Acid Generation from Alunite and Jarosite Bearing Materials

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Abstract

Weathering products from sulphide oxidation include the aluminium and iron hydroxy-sulphate minerals, alunite and jarosite. Dissolution of these minerals, if coincident with precipitation of iron and aluminium hydroxides can result in acid generation. Due to their low solubility, acid production would be slow for the expected rates of water flux through waste landforms and slower than acid production from oxidation of primary sulphide minerals.

Results from leach studies have been investigated using geochemical modelling techniques; solubility controls were identified and aluminium and iron activity diagrams generated.

Conclusions from the work include:

- Alunite and jarosite dissolution has an important influence on the pH of contacting waters. In materials that contain negligible neutralising capacity, final pH values can be as low as 4.
- The most acidic pH values often coincide with the relationship between alunite and jarosite dissolution and precipitation of relatively crystalline hydroxides (gibbsite and crystalline $Fe(OH)_3$). If the aluminium and iron solubility is controlled by an alternative, more soluble phase (e.g. boehmite, amorphous $Fe(OH)_3$), final pH values are near-neutral.

Management of wastes containing hydroxy-sulphate minerals should include co-disposal with materials that contain neutralising potential and/or strategies that reduce the water flux through the wastes. This will minimise the flux of acid and contaminants that can be released from hydroxy-sulphate minerals.

Key Words: hydroxy-sulphate, dissolution, solubility, geochemical modelling.

Introduction

Common secondary products after sulphide oxidation include a range of more soluble (e.g. gypsum) and less soluble (e.g. alunite and jarosite) sulphate minerals. Some of these sulphate mineral products represent stored acidity. For example, alunite and jarosite dissolution can be expressed by the reaction given below:

$$KM_3(OH)_6(SO_4)_2\ [solid] \rightarrow K^+ + 3\ M^{3+} + 6\ OH^- + 2\ SO_4^{2-} \quad (1)$$

where M is Al^{3+} or Fe^{3+} for alunite and jarosite, respectively. Aluminium or iron released by the dissolving alunite or jarosite may precipitate, for example, as gibbsite or ferrihydrite:

$$3\ M^{3+} + 6\ OH^- + 3\ H_2O \rightarrow 3\ M(OH)_3\ [solid] + 3\ H^+ \quad (2)$$

Combining Reactions (1) and (2) gives an overall net acid-generating reaction:

$$KM_3(OH)_6(SO_4)_2\ [solid] + 3\ H_2O \rightarrow 3\ M(OH)_3\ [solid] + 3\ H^+ + K^+ + 2\ SO_4^{2-} \quad (3)$$

The stratigraphical sequence in the Pilbara, Western Australia, includes shale (including black shale) and lignite lithologies, both of which are known hosts for sulphide mineralisation (Green and Borden, 2011). Some portions of the sequence are oxidised, and a range of sulphate reaction products have been observed. This paper describes results from kinetic tests conducted on Pilbara materials that contained low quantities of sulphide, but significant quantities of the secondary sulphate product, alunite. These tests have given valuable insights to the potential range of pH in water contacting such wastes.

Discussion of results from the kinetic testing has been augmented by a review of static leach extract data made available by Rio Tinto Iron Ore (RTIO). RTIO has a large database of short-term (static) leach extract results collected over a period of many years during ongoing geochemical characterisation programmes. Results relate to many rock types, from a range of operations across the Pilbara. Typically the extracts are based on analysis of solutions after a solid/de-ionised water contact test at a ratio of 1:2.

Methods and Materials

Samples

One sample of black shale (Mount McRae Shale (MCS)) and three samples of iron-rich materials (two from the Dales Gorge Member and one from the Whaleback Shale Member) were assessed. The samples were sourced from drill cuttings (using a reverse circulation percussion method). Following rough-crushing, dry sieving indicated that more than half the particles (by weight) were less than 1 mm in size.

Kinetic Test Method

The kinetic leach test method was based on the AMIRA free draining method (AMIRA, 2002), which is designed to measure rates of sulphide oxidation. In summary, the AMIRA method involves placing a sample of crushed rock on a mesh in a free-draining container and subjecting it to periodic leaching with a known volume of de-ionised water. The sample is leached every four weeks, and is moistened by the addition of a small volume of de-ionised water during the intervening weeks. Heat lamps are applied at regular intervals to ensure the sample dries out between solution applications. After each leach cycle, the leachate draining from the sample is collected and analysed.

In the current work, modifications to the standard free-draining method included:

- An initial rinse-phase. Sufficient volume of deionised water was used to remove pre-existing soluble salts.
- Changes to the time period between leach events. For most of the test duration, leaching was every four weeks as per the procedure. However, additional leach events were included at certain points during the tests to investigate the influence of shorter elapsed times between leach events.
- Changes to the water/rock contact time. At the end of the tests, the final leach solution was re-circulated a number of times through the material. By re-circulating the leachate, the contact time between the solution and the sample was increased. This re-circulation step was undertaken to assess whether slow dissolution of less readily soluble minerals could limit the mass of solute leached during individual leach events.

The kinetic tests were operated by Graeme Campbell and Associates Pty Ltd with analytical support from SGS Australia Pty Ltd and Genalysis Laboratory Services Pty Ltd.

Geochemical modelling

Geochemical modelling was undertaken using PHREEQC Interactive, Version 2.12.5.669 (Parkhurst and Appelo, 1999). Thermodynamic data used were those contained in the HATCHES thermodynamic database, NEA v19 (Bond *et al.*, 1997). Supplemental data for K-jarosite were based on information given in Baron and Palmer, 1996. Alunite dissolution was based on data provided in 'phreeqc.dat', one of the databases distributed with PHREEQC.

