Weathering and Oxidation Rates in Black Shales – A Comparison of Laboratory Methods

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ABSTRACT

Kinetic testing has been conducted on six samples of sulfidic Mount McRae Shale from the Pilbara, West Australia. The total sulfur content of the samples ranged from 0.2 to 8.9%. Whilst the sulfide mineralization was predominantly pyrite, the bulk mineralogy of the samples was dominated by silicates and iron oxides. Acid neutralizing capacity was low and sample classification ranged from Uncertain (UC) for the low sulfide samples, to potentially acid forming (PAF) for the higher sulfide samples.

Various small scale test methods have been developed within the industry to assess the rate of oxidation and solute release from mine waste materials. Whilst humidity cell tests (HCTs) were developed in North America as part of the MEND program, an alternate but similar free draining method was developed in Australia, referred to as the AMIRA free-draining method. These methods are conducted at a similar scale, but differ primarily in the frequency of irrigation, and the temperature at which testing is undertaken. The methods were compared to assess the implications on leach rates and water quality predictions.

Under acidic conditions, both test methods generated similar trends, and produced approximately equivalent results. One sample contained neutralizing capacity and the two methods yielded different pH profiles; the HCT remained circum neutral, whilst the AMIRA test developed acidic conditions. A possible cause of the discrepancy is comparatively high consumption of neutralization capacity in the saline AMIRA leachate environment. Further work is required to develop a more robust understanding of neutralization processes, and their effectiveness, as a function of leachate salinity.

The test results for acidic conditions would yield similar outcomes when used as the basis for water quality predictions at a larger scale, however, this was not the case for the sample containing reactive ANC.

Keywords: Sulfide oxidation, kinetic testing

INTRODUCTION

The stratigraphic sequence in the Pilbara, Western Australia, includes shale and lignite lithologies, both of which are known to host sulfide mineralization (Green and Borden, 2011). Extensive geochemical characterization programs have been conducted to build an understanding of the geochemical behavior of these materials.

Laboratory-scale testing methods are employed to give insights into sulfide oxidation rates, acid/neutralization potential of the material and solutes released. The results are the foundation for predictive modelling of future mine-affected water quality and are used to guide mine waste management decisions (Green and Borden, 2011; MEND, 2009; INAP, 2009).

In the current study, two kinetic test methods were evaluated in parallel: i) AMIRA free-draining columns and ii) humidity cell tests (HCTs). In addition, the work was performed to compare the results from the two methods in order to evaluate the test method constraints, functionality and reliability or accuracy.

METHODS AND MATERIALS

Two kinetic test methods were employed:

- **AMIRA Free-Draining Column Method** (AMIRA, 2002). The method involves placing 2 kg dry weight of crushed rock (< 10 mm) on a mesh in a free-draining container and subjecting it to periodic leaching with a known volume of de-ionized water (400 mL/kg). The sample is flushed once every four weeks. In the weeks between flush events, the sample is moistened by the addition of a small volume (100 mL/kg) of de-ionized water. Heat lamps are applied at regular intervals to ensure the sample dries out between solution applications and to ensure that the temperature remains in the range 30 to 35 °C.
- **Humidity Cell Test Method** (MEND, 2009). Humidity cell tests (HCT) involve loading approximately 1 kg dry weight of crushed rock (< 10 mm) into a humidity cell. In the initial week (Week 0) the sample is wetted and flushed. This is followed by a weekly cycle, involving continuously pumping dry air for three days, and humid air for a subsequent three days, through the sample. The sample is then flushed with 500 mL of de-ionized water on the seventh day. Tests are operated at ambient laboratory temperature, approximately 23 °C.

In both methods, after each leach cycle, the leachate draining from the sample is collected and analyzed.

Six rock samples sourced from Mount McRae Shale were selected to represent a range of sulfur contents and various classifications, as shown in Table 1. Four samples were subjected to both kinetic testing methods. Since insufficient sample mass was available for the remaining two samples to conduct both methods, one was tested as an AMIRA column and the other as a HCT.

