Applicability of the chromium reducible sulfur test for acid metalliferous drainage prediction in hard rock mining

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ABSTRACT

The potential for Acid and Metalliferous Drainage (AMD) from waste rock in mining operations is a key issue which must be addressed at all stages, from the initial mining proposal to rehabilitation and site closure. The Chromium Reducible Sulfur (CRS) method was originally introduced into Australia as a rapid and cost-effective method to estimate the acid production potential of acid sulfate soils. However, concerns are being raised over its potentially inappropriate use without supporting scientific evidence to assess the AMD potential of mine wastes in hard rock mining, especially those containing base metal (lead, zinc, copper and nickel) sulfides.

This paper outlines the results of a comparative laboratory study of 55 Western Australian mine waste samples and mineral specimens for AMD potential using CRS results from routine commercial laboratories normally handling soil samples as well as conventional approaches. CRS was found to be generally suitable for many applications, particularly for common iron sulfides at low to moderate concentrations (relevant to many iron ore, mineral sands and gold mining operations). However, CRS was not a reliable predictor of potential acid production from samples containing elevated concentrations of iron sulfides, base metal sulfides, arsenopyrite or molybdenite. Issues with CRS precision and bias were also indicated. A good understanding of sulfide mineralogy is required for accurate AMD predictions of these types of mine wastes, and cannot be obtained from any single test.

1. Introduction

The Chromium Reducible Sulfur (CRS) method is now a routine commercial laboratory method originally introduced into Australia to estimate the acid production potential of acid sulfate soils (Sullivan et al., 1999, 2000; Ahern et al., 2004; ISO, 2014a,b) and coal mine wastes (Schumann et al., 2012), usually siliceous materials containing relatively low concentrations of iron sulfides. However, it is being increasingly used to assess Acid and Metalliferous Drainage (AMD) potential from hard rock mine waste, despite limited validation data to demonstrate its suitability for mineralized rocks, especially those containing base metal sulfides. Conventional AMD characterization relies on a combination of several different analytical methods, so the appeal of CRS as a single test with reduced analytical costs and time savings, is understandable but requires investigation. The purpose of the present work was an initial examination of results for CRS by standard commercial laboratory methods validated for soils (but not waste rock) versus conventional AMD assessment using multiple techniques.

1.1. Acid generation in hard rock mining

Acid generation typically occurs when acid-forming sulfur minerals (usually containing iron as the dominant base metal, for which pyrite (FeS_2) is most common mineral) are exposed to both oxygen and water, reacting to produce sulfuric acid and a characteristic yellow-orange precipitate, simplified as ferric hydroxide ($Fe(OH)_3$), as summarized by Equation (1).

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 16H^+ + 8SO_4^{2-} \qquad (1)$$

Provided that complete oxidation of the sulfide minerals proceeds according to the stoichiometry of Equation (1), the Maximum Potential Acidity (MPA) can be calculated from the total sulfur concentration (% by weight) by multiplying by a factor of 30.6 (Equation (2)).

$$\text{MPA (kg } H_2SO_4/t) = 30.6 \times \text{Total S (\%)} \qquad (2)$$

The use of total sulfur is the most conservative approach because some sulfur may occur in forms other than pyrite (FeS_2). If the sulfur-

Table 1
Sulfur mineral classes and acid formation Potential.[1]

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 ($KAl_3(OH)_6(SO_4)_2$)	Produce some acid by hydrolysis
Reduced Sulfur Species	Thiosulfates, sulfites, polythionates	Thiosulfate ($S_2O_3^{2-}$) Dithionate ($S_2O_6^{2-}$)	Produce some acid by oxidation
	Elemental sulfur	Sulfur (S)	Produces 30.6 kg[2] H_2SO_4/t by bacterial oxidation
Sulfides	Iron sulfides	Pyrite (FeS_2) Marcasite (FeS_2)	Produce 30.6 kg[2] H_2SO_4/t by oxidation
		Pyrrhotite ($Fe_{(1-x)}S$)	Produces <30.6[2] kg H_2SO_4/t by oxidation, depending on oxygen supply
	Mixed iron-base metal sulfides	Chalcopyrite ($CuFeS_2$) Pentlandite ($(Fe,Ni)_9S_8$) Bornite (Cu_5FeS_4)	Produce <30.6[2] kg H_2SO_4/t 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 in the pure mineral forms.
	Arsenic and molybdenum sulfides	Arsenopyrite (FeAsS) Realgar (As_4S_4) Molybdenite (MoS_2) Orpiment (As_2S_3)	May produce >30.6[2] kg H_2SO_4/t by oxidation

[1] *(Price 2009)*

[2] *Acid Formation Potential values apply to samples containing 1% sulfur by weight*

containing mineralogy is known, then allowance can be made for non acid-generating and lesser acid-generating sulfur forms to provide a better MPA estimate. Sulfate minerals (gypsum, anhydrite, barite, celestite), and organic sulfur, for example, are non acid-generating sulfur forms. Other base metal sulfides such as chalcocite, sphalerite and galena yield less acidity than pyrite and, in some cases, are non-acid-generating or even acid-consuming. Table 1 summarizes the acid formation potential of different sulfur minerals.

1.2. Measurement of AMD

MPA, as it assumes all sulfur present is oxidizable, greatly overestimates the potential acidity of mineral wastes in deeply weathered (oxide) or partly weathered (transition) regolith. As a result, a number of more complex techniques have been developed to better estimate AMD.

Waste rock characterization 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, Innovation and Science (DIIS, 2016). Tests aim to identify the distribution and variability of key geochemical parameters such as sulfur content, sulfur speciation, Acid

Neutralizing Capacity (ANC) and elemental composition, along with acid-generating and element leaching characteristics under neutral, acidic or alkaline conditions.

AMD estimation invariably commences with the Acid Base Account (ABA) using static test procedures that rely on the estimation of sulfide-S as an indicator of acid formation potential, and titrimetric analyses to determine ANC.

Sulfide-S can be measured by:

- Direct measurement, using reactions that specifically measure reduced (sulfide) forms of sulfur. The CRS method is the main example of this.
- Indirect measurement, which requires separate measurements of total S (usually by a combustimetric procedure) and sulfate-S (typically involving extraction with a dilute, non-oxidizing, hydrochloric acid solution).
- Measuring 'oxidizable'-S, which is defined as the increase in concentration of soluble sulfate-S when reacted with a strong oxidizing 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 measuring acid