Using Chromium Reducible Sulfur for AMD Prediction

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Abstract

The potential for acid and metalliferous drainage (AMD) from waste rock and tailings in hard rock mining is a key issue which is required to be addressed at all stages of mining from the Mining Proposal to Mine Closure Plans. Draft changes to current waste characterisation guidelines are being considered by DMP as part of an overall review of Mining Proposal guidelines.

Waste characterisation in Western Australia has generally been undertaken using standard static and kinetic testing methodologies specified in Australian Minerals Industry Research Association (AMIRA) (2002), the Global Acid Rock Drainage (GARD) Guide (INAP 2009) and the Commonwealth Department of Industry, Tourism and Resources (DITR 2007). In recent years however, some companies have used different analytical methods focusing on a single test, chromium reducible sulfur (CRS), rather than conducting multiple tests, with the main driver for this being reduction in analytical costs and time savings. MBS Environmental participated with the ChemCentre as part of a Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) funded project to determine whether the CRS method could be reliably used for waste rock characterisation for hard rock samples from Western Australia. The CRS method was originally developed for use in coal mine and acid sulfate soils studies, but has recently been used in various assessments of AMD potential from hard rock mine waste in WA, despite limited validation data. This paper outlines the results of a comparative laboratory study of 54 mine waste samples (from gold, iron ore, copper, nickel and lead/zinc mines) and pure mineral specimens from WA for AMD potential. Key findings are:

- CRS appears generally suitable for application in many instances – especially for common iron sulfides at low to moderate concentrations. Examples include iron ore, mineral sands and gold mining operations. This means there are opportunities to use this method to reduce analytical costs and time.

- Caution and a full knowledge of the properties of minerals present must be applied for high concentrations of iron sulfides or sulfides other than iron (especially lead, zinc, copper and nickel sulfides).

- Arsenopyrite, which is often present in various mine wastes as an accessory sulfide, did not give a result by the CRS method, but did produce acid when oxidised in the laboratory.

- There was evidence for substantial inter-laboratory bias (and intra-laboratory variation) in CRS results from commercial laboratories in WA. This raises concerns about its use alone to predict AMD.

- Unlike most other test methods, there appears to be no available standard reference material for CRS analysis by laboratories to limit bias or errors. Inter-laboratory trials for low level acid sulfate soils are not considered appropriate for hard rock mine samples.

Care needs to be undertaken when commissioning waste characterisation studies to make sure the analytical methods are appropriate for the project and potential cost and time savings do not jeopardise the technical validity of the data being used for mine waste management planning.

Introduction

Concerns have been raised by industry regarding the possibly inappropriate use of the Chromium Reducible Sulfur (CRS) method to estimate the acid production potential of mining related waste rocks. The CRS method was originally introduced into Australia to estimate the acid production potential of acid sulfate soils (ASS). It is being increasingly used to assess Acid and Metalliferous Drainage (AMD) potential from sulfidic mine waste, despite limited validation data to demonstrate its suitability for mineralised rocks, especially those containing base metal sulfides.

AMD assessment invariably commences with the Acid Base Account (ABA) using 'static' test procedures that rely on the estimation of "total oxidisable sulfur" (TOS) as an indicator of acid formation potential and measurement of Acid Neutralising Capacity (ANC), supplemented by mineralogical analyses, to indicate the capacity of mine waste to neutralise acidity.

TOS in mine waste samples is defined as the concentration of reduced forms of sulfur that can be oxidised by reaction with strong oxidising substances including oxygen and hydrogen peroxide. Some, but not all, sulfur minerals containing TOS result in acid formation. Generally, the acid forming sulfur minerals contain iron as the dominant base metal. The acid formation potential of other base metal sulfides is typically less than that of pyrite (FeS_2), which is usually the cause of AMD related issues in coal mines, acid sulfate soils, iron ore and gold mines.

Laboratory measurement of TOS has traditionally relied on two laboratory methods; measurement of total sulfur (usually by a combustimetric procedure) and sulfate-S, which typically involves extraction with a dilute, non-oxidising, hydrochloric acid solution. The appeal for using the CRS procedure is that a single laboratory test may be used as a surrogate for TOS.

The use of the CRS test as an alternative to conventional measurements of TOS for estimating the acid production potential of waste rocks was investigated in this study by testing a wide range of hard rock mine wastes (i.e. other than coal and ASS) from Australasia.

The generation of acid (H^+) occurs typically when iron sulfide minerals, notably pyrite (FeS_2), are exposed to both oxygen (from air) and water. Sulfide oxidation produces sulfuric acid and a characteristic yellow-orange precipitate, simplified as "ferric hydroxide" ($Fe(OH)_3$), as summarised by Equation 1.

$$\text{Equation 1:} \quad 4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 16H^+ + 8SO_4^{2-}$$
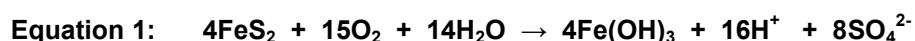
Key stakeholders in mining project development, including mining companies, finance companies and Government regulators, recognise the need to ascertain the risk of AMD very early in project development.

Geochemical mine waste assessment aims to identify the distribution and variability of key geochemical parameters (such as sulfur content, ANC and elemental composition) and acid-generating and element leaching characteristics under neutral, acidic or alkaline conditions. Exploration usually provides the earliest indication of AMD risk. Modern and rapid multi-element techniques such as X-Ray Fluorescence (XRF) spectrometry and Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) analysis of exploration drill core materials provides substantial amounts of data relating to concentrations of sulfur as well as the primary target element and associated indicator elements.

If most of the measured total sulfur content is present as sulfide minerals, an estimate of the Maximum Potential Acidity (MPA) can be made. Provided that complete oxidation of a sulfide mineral such as pyrite proceeds according to the stoichiometry of Equation 1, MPA (expressed in units of kilograms of sulfuric acid, H_2SO_4, per tonne) can be converted from the total sulfur concentration (% by weight) by multiplying by a factor of 30.6 (Equation 2).

Equation 2:   MPA (kg H2SO4/t) = 30.6 * Total S (%)

However, if the sulfide mineral forms are known, then allowance can be made for non-acid- generating and lesser acid-generating sulfur forms to provide a better MPA estimate. The use of total sulfur is a conservative approach because some sulfur may occur in forms other than pyrite. Sulfate-S minerals (gypsum, anhydrite, alunite), elemental (native) sulfur and organic sulfur, for example, are non-acid-generating sulfur forms. Also, some sulfur may occur as other base metal sulfides such as chalcocite, sphalerite and galena which yield less acidity than pyrite or, in some cases, are non-acid-generating or even acid-consuming.