In later stages of AMIRA testing for samples ETD297 and EUG180, insufficient leachate was generated to meet analytical requirements – possibly because physical properties of the samples were changing over time (e.g. reduction in porosity, permeability, leading to an increase in moisture retention). Consequently from approximately Week 40 onwards these samples were flushed at a higher rinse volume (500 mL/kg).

All testing and analyses were undertaken at the SGS Laboratories in Perth.

Table 1 Acid-Base Accounting Results and Sample Classification

Parameter	Units	Sample ID					
		EPP357	ETD297	EUG180	EZL155	ESI115	EUE765
Sulfur speciation and potential acid generation potential							
Total S	%	0.16	0.55	1.4	1.8	5.1	8.9
CRS	%	n.m.	n.m.	0.9	n.m.	3.4	6.3
HCl soluble SO_4 - S	%	0.08	0.05	0.3	1.3[4]	0.3	0.9
Pyrite-S[1]	%	n.d.	0.4	1.0	1.7	4.0	8.8
Jarosite-S[1]	%	n.d.	n.d.	0.1	n.d.	0.3	0.4
MPA	kg H_2SO_4/t	4.9	16.8	42.8	55.1	156.1	272.3
AP	kg H_2SO_4/t	2.4	15.2	32.7	15.3	146.3	244.2
Carbon speciation and acid neutralization capacity							
TOC	%	n.m.	0.96	1.4	3.4	0.53	2.1
TIC	%	n.m.	0.13	0.08	0.24	0.65	0.14
Siderite-C[1]	%	n.d.	n.d.	n.d.	n.d.	0.6	n.d.
ANC	kg H_2SO_4/t	<1	8.2	4.7	9.6	4.4	<1
CarbNP[2]	kg H_2SO_4/t	-	10.6	6.5	19.6	53.1	11.4
Net acid generation (NAG) test results							
NAG pH	pH Unit	4.7	7.1	3.1	2.5	2.2	2
NAG (pH 4.5)	kg H_2SO_4/t	0.5	0.5	4.9	33	33	210
NAG (pH 7.0)	kg H_2SO_4/t	1.5	<0.5	10	44	59	230
Acid Base Accounting and Sample Classification							
NAPP[3]	kg H_2SO_4/t	3.9	8.6	38.1	45.5	151.7	271.3
NPR[3]	-	0.2	0.5	0.1	0.2	0.1	0.1
Classification	AMIRA	UC(NAF)	UC(NAF)	PAF-LC	PAF	PAF	PAF

n.d.=not detected; n.m.=not measured

S – Sulfur; SO_4 – Sulfate; CRS=Chromium reducible sulfur; ANC – Acid Neutralizing Capacity; NAG – Net Acid Generation; MPA – Maximum Potential Acidity; AP – Acid potential; TIC=Total Inorganic Carbon; TOC=Total Organic Carbon; CarbNP – Carbonate Neutralizing Potential; NAPP – Net Acid Producing Potential; NPR – Net Potential Ratio; NAF – Non Acid Forming; UC – Uncertain; PAF – Potentially Acid Forming; LC – Low Capacity.

Notes:
[1]   Calculated from XRD results.
[2]   CarbNP was calculated from the total inorganic carbon content of the sample.
[3]   NAPP and NPR calculated using the ANC and MPA.
[4]   Anomalous (high) as it is inconsistent with other results for this sample, e.g. the pyrite content as determined by XRD, and the NAG test results.

