USING CHROMIUM REDUCIBLE SULFUR TO PREDICT ACID FORMATION POTENTIAL


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ABSTRACT

Generation of acid and metalliferous drainage (AMD) from waste rock and tailings in hard rock mining is a significant issue which requires management throughout the mining process, from initial impact assessment applications to closure. Draft Western Australian DMP Mining Proposal guidelines are considering various possible changes to waste characterisation methodology.

In Western Australia, standard static and kinetic waste characterisation methodologies, largely those published in 2002 by the Australian Minerals Industry Research Association (AMIRA), are usually applied. Typically, acid base accounting (ABA) procedures are used (oxidisable sulfur plus acid neutralisation capacity). A complementary method for estimating the acid production potential is direct measurement of sulfide sulfur (instead of oxidisable sulfur) as Chromium Reducible Sulfur, CRS, which was developed for analysis of acid sulfate soils that also contain significant amounts of non-acid forming organic sulfur.

Concerns have arisen in industry on the possible inappropriate use of CRS for AMD prediction of hard rock mining wastes with limited knowledge or validation data on its suitability, in particular for base metal sulfides. Reasoning for the use of CRS over conventional ABA methodologies surrounds cost and time savings.

This paper compares CRS methodology with conventional ABA methodologies to predict acid production potential in hard rock mining wastes. The results demonstrate that CRS is a potentially useful tool for ABA, although it is still recommended that ABA tests are used in conjunction with CRS to incorporate acid neutralising/consuming effects when predicting AMD.
1.0 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) and other material likely to contain organic sulfur, mainly coal. The CRS method has been shown to be suitable for measurement of pyritic sulfur with no interferences from organic sulfur in coal wastes (Stewart et al. 2009). 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.

Oxidation of some, but not all, sulfur minerals containing TOS results 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. Sulfide minerals, such as pyrite, undergo oxidation by reaction with atmospheric oxygen and water, generating acid (H$^+$) and a yellow-orange precipitate, simplified as “ferric hydroxide” (Fe(OH)$_3$) (Eqn [1]).

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 16H^+ + 8SO_4^{2-}$$

[1]

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.

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, which assumes all sulfide sulfur to be present as pyrite based on the conversion factor of 30.6. 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.

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 there is a detailed understanding of the sulfur minerals present.

Sulfide-S can be measured in the laboratory by three methods, either by direct (e.g. CRS) or indirect measurements including separate measurements of total S and sulfate S and measurement of “oxidisable-S” by oxidation with hydrogen peroxide (H$_2$O$_2$). 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.

A more specific method for direct 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$_2$S), 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 dominant sulfide mineral (with marcasite), it is being increasingly used for studies of hard rock mining in WA and elsewhere in Australia where other forms of sulfur are dominant. Few papers (for example, Schumann et al. 2012, have 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.

### 2.0 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.
2.1 Mine Waste Samples

A total of 55 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 1. The rock and tailings samples selected for analysis vary in the amount of total sulfur, their acid neutralisation capacity and the minerals with neutralising value present. The following sulfide minerals were included in this cohort of samples:

- Iron sulfides (pyrite FeS$_2$, pyrrhotite Fe$_{(1-x)}$S, marcasite FeS$_2$).
- Copper sulfides (chalcopyrite CuFeS$_2$, chalcocite, Cu$_2$S).
- Arsenopyrite FeAsS.
- Molybdenite, MoS$_2$.
- Stibnite Sb$_2$S$_3$.
- Galena, PbS.
- Sphalerite, ZnS.
- Pentlandite, Fe,Ni(S).

Table 1. Sample descriptions

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

* Sample was diluted with quartz prior to analysis

2.2 Methods

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.
Assessment of CRS Methodology for Hard Rock Mining

- Sulfate-S.
- Acid Neutralising Capacity (ANC)
- 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.

3.0 RESULTS AND DISCUSSION

3.1 Acid Base Accounting

Total sulfur concentrations ranged from <0.01% to 35.8%. 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%).

In most cases, sulfate-S was a minor proportion of total sulfur, indicating most of the sulfur was present in an oxidisable (sulfide) form. 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 (CaSO₄·½H₂O) and gypsum (CaSO₄·2H₂O).

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. These comprised waste samples from iron ore, lead-zinc mine and a chalcocite (Cu₂S) specimen where positive NAPP values were paired with NAG pH values of greater than 4.5.

3.2 Mineralogy

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 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 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.

### 3.3 Comparison of CRS and TOS Methods

A comparison of TOS with CRS for samples containing total sulfur concentrations below 10% was performed by plotting TOS versus CRS. 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.

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 a statement by Plumlee and Logsdon (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 (BaSO₄) and celestite (SrSO₄), will be included in the TOS fraction in such samples. Thus the acid formation potential will be over-estimated.

