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Leach column study of the net solute load response to installing infiltration-limiting dry cover systems over acid-forming waste piles

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Abstract

Store-and-release (SAR) covers are often installed over sulphidic mine waste to limit the generation and transport of acidic and metalliferous drainage by reducing water percolation to these wastes. SAR covers act to reduce both the net volume and the frequency of percolation events by buffering the underlying waste from smaller rainfall events that would have otherwise penetrated to the waste and by enhancing evapotranspiration of stored pore-water. While water content has been shown to significantly impact the rate of sulphide oxidation in numerous studies, there is currently no established relationship between percolation volume and acidity load. This project investigates whether reducing incident water percolation with a SAR cover simply results in more-concentrated deep drainage containing a comparable acidity load, with no net benefit from SAR installation.

The relationship between percolation volume and acidity load was tested by leaching three columns of a composite marcasite:quartz material (1:300) weekly with deionised water to achieve regular drainage via vacuum extraction equivalent to pore volumes of 0.3, 0.5 and 0.7. A fourth column was run at the mid-range drainage rate but leached fortnightly to investigate the impact of varying percolation event frequency. Vacuum extraction of pore water enabled precise regulation of column water content to ensure comparable oxidation conditions between the four columns in the inter-leach period. Normal operation of columns ceased after 11 weeks. The twelfth and final week consisted of a large flush event for all four columns, where the equivalent of 1.05 pore volumes of drainage was extracted.

Drainage after the first percolation event stabilised around pH 2.5 for all columns. Analysis of drainage quality found that a 60% reduction in drainage volume over the 11 weeks of normal operation resulted in a 13% decrease in cumulative acidity load and a 30% reduction in cumulative sulphate (SO_4*) load. The primary mechanism for this reduction in solute load with reduced percolation volume was the capacity of discrete infiltration events to flush oxidation products and expose fresh sulphide surfaces to reaction. Altering the percolation event frequency from weekly to fortnightly resulted in 47% and 41% reductions in realised acidity and* SO_4 *loads, respectively, indicating that changes to the frequency of percolation events had a stronger impact on acidity and* SO_4 *load than the net volume of discrete percolation events. Acidity loads in the final high volume flush event were 1.1–2.8 times greater than the previous week, illustrating that significant generated acidity was not mobilised at previous lower percolation volumes.*

Results from this study illustrate that solely decreasing the volume or frequency of discrete percolation events may reduce the net acidity load experienced in deep drainage. SAR covers act to enhance both of these factors whilst also reducing material water content, with these three factors all acting in concert capable of significantly lowering the acidity load reporting to waste pile deep drainage.

1 Introduction

Typical management of sulphidic mine waste where site and climatic conditions preclude material inundation is to limit water infiltration through waste rock by installing a material store-and-release (SAR) cover. SAR covers are designed to have high water storage (ΔS) and evapotranspiration (ET) capacity to

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optimise the water balance equation (Equation 1) and subsequently reduce percolation volume (V) from precipitation (P). The runoff term (R) is not specifically influenced by SAR cover installation.

$$V = P - R - \Delta S - ET \tag{1}$$

SAR covers act to reduce both the net volume and the frequency of percolation events by buffering the underlying waste from smaller rainfall events that would otherwise have penetrated whilst simultaneously enhancing evapotranspiration of stored pore-water. Campbell (2004) outlined the particular suitability of SAR covers to interior Australia's highly arid conditions, where potential evaporation greatly exceeds precipitation in all but the most intense (and typically brief) downpours. In Western Australia's Pilbara region, trial SAR covers at the Mt. Whaleback (O'Kane and Waters, 2003) and Mt. Tom Price mines (Shurniak et al., 2012) have decreased net percolation rates to underlying waste rock significantly, verifying the ability of these covers to perform as designed. Nevertheless, net percolation did still occur through covers at both these sites during high-intensity rainfall events. The mechanism through which reducing percolation volume results in a reduction in acidity generation and solute load in deep drainage is unclear, leaving open the possibility that reducing percolation volume only results in a more-concentrated drainage containing a comparable acidity and solute load and no net benefit from SAR cover installation.

Iron sulphides, predominantly in the form of pyrite (isometric FeS_2) or related minerals such as marcasite (orthorhombic FeS_2), may oxidise when exposed to water and oxygen. The rate of iron sulphide oxidation is influenced by sulphide morphology, particle size, temperature, water availability, oxygen availability, bacterial activity and Fe^{3+} availability. As the orthorhombic polymorph of pyrite, marcasite is more reactive and susceptible to weathering and oxidation due to its less stable mineral structure (Wang et al., 2007). Oxidation of pyrite or marcasite releases the same amount of acidity per mole oxidised and acts to lower pH where neutralising minerals are absent, thereby increasing the solubility of various contaminant trace metals, creating what is collectively known as acidic and metalliferous drainage (AMD). The metal and acidity load realised from oxidation of sulphidic minerals is dependent on the solubility of the secondary sulphate minerals that form from pyrite oxidation products (Li et al., 2007). Highly soluble ferrous-sulphate salts will completely dissolve (melanterite has a solubility over 200 g/L) with minimal percolation volume, resulting in pulses of concentrated drainage following extended dry periods. Other secondary sulphate minerals such as jarosite ($KFe_3(OH)_6(SO_4)_2$) or alunite ($KAl_3(OH)_6(SO_4)_2$) that have a clear solubility limited dissolution rate will produce acidity and solute loads positively correlated to incident percolation volumes, making SAR covers an ideal closure option for these sparingly soluble potentially acid-forming (PAF) minerals.

