



SULFUR MINERAL PHASE IDENTIFICATION AND ASSESSMENT OF AMD RISK: A REVIEW OF SITE-SPECIFIC ANALYTICAL TOOLS

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ABSTRACT

It has been widely documented that sulfur speciation and mineralogy are key controls of AMD risks posed by sulfur-bearing waste rock and tailings materials. Processing to recover sulfur-bearing ore can alter the natural S-speciation, causing the formation of different and often amorphous S-bearing phases. Predicting AMD and NMD risk from this array of sulfur minerals is challenging and requires a combination of chemical and mineralogical testing.

Acid-generation risk evaluation using sulfide S as a proxy is dependent on the accuracy of the analytical method to determine only and all available sulfide-S. Mineralogical analyses such as XRD and SEM have been used to identify sulfur mineral phases to resolve these analytical challenges. However, limitations relating to sensitivity of the methods, crystallinity of the minerals and their chemistry mean that these mineralogical methods provide only part of the solution. We present a detailed case study of waste materials from hydrothermally-altered ore deposit containing alunite and jarosite-group minerals alongside various sulfide minerals which require the use of a suite of analytical tools to assess true AMD risk. The broad speciation of sulfates, particularly amorphous phases, can be difficult to resolve hindering the understanding of their impact on seepage quality. AMD risks are often controlled by phases that are misreported in terms of chemistry, undeterminable in terms of structure, but able to generate acidity or leach trace metals in circum-neutral waters. We present a second case study where variable crystallinity of gypsum formed in tailings produced from the processing of sulfidic ore is identified as the driver for the release of metals and metalloids. The metals and metalloids are associated with the amorphous fraction of the gypsum which is more reactive. When the tailings are leached (for example using upflow columns or in the field) the reactive amorphous gypsum releases metal and metalloids from the phase as it dissolves.

Because of the ubiquitous and complex nature of sulfur minerals in many sites that pose AMD risks, these examples have widespread applications in industry.

Keywords: Alunite, jarosite, arsenic, SEM, NAG testing, gypsum

1.0 INTRODUCTION

Sulfide minerals concentrate metals to mineable concentrations (Vaughan and Corkhill 2017) and are therefore ubiquitous in metal mines. Since these minerals are so prevalent



and the sulfur they contain can be oxidised to produce acid, the sulfur speciation, mineralogy, evolution and behaviour as the ore is recovered and processed, and long term behaviour in mine waste streams is key to the risks posed by the ore recovery operations.

Characterisation of S-bearing minerals is very challenging because of their many forms (e.g. Vaughan and Corkhill 2017), differences in mineral chemistry (particularly trace metal profile) and overlapping (or sometimes lacking) structure as well as size and crystallinity. The properties of these minerals control acid and metalliferous drainage (AMD) behaviour including reactivity, acid generation, and mechanism of metal release (Plumlee 1999). Sulfur speciation is one of the key parameters that impact the acid-generation potential. Sulfide minerals such as pyrite and pyrrhotite contain sulfur in a reduced form and release acidity and mobilise metals upon oxidation of the sulfide sulfur (sulfide-S). In contrast, sulfur in sulfate minerals such as the common mineral gypsum is fully oxidised and does not release acidity on oxidation or upon mineral dissolution. However, between these end members a host of S-bearing minerals can form (for example the sulfate minerals melanterite, jarosite and alunite), that may or may not release different amounts of acidity depending on the conditions and oxidation pathways. The texture (for example particle size) and crystallinity of the minerals on the other hand generally control their reactivity, with finer or amorphous materials being more reactive due to either their greater surface area, and metastability of amorphous phases relative to phases with well-developed crystal structures. The presence of 'impurities' (such as trace metals that substitute for elements within the mineral lattice) can distort the mineral structure, destabilising it and enhancing the mineral dissolution. Therefore, to reliably predict the full environmental risk profile of mine waste over time, it is important to understand not only the sulfur content, but also its speciation and evolution alongside that of the metals and metalloids of concern, from the ore and into the mine waste and tailings following mining and processing.

Analytical determination of the chemistry of the rock and its acid-producing properties is routinely used to characterise the waste materials in terms of AMD risk. Acid-generation risk is typically evaluated based on sulfide-S content since it is assumed that all acid is generated from the oxidation of sulfide-S. Sulfide-S is typically determined chemically, by extraction of the sulfide-S and subsequent LECO analysis method (Price 2009) with the inherent assumption that the extraction targets sulfide S only. However, other S-bearing minerals can be susceptible to the extraction process, resulting in unrepresentative results where a mixture of S-bearing minerals exists and particularly when alunite is present. In addition, the solubility of secondary S-bearing minerals (e.g. gypsum), including under neutral pH conditions, makes understanding their formation, associations with trace metals and dissolution behaviour central to seepage quality prediction.