Results

Sample Characteristics

The mineralogical composition of the samples is given in Table 1. Some acid-base accounting properties are summarised in Table 2. The total sulphur content of the samples ranged from 0.4 to 2.21 wt%; most of the sulphur was present in the form of alunite. Mineralogical investigation (X-ray diffraction) did not identify sulphide minerals in any of the samples, and the chromium-reducible sulphur results confirmed that the sulphide-sulphur content of the samples was low.

The soluble sulphate component of the sample was determined by a hydrochloric acid (HCl) digest and was very low in comparison to the alunite content estimated by X-ray diffraction. This would suggest that the alunite was relatively insoluble in HCl. This is significant because it suggests that routine acid-base accounting testwork may underestimate the sulphate sulphur content of samples when alunite (or jarosite) is present. In the case of the MCS sample, even the more aggressive *aqua regia* digest (expected to target all sulphur species excepting organic, and possibly elemental sulphur) did not dissolve much of the alunite. Under the very acidic conditions of both these digests, the observed very low solubility of alunite is counter to expectation. As will be discussed later in this paper, slow reaction kinetics are not believed to play a role. Possibly alunite solubility is suppressed by, for example, high dissolved potassium in the digest solutions.

X-ray diffraction (XRD) appears to be the most reliable method for determining the presence of less soluble sulphate minerals such as alunite (and by analogy, jarosite). However, it should be noted that XRD detection limits are relatively high (approximately 1 wt%). Thus, low quantities of these minerals may go undetected.

Table 1: Summary of Sample Mineralogy

Mineral	%	EAW096	EAW152	EAW153	WS1AVES
		Black MCS	DG (Ore)	DG (Waste)	WS
Amorphous/unknown Content	%	29.5	2.1	8.5	0.1
Quartz	%	51.0	0.3	0.6	1.3
Hematite	%	7.3	37.5	22.8	44.7
Goethite	%	-	59.0	55.8	49.6
Alunite	%	12.2	1.1	7.8	4.3
Kaolinite	%	-	-	4.5	-

DG – Dales Gorge Member; MCS – Mount McRae Shale; WS – Whaleback Shale Member

Table 2: Summary of Sample Acid-Base Accounting Properties

SAMPLE ID	Units	EAW096	EAW152	EAW153	WS1AVES
Sample types		**Black MCS**	**DG (Ore)**	**DG (Waste)**	**WS**
Acid neutralising capacity	kg(H_2SO_4)/t	2.7	<0.5	<0.5	<0.5
Total S (Leco)	%	2.21	0.4	1.52	0.4
Soluble sulphate sulphur[1]	%	0.15 (0.27)	0.18	0.20	0.08
Alunite sulphur (calculated from XRD)[2]	%	1.89	0.17	1.21	0.67
Sulphide S (total S minus soluble and alunite sulphur)	%	0.17	0.05	0.11	<0.01
Sulphide S (Cr-reducible)	%	<0.02	0.01	0.012	n.m.
Acid Potential[3]	kg(H_2SO_4)/t	5.2	1.5	3.4	<0.1
NAG pH	pH Unit	6.3	3.9	3.7	4.4
NAG (pH 4.5)	kg(H_2SO_4)/t	<0.1	0.8	1	<0.1
NAG (pH 7.0)	kg(H_2SO_4)/t	1	3.8	4.3	4.2
Net Acid Producing Potential[3]	kg(H_2SO_4)/t	2.5	1.0	2.9	-
Neutralisation Potential Ratio[3]	-	0.5	0.3	0.1	-

NAG – Net Acid Generation; DG – Dales Gorge Member; MCS – Mount McRae Shale; WS – Whaleback Shale; n.m. = not measured

Note : [1] HCl digestible sulphur (*aqua regia* digestible sulphur)

[2] Calculated from the alunite content using an S/alunite mass ratio of 0.155

[3] Calculated based on the larger of the two estimates of sulphide sulphur content

Leachate pH and sulphate release

Figure 1 shows the kinetic test leachate pH, plotted as a function of time for the four samples tested. Only the black MCS sample contained measureable neutralising potential (2.7 kg(H_2SO_4)/t). The leachate pH from this sample remained near-neutral throughout the test, typically between pH 6 and 7.5. The leachate pH of the other samples stabilised at approximately pH 4 to 4.5. The leachate pH was not influenced significantly by either the frequency of leach events, or the 'duration' of water/rock contact, suggesting equilibrium conditions had been achieved.

Figure 2 shows dissolved sulphate concentrations in the leachate plotted as a function of time. The higher initial sulphate concentrations represent the flushing of soluble sulphate salts from the samples. Based on geochemical modelling some of this sulphate was sourced from the dissolution of gypsum as the Week 0 leachate for the black MCS sample was assessed as close to equilibrium with respect to gypsum. [Note that the mass of sulphate leaching in early column rinses for this sample is in excess of that expected based on the sample characteristics given in Table 2. According to Table 2, all four samples had similarly low quantities of soluble sulphate. In the case of the black MCS sample, we believe that the sub-sample used for kinetic testing had higher soluble salt content than the sample used for the static testing]. The other leachates shown in Figure 2 were under-saturated with respect to gypsum. Soluble sulphates are expected to leach completely during the initial leach cycles explaining the decline in dissolved sulphate concentrations with time.

