Characterising the Acid Generating Potential of Mine Wastes by means of Laboratory-scale Static and Biokinetic Tests

Jennifer L. Broadhurst[1], Christopher G. Bryan[2], Megan Becker[1], Jean-Paul Franzidis[1], Susan T.L. Harrison[1]

[1]*Minerals to Metals, University of Cape Town, South Africa, jlb@absamail.co.za*
[2]*Environment and Sustainability Institute, University of Exeter, United Kingdom, C.G.Bryan@exeter.ac.uk*

Abstract The reliable prediction of acid rock drainage risks associated with sulfide mine wastes plays an important role in planning for their disposal. This paper explores the application of a novel biokinetic test, in combination with conventional static chemical tests, for the rapid and effective characterisation of the acid generating potential of a number of mine wastes from the processing of both hard-rock ores and coal. Findings also highlight the need to consider microbial colonisation and the effects of such on the relative kinetics of the acid forming and neutralising reactions.

Keywords Acid rock drainage, sulfide mine waste, static tests, biokinetic tests

Introduction

Wastes from the extraction and beneficiation of sulfide-bearing hard rock ores and coal deposits may contain significant quantities of sulfide minerals, particularly pyrite, which are susceptible to oxidative dissolution in the presence of water and oxygen, giving rise to the formation of acid rock drainage (ARD). In order to be effectively managed, the long-term acid generating potential of mine wastes first need to be accurately and reliably characterised using simple, robust and precise testing procedures. Whilst the chemical oxidation of pyrite occurs at a relatively slow rate, the formation of ARD is greatly accelerated in the presence of naturally-occurring acidophilic micro-organisms (Bryan 2006, Johnson and Hallberg 2005).

Typically, predictions of the acid generating potential of mine wastes are based on static and kinetic chemical tests (INAP 2009, Smart *et al.* 2002, Price 2009). Static chemical tests, such as acid base accounting (ABA) and net acid generation (NAG), provide an indication of the absolute potential of a material to generate acid over geographical time, but do not take into account reaction kinetics. These tests are thus mainly used as initial screening tests, whereby materials are classified in accordance with universally accepted criteria. Kinetic tests are designed to provide information on the time-related acid generating potential of a material. The most common kinetic tests include humidity cell tests and leach column tests, both of which provide long-term dynamic weathering data. A major drawback of these standard kinetic tests is the time required to generate meaningful data, which may often run into years. Furthermore, standard kinetic tests do not take microbial activity into account-this despite the fact that microbial colonisation of sulfide-bearing waste rock or tailings is inevitable (Bryan 2006). Finally, both humidity cells and leach column tests are carried out using a large particle size distribution of heterologous ore which limits reproducibility.

In an attempt to address the short-comings of standard humidity and leach column tests, a microbial shake flask test was developed by Duncan and Bruynesteyn (1979) and subsequently modified and refined in a more recent study by Hesketh *et al.* (2010a). This paper extends the application of the biokinetic shake flask tests to a range of sulfide-bearing mine wastes from different sources and origins, and demonstrates its role in both validating and enhancing the results from standard static chemical tests.

Methods

Chemical static and biokinetic shake flask tests were carried out on the following mine waste samples:

