CLASSIFICATION AND MANAGEMENT OF WASTE ROCK FROM IRON ORE DEPOSITS CONTAINING SECONDARY ACID SALTS

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ABSTRACT

The standard approach to Acid and Metalliferous Drainage (AMD) hazard classification is to assume that sulfur is entirely bound in the sulfide minerals pyrite / marcasite, where acidity is released via oxidation. However, particularly in weathered rocks, sulfur may be bound in various minerals, some of which do not generate acid (e.g., gypsum), whilst others generate less acid relative to pyrite via dissolution and re-precipitation (e.g., alunite). Hence, the actual AMD hazard posed by weathered or partially weathered materials (hereafter 'weathered') which contain MPA values dominated by secondary acid sulfate minerals cannot accurately be assessed using total sulfur concentrations alone. These differences in the magnitude and mechanism of acidity release warrant a different approach to classifying and managing 'weathered' PAF (W-PAF) materials.

A range of laboratory-based leaching and dissolution tests were developed to determine whether the AMD hazard posed by W-PAF materials could easily and rapidly be assessed. This included variable leach ratios (1:2 to 1:400), sequential leaching, and titrations with a strong base. These leach tests did not mobilise all the potential acidity due to the low solubility of alunite, and hence such tests are unable to quantify the actual AMD hazard posed by alunite-bearing W-PAF materials.

At BHP's Pilbara Marra Mamba iron ore deposits, Proterozoic materials from above the water table generally have MPA values dominated by alunite-natroalunite, with minor contributions from pyrite in some samples. At these deposits, only a small proportion (i.e., <5%) of the waste rock is classified as potentially acid forming (PAF), due to the presence of alunite-natroalunite, with the remaining (>95%) classified as non-acid forming (NAF). Currently BHP selectively manages W-PAF waste, by encapsulating it with NAF wastes.

To determine if BHP's current W-PAF waste management approach is fit for purpose, and/or identify potential improvements, a series of column leach tests were undertaken. Column leach tests were conducted at two different NAF-PAF ratios (90:10 and 75:25), with column configurations designed to test the relative benefits of different waste disposal configurations in terms of leachate water quality.

It was found that the best leachate quality was obtained from columns where W-PAF or commingled NAF/W-PAF materials were encapsulated with NAF materials. This column leach testwork supports BHP's current waste disposal strategy, where all W-PAF material is encapsulated by NAF material. However, it also suggests that co-mingling of W-PAF and NAF waste would achieve similar leachate quality as the current management approach.

Keywords: AMD/ARD Management, Secondary Acid Salts, Alunite, Column Leach

1.   INTRODUCTION

BHP discriminates 'weathered' from 'fresh' Proterozoic waste rock materials based on their position relative to the current water table. Materials from below the water table (BWT) are assumed to be fresh, and materials from above the water table (AWT) are assumed to be 'weathered'. This distinction is generally supported by mineralogical data, where most samples from BTW have Maximum Potential Acidity (MPA) values dominated by pyrite / marcasite, and most samples from ATW have MPA values dominated by secondary sulfate minerals (e.g., alunite).

The AMD classification system implemented at WAIO deposits uses MPA and Acid Neutralising Capacity (ANC) to calculate Net Acid Production Potential (NAPP) values, which are used to discriminate PAF from Non-Acid Forming (NAF) waste. One of the key assumptions of this classification is that the total S used to estimate the MPA is entirely bound in the acid generating sulfide minerals pyrite / marcasite [FeS_2] (i.e., MPA = Total Sulfur × 30.6). This assumption is likely valid for fresh waste rock. However, it is potentially leading to an overestimate of NAPP values of 'weathered' samples, and therefore overestimating the geochemical hazard, leading to an over-management of waste rock.

Total S generally does not provide a reliable estimate of the MPA of weathered samples (e.g., where sulfur may be bound in other minerals such as alunite or gypsum). Therefore, alternative methods were explored to determine whether other variables could be used in lieu of total S, when the mineralogical composition of weathered waste was not fully understood. An initial investigation was conducted to assess if paste pH could be used to discriminate between NAF and weathered PAF (W-PAF) wastes and quantify the MPA for weathered wastes. However, this testwork showed that paste pH values were controlled by saturation of a low solubility acid-generating mineral. Hence the MPA could not be assessed by the paste pH method.

To resolve the actual Acid and Metalliferous Drainage (AMD) hazard posed by these 'weathered' materials, as well as better understand the mechanisms and magnitude of acidity release, a detailed laboratory leaching program was undertaken. This procedure involved, sequential leaching (up to 1:6), titrations with a strong base (NaOH), high dilution leaching (up to 1:400), and mineralogical analyses of spent (leached) solids (further procedural details provided in Section 2.3.4).

