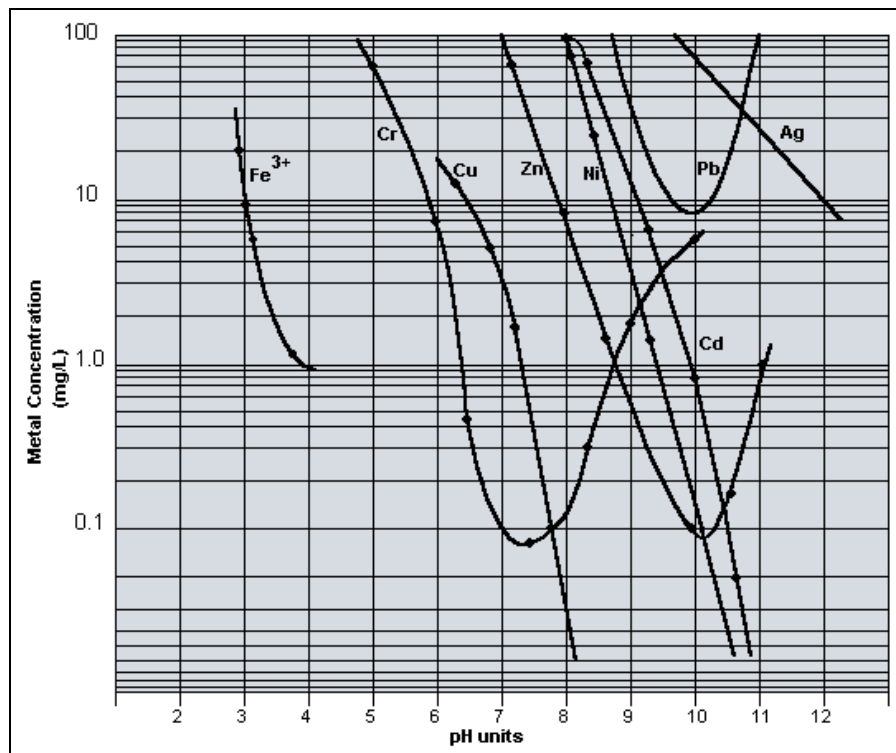


Neutral Mine Drainage

Many of the environmental impacts resulting from AMD are not caused directly by the acidity of the leachate, but by elevated concentration of toxic metals such as copper, aluminium, manganese and

zinc dissolved from minerals by the released acidity. However, some metals and metalloids can be released by oxidation and leaching of waste rock and tailings under both neutral and even alkaline conditions. The amount of dissolved metals is effectively controlled by the pH of seepage and mineralogy of the waste rock or tailings. Under oxidising conditions, metal ions such as nickel, lead, cadmium and zinc are present mainly as hydroxide weathering products, the solubility of which is very much controlled by pH of seepage. Figure 2 demonstrates the influence of seepage pH on metal ion solubility.

Figure 2: Solubility of Metal Ions as Determined by pH of Seepage



In addition to metals, other contaminants such as metalloids, salts, and anionic contaminants may be leached from other fresh or waste rock under neutral or alkaline seepage conditions. Common anionic environmental contaminants include fluoride, nitrate, hexavalent chromium (which can be produced in small amounts by oxidation of chromium minerals), arsenic and selenium.

MBS Environmental tests for the presence of these potential contaminants using various laboratory water leachate tests. The Australian Standard Leach Procedure (ASLP, Australian Standard AS4439.3-1997) has been developed to assess leachate water quality of wastes designated for landfill disposal. Extractions with oxygenated deionised water and finely ground waste rock and tailing samples provides useful information for identifying potential contaminants that may leach from waste rock stockpiles and TSFs. Filtered leachates are routinely analysed for major cations (Ca, Mg, Na, K), anions (Cl, SO₄, F, NO₃), metals (Ag, Al, Ba, Bi, Be, Cu, Cr, Co, Cd, Fe, Hg, Mn, Mo, Ni, Pb, Tl, U, V and Zn) and metalloids (As, B, Sb, Se and Si).

Case Study: Thallium in Lead/Zinc Tailings

Thallium is a common contaminant in lead and zinc ore. Thallium is highly toxic within the environment with acute effects including animal deaths and low growth rates in plants, or death. Acute effects are typically seen two to four days after animals or plants are initially exposed to excessive levels of thallium. Thallium has high acute toxicity to aquatic life. The absence of water quality criteria for this element in the ANZECC 2000 water quality guidelines is due to its rarity and the absence of environmental impact information in an Australian context, and does not indicate that thallium is not a potential environmental hazard.

There is very limited data available to evaluate the chronic effects of thallium on plants, birds or terrestrial animals. However, chronic effects may include shortened lifespan, reproductive problems, lower fertility and changes in appearance or behaviour in exposed animals. These effects can be seen long after the initial exposure. Thallium compounds can also be bioaccumulated within plant and animal tissue, causing chronic health problems to sensitive organisms which can be transferred to other trophic levels.

