

Weathered Sulfidic Waste – Laboratory-Scale Tests for Assessing Water Quality in Backfilled Pits

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Abstract

Closure options under consideration at some iron ore mine sites in Western Australia include backfilling with mineralised and/or non-mineralised waste rock. Post-closure, following groundwater rebound, flow-through conditions may develop in the backfill located within the saturated zone below the water table and may release solutes accumulated from previous oxidation. The release of solutes may impact on the receiving groundwater quality. It is therefore important to quantify the potential for solute release under these conditions to understand the potential impacts that result.

Geochemical characterisation programmes are the foundation for assessing the potential solute release that may occur to water that has contacted the backfill. Such programmes generally comprise laboratory scale static and kinetic methods designed to obtain data relevant to the closure options under consideration. The tests generally are carried out under ambient atmospheric conditions which may not be representative of the conditions in the porewater of backfill after groundwater rebound. To complement standard testing techniques, SRK employ a saturated column test which is designed to generate site-specific data for solute leaching under the anoxic conditions that may occur within the inundated backfill.

This paper presents the findings of saturated column test work carried out on samples of waste rock from BHP’s Eastern Ridge mine located in the Pilbara, Western Australia. The samples were sulfidic, and had been subjected to ‘accelerated’ weathering and oxidation in free- draining columns prior to saturated column testing.

1. Introduction

BHP are exploring closure options for open pit mines at their Eastern Ridge operations located in the Pilbara region of Western Australia. Options include leaving the pits open or backfilling them on cessation of mining (Figure 1). In areas of net evaporation such as the Pilbara, an open pit will likely become a local groundwater sink (Figure 1A). Where backfill is placed to above the pre-mining water table, evaporative losses will be eliminated, and flow-through conditions are likely to develop following groundwater rebound (Figure 1B). Backfill may include mineralised and non-mineralised waste rock. In a flow-through system, backfill located below the water table may release pre-existing solutes to the downstream groundwater system. Quantification of the potential for solute release under these conditions is important to understand the possible impacts that the backfill could have on post-closure groundwater quality.

Previous testwork examined solute release from low sulfur material (Watson et al, 2016). The current paper extends the dataset to include weathered sulfidic or potentially acid forming (PAF) material.

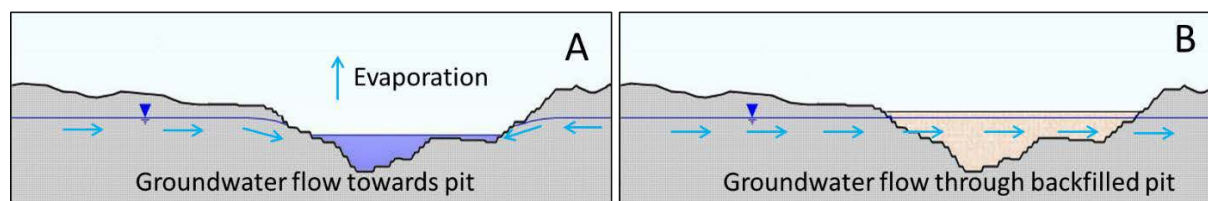


Fig. 1. Effect of pit management on groundwater flow

2. Method

Two PAF-classed McRae Shale samples were subjected to free draining kinetic column tests to simulate weathering. The tests were carried out over a period of 51 weeks using a modified AMIRA test method (samples were rinsed on a weekly, rather than monthly basis; average weekly rinse volume was 400 mL/kg). On completion of the AMIRA tests, the samples were placed into storage for a period of twelve months (covered, on laboratory bench). The samples were then loaded into columns, with the sample effectively filling the whole column. The columns were equipped with an inlet at the base of the column, and an outlet at the top, and sealed for saturated column test work. Figure 2 illustrates the test setup.

