Geochemical assessment of Metal/Metalloid release by contrasting laboratory methods; The importance of secondary minerals ◎

R.J. Bowell[1,2], D.J. Sapsford[2], B.M.Dey[2], K.P. Williams[2]

[1]*SRK Consulting, Churchill House, 17 Churchill Way, Cardiff, Wales, UK CF10 2HH rbowell@srk.co.uk*
[2]*School of Engineering, Newport Road, Cardiff, Wales, UK*

Abstract

Polymetallic arsenic-rich mineralized waste from Penberthy Croft, an abandoned copper-tin mine in South West England, hosts a unique assemblage of more than 200 oxide zone minerals. In addition, sulfide minerals, are also present in the exposed mine waste. Such material exposed to oxygen and water can generate acidic drainage with levels of metals/metalloids and present a potential environmental hazard. A challenge in the management of such waste is the prediction of long term future changes in the material with the most common method of humidity cell tests requiring a long lead period for prediction and uncertainty in the termination of the tests when they are considered complete.

The aim of the study was to assess different methods for the prediction of long term potential for metal/metalloid and acid release. This evaluation was achieved comparing results of agitated bottle roll tests and selective chemical extraction (SCE) to the results of humidity cell testwork on the sample material. Material characterization utilized mineralogy, whole rock geochemistry and aqua regia digest to select representative samples.

From the extraction results the agitated bottle roll tests provided a high concentration of metals and metalloids from the partly oxidized dominated samples to an aqua regia digest. By contrast, both the sulfide dominated samples and the pure oxide sample showed significantly lower concentration of metals in the bottle roll rinse tests compared to aqua regia. Utilizing selective extraction, the results can be interpreted in terms of potential mineral fractions showing release of highly soluble secondary forms but not iron oxides or sulfide mineral fractions.

Agitated oxygenated bottle roll tests could generate similar total release to standard humidity cells at various times for each material, particularly for reactive sulfide and partly oxidized sulfide samples but also consistent results for less reactive sulfides. The accelerated rate of oxidation within the cells provide a good determination of mineral reactions and a clear plateau in the results may be indicative of termination in reaction of available sulfides. Mass balance calculations from residue samples indicated similar release mass in the two tests. By comparison the oxide material showed similar release quantum to the sum of weeks 1-4 of the humidity cell results.

Keywords: ARDML prediction, laboratory testwork, secondary minerals

Introduction

Sulfide oxidation occurs when oxygen and water contact sulfide mineral surface and is catalysed by bacteria and ferric iron in nature (Nordstrom, 2011). The result is the potential generation of acidic sulfate-rich waters hosting variable concentrations of metals and metalloids. Dependent on the presence of minerals able to neutralize acid and attenuate metals and metalloids. The prediction of such reactions is an important aspect in the environmental assessment of mine waste (Blowes et al 2014; Williams and Diehl, 2014). Standard practice in the mining industry is the application of leach tests particularly humidity cells (Williams and Diehl, 2014). These are cells or columns executed with repeated cycles of alternating dry and humidified air

cycles used to simulate element release under accelerated weathering conditions. They provide information on element release but limited speciation information inside the cell and in recent years these have come under scrutiny and may not always deliver the expected results and are sensitive to a number of potential artefacts in the operation and mechanism of the test undertaken (Sapsford et al 2009; Erguler and Erguler, 2015; Maest and Nordstrom 2017).

To assess the chemical and mineralogical changes in the weathering of sulfide material and thereby better understand their retention and release during weathering, selective chemical extraction was applied (Keon et al 2001). Unfortunately, the performance of such tests is prone to limitations due to incomplete dissolution of non-target phases (Tlustoš et al 2005) as well as incomplete removal due to re-adsorption or re-precipitation. In addition, another partial extraction method, bottle roll leaching was also assessed. These are a traditional metallurgical test used to determine "maximum" extractable metal in the presence of a reagent and like selective chemical extraction has limitations. The results were mass balanced and compared back to the whole rock geochemistry to assess quantum of elements mobilized over a given period of time and compared to mineral speciation to predict potential mechanisms of release in the cells. Although other factors such as particle size, frequency of sampling and presence of bacteria are important (Sapsford et al 2009; Erguler and Erguler, 2015; Maest and Nordstrom 2017) in this paper the focus is only on the mineralogical controls.