In later stages of the tests, there are two possible sources of sulphate:

- Sulphate derived as a product of oxidation of sulphide in the samples. Between leach events, the samples are maintained in a moist, aerated condition and any sulphides present would oxidise, resulting in the accumulation of sulphate reaction products.
- Sulphate derived from dissolution of alunite present in the sample. Although relatively insoluble, some limited amount of dissolution would be expected to occur during each leach event.

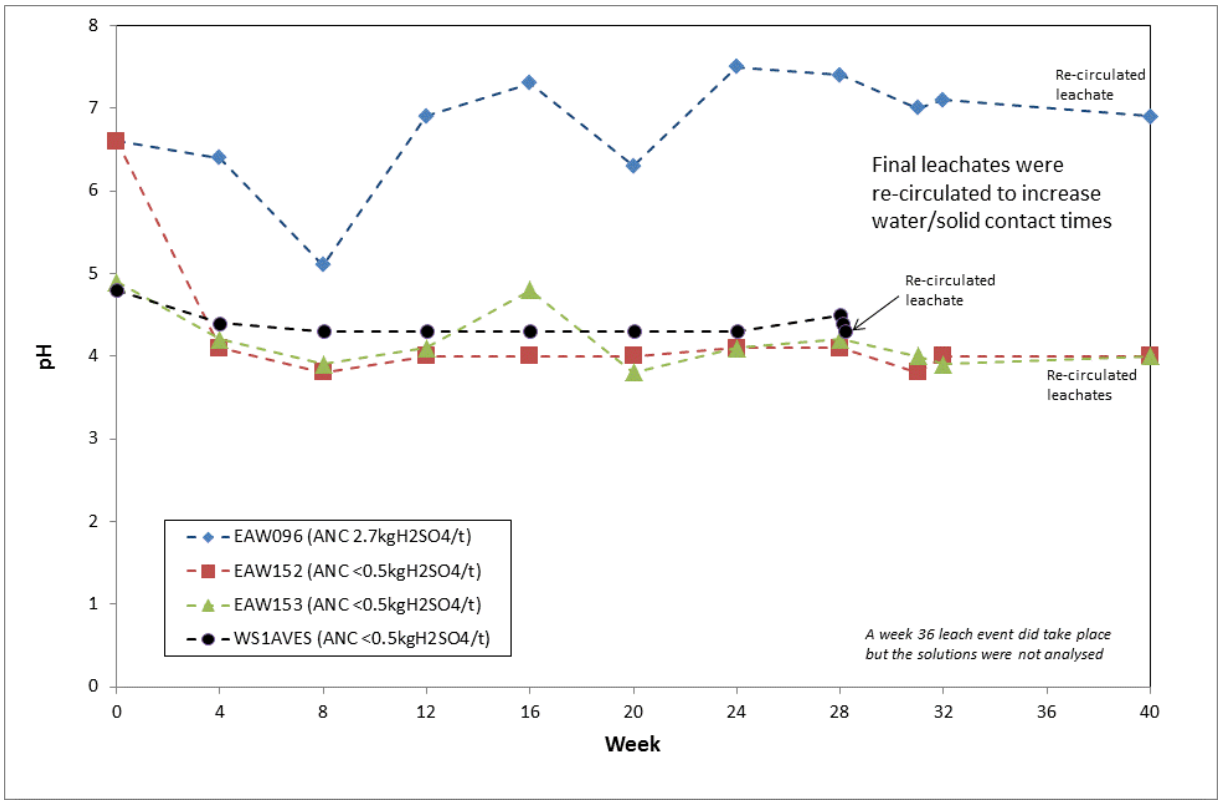

Figure 1: Leachate pH, as a function of time

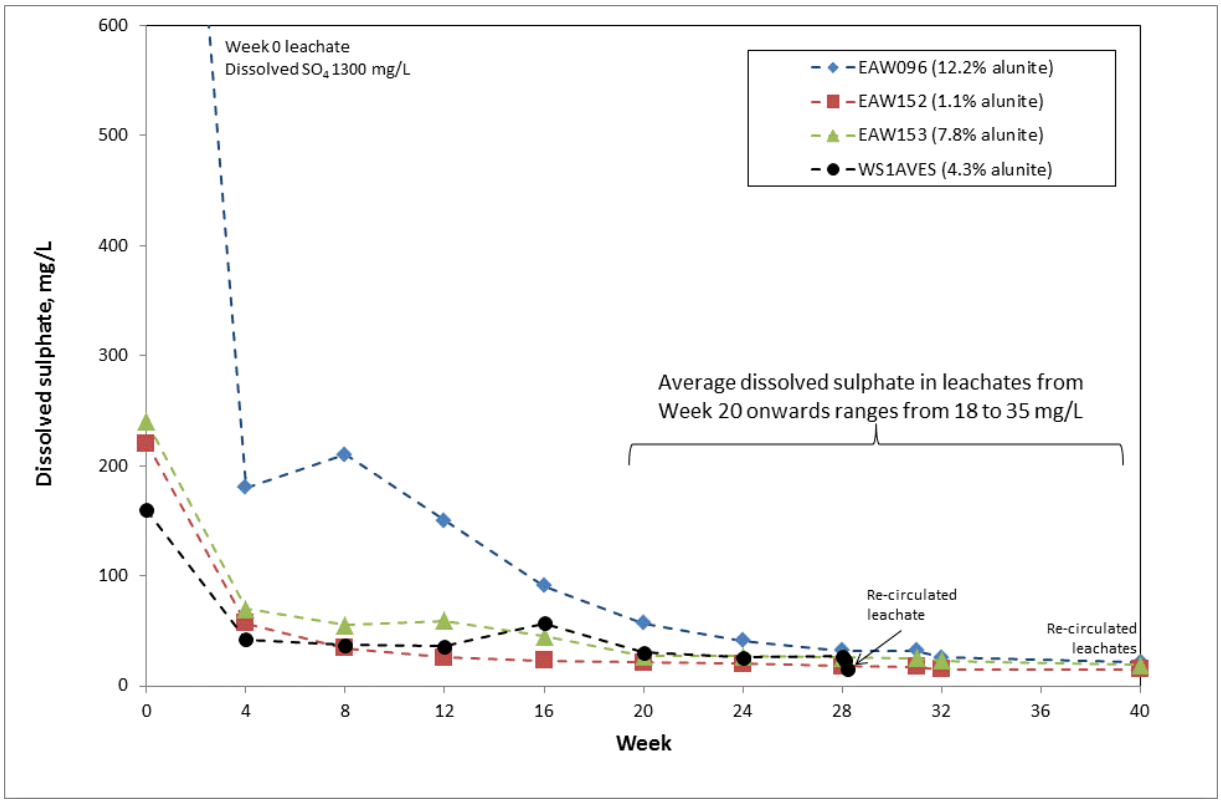

Figure 2: Dissolved sulphate in leachate, as a function of time

The samples contained very low to negligible sulphide (Table 2) and the main source of sulphate in the late stage leachates is alunite dissolution. This conclusion is supported by the observation that the mass of dissolved sulphate in the leachates did not fluctuate in response to variation in the leaching frequency, indicating equilibrium conditions rather than time dependent sulphate generation from oxidation reactions. Generally, leaching events took place at four weekly intervals (Figure 2). In three tests (EAW096, EAW152 and EAW153) an 'extra' leaching event took place during Week 31, introducing a different leaching interval before and after this event (three weeks and one week, respectively). In the fourth test (WS1AVES), during Week 28, a series of three leach events took place. The first event was the normal four-weekly leach. Immediately following drain-down of the first leach solution, a second leach event was performed, and the leachate collected for analysis. Finally, a third leach event was performed involving re-circulation of the leach solution. Had sulphide oxidation been the dominant control on sulphate production in the tests, the mass of sulphate accumulated (per kg sample) would be influenced significantly by the time interval that had elapsed between leach events. As shown in Figure 2, only very modest reductions in the dissolved sulphate were observed after short elapsed time intervals.

Alunite dissolution in the tests did not appear to be influenced by slow reaction kinetics. The dissolved sulphate concentration did not increase for increased water contact times as would be expected for a kinetically controlled reaction. Dissolved sulphate concentrations in all the kinetic tests reached a steady level in the relatively narrow range of 15 to 35 mg/L, irrespective of the mass of alunite present in the sample. Alunite has a low solubility under the test conditions with the dissolution of only 5 to 9 mg sulphate (per kg sample) (equating to between 0.001 to 0.002 wt% alunite).

Minor and trace element release