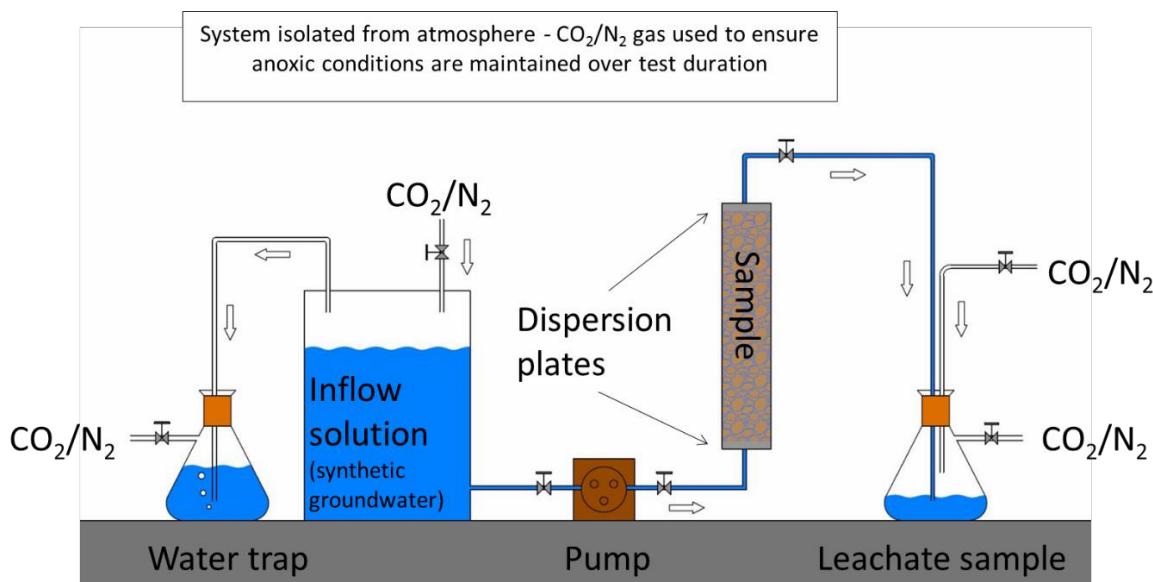


Fig. 2. Saturated column set up

Column inflow for this test was a synthetic groundwater solution. A synthetic solution was prepared by mixing common salts (such as NaHCO_3 , MgSO_4 and NaCl) in deionised water at a ratio to replicate their approximate concentrations in the site groundwater. Anoxic conditions in the synthetic water were achieved by bubbling a mixture of CO_2/N_2 gas through it (comprising 0.5% CO_2 and 99.5% N_2).

Anoxic water was introduced at the base of the column and pore gas displaced to ensure that the samples remained saturated. To maintain de-oxygenated conditions, the head space in

the sample collection vessels and within the initial inflow solution reservoir was filled with the inert CO_2/N_2 gas mixture, as illustrated in Figure 2. The saturated column tests were operated by displacing one pore volume per week.

At the time of preparing this paper, 19 pore volume displacements had been completed. The leachate samples were analysed for a range of parameters including pH, electrical conductivity (EC), oxidation-redox potential (ORP), dissolved oxygen (DO), major cations and anions and a suite of over 20 minor elements. In addition, the water in the inflow water reservoir was sampled and analysed frequently throughout the testing period to verify the inflow composition.

3. Sample Properties

The McRae Shale sample properties prior to kinetic testing are summarised in Table 1. The samples were classified as acid generating; the sulfur contents were 4.8 % and 10.5 % respectively, and were enriched with a range of elements (i.e. elements present at concentrations that were elevated when compared to crustal averages, and gave calculated global abundance indicators, GAIs, of 3 or more).

