

Iron Sulfides Ain't Iron Sulfides. A Comparison of Acidity Generated During Oxidation of Pyrite and Pyrrhotite in Waste Rock and Tailing Materials

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ABSTRACT

It is generally recognized that acid and metalliferous drainage (AMD) occurs as a result of oxidative dissolution of iron-containing sulfide minerals, while oxidation of sulfides containing low or no iron such as sphalerite or galena do not generally result in highly acidic drainage, but may lead to elevated concentrations of sulfate and metals, e.g. Zn, Pb. Therefore common understanding suggests that the amount of iron sulfide present in an ore deposit or mine waste plays a crucial role in determining the characteristics of the mine drainage. It is generally less appreciated that the oxidative behavior of different iron sulfide minerals varies appreciably, and the characteristics of mine drainage depends markedly on the particular iron sulfide minerals present.

In order to quantify differences in the oxidative behavior of pyrite and pyrrhotite-containing wastes, both simulated sulfidic mine wastes and actual mine tailings were leached under kinetic leach column test conditions. Synthetic mine wastes containing 5 wt% pyrite or pyrrhotite, together with 5 wt.% chlorite, 10 wt.% amazonite and 80 wt.% quartz, produced 71 % and 6 % respectively of the expected acidity based on acid base accounting during 120 weeks of leaching. Nickel mine tailings containing nearly 30 % pyrrhotite also produced much lower than expected acidity (<1 %) after 107 weeks of leaching.

Sulfur speciation analysis of both solids and the drainage demonstrate that, for both the simulated pyrrhotite mine waste and the nickel mine tailings, around 85 % of the oxidized sulfur converted to elemental sulfur, a reaction path which does not generate acidity. In contrast, for the simulated pyrite mine waste, only 2 % of the oxidized sulfur converted to elemental sulfur, with the majority oxidising through to sulfate. While elemental sulfur can further oxidize to sulfate with concomitant acid production, this reaction is very slow in the absence of oxidative bacterial catalysis. Analysis of the oxidized zone of the nickel mine tailings storage facility also demonstrated the predominant oxidation product to be elemental sulfur, suggesting that even in field conditions, pyrrhotite oxidation will likely produce significantly less acidity than is predicted by standard AMD assessment methods.

Keywords: pyrite, pyrrhotite, acid potential, elemental sulfur

INTRODUCTION

In the assessment of the acid generating potential of a mine waste material, the initial screening method usually includes acid base accounting (ABA) and, in some cases, the net acid generation (NAG) test (INAP, 2009). In its most basic form, ABA includes calculation of the acid potential (AP) of a waste usually by determining the sulfide content of the material. The use of sulfide content without further distinction between the various sulfide minerals is based on the abundance of iron sulfides, particularly pyrite, in mine wastes. AP is then calculated from the sulfide sulfur content based on the stoichiometry of the reaction of pyrite with oxygen and water to produce one mole of sulfuric acid per mole of sulfur. It is generally regarded that other iron sulfides such as pyrrhotite, marcasite and arsenopyrite will also react similarly to produce acid, while some sulfides such as sphalerite and galena, which can undergo oxidative dissolution to release metal ions and sulfate without iron oxyhydroxide precipitation, may not produce much if any acidity (INAP, 2009, MEND, 2009, DTIR, 2007).

Under the conditions of the accelerated oxidation NAG test (hydrogen peroxide), results from testing of various individual sulfide minerals suggest that all iron sulfides react in a similar way to pyrite, producing one mole of sulfuric acid per mole of sulfur (Stewart et al., 2003, Jennings et al., 2000). Therefore in the use of these simple screening methods for assessment of acid potential, there is generally no consideration given to different potential reaction pathways for oxidative dissolution of the various iron sulfides and the possible effects of these reaction pathways on drainage chemistry. However, a number of studies have identified that, unlike the oxidative dissolution of pyrite where sulfate is invariably the major final product of sulfide oxidation, during oxidation of pyrrhotite significant quantities of elemental sulfur have been identified (Cruz et al., 2005, Belzile et al., 2004, Mikhlin et al., 2002, Kalinkin et al., 2000, Nicholson & Scharer, 1994). In addition to laboratory studies, investigations into weathering of pyrrhotite in site tailings storages have shown that elemental sulfur is present as a result of pyrrhotite oxidation (McGregor et al., 1998, Janzen et al., 1997).

