



Acid–base accounting assessment of mine wastes using the chromium reducible sulfur method

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ABSTRACT

The acid base account (ABA), commonly used in assessment of mine waste materials, relies in part on calculation of potential acidity from total sulfur measurements. However, potential acidity is overestimated where organic sulfur, sulfate sulfur and some sulfide compounds make up a substantial portion of the sulfur content. The chromium reducible sulfur (CRS) method has been widely applied to assess reduced inorganic sulfur forms in sediments and acid sulfate soils, but not in ABA assessment of mine wastes. This paper reports the application of the CRS method to measuring forms of sulfur commonly found in mine waste materials. A number of individual sulfur containing minerals and real waste materials were analyzed using both CRS and total S and the potential acidity estimates were compared with actual acidity measured from net acid generation tests and column leach tests. The results of the CRS analysis made on individual minerals demonstrate good assessment of sulfur from a range of sulfides. No sulfur was measured using the CRS method in a number of sulfate salts, including jarosite and melanterite typically found in weathered waste rocks, or from dibenzothiophene characteristic of organic sulfur compounds common to coal wastes. Comparison of ABA values for a number of coal waste samples demonstrated much better agreement of acidity predicted from CRS analysis than total S analysis with actual acidity. It also resulted in reclassification of most samples tested from PAF to NAF. Similar comparisons on base metal sulfide wastes generally resulted in overestimation of the acid potential by total S and underestimation of the acid potential by CRS in comparison to acidity measured during NAG tests, but did not generally result in reclassification. In all the cases examined, the best estimate of potential acidity included acidity calculated from both CRS and jarositic S.

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1. Introduction

The acid–base account (ABA) is one of the most commonly used methods in the assessment of mine waste materials for acid forming characteristics (INAP, 2009). The ABA method involves static laboratory procedures that evaluate the balance between acid generation processes (primarily oxidation of sulfide minerals) and acid neutralizing processes (dissolution of alkaline carbonates, displacement of exchangeable bases, and weathering of silicates).

The values arising from the ABA method are often referred to as the maximum potential acidity (MPA) and the acid neutralizing capacity (ANC). The difference between the MPA and the ANC is referred to as the net acid producing potential (NAPP). The usefulness of the NAPP value obtained for a given sample will of course depend on how well both the MPA and the ANC values determined for the sample represent the behavior of the waste material in the environment.

In its simplest form, MPA is calculated from the total sulfur content of the sample using the formula:

$$\text{MPA}(\text{kg H}_2\text{SO}_4/\text{t}) = (\text{Total \%S}) * 30.6. \quad (1)$$

The 30.6 factor is based on the assumption that all sulfur measured by the total S method can be oxidized to produce 1 mol of sulfuric acid per mole of sulfur, as for example occurs during the oxidation of pyrite. However, it is widely recognized that this approach is highly conservative as this assumption is invalid for many waste samples.

To address this issue, several approaches aimed at speciating sulfur types in both coal and base metal mine wastes have been investigated. Various extraction methods have been used (Day et al., 2000; Lapakko, 2002), but it is generally recognized that these methods lack the precision of the high temperature combustion total S method (Kania, 1998) and are not always particularly selective (Jennings and Dollhopf, 1995). The net carbonate value (NCV) method (Lapakko, 2002) is an acid base accounting approach in which the acid potential of a sample is calculated from Leco total S, Leco total C, Leco S after pyrolysis (non-acid sulfide portion) and Leco C after HCl digestion

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(non-carbonate C portion). The acid forming component of the sample is represented by the difference between the total S and S after pyrolysis, and the acid consuming component is represented by the difference between the total C and the C after HCl digestion. Previous investigations showed that the NCV was a useful way of estimating the acid generating S content of metalliferous waste samples (Smart et al., 2006). However, it was apparent that the sulfur content produced by this method would include sulfur from both pyrite and organic sulfur compounds, and hence not provide the required differentiation between these two major sulfur forms commonly present in coal waste materials. Similarly, methods based on selective extractions such as the modified acid base accounting procedure described by Lawrence and Wang (1996), which uses hydrochloric acid leach to determine sulfate sulfur, are unlikely to distinguish between pyritic and organic sulfur forms, while multiple extraction procedures such as that of Sobek et al. (1978) can introduce analytical uncertainty due to the cumulative nature of the analytical error (Mills, 1998).