To support refinement of the optimal management strategy for disposal of W-PAF wastes, a preliminary assessment was undertaken (via bottle roll tests), to test whether comingling W-PAF with the significantly larger mass of NAF wastes could potentially be a viable management option. Larger scale column leach tests were then established to identify the optimum waste disposal configurations for the management of poor water quality from W-PAF waste materials and provide more accurate constraints on expected leachate chemistry.

2.   METHOD

2.1.   Sample Selection and Existing Geochemical Data

Nine waste rock samples, statistically representative of weathered waste, were subject to leaching and dissolution tests. These samples were selected from an extended assay database, and hence their static geochemical properties were well constrained (e.g., paste pH and EC, major and trace element geochemistry, NAG suite, ANC, total carbon, sulfur, sulfate, and sulfide). All samples were derived from <50 meters depth (i.e., AWT) at a Marra

Mamba iron ore deposit currently mined by BHP. The samples covered a range of total sulfur concentrations (0.08 – 1.5 wt.%) and all returned paste pH values <4.5 during the previous phase of testwork (i.e., potentially classifiable as PAF).

2.2.   Static Geochemical Characterisation

The samples subject to the leaching program were analysed for the additional parameters listed below.

- High precision Quantitative X-Ray Diffraction (QXRD). This provides full speciation of carbon and sulfur bearing minerals, which can be used to independently calculate acid base accounting parameters (ANC, MPA, and NAPP values). In addition, QXRD analyses were performed on solids before and after leaching to resolve subtle changes in a sample's mineralogy due to mineral dissolution.

- Sulfur speciation via laboratory based selective chemical extraction, including S_{HCl}, S_{KCl} and pH_{KCl} (to supplement available total sulfate and S_{Cr} data). These parameters can provide constraints on the various acid generating and non-acid generating sulfur bearing minerals present.

- Acid Neutralising Capacity (ANC). Whilst ANC values measured by BHP were available for these samples, the ANC concentrations were re-analysed (by ALS) for independent verification.

2.3.   Estimation of MPA Values

2.3.1.   Sequential Leaching

Previous paste pH investigations showed that a 1:2 dilution ratio was insufficient to release the MPA of 'weathered' samples, due to the low solubility of the acidity generating mineral(s). Therefore, the samples were subject to sequential leaching in an attempt to release the MPA and assess the acidity release mechanisms of the samples.

Samples were subject to a 24-hour bottle roll (1:2 dilution ratio). The supernatant water was then decanted and analysed for pH, EC, acidity, major ions (Ca, K, Na, Mg, SO_4, Cl), and dissolved metals and metalloids (Al, As, Cd, Cr, Co, Cu, Se, Fe, Pb, Mn, Ni, and Zn). Following which, the equivalent volume of water removed was replaced with deionised (DI) water, and the 24-h bottle roll repeated. The samples were leached for a total of four cycles yielding total dilution ratios of up to 1:6.

2.3.2.   Sodium Hydroxide (NaOH) Titrations – Laboratory and Modelled

The results of the sequential leaching testwork (see above) indicated that even after sequential leaching the pH was still buffered at weakly acidic values (i.e., the MPA could not have been released). Therefore, it was decided to titrate sample slurries with NaOH, in an attempt to increase the dissolution rate of the acidity generating phase(s) through the introduction of alkalinity. The samples were titrated to a final pH value of 10, and in a separate test to a final pH value of 8. In addition to laboratory-based titrations, the same titrations were modelled using PHREEQC. Modelling provides an additional point of comparison, as unlike the laboratory titrations, the modelling is not limited by reaction kinetics and immediately proceeds to equilibrium.

2.3.3.   High Dilution Ratio Leaching

Finally, non-sequential high dilution ratio leach tests (24-h bottle roll) were conducted. Four leaches were performed on each sample with dilution factors of 1:50, 1:100, 1:200, and 1:400. The leachate was analysed for pH, EC, major ions (Ca, Mg, K, Na, SO_4, Cl) and dissolved metals (Fe, Al, Zn, and Mn - metals consistently above detection limits in previous analyses). The acidity was calculated from the leachate chemistry (using dissolved metal concentrations and pH).

2.3.4. Analysis of Spent (leached) Solids

To conclusively identify the mineral(s) responsible for acidity release, the sample with the highest total sulfur / alunite concentration (1.5 and 11.8 wt.%, respectively) was subject to accelerated leaching, with the mineralogy determined by QXRD before and after leaching. Accelerated leaching involved a 1:200 dilution ratio leach at 85°C with a small amount of MgO added to introduce alkalinity. The increase in temperature and pH were designed to facilitate the dissolution of acid generating mineral(s).

