WEATHERING BEHAVIOUR OF MINE TAILINGS AND WASTE ROCK: A SURFACE INVESTIGATION[1]

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Abstract: A study focussing on the ion movement in the near surface of sulphide minerals was conducted to better understand the weathering mechanisms of mine waste materials. Tailings and waste rock samples from Canadian mines were subjected to controlled weathering studies using various chemical leachants. Leachates were analyzed for various parameters, and petrographic analyses were conducted on the solid residues. Laboratory oxidation studies of pure pyrrhotite and arsenopyrite were carried out using the surface techniques X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES). The data derived from the weathering study and the surface techniques were correlated to determine mechanisms of oxidation. Several results were observed during the project: Ferric iron constitutes one third of the iron present in pyrrhotite, sulphide oxidation is initiated when rock is blasted, sulphide sulphur is oxidized to di- and poly-sulphides prior to forming sulphates, and significantly more sulphate is produced upon exposure to aqueous environments than to air alone.

Introduction

Acid rock drainage (ARD) is a significant environmental concern to the mining industry. Much effort has been expended over the last decade to develop methods of preventing, predicting, controlling and treating ARD. An important starting point for all ARD research is understanding the mechanisms of ARD. The objective of this research is to expand our knowledge of ARD fundamentals.

A study of ion movement in the near surface of pyrrhotite and arsenopyrite revealed some of the mechanisms involved in ARD development. This study was carried out by conducting X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES) on pure minerals and petrographic analyses on laboratory-weathered tailings and waste rock. The results of the petrographic analyses served as a link between the two sets of information obtained from the laboratory-weathered material and from the pure minerals.

This paper will focus on the pyrrhotite experiments.

Methodology

The project was conducted as two parallel research programs: Examination of pyrrhotite surfaces using XPS and AES, and controlled laboratory weathering of tailings and waste rock containing pyrrhotite. The analytical procedures used are presented in two subsections, representing each program.

Mineral Surface Investigations

Three different analytical techniques were considered in this research: secondary ion mass spectrometry (SIMS), X-ray photoelectron spectroscopy (XPS), and auger electron spectroscopy (AES). As a result of the limitations encountered with SIMS, only XPS and AES were employed in surface investigations conducted on pyrrhotite.

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Sample Preparation of Pyrrhotite and Arsenopyrite. Research-grade pyrrhotite from Santa Eulalia, Chihuahua, Mexico was used in this study. Crystallographic properties were investigated by X-ray diffraction methods. Mineral composition was determined by repeated electron microprobe analyses.

Mineral fragments approximately 2 to 3 mm^3 were cleaved from the research-grade samples. Fragment faces were polished with P 800 silicon carbide paper to provide quick recognition of fresh fracture faces. Following polishing, the grains were ultrasonically cleaned for 2 min with methanol. Samples were dried in a low-vacuum desiccator.

Characterization of initial mineral surface chemistry was achieved by analyzing samples fractured under high vacuum in the XPS instrument. Transfer to the AES instruments was performed using a nitrogen-filled glove bag to prevent reaction with the atmosphere. Pyrrhotite samples were also analyzed after exposure to air at room temperature and atmospheric pressure for periods of 6.5 and 50 h, after 8 h of distilled water leaching, and after 8 h of sulphuric acid solution leaching.

Experiments Employing XPS. In the XPS experiment, X-ray photons interact with surface atoms to eject core level electrons. The atoms from which photo-ejected electrons originate are determined by the binding energies of the ejected electrons. Photoelectrons typically originate in the first 5 to 50 Å below the surface.

Survey scans were used to determine the elements present at the pyrrhotite surface. Emphasis was placed on the variations in the surface composition between samples rather than the absolute composition of each particular sample surface. Chemical state information was obtained from narrow-region photoelectron spectra, resolved by a peak-fitting routine using a Shirley-type background (Shirley 1972) and an 80% Gaussian, 20% Lorentzian peak model. Photoelectron binding energies for the vacuum-fractured sample were assigned relative to the monosulphide (S^{2-}) peak at 161.25 eV.