Paktunc (1999) recognized the problems associated with evaluating MPA and suggested that a mineralogical approach may be a better alternative. He indicated that to take into account the presence of various sulfides in a sample, the (chemical) MPA should be calculated according to the equation:

$$MPA = \sum_{s=1}^m \frac{n_s \times 98 \times X_s \times 10}{w_s} \quad (2)$$

where n_s is the number of moles of sulfuric acid produced when 1 mol of the sulfide mineral s is oxidized, w_s is the molecular weight of the sulfide mineral s , m is the number of sulfide species present in the sample and X_s is the wt.% of the sulfide s in the sample. This method requires a detailed knowledge of the sulfide mineralogy of the sample, which will limit its use as part of a large sample volume screening tool such as ABA.

The chromium reducible sulfur (CRS) method, originally developed for sulfur speciation in sediments (Cornwell and Morse, 1987; Morse and Cornwell, 1987; Zhabina and Volkov, 1978), has found widespread application in assessment of the acid producing characteristics of acid sulfate soils (Burton et al., 2008; Ward et al., 2004; Sullivan et al., 2000). CRS analysis is based on the conversion of reduced inorganic sulfur to H_2S by a hot acidic $CrCl_2$ solution; the evolved H_2S is trapped in a zinc acetate solution as ZnS. The ZnS may be quantified by iodometric titration. Alternatively, H_2S can be quantified directly using a specific gas sensor. CRS is selective to inorganic sulfur with an oxidation state of less than +6 (Burton et al., 2008). The reaction may be as simple as the dissolution of monosulfide in the presence of acid to form H_2S , or may involve reduction of the S–S bond in disulfides such as pyrite to liberate H_2S , or both processes may take place (Luther, 1987).

Several studies have investigated recoveries of individual mineral samples and demonstrated that disulfides such as pyrite and monosulfides such as pyrrhotite, sphalerite, and amorphous and crystalline iron monosulfides (greigite and mackinawite) are quantitatively recovered, while the sulfur in sulfate salts such as barite, gypsum and sodium sulfate is not recovered during the CRS assay (Kallmeyer et al., 2004; Ulrich et al., 1997; Cornwell and Morse, 1987). The CRS method is also reported to include intermediate sulfide oxidation products such as thiosulfate and polythionates (Ward et al., 2004), which will liberate acid on further oxidation to sulfate. In addition, a number of organic sulfur compounds such as amino acids, proteins and organic sulfates have been assayed by CRS and, based on these compounds, it appears that organosulfur compounds are also not included in the CRS assay (Sullivan et al., 1999; Canfield et al., 1986; Wieder et al., 1985). The recovery of elemental sulfur by CRS analysis appears to be related to the particle size and crystallinity of the material, but addition of solvent (e.g. acetone) prior to analysis results in

quantitative recovery, suggesting heterogeneous reduction of elemental sulfur by Cr(II) is less favorable than homogeneous reaction in solution (Hsieh and Shieh, 1997; Fossing and Jørgensen, 1989; Hsieh and Yang, 1989).

These results suggest that the CRS method may be useful in measuring the acid producing sulfur content of base metal mine wastes and particularly coal waste samples where exclusion of organic sulfur from the MPA calculation is desired. The CRS method has been applied to analysis of some base metal mine wastes, particularly sulfide tailings (Praharaj and Fortin, 2008; 2004; Schippers et al., 2007; Budakoglu and Pratt, 2005) and waste rock (Wilkin and Bischoff, 2006), as part of sulfur speciation work. It has also been used as part of sulfur speciation schemes for coal (Bottrell et al., 1994) and oil shales (Tuttle et al., 1986), but has not been used for ABA assessment of these types of materials.