Therefore better understanding of the current methods for example gained through combining analytical methods is required for accurate determination of sulfide S content and mineral associations to reliably use for acid generation prediction.

2.0 METHODOLOGY

The accuracy and representativeness of analytical methods is affected by the properties of the sample. For commonly used tests some such analytical artefacts are well constrained and understood (Price 2009), however for complex materials with unusual combinations of minerals, or ones resulting from weathering of the primary minerals and therefore precipitation of poorly crystalline and mixed secondary minerals, the analytical results can be challenging to interpret. Since the analytical method used for the examples discussed in this paper uses standardised protocols, details of the methodology are not included,



however, the specific aspects of the methods that affect their reliability for interpretation are highlighted.

2.1 Geochemical tests

The AMD risk from mine waste is related to the amount of sulfides present, as their oxidation drives acid production. Key analyses used to characterise the potential acid or base character of waste rock include quantification of total sulfur and sulfide sulfur, total and inorganic carbon, and direct methods to measure acidity generated or available buffering under a range of conditions (for example net acid generation (NAG) test and total actual acidity test).

The sulfide S content is used to calculate the acid generation potential of the rock upon complete oxidation. Sulfide S content can be measured directly using the chromium reducible sulfur method, where the reduced inorganic sulfur is reduced to H_2S by hot acidic $CrCl_2$ solution. The H_2S is converted to ZnS in a zinc acetate solution and Zn quantified to give direct measurement of the amount of sulfide that was reduced in the test (Queensland Department of Natural Resources, Mines and Energy, 2004). The method is designed for low sulfide-S samples and may not yield representative results for samples with sulfide-S content $>3\%$. This test is relatively more costly and time-consuming than other sulfide-S tests and as such has not been adopted widely for sulfide-S quantification.

Instead, sulfide-S is often determined as the difference between the total sulfur (e.g. quantified by pyrolysis/IR (LECO) and sulfate sulfur (quantified by extracting the sulfates present in the sample using a reagent). This means that the technique may over-estimate the true sulfide content of the sample if more-stable sulfates are not dissolved. Two common reagents are HCl (referred to as SxS value herein) and Na_2CO_3 (also sodium carbonate insoluble sulfur, or SCIS). S-bearing minerals are differently soluble in HCl and Na_2CO_3 , and some limitations are known. The potential under-reporting of sulfide-S by the dissolution of sulfides like pyrrhotite by HCl is one such limitation (Jennings and Dollhopf (1995)), but is unlikely to impact the study results since the sulfides in the deposit were dominated by pyrite (with pyrrhotite generally absent). However, little data is available on the relative solubility of sulfates, particularly alunite group minerals ((including alunite, which is considered not acid-forming, and potentially jarosite, which is an acid-forming sulfate) and therefore the impact of their presence on the sulfide-S. Since the amount of these minerals across the deposit is variable, and not determined for every sample for which SxS or SCIS value is available, it is not possible to apply a reliable correction for the over-estimation or determine which extraction is more accurate without additional testing.

Since acidity from sulfides is generated by their oxidation a direct acidity generation test related to the oxidisable sulfide content (NAG test) can be carried out to quantify the AMD potential instead. The test is based on boiling the sample with peroxide to oxidise the reactive sulfides, generating acidity which is measured by back-titration to pH7 and reported as acidity, to pH4.5 and pH7 (the pH of the solution prior to titration is also reported as the NAG pH). In addition to the standard test limitations relating to the reagent and boiling manipulation (Charles et al 2015), this method is susceptible to under-reporting the pH on samples with negligible sulfide content due to residual peroxide acidity, both due to pH probe effects and addition of acidic stabilisers (Parbhakar et al. 2018, Barnes et al. 2015). On the other hand, since NAG testing is static and reflects the end point of the acid production and neutralisation processes. In the presence of carbonates low NAG acidity and neutral NAG pH can be reported despite presence of sulfides in the sample, due to the buffering from carbonate dissolution. In these cases, while the NAG test can be an indicator of the steady state of pH of the materials, it will not correlate to the amount of sulfide present



in the sample. For samples with high sulfide content, a multi-stage NAG test may be required to avoid underestimation of acidity generation due to incomplete oxidation due to insufficient peroxide used in the standard single step test.

It is noted that while not the focus of this paper, results produced by other tests (such as standard upflow testing and total actual acidity testing) are included within. Both tests followed standard procedures by accredited laboratories.