The availability of oxygen and water to the surface of reactive iron sulphide particles is critically important to their rate of oxidation and subsequent generation of acidity (Evangelou and Zhang, 1995). At saturated to near-saturated conditions, sulphide oxidation is known to be limited by the very slow diffusive transport of oxygen (Rose and Cravotta, 1998). Therefore, opportunities to back-fill PAF sulphidic material below the water table (BWT) upon mine closure should always be preferentially chosen where conditions are suitable and costs are not prohibitively large. Material bearing PAF sulphate minerals, however, should not be stored BWT because the dissolution-derived acidity load will increase from these wastes due to greater water availability.

If a large amount of sulphate has accumulated in sulphidic waste due to oxidation, a specific assessment of the materials' acid-generating characteristics under both saturated and unsaturated conditions will inform whether BWT placement is the appropriate storage option to select. Even if back-filling PAF material is the chosen closure option, temporary storage of this material above water table (AWT) until in-pit mining ceases may require substantial temporary AMD management. At the other end of the H_2O availability spectrum, disposal of sulphidic waste rock AWT in very dry conditions where water is completely excluded may minimise potential acidity because there is no water available for oxidation or to act as a transport mechanism. The spectrum of saturation conditions between water excluded and fully saturated will oxidise sulphides more rapidly than either extreme because both water and oxygen are more available to the reactive particle surface. Hollings et al. (2001) found that the rate of pyrite oxidation was maximised at a particular water content where both water and oxygen were optimally available at circa 5–10 wt.% (12–25% saturation), while at very low and very high water contents, León et al. (2004) found that pyrite oxidation was significantly inhibited. Often there is sufficient water in waste dump humidity alone to enable the oxidation of sulphides (Czerewko and Cripps, 2006). Where this is the case, pyrite is decomposed and the reaction is slowed due to the formation of hydrated iron sulphate salts such as melanterite ($FeSO_4.7H_2O$) or rozenite ($FeSO_4$) (Czerewko and Cripps, 2006).

Reducing flushing volume and frequency is likely to prevent the exposure of fresh sulphide mineral surfaces to oxidation, potentially decreasing solute load (Song and Yanful, 2008). The long-term oxidation of a sulphidic waste rock dump can therefore be reduced through decreased infiltration, which effectively spreads acid generation from these wastes over a longer time period and reduces the requirement for treatment of acidic water (Song and Yanful, 2008). The increased residence time caused by a decrease in flushing frequency also enables greater participation of aluminosilicate neutralising minerals in determining drainage quality (Adu-Wusu, 2005, in Song and Yanful, 2008).

This study aimed to investigate the effectiveness of infiltration-limiting SAR covers at mitigating the discharge of pollutants from their underlying acid-generating wastes. A column leach experiment was undertaken to verify the relationship between infiltration volume and net solute load reporting to drainage. This project was conducted because an improved understanding of this relationship will better inform the future long-term management of acid-forming wastes, with the potential for adjustments to be made to SAR cover design to optimise performance from a hydrogeochemical perspective and verify overall efficacy.

2 Methodology

2.1 Material preparation

A marcasite-quartz rock sample was supplied by Earth Systems (Melbourne) and ground and sieved to < 150 µm. X-ray diffraction (XRD) analysis conducted on this material found it was 65.4% FeS_2 and 34.6% SiO_2. Fine grade (96.3% between 106 and 300 µm) quartz sand (99.58% SiO_2) was used as an inert filler material. The quartz sand was rinsed with 10% hydrogen peroxide (H_2O_2) overnight to remove any traces of organic matter prior to successive rinsing with deionised (DI) water and drying at 110°C. The marcasite-quartz rock sample was very thoroughly mixed together manually with the washed quartz sand at a mass ratio of 1:199, yielding a FeS_2:SiO_2 of 1:306 (by ideal XRD composition). This composite material is hereafter referred to by the moniker PYT.

