

A SIMPLIFIED METHOD FOR ESTIMATION OF JAROSITE AND ACID-FORMING SULFATES IN ACID MINE WASTES¹

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Introduction

In standard acid base accounting methods, estimation of net neutralizing potential (NNP) from acid mine wastes is made by subtracting the acid potential (AP) from the neutralizing potential (NP). The AP estimate is determined from the total %S assay x 30.6 assuming that all S reacts according to the pyrite oxidation stoichiometry (Equation 1). It is well recognised that this estimate can be incorrect when other sulfides and acid-forming sulfates are present in the waste (e.g. Paktunc, 1999; White III et al., 1999; Weber et al., 2004).



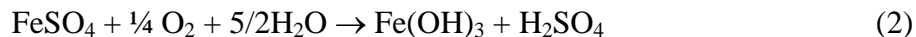
This estimate can be improved by using the net carbonate value (NCV) sulfide S method (Bucknam, 1998; Lapakko 2002). The NCV method measures reactive sulfide S by heating the sample at 550°C for one hour to convert reactive sulfide to S dioxide (pyrolysis). The sulfide content is determined as the difference between total S in the sample and in the residue after heating. This method does not include recovery of potentially acid producing secondary sulfates formed from pyrite oxidation as present in many mine wastes. Therefore, content of the acid producing sulfates in the sample need to be determined in addition to the NCV method. The amount of acid produced per unit of oxidised pyrite from the sulfates depends upon the type of the sulfates formed under different reaction conditions. If iron precipitates of goethite or ferrihydrite form from the Fe⁺³ produced in the oxidation, then the full 3 H⁺ units of acidity are released. However, if oxidation is incomplete, reducing conditions are maintained or wetting/drying cycles occur, ferrous salts can form retaining stored acidity in the waste as seen in the MEND Waite Amulet study (Nesbitt and Jambor, 1998). If hydrolysis is incomplete, jarosite can precipitate at pH below about 3.5 releasing only 2 H⁺ per Fe⁺³ formed (van Breeman, 1976; Lapakko and Berndt, 2003). This is commonly found in weathered coal and laterite Ni mine wastes where the pyrite is often highly reactive, especially framboidal pyrite. Schwertmannite can also form from incomplete hydrolysis but since this releases 2.6 H⁺ per Fe⁺³ (Piene et al., 2000), the error is not as significant. If hydrolysis is complete, water

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soluble melanterite (Equation 2) and jarosite, which is soluble above about pH 4.7, will undergo hydrolysis (Equation 3) to release the stored acidity.



These reactions and the stored acidity are well recognised in acid sulfate soil assessment procedures. In Australia, a standard method for laboratory analysis of jarosite is included in the Queensland Acid Sulfate Soil Technical Manual (Ahern et al., 2004) but this method is designed for low pyrite concentrations, does not estimate ferrous salt stored acidity, and it can take up to 3 days to complete the sequential extractions. It is also recognised that procedures for estimation of soluble salts and jarosite have been addressed in mine wastes (Yin and Catalan, 2002; Leinz et al., 2000), but these sequential extraction methods are also time consuming particularly where the waste contains gypsum, epsomite and non-acid producing sulfides.

There is a need for an effective, fast method able to be used at most operating sites to quantify secondary sulfate salts such as jarosite and melanterite in mine wastes for more accurate estimation of AP. We report here the development of a simple method, tested on both synthetic and mining-derived wastes, as part of the Australian Minerals Industry Research Association Project P387B - Neutralising Mineral Reactions in Acid Mine Drainage Control (Smart et al. 2005).

Extraction Method

The Suspension Peroxide Oxidation Combined Acidity & Sulfur (SPOCAS) methods have been developed in Australia as a standard for routine laboratory analysis of existing acidity and of the potential acid production from oxidation of iron sulfides in acid sulfate soils (Ahern et al., 2004). The complete SPOCAS method provides 12 individual analyses, enabling the quantification of some key fractions in soil samples, leading to better prediction of likely acid-generating potential. Two of the analyses, which are closely related to this work, are the titratable actual acidity and residual acid soluble S measurements. In the former, a 1 M KCl extraction procedure is performed on a soil sample, followed by a subsequent titration to measure soluble and exchangeable S acidity. In the latter, 4M HCl acid extraction is conducted on a sample residue remaining after peroxide digestion and titration to determine S from jarosite and other insoluble sulfate-containing compounds present in the soil sample.