Experiments Employing AES. In the AES experiment, a high energy electron beam (1 to 10 kV) is focused at a sample surface, resulting in the inner shell ionization of a surface atom. As the ionized surface atom relaxes, excess energy is dissipated by either fluorescence or the ejection of an electron with characteristic kinetic energies of the donor atom (Auger 1975).

Acquisition of AES spectra was accomplished using a scanning Auger microprobe, equipped with a secondary electron detector and an Ar^+ ion gun. AES data collection was in two modes, survey and profile. Semiquantitative surface compositions were calculated using peak heights and sensitivity factors of data collected in survey mode. AES depth profiles were collected with reference to sputter time rather than depth. Time was converted to depth using the sputter erosion rate. The standard sputter rate for iron oxides is approximately 100 Å min^{-1} ±20% (Nicholson et al. 1990). The sputter rate of unoxidized pyrrhotite surfaces was measured to be approximately 0.4 Å min^{-1}.

Controlled Laboratory Weathering Tests

Samples of tailings and waste rock were subjected to several controlled laboratory weathering tests. These tests are described below.

Acid Base Accounting (ABA). ABA tests were conducted in duplicate on all samples, according to standard procedures (Sobek et al. 1978). Neutralization potential was determined by a modified method by employing hydrochloric acid digestion at ambient temperature for 24 h.

Humidity Cell Program. One kilogram of tailings was added to each of six humidity cells (HC-1, HC-2, HC-3, HC-4, HC-5, HC-6), and 1 kg of waste rock, crushed to -¼ in, was added to each of six additional humidity cells (HC-7, HC-8, HC-9, HC-10, HC-11, HC-12). The tailings and waste rock contained in all cells were weathered according to a 30-week, three stage program:

- 2-week leaching program using deionized water as the leachant, according to standard humidity cell protocol;
- 8-week leaching program using six different chemical solutions for each of the six cells containing tailings and waste rock, according to the standard wet-dry humidity cell protocol; and
- 20-week leaching program in which the same solutions employed in the 8-week program are maintained as continuous covers for each of the respective tailings and waste rock cells.

The standard protocol for humidity cell tests is outlined in the BC Draft ARD Technical Guide (1989): (1) dry air is passed over the samples from day 1 to day 3; (2) humidified air is passed over samples from day 4 to day 6; and (3) the sample is leached on day 7. The leachants used to simulate disposal conditions were selected from Engler et al. (1976) and modified in strength for the purpose of this study (table 1).

Table 1. Leaching conditions

Test	Leachant	Simulated Disposal Environment
HC-1 HC-7	Deionized water	Natural precipitation.
HC-2 HC-8	Dilute acetic acid (pH 3.5)	Landfills, water bodies with high organic content, and fermentative waters/bogs.
HC-3 HC-9	Oxalic acid (0.004M) and ammonium oxalate (0.004M)	Bottom and middle region of deep water disposal environments.
HC-4 HC-10	Sulphuric acid (pH 2.5)	Acidic drainage, pore water, lakes, and tailings ponds.
HC-5 HC-11	Hydrogen peroxide solution (0.1% w/w)	Oxygenated waters and sulphide-oxidizing environment.
HC-6 HC-12	Sodium hydroxide (pH 11.0)	Alkaline drainage, pore water, mill effluent, and some environments.

Leachate samples collected from the 12 humidity cells were analyzed for pH, Eh, conductivity, acidity, alkalinity, sulphate, and dissolved metals. The pH of leachates was measured with a combination electrode, and Eh was measured with a combined platinum-reference electrode. Sulphate was measured gravimetrically. Dissolved metal levels were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) upon filtration of leachates through a 0.45 μm-filter.

Quality-control methods, including calibration programs for each method, duplicate analyses, standard solution analyses, and blanks were implemented to ensure the integrity of results collected on leachates.

Cumulative release of sulphate and metals were plotted against time to identify trends.

The saturation indices for 214 minerals were calculated using the geochemical modelling software package SOLMINEQ.88. Using leachate data and established thermodynamic data, relationships between solid and liquid phases were established.

Petrographic Analysis. Upon completion of the 30-week weathering program, a sample from each of the tailings and waste rock humidity cells was subjected to petrographic analysis. Tailings samples consisted of vertical crosssections of the tailings bed and waste rock samples consisted of grab samples from the humidity cells. Waste rock samples consisted of material from various depths in the cells, however, vertical layering was not preserved.