RESULTS

Figure 1 and 2 show leachate pH and calculated sulfate release rates for each test, as a function of time. As applicable results from both AMIRA columns and humidity cell tests are shown on the same plot for ease of comparison.
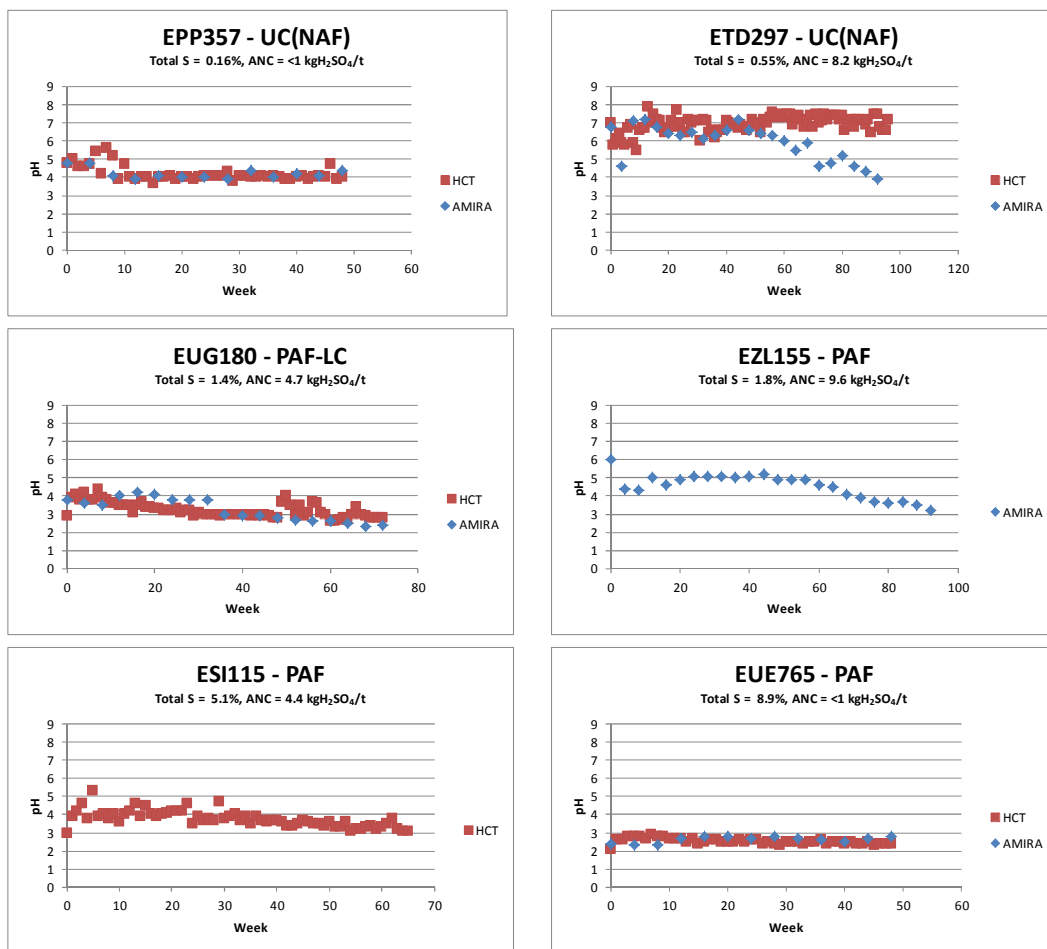
Figure 1 Leachate pH as a Function of Time
[The plots are arranged in order of sulfur content, reading from left to right]