Site Description

Penberthy Croft is situated approximately 1.5 km northeast of the village of Goldsithney in the parish of St Hilary, Cornwall. It produced tin, copper and lead from a series of predominantly east-west lodes hosted by rocks of the Mylor Slate formation of Upper Devonian age. The mines were active in the 17th and 18th century (Betterton, 2000). Initially worked for high grade cassiterite lodes they were subsequently mined through to the mid-20th century for the rich copper supergene zone and the mixed copper-tin lower grade hypogene mineralization. The mineralisation

is a multi-stage, polymetallic hydrothermal vein system and consists of several, but distinct overlapping assemblages: Minor, burial-related quartz-albite-anatase-monazite veins of a pre-tectonic, metamorphic origin; main-stage high-temperature hypothermal-mesothermal Sn-Cu-As-W veins; later lower-temperature epithermal Pb-Zn sulfide mineralisation; and a late-stage, low-temperature Fe-Mn mineralisation.

Subsequent supergene oxidation and weathering of lodes resulted in the formation of complex gossans with oxide and supergene enrichment zones. Post-mining formation of other minerals both underground and on the dumps, has resulted in a very large variety of mineral species in a small area. These in order of approximate abundance include arsenates, arsenate-sulfates and phosphates. The greatest diversity in terms of species has been located in five main areas of the old dumps: Three in the western and two in the eastern section of the workings. Most minerals here are found as good quality subhedral to euhedral microcrystals with occasional miniature specimens. Brecciation, fracturing, silicification, chloritization and carbonatization are abundant. The mineralisation formed over a very wide period of time extending from the Upper Palaeozoic through to the Cenozoic.

An extensive suite of supergene minerals has been found in the deposit and on the associated dumps including, in approximate order of abundance, arsenates, sulfates, arsenate-sulfates and phosphates with various oxide, carbonate, hydroxide and sulfide minerals also present (Betterton, 2000). The site has been listed as a SSSI by English Nature for its mineralogy in 1993.

Methods

Sample Description

For the purpose of this study, four samples were composited from surface material on the dumps at Penberthy Croft and these are summarised in Table 1.

Mineralogical identification was by fine powder X-Ray Diffraction (XRD). Samples were prepared from the testwork material as dry powders (for SEM). XRD analysis was carried out on pulverised samples of the precipitates. Bulk analyses were carried out on

Table 1. Summary description of the four laboratory samples

Sample	Sample Description	Major mineralogy
PC001	Reactive sulfides, no secondary minerals	Pyrite, marcasite, chalcopyrite, sphalerite, galena, tennantite, arsenopyrite, quartz, chlorite, siderite
PCCOO2	Low reactivity sulfides Minor secondary minerals	Chalcocite, sphalerite, galena, quartz, muscovite, calcite, siderite, ankerite, linarite, anglesite
PC003	Oxide ore	Goethite, quartz, scorodite, hidalgoite, kaolinite, monazite-La, duftite, dolomite, birnessite
PC004	Transitional oxide/sulfide	Balydonite, beudantite, pharmacosiderite, goethite, olivenite, annabergite, duftite, malachite, hidalgoite, stilpnomelane, carminite, pyrite, chalcopyrite, arsenopyrite, quartz, kaolinite, orthoclase, beaverite, brothanthite, mixite

the samples. Scans were run using the Philips PW1710 Automated Powder Diffractometer using Cu Kα radiation at 35kV and 40mA, between 2 and 70° 2θ at a scan speed of 0.04° 2θ/s. From the scans, phases were identified using Philips PC-Identify software and from the peak areas, semi quantitative analysis was performed and a percentage of each phase present calculated. Weighting factors were applied where necessary.

Two methods of Whole Rock Geochemistry were undertaken, analysis by X-Ray Florescence using a factory calibrated Olympus Delta hand held instrument and additionally in the laboratory utilizing an Aqua Regia digest comprised of 3:1 concentrated nitric and hydrochloric acid and adjusted to a 3M solution.