Dissolved concentrations of selected minor and trace elements in the leachates are summarised in Table 3. The initial rinse (Week 0) is generally coincident with higher minor and trace element concentrations than later leachates, suggesting that soluble salts represent a possible source of these elements in the short-term.

Although it is possible that pure minor element salts were present, it is more likely that minor elements were incorporated within major element salts, perhaps as impurities or having substituted for one of the major components (a solid solution). It is notable that the black MCS sample (EAW096), which contained the highest quantity of soluble sulphate (probably gypsum), also had the highest short-term release of elements such as arsenic, barium, molybdenum, selenium and strontium. Release of some of these elements could be linked to the dissolution of a potential host sulphate salt such as gypsum. Arsenic, molybdenum and selenium are chemically analogous to sulphur and could substitute for sulphate. Barium and strontium are chemically analogous to calcium and could also be incorporated in the gypsum matrix, or be present as sulphate minerals in their own right (e.g. geochemical modelling suggests that barite, $BaSO_4$, is close to equilibrium in some of the leachates).

Alunite and jarosite may also represent sources of minor and trace elements. Both minerals have the general formula $AB_3(XO_4)_2(OH)_6$, and are known to form complex solid solutions (Dill, 2001). In the formula, 'A' sites are occupied by large cations such as Na, K, U, Pb, alkaline earths, or rare earth elements and 'B' sites are occupied by cations of the elements, Fe, Al, Cu and Zn. The 'X' in the anionic component XO_4^{x-} is dominated by S or P. Given the low solubility of alunite observed in these tests, it is expected that dissolved concentrations of trace components will be maintained at very low levels. .

Other potential sources of minor and trace elements in the leachates include iron oxide and clays, and oxidation of trace sulphide minerals. Both oxide and clay mineral groups can incorporate these elements as impurities, and have a strong potential to adsorb elements via surface interactions. Changes in solution conditions, in particular decreasing pH, may lead to release of adsorbed solutes (desorption of cationic species, possibly combined with dissolution of the adsorbent itself). This may be the case for elements such as cadmium, cobalt, zinc and uranium – all of which tend to show higher concentrations in the more

acidic long-term leachates. Elements such as arsenic, molybdenum and selenium, which tend to form negatively charged oxyanions under oxic conditions tend to sorb more strongly under acid conditions, possibly explaining the lower concentrations of these elements in the acidic long-term leachates.