The SPOCAS procedures have been modified here to a single, simpler, effective method to speciate non-sulfide S in synthetic and mining-derived mine waste samples. A four-step sequential extraction procedure has been established:

- 1) Distilled water extraction (3 min with magnetic stirrer at room temperature) to extract soluble Fe^{+2} salts, epsomite and gypsum (<10 wt%); oxidise solution with 2 drops of 30% H_2O_2 ; assay solutions for acidity, Fe, Mg, Ca and total S.
- 2) 1M KCl extraction (4 h) to extract higher (>10%) contents of gypsum and epsomite;
- 3) Roast at 550°C in air (1 h) to remove pyrite and reactive sulfides;
- 4) 4M HCl extraction (16 h with magnetic stirrer at room temperature) for jarosite extraction (Dilute extracts ten-fold before ICP S assay).

Step 2 can be removed if gypsum and epsomite content is low, and Step 4 can be replaced by a solid assay for S.

Synthetic Mine Wastes

The sequential extraction procedure was used to estimate melanterite, epsomite, gypsum and jarosite concentrations in a synthetic waste samples as specified in Table 1. Complete (100%) extraction of melanterite, epsomite and gypsum, measured by the assays for Fe, Mg and Ca, was found in 5 duplicate sets of repeat samples. Complete removal of pyrite in the roasting step was also confirmed by XRD and total S assay. Jarosite extraction was after roasting and 4M HCl treatment was confirmed by both solution assay for S and by solid assay (<0.05% in residue).

These tests also established that:

- 3 min water extraction, instead of 1 M KCl extraction, can effectively remove melanterite and epsomite in the sample.
- Gypsum is fully dissolved in water (1g solid/40 ml liquor) when its content is < 9 wt%.
- Pyrite and jarosite are water insoluble.
- High gypsum contents (>15%) passivate pyrite pyrolysis and must be removed prior to roasting as in Step 2.
- Jarosite decomposes during roasting at 550°C, according to Equation 4 (Drouet and Navrotsky, 2003).
- Repeatability >95% was measured for each extraction.

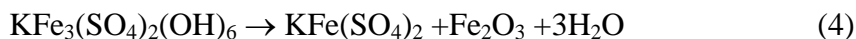


Table 1: Mineral composition of the synthetic mine waste sample.

Mineral	Stoichiometry	Mass Fraction	
		(wt%)	S (wt%)
Melanterite	FeSO ₄ ·7H ₂ O	5	0.6
Epsomite	MgSO ₄ ·7H ₂ O	5	0.7
Gypsum	CaSO ₄ ·2H ₂ O	5	0.9
Jarosite*	Na _{0.88} K _{0.12} Fe _{2.96} Al _{0.04} (SO ₄) ₂ (OH) ₆	5	0.7
Pyrite*	FeS ₂	5	2.7
Quartz*	SiO ₂	75	0
Total		100	5.5

*Natural minerals, purity of jarosite, pyrite and quartz are 94.5%, 97.0% and 98.6% respectively.

Laterite Nickel Tailings

The sequential procedure was tested on a mine waste sample of laterite Ni tailing residue with mineralogical abundance estimated, shown as Sample 1 in Table 2, based on multi-element extraction procedures similar to those in Leinz et al., 2000. In this procedure, the jarosite content is inferred by difference in the extraction sequence. Since the original laterite Ni tailings sample

did not contain any sulfide minerals, another sample was also prepared as a mixture of 5 wt% pyrite added to 95 wt% of the laterite Ni sample with overall mineralogy shown as Sample 2 in Table 2. This pyrite was added in order to test if roasting in Step 3 would remove the pyrite from an original waste sample.

Due to the high gypsum content in the samples (Table 2), a low ratio of solid to solution (1g : 80 ml) was adopted for water extraction tests to ensure removal of all the gypsum during the water extraction step. Considering natro alunite as a jarosite, the total jarosite content is 13.4% in the laterite Ni tailings residue Sample 1 and 12.7% in the pyrite/laterite mixture Sample 2.