While some mineral deposits, notably coal and deep sulfide intrusions into fresh rock, do contain most of the total sulfur as sulfide minerals (especially pyrite), others do not. Many gold and iron ore deposits in Western Australia occur in deeply weathered (oxide) or partly weathered (transition) regolith. In such circumstances, almost all of the original sulfide minerals have completely oxidised to sulfate salts (such as gypsum and epsomite /kieserite) or partly converted into iron or aluminium 'sulfo-salts' such as jarosite ($KFe^{3+}_3(OH)_6(SO_4)_2$) or its aluminium equivalent, alunite. In these cases, the use of MPA as a measure of potential acidity greatly overestimates the actual acidity measurements in the laboratory or field. Sulfates produce no acidity at all, while 'sulfo salts' such as jarosite release a form of "residual" acidity by reaction with water.

The observations described above indicate that the amount of potential acidity produced from sulfur minerals is variable and cannot be predicted with any confidence unless detailed understanding of the

sulfur minerals present is well understood. Table 1 summarises the acid formation potential of different sulfur minerals.

Table 1:   Sulfur Mineral Classes and Acid Formation Potential

Sulfur Form	Sub-Class	Examples	Acid Formation Potential
Sulfate	Alkali and alkaline earth sulfate salts	Gypsum ($CaSO_4.2H_2O$) Epsomite ($MgSO_4.7H_2O$) Barite ($BaSO_4$)	Nil
	Iron and aluminium sulfates	Jarosite ($KFe^{3+}_3(OH)_6(SO_4)_2$) Alunite ($KAl_3(OH)_6(SO_4)_2$)	Produces some acid by hydrolysis
Reduced Sulfur Species	Thiosulfates, sulfites, polythionates	Thiosulfate ($S_2O_3^{2-}$) Dithionate ($S_2O_6^{2-}$)	Produces some acid by oxidation
	Elemental sulfur	Sulfur (S)	Produces 30.6 kg H_2SO_4/tonne by bacterial oxidation
Sulfides	Iron sulfides	Pyrite (FeS_2) Marcasite (FeS_2)	Produce 30.6 kg H_2SO_4/tonne by oxidation
		Pyrrhotite ($Fe_{(1-x)}S$)	Produces <30.6 kg H_2SO_4/tonne by oxidation, depending on oxygen supply
	Mixed iron-base metal sulfides	Chalcopyrite (CuFeAs2) Pentlandite (($Fe,Ni)_9S_8$) Bornite (Cu_5FeS_4)	Produces <30.6 kg H_2SO_4/tonne by oxidation, depending on iron to base metal ratio
	Base metal sulfides	Chalcocite (Cu_2S) Covellite (CuS) Galena (PbS) Sphalerite (ZnS)	Do not produce acid by oxidation
	Arsenic and molybdenum sulfides	Arsenopyrite (FeAsS) Realgar (As_4S_4) Molybdenite (MoS_2) Orpiment (As_2S_3)	May produce >30.6 kg H_2SO_4/tonne by oxidation

Sulfide-S can be measured in the laboratory by three methods, either by direct or indirect measurements as described below.

- Direct measurement, utilising reactions that specifically measure reduced (sulfide) forms of sulfur. The CRS method is an example of this.

- Indirect measurement, which requires separate measurements of total S and sulfate S.

- Measuring "oxidisable"-S, which is defined as the increase in concentration of soluble sulfate-S when reacted with a strong oxidising agent such as hydrogen peroxide (H_2O_2).

In 2002, the Australian Mineral Industries Research Association (AMIRA 2002) advocated the use of "sulfide-S" measured by the difference of total S and sulfate-S as the preferred method of acid formation potential. Sulfate-S can be measured by two wet chemical procedures; extraction with 4 M HCl or fusion with sodium carbonate. The latter is considered more accurate as it measures sulfate salts that are not effectively dissolved by 4 M HCl; these include barite ($BaSO_4$) and celestite ($SrSO_4$). However, the 4 M HCl extraction procedure is more commonly used as it is considerably less tedious and therefore relatively inexpensive.

The amount of acid (in kg H_2SO_4/t) that can be formed by complete oxidation of sulfide-S is known as the Acid Potential (AP), which is calculated from total-S and sulfate-S concentrations using Equation 3. The total S minus the sulfate-S in the calculation of AP is termed total oxidisable sulfur (TOS).

Equation 3:   AP (kg H2SO4/t) = 30.6 * [Total S (%) - Sulfate S (%)]

Determination of AP is significantly more expensive than determination of MPA as it requires two laboratory procedures to determine total S and sulfate S. As acid formation risk potential for a new mining project can potentially involve analysis of thousands of geological samples, there is a strong incentive for laboratories to develop single test for measuring potentially acid forming forms of sulfur, viz "oxidisable"-S or sulfide-S.

The AMIRA Net Acid Generation (NAG) test is a modification for waste rock material of the Suspension Peroxide Oxidation Combined Acidity and Sulfate procedures (SPOCAS), which were introduced to Australia in the 1990s for assessing acid sulfate soils, ASS (AS 4969.12 2009). Acid sulfate soils usually contain relatively low concentrations of highly reactive microcrystalline pyrite and other iron sulfides. The NAG test is part of; (i) the AMIRA (2002) procedure and (ii) the Australian Government Guidelines on Managing Acidic and Metalliferous Drainage procedure (DITR 2007). The NAG test involves the measurement of net acidity following laboratory oxidation with peroxide with allowance for much higher concentrations of sulfides.

More recently, a more specific method for laboratory measurement of sulfide-S has been developed, initially for measuring sulfide-S in ASS materials. The method utilises the specificity of chromous ions (Cr^{2+}) in 6M HCl solution to convert sulfide-S to hydrogen sulfide gas (H_2S), which is subsequently absorbed by a gas scrubbing solution and measured by a conventional wet chemistry titration method. Reduced forms of sulfur measured by this procedure are collectively termed 'Chromium Reducible Sulfur' (CRS).

The CRS test was introduced into Australia as a rapid assessment tool for acid formation from ASS based on its previously established specificity for determining sulfide-S in the presence of organic forms of sulfur in coal samples. Although there is ample validation data to demonstrate the suitability of CRS for predicting acid formation potential in ASS, coal and various mine wastes in which pyrite is the exclusive sulfide mineral, it is being increasingly used for studies of hard rock mining in WA and elsewhere in Australia where other forms of sulfur are dominant. Only one paper (Schumann *et. al.* 2012), has to date examined using CRS for some, but not all, of the sulfide minerals examined in the present study relevant to hard rock mining.

This study aims to address emerging issues concerning the inappropriate use of the CRS method to estimate the acid production potential of waste rocks containing a diverse range of sulfidic minerals, some of which may be acid forming.

This study also compares CRS with the AMIRA method for determining sulfide-S and the suitability or otherwise for acid formation estimation in a wide range of mine wastes (other than coal and ASS) from Australasia.