Table 1 shows some potential overall reaction pathways for the dissolution of pyrite and pyrrhotite, ranging from oxidative dissolution to produce iron oxyhydroxide and sulfate (2 moles H⁺ produced per mole S) to non-oxidative dissolution to hydrogen sulfide (2 moles H⁺ consumed per mole S). It is clear from these equations, that the pathway(s) along which iron sulfide dissolution occurs will influence the amount of acidity produced (or consumed) with direct consequence on drainage quality. It is also apparent that if oxidation of pyrrhotite proceeds only as far as elemental sulfur, then no proton acidity will be produced. If this reaction pathway becomes the dominant path for oxidative dissolution, then AP and NAG measurements will likely greatly over estimate the amount of acidity that can be expected from pyrrhotite containing waste materials.

In order to determine and quantify the different reaction pathways of various sulfide minerals during oxidation, we have investigated the behavior of simulated mine wastes containing various sulfides including pyrite and pyrrhotite using kinetic leach column tests (AMIRA 2002). At the same time, as part of investigations into the geochemistry of tailings in the tailings storage facility (TSF) at the Savannah Nickel Mine (SNM) in the Kimberly region of Western Australia (Robertson et al. 2015), we have studied the oxidative behaviour of pyrrhotite-containing tailings both in laboratory leach columns and *in situ* in the SNM TSF. This paper details the results of these investigations, including quantification of the relative amounts of various reaction products and the subsequent acidity produced.

Table 1 Different reaction pathways for oxidative and non-oxidative dissolution of pyrite and pyrrhotite and the corresponding number of protons released per S

Product	Sulfide	Reaction	H ⁺ Released/S	H ⁺ Stored/S
Goethite & sulfate	Pyrite	$\text{FeS}_2 + 3.75\text{O}_2 + 2.5\text{H}_2\text{O} \Rightarrow \text{FeOOH} + 2\text{SO}_4^{2-} + 4\text{H}^+$	2 (100%)	0 (0%)
	Pyrrhotite	$\text{Fe}_{(1-x)}\text{S} + 0.75(3-x)\text{O}_2 + 0.5(3-x)\text{H}_2\text{O} \Rightarrow (1-x)\text{FeOOH} + \text{SO}_4^{2-} + 2\text{H}^+$	2 (100%)	0 (0%)
Goethite & jarosite	Pyrite	$\text{FeS}_2 + 3.75\text{O}_2 + 2.5\text{H}_2\text{O} + 1/3\text{K}^+ \Rightarrow 1/3\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 + 4/3\text{SO}_4^{2-} + 3\text{H}^+$	1.5 (75%)	0.5 (25%)
	Pyrrhotite	$\text{Fe}_{(1-x)}\text{S} + 0.75(3-x)\text{O}_2 + 0.5(3-x)\text{H}_2\text{O} + 1/3(1-x)\text{K}^+ \Rightarrow 1/3(1-x)\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 + 1/3(1+2x)\text{SO}_4^{2-} + (1+x)\text{H}^+$	1+x (55% for Fe _{0.9} S)	1-x (45% for Fe _{0.9} S)
Goethite & elemental sulfur	Pyrite	$\text{FeS}_2 + 0.75\text{O}_2 + 0.5\text{H}_2\text{O} \Rightarrow \text{FeOOH} + 2\text{S}$	0 (0%)	2 (100%)
	Pyrrhotite	$\text{Fe}_{(1-x)}\text{S} + 0.75(1-x)\text{O}_2 + 0.5(1-x)\text{H}_2\text{O} \Rightarrow (1-x)\text{FeOOH} + \text{S}$	0 (0%)	2 (100%)
Sulfide	Pyrrhotite	$\text{Fe}_{(1-x)}\text{S} + 2\text{H}^+ \Rightarrow (1-3x)\text{Fe}^{2+} + 2x\text{Fe}^{3+} + \text{H}_2\text{S}$	-2 (-100%)	4 (200%)

METHODOLOGY

Kinetic leach column tests using simulated sulfidic mine wastes

To compare the oxidative behaviour of pyrite and pyrrhotite under conditions that might be comparable to the oxidative zone of a waste rock storage facility, simulated sulfidic mine wastes containing either pyrite or pyrrhotite were subjected to leaching for a period of 120 weeks. In addition to 5 wt.% sulfide, the simulated sulfidic wastes also contained 5 wt.% chlorite, 10 wt.% amazonite and 80 wt.% quartz. Leaching was conducted using the standard kinetic leach column method (AMIRA 2002).