- Untreated copper sulfide tailings: Sample represented typical tailings from the flotation of porphyry-type copper sulfide ores, with the sulfide minerals comprising mainly pyrite (≈7 % by mass) and minor quantities of chalcopyrite (≈0.5 % by mass).
- Desulfurised copper sulfide tailings: Sample prepared from the untreated copper sulfide tailings in a two-stage batch desulphurization flotation process, as described in Hesketh *et al.* (2010b).
- Copper sulfide waste rock: Sample of waste rock prepared from a blend of low-grade porphyry copper sulfide and complex base-metal sulfide ores. The sulfide minerals comprised mainly pyrite (≈ 2.6 %) and no carbonate minerals were detected by XRD.
- Nickel-pyrrhotite flotation tailings: Sample prepared from a low-grade nickel sulfide (pentlandite) ore in a laboratory-scale batch flotation cell (Chimbganda *et al.* 2013). Pyrrhotite was identified as the major sulfide mineral and calcite as the major carbonate. The ore also contained relatively reactive silicate minerals, such as olivine (≈4 %).
- Gold tailings: Sample prepared through the crushing and screening of a Witwatersrand gold ore. Mineralogical analysis indicated that pyrite is the major sulfide mineral (≈1 %) and calcite the major carbonate mineral.
- Coal waste slurry: Two samples of fresh ultra-fine thickener underflow procured from two different coal processing plants in the Middelburg area, South Africa. Sample 1 was screened into various size fractions, prior to further testwork. The coal slurry samples contained 25–40 % ash-forming minerals, comprising mainly quartz and kaolinite with minor quantities (<5 %) of pyrite, calcite, dolomite and sulfate minerals.
- Untreated coal discard: Sample generated at a South African power station, through the destoning of a low-grade coal by means of an experimental X-ray sorter. The discard had an ash content of 56.4 %.
- Desulfurised coal discard: Sample prepared from the untreated coal discard sample in a two-stage flotation process as described by Kazadi Mbamba *et al.* (2012), using oleic acid to recover coal in the first-stage float and xanthate to remove sulfide minerals in the second flotation stage. The desulfurised tailings comprised 36 % of the feed discards, and had an ash content of 82.4 %.

Static tests were conducted on all samples using both the ABA and NAG test methodologies. The ABA test measures the net acid producing potential (NAPP), which represents the balance between the maximum potential acidity (MPA) and the acid neutralising capacity (ANC). The MPA was based on the total LECO sulfur concentration in the case of the wastes from the processing of hard-rock ores, and the sulfide sulfur content (as determined by the standard ISO 157: 1996 method) in the case of coal wastes. ANC was determined empirically in accordance with the method proposed by Skousen *et al.* (1977). NAG tests were conducted according to the method described by Smart *et al.* (2002). This method measures the acid forming potential, by allowing both the acid–forming and neutralising reactions to occur simultaneously, using H_2O_2 as an oxidant. The waste samples were subsequently classified using a slightly modified version of the combined ABA/NAG classification system, proposed by Smart *et al.* (2002).

Biokinetic tests were carried out on all waste samples in accordance with the standard batch method described in Hesketh *et al.* (2010a). In this test, 7.5 g of sample, with a particle size of <150 µm, is added to a basal salts medium at pH 2.0, prior to inoculation with an active, mixed microbial bioleaching culture. The prepared flasks are subsequently maintained at 37 °C on an orbital shaker at 150rpm for a period of approximately 90 days. In order to better present an open flow-through system, a dynamic (semi-continuous) version of the standard batch biokinetic test was also carried out on selected samples under circum-neutral pH conditions. In these tests, the initial pH of the basalt salts medium was adjusted to a value of 6 prior to the introduction of the waste sample. This was followed by intermittent removal and replacement of 90 % of the supernatant during the course of the shake flask test.

Results

Static test results for the wastes from the processing of hard-rock ores (table 1 and fig.1) indicate that the untreated sulfide tailings and waste rock samples investigated are all classified as acid generating. The low-sulfur copper tailings sample, generated through the desulfurisation flotation of the copper sulfide tailings, is classified as non-acid forming.

The results of standard batch biokinetic tests (fig. 2) yielded the same results as the static tests in terms of classification *i.e.* all untreated mine waste samples tested were net acid generating, under conditions of microbial activity, whilst removal of the sulfide by means of flotation effectively removed the long-term ARD risk.

