Understanding Mineralogy as a tool for Acid Rock Drainage (ARD) Characterisation

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Abstract

Accurate characterisation of ARD potentials is required for the development of suitable waste management strategies. Laboratory-scale static tests, provide information on the ARD capability of the waste, but not the behaviour of the individual minerals. This behaviour is dependent on the conditions within the static and Biokinetic tests. Dissolution of the carbonate and reactive silicates contributed to the neutralising capacity. Mineral behaviour within the static tests provided an indication of behaviour within Biokinetic tests. Elemental concentrations within leachate solutions supported the findings from the leach residues. The integration of the mineralogical and leachate analysis allows for better understanding of the ARD behaviour of sulfidic wastes.

Keywords: Mineralogy, Static Tests, Biokinetic Tests, Acid Rock Drainage

Introduction

Acid rock drainage (ARD) is one of the most serious pollution problems facing the mining of sulfidic ores. ARD pollution is characterised by acidic pH, and elevated concentrations of deleterious elements and soluble salts. The acidic nature of the pollution is due to the oxidation of sulfide minerals, which occurs naturally in the presence of water and oxygen. This oxidation, however, may be accelerated through the metabolic action of Fe- and S-oxidising micro-organisms. The accurate and reliable characterisation of the ARD potentials will allow for a more sustainable approach to waste management through the optimisation of cleaner production principles within the mining industry.

To limit the number of samples and the associated cost of analysis, a sequential approach is used in the characterisation and prediction of ARD hazards (Parbhakar-Fox and Lottermoser, 2015). The initial stage consists of acid-base accounting, with a balance of the acid-generating and acid-neutralising potentials of the waste providing an estimate of the net acid producing potential (NAPP). This assessment is performed using laboratory-scale tests. In addition, net acid generation (NAG) tests are performed, with the pH of the final solution indicating the potential for net acidity generation (Miller et al., 1997). Following static tests, potentially acid forming samples undergo kinetic testing to evaluate the rate of ARD generation and its potential composition. Samples which are found to be non-acid forming (NAF) are eliminated from the ARD protocol (Smart et al., 2002). A number of previous researchers have documented the various short-comings of this approach and the test methods involved (Dold, 2017, Parbhakar-Fox and Lottermoser, 2015).

However, the simplicity, speed and low cost of the laboratory tests ensures their continued use as the initial stage in the characterisation of potential ARD hazards (Smart et al., 2002). The reliability of these tests, therefore, remains a key parameter in the characterisation of the ARD hazards associated with mine wastes. In particular, studies have suggested the inclusion of sample mineralogy to provide understanding of the behaviour of individual minerals in the overall ARD generation process (Becker et al., 2015, Brough et al., 2013). Such information may be used directly for an estimation of the acid generating and acid neutralising capability of the wastes (Paktunc, 1999, Bouzahzah et al., 2014).

This study investigates the behaviour of individual minerals under the static and Biokinetic test conditions, through analysis of leach residues. This allowed for assessment of mineral reactivity as a function of test conditions, with a deeper understanding of the test results gained. Changes in sample mineralogy were supported through analysis of the elemental concentrations within the leachate solutions.

Materials and Methods

Two waste rock samples sourced from a greenstone belt gold deposit were used in this study. Statistically representative samples were prepared for use in the static and Biokinetic tests (Opitz et al., 2016). Mineral grades were quantified using QEMSCAN® analysis on an FEI QEMSCAN® 650F at the University of Cape Town and complimented by electron micro-probe analysis (EMPA) of various silicate minerals to accurately determine their end-member compositions.

Acid-generating sulfides included pyrrhotite (5.8 wt.%; 0.9 wt. %) and pyrite (1.2 wt.%; 6.0 wt. %) for the two waste samples, whereas the acid neutralising potential was due to fast-weathering calcite (0.9 wt.%; 2.8 wt. %), intermediate-weathering chlorite (1.4 wt.%; 0.7 wt. %) and biotite (1.7 wt.%; 15.5 wt. %), and slow-weathering magnetite (33 wt.%; 16 wt. %)(Opitz et al., 2016).Classification of the ARD potentials of both samples was performed using acid-base accounting. The acid neutralising capacity (ANC) was determined experimentally using the method outlined in Weber et al. (2004). Single stage Net acid generation (NAG) tests were performed using reaction of the wastes with a 15 % H_2O_2 solution (Miller et al., 1997). Further details are provided in Opitz et al. (2016), with a summary of the characterisation results presented in **Table 1**.

Biokinetic tests provided an understanding of the ARD generation under microbially-mediated conditions. Analysis of the solution pH with time (Figure 1) allowed for assessment of the relative rates of acid-neutralisation and acid-formation within the triplicate tests. For sample A, the rise in pH from reaction with calcite was followed by a decrease as a consequence of acidity formation. For sample B, however, the solution pH increased above conditions favourable for microbial growth and activity.