2.2 Mineralogy testing

The mineralogy of a sample is typically determined by x-ray diffraction, which is a method that provides information of the crystal structure of the sample materials. The diffractogram is interpreted using standard software to identify the mineral phases present based on their known structures. Diffractograms however do not provide information directly about the chemical composition of the minerals. Because of this isomorphous minerals or end members of a solid solution series cannot be distinguished by this technique alone. Quantification is based on the areas under the curve using the Rietveld refinement. These areas will be skewed if the particles are very fine (nm scale), or the mineral is poorly crystalline as these cause broadening of the diffraction peaks. Crucially, XRD cannot identify non-crystalline (amorphous) phases such as iron hydroxides or some sulfates (including amorphous fractions of gypsum) that can often form as secondary minerals in mine waste, since they lack the structure to generate the XRD peaks. If present in high quantities which is likely for mine waste, the presence of such amorphous phases increases the background noise level, decreasing intensity of the XRD pattern and accuracy of interpretation.

Mineralogy can also be investigated visually and through a chemical analysis using scanning electron microscopy with energy dispersive spectrometry (SEM-EDS). This technique does not provide structural information, therefore the mineralogy is based on composition alone. While this can be reliable for well-formed standard phases and can give information on minerals from solid solution series, it may not be able to characterise mixtures of fine or amorphous minerals or accurately distinguish between coatings and the grain they are formed on, potentially mis-identifying the mixture as one whole mineral rather than two separate mineral fractions.

2.3 Combining chemical and mineralogical analyses

The methods described above are informative, but can be limited in application of individual results as they reflect the conditions for which they were designed and tested in a laboratory, while heterogeneity at scale in field settings may mean 'one size does not fit all'.

Combining methods is potentially very powerful. Such an approach allows the use of the benefits of one test (e.g. well understood and cheaper tests such as industry standard SxS, SCIS or NAG test, for which most mine sites have extensive data) to be combined with the benefits of another (CRS, XRD, total actual acidity, SEM). Targeted specialised testing (for example sequential extraction XRD (Dold 2003)) can improve the accuracy of interpretation of existing results of single tests. Then the strengths of one test can be used where there are ambiguities in the other to decrease the uncertainties stemming from the specific method and provide more reliable information for behaviour prediction within acceptable costs or timeframes.

We show how standard geochemical tests do not accurately characterise the waste materials from two sites, requiring combinations of geochemical and mineralogical testing

to quantify the sulfide S content of the waste rocks of a hydrothermal deposit and identify the arsenic-bearing phases in carbon-in-leach tailings.

3.0 RESULTS

3.1 Sulfur mineral proxies

The results discussed here are excerpts from extensive geochemical and mineralogical testing of rock from an epithermal acid sulfate volcanogenic gold deposit with dominant sulfide mineral being pyrite with some chalcopyrite and enargite. The local geology of the pit from which the materials were sourced is described as being dominated by volcanic dome complex. The overall facies comprise about two thirds coherent porphyritic andesite and dacite interspersed with intervals of non-stratified, matrix-supported polymictic phreatomagmatic breccias and hydrothermal breccias. The variations of breccia types apparently associated with multiphase magmatic activities generated the development of acid sulfate alteration and ore deposition from the convective hydrothermal fluids. The pit itself is situated within an advanced argillic altered facies. The advanced argillic alteration is dominated by alunitic alteration followed by kaolinite-dickite alteration and siliceous alteration. The alunite alteration is wide-spread along a NE-SW structure and envelopes siliceous alteration. It is the prevalence of alunite through this deposit, which presents a challenge to using typical chemical proxies for mineralogical interpretation and AMD prediction at this site.

Figure 1 (top) shows the relationship of the results of different chemical methods of quantifying sulfide S content with the total S content of the samples.

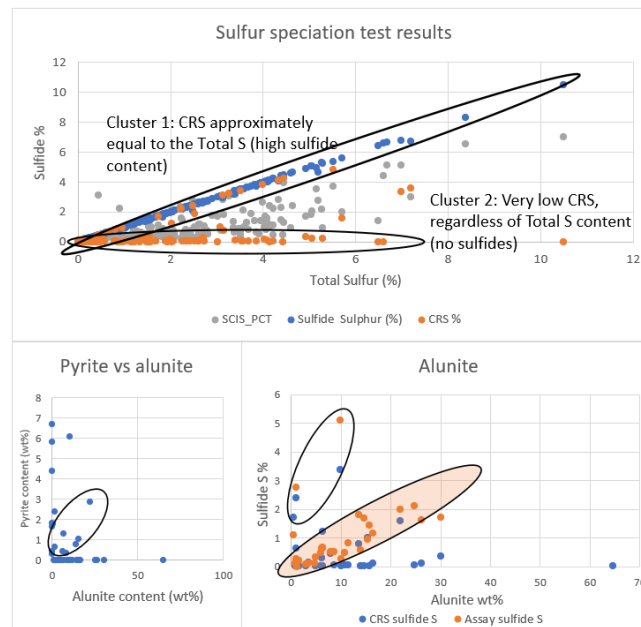


Figure 8. Top: Scatter plot of the sulfide S results from different tests vs the total sulfur determined by SCIS method. Sulfide sulfur is the sulfide content determined by difference using the HCl extractable sulfate. CRS reflects the chromium-reducible sulfur. Bottom left: scatter plot of the pyrite content vs alunite content. Bottom right: sulfide S content vs alunite content