Table 1. Sample properties

Group	Parameter	Units	Sample ID	
			HEA0320-20-PAF	HEA0320-26-PAF
Saturated Column Loading	Sample mass	kg	0.74	1.5
	Pore volume	mL	236	402
Acid Base Account ^[1]	Total Sulfur	%	4.8	10.5
	ANC	kgH ₂ SO ₄ /t	7.4	3.7
	NAG pH	pH	2.3	2.1
	NAG to pH 4.5	kgH ₂ SO ₄ /t	115	226
	Class	-	PAF	PAF
Minor Element Content (GAI) ^{[1][2]}	As	ppm	197 (6)	169 (6)
	Bi	ppm	3.1 (5)	2.1 (4)
	S	ppm	48,000 (6)	105,000 (7)
	Sb	ppm	5.2 (4)	4.8 (3)
	Se	ppm	4.0 (5)	9.0 (6)
	Te	ppm	0.66 (6)	0.72 (6)
Mineralogy ^[1]	Pyrite	%	3.9	14.9
	Quartz	%	28.5	42.5
	Hematite	%	1.1	1.2
	Rutile	%	0.4	0.5
	Muscovite	%	30.5	21.3
	Kaolinite	%	1.1	2.7
	Amorphous	%	34.4	16.9

Notes: [1] Prior to commencing AMIRA testing; [2] Calculation of GAI values is described in Förstner and Calmano (1993) and the average crustal abundances used are documented in Bowen (1979); ANC – acid neutralising capacity; NAG – net acid generated; PAF – potentially acid forming.

4. Results and Discussion

Solute leachability at laboratory scale is generally controlled by the reactivity of mineral sources under the conditions of the test. Potential solute sources are:

- Dissolution of readily soluble minerals and salts (e.g. gypsum, chlorides) – these could be expected to leach completely in the first few pore volume displacements, especially if they are present in small quantities.
- Sparingly soluble minerals (e.g. hydroxysulfates, oxides) – such minerals may take much longer to leach, even if present in small quantities, and may represent a potential source of contaminants for many leach cycles.
- Interactions involving mineral surfaces, such as ion exchange and sorption/desorption.

4.1. Major Parameters

As noted above, the samples were placed in storage for a period of 12 months following AMIRA testing and before saturated column testing commenced. Plots of pH, SO₄, Ca, Si, K and Fe, illustrating the transition from the weekly flushed AMIRA tests to the once weekly pore volume displacements for the saturated column tests, are shown in Figure 3.