2.2 Characterisation

The chemical composition of the marcasite-quartz rock sample was assessed by both X-ray fluorescence (XRF) and acid digest by the NATA-accredited laboratories of SGS, Newburn, Western Australia (Table 1). Standard acid digest procedure involves the digestion of sample in four acids (HCl, HNO_3, HF and $HClO_4$) prior to measurement of element concentrations by inductively coupled plasma (ICP) spectrometrical methods. Particle density of the PYT sample was determined by the pycnometer (100 mL) method conducted in triplicate. Bulk density was measured by the core method on post-leach samples of each of the four columns. Paste pH and electrical conductivity (EC) were determined by the standard AMIRA (2002) method, whereby 25 g of pulverised sample were added to 50 g DI water and allowed to equilibrate overnight. Standard acid base accounting procedures – acid neutralising capacity (ANC), maximum potential acidity (MPA), single addition net acid generation test (NAG) – were performed by SGS following the industry standard AMIRA (2002) methods. Sulphur content was determined using XRF, the LECO analyser (combustion and infrared detection) and by deduction from known XRD composition and sample quartz:marcasite ratio.

2.3 Leach columns

Four columns of the PYT sample were created using 240 mm plastic Buchner funnels (Kartell). Filter paper (240 mm-MN615) was used to support a 6 kg sample. Heat lamps (150 W) were installed 300 mm above the column surface and used to dry the column out between percolation events (Figure 1A). Additionally, column surface temperatures were further regulated through the use of a thermostat placed 5 cm above the column surface controlling heat lamp operation to maintain surface temperature between 28 and 32° C. The regulated heat lamp apparatus was operated day and night during the inter-leach period and switched off 12 hours prior to a percolation event, and was only restarted following water extraction 24 hours after water addition. Water residence time was 24 hours. This methodology is essentially a variation to the standard AMIRA (2002) method, but using larger columns than the standard 175 mm, more precise temperature regulation and varied water application scheme. The larger pore volume (PV) of 1,458 mL enabled greater variation in water application volumes that managed to maintain unsaturated conditions whilst producing the minimum 300 mL volume of water required for chemical analysis (acidity titration, ion chromatography and ICP for metal analysis). Drainage was collected underneath the column (Figure 1B) via vacuum extraction with a vacuum pump and Buchner flask. The laboratory was air-conditioned to maintain room temperature over the warm summer months (Nov–Feb).

Table 1 Comparison between XRF and Acid Digest results for the pure marcasite-quartz rock sample; higher values between the two methods are shaded dark green; LOR = Limit of reporting

	XRF LOR	XRF	Acid Digest LOR	Acid Digest
Units	%	%	%	%
Al	*0.01*	0.25	*0.01*	0.29
As	*0.01*	< 0.01	*0.0001*	0.0004
Ba	*0.01*	< 0.01	*0.0002*	0.0026
Ca	*0.01*	0.02	*0.005*	0.007
Cl	*0.005*	0.012	*0.0005*	0.027
Co	*0.01*	< 0.01	*0.00001*	0.0015
Cr	*0.01*	0.09	*0.001*	0.088
Cu	*0.01*	<0.01	*0.0002*	0.0014
Fe	*0.01*	26.4	*0.01*	29
K	*0.01*	0.05	*0.01*	0.053
Mg	*0.01*	0.04	*0.002*	0.023
Mn	*0.01*	0.02	*0.00005*	0.016
Mo	*0.01*	< 0.01	*0.00001*	0.00008
Na	*0.01*	0.11	*0.005*	0.02
Ni	*0.01*	0.01	*0.0002*	0.01
Pb	*0.01*	0.01	*0.0001*	0.0014
S	*0.01*	21.4	–	–
Sb	*0.01*	< 0.01	*0.0001*	0.00004
Sr	*0.01*	< 0.01	*0.0001*	< 0.0001

U	*0.005*	0.011	*0.000005*	0.00053
Zn	*0.01*	< 0.01	*0.0005*	0.0042

Column commissioning involved an initial flushing event at 500 mL/kg (2.05 PV) to produce drainage with conductivity below 100 µS/cm and pH above 5. Detailed chemistry of this initial flush was not tested. Water application volumes were designed to achieve drainage of 400 mL, 700 mL and 1,000 mL as specified in Table 2. The actual application volume for each column was back-calculated from the drainage produced the previous week and iteratively revised to account for minor variations in stored water. This iterative solution proved very successful at accurately predicting drainage volumes for all four columns after the first two to three iterations. The bulk of pore water was always removed via vacuum, achieving water contents that would not have been possible using the standard AMIRA technique. The higher standard error for PYT3 volumes in Table 2 was due to an inadvertent application of the PYT4 application volume to PYT3 in the eleventh week. Column gravimetric water content was determined by regular weighing of each column and comparison to the pre-leach oven-dried weight.

(a)

(b)

Figure 1 (a) Kinetic column leach experiment set up; and (b) Drainage was collected under funnels by vacuum extraction

Leachates were assessed by inductively coupled plasma optical emission spectrometry (ICPOES) (method AN320/321) for major cations, inductively coupled plasma mass spectrometry (ICPMS) (method AN318) for trace metals and ion chromatography for Cl and SO_4 by SGS Laboratories. Acidity was determined using the standard hot acidity titration method (APHA, 1998) that uses hydrogen peroxide with boiling and cooling stages prior to titration to account for potential acidity from metal hydrolysis.