The high toxicity of thallium is attributed to an affinity for sulphur-containing enzymes and resembles other heavy metals such as mercury and lead in this respect. The similarity of the Tl^+ and K^+ ions also allows thallium to inhibit important biological functions controlled by potassium ions.

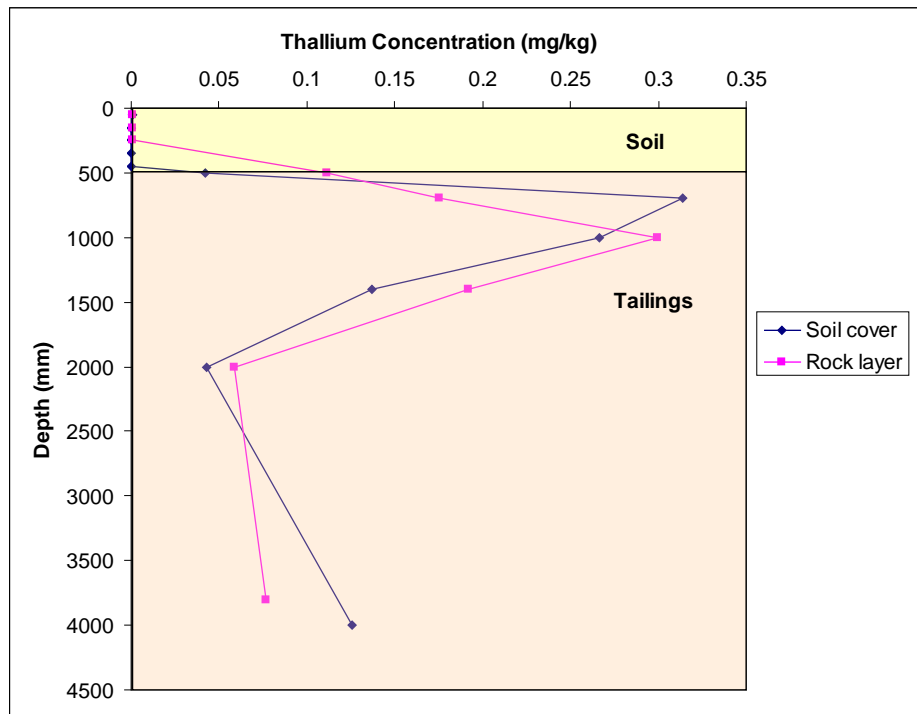
Thallium in tailings produced by a former lead and zinc mine in the north of Western Australia was shown to be associated with residual galena (PbS). Thallium sulphide is extremely insoluble and does not present an environmental risk in this form. Oxidation of lead sulphides releases both lead and associated thallium. Although the tailings contain significant amounts of reactive pyrite, they are classified as NAF because approximately 80% of the gangue is acid-consuming calcite.

Lead ions (Pb^{2+}) produced by oxidation of galena is not mobile in the tailings because its solubility is controlled by sparingly soluble mineral phases including lead carbonate, lead sulphate and lead hydroxides. Unlike lead ions, thallium ions (Tl^+ and Tl^{3+}) do not form insoluble sulphate, carbonate and hydroxide minerals. Thallous chloride ($TlCl$) is only slightly soluble in water. Concentrations of water-soluble thallium in 18 samples of tailings ranged from 0.06 milligrams per kilogram in unoxidised tailings to 0.39 milligrams per kilogram in oxidised tailings at or near the surface of the TSF.

A rehabilitation plan for the TSF considered potential for capillary rise of soluble toxicants, including thallium, into the revegetated soil cover. A trial was established to investigate TSF cover designs incorporating different amounts of soil and rock in a 500 millimetre thick cover. Samples of soil from the cover, palatable plants and underlying tailings were collected and analysed for various potential contaminants, including thallium. After a period of 12 months, covers incorporating either 400 millimetres of a gravelly subsoil or 300 millimetres of gravelly subsoil over a 100 millimetre waste rock

layer were highly effective for preventing ingress of thallium from underlying tailings, as shown by Figure 3.