Materials and Methods

A range of representative mining related waste rocks and process tailings containing various sulfur minerals and representative of base metal, precious metal, ferrous metal and other metal deposits have been be sourced from mining companies and the WA Department of Mines and Petroleum's Geological Survey group.

These samples were properly catalogued and contain varying amounts of sulfur. The rock and tailings samples selected for analysis also vary in their acid neutralisation value and the minerals with neutralising value present.

Rocks composed of sulfur-containing minerals included in the study consisted of:

- Iron sulfides (pyrite FeS_2, pyrrhotite $Fe_{(1-x)}S_x$, marcasite FeS_2).

- Copper sulfides (chalcopyrite $CuFeS_2$, chalcocite, Cu_2S).

- Arsenopyrite FeAsS.

- Molybdenite, MoS_2.

- Stibnite Sb_2S_3.

- Galena, PbS.

- Sphalerite, ZnS.

- Pentlandite, Fe,Ni(S).

Mine Waste Samples

A total of 54 samples were supplied from mining operations in Australia and overseas. Included with the study was a quartz sample used as a control blank. A summary of the details of the samples are shown in Table 2.

Table 2:   Information on the Samples Provided for this Study.

Number of Samples	Sample Type	Mine/Mineral Type
5	Process tailings	Nickel-copper
6	Tailings	Gold
10	Waste rock	Iron
6	Waste rock	Iron
7	Tailings and waste rock	Gold
1	Copper concentrate	Copper
1	High iron/nickel sulfide scale deposit	Nickel
10	Tailings and waste rock	Poly-metallic sulfides
3	Mineral specimen*	Arsenopyrite, stibnite, chalcocite ore
5	Tailings, waste rock and mineral specimens	Copper, iron, sulfidic gneiss, marcasite in calcite, molybdenite
1	Control blank	Quartz

* *Sample was diluted with quartz prior to analysis*

Sample Analysis

The samples were pulverised by ring-milling to -75 µm. The following analyses were performed on the samples :

- Mineral characterisation by XRD and SEM, on a set of 31 representative samples.

- Total sulfur.

- Sulfate-S.

- Acid Neutralising Capacity (ANC)

- Chromium-reducible sulfur (CRS) (performed by three laboratories outside of ChemCentre).

- Net Acid Generation (NAG), measuring NAG pH, NAG to pH 4.5 and NAG to pH 7.0.

- Total elemental analysis by acid digestion, ICP/AES and ICP/MS for Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se and Zn.

## Results and Discussion

Acid Base Accounting

Total sulfur concentrations ranged from <0.01% to 35.8% (Figure 1). Twelve samples (22%) contained total sulfur concentrations below a value of 0.3%, which has traditionally been considered as presenting a low risk of producing AMD in the arid and semi-arid regions of Australia. The highest total sulfur concentrations were recorded in a sample of copper concentrate (35.8% S) and a sample of lead-zinc ore (32.8%).
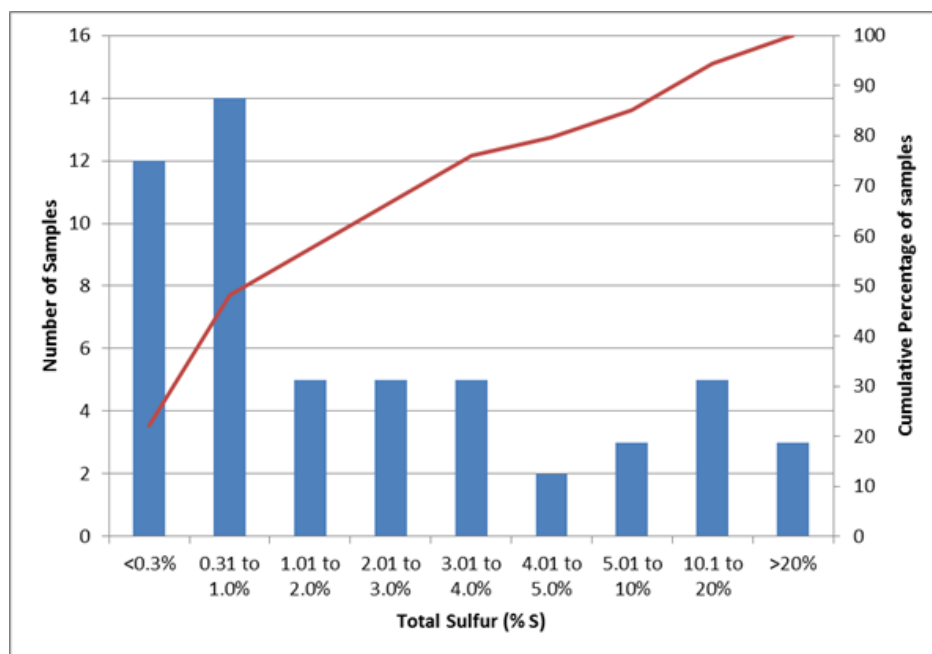
Figure 1: **Distribution of Total Sulfur Concentrations Across Samples**

In most cases, sulfate-S was a minor proportion of total sulfur, indicating most of the sulfur was present in an oxidisable (sulfide) form. As shown in Figure 2, notable exceptions were:

- Several samples of process tailings, notably two samples of lead-zinc tailings from Western Australia containing 2.95 and 5.3% sulfate-S.

- A sample of a pipe scale material from a nickel mine in Western Australia. All of the sulfur was present as calcium sulfate minerals bassinite ($CaSO_4 \cdot \frac{1}{2}H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$).
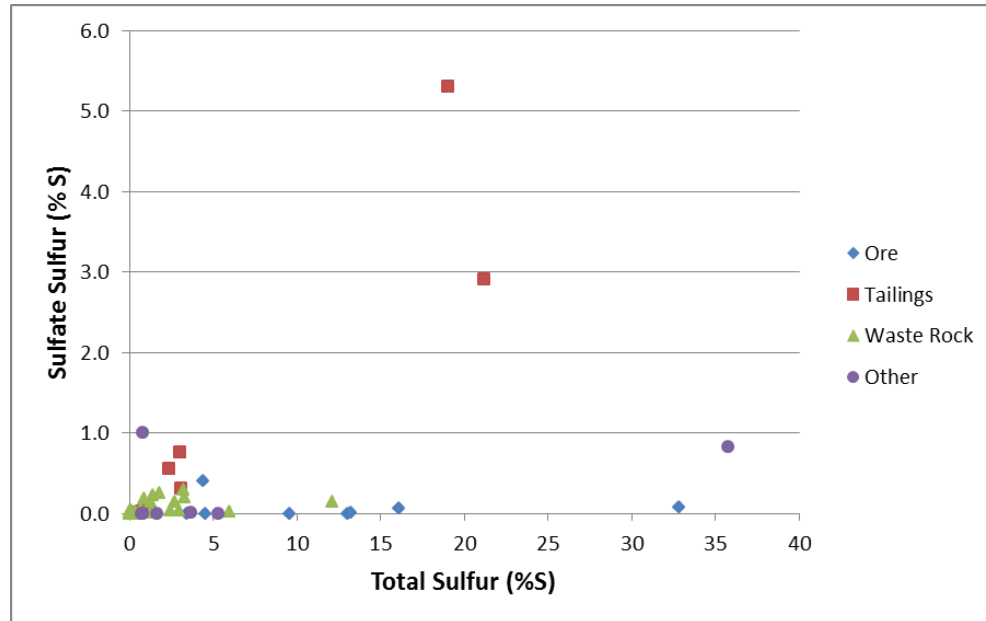
Figure 2:   Sulfate_S Compared with Total Sulfur