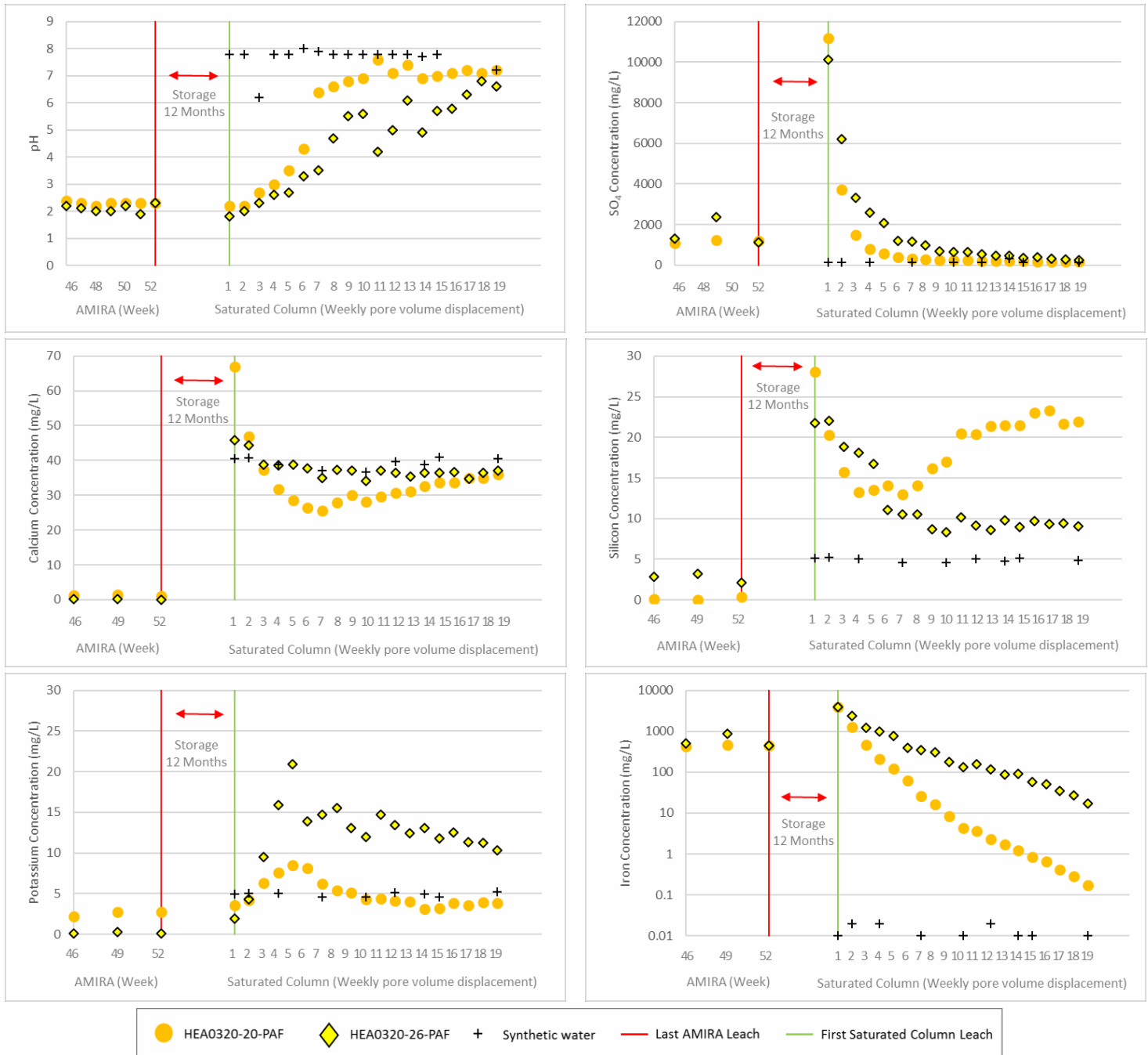


Fig. 3. Column output – pH, SO₄, Ca, Si, K and Fe

The pH of the leachate from AMIRA free draining columns was acidic (around pH 2). Initially, the pH of the outflow from the saturated columns was also acidic, but increased to values close to the inflow solution (i.e. circum neutral) after about seven and 10 pore volume displacements for the lower sulfur sample (HEA320-20-PAF) and 15 pore volume displacements for the higher sulfur sample (HEA320-26-PAF). This represents a flushing of stored oxidation products from the samples.

Under the anoxic conditions of the test, oxygen is no longer available for sulfide oxidation (dissolved oxygen in the saturated columns remained between 0.1 and 2 mg/L). Acid production at the lower oxygen concentration is precluded and the residual acidity is removed by flushing and minor neutralisation by alkalinity present in the inflow solution.

The outflow SO_4 decreases with successive pore volume exchanges, trending towards concentrations equivalent to that of the inflow, confirming that no further oxidation was occurring.

Iron concentrations from the saturated columns followed a trend similar to that of SO_4 (note the log scale used on the y-axis). Fe speciation test work indicated that Fe^{2+} (reduced form of Fe) was the dominant species in solution.

In response to pH increases, mineral solubility controls will come into play; many minerals are less soluble at near-neutral and alkaline pH. Possible solubility control phases were assessed using geochemical modelling techniques (PHREEQC modelling software – v3.3.7.11094, Parkhurst and Appelo, 2013). Measured outflow solute concentrations were used to calculate saturation indices (SI) for key mineral phases. The focus of the calculations was to identify minerals close to equilibrium with the measured outflow water (i.e. SI values close to zero). Such minerals may have dissolved to attain equilibrium with the water (or may be precipitating from solution) and therefore may be used to infer solubility controls or limitations within the tests. PHREEQC modelling indicated that the following minerals were generally near equilibrium at the higher pH values observed in the later stages of the tests:

- Carbonates – Calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$) and NiCO_3
- Hydroxysulfates – Jarosite ($\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$)
- Oxides and Oxyhydroxides – Boehmite and diaspore (both $\text{AlO}(\text{OH})$)
- Halides – Fluorite (CaF_2).