Leachate solution prior to the neutralisation step was recovered from the static tests, with liquid samples collected from the Biokinetic tests prior to commencement and daily thereafter. Solution analysis was performed for major elements (Al, Ca, Fe, K, Mg, Na) using induced coupled plasma optical emission spectrometry (ICP-OES) using a Varian 720 machine. Solid residues were collected upon the completion of the ARD laboratory tests, with mineralogical assessment performed using QEMSCAN. The extents of mineral reaction are presented as range, following the calculation presented in (Becker et al., 2015).

Results

Decreases in mineral content, as a percentage change from the feed material, are presented in **Table 2**. The reaction of the acid-consuming minerals was observed within all tests performed for both samples, while the depletion of the sulfides was predominately within the NAG and Biokinetic tests. The leach residues from the ANC tests from both samples confirmed the completion dissolution of calcite, as specifically targeted by the test conditions. In addition, dissolution of the reactive silicates (chlorite and biotite), and the Fe-oxyhydroxides were observed for both waste samples. The decreases in Fe-oxyhydroxides (1-30 %) and sulfides (1-30 %) (**Table 2**) are in agreement with Becker et al. (2015), where dissolution of these minerals was observed under similar test conditions. In particular, a reduction in pyrrhotite content was observed in the ANC residues for both samples, indi-

***Table 1:** ARD characterisation results for the two waste rock samples indicating the overall acid generation classification of both samples. From: Opitz et al. (2016).*

Waste Sample	MPA [kg H_2SO_4 / ton]	ANC [kg H_2SO_4 / ton]	NAPP [kg H_2SO_4 / ton]	NAG pH	ARD Classification
Sample A	70.2 ± 0.7	53.2 ± 1.8	17.0 ± 1.9	2.5 ± 0	Potentially acid forming
Sample B	98.8 ± 1.4	95.7 ± 1.9	3.2 ± 2.4	2.7 ± 0	

cating fairly extensive dissolution under the relatively aggressive leach test conditions.

NAG tests are designed to provide an indication of net acidity generation upon simultaneous oxidation of the sulfide minerals and reaction of the neutralising minerals. For both samples, dissolution of pyrrhotite and pyrite was observed within the single stage NAG tests. Decreases in the calcite, chlorite and biotite content were due to reaction with the acidity produced from sulfide oxidation. The differences in extent of chlorite dissolution between ANC and NAG tests were due to the milder test conditions with respect to acid molarity.

In contrast to the NAG test conditions, oxidation within the Biokinetic tests was facilitated through microbial (re)generation of soluble ferric iron. The mineralogical changes as a consequence of the Biokinetic tests were different for the two samples, related to the acid neutralising content of the wastes (**Table 1**), which affected the pH conditions within the two experimental systems. The Biokinetic test results (Opitz et al., 2016) indicated a varied immediate response in solution pH for the two waste samples. Tests performed on sample A illustrated an initial dominance of acid neutralisation followed by acid generation. The favourable microbial conditions allowed for microbially-mediated oxidation of the pyrrhotite (>90 %) and pyrite (61-90 %), with the acidic environment leading to the dissolution of acid consuming minerals (> 90% calcite; 31-60 % chlorite). In contrast, the neutralisation content of sample B was sufficient to ensure pH levels rose to pH 7.0 over the initial 3 days. These pH levels were maintained for the duration of the experiment with limited acid generation observed. These unfavourable microbial conditions, limiting the solubility of the ferric iron oxidising agent. The pyrrhotite and pyrite oxidation observed within these residues were a result of initial reaction of the sulfides with ferric iron added as part of the inoculum solution. In addition, formation of iron-sulfate precipitates within both experimental systems occurred, as indicated by the increase in the sulfate composition of the test residues.

Analysis of the solution composition of the static and Biokinetic tests (Figure 2) supported the observations from the mineral residues. Greater concentrations of Al, Ca, K and Mg were observed in the ANC test solutions as compared to the NAG and Biokinetic tests. This is consistent with the greater dissolution of chlorite under the more aggressive leach conditions in the ANC tests. Differences in Fe concentrations between the tests are due primarily to differences in solution pH. Higher Fe concentrations were observed un-