On the basis of conventional acid base accounting, NAG pH values and net acid production potential (NAPP) calculated for TOS were:

- 10 samples (18%) were classified as barren. Most were samples of iron ore mine waste.

- 13 samples (24%) were classified as non-acid forming (NAF).

- 28 samples (51%) were classified as potentially acid forming (PAF).

- 4 samples (7%) were classified as Uncertain:
    – Sample 14A0358/004, iron ore mine waste, had a positive NAPP value, but a NAG pH >4.5.
    – Sample 14A0377/012, lead-zinc mine waste, had a positive NAPP value, but a NAG pH >4.5.
    – Sample 14A0377/019, lead-zinc mine waste, had a positive NAPP value, but a NAG pH >4.5.
    – Sample 15S0600/003, a specimen of mineral chalcocite (Cu_2S), had a positive NAPP value, but a NAG pH >4.5.

Elemental Composition and Mineralogy

Generally, elevated metal concentrations and associated Global Abundance Index (GAI) values were elevated for the target metal of most mine waste samples.

As expected, pyrite was the dominant sulfide mineral in most gold and iron ore mine waste samples. It was also present as an accessory sulfide mineral with some of the base metal (copper, nickel and zinc) mine waste samples. Pyrrhotite was the dominant iron sulfide mineral associated with pentlandite in nickel mine samples and in gold tailings and waste rock from one particular gold mine in Western Australia.

Marcasite (FeS_2) was confirmed by XRD as being the only iron sulfide mineral recorded in a sample of mine waste from a lead-zinc mine on the Lennard Shelf in the Kimberley region of WA.

Although arsenopyrite was only detected by XRD in one sample, several gold mine waste samples contained slightly elevated arsenic (>100 mg/kg). These samples are suspected of containing trace amounts of arsenopyrite as this mineral was observed by project geologists in corresponding ore samples and drill core material. One sample of iron ore mine waste contained elevated arsenic (281 mg/kg), but the arsenic in this sample was suspected to be present as oxidised arsenic adsorbed to hydrous iron oxides (mainly goethite). Consistent with this, the corresponding TOS concentration was found to be very low at 0.01% (100 mg/kg).

Cadmium, antimony and selenium were recorded in elevated concentrations as significant non-target elements in samples of mine waste from nickel (selenium only), lead-zinc, copper and iron ore deposits.

Assessment of the CRS Method

CRS and TOS Comparisons

Figure 3 compares TOS with CRS for samples containing total sulfur concentrations below 10%. Typical recoveries of CRS compared to TOS were 80-90%, with only one sample containing CRS (2.55%) at a concentration greater than that of TOS (2.22%). This was a sample of gold process tailings in which pyrrhotite was the dominant sulfide mineral.

Generally, recoveries of calculated oxidisable sulfur by the CRS method were consistent with those reported for high purity sulfide minerals by Schumann *et al.* (2012). Two notable exceptions for which CRS concentrations were below the laboratory reporting limit (0.005%), despite containing significant concentrations of TOS were:

- A sample of arsenopyrite containing 0.71% TOS. This sample was analysed for CRS by two laboratories. Although the presence of arsenopyrite was confirmed by XRD to be the sole sulfide mineral, the lack of CRS is not consistent with the findings of Schumann *et al.* (2012) who recorded recoveries of CRS versus total S of 81% to 83%.

- A sample of molybdenite blended with quartz. Results for analysis of this sample for TOS and CRS were 3.67% and 0.046%, respectively, with the CRS procedure recovering only 1.3% of TOS.
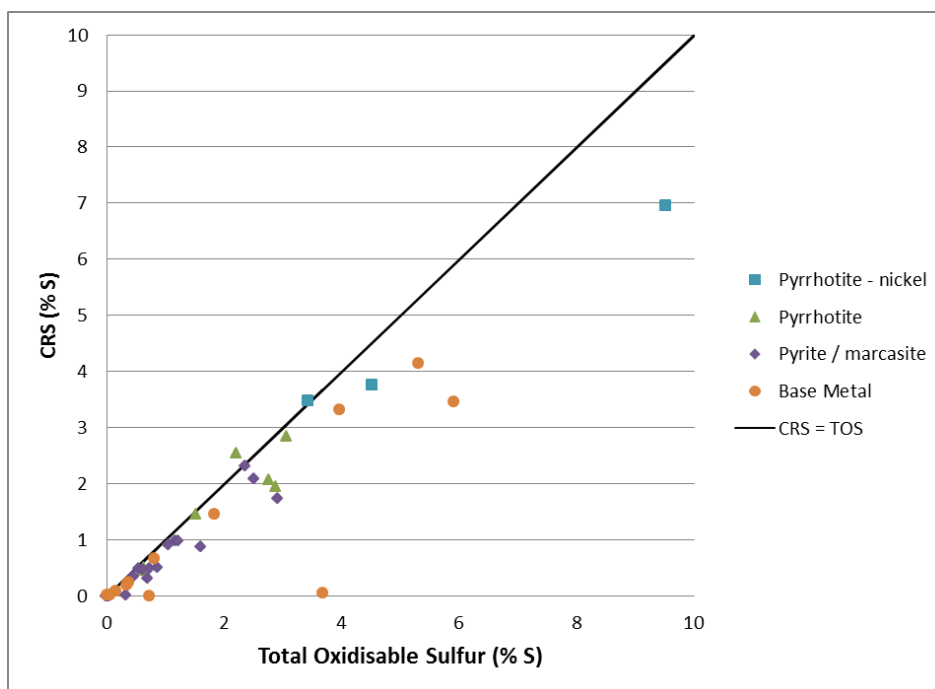
Figure 3:   Total Oxidisable Sulfur (TOS) Compared with Chromium Reducible Sulfur (CRS)

These results generally support the findings of Schumann *et al.* (2012) that the CRS method is effective at recovering most of the oxidisable sulfide from iron, copper, nickel, lead and zinc sulfides. In the case of iron sulfides, high recoveries were recorded for samples containing pyrite, pyrrhotite or marcasite – as expected based on earlier ASS studies.