Thin sections were examined, in transmitted and reflected light modes, using a petrographic microscope. Mineral identifications were made by standard observations of optical and physical properties. Observations of particle size were made using a calibrated eyepiece scale. Mineral abundances were estimated. Conclusions were based on observations of spatial distributions and textural relationships of the identified components.

Results

Surface Investigations

Data obtained from the XPS and AES analyses of research-grade pyrrhotite are summarized in tables 2 and 3.

Table 2. Iron, sulphur and oxygen species identified by XPS experiments on pyrrhotite, percent.

Spectrum	Vacuum Fractured	Air oxidized (6.5 h)	Water leached (8 h)	Sulphuric acid leached (8 h)	
				Smooth textured	Mosaic textured
Iron:					
Fe(II)-S	63.86	37.78	32.77		11.93
Fe(III)-S	33.18		23.84		19.55
Fe(III)-O		51.90	43.39	100.00	68.52
Sulphur:					
Monosulphide	77.40	64.00	61.45	7.71	31.10
Disulphide	12.00	18.80	21.27	12.00	20.75
Polysulphide	10.60	6.80	9.23	15.17	12.69
Elemental sulphur		3.40		7.01	3.29
Sulphite		3.30		4.12	
Sulphate		3.80	4.93	53.99	32.17
Iron sulphate			3.12		
Oxygen:					
Oxide-oxygen	20.00	29.10	25.28	31.52	17.28
Hydroxide	55.40	57.10	51.61	54.92	56.49
Adsorbed water	24.60	13.80	18.49	13.56	26.23
Iron sulphate			18.49		

Table 2 contains three components: the iron spectrum, the sulphur spectrum and the oxygen spectrum. Percentages represent contributions of a particular chemical species towards the overall spectrum for an element. The concentration of elements at the mineral surface is summarized in table 3.

Table 3. Atomic concentrations of surface atoms in pyrrhotite determined by AES, percent.

	Pyrrhotite					
	Vacuum fractured	Air oxidized (6.5 h)	Air oxidized (50 h)	Water leached (8 h)	Sulphuric acid leached (8 h)	
					Smooth textured	Mosaic textured
Carbon				49.00	37.00	14.00
Oxygen	12.00	29.00	37.00	24.00	30.00	48.00
Sulphur	46.00	24.00	15.00	6.00	16.00	11.00
Iron	40.00	47.00	48.00	21.00	17.00	27.00

Several points are noted from these results. First, iron is present in both ferric and ferrous ionic forms. Second, oxidized species of sulphur were detected in the vacuum-fractured pyrrhotite in the upper layers. The amount of sulphide sulphur decreases as the oxidizing potential of the environment increases. As sulphide sulphur decreases, the amount of oxidized sulphur species increases. Finally, iron is present predominantly as the ferric ion in all the experiments except the vacuum-fractured pyrrhotite experiment.

Controlled Laboratory Weathering Tests

Acid Base Accounting. ABA data are summarized in table 5. Samples of unweathered, naturally weathered, and laboratory-weathered tailings were analyzed. Naturally weathered tailings have been exposed for approximately 10 years. Both unweathered and naturally weathered tailings have a net neutralization potential (NNP) of -90 t $CaCO_3$ equivalent per 1 000 t waste. Except for the sodium hydroxide leached cell, NNP results for tailings weathered in the laboratory for 30 weeks show no significant changes in comparison to values obtained for unweathered and naturally-weathered tailings. The laboratory-weathered tailings exhibit decreases in total percent sulphur.

Table 5, Acid base accounting analysis of laboratory-weathered tailings.