The biokinetic test results also show that the acid neutralising reactions occur more rapidly than pyrite oxidation, with the pyrite-bearing wastes becoming net acid consuming in the initial leach stages. This neutralising capacity is, however, generally short-lived (<15 days) for wastes that have not been desulfurised, and the acidification observed in the biokinetic tests thus ultimately exceeds that predicted by the static tests (final biokinetic pH values are lower than the NAG pH values). This is particularly the case for the pyrrhotite-bearing nickel sulfide tailings which, despite the

Waste description	Total S (%)	ANC (kg/t H_2SO_4)	NAPP (kg/t H_2SO_4)	NAG pH
Untreated copper sulfide tailings	3.84	23.2	94.8	2.57
Desulfurised copper sulfide tailings	0.21	28.7	-22.3	5.71
Copper sulfide waste rock	3.39	3.39	92.8	2.63
Nickel-pyrrhotite flotation tailings	3.59	89.4	20.3	3.19
Gold tailings	1.41	16.5	24.9	2.51

Table 1 *Static ARD test results for wastes from hard-rock ore processing*

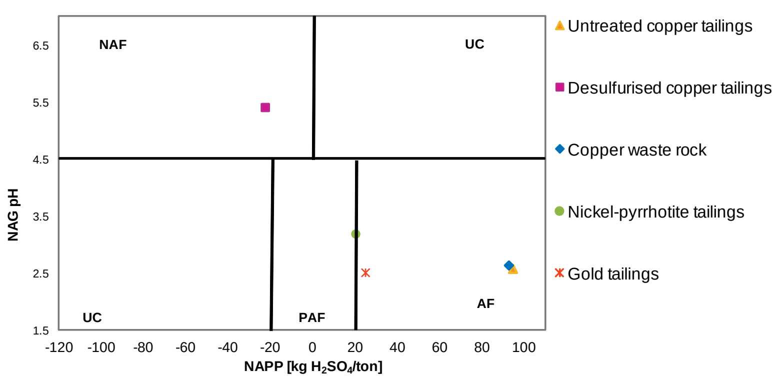

Fig. 1 *Static ARD classification plot for the wastes from hard-rock ore processing (NAF: non- acid forming, UC: uncertain, PAF: potentially acid forming and AF: acid forming)*

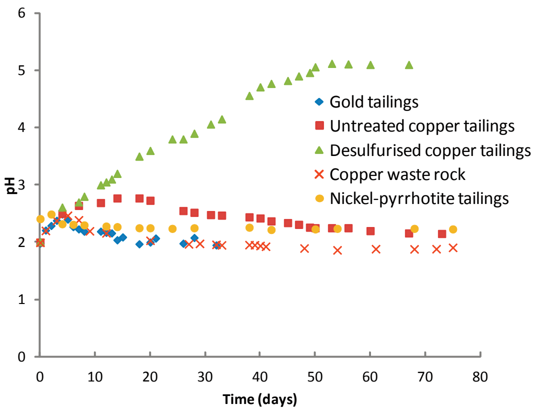

***Fig. 2** Batch biokinetic test results for wastes from the processing of hard-rock ores*

relatively high ANC, exhibited acid generating behaviour after the first day. This can be attributed to the relatively rapid kinetics of pyrrhotite oxidation in comparison to that of pyrite (Janzen *et al.* 2002).

Static test results for the coal waste samples (tab.2 and fig. 3) indicate that the untreated coal discards are acid forming, the coal waste slurry 1 potentially acid forming, and the coal waste slurry 2 and the desulfurised coal discards both non-acid forming.

In accordance with Miller (2008), the standard NAG test may overestimate the acid generating potential of samples with relatively low acid generating potential (*i.e.* those falling in the PAF region of the graph), due to organic acid effects. However, biokinetic tests (fig. 4) confirmed that samples classified as either acid forming or potentially acid forming on the basis of static chemical tests are also acid generating under conditions of microbial colonisation. In agreement with the static chemical tests, biokinetic tests indicate that coal waste slurry 2 and the desulfurised coal discards are both non-acid generating. A comparison of the leach behaviour of the -75 µm fraction of coal slurry waste 1 under biotic and abiotic conditions confirms, furthermore, that microbial activity plays a significant role in acid generating behaviour. As in the case of the wastes from hard-rock ore processing, the biokinetic test results indicate that, although the samples classified as PAF and AF are initially acid consuming, this acid neutralising capacity is consumed relatively rapidly. This is of relevance when considering a tailings deposit where soluble fractions are transported away from the waste material, and thus are not