The very low recovery of oxidisable sulfur in molybdenite is consistent with the statement by Plumlee (1999) that this mineral is characterised by high resistance to atmospheric oxygen. Further work will be required to assess the recovery of oxidisable sulfur in arsenopyrite by the CRS method; this study indicated that the sulfur present as arsenopyrite was not recovered as CRS, contrary to earlier findings by Schumann *et al.* (2012).

Although CRS results are typically lower than TOS for most samples assessed, this finding does not necessarily mean that the CRS method is inferior to TOS for determining sulfide sulfur content. As the sulfate-S procedure used to calculate TOS involved extraction with dilute HCl, non-acid forms of sulfate-S, such as barite ($BaSO_4$) and celestite ($SrSO_4$), will be included in the TOS fraction in such samples. Thus the acid formation potential will be over-estimated.

**Comparison of NAPP (from TOS and CRS) with NAG Test Results**

As discussed in the Introduction Section, oxidation of sulfide minerals produces variable amounts of acidity. Base metal sulfides including chalcocite, galena and sphalerite produce little or no acid, while iron sulfides can produce a maximum of 30.6 kg H_2SO_4/t for every 1% sulfide-S in mine waste samples.

NAG acidity to pH 4.5 and pH 7.0 (generated from simulated oxidation with hydrogen peroxide) was compared to calculated NAPP predicted from either TOS or CRS in order to compare the methods. Figure 4 and Figure 5 respectively show the relationships of NAG to pH 4.5 with NAPP values calculated from TOS and CRS. Figure 6 and Figure 7 show the relationships of NAG to pH 7 with NAPP values calculated from TOS and CRS, respectively. For clarity, only samples with NAPP values less than 200 kg H_2SO_4/t are shown.

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Significant observations are summarised as follows:

- All samples with negative NAPP values (no acidity generation predicted), whether calculated from TOS or CRS results, produced no acidity under conditions of the NAG tests. Sulfide minerals present in these samples were either pyrite or copper, lead or zinc sulfides.

- Only one sample produced more acidity to both pH 4.5 and pH 7.0 by the NAG test than predicted by the NAPP value calculated from TOS (Figure 4 and Figure 6). This sample contained molybdenite, which was predicted to be theoretically capable of producing more acidity on a sulfur weight basis than iron sulfides. The NAPP calculated by CRS for the same sample (Figure 5 and Figure 7) was grossly underestimated and hence TOS is more predictive for potential oxidation of molybdenite.

- Acid production as measured by the NAG test to pH 4.5 for PAF samples containing either pyrite or pyrrhotite in gold tailings were similar to or slightly lower than that predicted by NAPP values calculated from TOS concentrations. This is consistent with behaviour of these iron sulfide minerals discussed in the Introduction. Agreement with NAG pH 7 acidity values (Figure 6), was closer again. CRS generated NAPP versus NAG acidity followed the same trend but was more variable.

- Samples containing significant amounts of nickel sulfides, chalcopyrite or chalcocite produced substantially less acidity to pH 4.5 and pH 7 by the NAG test compared to predicted NAPP values calculated from either TOS or CRS. This is consistent with these base metal sulfide minerals having none or low actual acid production potential. NAG acidity measured to pH 7.0 for PAF materials is always greater than that measured to pH 4.5 due to the consumption of alkali by dissolved base metals (e.g. Cu^{2+}, Zn^{2+} and Ni^{2+}) released by peroxide oxidation of sulfide minerals containing these elements.

- NAG to pH 4.5 exceeded the NAPP calculated from CRS (i.e. underestimated laboratory simulated acid production) for six samples (Figure 5). Four of these samples also produced substantially more acidity to pH 7 under conditions of the NAG test compared to that predicted by NAPP calculated from CRS (Figure 7). These samples comprised:
    - A sample containing significant arsenopyrite. The NAG test resulted in oxidation of arsenopyrite producing 23 kg H_2SO_4/t of acidity to pH 7. Only 1 kg H_2SO_4/t of acidity was predicted by NAPP calculated from CRS.
    - A sample of sulfidic gneiss. The NAG test produced 32 kg H_2SO_4/t of acidity to pH 7. Only 6 kg H_2SO_4/t of acidity was predicted by NAPP calculated from CRS (NAPP from TOS was 28 kg H_2SO_4/t). This sample did not contain significant base metals, although the pyrite crystals were noted as particularly coarse.
    - A sample of waste rock from a gold mine in WA with gold mineralisation associated with Banded Iron Formation (BIF). Pyrrhotite was the only sulfide mineral identified by XRD. The NAG test produced 69 kg H_2SO_4/t of acidity to pH 7, which was approximately 40% greater than the 50 kg H_2SO_4/t of acidity predicted by NAPP calculated from CRS (NAPP from TOS was 79 kg H_2SO_4/t).
    - A sample of sulfidic iron ore mine waste. The NAG test produced 66 kg H_2SO_4/t of acidity to pH 7. Only 24 kg H_2SO_4/t of acidity was predicted by NAPP calculated from CRS (NAPP from TOS was 60 kg H_2SO_4/t).
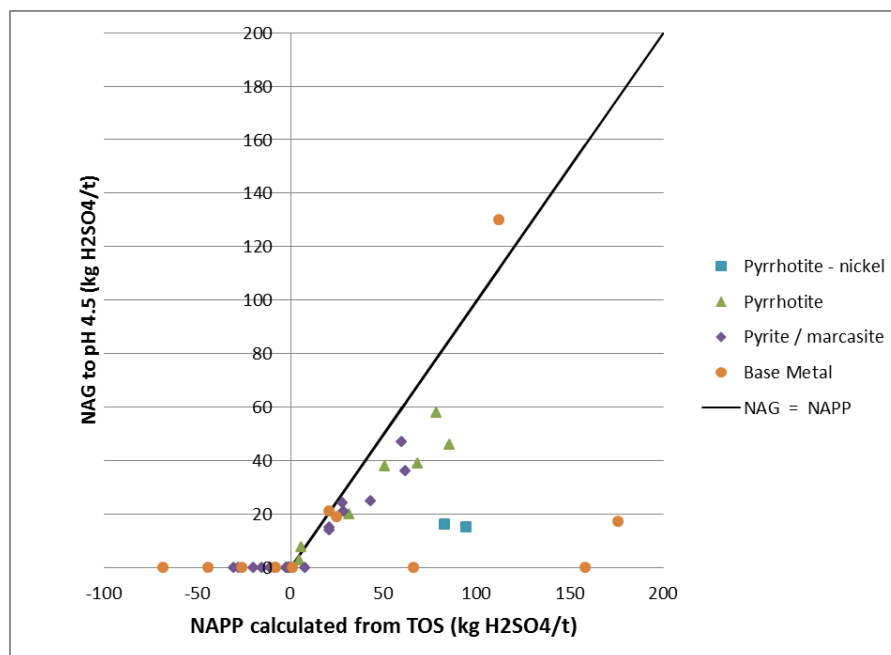
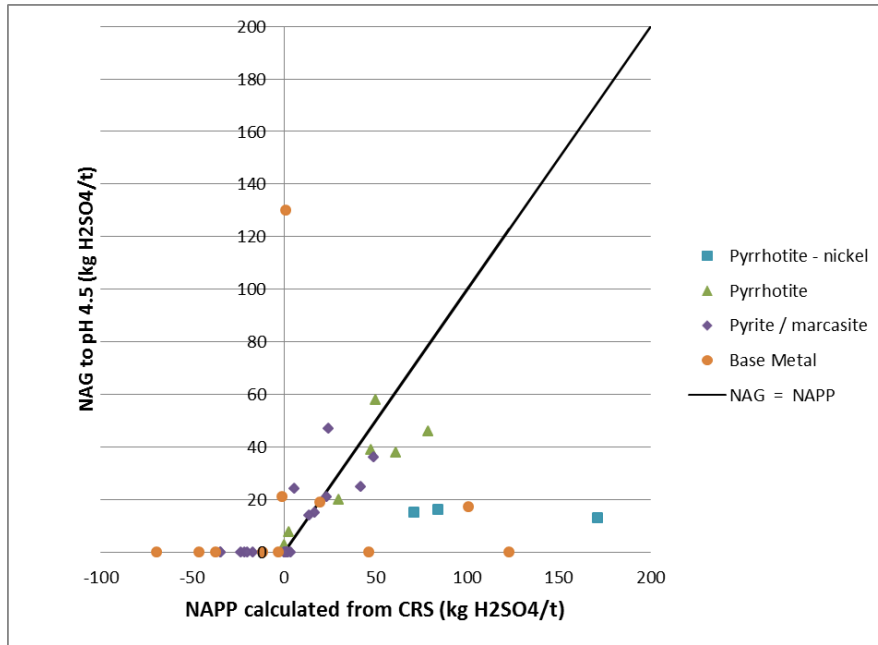**Figure 4:** NAPP Calculated from TOS Compared with NAG to pH 4.5.