The plot for Ca shows that concentrations were very low in the AMIRA leachate; however, concentrations in the saturated column tests were influenced by the presence of Ca in the inflow (synthetic groundwater). Whilst outflow concentrations from HEA0320-26-PAF were equivalent to the inflow over the test duration, outflow concentrations from HEA0320-20-PAF were lower than the inflow for a portion of the test. A similar result was observed for Mg. The reduction in concentration appears to correspond with an increase in K concentration in the outflow. The change in concentrations may occur as a result of cation exchange, where Ca^{2+} and Mg^{2+} in solution exchanges for K^+ present on mineral surfaces (for example in the clay/ amorphous material).

The dissolved Si concentration trend for HEA0320-26-PAF was similar to that for SO_4 , but stabilised at about 10 mg/L (which was above the inflow concentration of 5 mg/L). However, the Si concentration for the leachate from sample HEA0320-20-PAF initially decreased (similar to that for sample HEA0320-26-PAF) but then increased to about 20 mg/L, which was elevated above the inflow. These results suggest dissolution of a Si-bearing mineral under the conditions of the test.

4.2 Minor Elements

Plots of As, Pb, Sb, Mo and F as a function of time are shown in Figure 4.

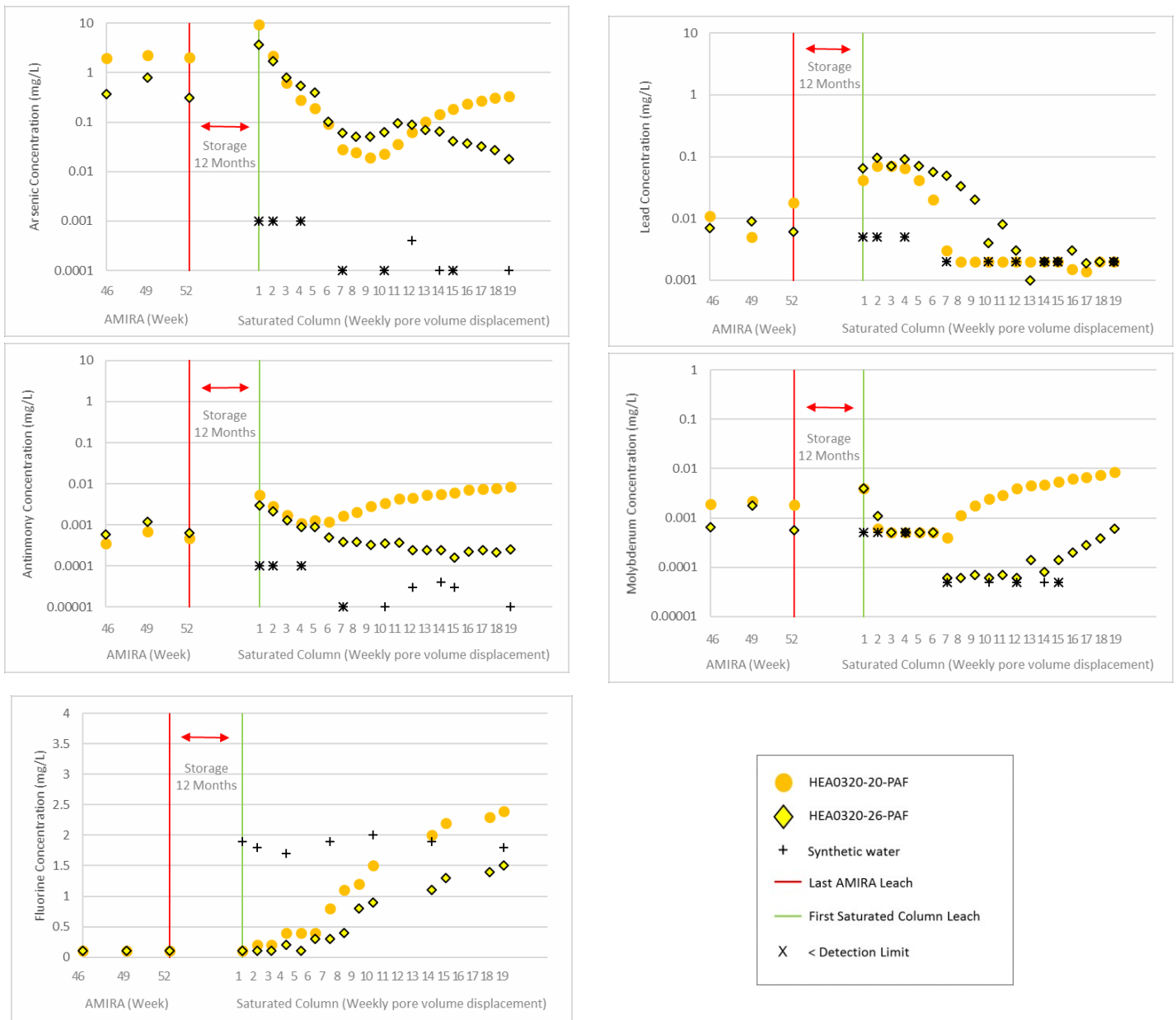


Fig. 4. Column output – As, Pb, Sb, Mo and F

Minor element leaching trends were as follows:

- Ag, Bi, Cd, Cr, Hg, Mn, Se, Sn, Th, Ti, Tl, U and V leached from both saturated columns at concentrations that were low (close to the method detection limit or below it).
- Al, B, Co, Cu, Pb (Figure 4), Sr and Zn showed a similar trend to Fe (Figure 3); however, outflow concentrations were similar to those in the inflow by the end of the test.