All of the individual mineral samples used for producing the simulated sulfidic mine wastes were characterized by bulk assay and quantitative XRD analysis. The results show that pyrite and quartz were essentially pure minerals (>98%). The pyrrhotite sample contained 65 wt.% pyrrhotite, 10 wt.% pentlandite and 8 wt.% chalcopyrite. Scanning electron microscopy (SEM) analysis using energy dispersive x-ray spectroscopy (EDS) suggested an average iron content of 46.5 atomic % in the pyrrhotite, which is close to that for the iron deficient monoclinic pyrrhotite Fe₇S₈. Analysis results for the chlorite sample indicate it contained around 75% chlinoclore, with 15% quartz and 10% albite. The amazonite was an 80:20 mixture of microcline and albite.

Kinetic leach column tests using pyrrhotite tailings from SNM

Quantitative XRD analysis of the fresh tailings from SNM indicated a pyrrhotite content of 29.1%, which, if it is assumed that the sulfide content is 11.4% (Total S 11.5% - sulfate S 0.1%), is very close to the 29.3% pyrrhotite calculated from the sulfide S content assuming a formula of Fe_{0.90}S for the pyrrhotite determined by EDS analysis. SEM-EDS analysis identified essentially pyrrhotite as the only sulfide, with very minor amounts of mackinawite ((Fe, Ni)_(1+x)S). No pyrite was found. XRD analysis using a high intensity, high resolution synchrotron source indicated the pyrrhotite in the fresh tailings was around 90% hexagonal, consistent with an average iron content of 47.4 atomic % (Fe_{0.90}S).

XRD analysis identified both anthophyllite and ferroan enstatite as magnesium bearing silicates in the tailings. SEM analysis confirmed the presence of magnesium iron silicate phases, which are likely to contribute significantly to the neutralising potential (NP) of the tailings. Inorganic carbon analysis indicated there are no carbonates in the fresh tailings (inorganic C <0.02%).

Fresh tailings collected from the SNM concentrator were placed into columns 150 mm diameter by 600 mm height. The columns were constructed in four segments, each segment containing liquid and solids sampling points. The tailings were placed into the columns as slurries in process water as received. Approximately 15 kg of tailings (dry weight) were packed into each column. After allowing the bed to consolidate, water was allowed to drain from the columns. The consolidated tailings bed had a porosity of close to 0.40, similar to that estimated for the tailings in the SNM TSF.

KLC tests were run with tailings at 50 and 75 % average saturation. However, after allowing Column 1 (target 50 % saturation) to drain under gravity for four months the average degree of saturation of the tailings bed had not dropped below 75 %, presumably due to the high suction pressure of this material. Following the first flush, Column 1 was allowed to drain until no further water was collected. Vacuum was then applied to the column until sufficient water was removed to give an average degree of saturation of 50%. After about six months of operation, it was found that small volumes of water were required to be added to Column 2 to maintain 75% average saturation.

Flushing of the tailings was achieved by adding 3 L of deionized water to the columns and allowing the flush water to remain in the column for 24 h prior to draining. Water was collected in clean plastic-lined foil bags so that air was excluded during collection. pH and oxidation-reduction potential (ORP) measurements were made at each of the liquid sampling points (top, middle and bottom segments) for each column immediately prior to collection of the flush water. Flushes were conducted at weeks 16, 26, 39, 52, 65, 78, 91 and 107. Solids were sampled from each segment following flushes at weeks 26, 52, 78 and 107. Approximately 10 g of wet solids were removed from each sampling point by inserting a hollow tube through the entire width of the column. The samples were weighed and then dried under vacuum at 50°C prior to analysis.

Characterization of sulfur species in tailings from SNM

Core samples from TSF1 at SNM were collected using a drilling rig fitted with an auger bit in which the core was collected in 40 mm diameter tubes, each of 700 mm length. Using this method, the cores had very limited exposure to air during sampling and no drilling water was used so pore water was not diluted during sampling. Samples from the drill holes were bagged immediately in air tight plastic bags and transported to the metallurgical laboratory on site as collected.

Measurements including pore water pH, Eh and dissolved oxygen (DO) were made in a glove bag under an argon atmosphere. Remaining pore water was filtered and appropriately preserved and then transported to our laboratories in Adelaide. The remaining core samples were frozen and transported to Adelaide without thawing. Samples were stored frozen until they were analysed when they were thawed and a portion dried under vacuum at 50°C.