Figure 5:   NAPP Calculated from CRS Compared with NAG to pH 4.5.
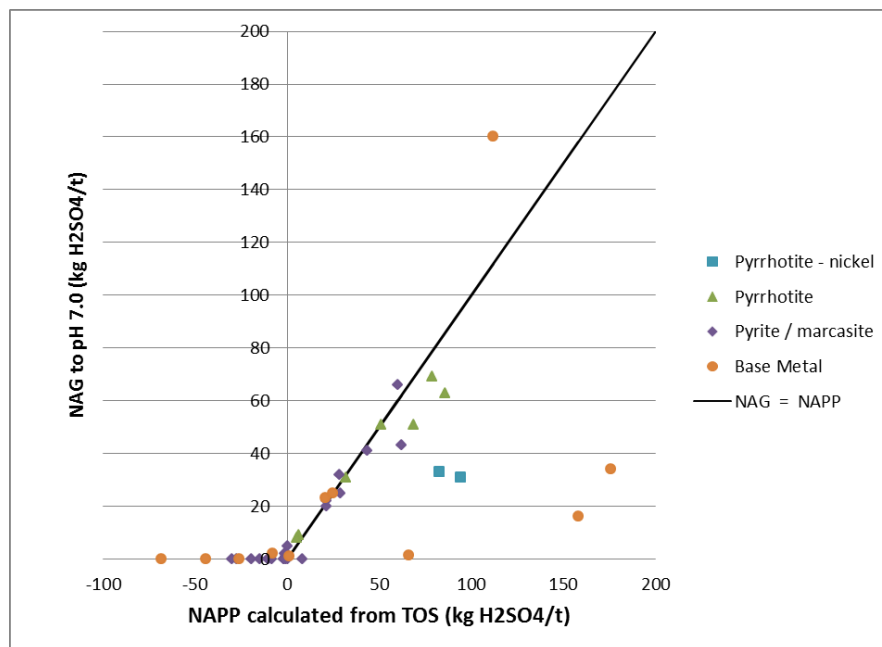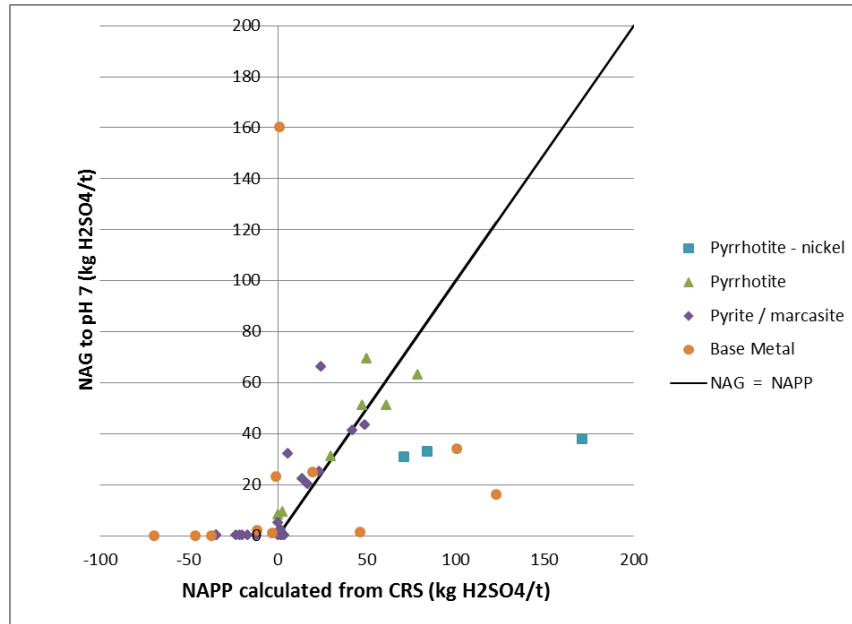

Figure 6:   NAPP Calculated from TOS Compared with NAG to pH 7.

Figure 7: NAPP Calculated from CRS Compared with NAG to pH 7.

Comparison of Acid Formation Potential Predictions

AMIRA (2002) uses a procedure in which calculated NAPP values (calculated from TOS) are compared with NAG pH values, resulting in four quadrants, as shown in Figure 8 corresponding to NAF (upper left quadrant), PAF (lower right quadrant) and Uncertain (upper left and lower right quadrants) classifications.