2.4. Assessing Optimal Waste Management

2.4.1. Commingling Bottle Roll Tests

Bottle roll testwork was conducted to provide preliminary indications of whether co-mingling weathered PAF and with the volumetrically dominant NAF materials could prevent low pH drainage from 'weathered' waste materials. In total, six co-mingling bottle tests were performed, covering Proterozoic and Tertiary Detrital materials with MPA values dominated by alunite. The acid base accounting (ABA) parameters of the starting materials and commingled composites, as well as the mixing ratios are provided in Table 1. The mixing ratio of 95:5 (NAF:W-PAF) reflects the approximate maximum proportion of W-PAF waste encountered at BHP's WAIO Mara Mamba deposits, whereas the 90:10 mixing ratio is intended to test conditions with theoretically greater acidity generating potential.

Table 1 Summary of the acid base accounting parameters of materials subject to the commingling bottle roll tests.

Test	Sample Type	1	2	3	4	5	6
ANC (kg H_2SO_4 / tonne)	NAF	2.7	2.7	2.7	2.7	2	2
MPA (kg H_2SO_4 / tonne)	NAF	0.2	0.2	0.2	0.2	0.6	0.6
ANC (kg H_2SO_4 / tonne)	PAF	0	0	0	0	0	0
MPA (kg H_2SO_4 / tonne)	PAF	4.9	4.9	4.6	4.6	22	22
NAF : weathered PAF (Mass Ratio)	-	95:5	90:10	95:5	90:10	95:5	90:10
Alunite (wt.%)	Mix	0.09	0.13	0.08	0.1	0.45	0.71
MPA* (kg H_2SO_4 / tonne)	Mix	0.45	0.65	0.44	0.63	1.61	2.54
ANC (kg H_2SO_4 / tonne)	Mix	2.57	2.45	2.57	2.45	1.9	1.82
NAPP (kg H_2SO_4 / tonne)	Mix	-2.12	-1.81	-2.13	-1.83	-0.29	0.72
ANC / MPA ratio	Mix	5.7	3.8	5.9	3.9	1.2	0.7

* For the purpose of this leaching test procedure MPA values were calculated by multiplying total sulfur by 22.9, as most of the MPA is bound in the minerals alunite / natroalunite.

2.5. Column Leach Testwork

2.5.1. Sample Preparation

Column leach testwork was designed to assess the optimum NAF and W-PAF waste disposal configurations to manage PAF waste as per BHP's AMD management requirements.

Two large composite starting materials (NAF and W-PAF) were produced from Proterozoic waste samples (Marra Mamba and Wittenoom formations), with the aim of simulating the typical composition / ABA parameters of waste materials representative of these Formations. These two starting materials were used for all the column leach tests described below and were analysed for the following static geochemical parameters to ensure they were homogeneous and representative.

- QXRD mineralogy.
- Major and trace element geochemistry.
- Acid base accounting (Total Carbon, Total Sulfur, MPA, ANC, NAPP, Chromium Suite [pH_{KCl}, TAA, S_{Cr}, S_{KCl}, S_{HCl}, S_{NAS}]).
- Net Acid Generation (NAG) suite and NAG leachate chemistry.
- Acid Buffering Characteristics Curve (ABCC).

2.5.2. Column Configuration

In total, 12 columns were established consisting of two baselines and five different waste configurations representing different waste disposal arrangements (see **Fig 1** below).
The tests on different waste configurations were each run at two NAF:W-PAF mass ratios, nominally 90:10 (**B1-F1**) and 75:25 (**B2-F2**) (Fig 1). The ratio of NAF:W-PAF chosen for the column leach tests were selected to represent theoretically higher acidity generating conditions (i.e., worst case scenarios), noting that across BHP's Pilbara Marra Mamba deposits, the maximum proportion of W-PAF waste is less than 5%.

Columns configurations **B** to **F** were designed to test the following waste rock dump construction methods:

- **A1** W-PAF baseline
- **A2** NAF baseline.
- **B** tests the efficiency of an NAF basal layer under W-PAF materials.
- **C** tests the efficiency of an NAF cover over W-PAF materials.
- **D** tests the efficiency of commingling NAF and W-PAF materials.
- **E** tests the efficiency of encapsulating W-PAF within NAF.
- **F** tests the efficiency of encapsulating commingled NAF and W-PAF within NAF.

2.5.3. Leachate Analyses

Each column was irrigated weekly with DI water (600 ml). The resulting leachate was analysed for pH, EC, alkalinity / acidity, major ions (SO_4, Cl, Ca, Mg, Na, K) and dissolved metals and metalloids (Fe, Al, Mn, Cu, Pb, Zn, Cd, Co, Ni, Cr, As).

3. RESULTS AND DISCUSSION

3.1. Classification of 'Weathered' Waste Rock – Leaching and Dissolution Test

3.1.1.   QXRD Mineralogy

The mineralogy of Proterozoic waste samples from AWT suggests they are 'weathered' or mostly 'weathered'. The sulfur bearing phases identified include 'alunite' (solid solution between alunite [$KAl_3(SO_4)_2(OH)_6$] and natroalunite [$NaAl_3(SO_4)_2(OH)_6$]), gypsum, and jarosite, with trace pyrite detected in some samples. For all Proterozoic samples the MPA values calculated from QXRD mineralogy are dominated by secondary sulfate minerals, supporting classification as 'weathered'. Dolomite was the only ANC providing mineral detected in these samples, although dolomite is either below detection limits, or occurs in very low concentrations (0.1 wt.%).