Sample	Total S, %	Paste pH	NP	MPA	NNP
Unweathered	3.13	7.8	7.8	97.8	-90.0
HC-1	3.07	6.8	6.1	95.9	-89.8
HC-2	3.09	6.9	5.6	96.6	-91.0
HC-3	3.06	6.5	5.4	95.6	-90.2
HC-4	3.00	6.0	4.0	93.8	-89.8
HC-5	3.01	6.7	4.5	94.1	-89.6
HC-6	2.87	7.5	6.2	92.8	-86.6

HC-1= deionized water leached
HC-2= acetic acid leached
HC-3= ammonium oxalate/oxalic acid leached
HC-4= sulphuric acid leached
HC-5= hydrogen peroxide leached
HC-6= sodium hydroxide leached
NP = neutralization potential in t $CaCO_3$ equivalent per 1 000 t waste
MPA= maximum potential acidity in t $CaCO_3$ equivalent per 1 000 t waste
NNP = net neutralization potential in t $CaCO_3$ equivalent per 1 000 t waste

Waste rock materials collected from a waste rock pile were analyzed before and after the laboratory weathering program, as summarized in table 6. Unweathered waste rock produced a net neutralization potential (NNP) of -7.6 t $CaCO_3$ equivalent per 1,000 t waste. Four of the six laboratory-weathered samples had NNP values equal to or less than the value obtained for unweathered material, while the remaining two samples had an NNP value greater than the unweathered material.

Table 6. ABA analysis of laboratory-weathered waste rock.

Sample	Total S, %	Paste pH	NP	MPA	NNP
Unweathered	0.56	7.8	9.9	17.5	-7.6
HC-7	0.40	6.8	4.8	12.5	-7.7
HC-8	0.31	6.9	3.3	9.7	-6.4
HC-9	0.42	6.5	3.8	13.1	-9.3
HC-10	0.35	6.0	3.0	10.9	-7.9
HC-11	0.47	6.7	3.2	14.7	-11.5
HC-12	0.66	7.5	4.8	20.6	-15.8

HC-7 = deionized water leached
HC-8 = acetic acid leached
HC-9 = ammonium oxalate/oxalic acid leached
HC-10 = sulphuric acid leached
HC-11 = hydrogen peroxide leached
HC-12 = sodium hydroxide leached

Humidity Cell Program. The results of the humidity cell program on tailings and waste rock material are summarized in tables 7 and 8, respectively.

Table 7, Physical and chemical characteristics of tailings leachates.

Physical and chemical characteristics	Trends
pH	· Alkaline or alkaline-to-neutral throughout tests in all cells, except the sulphuric acid cell. · In the sulphuric acid cell, pH increased gradually upon establishment of saturated conditions, reaching 4.5 in the final cycle. · Aside from the sulphuric acid cell, the most significant drop in pH (from 7.8 to 5.4) was observed in the hydrogen peroxide cell in the 14th week (this decline was not accompanied by a significant increase in SO_4 levels). · A slight drop in pH (from 8.3 to 7.5) was accompanied by a peak in SO_4 levels in week 10 during unsaturated conditions in the sodium hydroxide cell. · Large fluctuations in pH during saturated leaching conditions (aside from the sulphuric acid cell) were observed in the hydrogen peroxide cell.
Eh	· An oxidizing environment dominated in all cells, the highest Eh values being measured in the sulphuric acid cell.

Table 7, Physical and chemical characteristics of tailings leachates (continued).

SO_4 levels	· Cumulative SO_4 curves indicate that SO_4 production in the first 10 weeks was as follows (cumulative SO_4 values at week 10 are given in brackets): SO_4 hydrogen peroxide cell (2162 mg/kg) > SO_4 sodium hydroxide cell (2054 mg/kg) > SO_4 sulphuric acid cell (1879 mg/kg) > SO_4 ammonium oxalate/oxalic acid cell (1230 mg/kg) > SO_4 deionized water cell (1017 mg/kg) > SO_4 acetic acid cell (798 mg/kg). · During maintenance of continuous solution covers, beginning with week 12, SO_4 production was highest in the sulphuric acid cell and decreased as follows (cumulative SO_4 values at week 30 are given in brackets): SO_4 sulphuric acid cell (4960 mg/kg) > SO_4 hydrogen peroxide cell (3994 mg/kg) > SO_4 sodium hydroxide cell (2767 mg/kg) > SO_4 ammonium oxalate cell (2072 mg/kg) > SO_4 deionized water cell (1749 mg/kg) > SO_4 acetic acid cell (1031 mg/kg).
Acidity	· Minority acidity measured throughout tests in all cells, except the sulphuric acid leached cell.
Alkalinity	· Largest variations in the hydrogen peroxide cell. · High alkalinity levels in the ammonium oxalate/oxalic acid cell.
Metal levels	· Iron levels lower than 10 ppm were reported in all cells except the sulphuric acid cell. · The highest arsenic levels were reported for the ammonium oxalate/oxalic acid cell. · Calcium concentrations lower than the deionized water cell were measured only in the ammonium oxalate/oxalic acid cell.

Table 8. Physical and chemical characteristics of waste rock leachates.

Physical and chemical characteristics	Trends
pH	· Alkaline, acidic and neutral-to-alkaline in the leachates from sodium hydroxide, sulphuric acid and deionized water, respectively. · Ammonium oxalate/oxalic acid and acetic acid leachates initially acidic, then upon establishment of saturated conditions, neutral. · Leachate from the hydrogen peroxide cell initially alkaline, then acidic. Indication of acid generation throughout the weathering program.
Eh	· An oxidizing environment dominated in all cells, the highest Eh values being measured in the sulphuric acid cell.
SO_4 levels	· Noticeably higher cumulative sulphate levels in the sulphuric acid (356 mg/kg) and hydrogen peroxide (646 mg/kg) cells compared to the acetic acid, ammonium oxalate/oxalic acid, and sodium hydroxide cells (206 - 218 mg/kg) at week 30. De-ionized water cell was intermediate at 308 mg/kg. · A 10-week lag in sulphate production observed in the hydrogen peroxide cell (138 mg/kg at week 10). Other cells showed low cumulative sulphate levels.

Table 8. Physical and chemical characteristics of waste rock leachates (continued).

Metal levels	· With the exception of ammonium oxalate/oxalic acid and sulphuric acid cells, iron concentrations were less than 2 ppm. · Arsenic levels remained below 0.1 ppm in all cells except the ammonium oxalate/oxalic acid cell where it reached levels of 0.14 ppm. · Sulphuric acid, ammonium oxalate/oxalic acid, and hydrogen peroxide leachates show cumulative calcium concentrations of 100 and 45 ppm, respectively.

Petrographic Analyses. Petrographic analyses were conducted on unweathered, naturally weathered and laboratory-weathered tailings and waste rock material. These studies revealed varying degrees of red-brown stains on fragments of waste rock. The sulphuric acid leached cell displayed the most strongly developed staining. However, no effects on the sulphides were recognizable in any of the six laboratory-weathered waste rock samples.

Tailings material clearly showed the effects of laboratory weathering. All samples, except the sodium hydroxide cell, displayed brown staining. The depth of this staining was consistent in the deionized, acetic acid, and ammonium oxalate/oxalic acid leached cells at 1 to 2 mm. Unoxidized sulphides were present throughout the samples, including the zone of staining. Sulphuric acid and hydrogen peroxide leached tailings had the thickest zones of brown staining (approximately 5 mm). These two samples were the only cells to display appreciable sulphide destruction. Sulphides in the upper four-fifths of the stained zone in the hydrogen peroxide leached tailings were almost completely destroyed. In the sulphuric acid leached tailings, unoxidized sulphides were present at the surface, but sulphides were completely oxidized in the slimes-enriched areas of the stained zone.

The naturally weathered tailings were obtained from the same mine as the tailings material used in the laboratory weathering program. Several differences were observed between this material and the unweathered material. The sulphide content of naturally weathered tailings was 0.5%, compared with 17% in unweathered material, based on observations during the petrographic analyses. Also, the particle size was in the range of 10 to 50 µm, as opposed to fresh tailings, which had a size range of 10 to 200 µm. Ferruginous secondary minerals occurred as diffuse stains and coatings on silicates, and as discrete, diffuse-margined grains probably representing the oxidized remnants of the original sulphide particles. Surviving sulphides typically displayed encapsulation by limonite.

Discussion

Although direct correlations between mineral surface chemical studies and leachate chemistry studies could not be made, valuable information was still obtained. Petrographic analyses of laboratory-weathered materials provided a valuable link to relate information obtained from the surface studies of pure minerals and from the leaching studies of natural waste materials.

Initiation of Oxidation - Ferric Iron Sites

The data from XPS and AES studies provide evidence that ferric iron is present in pyrrhotite, as opposed to pyrite, which contains ferrous iron only. The initiation of oxidation is expected to occur in the vacant cation sites within in the pyrrhotite crystal structure. Oxidation continues through redox reactions involving ferric iron. The vacuum-fractured mineral experiments suggest that the process begins at the fracturing stage.

Exposure-Related Weathering Behaviour

According to surface investigations and petrographic analyses, surface appearance and structure of alteration layers appear to vary according to exposure conditions. The tailings material leached by hydrogen peroxide and sulphuric acid displayed the greatest depletion in sulphide content, limnotization, and staining compared with other humidity cell leaching conditions. Naturally weathered tailings also showed considerable sulphide destruction. Air-oxidized pyrrhotite produced surface iron oxide, while deionized water and sulphuric acid leached pyrrhotite produced surface iron oxyhydroxide.

Sulphate Production

Different surface layers were produced as a result of air-oxidation and deionized water leaching. It was also observed that deionized water leaching produced twice as much sulphate as air-oxidation according to XPS. Sulphuric acid-leaching produced the most sulphate according to surface investigations (XPS) conducted on pyrrhotite. Net sulphate levels in the sulphuric acid cell leachates for tailings were significantly higher than from other tailings cells. Compared to sulphate generated in the hydrogen peroxide cells, these higher levels are assumed to be due to the presence of ferrous rather than ferric iron sulphates. The rate of sulphate release remained constant or decreased in five of the six cells after the samples were immersed after week 10. Sulphate production decreased after week 20 in the sulphuric acid-leached cell. The cumulative sulphate in the tailings leachates account for the reduction of sulphur required to reduce the maximum potential acidity (MPA) values reported in the tailings ABA results. The hydrogen peroxide-leached waste rock was the only sample reporting increased sulphate release rate after the samples were immersed. Cumulative sulphate levels did not account for all the sulphur reductions suggested by the waste rock MPA results.

Release of Iron

The extensive depletion of sulphides in the hydrogen peroxide leached tailings compared with those from other cells did not correspond to higher dissolved iron levels. Hydrogen peroxide and sodium hydroxide cell leachates contained the lowest iron levels, while the sulphuric acid cell leachates contained the highest. High iron, sulphate and acidity levels in the sulphuric acid cell leachates are expected to be due, in part, to bacterial catalysis, although this was not confirmed. The low iron levels observed in hydrogen peroxide cell leachates can be attributed to the low solubility of Fe(III) under the prevailing pH conditions. The iron levels in ammonium oxalate/oxalic acid cell leachates is expected to be due to the chelating effects of the leachant.

Conclusions

Oxidation state and depth profile information obtained from the experiments conducted on research-grade pyrrhotite produced some very significant and relevant findings with respect to understanding and predicting ARD potential. Some of the following conclusions will require further work to verify their validity.

The vacuum fractured pyrrhotite experiment provided many insights into the initiation of the oxidation process. One-third of the iron in pyrrhotite is present as Fe(III). The first step in the ARD process may begin with the redox reaction between sulphur (oxidizing) and ferric iron (reducing). This first step is initiated when the rock is blasted, not upon exposure to air. Upon exposure to air, the reduction of molecular oxygen to oxide oxygen may be facilitated by the vacant cation sites created by the presence of ferric iron in the crystal structure. The presence of ferric iron in addition to ferrous iron provides a possible explanation for the higher reactivity of pyrrhotite relative to pyrite.

Sulphide sulphur is oxidized to di- and poly-sulphides prior to forming sulphate.

Exposure to oxygenated aqueous environments during the XPS and AES experiments produced significantly more sulphate than exposure to air at room temperature and pressure. Exposure to aqueous environments also produced hydrated iron oxides rather than iron oxide. Previous isotope studies (Taylor et al. 1984, Reedy et al. 1990, and Van Everdingen and Krouse 1985) indicate the involvement of water-derived oxygen in the formation of sulphate in addition to atmospheric-derived oxygen. Directed studies involving mine waste materials are required to confirm suggestions that water is an important source of oxygen in the production of sulphate.

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