Table 2: Mineralogical composition of laterite Ni tailing residue Sample 1 and the same sample with 5 wt% pyrite added in Sample 2.

Mineral	Stoichiometry	Sample 1	Sample 1	Sample 2	Sample 2
		Mass Fraction (wt%)	S (wt%)	Mass Fraction (wt%)	S (wt%)
Hydrated Lime	Ca(OH) ₂	0.3	0.0	0.3	0.0
Gypsum/Anhydrite	CaSO ₄	13.0	3.1	12.4	2.9
Epsomite	MgSO ₄	7.7	2.1	7.3	2.0
Magnesium Oxide (as Silicates)	MgO	2.9	0.0	2.8	0.0
Natro Alunite	NaAl ₃ (SO ₄) ₂ (OH) ₆	5.6	0.9	5.3	0.9
Natro Jarosite	NaFe ₃ (SO ₄) ₂ (OH) ₆	0.1	0.0	0.1	0.0
K-Jarosite	KFe ₃ (SO ₄) ₂ (OH) ₆	1.5	0.2	1.4	0.2
Hydronium Jarosite	H ₃ OFe ₃ (SO ₄) ₂ (OH) ₆	6.2	0.8	5.9	0.8
Haematite	Fe ₂ O ₃	23.7	0.0	22.5	0.0
Manganese Hydroxide	Mn(OH) ₂	0.3	0.0	0.3	0.0
Quartz	SiO ₂	27.8	0.0	26.4	0.0
Halite	NaCl	2.6	0.0	2.4	0.0
Pyrite	FeS ₂	0.0	0.0	5.0	2.6
Other		8.3	0.0	7.9	0.0
Total		100	7.1	100	9.3

Figure 1 shows the results of the four-step procedure applied to Sample 1, mine waste laterite Ni tailing residue sample. All of the epsomite and gypsum in the sample was completely removed by the initial water extraction step. Recoveries higher than 100% probably represent small additions to the Mg and Ca assays from ion exchange and dissolution of other minerals in the waste but these contributions do not compromise the removal of the epsomite and gypsum before the jarosite extraction. Since Sample 1 does not contain pyrite or other reactive sulfides, this may suggest that the roasting Step 3 could be deleted. However, without roasting, only 39%

of total jarosite (Table 1) was extracted by 4M HCl. In contrast, approximately 80% of total jarosite was effectively dissolved by 4M HCl after first roasting the sample. This shows that the roasting procedure, which transforms jarosite into ferric sulfate (Equation 4), is necessary prior to 4M HCl extraction for determination of jarosite S in the mine waste samples regardless of pyrite content.

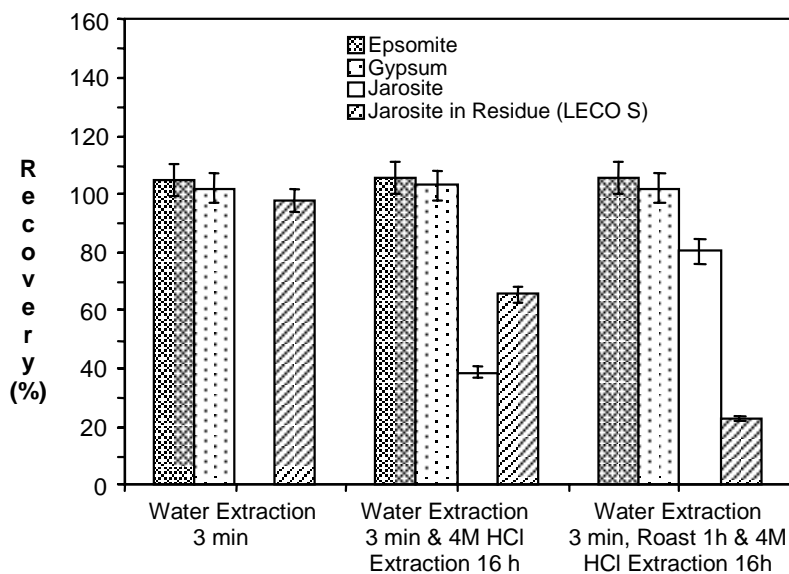


Figure 1: Mineral recovery from sequential steps for laterite Ni tailing residue Sample 1 containing 7.7% epsomite, 13% gypsum and 13.4% jarosite.