Analysis of column leachates and solids, and tailings storage facility pore waters and solids

Samples of simulated sulfidic mine waste, fresh tailings and TSF core samples from SNM were characterized using standard static test procedures (NP, total S, chromium reducible sulfur (SCR), NAG) in addition to mineralogical analysis by quantitative XRD and SEM-EDS analyses. Sulfur speciation analysis was conducted on both fresh tailings and on samples of weathered tailings from

the kinetic leach column tests and on core samples collected from the SNM TSF. Sulfur speciation analysis was also conducted on solids removed from the kinetic leach column tests conducted on simulated sulfidic mine wastes after 120 weeks of leaching.

NP and NAG analyses were conducted according to the methods described in the AMIRA ARD Test Handbook (AMIRA 2002). S_{CR} analysis was conducted using the method of Sullivan et al. (2004). Sulfur speciation analyses were carried out using the methods of Li et al. (2007) and Stewart et al. (2009). Because of the high concentration of pyrrhotite in the SNM tailings samples, it is likely that pyrolysis of the tailings does not result in complete removal of the pyrrhotite (Li et al., 2007). Therefore a portion of the pyrrhotite would report as HCl extractable sulfur which also includes insoluble sulfates such as jarosite. Consequently HCl extractions were not conducted and estimates of jarosite content were not made. Determination of elemental sulfur was achieved by extraction of the solids with acetone followed by analysis of the extract by liquid chromatography (McGuire and Hamers, 2000).

RESULTS AND DISCUSSION

Kinetic leach column tests using simulated sulfidic mine wastes

During KLC testing of the simulated sulfidic mine wastes containing pyrite and pyrrhotite, coloration of the pyrrhotite waste suggested significant oxidation had taken place, but acidity measured in leachates was surprisingly low in comparison to the expected acidity based on either ABA or NAG tests (Table 2). In an attempt to understand the lower than expected leachate acidity, sulfur mass balance was undertaken to determine reaction pathways of sulfide oxidative dissolution. Sulfur mass balance included sulfur species contained in leachates, sulfur in acetone extracts of solids (elemental sulfur) and sulfur species in 1M KCl extracts of the solids (soluble sulfates, e.g. gypsum, melanterite, etc.).

Based on sulfur mass balance undertaken at 120 weeks of leaching, less than 20 % of pyrite and more than 70 % of pyrrhotite had undergone oxidation, consistent with the visual evidence that suggested substantial oxidation of the simulated pyrrhotite waste and in line with previous studies, which suggest pyrrhotite oxidation rates one to two orders of magnitude higher than for pyrite (Belzile et al., 2004). Correction of expected acidities based on the amount sulfide oxidized, gave much closer agreement with measured acidity for the simulated pyrite waste, but the measured acidity was still significantly lower than that expected from oxidation of the simulated pyrrhotite waste if oxidation was assumed to proceed to goethite and sulfate (Table 2). However, the sulfur mass balance indicated that the dominant (85 %) sulfur oxidation product in the case of the simulated pyrrhotite waste was not sulfate but elemental sulfur (Table 2), a reaction which will not produce acidity (Table 1). Further correction of the expected acidity to take into account oxidative dissolution to elemental sulfur, shows much closer agreement with the measured acidity for the simulated pyrrhotite waste.

Further analysis of leachate solutions and 1M KCl extracts of the solids were undertaken to determine the processes that may lie behind the difference in measured and expected acidity, even after reaction to elemental sulfur is taken into account. The results of these analyses are shown in Figure 1. The figure shows the titrated acidity (released acidity) together with stored acidity measured by titration of the KCl extract. It also shows released and stored alkalinity, which were calculated from concentrations of Ca, Mg and Na in leachates and KCl extracts respectively,

assuming the presence of these ions results from neutralising reactions. When stored and released acidities and alkalinities are combined, their sum is in good agreement with the expected acidities (Fig. 1). The results demonstrate that for the pyrite waste, the majority of acidity is released, with minor stored acidity and limited neutralization provided by chlorite in the simulated waste. In the case of the simulated pyrrhotite waste, the proportion of expected acidity which was released under KLC conditions was much less, with more stored acidity and some neutralising by chlorite (Jambor et al., 2007).