The SxS results (in blue) are a very close match to the total S value of each sample, forming a straight line. The assay testing using the SCIS method vary between this 1:1 relationship and zero with little correlation between sulfide S content and total S value. Use of CRS to determine the sulfide S content formed the data into two clusters relative to total S – Cluster 1 had CRS value very similar to the total S value (and therefore approximately matched the SxS result for those samples), and Cluster 2, where CRS was negligible regardless of the total sulfur value (i.e. these samples appeared to contain no sulfides and the presence of sulfate minerals).

Combined with mineralogical testing, the results show that while the SxS value increased with increasing alunite content (confirming results from this method include the alunite content as well as any present sulfides), for the majority of these samples CRS was negligible where alunite was high and was therefore not affected by the presence of alunite.

Using the sulfide sulfur value from the SxS method to calculate the Net Acid Producing Potential ($NAPP_{SxS}$, calculated as maximum potential acidity based on sulfide sulfur content (MPA_{SxS}), minus acid-neutralisation capacity (ANC)) overestimates the acid generating properties of the majority of the samples in this example, relative to their NAG properties (see Figure 2). Since the deposit has generally low buffering, it is unlikely that many samples will have high NAG pH (4 or above) while also containing high sulfide sulfur (resulting in $NAPP$ values over ~ 10 kg H_2SO_4/t). Combining the $NAPP_{SxS}$ value (which uses the SxS value as a proxy for the true sulfide S content), with the results of the CRS test allowed for samples where SxS over-estimated sulfide S content due to presence of alunite to be identified. The majority of samples with CRS value (and therefore likely true sulfide S content) of $<0.3\%$ had NAG pH above 4, which matches the understood relationship between these variables. Samples with CRS value $>0.3\%$ had NAG pH of 3 or less confirming also that CRS was able to capture higher-sulfide samples reliably.

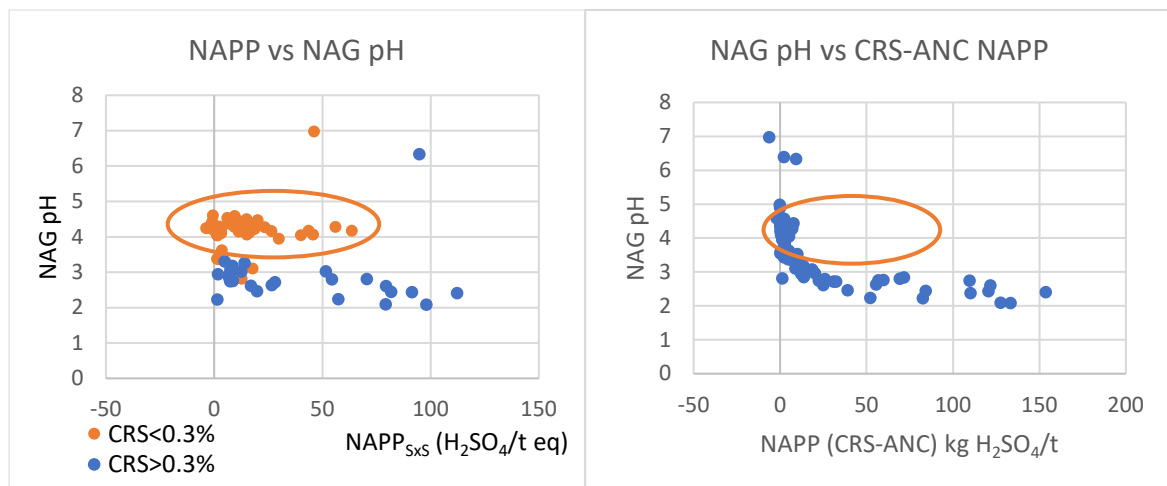


Figure 9. Scatter plots of $NAPP (SxS \cdot 30.63 - ANC)$ vs NAG pH by CRS grade (left) and $NAPP (CRS - ANC)$ vs NAG pH (right). The oval indicates samples where SCIS test over-estimated the true sulfide S content.