Selective Extraction

A selective extraction to a sub-split of each of the samples to determine them major mineral hosts for metals in the samples. This approach utilized a previously published scheme (Keon et al 2001; Bowell et al 2013). The method applied was completed to determine metal and metalloid speciation and mobility in the material. It utilizes a comprehensive 8-step extraction scheme (Keon et al. 2001), which includes the following extraction steps: (i) 1M $MgCl_2$ (for ionically-bound As); (ii) 1M NaH_2PO_4 (strongly adsorbed); (iii) 1M HCl (acid volatile sulphides, carbonates, Mn-oxides and very amorphous Fe oxyhydroxides); (iv) 0.2M oxalate/oxalic acid (amorphous Fe oxyhydroxides); (v) 0.05M Ti(III)–citrate-EDTAbicarbonate (crystalline Fe oxyhydroxides); (vi) 10M HF (As oxides and silicates); (vii) 16M HNO_3 (pyrite, arsenopyrite, tenan-

tite, chalcopyrite, and pyrrhotite); and (viii) hot 16M HNO_3+ 1M HF +30% H_2O_2 (recalcitrant minerals such). This work was completed at the School of Engineering,Cardiff University and involved analysis by ICP-AES. Precision from standard solution analysis was ±5%.

Agitated Oxygenated Bottle Roll Tests

The bottle roll tests involved the placement of 3 kg charge of rock material into a 10 L barrel that was also filled with 3 L of water and had an air line into the barrel. This was placed on an agitated roller table and run continuously for 24 hours. The solution was then decanted and analysed.

Humidity Cell Test

The ASTM Procedure for humidity cell tests (ASTM D-5744-13e1) was applied in this study. The test follows a seven-day cycle during which water is trickled over the rock. After draining, dry air is circulated through the cell for 3 days followed by humidified air at 25ºC for 3 days. On the seventh day, the sample is rinsed with an equal mass of distilled water and the extracted solution is collected for analysis. The leachate from the test is then chemically analysed by kone analyser for anions and ICPOES for metals and metalloids. Element release percentage was determined against a re-constituted head grade for the column utilizing released element concentrations and residue material concentration.

Results

Whole Rock Geochemistry

Selected results of Aqua Regia and XRF analysis of the four samples are provided in Table 2.

Table 2. Whole Rock Geochemistry for As, Pb in ppm and Sulfide-S in wt%

Element	Leco/XRF	Aqua Regia-ICPOES	Sample
Sulfide-S	3.76		PC001
	1.48		PC002
	0.09		PC003
	0.75		PC004
Arsenic	785	543	PC001
	46.7	23.4	PC002
	39.4	37.6	PC003
	553	497	PC004
Lead	13,300	11,800	PC001
	26,500	19,600	PC002
	350	298	PC003
	13,700	12,900	PC004

These show reasonable correlation in the oxide and partially oxidized samples but less so with the primary sulfide samples indicating a portion of the metals in these samples (and probably sulfide minerals) are encapsulated in resistant materials such as feldspar or quartz.

Selective Extraction

The selective extraction results demonstrate that in all samples some arsenic is present in secondary minerals (Figure 1) even in relatively apparent primary sulfide samples reflecting the challenge of sampling dump material. However, in the sulfide samples at least 60% or more of the arsenic is present as exposed sulfide minerals or as sulfides encapsulated in resilient silicate minerals.

By contrast lead is dominated by its presence in galena in the primary samples or by anglesite, cerussite and bayldonite in the secondary material. Although secondary in nature these minerals have low solubility

compared to other secondary minerals and as such limit the mobility of lead in the environment.

Copper and zinc show a similar trend to lead but both contain a higher fraction in the amorphous oxide and strongly adsorbed fractions. Iron is dominated in the sulfides in PC001 and PC002 and as crystalline oxides in PC003. In PC004 it shows even distribution between carbonate fraction and crystalline oxide fraction.

Bottle roll tests

The four samples were subject to a 24-hour agitated oxygenated leach in a 1:1 mix with a reagent. In metallurgical work this is a common test using an acid leach, however in this study distilled water was used. The results for selected metals is shown in Table 3.

The addition of oxygen to an agitated leach certainly increases the potential to leach metals from the assemblages. The similarity in arsenic leaching levels in PC001, 002 and
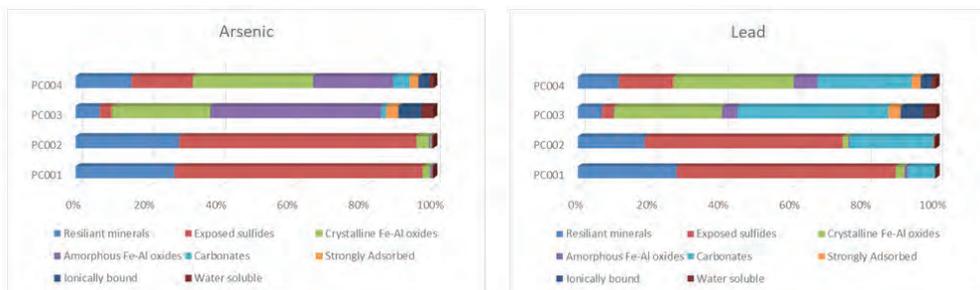
Figure 1 Results of Selective Extraction Testwork for Arsenic and Lead