Although a range of sample classifications was represented - UC(NAF), PAF-LC and PAF (see Table 1 footnote) - most of the tests progressed to acidic conditions (stable long-term average leachate pH values ranging from 2 to 4). The exception was the HCT test for sample ETD297 which remained circum neutral throughout (92 weeks). Though circum neutral at first, the AMIRA test for this sample progressed to acidic conditions at around Week 48 (not long after the increasing the rinsing volume from 400 mL/kg to 500 mL/kg).
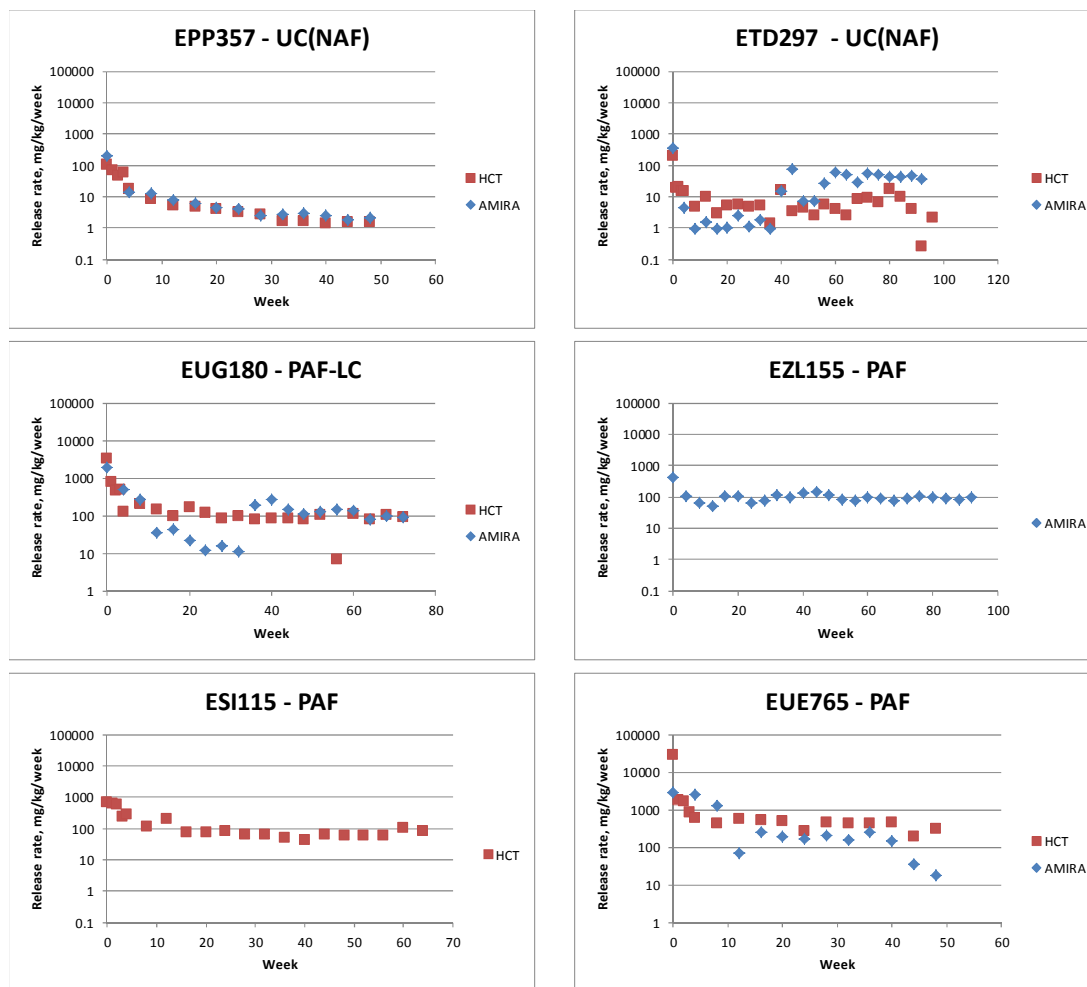
Figure 2 Calculated Sulfate Release Rate as a Function of Time.
[The plots are arranged in order of sulfur content, reading from left to right]

Sulfate release was highest in the early cycles of testing, and decreased in subsequent cycles, for the majority of tests, irrespective of test method. This reflects leaching of pre-existing readily soluble sulfate from the samples. The sulfate concentrations tended to stabilize at an approximately constant value in later stages for many of the tests, allowing calculation long-term average sulfate release rates. Exceptions were:

- AMIRA tests for samples ETD297 and EUG180 which showed a significant increase in release rate (by an order of magnitude or more) coincident with the increase in rinse volume
- AMIRA test containing sample EUE765 which showed a progressive decrease in release from Week 40 onwards.

Table 3 tabulates average release rates calculated for selected parameters.