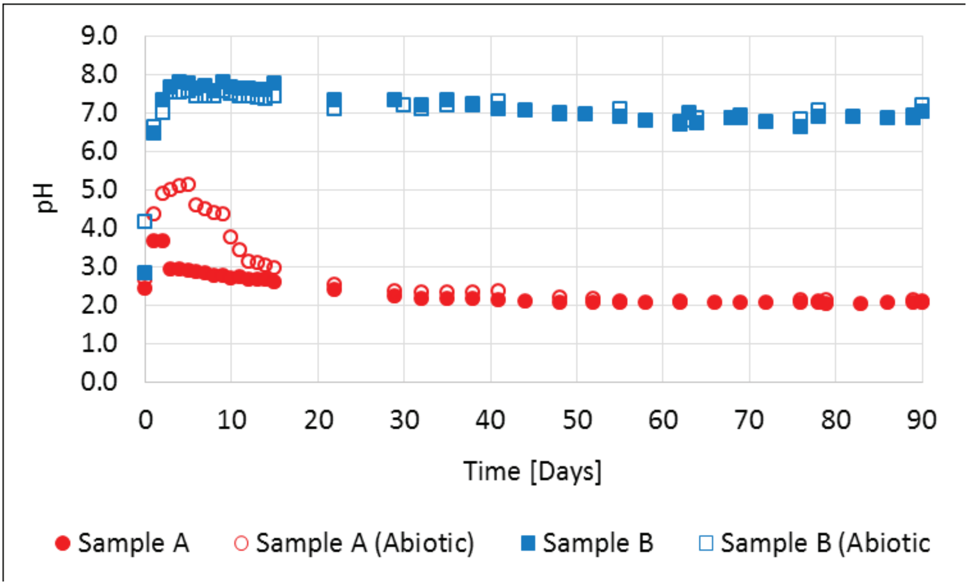

Figure 1: pH profile of the Biokinetic tests performed on samples A and B, for biotic (closed symbols) and non-inoculated (open symbols) experiments (Opitz et al., 2016).

der acidic conditions, with the formation of Fe-bearing sulfate precipitates at the elevated pH conditions within the Biokinetic test performed on sample B. Similar Mn concentrations were observed with all characterisation tests.

Discussion

The role of reactive silicates to the acid neutralising capacity of waste samples has been demonstrated previously (Becker et al., 2015, Lawrence and Scheske, 1997, Jambor et al., 2002). Such minerals, however, are not often included in estimations of the neutralising potential based on sample mineralogy. The dissolution of these minerals under ANC test conditions, however, indicates their inclusion in the experimental quantification of the acid neutralising capacity of the samples. In addition, dissolution of these silicates within the Biokinetic tests, with conditions similar to those within waste deposits, indicates the contribution of such minerals to ARD generation. Dissolution of pyrrhotite within the ANC tests highlighted the behaviour of sulfide minerals which undergo dissolution through proton attack. For pyrrhotite, the acid consumption upon dissolution within the ANC test may be offset by the acid released during precipitation of the ferric iron resulting from its dissolution. However, for non-ferrous sulfides such as galena (0.03 wt. %), this offset may not occur, with the potential for these minerals to contribute to acid-neutralisation and acid-generation estimates simultaneously.

The dissolution of the reactive silicates and Fe-oxyhydroxides within the NAG tests indicates the dissolution of these minerals by acidity produced through the oxidation of the sulfide minerals. The acid consuming behaviour, therefore, is accounted for through measurement of the NAGph upon completion of the single-stage NAG test. The lack of complete sulfide oxidation in the residue of this test, however, implies a remaining potential for acidity formation, and indicates the underestimation of the total ARD generation potential from the single-stage NAG test.

Quantification of the ARD potentials from mineralogical estimates and static characterisation tests provides an indication of the ARD potential of the wastes over geological time frames. No information on the relative rates of acid neutralisation and generation, however, is obtained. The importance of this knowledge is illustrated by the Biokinetic test results of the two samples. The greater calcite content in sample B led to a greater elevated in initial solution pH as compared to the tests performed on sample A. The resulting unfavourable microbial conditions limited the information gained on microbially-mediated sulfide oxidation for this sample. The suitable acidic and oxidative conditions within the Biokinetic tests performed on sample A, however, resulted in sulfide mineral oxidation, illustrated by the reduction in solution pH by day 3 (Figure 1) and the decrease in sulfide mineral content grade of this sample. In addition to the increase in acidity as a consequence of sulfide oxidation, the increase in sulfate content within the leach residues,

Table 2: *Changes in mineral composition presented as a percentage of the initial amounts as quantified from the leach residues following static and Biokinetic tests performed on waste sample A and B.*

Mineral Phase	Sample A [%]			Sample B [%]		
	ANC	NAG	Biokinetic	ANC	NAG	Biokinetic
Pyrrhotite	61-90 %	61–90 %	>90 %	1–30 %	31-60 %	1-30 %
Pyrite	0 %	61–90 %	61–90 %	0 %	61–90 %	1–30 %
Calcite	> 90 %	> 90 %	> 90 %	> 90 %	> 90 %	> 90 %
Chlorite	61-90 %	31–60 %	31-60 %	61-90 %	31–60 %	31-60 %
Fe-oxyhydroxides	1–30 %	1-30 %	1–30 %	1–30 %	1-30 %	1–30 %
Biotite	1–30 %	1–30 %	1–30 %	1–30 %	1–30 %	1–30 %
Actinolite	1-30 %	1-30 %	1-30 %	31-60 %	31-60 %	31-60 %
Albite	0 %	0 %	0 %	0 %	0 %	0 %
Quartz	0 %	0 %	0 %	0 %	0 %	0 %
Sulfates	31-60 %	31-60 %	< 0 %	31-60 %	31-60 %	< 0 %