Table 2 Comparison of expected and measured acidity in leachates after 120 weeks of KLC testing conducted on simulated sulfidic wastes containing either pyrite or pyrrhotite

Sulfide	AP (kg CaCO ₃ /t)	NAG (kg CaCO ₃ /t)	Titrated leachate acidity (kg CaCO ₃ /t)	Total sulfide oxidized (%)	Expected acidity (kg CaCO ₃ /t)	Relative amount oxidized to S ⁰ (%)	Expected acidity S ⁰ excluded (kg CaCO ₃ /t)
Pyrite	84	65	10	17	14	2.0	14
Pyrrhotite	50	32	2.0	73	37	85	5.6

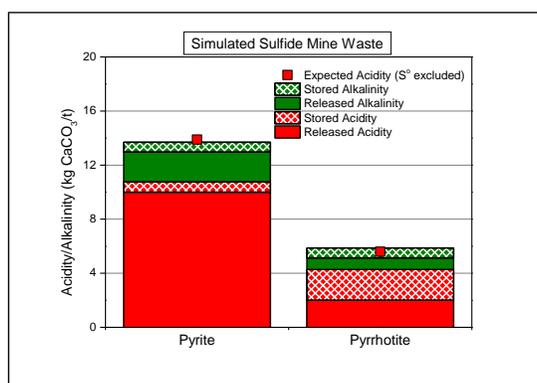


Figure 1 Acidity and alkalinity measured in leachates (released) and in KCl extracts of solids (stored) after 120 weeks of KLC testing conducted on simulated sulfidic mine wastes containing either pyrite or pyrrhotite

Kinetic leach column tests using pyrrhotite tailings from SNM

Similar to observations made during KLC tests of simulated pyrrhotite waste, visual inspection of the SNM tailings during column leach testing suggested extensive oxidation, but acidities measured in leachates remained low (Table 3) and in the case of the tailings leached at an average saturation of 75 %, almost non-existent (Table 4). With a pyrrhotite content of around 30%, these tailings were predicted to be strongly acid producing. Sulfur mass balance analysis indicated around 40% of the pyrrhotite had undergone oxidation during two years of leaching at 50 % average saturation and around 10% was oxidized during two years of leaching at 75 % average saturation (Tables 3 and 4), suggesting both columns should have produced substantial acidity if oxidation had proceeded to sulfate (Table 1). However, as for the simulated pyrrhotite waste, sulfur analysis demonstrated that the major pathway for pyrrhotite oxidation during leaching of the SNM tailings was via oxidation

to elemental sulfur, with around 90 % of oxidized sulfur in the tailings leached at 50 % saturation and around 80 % of oxidized sulfur in the tailings leached at 75 % saturation, reacting to produce elemental sulfur and no acidity (Tables 3 and 4). When this non-acid producing reaction pathway is taken into account, expected and measured acidities are much closer, although there was still significantly less measured acidity than expected, especially for the column leached at 75 % saturation.

Table 3 Comparison of expected and measured acidity in leachates during 107 weeks of leaching of SNM tailings with and average saturation of 50%

Leaching time (weeks)	AP (kg CaCO ₃ /t)	NAG (kg CaCO ₃ /t)	Titrate leachate acidity (kg CaCO ₃ /t)	Total sulfide oxidized (%)	Expected acidity (kg CaCO ₃ /t)	Relative amount oxidized to S ⁰ (%)	Expected acidity S ⁰ excluded (kg CaCO ₃ /t)
26			0.03	7.6	27	91	2.5
52	356	213	5.2	25	87	88	11
78			7.4	44	155	90	16
107			9.3	39	139	88	17

Table 4 Comparison of expected and measured acidity in leachates during 107 weeks of leaching of SNM tailings with and average saturation of 75%

Leaching time (weeks)	AP (kg CaCO ₃ /t)	NAG (kg CaCO ₃ /t)	Titrate leachate acidity (kg CaCO ₃ /t)	Total sulfide oxidized (%)	Expected acidity (kg CaCO ₃ /t)	Relative amount oxidized to S ⁰ (%)	Expected acidity S ⁰ excluded (kg CaCO ₃ /t)
26			0	2.0	7.1	80	1.4
52	356	213	0.02	7.9	28	79	5.9
78			0.03	10	36	79	7.7
107			0.05	9.5	34	73	9.2

The results of a similar analysis of stored and released acidity and alkalinity in leached SNM tailings to that conducted for the simulated sulfidic wastes are shown in Figure 2. Again, when stored and released alkalinity (neutralized acidity) are summed together with stored and released acidity, there is good agreement with the expected acidity based on the total amount of sulfide oxidized and the percentage of reaction leading to elemental sulfur. In some cases, the expected acidity is not entirely accounted for by the measured neutralization and stored and released acidity. These small differences are likely due to stored acidity in jarosite which was not quantified, but was detected during XRD analysis of the leached tailings.