In this study, a comparison was made between the AMIRA (2002) based acid formation potential classifications (Figure 8) and those provided by use of CRS instead of TOS (Figure 9). Comparing Figure 8 with Figure 9 indicates very little difference between the two methods for calculating NAPP for the particular samples involved.

Table 3 summarises the number of samples classified as either; Barren, NAF, PAF or Uncertain according to classification procedures based on either AMIRA 2002 (using TOS to calculate NAPP) and CRS to calculate NAPP.
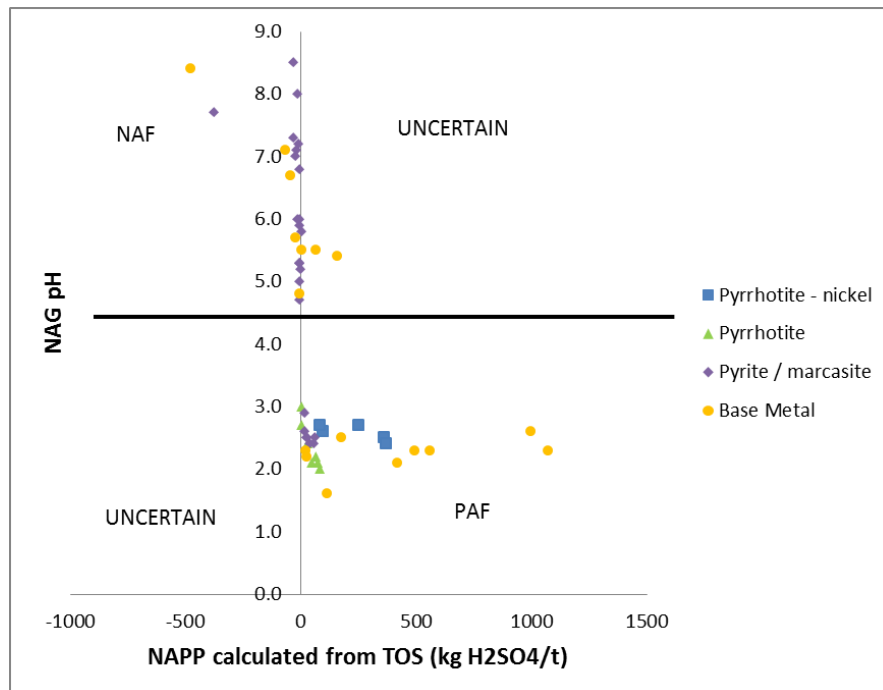
Table 3: Acid Formation Potential Classifications Based on TOS (AMIRA 2002) and CRS.

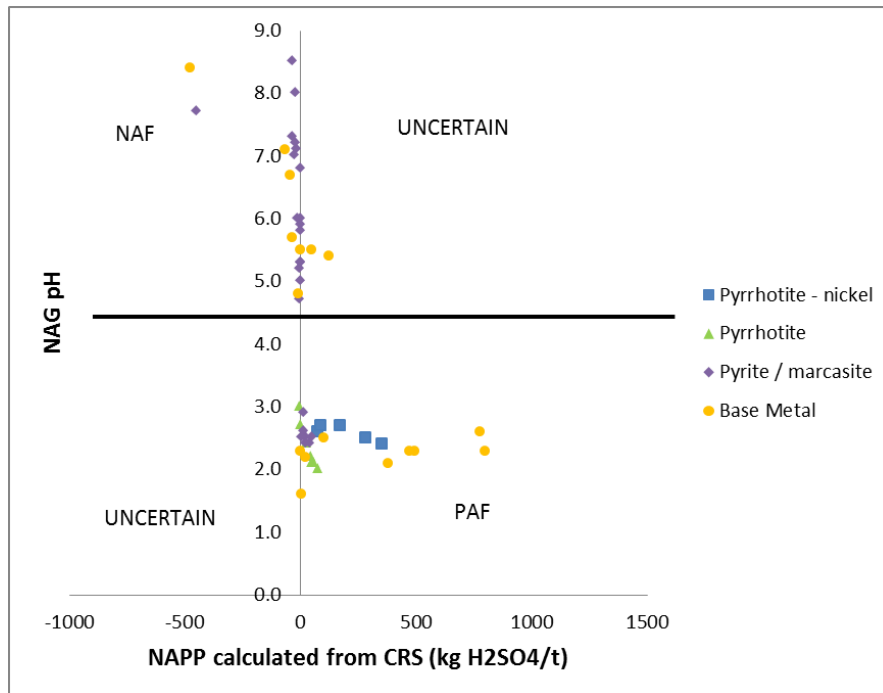| Acid Formation Potential	AMIRA (2002) based on TOS	NAPP Calculated from CRS
Barren	10 samples (18%)	11 samples (20%)
NAF	13 samples (24%)	13 samples (24%)
PAF	28 samples (51%)	25 samples (45%)
Uncertain	4 samples (7%)	6 samples (11%)

Of the 55 samples studied, only four were classified differently by the two procedures. These samples were:

- One sample of iron ore mine waste which was classified as Uncertain by the AMIRA (2002) procedure and Barren by the CRS procedure. The different classifications resulted from higher TOS (0.33%) compared to CRS (0.017%).

- A sample of gold mine waste containing pyrrhotite was classified as PAF by the AMIRA (2002) procedure and Uncertain by the CRS procedure. The different classifications resulted from higher TOS (0.62%) compared to CRS (0.458%).

- The molybdenite sample was classified as PAF by the AMIRA (2002) procedure and Uncertain by the CRS procedure. The different classifications resulted from much higher TOS (3.67%) compared to CRS (0.046%).

- The arsenopyrite sample was classified as PAF by the AMIRA (2002) procedure and Uncertain by the CRS procedure. The different classifications resulted from much high TOS (0.71%) compared to CRS (<0.005%).

In each case described above, the different classifications resulted from substantially lower estimates of oxidisable sulfide-S provided by the CRS method compared to values calculated as TOS.

Figure 8:   **Acid Formation Potential Classification According to AMIRA 2002, NAPP Calculated from TOS.**

Figure 9:   Acid Formation Potential Classification based on NAPP Calculated from CRS

Intra-Laboratory and Inter-Laboratory Quality Control Comparisons

Three commercial laboratories in Perth, Western Australia, were used for analysis of selected samples by the CRS method to determine the robustness of the method when used by different analysts in different laboratories.

Laboratories A and B provided duplicate results for five and seven samples, respectively. These pairs of values provide an indication of reproducibility within each laboratory's test method. The standard metric for intra-laboratory reproducibility is the Relative Percentage Difference (RPD%) and it is defined by Equation 4:

Equation 4:   RPD(%) = 100 * (Higher Value – Lower Value) / (Average Result)

The average calculated %RPD values for Laboratories A and B were 46.2% and 8.8% respectively. However, the %RPD value for Laboratory A was positively biased as the samples selected for duplicate analysis were those already identified as having anomalous comparisons between total S and CRS. A intra-laboratory RPD% value of 8.8% for Laboratory B is considered acceptable for this type of method over the range of total sulfur concentrations in the samples submitted.