Figure 3: Profile of Water Soluble Thallium in TSF Cover and Tailings



Soil Characterisation

Characterisation of soil for chemical and physical properties should also be conducted as part of waste characterisation, as selection and placement of appropriate soil types is essential for effective rehabilitation of waste rock stockpiles and TSFs. Soil characterisation services provided by MBS Environmental focus on three areas:

- Elemental composition.** Contaminated Sites legislation introduced into Western Australia have implications for mine site rehabilitation and closure. To ensure compliance with these regulations, it is helpful (but not essential) that the concentrations of heavy metals in soil and waste rock rehabilitation materials comply with current Ecological Investigation Levels (EILs). DEC updated EILs for soil in February 2010. Current EILs for metals commonly encountered in mineralised areas are presented in Table 2. Significant changes include an increase from 50 to 400 milligrams per kilogram for chromium and from 300 to 600 milligrams per kilogram for lead.
- Stability to erosion.** Waste rock stockpiles containing dispersive soils or clay-rich waste rock are prone to slumping and/or severe water erosion. MBS Environmental includes assessment of soil and clay-rich waste rock materials for factors that are known to be important for mechanical stability. These include particle size distribution, slaking and dispersion potential using the Emerson Test and sodicity. If results from these tests indicate potential stability

problems, additional testing of large samples using rainfall simulators is recommended. Several companies in Western Australia offer such services to the mining industry.

- **Bioavailability of Nutrients and Heavy Metals.** It is well known that total element concentrations of plant nutrients in soil are a very poor predictor of deficiency and toxicity. The same is usually true of heavy metals contaminants, particularly those such as cadmium and nickel which simulate essential nutrients such as zinc and copper. MBS Environmental uses the recently introduced Mehlich 3 soil test (Walton and Allen 2004) to measure the bio-available forms of nutrients (Ca, Mg, Na, K, P, S, B, Cu, Fe, Mn, Mo, Zn), metals (Cd, Co, Ni, Pb) and metalloids (As, Se). Analysis of several samples of subsoils from the northern and eastern goldfields in Western Australia has indicated levels of extractable boron that would be considered toxic to crop plants.

Table 2: Revised EIL Values for Soil in Western Australia

Metal/Metalloid	Units	EIL
Arsenic	mg/kg	20
Barium	mg/kg	300
Cadmium	mg/kg	3
Chromium (Cr III)	mg/kg	400
Chromium (Cr VI)	mg/kg	1
Cobalt	mg/kg	50
Copper	mg/kg	100
Lead	mg/kg	600
Manganese	mg/kg	500
Mercury	mg/kg	1
Molybdenum	mg/kg	40
Nickel	mg/kg	60
Tin	mg/kg	50
Vanadium	mg/kg	50
Zinc	mg/kg	200

Conclusions

Reliable waste characterisation data is a prerequisite for effective rehabilitation of Waste Rock Stockpiles, Tailings Storage Facilities and other areas disturbed by mining activities. Comprehensive waste characterisation requires considerable expertise and experience in the fields of geology,

mineralogy, geochemistry and soil science. If any of these disciplines are not utilised to their full capability, there is potential for significant damage to the environment if the waste characterisation does not identify specific risks. Alternatively, over estimation of risks by erroneous interpretation of analytical data or by use of inappropriate test methods can cost mining companies millions of dollars in unnecessary mitigation measures.

This paper describes case study in which the potential for AMD to be generated by waste rock stockpiles and TSFs may be either greatly overestimated or underestimated by applying current guidelines without a detailed understanding of the underlying mineralogy and geochemistry.

Western Australian regulations and guidelines recognise the potential for AMD and saline mine drainage to impact upon the local environment. The possibility of metals, metalloids and anions leaching in neutral mine drainage is often not considered, especially for some of the more unusual elements such as boron, thallium, bismuth and selenium. The high toxicity and unusual geochemistry of the heavy metal thallium are of particular concern. Identification of these potential risks by comprehensive waste characterisation allows development of appropriate mitigation strategies.

Bibliography

Campbell, G.D. *Acid Formation Potential of Mine-Wastes: Sampling, Testwork and Interpretation Approaches for the WA Goldfields*. Goldfields Environmental Management Workshop, 2006. 145-152.

DEC, 2010. *Assessment levels for Soil, Sediment and Water*. Contaminated Sites Management Series, February 2010.

DITR, 2007. *Managing Acid and Metalliferous Drainage*. Department of Industry, Tourism and Resources. February 2007.

DMP, 2006. *Mining Proposals in Western Australia*. Originally released February 2006.

International Network for Acid Prevention. Global Acid Rock Drainage Guide. http://www.gardguide.com/index.php/Main_Page (accessed 28 April 2010).

Jasper, D. and Braimbridge, M. *Waste Characterisation for Optimal Landforms*. Goldfields Environmental Management Workshop, 2006. 128-127.

Loch, R. and Vacher, C. *Assessing and Managing Erosion Risk for Constructed Landforms on Minesites*. Goldfields Environmental Management Workshop, 2006. 121-127.

Sobek A.A., Schuller W.A., Freeman J.R. and Smith R.M. (1978). "Field and Laboratory Methods Applicable to Overburdens and Minesoils", EPA-600/2-78-054.

Walton, K. and Allen, D. *Mehlich No 3 Soil Test – The Western Australian Experience*. 3rd Australian New Zealand Soil Conference, Sydney, December 2004.