Table 3 Average Release Rates Calculated for Selected Parameters

Sample	Lithology	Test duration, weeks	Week Trends Stabilised	Leachate pH	Average release rates, mg/kg/week[1]										
					SO₄	Ca	Fe	K	Mg	Si	Co	Cu	Ni	Se	Zn
AMIRA Columns															
Approx. detection limit[2]					*0.07*	*0.01*	*0.0003*	*0.007*	*0.007*	*0.001*	*0.00007*	*0.00007*	*0.00007*	*0.0002*	*0.00007*
EPP357	LGG	48	32	4.2	2	0.3	0.0003	0.08	0.3	0.5	0.0002	0.00007	0.0008	0.0002	0.0008
ETD297	SHL	96	40[3]	4.5	41	9.0	0.035	0.6	2.8	0.9	0.007	0.0011	0.012	0.001	0.013
EUG180	SHC	72	40[3]	2.6	119	3.3	4.8	0.06	3.7	1.0	0.2	0.1	0.8	0.006	3.0
EZL155	SHL	96	20	3.8	95	3.1	0.182	2.5	1.2	0.4	0.10	0.057	0.2	0.002	0.9
EUE765	SHC	48	16[4]	2.7	195	0.9	71	0.03	4.7	0.1	0.03	0.05	0.08	0.0009	0.05
Humidity Cell Tests															
Approx. detection limit[2]					*0.4*	*0.08*	*0.002*	*0.04*	*0.04*	*0.008*	*0.0004*	*0.0004*	*0.0004*	*0.0008*	*0.0004*
EPP357	LGG	48	32	4.0	2	0.08	0.002	0.1	0.08	0.6	0.0004	0.0004	0.0008	0.0008	0.002
ETD297	SHL	120	12	6.9	6	2.9	0.02	0.5	0.8	1.0	0.0004	0.0004	0.0004	0.0008	0.003
EUG180	SHC	72	32	2.9	83	0.5	3.2	1.0	1.7	4.3	0.1	0.1	0.5	0.006	1.9
ESI115	SHC	72	20	3.4	70	2.8	8.1	0.3	4.3	0.8	0.03	0.0006	0.07	0.0014	0.2
EUE765	SHC	48	16	2.5	394	0.1	152	0.2	5.3	4.3	0.03	0.07	0.1	0.007	0.07

Grey values are close to the approximate detection limits

Notes:

[1]   Calculated from later column leachates, after most chemical parameters start showing stable trends (the week when stable conditions were attained is shown).

[2]   Some calculated release rates are based on detection limit values and are therefore overestimates. The detection limit given in the table is approximate because, for the same analytical detection limit, the calculated release rate varies according to the volume of leachate collected and the mass of solid in the column.

[3]   Average rates are based on data collected after the rinse volume had been increased.

[4]   For this test, trends showed a sharp decline after 36 weeks, possibly due to armouring of reactive surface (see main text for discussion). The average release rates have been calculated using the data obtained between Week 16 (trends stabilised) and Week 36 (immediately prior to the declining trend).

DISCUSSION

Sulfide Oxidation, Acid Generation and Neutralization

Sulfate release rates from kinetic columns can be used to infer sulfide oxidation rates, assuming that no other geochemical processes increase or decrease sulfate concentrations in the leachates. PHREEQC modeling indicated that gypsum solubility may have controlled sulfate release in some of the early leaching cycles. At later stages, other sulfur-bearing minerals, e.g. hydroxysulfates such as jarosite, may have influenced leachate chemistry. However, the influence of these minerals on sulfate concentrations would have been limited by the low concentrations of other mineral constituents such as Al, K or Fe.

Figure 3 plots the average sulfate release rates against the sulfide sulfur content of the sample. The results from AMIRA columns and HCTs show the same general trend toward higher sulfate release rates as the sulfide sulfur content increases.
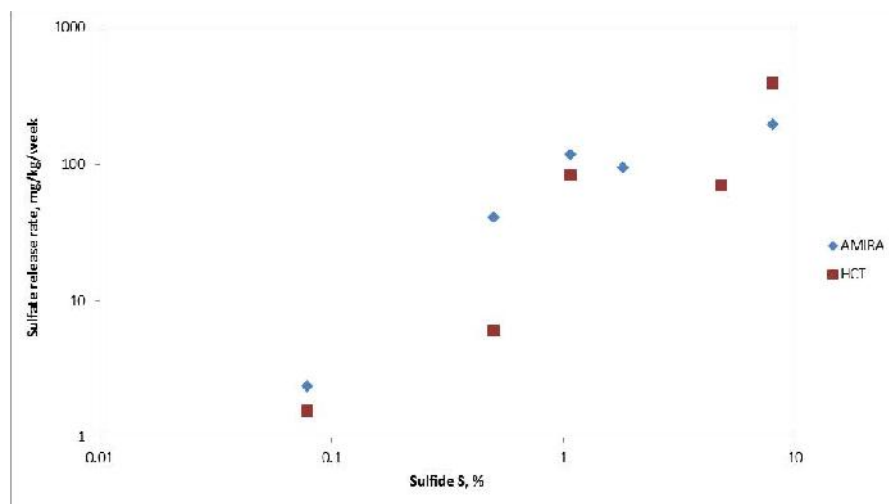