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

In this study, 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. Key observations included:

- All samples for which negative NAPP values were calculated (no acid generation predicted) from both TOS and CRS calculations had good agreement with NAG values. Minerals comprised iron or copper, lead or zinc sulfides.
- Good agreement between acid production prediction of NAG 4.5 and NAPP using TOS and better correlation observed for NAG 7.0 versus NAPP. NAPP calculated using CRS showed the same trends, but tended to be more variable.
- Only one sample (molybdenite) produced more acidity for both NAG 4.5 and 7.0 compared to calculated NAPP values using TOS. NAPP calculated using CRS for the same sample substantially underestimated the acid production potential using ABA methodology. Molybdenite, however, oxidises very slowly (Plumlee and Logsdon (1999)) and the rate of acid formation is usually very slow under laboratory and field conditions.
- Consistent results between TOS and CRS calculated NAPP versus NAG for low acid producing sulfide minerals (nickel sulfides, chalcopyrite and chalcocite) where NAG values were significantly less compared to the calculated NAPP.
- NAG to 4.5 exceeded calculated NAPP values using CRS for six samples of which four also exceeded NAG 7.0 compared to predicted NAPP. These samples notably contained sulfidic minerals including arsenopyrite, pyrite and pyrrhotite.

3.5 Comparison of Acid Formation Potential Classifications

Acid formation potential classification methodology was based on the four-quadrant approach outlined by AMIRA (2002) using calculated NAPP versus NAG pH values. Very little difference was observed for calculating NAPP from TOS and CRS for samples under investigation. Table 2 compares the acid formation potential classifications using NAPP calculated according to the AMIRA (2002) method (using TOS) and CRS.

Of the 55 samples studied, only four were classified differently by the two procedures. The discrepancies between classifications using TOS and CRS mainly concerned higher TOS values compared to CRS. Samples that were classified differently comprised iron ore, gold mine waste, arsenopyrite and molybdenite.
Table 2. Acid formation potential classifications based on TOS (AMIRA 2002) and CRS

<table>
<thead>
<tr>
<th>Acid Formation Potential</th>
<th>AMIRA (2002) based on TOS</th>
<th>NAPP Calculated from CRS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barren</td>
<td>10 samples (18%)</td>
<td>11 samples (20%)</td>
</tr>
<tr>
<td>NAF</td>
<td>13 samples (24%)</td>
<td>13 samples (24%)</td>
</tr>
<tr>
<td>PAF</td>
<td>28 samples (51%)</td>
<td>25 samples (45%)</td>
</tr>
<tr>
<td>Uncertain</td>
<td>4 samples (7%)</td>
<td>6 samples (11%)</td>
</tr>
</tbody>
</table>

3.6 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.

Only two 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%). There was a significant difference for average RPD% between Laboratories A and B (46.2 versus 8.8%, respectively). Laboratory A provided duplicate results for samples known to have anomalous comparisons between total S and CRS (positively biased). The RPD% of 8.8% provided by Laboratory B is considered acceptable for this type of method and range of total sulfur concentrations.

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 3.

Table 3. Comparison of CRS results from laboratories A and B

<table>
<thead>
<tr>
<th>Statistical Parameter</th>
<th>Total S Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Number of samples</td>
<td>25</td>
</tr>
<tr>
<td>Laboratory A, Mean (% S)</td>
<td>0.26%</td>
</tr>
<tr>
<td>Laboratory B, Mean (% S)</td>
<td>0.21%</td>
</tr>
<tr>
<td>Significance</td>
<td>P &lt;0.01</td>
</tr>
</tbody>
</table>

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.

4.0 CONCLUSIONS

Results of CRS versus TOS using the AMIRA (2002) method were generally in agreement for most samples. 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. Only small proportions of total sulfur in arsenopyrite and molybdenite minerals was measureable as CRS. These minerals are not soluble in 6M HCl used during CRS, which may explain the low recoveries. TOS is therefore a more conservative estimation of acid forming sulfides, but may also lead to over-prediction of acid potential if mineralogy is not understood.

Overall, there were only four disagreements between acid forming classifications when comparing TOS and CRS derived NAPP calculations. The following comments are considered relevant for use of the CRS method according to waste type:

- Iron ore waste samples had good agreement or slightly lower than TOS. CRS is considered the preferred method for analysis of these waste types given the often noted presence of barite and celestite in these rock types.
- Gold mine waste samples generally contain iron sulfides as the dominant acid forming sulfide and good predictions for acid potential based on CRS should be possible for this mine type, provided arsenopyrite levels are not significant.
- Samples containing copper or nickel sulfides have variable acid production based on iron content rather than sulfide, copper or nickel. Pyrrhotite, chalcopyrite and pentlandite are common iron sulfide minerals in these rock types and are typically less than acid formation predicted by standard ABA parameters. CRS should at least be combined with NAG acidity and mineralogy measurements to better predict AMD potential.
- Lead/zinc deposits typically contain galena and sphalerite which are non-acid forming and usually give false positive results by application of ABA methodology. The differences between TOS and CRS are therefore not considered problematic.
- CRS results were found to be significantly variable within and particularly between commercial 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.

Funding for this project by the Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) is acknowledged.
REFERENCES