The NAPP values calculated from QXRD mineralogy range from 0.4 to 42 kg H_2SO_4 / tonne and are broadly consistent with NAPP values derived from conventional static geochemistry. Although, in samples where alunite / gypsum / jarosite concentrations are elevated, QXRD (which provides full sulfur speciation), returns slightly lower MPA values compared with those based on the assumption that all sulfur is bound in pyrite (ie. 30.6)

3.1.2.   Sulfur Speciation and Acid Neutralising Capacity

In general, the sulfur speciation estimated by selective solvent extraction methods do not correlate with the expected forms of sulfur detected by QXRD. For example, S_{Cr} does not correlate with the concentration of pyrite, S_{HCl} - S_{KCl} does not correlate with the concentration of alunite, and S_{KCl} does not correlate with the concentrations of gypsum.

Discrepancies between S_{Cr} and QXRD pyrite could be due to the low concentrations of sulfide sulfur / sulfide minerals, introducing large relative errors. However, the lack of correlation between S_{HCl} - S_{KCl} and alunite concentrations cannot be attributed to low concentrations (i.e., alunite concentrations are up to 11.8 wt.%). Rather, this discrepancy is likely due to chemical extraction methods being nonselective. For example, previous studies show that alunite is not readily soluble in HCl (e.g., Linklater *et al* ., 2012). On the other hand, alunite concentrations determined by QXRD are considered accurate, due to strong correlations between QXRD alunite concentrations and total sulfate measurements; as well as between QXRD alunite concentrations and theoretical alunite concentrations calculated from XRF major element chemistry (Al, S, and Na + K concentrations) by assuming ideal mineral stoichiometry.

Laboratory measured ANC concentrations (AMIRA, 2002) are below detection limits for all samples. This is broadly consistent with QXRD, which did not detect any ANC providing minerals in most samples, or returned very low concentrations of dolomite in the remaining samples (i.e., 0.1 wt.%)

3.1.3.   Sequential Leaching

Sequential leaching was performed to subject the samples to higher dilution ratios than the paste pH method in an attempt to release the MPA. However, the leachate pH of all samples remained stable (i.e., 3.8 to 4.5) despite increasing dilution ratios. The similar leachate pH values for all Proterozoic materials likely indicates a similar mineral assemblage (e.g., alunite) is responsible for buffering the leachate at acidic pH values.

The final (1:6) leachate contained elevated concentrations of SO_4 (up to 85 mg/L), Cl (up to 115 mg/L), Na (up to 52 mg/L), Mg (up to 23 mg/L), K (up to 8 mg/L), Al (up to 0.7 mg/L), and Zn (up to 7.8 mg/L). Except for Cl and Mg, these elements can be released by the dissolution of alunite. Whilst correlations between Na, K, and SO_4 concentrations in the

leachate suggest partial alunite dissolution, the Al (and to a lesser extent SO_4) concentrations are lower than expected for the ideal stoichiometry of alunite. This may indicate incongruent dissolution / reprecipitation of secondary Al (possibly SO_4) bearing minerals (e.g., gibbsite [$Al(OH)_3$] or felsöbányaite [$Al_4(SO_4)(OH)_{10} \cdot 4H_2O$]).

Acidity values calculated from the leachate chemistry are low, with most samples yielding <12 mg $CaCO_3$/L. The leachate acidity of all samples is dominated by acid (H^+), with major contributions from dissolved Al, and in some samples Zn. Nevertheless, dilution ratios up to 1:6 were insufficient to release the stored MPA of these samples.

Leachate from early leach cycles were relatively enriched in Cl (up to 425 mg/L), Mg (up to 50 mg/L), and Na (up to 170 mg/L), with elevated in EC values of 400-1,500 μs/cm. In subsequent leach steps the concentrations of these elements follow trends expected from dilution, despite the pH remaining stable. This indicates that the acidity generating mineral(s) are not the major control on leachate EC. Instead, the EC is likely to be initially controlled by dissolution of highly soluble chloride minerals (note: halite [NaCl] has been detected by QXRD in waste rock samples from the WAIO deposits).

3.1.4. Sodium Hydroxide (NaOH) Titrations – Laboratory and Modelled

When samples were titrated to a final pH of 10, most behaved as would be expected if alunite was the main control on acidity release. That is, samples with higher alunite concentrations required more NaOH addition to increase the pH.

To investigate potential kinetic controls on acidity release, a coarse-grained and a fine-grained split of one sample was titrated with NaOH. The fine grain size fraction required more NaOH addition to increase the slurry pH, suggesting that kinetic factors may be limiting dissolution of the acidity generating minerals in most samples.