- Trends for As (Figure 4), Sb (Figure 4) and U were similar for both samples at the start of saturated column testing. Initial concentrations were higher in the outflow compared to the inflow but showed a decreasing trend. In later stages of the test, outflow concentrations from HEA0320-20-PAF increased.
- Initial inflow and outflow Mo concentrations (Figure 4) were close to the method detection limit for both samples. However, increasing concentrations in the outflow were observed in later stages of the test. The increase in Mo concentration appears to coincide with depletion of Pb (and possibly Al). A trend similar to that observed for Mo was noted for U.

- Concentrations of F were lower in the outflow than the inflow at the start of the test, but steadily increased to values similar to the inflow concentration by the end of the test.

Correlations between minor elements and major parameters may be used to infer sources of minor elements. Pearson coefficients were calculated for a range of minor elements with selected major parameters (i.e. pH, SO₄, Ca, Mg, K and Si). For minor elements, the analysis focused on those with dissolved concentrations that were above detection limits for the majority of the test. Correlations were initially assessed for the whole data set (Weeks 1 to 19); however, due to the variability in outflow concentration for Ca, Mg, K and Si, correlations were re-evaluated based on data generated for pore volume exchanges between Weeks 1 and 6 (where trends are dominated by flushing of accumulated salts) and between Weeks 7 and 19 (where alternative trends are shown). Selected calculated Pearson coefficients for Weeks 7 to 19 are shown in Table 3.