Further testing was carried out to better understand which mineral is captured by the different sulfide quantifying tests. The abundance of key acid-producing minerals (jarosite by dissolution and pyrite upon oxidation) was related to either the CRS-determined sulfide

S content or the NAG pH or acidity (Figure 3). NAG acidity increased linearly with increasing pyrite content, indicating this test is able to identify samples that contain pyrite, however, some samples have high sulfide S and low NAG acidity since they contain buffering minerals. In this deposit this distribution of sulfides and carbonates occurs in the less altered rocks (argillic alteration, AR), where the alteration intensity was too low to form alunite. For these samples a combination of knowledge of the lithology and geochemical result can be used to define the materials for which alunite would not affect the sulfide S result.

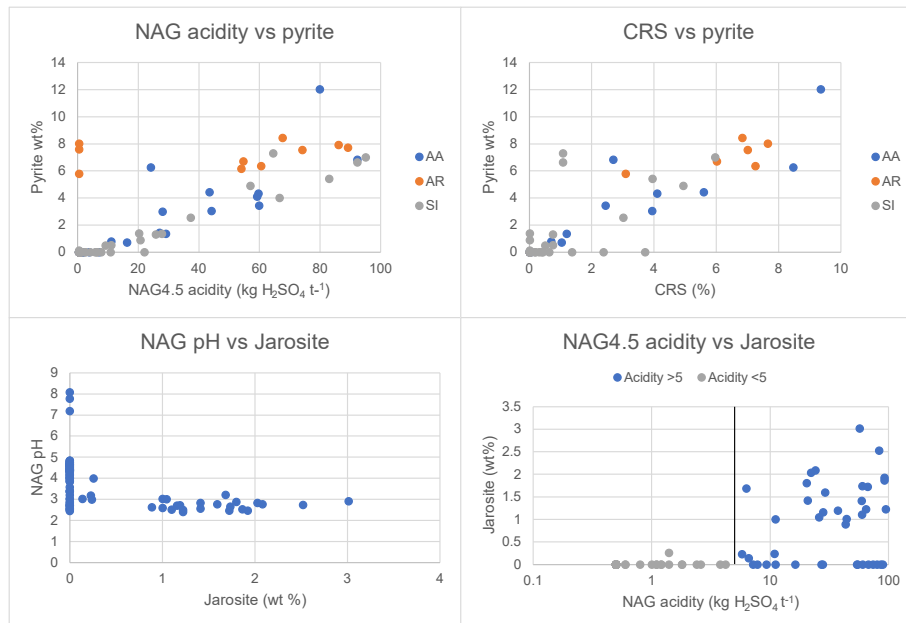


Figure 10. Scatter plots of NAG acidity to pH4.5 vs pyrite (top left), CRS vs pyrite (top right), NAG pH vs jarosite (bottom left) and NAG acidity to pH 4.5 vs jarosite (bottom right)

CRS also increased overall with increasing pyrite content, however the relationship was less clear, indicating that this parameter alone is not as reliable as NAG acidity in predicting AMD risk at this site. The NAG test reliably showed that samples with negligible acidity also contained negligible jarosite amounts. NAG acidity for samples containing either pyrite or jarosite or both exceeded 5 kg t⁻¹ H₂SO₄. The results show that for this deposit the NAG test is able to capture the acidity that would be generated both by oxidation of the sulfides and that generated by the dissolution of the already-oxidised materials such as jarosite (which will not be captured by the sulfide S test or CRS test), however, the results of the NAG test alone cannot distinguish between pyrite-associated acidity or jarosite associated acidity. Ongoing work for this site includes detailed sulfur mineralisation system research that considers the potential use of mineralogically and geochemically characterised lithotypes that can be identified based on core photographs to delineate materials where alunite is absent (and therefore sulfide-s test results can be considered reliable), alunite is present and pyrite is absent (and therefore the sulfide S result is inaccurate, but can be considered to be negligible) and where pyrite is present (with sulfide S results indicating significantly acid-generating materials regardless of the accuracy of the value, e.g. where sulfide S value exceeds 4).