Wolkersdorfer, Ch.; Sartz, L.; Weber, A.; Burgess, J.; Tremblay, G. (Editors)

Table 3. *Results of Bottle Roll Tests (in mg/L)*

Element	PC001	PC002	PC003	PC004
Arsenic	216	11.3	38.5	172
Copper	439	332	42.7	566
Iron	1070	238	334	411
Lead	89.7	130	5.6	17.8
Zinc	2100	2460	32.1	1760
Cadmium	71.4	65.4	11.4	26.7
pH	2.87	4.2	5.73	3.36

004 is perhaps a reflection of the dominant arsenic speciation in the crystalline secondary mineral fraction.

Humidity Cell Tests

Humidity cell tests were executed on the four samples for 100 weeks and during this time showed variable trend, consistent with typical humidity cells. Triplicates of the main cell were also run such that sacrificial cells could be terminated at weeks 4, 20 and 40 as well as week 100.

From the results in Table 4 it can be observed that utilising parts of the selective chemical extraction results it is possible to obtain similar mass balances for element release to those for different stages in the humidity cell.

The results indicate that by week 4 of the humidity cell most of the weakly held and water-soluble components are removed. This reflects benefit of flushing. Importantly the general held view that secondary minerals are flushed in early irrigation is not supported here and suggests secondary minerals are more complex. By week 20 of the humidity cell a portion of the secondary minerals are mobilized particularly soluble sulfates and simple salts. By week 40 only a small incremental amount of secondary minerals are mobilized and still no where near the balance of secondary minerals. For these samples the combination of cyclic irrigation and oxidation appear to mobilize much of the exposed sulfide in these samples as well as the majority of secondary minerals. The element release observed in the agitated leach bottles was not observed in week 40 and by qualitative estimate from leachate chemistry took until week 53 to see similar releases from the sulfide fraction. This indicates that for this material at least, a 52 week plus humidity cell program is required to leach the more reactive sulfide component and more than 100 weeks to leach the exposed sulfide component.

Discussion

Agitated oxygenated bottle roll tests were able to generate similar total release to standard humidity cells at various times for each material, particularly for reactive sulfide and partly oxidized sulfide samples but also consistent

Table 4. *Mass Balance Release Rates, humidity cells, bottle rolls and prediction of labile load from SCE analysis for Arsenic*

Test	PC001	PC002	PC003	PC004
Water soluble (SCE)	0.2	0.5	9.8	4.2
Secondary Minerals	2.8	4.2	80.1	63
Exposed sulfides	69.4	66.4	3.4	17.2
Agitated Bottle Roll	27.6	24.1	97.7	31.1
Humidity cell, week 4	0.4	0.4	7.2	5.3
Humidity cell, week 20	2.6	3.7	90.2	34.7
Humidity cell week 40	3	4.1	92.3	36.4
Humidity cell week 100	65.7	68.3	93	82.6

results for less reactive sulfides. The accelerated rate of oxidation within the cells provide a good determination of mineral reactions and a clear plateau in the results may be indicative of termination in reaction of available sulfides. Mass balance calculations from residue samples indicated similar release mass in the two tests. By comparison the oxide material showed similar release quantum to the early weeks 1-4 of the humidity cell results.

All leaching tests, including HCTs provide only partial information about the redistribution of elements within the material being tested (Nordstrom and Maest, 2017). In this context, the protocols tested here appear complementary to each other and ideally if combined provide an integrated approach to characterizing geochemical weathering of mine waste and allow better conceptualization of the mechanisms dominating redistribution of chemical elements in weathering.

Conclusions

Mineralogy is an important control on water-rock interaction in the assessment of mine waste geochemistry. Artefacts in leaching protocols are not uniform with different mineral assemblages and understanding this is an important factor in the design of a laboratory program. Development of the understanding of mineralogy of a mine waste in critical not only in the interpretation but also the design of leaching tests and should be integral data collected prior to and during their execution.

Acknowledgements

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