The statistical significance in variability of the CRS results provided by Laboratories A and B was assessed using the T-test (paired sample, two-tail test). Comparisons were made for samples grouped by their total sulfur concentrations as; relatively low (<1% S), moderate (1 to 10% S) and high (>10% S). The mean

values for these sample groupings and the significance of the differences between the mean values are presented in Table 4.

Table 4:   Comparison of CRS Results from Laboratories A and B.

Total Sulfur Concentrations	<1%	1% to 10%	>10%
Number of samples	25	13	6
Laboratory A, Mean (% S)	0.26%	3.48%	18.0%
Laboratory B, Mean (% S)	0.21%	2.47%	13.8%
Significance	P <0.01	P <0.01	P <0.01

With the exception of one sample, the CRS concentrations reported by Laboratory A were greater than those reported by Laboratory B. For samples containing 1% to 10% total S (13 samples) the mean values for Laboratories A and B were 3.48% and 2.47% respectively, representing a relative positive bias of approximately 40%. This would therefore result in a significant positive bias of approximately 40% in the AP values calculated from the CRS results provided by these laboratories.

Note that this assessment only indicates a statistically significant difference in CRS results provided by Laboratories A and B, it does not imply that one Laboratory is more accurate than the other. Accuracy (versus reproducibility) of results provided by an individual laboratory can only be determined by the laboratory undertaking analysis of a relevant "Certified Reference Material" (CRM) or "Standard Reference Material" (SRM). To our knowledge, there is currently no organisation using or commercially supplying CRMs or SRMs for ABA measurements, including analysis for non-sulfate-S.

Conclusions

A total of 55 samples of multiple sulfide mineral types and across four of the major Australian resource deposits (iron ore, gold, lead/zinc and copper/nickel) were examined for ABA predictions based on both TOS (AMIRA 2002 and DITR 2007) and CRS (ISO 14388-1:2014) methodologies. Samples included waste rock, tailings, ore, mineral concentrates and high purity mineral specimens. Comparison of these two approaches to ABA was made for the various samples in the context of the determined mineralogy, sulfide form and elemental composition. Below is a summary of the key findings from this study.

Results of CRS versus TOS using the AMIRA (2002) method were generally in agreement for most samples (Figure 3). CRS results were typically lower than calculated TOS, but TOS can also include acid insoluble sulfates such as barite and celestite which do not contribute to acid formation. TOS is therefore a more conservative estimation of acid forming sulfides, but may also lead to over-prediction of AP if mineralogy is not understood.

The CRS results were found to be significantly variable within and particularly between laboratories. This variability alone raises concerns on the reliability of this method, and especially if the CRS method is applied in isolation from other tests for the "acid formation potential" classification of mine waste material. The results of CRS used in comparison to TOS in this study were largely derived from Laboratory A, which gave higher results (and closer to TOS values) than subsequent analysis performed by Laboratory B. The variability issues of the CRS method may be due to one or more of the following;

- Inappropriate operator technique (CRS is a manual intensive method dependent on operator skill).

- Wrong sample dilution and handling of high and possibly over-range sulfide samples (e.g. > 5% S) for a method designed for low sulfide containing soils.

- An apparent lack of any use of suitable CRMs or SRMs to; (i) ensure the proficiency in reporting of CRS data and (ii) determine the possible contributing factors for poor quality data.

Very significant differences between CRS and TOS were noted for two particular mineral types:

- Arsenopyrite - gave less than reportable sulfide-S by the CRS method from repeat analysis and the measured TOS was 0.71% S. These results contradict those of Schumann *et al.* (2012), who reported arsenopyrite recoveries of 81 and 83% for two samples. Arsenopyrite can be a significant mineral in some Western Australian gold deposits and hence further study of this mineral is warranted; and

- Molybdenite - gave a very low result of 1% recovery for CRS (0.046% S) versus TOS (3.67% S). Although molybdenite is not commonly found in Australian deposits, the results from this study suggest that the CRS method cannot accurately predict the acid formation potential of mine waste material if this mineral is present. TOS itself still underestimates the actual AP for this mineral but not to the degree that CRS underestimates.

Both arsenopyrite and molybdenite are highly insoluble in the 6M HCl used for CRS determinations, and this may be the cause of very low recoveries for these minerals in the standard CRS procedure.

Overall the CRS method resulted in only four disagreements with the TOS (AMIRA 2002) approach for the ABA classifications of material (PAF/NAF/Uncertain) for the 55 samples studied (noting this is based on the numerically higher set of CRS results reported by Laboratory A). Two of these samples were arsenopyrite and molybdenite noted above. One sample was an iron ore sample and the other a pyrrhotite containing gold mine waste. The general observations on AMD predictions using the CRS method arising for the following resource types are:

- Iron ore mine waste sample results for CRS gave generally good agreement or slightly lower than TOS. However, CRS may be considered the preferred procedure to measure sulfides for these iron

sulfide based wastes given the often noted presence of barite and celestite in various iron ore deposits (particularly BIF). One exception was noted for a sulfidic gneiss sample which produced significantly more acidity (NAG to pH 7) than the CRS method predicted. Presence of very coarse pyrite crystals was noted in this sample. Issues on variability of CRS data should be investigated further and resolved.

- Gold mine waste samples generally contain iron sulfides as the dominant acid forming sulfide and good predictions based on CRS should be possible for this mine type, provided arsenopyrite levels are not significant and any variability issues for CRS determination are resolved. The primary arsenopyrite sample in this study produced 23 kg H_2SO_4/t acidity from NAG to pH7, which was not predicted by CRS measurements.

- Copper/nickel deposits have variable acid production which is proportional to the iron content rather than total sulfide, copper or nickel. Thus, accurate prediction relies on knowledge of the mineral forms. Pyrrhotite is often the dominant iron sulfide present in nickel sulfide (pentlandite) deposits. Hence, acid formation from these minerals as well as from chalcopyrite (common in copper sulfide ores) is less than standard ABA predictions, which are based on pyrite and use a factor of 30.6 x sulfide-S (Equation 2). CRS measurements in these types of samples should be at least combined with NAG acidity determinations and mineralogy for better AMD predictions.

- Lead/zinc deposits - It was noted that many lead/zinc deposit samples in this study had significantly lower CRS recoveries versus TOS (five polymetallic lead/zinc/iron samples gave only 34 to 68% recovery). This difference may not be considered an issue since galena and sphalerite are regarded as non-acid forming minerals. However in practice, the application of either ABA sulfide determination method to these minerals will give false classifications as acid forming.

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