Figure 3 Sulfate Release Rate as a Function of Sulfide Content

Whilst sulfide content is interpreted as the primary variable controlling oxidation rates in the test materials, leachate pH clearly plays a role, explaining the higher sulfate release calculated in the AMIRA column (acidic) for sample ETD297 (about 0.5 % S) when compared to the equivalent HCT (circum neutral). The higher oxidation rate for the AMIRA test can be explained by:

- Catalysis by acidophilic bacteria is expected to be more effective under acidic conditions;
- An increased influence from ferric iron (Fe^{3+}) as an oxidant at acidic pH;
- Armoring of reactive surfaces is more likely under the circum neutral conditions of the HCT, and may have slowed reaction rates in this test.

Sample ETD297 was the only material that showed any evidence of effective neutralization during testing. In the early stages of both methods, circum neutral pH and $(Ca+Mg)/SO_4$ molar ratios in the leachates were interpreted as evidence of carbonate-based neutralization.

In the AMIRA test the leachate remained circum neutral until Week 40, when the pH started to decrease (Figure 1). The change in pH coincided with an increase in rinse volume. The increased rinse volume is

believed to have resulted in more effective flushing of accumulated products. The observed pH response suggests that either: (i) available neutralization capacity in the AMIRA method depleted at the same time as the operational conditions changed, or, (ii) the change in operating conditions somehow influenced the effectiveness of pH buffering in the material. The latter explanation is considered more likely, and could also explain why the results for the AMIRA test on sample EUG180 indicated a pH decrease coincident with a change in operating conditions (from pH 3 to pH 2; Figure 1).

Leachate pH is a complex balance of multiple influences, e.g. minerals that contribute acidity, and, minerals and aqueous complexes that can provide pH buffering. These complex equilibria are likely to be affected by changes in the leachate solute load (salinity). It appears that for the AMIRA test on sample ETD297 pH buffering was no longer effective following the increase in solute load. From that point onward in the test, increased oxidation rates (in response to the more acidic conditions) would have compounded the effect.

When compared to the AMIRA test leachates, solute concentrations in the HCT leachates were more dilute (due to more frequent rinsing with a higher volume of water). Perhaps for this reason, pH buffering remained effective for longer – explaining the continued neutralization observed in the HCT test for sample ETD297.

It is noteworthy that for all the samples the average Ca (and Mg) release is higher for the AMIRA tests than for the equivalent HCT tests, possibly indicating that the Ca/Mg mineral source is more reactive and/or soluble under the more saline condition of the AMIRA tests. In general terms, as most tests were acidic, this would indicate that pH neutralization is generally not effective (possibly indicative of a sideritic carbonate mineral source – siderite identified in ESI115, Table 1).

Elemental Release

Major elements, Al, Fe and Mn, and minor elements, As, Cd, Co, Cu, Ni, Sr, and Zn, release rates in general were in reasonable agreement between the two methods (Table 3 shows data for some of these elements); some deviations noted for sample ETD297 were related to the circum neutral pH observed for the leachates from the HCT method. Key controls on release were interpreted to be:

- Oxidizing sulfides – positive correlation with sulfate release suggested that some elements (e.g. Fe, Cu, As, Se) could be present in the matrix of the dissolving sulfide, whilst others (e.g. Al, Mg) could be sourced from minerals (e.g. carbonates, silicates) reacting in response to the acidic conditions produced by sulfide oxidation.
- Mn-bearing mineral – Cd, Co, Ni and Zn all showed strong correlation with Mn release. The identity of the mineral is unknown, possibilities are: manganese hydroxide, or Mn-bearing siderite or iron oxide. Release of Cd, Co, Ni and Zn (under acidic conditions) was also correlated to the bulk elemental content of the sample. As Mn itself did not correlate with bulk content it is inferred that only one of multiple Mn-bearing mineral sources in the material is reactive under the conditions of the tests.
- Mineral solubility – Fe and Al concentrations in some leachates were consistent with control by the solubility of iron and aluminium hydroxides and hydroxysulfates. Other possible solubility controls identified were amorphous silica (Si) and barite (Ba).