Table 2 Column water application and drainage volumes

Column	Percolation Event Frequency	Application Volume		Designed Drainage Volume	Actual Drainage Volume	
		Mean ± Standard Error	Mean Pore Volume		Mean ± Standard Error	Mean Pore Volume
PYT1	Weekly	950 ± 16 mL	0.651	400 mL	374 ± 26 mL	0.257
PYT2	Weekly	1,323 ± 25 mL	0.907	700 mL	659 ± 27 mL	0.452
PYT3	Fortnightly	1,307 ± 64 mL	0.896	700 mL	743 ± 68 mL	0.509
PYT4	Weekly	1,577 ± 18 mL	1.082	1,000 mL	969 ± 18 mL	0.665

3 Results

3.1 Water content

The gravimetric water content of the four columns decreased significantly in the six days from extraction (9.54% ± 0.23%) to water application (1.14% ± 0.04% for weekly and 0.36% ± 0.15% for fortnightly columns). Particle density averaged 2.623 kg/L over the triplicates, and bulk density averaged 1.602 kg/L. Combined, these values depict a material with 38.9% porosity and a pore volume of 1.458 L. Water application above 1PV on PYT4 produced minor free drainage in the 24-hour leach period as expected.

3.2 Geochemical characterisation

The neutral paste pH result produced by the PYT mixture (Table 3) was not typical of what would be expected from a PAF material, particularly given the acidic nature of drainage produced at all stages of the kinetic experiment. Both the sand and pure marcasite-quartz samples were oven-dried prior to their composition as the PYT mixture and had negligible water content. When combined, pulverised and tested for paste pH, the PYT material essentially transitioned immediately from water-limited conditions to oxygen-limited conditions; both conditions are likely to inhibit sulphide oxidation and may have been the cause of this neutral paste pH result. An acidic NAG pH of 3.2 supports the presence of oxidisable sulphides that did not react in the paste pH test. The majority of acidity was located below pH 4.5 in the form of free acid and soluble iron and aluminium, with only minor acidity associated with metallic ions contributing to acidity between pH 4.5-7. ANC was low at 2.4 kg H_2SO_4/t, however this value represents 67% of the also low MPA of 3.6 kg H_2SO_4/t. The PYT material would be classified as PAF-Low Capacity because it has a positive net acid production potential (NAPP) and an acidic NAG pH, whilst having a relatively low sulphur content of 0.12% S (Table 3). LECO sulphur was used for the NAPP calculation.

Table 3 Static geochemical results

	Test	Method	Units	PYT Composite
Physical Characterisation	Specific gravity	Pycnometer	–	2.630
	Particle density	Pycnometer	kg/L	2.623
	Bulk density	Core	kg/L	1.602
	Porosity	–	–	0.389
	Pore volume (for 6 kg column)	–	L	1.458
Geochemical Characterisation	Paste pH	AMIRA	–	6.91
	Paste EC	AMIRA	(µS/cm)	284
	Acid neutralising capacity	AN214	% $CaCO_3$	0.2
		AN214	kg H_2SO_4/tonne	2.4
	LECO total organic carbon	AN203	%	< 0.02
	LECO sulphur	AN202	%	0.12
	Sulphur by XRD composition	–	%	0.175
	Total sulphur by XRF	XRF78S	%	0.11
	Maximum potential acidity (LECO S)	AN202	kg H_2SO_4/tonne	3.6
	Net acid production potential (NAPP)	AN215	kg H_2SO_4/tonne	1.2
	pH_{OX} (NAG pH)	AN216	–	3.2

NAG as kg H_2SO_4/tonne to pH 4.5	AN216	kg H_2SO_4/tonne	3.2
NAG as kg H_2SO_4/tonne to pH 7	AN216	kg H_2SO_4/tonne	4

3.3 Kinetic leach columns

3.3.1 *Solute trends*

Trends in leachate pH and loading of Fe, Al, SO_4 and other major cations and anions (Ca, Cl, Mg, Na, Silica) are presented in Figure 2. Loads were calculated as mg/kg/week, therefore the load from each discrete PYT3 leach event was spread over two weeks (with the exception of the first and last week). The initial two weeks of column leaching had the highest pH and highest loading of most elements except Fe and SO_4.

The pH for all columns dropped marginally from the first week (pH 2.73–3.3) to the second week (pH 2.54−2.73) and thereafter remained stable around pH 2.5 (Figure 2). The pH of the lowest application rate column, PYT1, was generally lower than the other three columns, indicating a more concentrated solution. Loading of most metals and ions in solution (Al, Ca, Cl, Mg, Na, Si) decreased to negligible levels after six weeks, likely due to their exhaustion in their soluble-form. Discrete concentrations were generally higher for the lower leaching volumes. None of these elements were associated with acid production from FeS_2, so this result was expected. Conversely, Fe and SO_4 concentrations in column leachates were significantly elevated and experienced greater variability when compared to other analytes (Figure 2). Fe and SO_4 load rose or remained elevated up until week five, whereby loads stabilised somewhat and showed a decreasing trend, neglecting the final week large flush event.