Table 3: Sulphate, pH and minor and trace element concentrations in kinetic test leachates

	Initial rinse leachate concentration, mg/L (Week 0)				**Average leachate concentration, mg/L (Week 20 onward)**			
	EAW096	**EAW152**	**EAW153**	**WS1AVES**	**EAW096**	**EAW152**	**EAW153**	**WS1AVES**
pH	6.6	6.6	4.9	4.8	7.0	4.0	4.0	4.4
SO_4	1300	220	240	160	35	18	25	24
Al	<0.01	0.14	0.31	0.07	<0.01	1.08	1.27	0.07
As	0.02	0.002	0.003	0.005	0.002	0.0003	0.0002	0.0008
Ba	0.02	0.009	0.001	0.01	0.04	0.006	0.001	0.009
Cd	0.0002	0.0008	0.0005	0.00005	0.0001	0.001	0.002	0.0001
Co	0.008	0.002	0.003	0.001	0.0003	0.002	0.003	0.0007
Cu	<0.01	0.02	0.02	0.01	<0.01	<0.01	<0.01	<0.01
Fe	<0.01	0.06	0.08	<0.01	<0.01	0.07	0.12	0.02
Mo	0.0003	0.00007	0.00007	<0.00005	0.001	<0.00005	<0.00005	<0.00005
Ni	0.03	0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	<0.0005	0.008	0.004	0.001	0.001	0.001	0.0009	0.001
Sb	0.0001	0.0002	0.00006	0.00007	0.00006	0.00003	0.00001	0.00003
Se	0.2	0.002	0.004	0.006	0.009	0.0006	0.0006	<0.0005
Sr	0.2	0.1	0.02	0.2	0.03	0.01	0.003	0.06
U	0.00001	0.0001	0.0002	0.0001	0.000004	0.0002	0.0002	0.0001
Zn	0.1	0.1	0.07	0.02	0.02	0.04	0.03	0.02

Discussion

Alunite dissolution and influence on pH of contacting waters

In the three kinetic tests that contained negligible acid neutralising capacity (EAW152, EAW153 and WS1AVES), the leachate pH stabilised in the range pH 4 to 4.5. Figure 3 shows an aluminium activity diagram for aluminium in the leachates. The diagram shows mineral solubility expressed as a function of the activity of the Al^{3+} aqueous species. For simplicity, other aluminium aqueous species are excluded from the diagram. PHREEQC was used to calculate Al^{3+} activities in each leachate solution.

The majority of the results cluster close to the point where alunite and gibbsite solubility coincide. Note that the theoretical lines shown in the diagram should be considered as indicative only. Their positions on the figure are based on thermodynamic equilibrium constants usually derived for pure phases. The minerals forming in the tests may not be pure solids and accordingly, their solubility may be higher or lower than that indicated by the theoretical lines.

The tendency of the data to form clusters is consistent with the hypothesis that the pH is being controlled by the relationship suggested by Reaction (3) (see Introduction). In WS1AVES, the cluster is displaced slightly towards a higher pH (pH 4.5) and lower Al^{3+} activities, possibly suggesting a different aluminium hydroxide solubility in this sample (alternatively, a possible iron hydroxide influence on pH is discussed

in the next section). Results outside the clusters correspond to concentrations in the early leachates, and could indicate that gibbsite ($Al(OH)_3$) does not precipitate immediately.

The black MCS material (EAW096) contained a small amount of neutralising capacity (2.7 (kgH_2SO_4)/t) and pH in this test remained near-neutral. In some leach events, no dissolved aluminium was detected in the leachate. For leachates with detectable aluminium, the results plot close to the theoretical line for control by boehmite (AlOOH) solubility. These leachates were calculated to be over-saturated with respect to gibbsite. The 'clustering' is not as strong as for the other tests, although it is the case that the results are located proximal to where alunite and boehmite solubility coincide. The pH in this test may be influenced by interaction between alunite and boehmite. However, equally, an alternative process could control pH, e.g. carbonate neutralisation. It was noted that the $(Ca+Mg)/SO_4$ molar ratios in leachates from this test were in the range 1 to 2 (the bounding ratios expected for utilisation of carbonate buffering capacity).

The calculations suggest that aluminium hydroxide is more soluble in the black MCS test. Currently no unequivocal explanation exists for increased solubility. Possibly, solubility is affected by the pre-existing mineral content of the materials – new phases nucleate on existing mineral grains. The black MCS is dominated by quartz, whilst the other three samples are dominated by iron oxides (goethite and hematite).