Following titration to a final pH of ~10, sample slurries were then titrated to a final pH of ~8. The purpose of this additional test was to determine whether gibbsite saturation of the leachate was limiting acidity release at pH ~10 (e.g., Acero et al., 2015). Higher acidity values were recorded at titration to pH ~8 compared with titration to pH ~10, supporting the likely role of gibbsite precipitation in buffering the acidity release.

The titrations modelled using PHREEQC do not consider reaction kinetics and immediately proceed to the final equilibrium state. For this reason, the amount of NaOH added during the modelled titrations was much higher than in the conventional (partial) laboratory titrations. This again confirms that slow reaction kinetics hampered the release of the MPA of all samples. Nevertheless, more of the MPA was released in laboratory titrations compared with the previous sequential leach testwork.

3.1.5. High Dilution Ratio Leaching

A series of high dilution ratio leach tests were performed (from 1:50 to 1:400) to promote alunite dissolution. The majority of samples remained buffered at weakly acidic values (i.e., pH approx. ≤ 4.5). This includes samples with relatively high and low alunite concentrations (e.g., 11.8 wt.% and 0.1 wt.% respectively).

Despite acidic pH values, the calculated leachate acidity of all samples was very low (i.e., <7 mg $CaCO_3$/L), consistent with previous leach tests. The effective acidity released from the solid sample during the high-volume leach testwork was also very low for all samples (i.e., <1.5 kg H_2SO_4 / tonne). Despite high volume leaching, the MPA was still unable to be released due to the very low solubility and slow reaction kinetics of alunite.

3.1.6. Analysis of Spent (leached) Solids

The sample with the highest total sulfur and alunite concentrations (1.5 and 11.8 wt.%, respectively) was subject to QXRD analyses before and after accelerated leaching (see Section 2.3.4). The alunite concentration decreased from 11.8 to 9.3 wt.%, and the gypsum concentration decreased from 0.9 to 0.2 wt.% as a result of accelerated leaching. Whereas the concentrations of all other phases showed a concomitant increase. This confirms that the dissolution of alunite is responsible for acidity generation in these samples.

3.1.7. Preliminary Commingling Bottle Roll Tests

All co-mingled samples produced near neutral bottle roll leachate pH = 6.0 - 6.3 (Table 2), including the co-mingled sample with a positive NAPP value (i.e., Test 6). The pH of the leachate appears to be invariant of the ANC/MPA ratio, indicating that even at low concentrations, carbonate minerals can effectively neutralise the acidity generated by alunite. This is likely because the acidity release by alunite is limited to very low values due to low solubility and slow dissolution kinetics (see previous sections).

The only dissolved metal consistently above detection limits in bottle-roll leachate was Mn, albeit at low concentrations (<0.01 mg/L). As soluble Mn is commonly released by the dissolution of carbonate minerals, this may be expected from the commingling of NAF and W-PAF wastes. Sulfate (22-36 mg/L), Na (14-19 mg/L), and K (2-8 mg/L) concentrations in the leachate were relatively consistent across all co-mingle tests, consistent with the dissolution of alunite. From these initial bottle roll tests, it appears that the slow dissolution kinetics of alunite combined with its low solubility means that co-mingling of NAF and W-PAF wastes may be a viable option for managing such wastes.

Table 2 Summary of results from commingling bottle roll tests.

Test	1	2	3	4	5	6
NAF:PAF (Mass Ratio)	95:5	90:10	95:5	90:10	95:5	90:10
NAPP of mixture (kg H_2SO_4/ tonne)	-2.12	-1.81	-2.13	-1.83	-0.29	0.72
Leachate pH	6.26	6.06	6.30	6.03	6.27	6.04
Leachate EC (µS/cm)	148	190	135	157	103	125
Calculated leachate acidity (mg $CaCO_3$/L)	<1	<1	<1	<1	<1	<1
SO_4 (mg/L)	25	36	24	35	22	34
Mn (mg/L)	0.002	0.004	0.001	0.003	0.003	0.007

3.2. Column Leach Testwork

The preliminary commingling bottle roll tests provided promising results showing that co-mingling in addition to, or in-stead of encapsulation of weather PAF waste could be an effective management option for this waste type. However, these initial tests were limited in sample mass, artificially enhanced solubility-based acidity generation / neutralisation efficiency, prevented acidity release from oxidation of sulfide minerals (if present, due to saturation), and are could not test different waste rock disposal arrangement and dump construction options. Therefore, column leach testwork was designed to assess whether

the current W-PAF management strategy is effective in managing AMD, and potentially identify additional management options for W-PAF.

Acid base accounting parameters of the starting homogenised composite materials as well as the 90:10 and 75:25 NAF:W-PAF mixtures are reported in Table 3. Laboratory measured pH and EC results are provided below in **Fig 1** for the baseline columns and NAF:W-PAF co-disposal columns.