Waste description	Total S (%)	S^{2-} (%)	ANC (kg/t H_2SO_4)	NAPP (kg/t H_2SO_4)	NAG pH
Coal waste slurry 1: -75µm	2.08	1.00	27.7	2.9	2.50
Coal waste slurry 1: +212-315µm	1.03	0.64	28.2	-8.6	2.97
Coal waste slurry 2	0.82	0.50	131.9	-116.6	5.20
Untreated coal discards	5.11	3.30	55.6	101.0	2.20
Desulfurised coal discards	0.21	n/d	76.7	-70.6	5.90

***Table 2** Static ARD test results for coal processing wastes*

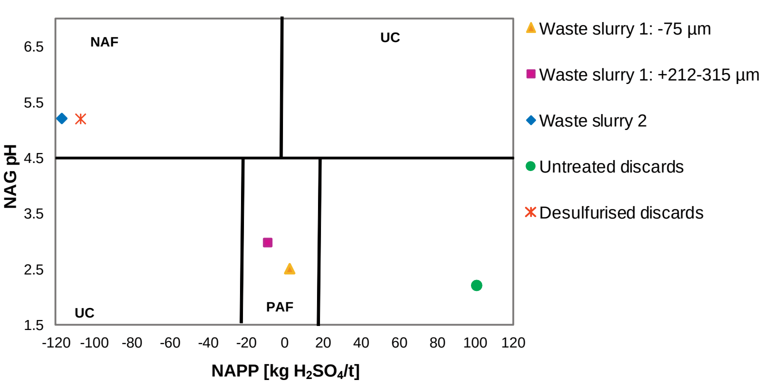

***Fig. 3** Static ARD classification plot for the coal processing wastes (NAF: non-acid forming, UC: uncertain, PAF: potentially acid forming and AF: acid forming)*

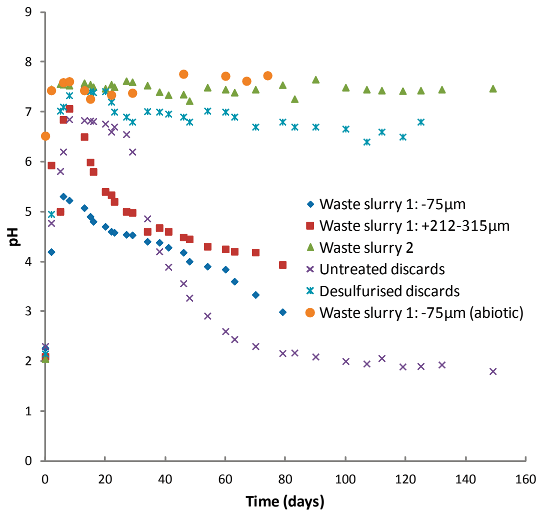

***Fig. 4** Batch biokinetic test results for wastes from coal processing*

available to neutralise acid generated through the oxidation of pyrite over the longer term.

Dynamic biokinetic leach tests on the two size fractions of coal waste slurry 1 (fig. 5) confirm that these samples eventually become net acid generating under conditions of microbial colonisation in a semi-continuous flow scenario, even when using a leach solution with a relatively mild circum-neutral pH (6). Mineralogical analysis of the leach residues indicated incomplete oxidation of pyrite over the 87 day biokinetic test period, particularly in the case of the coarser size fraction.

Conclusions

This study has demonstrated that the biokinetic test can be used to both validate and enhance the results of simple static tests, providing valuable additional information on the effect of microbial activity and the relative kinetics of the acid forming and neutralising reactions under stagnant and dynamic flow conditions. Such information provides a measure of the potential for conditions that promote bioleaching to be established and, ultimately, assists in the implementation of waste management strategies that are effective in both the short and long-term. The advantages of the biokinetic test over other conventional kinetic tests include its relatively simple and inexpensive methodology. The biokinetic test also delivers meaningful results pertaining to the long-term ARD generating potential of both fine and coarse wastes in a relatively short period of time (< 3 months for wastes from hard-rock ore processing, and 4–5 months for coal processing wastes).