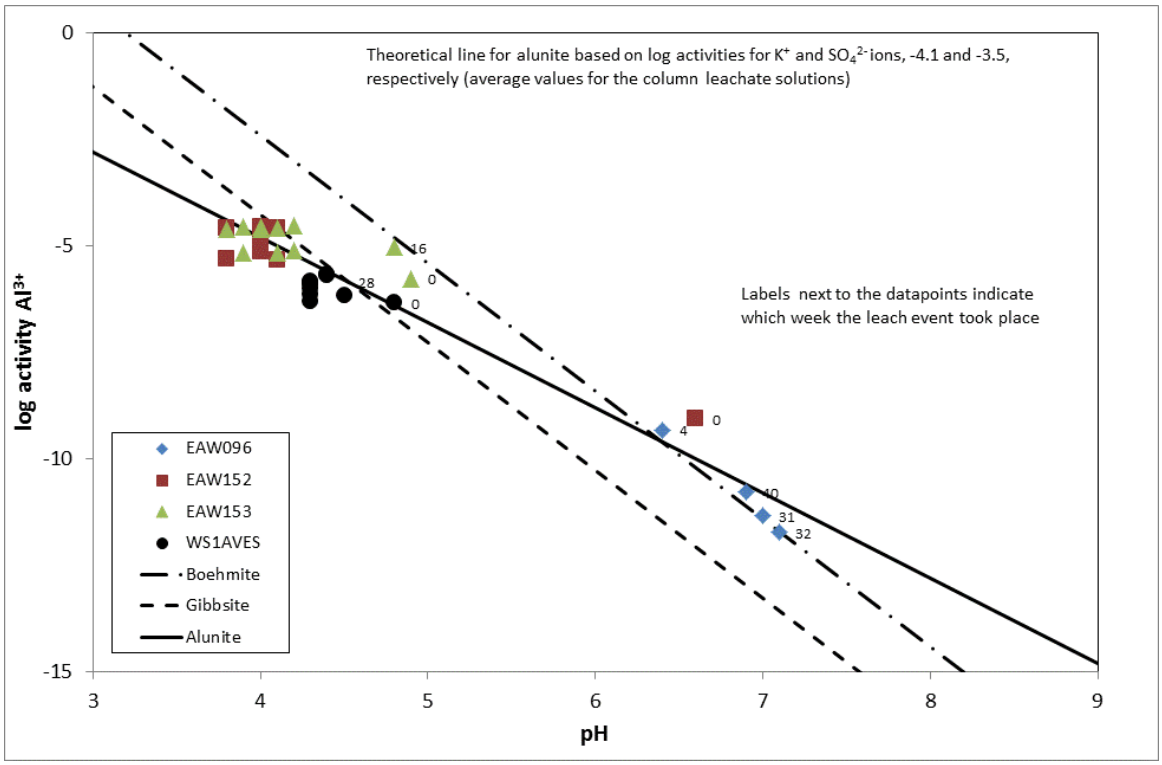

Figure 3: Leachate data plotted on an aluminium activity diagram (at 25°C)

Within the RTIO static leach extract test database there are also a significant number of test results that extend into the acidic pH range (less than 4). It is possible that alunite could be present in many of the samples tested and that in some cases, the pH is controlled by the alunite/gibbsite relationship. Figure 4 shows the aluminium activity diagram for the RTIO short-term (static) leach extract database (the kinetic leach test results are also shown for comparison). The results shown are limited to samples with low total

sulphur contents (less than 0.1 wt%). A range of lithological types are represented, including shales, banded iron formation rocks and samples from the overlying detrital formations.

The majority of the solutions are in the pH range 6 to 8, and the results plot close to or above the boehmite (AlOOH) solubility line. [The number of data points plotting above the boehmite line could suggest that a more soluble phase may control aluminium solubility in the materials. Alternatively, aluminium could be present in fine particulate (colloidal) form rather than as a dissolved species – which would also explain the degree of scatter shown by the data points when compared to the slope of the boehmite line.] In these tests it is assumed that excess neutralising capacity is available to maintain a neutral pH (as discussed for the kinetic test results).

The remainder of the data involve solution pH values in the acidic range. In these tests, there would be little or no neutralising capacity. The results for these samples are in reasonable agreement with the kinetic test results and would support the conclusion that alunite/gibbsite interactions can lead to acidic contact water, for cases where no neutralising capacity is available.