Table 3. Acid Base Accounting Parameters for the composite NAF and 'weathered' PAF starting materials, as well as the two different mixing ratios.

Parameter	Unit	NAF Starting Composite	W-PAF Starting Composite	90:10 (NAF:W-PAF)	75:25 (NAF:W-PAF)
Total Sulfur	%	0.01	0.2	0.03	0.06
Total Carbon	%	0.1	0.3	0.11	0.15
MPA$_{22.9}$*	kg H$_2$SO$_4$ / t	0.2	4.6	0.2	1.3
MPA$_{30.6}$†	kg H$_2$SO$_4$ / t	0.3	6.1	0.29	1.76
ANC	kg H$_2$SO$_4$ equiv./ t	4.8	0.9	4.3	3.8
NAPP$_{22.9}$*	kg H$_2$SO$_4$ / t	-4.6	3.7	-4.1	-2.5
NAPP$_{30.6}$†	kg H$_2$SO$_4$ / t	-4.5	5.2	-4.0	-2.1
NAGpH	-	8.0	4.3	-	-

*MPA (and NAPP) values calculated assuming all sulfur is bound in secondary acid sulfate salts such as alunite / jarosite (i.e., Total Sulfur × 22.9).

† MPA (and NAPP) values calculated assuming all sulfur is bound in pyrite / marcasite (i.e., Total Sulfur × 30.6).
W-PAF: Weathered PAF
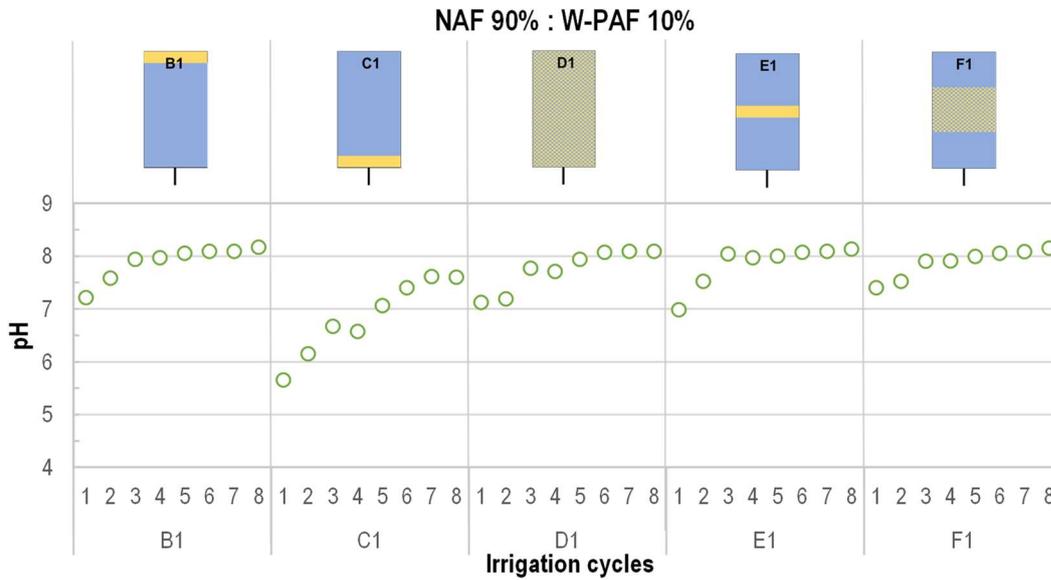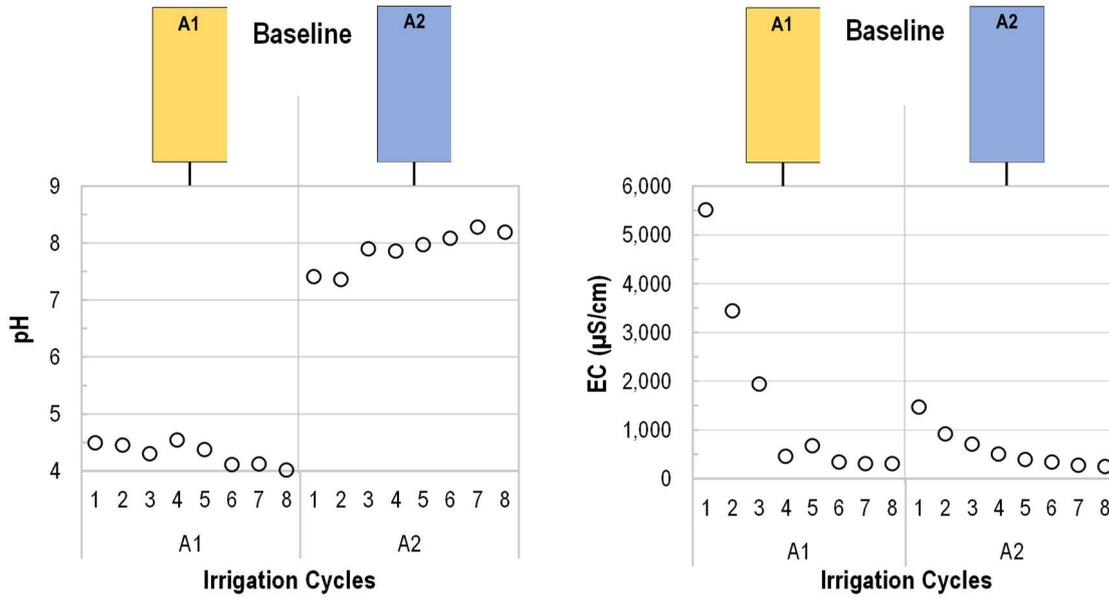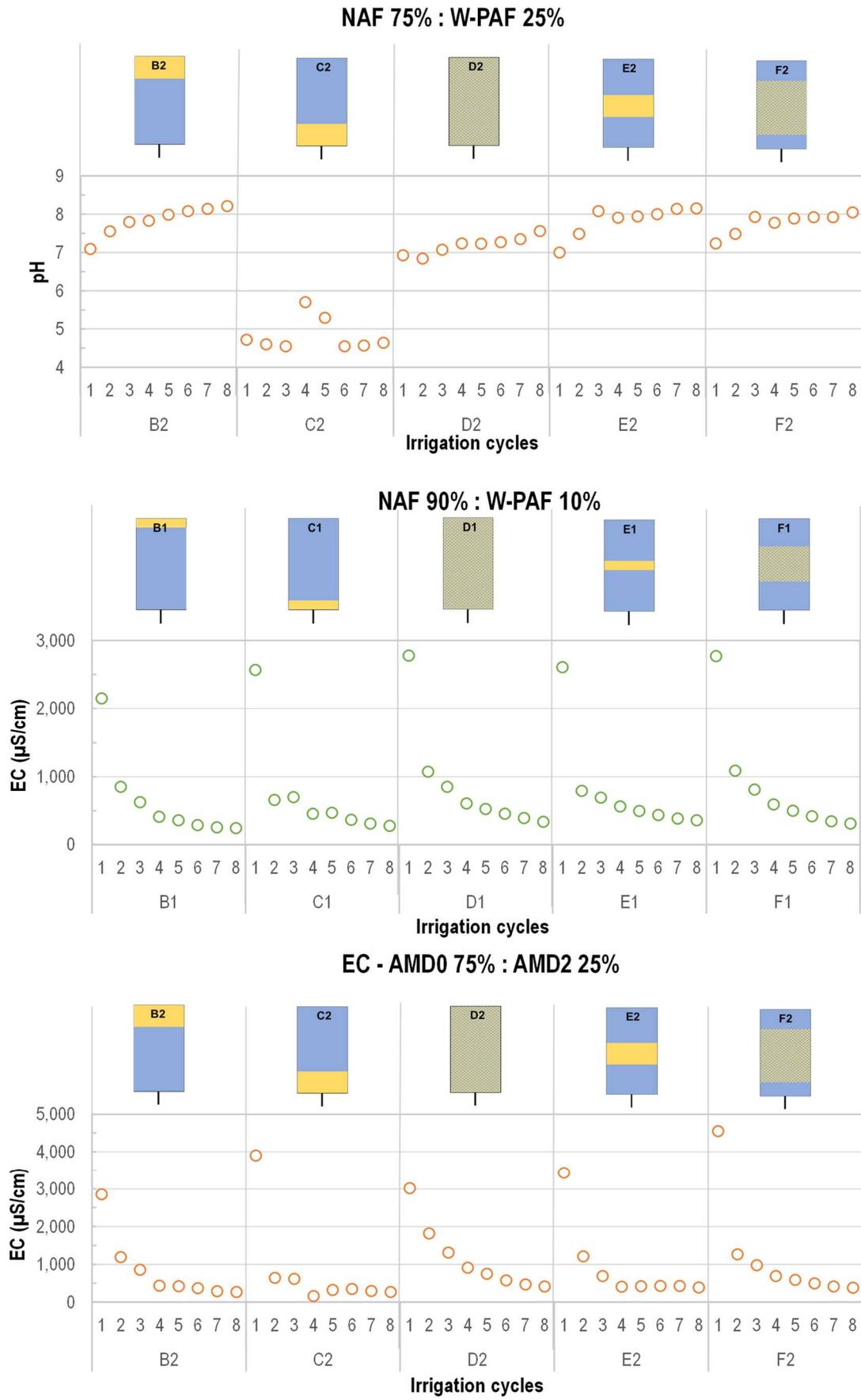
Fig 1 Summary of pH and EC results for the various column leach configurations.