However, approximately 20% of total S attributed to jarosite in Table 2 remained in the residue after roasting and the 4M HCl extraction. Increasing the roasting time to 2 h and diminishing the solid to liquid ratio for the 4M HCl extraction did not reduce this residual S assay. This suggests that an unknown S compound other than jarosite in the samples could not be removed by HCl. Whether this form of S exists in the original sample or is formed after roasting needs to be further investigated. Given these test results, it is unlikely to be jarosite or any other acid-producing salt. The results from tests on Sample 2 with 5% pyrite added to 95% laterite Ni tailings were similar to those from the laterite Ni tailing residue sample alone, as seen in Fig. 2 showing that the pyrite was effectively removed and did not have a significant effect on the final jarosite S determination.

Effect of Different Sulfide Minerals

To investigate the influence of sulfide minerals on the proposed method for jarosite determination, 4M HCl extractions on single mineral sulfide samples (5% S with quartz), both roasted and not roasted, were carried out. In summary, the results showed:

- Pyrite and arsenopyrite are removed by roasting at 550°C for 1 h and will not report to the 4M HCl extraction carried out after roasting as an interference in jarosite determination.
- The majority of pyrrhotite (86%) is removed by roasting. The remaining pyrrhotite is extractable by 4M HCl. This would only represent a serious interference in jarosite determination if there is a large percentage of pyrrhotite in the sample.

- About 50% of pentlandite is removed during roasting, but only a small fraction of the remaining pentlandite after roasting is extracted by HCl.
- Sphalerite and galena are not removed by the roasting procedure or appreciably extracted by subsequent HCl.
- Chalcopyrite, bornite, covellite, and chalcocite are partially removed by roasting and after roasting the remaining sulfides are readily extracted by 4M HCl. These sulfides are not appreciably dissolved by 4M HCl without roasting.
- Excluding the roasting procedure may be the most applicable method for jarosite S determination for wastes containing significant copper sulfides.

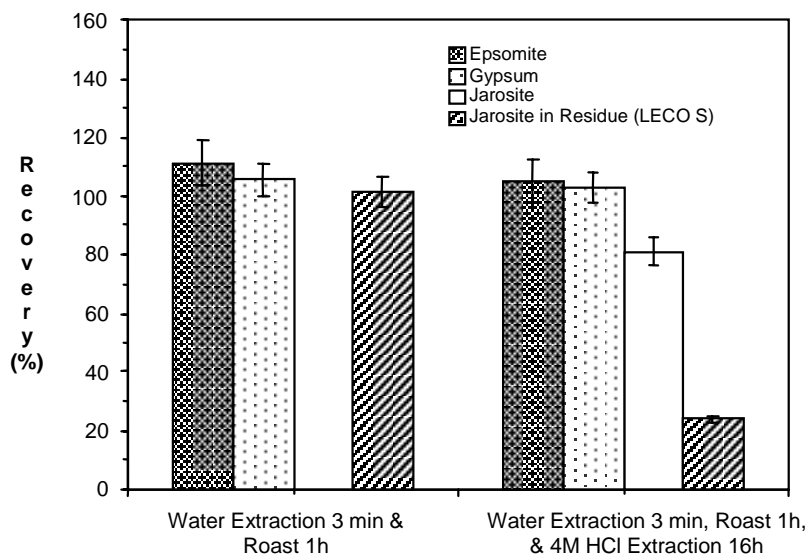


Figure 2: Mineral recovery from sequential tests for Sample 2 containing 7.3% epsomite, 12.4% gypsum, 5% pyrite and 12.7% jarosite.

Conclusions

The simplified four step method for estimation of non-sulfide stored acidity in mine wastes has been validated with both synthetic samples and a real laterite Ni tailings waste with relatively high jarosite content. Further testing and development of a data base needs to be completed but the method shows promise for reasonable estimates that will allow correction of AP in acid base accounting. This is particularly applicable to mine wastes with low sulfide content or in highly weathered samples.

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