3.3.2 *Trends in SO_4 and acidity*

Sulphate concentration generally declined over the duration of the experiment, while acidity trends were less uniform (Figure 3). SO_4 and acidity concentrations were almost always highest for PYT1, reflecting some concentration of solute load with decreasing volume. Cumulative SO_4 load was always highest in PYT4, the column leached at the highest rate. Initially, marcasite oxidation was more rapid in PYT4, as expressed through the most pronounced difference in SO_4 load at week four. However, the rate of oxidation decreased over time relative to PYT3 until at experiment completion the cumulative SO_4 loads for these columns were comparable. SO_4 loads from PYT1 were significantly lower than the higher drainage columns throughout the experiment, and PYT3 was lower again due to the decreased frequency of water application. A similar trend was expressed in the cumulative acidity load (PYT3 < PYT1 < PYT2 = PYT4), but the difference between the lower (PYT1) and higher (PYT2 and 4) drainage volumes was less pronounced. Acidity load in PYT2 and PYT4 were equivalent at all stages of the experiment. Cumulative acidity load was markedly lower in the fortnightly leached PYT3 column, indicating that both acidity and SO_4 load can be decreased significantly by reducing flushing frequency and increasing residence time in the column.

Plotting of cumulative SO_4 and acidity loads against extracted pore volume (Figure 3) showed that columns run at lower drainage rates were more concentrated (mg/L) but carried a lesser load (mg/kg) with each discrete leach event. This result supports the hypothesis that increased percolation through waste rock can expose a greater reactive surface of pyrite by flushing more oxidation products from the previous oxidation period.

3.3.3 *Total SO_4 and acidity load*

There were three distinct groupings of discrete leach event acidity loads for each column. Acidity loads below 40 mg $CaCO_3$ were from the initial flush event, and volumes above 1 PV from the final high volume flush event in week 12 had the greatest acidity loads (Figure 4). The third grouping contained the remaining 10 weeks of data. Interestingly, the week 11 PYT3 leach was accidentally run at the PYT4 application rate and yielded an acidity load greater than any column had achieved in any previous leach event. A similar trend is evident for realised SO_4 loads, with the exception of a grouping of four PYT4 data points above 120 mg/kg/event recorded during the first four weeks of the experiment. In general, the PYT1 column produced a lower SO_4 and acidity load than the others (more pronounced in SO_4 load), while similar loads were experienced by PYT2, 3 and 4. The fact that similar discrete loads of SO_4 and acidity were returned from PYT2 and PYT3 for each leach event (Figure 4) indicates that the oxidation reaction was mostly complete by the end of the first week. The very comparable acidity loads between PYT2 and PYT4 indicate that the variation in their percolation volumes did not noticeably influence marcasite oxidation or the transport of oxidation products. While percolation volume is obviously important because of the decreased load seen from PYT1, there appears to be a point at which constant higher percolation volumes do not increase the acidity and SO_4 loads experienced (Table 4).