Figure 2 shows that acidity released during oxidation of pyrrhotite in the SNM tailings comprised only a very small fraction of the total acidity generated and that the majority of the acidity has been neutralized, although at 50% saturation, there is also a significant fraction of stored acidity. Analysis of leachates and KCl extracts indicate that most of this neutralization comes from

magnesium bearing minerals, possibly enstatite. The results suggest that if the tailings can be maintained at near or above 75% saturation, then pyrrhotite oxidation is likely to be sufficiently slowed to allow the small amount of acidity generated from oxidation through to sulfate (Table 1), to be neutralized by reactive silicates present in the tailings. Under these conditions, released acidity is likely to be less than 1% of that predicted by ABA or NAG tests.

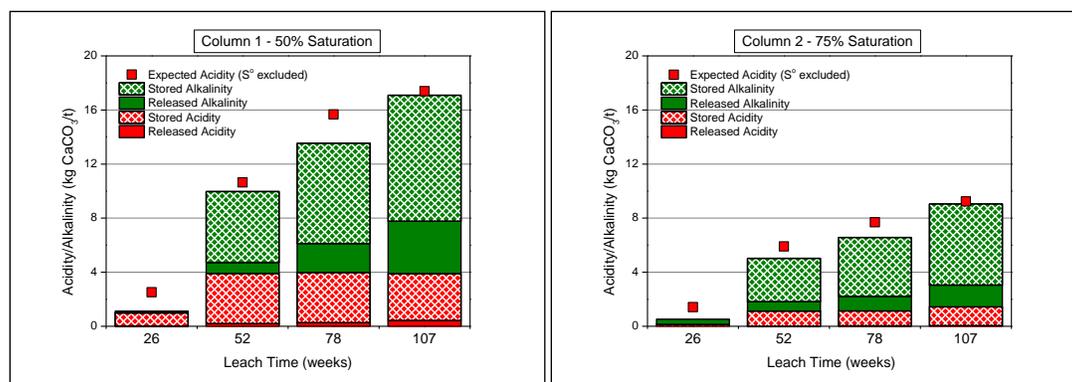


Figure 2 Acidity and alkalinity measured in leachates (released) and in KCl extracts of solids (stored), during 107 weeks of leaching of SNM tailings at an average saturation of 50% (left) and an average saturation of 75% (right)

Characterization of sulfur species in tailings from SNM

As a part of the study of geochemical reactions which occur during weathering of the SNM tailings, core samples were taken from several locations at the TSF. Core samples were taken through the full depth of the tailings deposited in the TSF and represented tailings deposited over about a five year period. Surface tailings, which had formed a hardpan, represented material deposited during the previous 1.5–2.5 years. Sulfur speciation analysis was undertaken on the core samples. The results of these analyses are shown in Figure 3.

For each core sample taken, in the oxidized hardpan layer, elemental sulfur was the dominant sulfur species present with only minor sulfide (pyrrhotite) remaining. It was not possible to determine with any accuracy the relative proportion of oxidation of pyrrhotite to elemental sulfur vs oxidation to sulfate, as the amount of sulfate produced could not be determined since it is not quantitatively retained within the hardpan. Nevertheless, an estimate of the relative amounts of oxidation to elemental sulfur and sulfate could be made based on the results of sulfur speciation. For example, if in the Geochem 4 hardpan sample it is assumed that the original sulfide sulfur content is similar to the sulfide sulfur content of the tailings immediately below the hardpan, then sulfide sulfur decreased from 9.2 to 1.0 %. At the same time the elemental sulfur content increased from 0.1 to 7.1 %. This equates to an 86 % conversion of sulfide sulfur to elemental sulfur, suggesting that oxidation to elemental sulfur is the dominant reaction pathway for oxidation of pyrrhotite in the TSF hardpan.

These results suggest that under the conditions prevailing in the TSF, further oxidation of elemental sulfur is very slow in comparison to pyrrhotite oxidation, and that therefore the acidity generated by pyrrhotite oxidation will be substantially less than that predicted from ABA and NAG tests. This

was confirmed by results of tailings pore water analysis and ground water monitoring around the TSF, which showed elevated concentrations of sulfate, Ca and Mg, but neutral pH and no acidity, results consistent with the laboratory-based leaching tests conducted on SNM tailings.