Comparison of Results from the Two Methods

Both methods were developed to measure sulfide oxidation and consequent solute release. The expectation is that all the soluble reaction products will be flushed entirely from the column during each irrigation event. The resulting leachate chemistries should therefore give a measure of the rate at which those reaction products are generated, provided the solutes are mobilized from the sample. Incomplete flushing of the oxidation products subject to solubility constraints would lead to underestimation of actual oxidation rates and solute release rates.

Table 3 Ratio of Calculated Average Long-Term Release Rates from HCTs: AMIRA Columns

Sample	Total S, %	Average long-term leachate pH		Rate HCT: Rate AMIRA[1]										
		AMIRA	HCT	SO$_4$	Cl	F	Al	Ca	Fe	K	Mg	Mn	Na	Si
EPP357	0.16	4.2	4.0	0.7	1.4	1.8	1.5	0.3	5.9	1.3	0.3	0.5	2.6	1.1
ETD297	0.55	4.7	6.9	0.1	1.5	4.5	0.4	0.3	0.7	0.8	0.3	0.0	0.4	1.2
EUG180	1.4	2.6	2.9	0.7	4.3	13.7	0.6	0.1	0.7	17.6	0.5	0.7	1.1	4.4
EUE765	8.9	2.7	2.5	2.0	5.3	19.5	1.0	0.2	2.1	7.2	1.1	0.5	5.4	47.6
				As	B	Ba	Bi	Cd	Co	Cr	Cu	Hg	Mo	Ni
EPP357	0.16	4.2	4.0	5.9	0.9	2.3	5.9	5.9	2.0	5.9	5.9	5.9	5.9	1.0
ETD297	0.55	4.7	6.9	5.1	2.4	0.7	4.5	0.4	0.1	6.0	0.5	6.0	10.8	0.0
EUG180	1.4	2.6	2.9	1.5	2.3	11.5	6.1	0.6	0.6	0.9	0.9	4.7	4.7	0.7
EUE765	8.9	2.7	2.5	1.6	9.7	68.5	5.5	1.6	0.9	1.4	1.5	5.3	5.3	1.6
				Pb	Sb	Se	Sn	Sr	Th	Ti	Tl	U	V	Zn
EPP357	0.16	4.2	4.0	5.9	4.7	4.9	5.9	0.2	5.9	5.9	5.9	5.9	5.9	2.8
ETD297	0.55	4.7	6.9	6.0	6.7	0.8	6.0	0.3	4.5	6.2	6.0	5.8	6.0	0.3
EUG180	1.4	2.6	2.9	4.7	5.3	1.2	4.7	1.6	0.6	4.7	4.7	0.9	1.1	0.7
EUE765	8.9	2.7	2.5	5.3	5.5	8.5	5.3	12.2	2.6	5.3	5.3	2.7	1.7	1.3

Notes:

[1] Grey shading indicates ratios for parameters leaching close to or below analytical detection limits in both test methods. For an equivalent analytical detection limit, where the detection limit is adopted for the calculation, the calculated release rate for an HCT will be five times that for an AMIRA column (due to the weekly versus 4-weekly rinse frequency, and accounting for the different rinse volumes involved)

Elements not unduly affected by proximity to detection limits in general indicated the following:

- Reasonable agreement was observed between the two methods with HCT:AMIRA ratios often between 0.5 and 2 (i.e. rates were within a factor of two) for many elements.
- For sample ETD297, ratios were often less than 0.5, suggesting a significantly greater release rate from the AMIRA test. Note that the AMIRA test was acidic, whilst the HCT was circum neutral.
- Ca (and Mg, except for sample EUE765) release was consistently greater from the AMIRA columns, by a factor of between 3 and 10 (i.e. giving ratios between 0.1 and 0.3). This may be indicative of a temperature response. However, systematic temperature effects are not evident for other elements, and therefore an alternative explanation such as the influence of salinity is considered more likely.

- K and Si release rates from the two methods were in reasonable agreement for the lower sulfide content materials, but were greater in the HCT for higher sulfide materials. For the higher sulfide materials, the behavior may reflect a combination of incomplete rinsing of products from the AMIRA test, and/or the influence of solubility constraints.

CONCLUSIONS

Relative Merits of the Two Methods

The AMIRA and HCT methods showed the same broad trends, and equivalent release rates were observed. It should be noted however that most of the materials tested contained little or no effective neutralizing capacity, and leachates were mostly acidic.

The sample that contained available neutralization capacity, ETD297, yielded different pH profiles for the two methods; the HCT remained circum neutral over a testing period of 92 weeks, whilst the AMIRA test yielded acidic conditions after 40 weeks. The differing pH trends were interpreted as evidence that, for the higher solute and acidity concentrations expected during an AMIRA rinse event, (carbonate) neutralization is consumed or dissolved at a comparatively higher rate, and is more easily 'overwhelmed' (or armoured be secondary minerals), than is the case for more dilute leachates and higher frequency of flushing that occur for the HCT method. This interpretation may explain the differing pH profiles obtained for the ETD297 sample, and also the observation that Ca and Mg release is consistently greater for the AMIRA methods than for the HCT method. This difference in test outcomes has important implications with respect to utilization of the results for water quality predictions.

In terms of operational performance, the following is noted:

- Release profiles calculated from the AMIRA method tended to show a greater degree of variability than for the equivalent HCT method – interpreted as an increased sensitivity to the efficiency of leaching during individual rinse events.
- Leaching of pre-existing soluble salts (where present) was completed in a shorter time frame in the HCT – due to the more frequent rinsing regime.
- Limits of detection were encountered more often for the HCT method. For slow reacting samples, the AMIRA method facilitated collection of quantitative release rates for a wider range of elements when compared to the HCT methodology.

Implications for Data Utilization in Water Quality Prediction

Generally, trends in kinetic test datasets are used to examine relationships between sample properties (e.g. sulfur content) and oxidation rates, and to build confidence in conceptual models of processes controlling solute release. The current dataset showed that for acidic operating conditions, both test methods generated similar trends, and produced approximately equivalent datasets for use as a basis for estimating potential seepage quality from acid generating materials.

Leachate pH is a key influence on many geochemical processes, and an important aim of kinetic testing is to gain insight to the effectiveness and availability of neutralization capacity present, and facilitate estimation of times to the onset of acidic conditions. The different trends shown by sample ETD297 have important implications; the AMIRA method and the HCT gave different test outcomes, and led to differing conclusions with respect to the timescale, or even the likelihood, that acid conditions would develop in waters contacting this material type. The main cause of the discrepancy is interpreted to be a

comparatively high consumption of neutralization capacity in the more saline AMIRA leachate environment.

The climate in the Pilbara is arid, characterised by hot summers with periodic heavy rain and mild winters with occasional rain. In a full scale waste rock facility, time periods between 'rinse' events may be long, and the volumes of water involved low. Thus, contact waters would be expected to be saline. It is possible therefore that the outcomes from the AMIRA method could be more representative of neutralization behavior in a larger scale facility.

The current study included only one sample that allowed insight to the effectiveness of neutralization processes in the tests. Also, the internal variability for each of the test methods (i.e. effects of subsample variability, method variability, flushing efficiency etc.) has not been established for either method. Further work, on sample types known to contain effective neutralization capacity, would be necessary to develop a more robust understanding of neutralization processes, and their effectiveness, as a function of leachate salinity.

ACKNOWLEDGEMENTS

REFERENCES

AMIRA AMIRA International Limited (2002), ARD Test Handbook: Project P387A Prediction and Kinetic Control of Acid Mine Drainage, May 2002.

Green, R. and Borden, R.K. (2011) Geochemical risk assessment process for Rio Tinto's Pilbara iron ore mines, Integrated Waste Management – Volume I (Ed. Sunil Kumar), 365-390. ISBN 978-953-307-469-6.

International Network for Acid Prevention (INAP) (2009) Global Acid Rock Drainage Guide (GARD Guide) - http://www.gardguide.com/.

MEND (2009), Prediction Manual for Drainage Chemistry from Sulphidic Geologic Materials. Report 1.20.1, December 2009