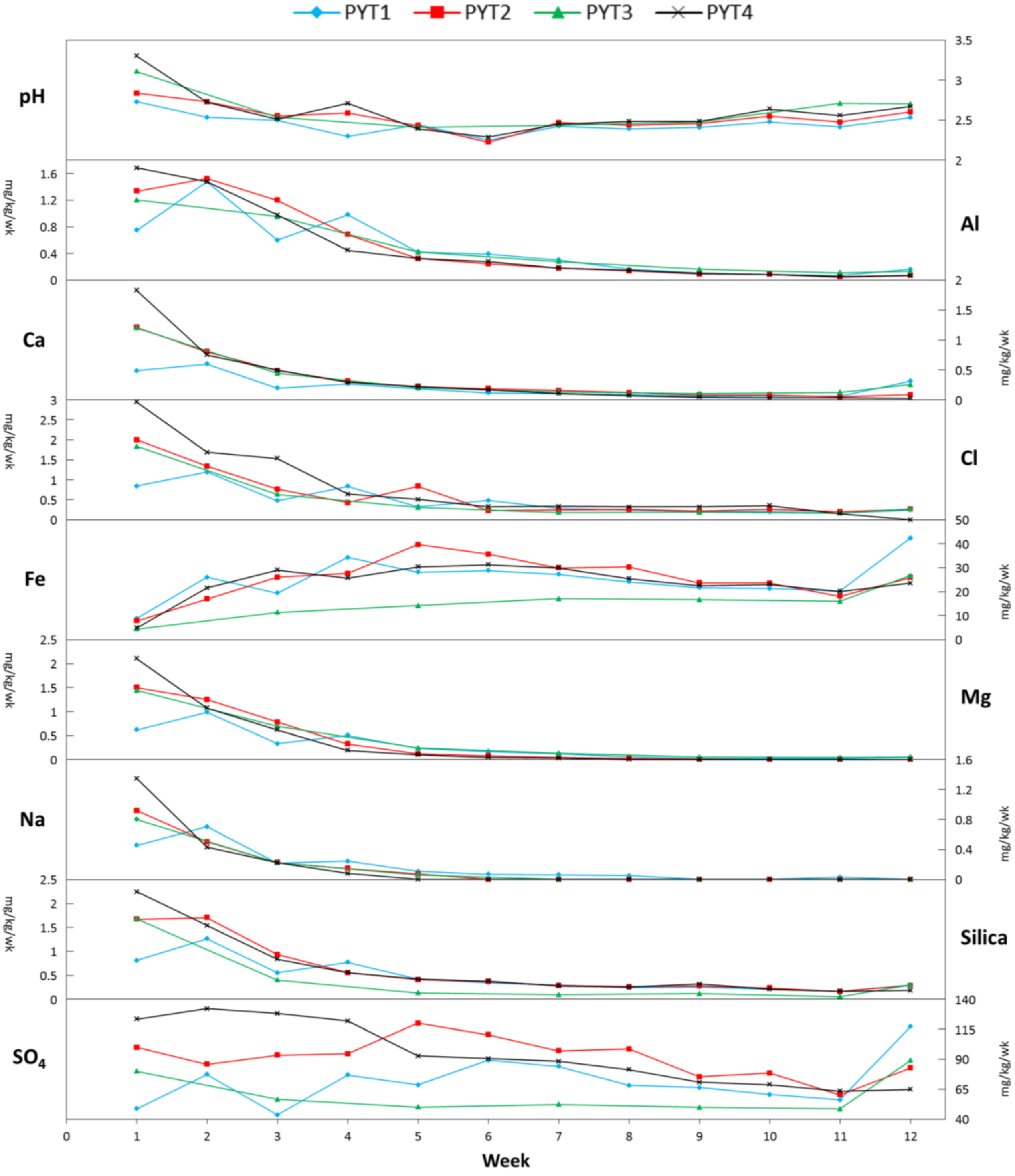

Figure 2 Trend in pH and loading of Al, Ca, Cl, Fe, Mg, Na, Silica and SO_4; week 12 consisted of a high volume flush event hence the elevated values