The following observations are noted with respect to the column leachate chemistry:

- The baseline W-PAF column consistently produced leachate with pH ≤ 4.5, whereas the baseline NAF column produced leachate with pH of ~8.
- Initial leach cycles exhibit elevated EC values attributed to dissolution of relatively soluble salts (elevated Cl and SO_4). However, EC values decrease over time and become dominated by SO_4.
- NAF materials are capable of neutralising the acidity from W-PAF materials and producing near neutral drainage, even in tests simulating conditions with theoretically greater acidity generating potential than is likely to be encountered at BHP WAIO sites (i.e., 75:25; NAF:W-PAF).
- In general, the neutralisation efficiency of NAF is optimised when it is exposed to acid conditions (i.e., placed as a basal layer beneath W-PAF). In contrast, when NAF is placed as a cap above W-PAF and exposed to near-neutral irrigation water (as opposed to acidic water), the neutralisation efficiency of NAF is significantly lower.
- The testwork supports the current management strategy of encapsulating W-PAF wastes with NAF wastes (i.e. configuration E). However, these tests also suggest that alternative management options are available to BHP, including the co-mingling of NAF and W-PAF.
- Whilst neutral leachate was achieved, detectable concentrations of dissolved Mn and Zn persist in leachate from many of the columns. However, because column leach tests do not use site specific fluid to rock ratios, the actual concentrations of these elements in waste rock dump leachate can not be established based on the current testwork. Rather the current tests only elucidate the relative benefits of different waste disposal configurations.

4. CONCLUSIONS

Proterozoic waste rock samples from BHP's Pilbara Marra Mamba deposits, derived from AWT have MPA values are generally dominated by the secondary sulfate mineral alunite and generally contain low ANC concentrations (e.g., <10 kg H_2SO_4 / tonne).

A series of leaching and dissolution experiments were conducted in an attempt to develop a rapid field-based test to define MPA values (rather than relying in routine mineralogical analyses), which could then be used to estimate NAPP values, and thus classify the samples as per current BHP AMD classification approach. In addition, the testwork was conducted to gain an understanding of the mechanisms and magnitude of acidity release from 'weathered' PAF samples and better define its AMD hazard.

All testwork (i.e., sequential leaching, high dilution leaching) yielded leachate buffered at weakly acidic values (pH ~4.2), indicating the mineral(s) responsible for generating acidity is sparingly soluble. The leachate contained elevated concentrations of SO_4, Na, K, Al, and Zn, which suggests dissolution of alunite, as confirmed by QXRD analyses of the spent (leached) materials. However, Al (and to a lesser degree SO_4) concentrations of the leachate are lower than expected for the dissolution of alunite, likely indicating incongruent dissolution and reprecipitation of secondary phases (e.g., gibbsite or felsöbányaite).

Modelling of mineral solubility using PHREEQC and mineralogical calculations both indicate that the theoretical MPA was not achieved during the laboratory leaching and dissolution testwork due to the low solubility of alunite and slow reaction kinetics. Hence such tests are inappropriate for assessing the MPA and therefore cannot be used to accurately assess

NAPP values for these samples. The calculated leachate acidity of most samples was low (<15 mg $CaCO_3$/L), where the acidity is dominated by acid (H^+) and dissolved aluminium. The implication is that leachate from W-PAF waste should have very low acidity concentrations, and therefore could be managed effectively by low ANC NAF waste. The testwork also suggests that the AMD hazard of W-PAF waste is relatively low due to the low acidity and metal mobilisation from such wastes.

Column leach testwork suggests that the current BHP waste management strategy for W-PAF waste is likely effective in preventing AMD generation and transport. However, the testwork suggests that alternative management options are available to BHP including comingling of NAF and W-PAF waste. Bottle roll and column leach tests show that typical NAF waste mined from Proterozoic formations has sufficient acid buffering capacity to manage the small amount of acidity released by the dissolution of alunite.

Column leach testwork was designed to assess the optimum NAF and W-PAF waste disposal configurations to avoid production of acidic leachate from waste rock dumps. This test work program indicates that the acid neutralisation provided by NAF materials is most efficient when in exposed to acid conditions (i.e., as a basal layer below PAF, rather than a cap overlying PAF). Increasing the thickness of the basal NAF layer results in slightly improved leachate quality. Whilst NAF materials are capable of effectively neutralising the acidity from alunite and producing near neutral drainage, even in tests simulating conditions with theoretically greater acidity generation potential (i.e., 75:25), low concentrations of Mn and Zn may persist. This column leach program demonstrates that the optimum waste rock dump design from the standpoint of leachate chemistry is where W-PAF, or commingled NAF:W-PAF materials, were entirely encapsulated within NAF materials (i.e., column configurations E and F). This column leach testwork supports BHP's current waste disposal strategy, where all W-PAF material is entirely encapsulated within NAF.

5.   REFERENCES

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