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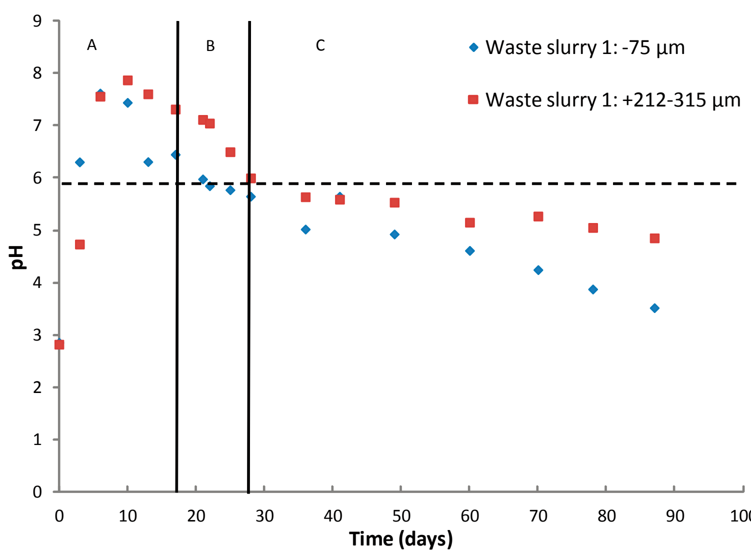

***Fig. 5** Dynamic biokinetic test results for wastes from coal processing at circum-neutral pH conditions (where A, B and C correspond to supernatant replacement intervals of 3, 8 and 14 days respectively)*

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References

Bryan CG (2006) A study of the microbiological populations of mine wastes, PhD thesis, School of Biological Sciences, University of Wales.

Chimbganda T, Becker M, Broadhurst J *et al.* (2013) Comparison of pyrrhotite rejection and passivation in two Nickel ores. Minerals Engineering, 46-47:38-44.

Duncan D, Bruynesteyn A (1979) Determination of acid production potential of waste materials. Metallurgy Society, AIME, paper A-79-29 AIME, Littleton, CO.

Hesketh AH, Broadhurst JL, Bryan CG, van Hille RP, Harrison STL (2010a) Biokinetic test for the characterisation of AMD generation potential of sulfide mineral wastes. Hydrometallurgy 104(3):459-464.

Hesketh AH, Broadhurst, JL, Harrison STL (2010b) Mitigating the generation of acid mine drainage from copper sulfide tailings impoundments in perpetuity: A case study for integrated management strategy. Minerals Engineering 23:225–229.

INAP (International Network for Acid Prevention) (2009) Global Acid Rock Drainage (GARD) Guide. Available at www. gardguide.com (accessed March 2013).

Janzen MP, Nicholson RV, Scharer JM (2000) Pyrrhotite reaction kinetics: reaction rates for oxidation by oxygen, ferric iron, and for nonoxidative dissolution. Geochimica et Cosmochimica Acta 64(9):1511-1522.

Johnson DB, Hallberg KB (2005) Acid mine drainage remediation options: a review. Science of the Total Environment 338:3–14.

Kazadi Mbamba C, Harrison STL, Franzidis J-P, Broadhurst J (2012) Mitigating acid rock drainage risks while recovering low-sulphur coal from ultrafine colliery wastes using froth flotation. Minerals Engineering 29: 13–21

Miller, S (2008) Development of ARD assessment for coal process wastes (ACARP project C15034). Environmental Geochemistry International Pty Ltd, Australia.

Price WA (2009) Prediction manual for drainage chemistry from sulphidic geological materials (MEND report 1.20.1). CANMET Mining and Mineral Science Laboratories, British Columbia, Canada.

Skousen J, Renton J, Evans, P *et al.* (1977) Neutralization potential of overburden samples containing siderite. J. Environmental Quality 26:673–681.

Smart R, Skinner B, Levay G *et al.* (2002) ARD Test Handbook (AMIRA project P387A: Prediction and Kinetic Control of Acid Mine Drainage), Ian Wark Research Institute and Environmental Geochemistry International, Melbourne, Australia.