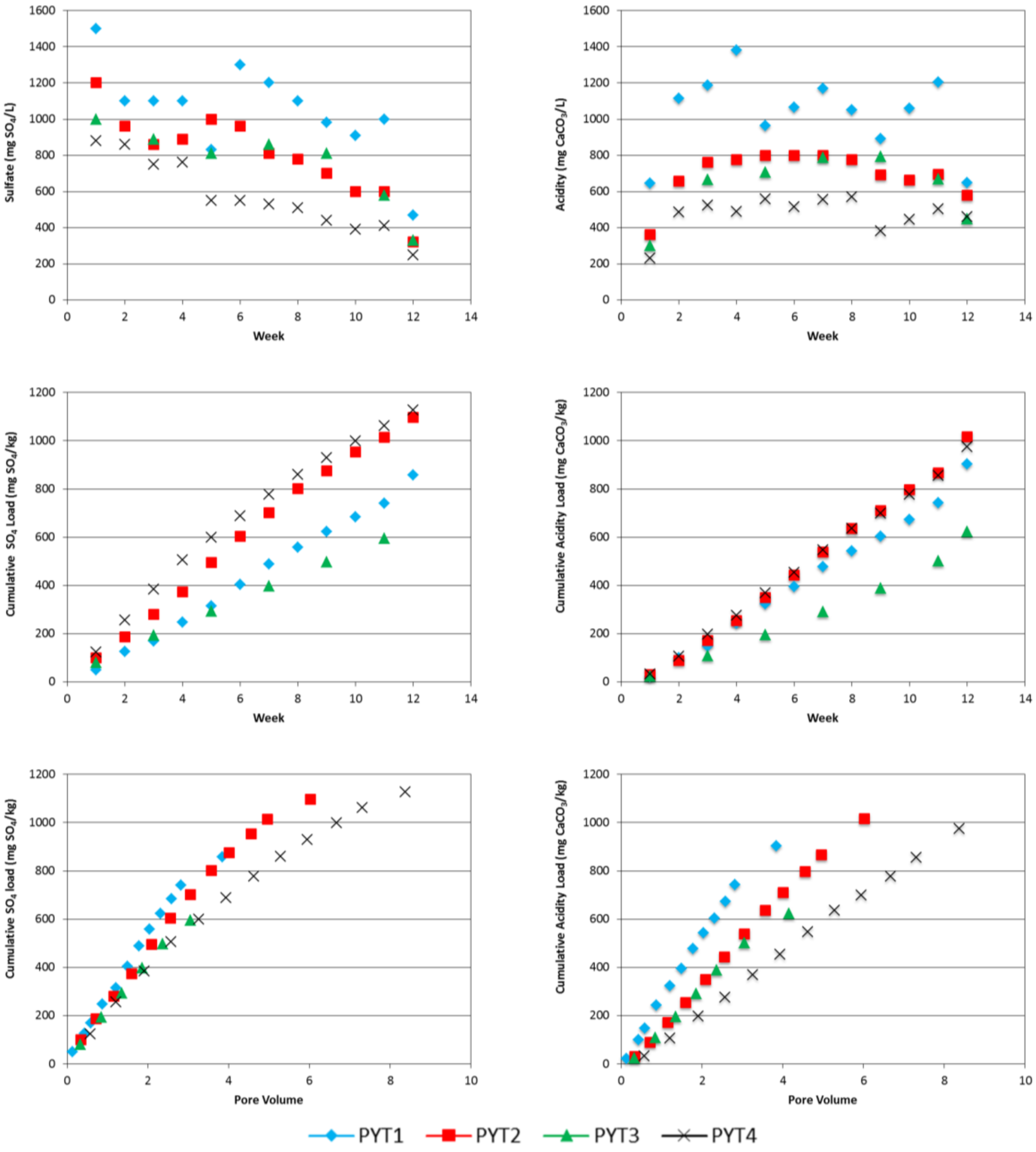

Figure 3 **Acidity and SO₄ concentration and cumulative load (mg/kg) against cumulative extracted volume and time**

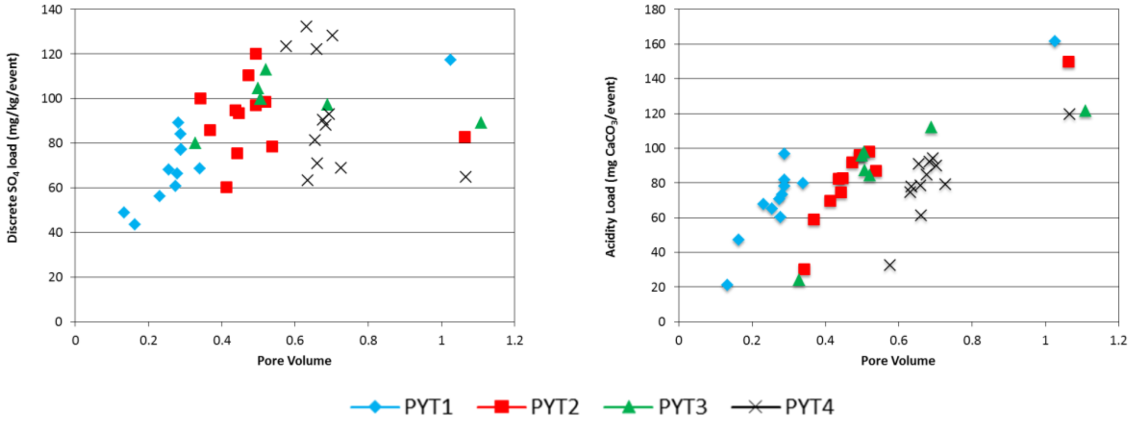

Figure 4 **Realised sulphate and acidity load per leach event against discrete extracted volume**

The total volume of applied water over the experiment duration was lowest for PYT3 (Table 4), while the lowest overall extracted volume was for PYT1. Comparisons between PYT1 and PYT3 cannot be made because there is no way to differentiate whether variations in application frequency or applied water volume were responsible for the lower loads experienced from PYT3. Acidity load for the PYT2 column was actually marginally greater than the PYT4 column, with the opposite case existing for the SO_4 load. Using SO_4 load as a proxy, approximately 25% of available sulphur was oxidised in the standard 11-week period for the PYT2 and PYT4 columns.

Table 4 Variation in realised acidity and SO_4 loads for the four columns up to week 11

Column	Total Volume Applied	Total Volume Extracted	Pore Volumes Extracted	Acidity Load	SO_4 Load	Original Sulphur Content	Residual Sulphur Content	Available Sulphur Oxidised
Units	mL	mL	-	mg $CaCO_3$/kg	mg SO_4/kg	%	%	%
PYT1	10,445	4,118	2.82	742	740	0.12%	0.098%	18.6%
PYT2	14,550	7,249	4.97	867	1,014	0.12%	0.089%	25.6%
PYT3	7,842	4,455	3.06	501	594	0.12%	0.102%	15.0%
PYT4	17,347	10,664	7.31	855	1,062	0.12%	0.088%	26.8%

3.3.4 Large flush event

The week 12 leach event consisted of a large flush event, with greater than 1PV extracted from each column. Comparing drainage from each of the columns was not possible because different proportions of sulphide had been oxidised in the period leading up to the twelfth week, therefore the composition of each column was not constant. However, the stark increase in both SO_4 and acidity load in the large flush event for all columns (except SO_4 in PYT4) shows that not all acidity generated from marcasite oxidation was being flushed from columns throughout the normal 11-week leaching period (Table 5). The SO_4 and acidity load for PYT1 that had the least volume of water extracted from it over the prior period had the highest SO_4 and acidity load in the final large flush event.