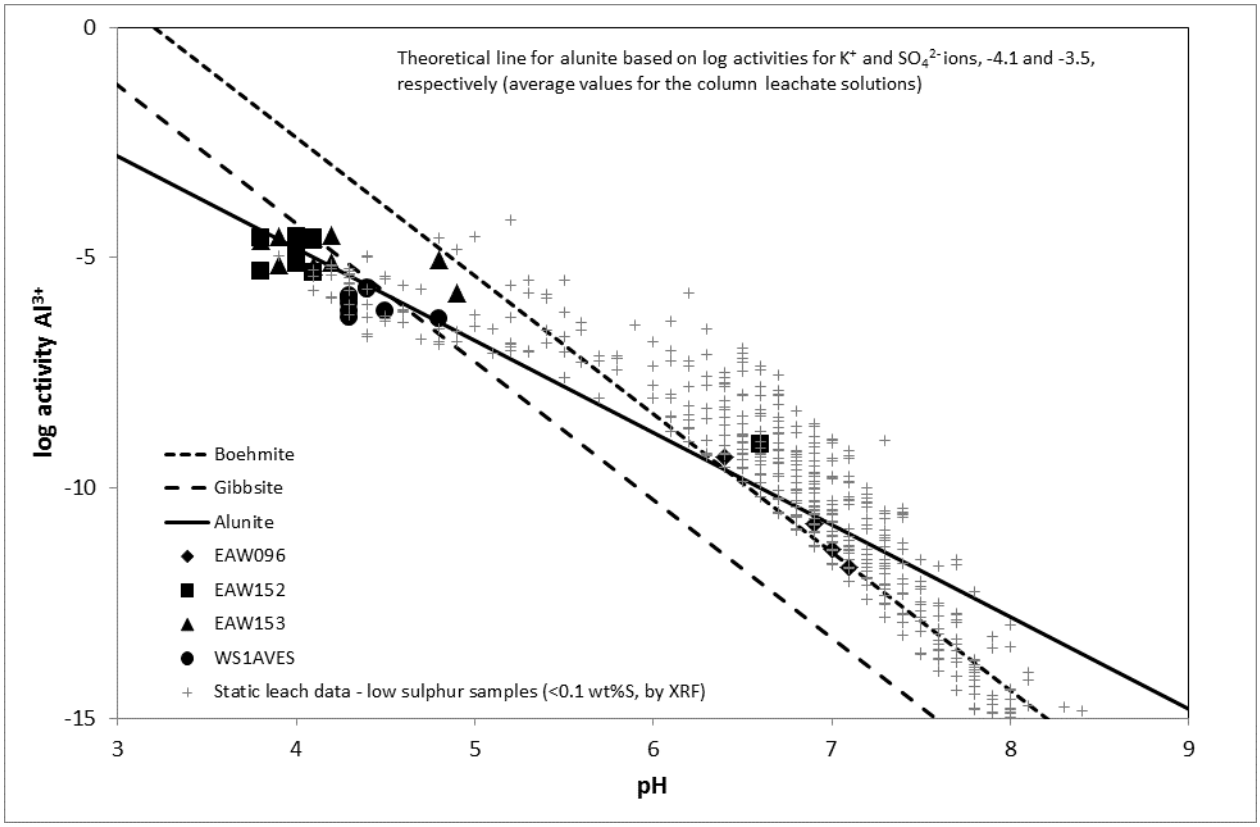

Figure 4: Static leach data compared to the leachate data, on an aluminium activity diagram (at 25°C)

Given that alunite dissolution can result in acidic leachate conditions, alunite-sourced acidity should be considered when estimating the acid potential of the sample. Based on the stoichiometry of Reaction (3) (see Introduction), the maximum acidity that would be generated from a sample containing 1% alunite-sulphur would be 22.9 kg(H_2SO_4)/t (i.e. 2 moles of sulphur (in alunite) give rise to 1.5 moles H_2SO_4 and 0.5 moles of the non-acidic K_2SO_4 salt). Table 4 compares estimates of sulphide-sourced and alunite-sourced acid potential for the samples.

Table 4: Comparison of Acid Potential Estimates

SAMPLE	Units	EAW096	EAW152	EAW153	WS1AVES
Sample types		Black MCS	DG (Ore)	DG (Waste)	WS
Acid Potential (Sulphide-sourced)[1]	kg (H_2SO_4)/t	5.2	1.5	3.4	<0.1
Acid Potential (Alunite-sourced)[2]	kg (H_2SO_4)/t	43.3	3.9	27.7	15.3
Total Acid Potential	kg (H_2SO_4)/t	48.5	5.4	31.1	15.3

DG – Dales Gorge Member; MCS – Mount McRae Shale; WS – Whaleback Shale Member.

Notes:

[1] Based on the sulphide S estimate given in Table 2 (total S minus soluble and alunite sulphur).

[2] Using the alunite sulphur estimate given in Table 2, and multiplying by a factor of 22.9 (based on the stoichiometry of Reaction 3, as discussed in text).

Accounting for alunite-sourced acid potential leads to significantly higher estimates of overall acid potential. However, due to the low solubility of alunite, the maximum amount of acid release during an individual leach event would be low. Typical equilibrated leachate acidities were low, ranging from 5 to 50 mg($CaCO_3$ eq)/L. The rate of acid release would be restricted by the volume of contact water that passes through the material. Coupled with the low rainfall environment, the rates of release would be very low and the duration of acid generation would tend to extend far into the future.

The role of jarosite

Whilst jarosite was not identified in mineralogical studies of the materials, it is possible that it is present, but at levels too low to be detected by XRD. Figure 5 shows the kinetic test results together with the RTIO static leach extract results (for the same suite of low sulphur content samples shown in the aluminium activity diagram) plotted on an iron activity diagram.

The kinetic test results for EAW152 and EAW153 plot some distance below the jarosite solubility line, and do not show a pH trend consistent with a jarosite solubility control. It is possible that no iron solubility control applies under the conditions of these tests.

The results for EAW096, and the majority of the static leach extractions fall into the near-neutral pH range (pH 6 to 8) and plot close to or above the amorphous $Fe(OH)_3$ solubility line. [As was the case with the aluminium results, the large number of points plotting above the amorphous $Fe(OH)_3$ solubility line could suggest that either (i) a more soluble hydroxide phase controls iron solubility in the materials (which means that jarosite would either not have been present, or would have been unstable under the test conditions and would have transformed to the hydroxide phase), or (ii) colloidal material has contributed to the range of dissolved iron concentrations measured.]

The results for sample WS1AVES, and a portion of the static leach test results, plot along a line consistent with a low solubility K-jarosite ($KFe_3(OH)_6(SO_4)_2$). Some of the results (including the WS1AVES results) cluster close to the point where low solubility K-jarosite and crystalline $Fe(OH)_3$ solubility coincide (at about pH 4.5). The separation of the test results for WS1AVES from the balance of the kinetic test results, together with the supporting static leach test results, may suggest that pH is being controlled by the relationship suggested by Reaction (3) (see Introduction). If jarosite interactions, rather than those of alunite, control pH in the WS1AVES leachate, this may explain the displacement of the WS1AVES 'cluster' on the aluminium activity diagram when compared to the EAW152 and EAW153 results.