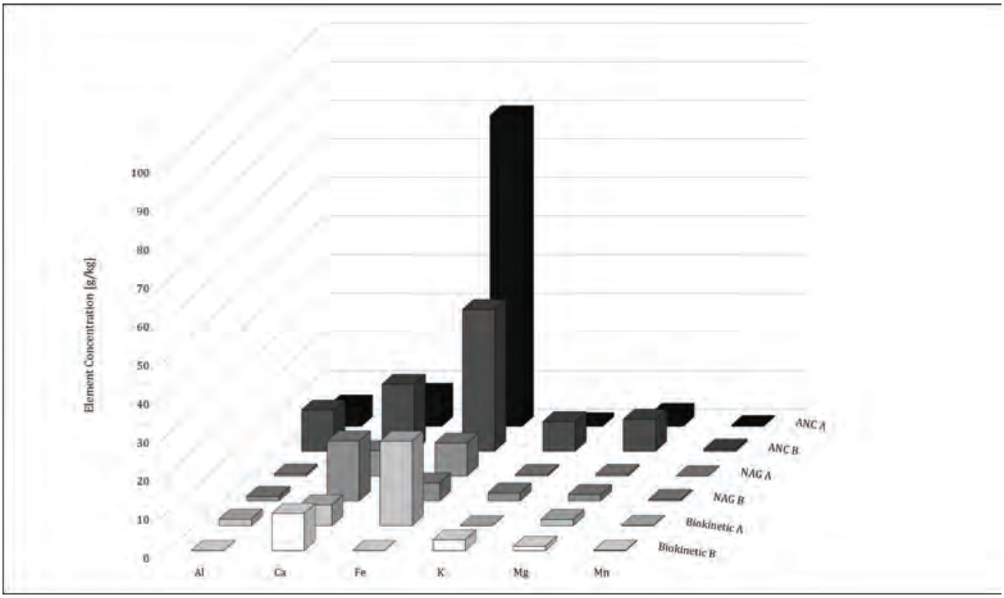

***Figure** 2: Solution concentrations at test termination for the static ARD and Biokinetic tests performed on waste samples A and B. Tests were performed in triplicate (n=3)*

indicates the formation of Fe-precipitates within this test. The sustained presence of these precipitates over the duration of the Biokinetic tests is consistent with the formation of insoluble jarosite precipitate within the acid–sulfate system (Nordstrom, 1982). Although the static test residues provides an indication of the minerals which may contribute to the ARD generation within the Biokinetic tests, accurate prediction of the behaviour and contribution of the individual minerals may require decoupling of the rates of acid-consumption and acid-formation. In addition, while analysis of the Biokinetic test solutions allows for identification of the mobilised elements, fundamental understanding of individual mineral behaviour with time is necessary for more detailed knowledge on elemental deportment.

Integration of the static and Biokinetic test results allow for knowledge of the possible drainage characteristics under “worst case scenarios” and conditions more typical of waste deposits. The combination of the leach residue analysis and quantification of elemental concentrations allows for identification of the minerals responsible for acid-formation and acid-neutralisation, and an understanding of the behaviour of the individual minerals under these conditions.

Conclusions

Partial dissolution of reactive silicate minerals and pyrrhotite were observed within the ANC tests performed on both samples. Dissolution of the Fe-oxyhydroxides and reactive silicate minerals within the NAG tests suggests the dissolution of these minerals may be expected within acid-sulfate systems. An underestimate of the total sulfide oxidation potential within the single-stage NAG solution is suggested by the substantial sulfide grade of the NAG residues. Integration of the leach residue analysis and soluble elemental concentrations from the static tests allowed for identification of the minerals likely to contribute to the ARD behaviour under Biokinetic test conditions. The accurate contribution of the individual minerals within this test, however, requires further development of Biokinetic tests where test solution is replenished with time. The elemental concentrations within the leachate solutions supported the dissolution of identified minerals from the test residues. The deportment of deleterious elements within Biokinetic tests, however, may only be considered upon the formation of acidic and oxidative conditions. There remains a necessity for integrated knowledge of detailed sample mineralogy and solution chemistry, both under chemical and biological conditions, in understanding the ARD potentials of sulfide wastes. An approach which includes of both of these aspects is required to provide accurate and reliable ARD characterisation and prediction.

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