Table 5 Drainage SO_4 and acidity load before (week 11) and after large flush event (week 12)

Column	SO_4 Load (mg SO_4/kg/wk)		Acidity (mg $CaCO_3$/kg/wk)	
	Week 11	Week 12	Week 11	Week 12
PYT1	56.2	117	67.7	162
PYT2	60.3	82.8	69.7	150
PYT3	48.6	89.1	56	122
PYT4	63.4	64.9	78	119

4 Discussion

4.1 Leach column procedure

The kinetic methodology utilised in this study ensured that columns remained unsaturated and fully oxic over their depth for the duration of the experiment. Water content during the inter-leach oxidation period was controlled by the consistent vacuum extraction of pore water (leaving all columns at similar water content after extraction) and the regulated drying of columns. While particle size has been shown to influence oxidation rates in other studies (Malmstrom et al., 2000), this factor was controlled due to the identical composition of each material mixture. For an unsaturated AWT waste dump, the availability of water to reactive particle surfaces is influenced by preferential flow, material hydraulic conductivity and water retention characteristics, with these factors in turn impacting the residence time and contact area exposed to percolation volume. The experimental work detailed in this study controlled for all of these factors through the use of a uniform, highly conductive sample. Variation in oxidation rate due to biological activity was not considered a factor due to the uniform composition of the composite material. Thermostat regulated heat lamps placed over columns ensured that column surface temperature was controlled over the entire duration of the experiment. Variations in leachate water quality between columns PYT1, 2 and 4 were therefore simply a result of the different applied and extracted water volumes, while variations between PYT2 and 3 were due to varying frequency of water application.

The frequency of water application used in this experiment was far higher than would be experienced in an arid climate. Likewise, the solid:water ratio present in this experiment was much greater than the norm for an arid region waste rock dump. Therefore, the results from this experiment are qualitative in nature only, and act solely to give an indication of the relative impact that changes in percolation volume and frequency caused by SAR cover installation may have on drainage quality from PAF wastes.

4.2 Material composition

The static geochemical test work predicted a leachate that would produce a neutral pH (paste pH of 6.91) and a material that could potentially buffer initial acidity load due to an ANC:MPA of 0.67:1. The source of this recorded ANC is unclear, specifically because of the defined marcasite:quartz nature of the PYT material. However, the immediate acidic pH of leachates from all of the PYT columns indicates there is negligible readily available ANC. Therefore, the recorded ANC value is either in error or in an unavailable form that does not influence the acidity load experienced.

4.3 Water quality

Elevated iron and SO_4 concentrations observed in leachates were due the oxidation of marcasite. Given the lack of auxiliary minerals to supply cations to form more complex secondary sulphate minerals, simple hydrated iron sulphate salts such as melanterite with a very high solubility were likely to form when pore waters concentrated in Fe and SO_4 became dehydrated.

The lack of a significant increase in discrete acidity or SO_4 loads for the fortnightly leached column when compared with the weekly leached column suggests that oxidation was largely inhibited during the second week, where lower water contents prevailed. This result concurs with observations by Song and Yanful (2008) that more frequent flushing increases overall oxidation rate specifically because it exposes fresh sulphide surfaces to oxidation more often. The longer residence time may also increase the import of aluminosilicate neutralisation reactions in a waste rock dump context, enabling them to react to a greater extent and buffer system pH more than would otherwise have been the case.

Overall, findings from this study found that long-term oxidation rates can be lowered by reducing percolation volume, supporting the theory that SAR covers can be an appropriate waste management technique. However, further work in this area is required to quantitatively assess the effectiveness of SAR covers as a closure design option, ideally on a much larger scale and with a natural PAF material. Such a study would target water contents and hydrological conditions more representative of real-world conditions.

While results from this study indicate that reducing percolation volumes will lower solute load, concentrations in drainage waters may still be higher than legislated site closure requirements, necessitating treatment. In such a scenario, a SAR cover has the additional benefit of reducing the volume of water requiring treatment and significantly reducing long-term treatment costs. For sites where this scenario prevails and is unacceptable, alternative PAF waste management techniques may be required.

5 Conclusions

This study focused on two physical factors that influence oxidation rates – discrete percolation event volume and percolation event frequency – in an attempt to investigate the relationship between reduced percolation rates and acidity discharge, all other factors are constant, with the intention of delineating whether SAR covers are able to lower long-term oxidation rates. It was shown that decreasing the volume of water percolating to PAF wastes could reduce the net solute load realised in drainage waters. In effect, reducing percolation volumes acts to delay acidity release and enables greater participation of slower aluminosilicate neutralisation reactions in determining the quality of drainage. The primary mechanism for a reduction in solute load with reduced percolation volume was the capacity of discrete infiltration events to flush oxidation products and expose fresh sulphide surfaces to reaction. The result of this research suggests there may indeed be merit in the use of SAR covers. However, a more definitive answer would require a site-specific assessment of PAF waste rock mineralogy, particularly with respect to what secondary minerals may form and their mobility.

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