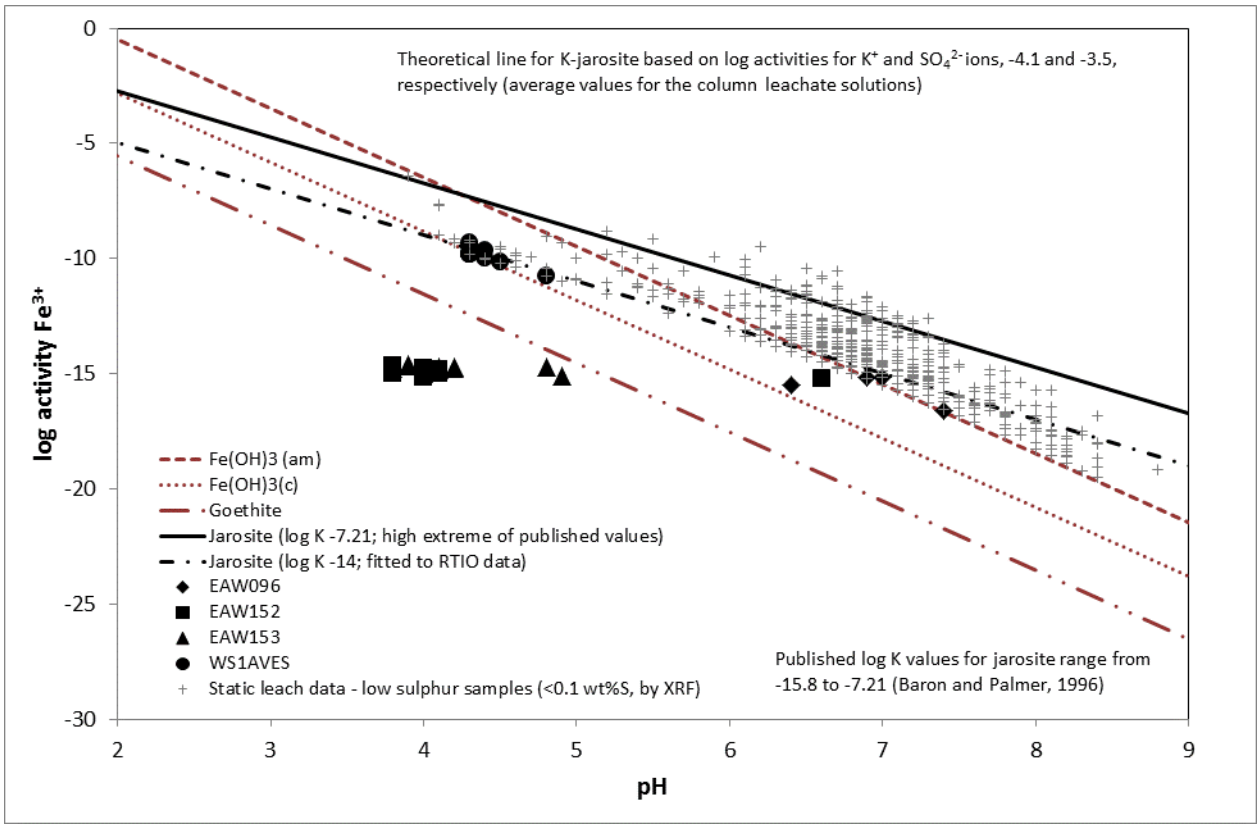

Figure 5: Kinetic and selected static leachate data plotted on an iron activity diagram (at 25°C)

Implications for Waste Management

The kinetic and static leach test results presented herein indicate that low quantities of alunite and jarosite may lead to a risk of acid generation. The magnitude of acid generation, is however, constrained by the low solubility of these minerals. The results indicate that equilibrium conditions are reached relatively rapidly and place an upper bound on the concentration of acidity that would be released (up to about 50 mg($CaCO_3$ eq)/L). The production of acidity would be directly proportional to the volume of water that passes through the material.

Management options that can mitigate risks of poor quality seepage from waste storage facilities containing such materials include:

- Co-disposal of alunite and jarosite-bearing materials with materials known to contain excess available neutralising capacity. For facilities with low water flux (see next bullet point) it may be possible to take additional credit for neutralising potential sourced from slow reacting aluminosilicates.
- Emplacement of covers designed to reduce water flux (e.g. store and release covers). Pore water residence time is not expected to influence acidity and solute loads and thus reducing water flux will reduce the flux of acid to the receiving environment.

It should also be emphasised that when the acid generation potential is based conservatively on the total sulphur content, the most common acid base accounting geochemical characterisation technique used by the mining industry, the sulphur associated with alunite and jarosite is already accounted for in the acid potential calculation. This is also the case if an HCl leach step is used to remove non-acid generating

sulphate minerals such as gypsum. The conclusions of this study do not therefore invalidate historical waste management practices based on common acid base accounting results. Analysis of the data presented in Figures 4 and 5 indicates that, for a 0.1% total sulphur cut-off, a small percentage (6%) of the sample set acidified to a pH of less than 5. Dispersed within any large-scale storage facility, it is expected that the influence of this small proportion of waste on overall seepage water quality would be low to negligible.

Conclusions

The materials discussed in this paper do not contain high levels of sulphides. They do however contain variable amounts of hydroxy-sulphate oxidation products, some of which have been demonstrated to represent a potential source of acidity. Acid and solute release is controlled largely by sulphate and hydroxide mineral solubilities. There is no strong evidence that solubility is subject to kinetic controls, and so acidity and dissolved solute concentrations are unlikely to be influenced by pore water residence times. Acidity release therefore would be constrained to an upper concentration level, and total loadings would be proportional to the water flux through the materials. Risks of poor quality seepage from such wastes can be mitigated by co-disposing the waste with materials known to contain excess available neutralising capacity. Encapsulation to minimise water flux through the facility over time will limit the overall release of acidity.

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List of Acronyms

RTIO – Rio Tinto Iron Ore
XRD – X-Ray Diffraction
MCS – Mount McRae Shale
DG – Dales Gorge
WS – Whaleback Shale