As part of our work in development of an acid rock drainage (ARD) assessment of base metal mine (Li et al., 2007) and coal wastes (Stewart et al., 2009), we investigated the utility of the CRS method for calculation of MPA. The CRS recoveries of sulfur from a wide range of the common individual sulfide minerals, some of which have not been reported previously, both acid producing (jarosite and melanterite) and non-acid forming (gypsum, barite etc.) sulfate salts and organic sulfur compounds were examined using the CRS method. Both total Leco S and CRS were applied to a number of base metal mine wastes and coal wastes to determine NAPP values of these materials. Comparison between the acid producing potential as determined by total S and CRS analyses was compared with actual acidity obtained from net acid generation tests (NAG) and column leach tests. The results of these investigations are reported here.

2. Methods

2.1. Preparation of individual mineral samples

The single minerals used for CRS tests were: melanterite ($FeSO_4 \cdot 7H_2O$, 99%, Chem-Supply, Australia); epsomite ($MgSO_4 \cdot 7H_2O$, 99%, Chem-Supply, Australia); gypsum ($CaSO_4 \cdot 2H_2O$, 99%, $CaCO_3 < 0.025\%$, $Fe < 0.002\%$, May & Baker LTD, Australia); sodium sulfate (Na_2SO_4 , 99.5%, BDH Chemicals Australia Pty Ltd); barite ($BaSO_4$, 99%, Sigma Aldrich); sulfur (99.999%, – 75 μm , Sigma Aldrich); dibenzothiophene ($C_{12}H_8S$, 98%, Sigma Aldrich); jarosite ($Na_{0.88} K_{0.12} Fe_{2.96} Al_{0.04} (SO_4)_2 (OH)_6$, 94.5%, 12.50% S, 3.85% Na, 0.88% K, 31.4% Fe, 0.22% Al, South Australian Museum); pyrite (FeS_2 , 97%, 44.6% Fe, 51.93% S, 0.7% Si, 0.42% Al, 0.15% Ca, 0.11% K, 0.04% Cu, 0.04% Zn, 0.01% As, Huanzala Mine, Peru); pyrrhotite ($Fe_{0.83}S$, 80%, 47.0% Fe, 32.6% S, 0.29% Si, 0.09% Cu, 4.64% Zn, 0.30% Pb, 1.45% C, North Bend Washington, USA); arsenopyrite ($AsFeS$, 99%, 34% Fe, 46% As, 19% S, Ward's Natural Science Establishment); chalcocyprite ($CuFeS_2$, 99%, 30.3% Fe, 34.4% Cu, 34.5% S, 0.06% Zn, 0.03% Pb, 0.04% Mn, 0.39% Si, 0.19% Ca, 0.07% Mg, Moonta Bay, South Australia, Australia); pentlandite ($(Fe_{4.5}Ni_{4.5})_8S_8$, 98%, 33.6% Fe, 32.6% Ni, 31.6% S, synthetic sample supplied by Anglo Platinum Research Centre), chalcocite (Cu_2S , 99%, 79% Cu, 20% S, Ward's Natural Science Establishment); covellite (CuS , 99%, 66% Cu, 33% S, Ward's Natural Science Establishment); bornite (Cu_5FeS_4 , 99%, 11% Fe, 63% Cu, 25% S, Ward's Natural Science Establishment); galena (PbS , 99%, 86.1% Pb, 13.2% S, 0.005% Cu, 0.14% Zn, 0.08% Fe, 0.005% Mn, 0.09% Si, 0.02% Ca, 0.005% Mg, Broken Hill, New South Wales, Australia) and sphalerite (ZnS , 99%, 66.7% Zn, 32.7% S, 0.25% Fe, 0.06% Cu, 0.07% Pb, 0.01% Mn, 0.07% Si, 0.19% Ca, 0.01% Mg, Elmwood Mine, Carthage, Tennessee, USA); quartz (SiO_2 , 98.6%, 46% Si, 0.03% Co, 0.02% Al, $K < 0.05\%$, $Fe < 0.01\%$, Ward's Natural Science Establishment).

The sulfide mineral samples were pulverized either by benchtop mill or mortar and pestle and sieved to – 75 μm . The sized samples were then washed once with aqueous solution adjusted to pH 1 with HCl for 1 min, rinsed 5 times with reagent water and rinsed

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