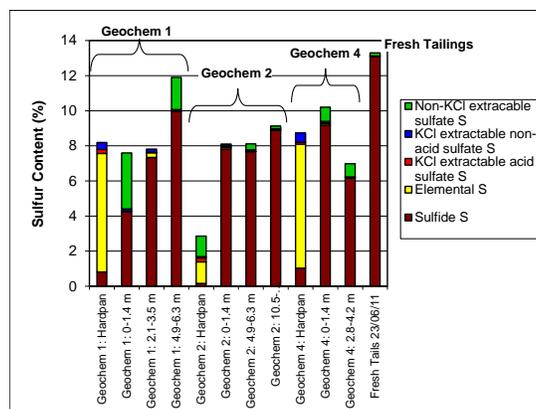


Figure 3 Results of sulfur speciation analysis of core samples taken from the SNM TSF

CONCLUSIONS

Oxidation of iron sulfides is recognized as being the cause of AMD, but generally no distinction is made between different iron sulfides in prediction of acid potential. Despite the fact that it has long been recognized that oxidation of pyrrhotite produces elemental sulfur as well as sulfate, with the former reaction generating no net acidity, there appears to have been no previous studies which have quantified the contribution of reaction to elemental sulfur to the overall oxidation of pyrrhotite. In this study, oxidation of simulated sulfide mine wastes containing pyrite or pyrrhotite under kinetic leach column tests conditions, demonstrated that oxidation of pyrite was dominated by the reaction to produce sulfuric acid (98 %), while pyrrhotite oxidation primarily (85 %) produced elemental sulfur and consequently significantly less acidity (~5 %) than would be expected based on AP calculations or NAG testing.

Similar results were obtained during column leaching of mine tailings containing around 30% pyrrhotite. About 90 % of oxidized sulfur in the tailings leached at 50 % saturation and around 80 % of oxidized sulfur in the tailings leached at 75 % saturation, reacted to produce elemental sulfur and no acidity. Consequently measured acidities were around 6 % of the predicted acidity in the tailings leached at 50 % saturation and less than 0.2 % of the predicted acidity in the tailings leached at 75 % saturation. The very low acidity from the tailings leached at 75% saturation was not only due to oxidation principally occurring via production of elemental sulfur, but also because the majority of acidity produced by the alternative oxidation pathway to sulfuric acid was neutralized by magnesium silicates also present in the tailings.

While further oxidation of elemental sulfur to produce sulfate and acid may occur, especially in the presence of bacterial catalysis, analysis of the oxidized zone of the tailings in the mine TSF suggests that, similar to laboratory column leach tests, *in situ* oxidation of pyrrhotite led to elemental sulfur as the main product. The results from the TSF suggest that further oxidation of elemental sulfur with natural bacterial populations is relatively slow in conditions at SNM. These results indicate that tailings and mine waste rocks where the major iron sulfide is pyrrhotite, are likely to produce

significantly less acid than those containing pyrite. The results of this study further suggest that if pyrrhotite oxidation can be sufficiently slowed, for example by maintaining adequate levels of saturation in tailings, then silicates present in many mine wastes may be reactive enough to neutralize most, if not all, of the acidity produced. In short, complete assessment of the acid potential of a mine waste material will include not only the amounts, but also the identities of any iron sulfides present.