3.2 Amorphous sulfur-bearing phases

A detailed study of the processed carbon in leach (CIL) tailings of a gold mine in Europe was conducted to understand the speciation and deportment of arsenic associated with these tailings. The ore deposit is composed of mafic tuffs, carbonated altered mafic tuffs, graphitic metasediment, black cherts and banded iron formation. The gold is largely related to arsenic and sulfur minerals, resulting in sulfur (S) and arsenic (As)-rich tailings at the end of the ore processing circuit. Because of the processing, S and As are re-distributed from the primary minerals into secondary phases that control the solubility of As. The results of upflow column testing are shown in Figure 4 and highlight a constant molar ratio of As to sulfate in the leachate, suggesting concurrent release (for example resulting from the dissolution of gypsum) that holds true for all three samples. This relationship is not apparent in the As-Fe plot, where Fe concentrations decrease faster than As concentrations (resulting in increasing As/Fe molar ratio with L/S ratio). The difference in relationship indicates that Fe mobilisation mechanisms differed to those for As and SO₄. Moreover, the As-Fe relationship differs between the spigot sample (which reflects fresh tailings at the end of processing) and the pond tailings (fine and coarse) where weathering due to ambient exposure has occurred, despite similarity in pH between samples at the same stages of the test (data not shown). It is noted that the fresh spigot sample released low concentrations of iron throughout the test, while As/Fe ratios for the weathered pond samples were lower (owing to greater Fe concentrations), suggesting some of the secondary Fe-bearing phases may be metastable. The spigot sample also had lower As/sulfate ratio compared to the other two samples. It is noted that the spigot sample contained ~22% calcium sulfate minerals, while the pond samples had less than 20%. This suggests that the As release from the spigot sample is predominantly related to gypsum dissolution, while after aging since deposition, some additional As may be released from phases that contain both sulfate and Fe, however, sulfate-related release remains dominant.

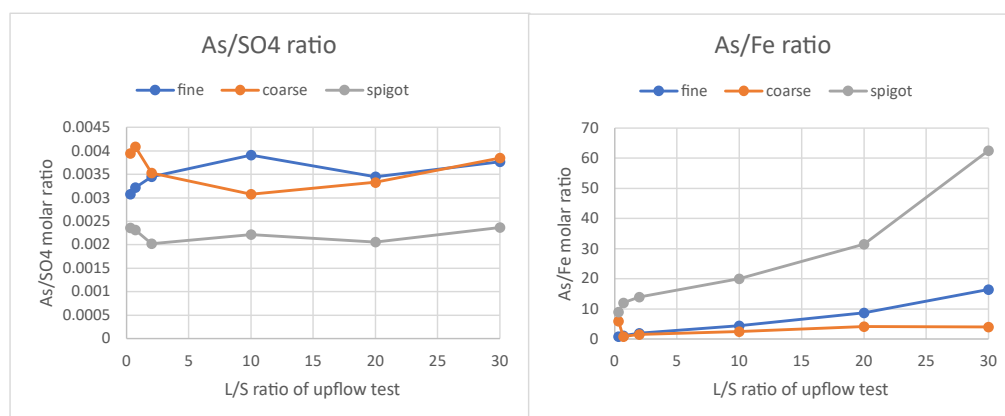


Figure 11. Molar ratio of arsenic to sulfate (A) and arsenic to iron (b) vs liquid to solid ratio of the test (L/S ratio) for three CIL tailings samples.

The elemental composition analysis of the bulk sample for key acid-base accounting parameters and Fe and S-bearing phases was compared to back-calculated composition from mineralogy assessment using XRD. This was also compared to the elemental composition-based mineralogy as derived using SEM-EDS analysis (Table 1).

The results show very good agreement between the total S and carbonate carbon (C-carb) values and XRD-derived and SEM-EDS-derived total S and calcite C values respectively.



This suggests both mineralogical and chemical methods of quantifying the abundance of these elements and the phases they are hosted in could be considered reliable overall. The results also indicate that most of the S and C-carb-bearing phases are likely relatively crystalline.

The S-speciation based on the mineralogy, however, suggests that the majority of the S reported by the SxS test is not representative of sulfide S, but rather is contained in the alunite-group mineral jarosite. This is an acid-producing sulfate and as such AP value based on the test-determined SxS is likely a suitable indicator of the acid-production potential for the samples, however, the mechanism of acidity release differs. Since jarosite is an already-oxidised phase, release occurs as a result of dissolution under appropriate conditions rather than oxidation of the tailings and will not be mitigated by methods used to prevent sulfide oxidation.

The Rietveld refinement identified phases, which overall contribute less than half of the Fe reported by the elemental composition analysis and EDS value. A proportion of the discrepancy could be explained by the mica present in the samples being the Fe-bearing type biotite rather than muscovite, however, this is insufficient to explain the difference. It is most likely that most of the iron reported by EDS, but not captured by XRD is amorphous Fe oxide-hydroxides.

Table 7. Comparison of S and C speciation and Fe content from mineralogy back calculation compared to ABA testing results

| XRD Parameter | XRD value | SEM-EDS value | Comparable parameter | ABA value | Comment |
|--|-----------|---------------|----------------------|-----------|---|
| Total S [%] | 5.68 | 5.85 | Total S [%] | 5.64 | Similar estimate of total S |
| Sum of gypsum, anhydrite and bassanite S [%] | ~3.4 | | Total S – SxS [%] | 3.9 | Sulfate ABA value exceeds equivalent XRD value by ~0.5% S, likely reflecting amorphous sulfate phases |
| Pyrite S [%] | ~0.5 | | SxS [%] | 1.8 | SxS average is significantly higher than the sulfide content by XRD |
| Jarosite S [%] | ~1.2 | | | | Jarosite-S is likely reported as SxS in the ABA tests (Price 2009) |
| Calcite C [%] | ~0.1 | | C-Carb [%] | 0.2 | Close agreement between carbonate content (XRD) and inorganic carbon (ABA) |
| Fe [%] | ~5.2 | 13.7 | Fe [%] | 13.9 | Fe is under-reported by XRD phase back-calculation, e.g. due to a significant proportion of Fe wt % being in amorphous phases |

The results clearly show that a significant proportion of the samples contains amorphous phases, which likely control the dissolution behaviour of the CIL-tailings. The amorphous materials contain Fe, As and S, and may be gypsum with sorbed Fe-As, Fe oxides,

hydroxides or hydroxy-sulfates with sorbed As, As-jarosite or mixture of all these different phases, which is too fine or amorphous to accurately determine the specific phase. It seems likely that the majority of the Fe-oxides and As-jarosite type mineralogy appears as coatings on other grains, while As- and Fe-bearing gypsum forms the majority of the amorphous mass noted in the CIL pond sample for example. The results show that while the Fe-As coatings contain As at a higher concentration than gypsum, the high abundance of gypsum means that this gypsum should be considered as a significant source of As within the CIL tailings.

Figure 5 shows an SEM image of the spigot sample, where a mixture of grains is visible. The mineral grains such as the Ti-maghemite (spectrum 18) have white coatings of a different chemical composition to the bulk grain (spectrum 19 and 20), notably containing ~20-30% Fe and ~20-30% As and likely reflecting Fe oxides or oxyhydroxides that incorporate or sorb As. The coating is thinnest on the least reactive quartz surfaces and thickest on clay grains such as illite (spectrum 17, chemical data not shown). Notably, the amorphous mass in the bottom left corner reflects gypsum chemical composition (spectrum 24) and contains a small fraction of As (~0.5%). This amorphous-gypsum-hosted-As is present in trace amounts making it difficult to detect and has the potential to be disregarded as not significant, particularly in relation to other As-bearing phases observed in Figure 5.

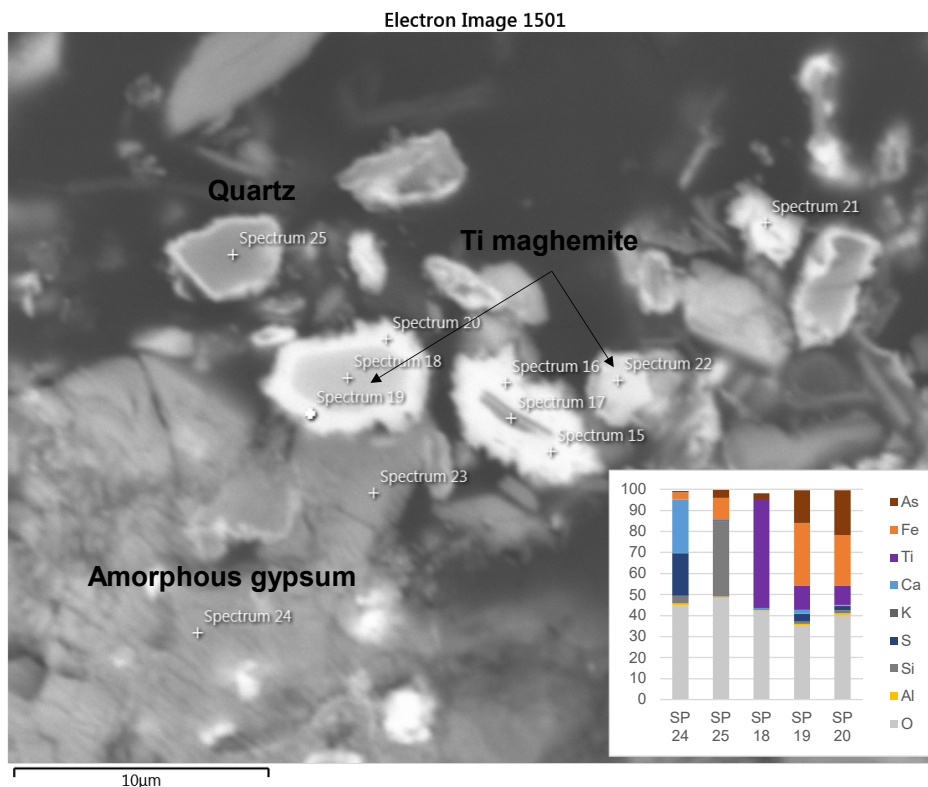


Figure 12. SEM image from CIL spigot sample showing grains of quartz and Ti-maghemite with an Fe-As-bearing coating, and amorphous gypsum mass. The inset stacked bar chart shows the elemental composition as normalised Wt% (determined by EDS of each spot (SP))



Uncertainties in quantification and partial overlap in the methods means that the amount of As within each phase and the prevalence of the phase and its importance in terms of seepage quality are not certain. The results indicated that:

- Arsenic in gypsum is up to 0.5wt% of the gypsum, and SEM shows it is predominantly in the amorphous calcium sulfate. This is consistent with fewer impurities remaining captured within the gypsum as it becomes more crystalline and less hydrated, since such impurities can distort the crystal structure.
- The amorphous fraction is noted to contribute ~13% of the XRD spectrum. It is not clear how much of the amorphous phase comprises gypsum, but this could equate to ~1%-2% of the As present in the CIL tailings being hosted within the gypsum and would be released as this gypsum dissolves, e.g. in circum-neutral pH.
- As is also present within the Fe oxides and As-jarosite grains and coatings, at higher concentrations (up to 25-30% of the weight of these phases). It is not clear whether this is sorbed or structurally bound, and the amount of As-jarosite relative to other mineral phases is not clear. However, it is also not clear whether these coatings are the same phases as the jarosite reported by XRD (in which case they would be crystalline). Assuming that is the case, jarosite-associated As would be the majority of As in the CIL tailings, 50%, equivalent to ~25000 mg/kg content in the tailings. Whether sorbed or structurally bound, As associated with those phases could be released upon decrease in pH (due to desorption or dissolution of the mineral phase), or as a result of Fe(III) reduction, which would dissolve the mineral phase and release Fe and As.

Understanding the distribution of arsenic within the secondary mineral phases in these tailings is key to identifying the controls which are most likely to suppress As mobilisation and maintain or improve the water quality from the facility. The key finding that As is associated with amorphous calcium sulfate at sufficiently high concentrations to maintain As concentrations of ~1 mg L⁻¹ indicates that limiting infiltration (which will limit seepage volume) could decrease the concentration of As in the CIL reclaim waters. The large amount of As associated with Fe-oxy-hydroxides or jarosite-type phases is a significant potential source of As if these phases are destabilised e.g. if acid conditions develop. Research is ongoing to understand the stability of the secondary phases under different conditions, and in turn the effect on As mobility.

4.0 DISCUSSION

The results from the research programs at these contrasting sites and variety of mine wastes indicate that understanding sulfur speciation and mineralogy is central to AMD risk prediction. Elucidating the relationships between the mineral structure, chemistry and crystallinity and the results of the standard tests and the impact of these properties on the leaching profile of mine waste materials clearly requires a combination of analytical approaches. Table 2 provides a summary of the tests discussed in this publication, and their advantages or limitations. Where a complementing method can be used to limit the uncertainty, this is discussed.

The presented examples highlight the potential pitfalls in basing predictions of AMD properties of waste rock on standard test results without thorough verification through cross-method interrogation. Our findings indicate that further research into the way S-mineralogy is captured by readily-available analytical methods is needed.



Table 8. Comparison of test methods and how accuracy can be improved through method combination (highlighted in bold).

| Parameter | High alunite deposit | Gypsum-containing tailings |
|--|--|--|
| SCIS or SxS test to determine sulfide S or predict MPA | Sulfide sulfur analysis is impacted by alunite content and if used for ABA, overestimates acid-forming potential NAG test could be used in combination or instead | Sulfide sulfur test over-estimated sulfide content (as confirmed by XRD). It captured Jarosite-S which can release acidity by dissolution but not by oxidation XRD test on a few samples can be used, since tailings have relatively uniform mineralogy |
| CRS test to determine sulfide S | Can provide reliable results of sulfide S for this deposit, but costs are higher and lab availability lower | Applicability not confirmed, does not assist with sulfate mineral identification |
| NAG acidity and pH | Direct measure of acid generation potential (in this case proportionate to sulfide S content). Low cost | Not an accurate measure of sulfide content due to presence of carbonates |
| Mineralogy by XRD | Expensive and limited application for pit-wide estimation due to material heterogeneity. Required for small scale comparative studies to confirm relationships between other results. | Required for initial characterisation, but limited in use due to presence of amorphous phases and variable chemistry minerals. Can be used in combination with SEM-EDS and compositional/ABA analyses to validate results. |
| Mineralogy and chemistry by SEM-EDS | Expensive for routine testing. Limited application due to material heterogeneity. | Required to understand the fine-scale chemistry and interpret some mineralogy based on chemistry and visual analysis. Gap still remains between the spatially-resolved chemistry provided by this technique and verifying its crystal structure (e.g. by XRD) |

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