Table 5. Pearson correlations calculated for Weeks 7 to 19

Element	HEA0320-20-PAF				HEA0320-26-PAF			
	pH	SO ₄	Ca	Si	pH	SO ₄	Ca	Si
Al	-0.49	0.43	-0.30	-0.33	-0.38	0.87	0.13	-0.27
As	0.35	-0.85	0.92	0.74	-0.86	0.74	-0.03	0.17
B	-0.59	0.95	-0.92	-0.88	-0.78	0.91	0.13	0.06
Ba	-0.61	0.83	-0.78	-0.74	0.77	-0.67	0.33	-0.19
Co	-0.83	0.94	-0.81	-0.88	-0.56	0.95	0.01	-0.31
Cu	-0.34	-0.16	0.37	0.64	-	-	-	-
Fe	-0.77	0.91	-0.81	-0.91	-0.75	0.99	0.05	-0.13
Mn	-0.10	0.63	-0.79	-0.63	-0.56	0.81	0.10	-0.17
Mo	0.55	-0.96	0.97	0.88	0.77	-0.81	0.21	0.04
Ni	-0.43	0.89	-0.84	-0.79	-0.78	0.88	0.19	0.13
Sb	0.59	-0.96	0.97	0.91	-0.50	0.77	-0.10	-0.04
Se	-0.28	0.54	-0.48	-0.32	-0.42	0.84	-0.01	-0.25
Sn	0.10	-0.47	0.49	0.49	0.32	-0.62	-0.04	0.10
Sr	-0.78	0.89	-0.77	-0.92	-0.77	0.95	0.11	-0.07
Tl	-0.66	0.96	-0.90	-0.93	-0.62	0.93	0.11	-0.15
U	0.57	-0.92	0.92	0.85	-0.31	0.71	0.27	-0.39
Zn	-0.72	0.95	-0.86	-0.95	-0.65	0.94	0.13	-0.12

Note: Green shading – correlations 0.7 or more; grey shading – correlations -0.7 or less.

For Weeks 7 to 19, positive correlations are indicated for several minor elements and SO₄, particularly in leachate from HEA0320-26-PAF. SO₄ was still leaching from the columns in concentrations greater than the inflow in Week 19, with concentrations being greatest from HEA0320-26-PAF. These correlations provide evidence that many of these elements were present in the matrix of sulfate salts, and that these salts are still being flushed from the HEA0320-26-PAF test.

For HEA0320-20-PAF, positive correlations were indicated between Ca, Mg and Si and the minor elements, As, Mo, Sb and U. This suggests that these minor elements are present within Ca, Mg and Si minerals. Plots for these minor elements (Figure 4) showed an increasing concentration trend in later pore volume exchanges.

It is also expected that F (Figure 4) is being influenced by ion exchange, where F⁻ is exchanging for Cl⁻. Due to the low concentrations of F and significantly higher concentrations of Cl, the increase in Cl in solution was not discernible.

4.3 Comparisons with Results from Low Sulfur Materials

Elements that leached from the low sulfur samples were As, Co, Mn, Mo, Sb, U and Zn. In most cases, the concentrations were relatively constant and low over the duration of the test, and it was concluded that their low rate of release was a result of dissolution of sparingly soluble minerals bearing these elements.

These elements also leached from the weathered sulfidic samples. Compared to the low sulfur samples, the weathered sulfidic samples leached:

- As (both samples) and Sb (HEA0320-20-PAF) at higher concentrations;
- Mo at concentrations that were rising to values similar to the low sulfur samples;
- U at lower concentrations.

5. Conclusions

The results indicated that initial pore water quality from the high sulfur PAF waste will be poor if allowed to oxidise prior to inundation. The presence of stored acidic oxidation products will result in low pH conditions and elevated solute concentrations. Over time and with successive pore volume exchanges, the stored oxidation products will be flushed from the waste rock and the porewater quality will resemble the groundwater quality.

The results further indicated the presence of solubility controlling mineral phases for a number of solutes, and consequently the number of pore volume displacements, before stored oxidation products will be flushed from the waste rock, will depend on the initial quantity of stored oxidation products present. For the test conditions and quantities of stored oxidation products present in the samples tested, the number of pore volumes required may range from six to more than 19 displacements.

6. References

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

Bowen HJM, 1979. Environmental Chemistry of the Elements, Academic Press, London. Förstner U, Ahlf W and Calmano W. Sediment quality objectives and criteria development in Germany. Water Science & Technology 28:307-316, (1993).

Parkhurst, D.L., and Appelo, C.A.J., 2013, Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497p., available only at <http://pubs.usgs.gov/tm/06/a43/>.

Watson, A., Linklater, C. and Chapman, J., Backfilled Pits – Laboratory-scale Tests for Assessing Impacts on Groundwater Quality, in proceedings of Life of Mine 2016, Brisbane, 28 to 30 September 2016.