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REFERENCES

- AMIRA/EGi (2002) ARD Test Handbook (Smart R, Skinner W, Levay G, Gerson A, Thomas J, Sobieraj H, Schumann R, Weizener C, Weber P, Miller S, Stewart W), *AMIRA International*, <http://www.amira.com.au/web/documents/downloads/P387AProtocolBooklet.pdf>.
- Belzile, N., Chen, Y-W., Cai, M-F., Li, Y. (2004) 'A review on pyrrhotite oxidation' *J. Geochem. Explor.*, vol 84, pp. 65–76.
- Cruz, R., González, I., Monroy, M. (2005) "Electrochemical characterization of pyrrhotite reactivity under simulated weathering conditions' *App. Geochem.*, vol 20, pp. 109–121.
- DTIR (2007). *Leading practice sustainable development program for the mining industry. Managing acid and metalliferous drainage*, Department of Industry, Tourism and Resources, Canberra, ACT, Australia.
- INAP (2009). *Global Acid Rock Drainage Guide (GARD Guide)*, Document prepared by Golder Associates on behalf of the International Network on Acid Prevention (INAP) <http://www.gardguide.com>.
- Jambor, J.L., Dutrizac, J.E., Raudsepp, M. (2007) 'Measured and computed neutralization potentials from static test of diverse rock types' *Environ. Geol.*, vol 52, pp. 1019–1031.
- Janzen, M.P., Nicholson, R.V., Scharer, J.M. (1997) 'The role of enhanced particle surface area, crystal structure and trace metal content on pyrrhotite oxidation rates in tailings' *Proceedings 4th International Conference on Acid Rock Drainage*, May 31-June 6, Vancouver, BC, Canada.
- Jennings, S.R., Dollhopf, D.J., Inskeep, W.P. (2000) 'Acid production from sulfide minerals using hydrogen peroxide weathering' *App. Geochem.*, vol 15, pp. 247–255.
- Kalinkin, A.M., Forsling, W., Makarov, D.V., Makarov, V.N. (2000) 'Surface oxidation of synthetic pyrrhotite during wetting-drying treatment' *Environ. Eng. Sci.*, vol 17, pp. 329–335.
- Li, J., Smart, R.StC., Schumann, R.C., Gerson, A.R., Levay, G. (2007) 'A simplified method for estimation of jarosite and acid-forming sulfates in acid mine wastes' *Sci Total Environ.*, vol 373, pp. 391–403.
- McGregor, R.G., Blowes, D.W., Jambor, J.L., Robertson, W.D. (1998) 'Mobilization and attenuation of heavy metals within a nickel mine tailings impoundment near Sudbury, Ontario, Canada' *Environmental Geology*, vol 36, pp. 305–319.

- McGuire, M.M., Hamers, R.J. (2000) 'Extraction and quantitative analysis of elemental sulfur from sulfide mineral surfaces by high-performance liquid chromatography' *Environ. Sci. Technol.*, vol 34, pp. 4651–4655.
- MEND, 2009. *Prediction Manual for Drainage Chemistry from Sulphidic Geologic Material*, MEND Report 1.20.1, Natural Resources Canada, www.mend-nedem.org.
- Mikhlin, Y.L., Kuklinskiy, A.V., Pavlenko, N.I., Varnek, V.A., Asanov, I.P., Okotrub, A.V., Selyutin, G.E., Solovyev, L.A. (2002) 'Spectroscopic and XRD studies of the air degradation of acid-reacted pyrrhotites' *Geochim. Cosmochim. Acta*, vol 66, pp. 4057–4067.
- Nicholson R.V., Scharer J.M. (1994) 'Laboratory studies of pyrrhotite oxidation kinetics' In *Environmental Geochemistry of Sulfide Oxidation*, ACS Symposium Series 550, CA Alpers and DW Blowes (Co-Eds.), American Chemical Society Washington DC.
- Robertson, A.M., Kawashima, N., Smart, R.St.C., Schumann, R.C. (2015) 'Management of pyrrhotite tailings at Savannah Nickel Mine – a decade of experience and learning' *Proceedings 10th International Conference on Acid Rock Drainage*, April 21–24, Santiago, Chile, Gecamin, Santiago, Chile, pp.
- Stewart, W., Schumann, R., Miller., S, Smart, R. (2009) 'Development of prediction methods for ARD assessment of coal process wastes' *Proceedings 8th International Conference Acid Rock Drainage*, June 22–26, Skelleftea, Sweden, <http://www.proceedings-stfandicard-2009.com/>
- Stewart, W., Miller., S, Smart, R , Gerson, A., Thomas, J., Skinner, W., Levay, G., Schumann, R. (2003) 'Evaluation of the net acid generation (NAG) test for assessing the acid generating capacity of sulfide minerals' *Proceedings 6th International Conference on Acid Rock Drainage*, July 14–17, Cairns, QLD, Australia, Australasian Institute of Mining and Metallurgy, pp. 617–625.
- Sullivan, L.A., Bush, R.T., McConchie, D., Lancaster, G., Clark, M., Lin, C., Saenger, P. (2004) *Chromium reducible sulfur (SCR)-method code 22B*. In: Ahern, C.R., Sullivan, L.A., McElnea, A.E. (eds). Laboratory method guidelines 2004 - acid sulfate soils. Queensland acid sulfate soil technical manual; Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia.