PYRRHOTITE OXIDATIVE DISSOLUTION:

REACTION RATES AND MECHANISMS

Minnesota Department of Natural Resources
Division of Lands and Minerals
Reclamation Section

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EXECUTIVE SUMMARY

This document provides a generalized description of oxidation rates, products, mechanism, and controlling variables of pyrrhotite oxidation under environmental conditions reported in seven references (listed in Table 1) judged to provide the most comprehensive and relevant information. Pyrrhotite oxidation is believed to occur through a series of steps which gradually remove iron from the crystal structure. Conceptually, the pyrrhotite structure passes through numerous intermediate forms from Fe_7S_8 to FeS_2 (either pyrite or marcasite) to Fe_yS, where y <0.5. The final oxidation products are Fe^{II}, which oxidizes to form iron oxyhydroxides, and sulfate and/or elemental sulfur. A fairly wide range of rates have been reported for pyrrhotite oxidation, from 10^{-8} to 10^{-10} mol/m²/s. The evidence for the effect that variables such as crystal structure, trace constituents, and pH is conflicting. The rate of pyrrhotite oxidation generally increases at elevated temperatures.

1. Introduction

Minnesota has an extensive mining industry and potential for mineral expansion and diversification. Iron mining began in Minnesota over a century ago and led to the taconite mining industry which, in 1996, shipped 45 million long tons of iron ore valued at 2.4 billion dollars (Minnesota Department of Revenue, 1997). Nonferrous mining development shows promise for the future. The state is presently the subject of extensive mineral exploration, with 59 leases covering over 26,000 acres of state land (MN DNR, 1998).

Considerable mineral potential for base and precious metals is associated with Minnesota's Precambrian rocks, specifically its Archean metavolcanics, metasedimentary formations and the Duluth Complex. The Archean metavolcanics and metasedimentary formations, or greenstone belts, of Minnesota extend north into Canada, where they have yielded substantial mineral production. These formations are potential hosts for gold, zinc-copper massive sulfides with various by-products, and magmatic sulfide deposits containing copper, nickel and platinum group elements. Recent exploration of greenstone belt metasedimentary formations has focused on gold, base metals, and silver-cobalt-copper deposits. The Duluth Complex contains an estimated copper-nickel resource of 4.4 billion tons (Minnesota Environmental Quality Board, 1979), as well as significant titanium resources. Drill core analyses have also revealed the presence of chromium, vanadium, cobalt, and platinum group elements.

If mineral development occurs, tailings and waste rock, as well as the mine itself will be wastes remaining after the operation is abandoned. The potential for generation of acidic mine waste drainage is the primary water quality concern, and this potential is largely determined by the mine waste composition. Iron sulfide minerals are often present in mines wastes, and their oxidation leads to the production of acid. The rate of acid production is directly related to the rate at which sulfide minerals present in the mine waste oxidize.

Understanding the relative rates and mechanisms of oxidation of specific iron sulfide minerals provides the background necessary to understand and evaluate literature regarding current developments relevant to environmental mine waste management. It also creates a foundation for calculating acid production rates in laboratory dissolution tests, and comparison of these rates to those of various rock types reported in the literature. Finally, the success of mitigation experiments can be evaluated in terms of reduced or slowed sulfide oxidation, if the rates of oxidation of sulfide minerals present in the waste material are known. Understanding the mechanisms by which specific sulfide minerals oxidize provides a framework through which results from laboratory dissolution tests and mitigation experiments can be interpreted. Furthermore, this information helps determine strategies for prevention and control of acid mine drainage.

2.   Scope And Objectives

The primary objective of this document is to provide a generalized description of oxidation rates, products, mechanism, and controlling variables of pyrrhotite oxidation. An extensive volume of literature has been published on the topic of pyrrhotite oxidation, and a partial bibliography of these titles is included in Appendix 1. A list of the most relevant references to pyrrhotite oxidation under environmental conditions is provided in Table 1. This document will review the information from seven of the references listed in Table 1 (Janzen, 1996; Janzen et al., 2000; Kwong, 1993; Lapakko, 1994; Lapakko and Antonson, 1994; Nicholson and Scharer, 1994; Pratt et al., 1994a, 1994b). These were judged to provide the most comprehensive and relevant information on the subject of pyrrhotite oxidation under environmental conditions. Additional references regarding pyrrhotite and oxidation of arsenopyrite are included in Appendices 2 and 3, respectively.

Table 1.   Summary of references to pyrrhotite oxidation.

Reference	Structure	Oxidation Rates	Oxidation Products	Mechanisms
Graham, AR, 1969, The Canadian Mineralogist, 10, 4-24. (#2902)	x			
Yund, RA; Hall, HT, 1969, Econ. Geol., 64, 420-23. (#2893)	x			
Schultz,HD; Proctor,WG, 1973 Appl. Spec. 27(5), 347-351. (#2893)	x			
Scott, SD; Both, RA, 1976, Proc. 25th Internat. Geol. Congress, 140-41 (#3409)	x			
Kissin, SA; Scott, SD, 1979, American Mineralogist, 64, 1306-10. (#3406)	x			
Kissin, SA; Scott,SD, 1982, Econ. Geol., 77, 1739-54. (#3407)	x			
Jongewaard, P., 1999, Geologist, EVTAC, Eveleth, MN, personal comm. (#3408)	x			
Yazawa, A; Eguchi, M, 1962, in Japanese? (#2892)		x		
Van Weert, G et al., 1974, CIM Bulletin, 97-103. (#2897)		x		

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| Reference	Structure	Oxidation Rates	Oxidation Products	Mechanisms
Bugajski, J; Gamsjager, H, 1982, Monatshefte fur Chemie, 113, 1087-92. (#2895)		x		
Buckley, AN; Woods, R, 1984, Proc. Internat. Symp. On Electrochemsitry in Mineral and Metal Processing, Electrochem. Soc. 286-302 (#2374)		x		
Ahonen, L et al., 1986, Fundamental and Appl. Biohydrometallurgy, 13-22. (#988)		x		
Ahonen, L; Tuovinen, OH, 1991, Appl. & Environ. Microbiol., 57(1), 138-45. (#1122)		x		
Xianjian, G; Chunpeng, L, 1991, Chin. J. Met. Sci. Technol., 7, 371-75. (#2837)		x		
Ahonen, L; Tuovinen, OH, 1992, Appl. & Environ. Microbiol., 58(2), 600-06. (#2484)		x		
Nicholson, RV; Scharer, JM, 1992, Abstracts of papers of the ACS, 204, #30. (#28)		x		
Li, J et al., 1993, EPD Congress, 229-44. (#2821)		x		
Linge, HG, 1995, Minerals Engineering, 8(7), 795-806. (#2836)		x		
Mizuta, T; Scott, SD, 1997, Econ. Geol., 92, 772-83. (#3404)		x		
Domvile, S et al., 1998, draft paper (#3405)		x		
Janzen, MP et al., 2000, GCA, 64, 1511-22 (#3942)		x		
Nicholson, RV; Scharer, JM, 1994, Environmental Geochemistry of Sulfide Oxidation, Chapter 2. (#987)		x		x
Hodgson, M; Agar, GE, Proc. Internat. Symp. Electrochem in Mineral and Metal Processing, 84, 185-201. (#2891)			x	
Ingraham, TR et al., 1972, Canadian Metallurgical Quarterly, 11(2), 407-11. (#347)			x	
Nickel, EH et al., 1974, Econ. Geol., 69, 93-107. (#62)			x	

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Reference	Structure	Oxidation Rates	Oxidation Products	Mechanisms
Steger, HF, 1977, Talanta, 24, 251-54. (#194)			x	
Steger, HF; Desjardins, LE, 1978, Chem. Geol., 23, 225-37. (#64)			x	
Steger, HF, 1979, Talanta, 26, 455-60. (#198)			x	
Hamilton, IC; Woods, R, 1981, J. Electroanal. Chem., 118, 327-43. (#59)			x	
Steger, HF, 1982, Chem. Geol., 35, 281-295. (#199)			x	
Steger, HF, 1982, Geostandards Newsletter, V1(2), 249-55. (#202)			x	
Reimers, GW; Hjelmstad, KE, 1987, US BOM RI 9118, 16p. (#229)			x	
Ahonen, L; Tuovinen, OH, 1989, Biotech. Lett., 11(5), 331-36. (#2339)			x	
Lapakko, KA; Wessels, JN, 1994, 40th Ann. Meeting Instit. On Lake Superior Geol., 29-30. (#2468)			x	
Ahmed, SM, 1995, Proc. Conf. Mining and the Environ., Sudbury, ON, 171-80. (#2716)			x	
Banerjee, A, 1976, Indian J. of Chem., 14A, 845-50. (#57)			x	x
Jones, CF et al., 1992, Appl. Surf. Sci. 55, 65-85. (#2907)			x	x
Pratt, AR et al., 1994, Geochim. Cosmochim. Acta, 58(2), 827-41. (#2334)			x	x
Pratt, AR et al., 1994, Geochim. Cosmochim. Acta, 58(23), 5147-59. (#2909)			x	x
Pratt, AR; Nesbitt, HW, 1997, Am. J. of Sci., 297, 807-28. (#3402)			x	x
Janzen, MP, 1996, MS thesis, U of Waterloo, ON Canada, 175p. (#2788)		x	x	x

3. Pyrrhotite Crystal Structure

Pyrrhotite has a chemical formula of $Fe_{1-x}S$, where $0 \leq x \leq 0.125$. Thus, the pyrrhotite formula may range from FeS to Fe_7S_8. The FeS end member has an orthorhombic structure. $Fe_{1-x}S$ intermediates such as Fe_8S_9, Fe_9S_{10}, and $Fe_{10}S_{11}$, have hexagonal structures and Fe_7S_8 is monoclinic. Pyrrhotite is typically found as mixtures of hexagonal and monoclinic phases.
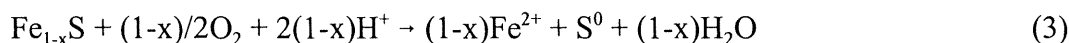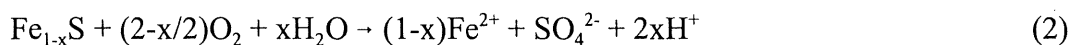
4. General Description of Mechanism and Reaction Products

Pyrrhotite oxidation occurs through a series of steps by which iron is gradually removed from the crystal lattice (Figure 1). In the initial step, oxygen partially oxidizes pyrrhotite to form marcasite or pyrite and Fe^{2+} intermediates:

$$2Fe_{x-1}S + (\tfrac{1}{2}-x)O_2 + (2-4x)H^+ \rightarrow FeS_2 + (1-2x)Fe^{2+} + (1-2x)H_2O \quad (1)$$
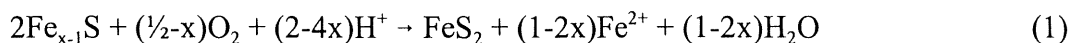
where, x can vary from 0 to 0.125 (Nicholson and Scharer, 1994; Janzen, 1996). Subsequent steps involve further oxidation of the marcasite or pyrite intermediate to an even more iron-depleted sulfide (Fe_yS), where y is less than 0.5. In the final stages, Fe_yS oxidizes to produce Fe^{2+}, sulfate and/or elemental sulfur.
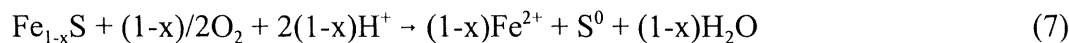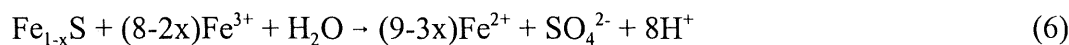
Two overall reactions have been proposed for the oxidation of pyrrhotite, one producing sulfate (Equation 2) and the other producing elemental sulfur (Equation 3):

$$Fe_{1-x}S + (2-x/2)O_2 + xH_2O \rightarrow (1-x)Fe^{2+} + SO_4^{2-} + 2xH^+ \quad (2)$$

$$Fe_{1-x}S + (1-x)/2O_2 + 2(1-x)H^+ \rightarrow (1-x)Fe^{2+} + S^0 + (1-x)H_2O \quad (3)$$

At any point during the oxidation, Fe^{2+} can be further oxidized to Fe^{3+}, which precipitates as $Fe(OH)_3$:

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \quad (4)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad (5)$$

However, at low pH, Fe^{3+} will remain dissolved and act as an additional pyrrhotite oxidant. This reaction may not proceed to completion, but instead produce elemental sulfur:

$$Fe_{1-x}S + (8-2x)Fe^{3+} + H_2O \rightarrow (9-3x)Fe^{2+} + SO_4^{2-} + 8H^+ \quad (6)$$

$$Fe_{1-x}S + (1-x)/2O_2 + 2(1-x)H^+ \rightarrow (1-x)Fe^{2+} + S^0 + (1-x)H_2O \quad (7)$$
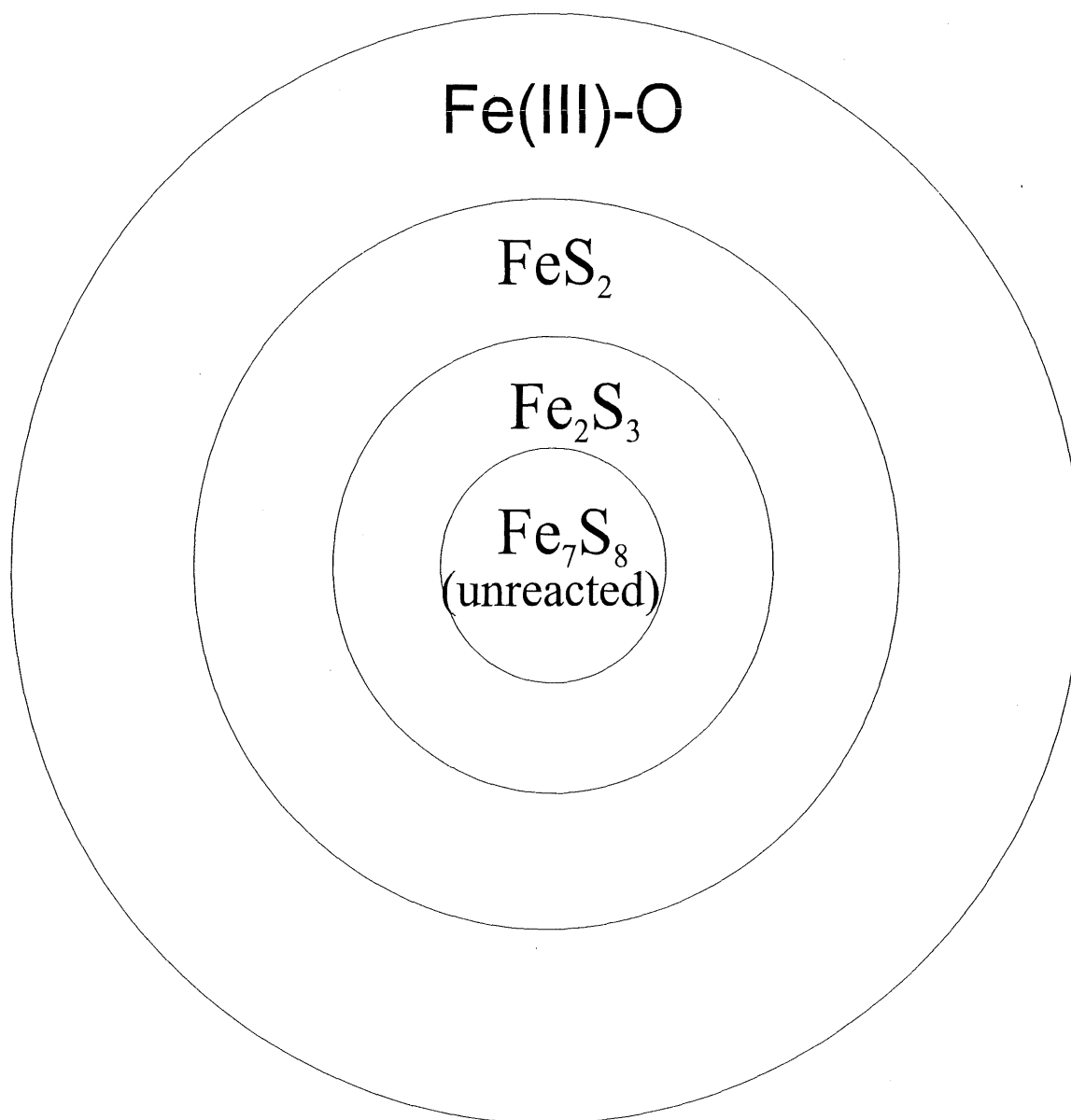
Figure 1.   Pyrrhotite oxidation takes place through a series of steps in which iron is gradually removed from the crystal lattice. At the surface of the crystal, an iron oxyhydroxide layer forms. Iron-depleted, or alternatively, sulfur-enriched intermediates form in layers between the oxide coating and unreacted pyrrhotite, Fe_7S_8.

Pratt et al. (1994a) determined the empirical formula of monoclinic pyrrhotite to be $Fe^{II}_5Fe^{III}_2S_8$. In the initial oxidation steps, oxygen adsorbs to vacant sites on the pyrrhotite surface that are created by the Fe^{III} substitutions into the crystal lattice. The Fe^{III}-S bond is the most reactive towards adsorbed oxygen (Pratt et al., 1994a, b). Thus electrons will be transferred to oxygen, reducing it to O^{2-} and oxidizing either Fe^{II} or S^{2-}. Oxygen does not diffuse into the crystal lattice nor does it exchange for S^{2-}. Electron transfer is promoted by the Fe^{III} located near the crystal lattice vacancies. Eventually a monolayer of Fe^{III}-O forms, and subsequent reaction requires iron to diffuse through this layer.

Iron diffusion probably results from a chemical potential gradient created between Fe^{II} and Fe^{III}. As the Fe^{III}-O layer grows, electron transfer will be inhibited by a lack of Fe^{II} (diminished gradient), and the rate of oxidation slows. Sulfide may also donate electrons to this process, which results in either sulfate (or other sulfoxy anion) release, elemental sulfur formation, or both. Sulfide oxidation results in a sulfur-depleted zone just beneath the Fe-OOH zone at the surface. The remaining sulfide apparently remains in the bulk pyrrhotite forming disulfides (the predominant form in pyrite) and polysulfides. The sulfur to iron ratio increases beneath the oxide layer due to iron diffusion to the surface. As the coating grows, Fe^{III} must diffuse towards the surface to facilitate further reaction. This loss of Fe generates a S-enriched zone between the S-depleted zone and the bulk pyrrhotite.

5.   Pyrrhotite Reaction Rates

Pyrrhotite oxidation rates under a wide variety of conditions have been reported in the literature. However, very few of these studies were conducted under environmental conditions (Ahonen and Tuovinen, 1991, 1992; Janzen, 1996; Janzen et al., 2000; Kwong and Ferguson, 1990; Lapakko, 1994; Lapakko and Antonson, 1994; Nicholson and Scharer, 1992, 1994). The following paragraphs summarize information from four of these papers. Notes on a greater range of publications are presented in Table 2.

Lapakko and Antonson (1994) measured the rate of sulfate release from sixteen 75-g samples of Duluth Complex rock containing pyrrhotite as the preliminary sulfide mineral. The Duluth Complex samples were rinsed weekly with deionized water and allowed to oxidize at approximately 26 °C and 58% relative humidity. The average rate of sulfate release was described by the equation:

$$[d(SO_4)/dt]_{avg} = (5.97 \times 10^{-13})S_T^{0.984} \quad (N = 32, r^2 = 0.801) \tag{8}$$

where, S_T represents the total solid-phase sulfur content of the sample. Assuming that all of the sulfate released was from pyrrhotite oxidation yields a pyrrhotite oxidation rate of 8.0×10^{-10} mol/m^2/s. Lapakko (1994) also determined the rate of sulfide oxidation in the Virginia Formation hornfels rock containing 14 wt% pyrrhotite in a similar set of laboratory experiments. The rate of sulfate release from these samples was $5.6 - 13 \times 10^{-12}$ mol/g/s.

Using the same assumptions as those used for the Duluth Complex samples yields a pyrrhotite oxidation rate of approximately 5.4×10^{-9} mol/m^2/s.

Table 2. Rates of pyrrhotite oxidation under environmental conditions that have been reported in the literature vary by several orders of magnitude.

Authors	Citation	Conditions	Reaction Rates
Ahonen, L Tuovinen, OH	Appl & Environ Microbiology 57, 1991	20% pyrrhotite, -590 um, 4,7,10,13,16,19,28,37,46°C	0.0143-0.1340 1/day
Ahonen, L Tuovinen, OH	Appl. & Environ. Microbiol., 58, 600-06, 1992	4, 7, 10, 13, 16, 19, 28, 37 °C	pyrrhotite > pentlandite
1. Janzen, MP 2. Janzen, MP Nicholson, RV Scharer, JM	1. MS Thesis, U of Waterloo, 1996 2. Geochim. Cosmochim. Acta, 64, 1511-1522, 2000.	non-oxidative dissolution: DO oxidation: Fe(III) oxidation:	5×10^{-10} mol/m^2/s 4×10^{-9} 3.5×10^{-8}
Kwong, YTJ Ferguson, KD	Acid mine drainage: Designing for mine closure, 1990	abandoned mine site	marcasite>pyrrhotite> chalcopyrite>pyrite= arsenopyrite
Lapakko, K	Proc. internat land reclam. and mine drainage, 1994	14% pyrrhotite experiments: control experiments:	1.5-2.2×10^{-12} mol/g-rock/s $5.7 - 13 \times 10^{-12}$
Lapakko, K Antonson, DA	ACS Symposium Series #550	26 °C 58% relative humidity	8.0×10^{-10} mol/m^2/s
Nicholson, RV Scharer, JM	Abstracts of papers 204th ACS. 1992	controlled T (25°C), P_{O2}, A_s, pH, and biotic activity	5×10^{-9} mol/m^2/s
Nicholson, RV Scharer, JM	Environmental geochemistry of sulfide oxidation, Ch2, 1994	pH 2, 3, 4, 6; T 10, 22, 33°C; $d_{avg} = 105$ um	$6 - 14 \times 10^{-9}$ mol/m^2/s

Nicholson and Scharer (1994) conducted kinetic experiments using a pneumatically mixed flow-through reactor to determine the rate of hexagonal pyrrhotite oxidation under environmental conditions. The experiments were conducted at pH values between 2 and 6 and temperatures between 10 °C and 33 °C. At pH 6 and 22 °C, the pyrrhotite oxidation rate was approximately 10×10^{-9} mol/m^2/s with an experimentally determined activation

energy of 100 kJ/mol. For the range of conditions tested, pyrrhotite oxidation rates ranged from 4 to 58 x 10^{-9} mol/m^2/s. The oxidation kinetics of pyrrhotite, pyrite, and three mixtures of the two minerals were also measured using fixed-bed reactors at 22 moles-Po/m^2/s and ambient oxygen pressures. The oxidation rate of pure pyrrhotite was 1.3 x 10^{-8} mol/m^2/s, approximately one hundred times higher than their measured rate of pure pyrite oxidation.

Janzen (1996, 2000) investigated rates of non-oxidative dissolution as well as oxidation rates by dissolved oxygen and ferric iron of twelve, museum grade, pyrrhotite samples. Oxidation studies were conducted using pneumatic reactors and stirred tank reactors at pH values between two and three and temperatures between 10 °C and 45 °C. The average non-oxidative dissolution rate was determined to be 5 x 10^{-10} moles-Po/m^2/s. The average oxidation rates by dissolved oxygen and ferric iron were 4 x 10^{-9} moles-Po/m^2/s and 3.5 x 10^{-8} moles-Po/m^2/s, respectively.

6.   Rate Controlling Variables

6.1   Crystal Structure

Janzen (1996) reviewed conflicting literature that described the different reactivities of various pyrrhotite phases. Monoclinic pyrrhotite was believed to oxidize both faster and slower than hexagonal pyrrhotite. It was further suggested that monoclinic pyrrhotite became enriched as the hexagonal pyrrhotite was preferentially oxidized. However, Janzen, himself, did not find any correlation between pyrrhotite oxidation rates using dissolved oxygen or ferric iron and crystal structure.

6.2   Trace Constituents

Kwong (1993) observed that pyrrhotite oxidation rates decreased in pyrrhotites with higher trace metal contents. This observation was explained in terms of a semi-conductor process where substitutions into the crystal lattice create positive or negative effective charges on the surface. A positive effective charge would result when an element to the right of iron on the periodic table (e.g. Co) substitutes for iron in the crystal lattice. This positive effective charge may inhibit electron transfer that occurs during pyrrhotite oxidation. Similarly, a negative effective charge occurs when the substitution involves an element to the left of iron on the periodic table, which may enhance electron transfer (and consequently, pyrrhotite oxidation). However, Janzen (1996) did not find any correlation between pyrrhotite trace metal content and rate of oxidation.

6.3   pH

Pyrrhotite oxidation rates by ferric iron have been found to generally increase as pH increases (Janzen, 1996). It was suggested that this pH dependence implied competition between H$^+$

and Fe^{3+} for adsorption sites on the pyrrhotite surface. However, these results were not consistent for all twelve of the pyrrhotite samples tested. Furthermore, the pH range tested by Janzen (1996) was 2 - 2.75, far below the pH of most natural waters. However, mine waste drainages may have pH values within this range.

6.4   Temperature

The Arrhenius equation has been shown to apply to pyrrhotite oxidation (Janzen, 1996). Both dissolved oxygen and ferric iron oxidation experiments obeyed an Arrhenius-type equation. Oxidation rates increased three to five times for a temperature increase of 20 °C when oxygen was the oxidant and two to eleven times for a temperature increase of 30 °C when ferric iron was the oxidant. Activation energies ranging from 47 kJ/mol to 63 kJ/mol suggested that the controlling mechanism involved breaking or forming of bonds.

7.   Direction of Future Work

Seven papers considered to be the most relevant to the topic of pyrrhotite oxidation under environmental conditions were summarized in this document. This document did not address pyrrhotite oxidation under conditions that may not naturally occur in the environment. This type of information is not immediately relevant to sulfidic mine waste management issues in Minnesota, although it may improve our understanding of the mechanisms and physical and chemical variables that affect pyrrhotite oxidation rates and products. This type of information may also provide insight into potential mitigation strategies to control pyrrhotite oxidation in mine waste materials.
A second objective is to broaden our knowledge base to include a range of sulfide minerals that may occur in Minnesota's sulfide-bearing rocks (e.g. pyrite, marcasite etc...). These minerals probably oxidize at different rates and by different mechanisms that pyrrhotite. Consequently, interpretation of results from laboratory dissolution and mitigative experiments is likely to vary with respect to the specific mineralogy of the mine waste material used. Finally, the potential interaction of more than one sulfide mineral within a given material should be investigated.

8. References

Ahonen, L., Tuovinen, O. H., 1991. Temperature effects on bacterial leaching of sulfide minerals in shake flask experiments. *Appl. and Environmental Microbiology*, 57, p. 138-145.

Ahonen, L., Tuovinen, O. H., 1994. Solid-phase alteration and iron transformation in column bioleaching of a complex sulfide ore. In: Environmental geochemistry of sulfide oxidation. ACS Symposium Series No. 550, American Chemical Society, Washington, DC, p. 79-89.

Janzen, M. P., 1996. Role of ferric iron, trace metal content, and crystal structure on pyrrhotite oxidation. master thesis, University of Waterloo, Waterloo, Ontario. 175 p.

Janzen, M. P., Nicholson, R. V., Scharer, J. M., 2000. Pyrrhotite reaction kinetics: reaction rates for oxidation by oxygen, ferric iron, and for nonoxidative dissolution. Geochimica et Cosmoschimica Acta, 64, 9, 1511-1522.

Kwong, Y. T. J., Ferguson, K. D., 1990. Water chemistry and oxidation mineralogy at Mount Washington - Implication to acid generation and metal leaching. In: Acid mine drainage: Designing for closure. Presented at GAC/MAC Joint Annual Meeting in Vancouver, May 16-18, BiTech Publishers Ltd., Vancouver, BC, 217-230.

Lapakko, K. A., 1994. Subaqueous disposal of mine waste: Laboratory investigation. In: Internat. Land Reclamation and Mine Drainage Conf. and the Third Internat. Conf. on the Abatement of Acidic Drainage, Pittsburgh, PA, April 24-29, p. 270-278.

Lapakko, K.A., Antonson, D.A., 1994. Oxidation of sulfide minerals present in Duluth Complex rock: A laboratory study. In: Environmental Geochemistry of Sulfide Oxidation, ACS Symposium Series No. 550, American Chemical Society, Washington, DC, p. 593-607.

MN DNR, 1998. October 1997 (Q2 F1998) report on state mineral leasing activities. MN Dept. Nat. Resour., Division of Minerals, mineral leasing and mineral rights management section, Saint Paul, MN.

Minnesota Department of Revenue, 1997. Personal communication with Tom Schmucker, Administrative engineer, Eveleth, MN.

Minnesota Environmental Quality Board, 1979. Regional copper-nickel study, Executive summary, volume 1. MN State Planning Agency, Saint Paul, MN. 118 p.

Nicholson, R. V., Scharer, J. M., 1992. Laboratory investigation of the controls on the rate of pyrrhotite oxidation. Abstracts of Papers 204 (American Chemical Society, 23 August, Ed: American Chemical Society), 30-GEOC.

Nicholson,R. V., Scharer, J. M., 1994. Laboratory studies of pyrrhotite oxidation kinetics. In: Environmental Geochemistry of Sulfide Oxidation, ACS Symposium Series No. 550, American Chemical Society, Washington, DC, p. 14-30.

Pratt, A. R., Muir, I. L., Nesbitt, H. W., 1994a. X-ray photoelectron and Auger electron spectroscopic studies of pyrrhotite and mechanism of air oxidation. *Geochim. Cosmochim. Acta* 58, 2, 827-841.

Pratt, A. R., Nesbitt, H. W., Muir, I. J., 1994b. Generation of acids from mine waste: Oxidative leaching of pyrrhotite in dilute H_2SO_4 solutions at pH 3.0. *Geochim. Cosmochim. Acta* 58, 23, p. 5147-5159.

APPENDIX 1

Annotated Pyrrhotite Bibliography

A1.1. Pyrrhotite Crystal Structure

2335. Arnold,RG (1967): Range in composition and structure of 82 natural and terrestrial pyrrhotites. Canadian Mineralogist 9(Part 1), 31-50.
   [COMPOSITION; LOW TEMP; METAL SULFIDES; MINERAL DISSOLUTION; MINERALOGY; PYRRHOTITE; STRUCTURE]

2886. Schultz,HD; Proctor,WG (1973): Application of electron emission spectroscopy to characterize sulfur bonds in coal. Applied Spectroscopy 27(5), 347-351.
   [COAL; ELECTROCHEMISTRY; IEE; IRON; ORGANICS; PYRITE; PYRRHOTITE; SPECTROSCOPY; STRUCTURE; SULFATE; SULFUR]

2893 Yund, R.A.; Hall, H.T. (1969): Hexagonal and monoclinic pyrrhotites. Econ. Geol. 64, 420-423.

Abstract. The sulfur-rich limit of hexagonal pyrrhotite below 290 °C is 47.45 atomic percent iron and is independent of temperature. Monoclinic pyrrhotite is metastable above 290 °C. This observation, combined with the reported conversion of a natural monoclinic pyrrhotite to the hexagonal form at 260 °C, suggests that monoclinic pyrrhotite may be metastable at lower temperature as well. The composition of monoclinic pyrrhotite seems to be a function of temperature, but experimental determination of its composition also depends on the decomposition rate if it is metastable.

The dry and aqueous synthesis of monoclinic pyrrhotite at low temperature (not inversion of hexagonal pyrrhotite on cooling) and its occurrence in low-temperature environments, indicates that the use of the composition of monoclinic pyrrhotite and the hexagonal pyrrhotite solvus for estimating formation temperatures is not justified unless the thermal history of the specimen is known.

Results. The experiments described here were designed to answer three questions. The first concerns the compositional limit or minimum iron content of hexagonal pyrrhotite below 325 °C. Both the slow cooling exsolution (pyrite exsolved at high-T) experiments and the solution (annealed) experiments indicate a compositional limit for hexagonal pyrrhotite of 47.45 atomic percent iron. The second question concerns the composition of monoclinic pyrrhotite. Apparently, the composition of monoclinic pyrrhotite varies (possibly up to 0.4 atomic percent) with temperature and the sulfur-rich limit. The third question had to do with the stability of monoclinic pyrrhotite. Their data indicate that monoclinic pyrrhotite is metastable between 290 °C and 308 °C.

2900. Arnold,RG; Reichen,Laura E (1962): Measurement of the metal content of naturally occurring, metal-deficient, hexagonal pyrrhotite by an x-ray spacing method. American Mineralogist 47(January-February), 105-111.
[ANALYTICAL METHODS; COMPOSITION; CONCENTRATION; METHODS; MINERALOGY; PYRRHOTITE; STRUCTURE]

2902   Graham, A.R. (1969) Quantitative determination of hexagonal and monoclinic pyrrhotites by XRD. The Canadian Mineralogist. 10, 4-24.

Abstract. Measurement of the difference in amplitude of components at about 51.75° and 51.40° 2Θ (Co Kα radiation) of the asymmetric XRD peak resulting rom partial superposition of strong diffractions from corresponding planes in hexagonal and monoclinic pyrrhotite structures allows rapid quantitative determination of amounts and proportions of these structures in certain sulfide ores carrying at least 3% of either pyrrhotite type. The differences in amplitudes from synthetic mixtures of the pure structures are divided by the amplitudes of a nearby diffraction peak from an internal standard added in constant proportion; and the resulting rations are plotted against the known proportions of either structure. The plot may be checked against weights of magnetic concentrates of monoclinic pyrrhotites from the ores under study. Determination rates of at least two to three samples per hour with an average error of about ±12% of the amounts present may be readily attained with suitable instrumentation. Economical and relatively precise contouring of sulfide bodies for the amounts and distributions of hexagonal (paramagnetic) and monoclinic (ferromagnetic) pyrrhotites is thus feasible.

2906. Arnold,RG (1966): Mixtures of hexagonal and monoclinic pyrrhotite and the measurement of the metal content of pyrrhotite by x-ray diffraction. American Mineralogist 51, 1221-1227.
[CRYSTALLIZATION; LABORATORY; MINERALOGY; PYRRHOTITE; XRD]

2907   Jones, C.F.; LeCount, S.; Smart, R.St.C. (1992): Compositional and structural alteration of pyrrhotite surfaces in solution: XPS and XRD studies. Applied Surface Sci. 55, 65-85.

Abstract. Ground pyrrhotite surfaces oxidized by exposure to (i) air, (ii) water and (iii) deoxygenated perchloric acid solution (0.05-1M) were examined using XPS and XRD. In air or water, the surfaces form amorphous layers containing carbonate species; sulfate species; iron (III) oxide/hydroxides; and an iron-deficient sulfide species with an S(2p) doublet shifted 1.0-1.8 eV to higher binding energy (BE). After acid reaction, the surface partly restructures to a crystalline, defective tetragonal

Fe$_2$S$_3$ product in which linear chains of S$_n$ atoms have a S-S distance similar to elemental sulfur (S$_8$) but the S(2p) BE is still 0.2-0.6 eV less than S$_8$. Initially, the acid-reacted surface may be partly hydrophobic, giving flotation separation, but, as oxidation proceeds, hydrophilic iron hydroxides deposit on the surface depressing flotation. The chemical forms of Fe and S in the surface layers are discussed in detail with changes in the proportion of the oxidized and iron-deficient sulfide products.

3406 Kissin, S.A.; Scott, S.D. (1979): Device for the measurement of sulfur fugacity mountable on the precession camera. American Mineralogist. 64, 1306-1310.

Abstract. A device for measurement of sulfur fugacities of single crystals of sulfides at elevated temperatures was designed for use with a precession camera and successfully employed in studies of pyrrhotite. The device contains the solid-state electrochemical cell Pt, Ag(s)|AgI(s)|Ag$_2$S(s), S$_2$(g), Pt and enables simultaneous determination of temperature, sulfur fugacity, and crystal structure. Trial studies confirmed that the stable pyrrhotite structure at 437 °C, 434 °C, and 320 °C is the 1C type. Measured sulfur fugacities for the crystals are slightly lower than calculated values from earlier data.

3407 Kissin, S.A.; Scott, S.D. (1982): Phase relations involving pyrrhotite below 350 °C. Econ. Geol. 77, 1739-1754.

Abstract. A hydrothermal recrystallization method was employed to determine the phase relations in the Fe-S system involving pyrrhotite between 350 °C and 115 °C. The superstructures of pyrrhotite, as designated by Nakazawa and Morimoto (1970, 1971), are considered to be thermodynamic phases. The solvus between pyrite and hexagonal (1C) pyrrhotite continues below 325 °C along the slope established by Toulmin and Barton (1964) to 308 °C, where a discontinuity marks the upper stability of the MC superstructure. The solvus then continues along a similar slope to 262 °C where, with the onset of the NA superstructure, there is a discontinuity and the curve reverses slope sharply. At 254 °C, monoclinic (4C) pyrrhotite becomes stable in the peritectoid reaction hexagonal (NA) pyrrhotite (47.30 at. % Fe) + pyrite = monoclinic (4C) pyrrhotite (47.25 at. % Fe). Monoclinic pyrrhotite exists over a range of compositions, the maximum being 46.4 to 46.9 at. % Fe at 115 °C. Hexagonal pyrrhotite is separated from Monoclinic pyrrhotite by a narrow miscibility gap down to the upper stability limit of the NC superstructure at 209 °C. Below 209 °C, the miscibility gap widens, with hexagonal (NC) pyrrhotite of 47.3 at % Fe coexisting with Monoclinic pyrrhotite of 46.9 at. % Fe. At the sulfur-rich limit of the stability field, Monoclinic pyrrhotite coexists with pyrite. The phases greigite, smythite, and marcasite were not encountered.

Our results are in reasonable agreement with those obtained previously by hydrothermal synthesis methods, but they are in disagreement with some results obtained in "dry" experiments which have produced metastable phase assemblages. The phase diagram is compatible with natural pyrrhotite occurrences and in particular with those from geothermal boreholes at Broadlands, New Zealand, from which samples were recovered at known quench temperatures. On the other hand, our studies cast considerable doubt on the validity of the "pyrrhotite geothermometer" as applied to ores.

3408. Jongewaard,Peter (1800): Notes on Pyrrhotite. Informal notes and information about pyrrhotite.
[CRYSTALLIZATION; MINERALOGY; PYRRHOTITE; STRUCTURE]

Notes. Pyrrhotite group represents iron monosulfides with the NiAs structures. These include hexagonal and Monoclinic pyrrhotite and troilite (troilite considered a polymorph). In pyrrhotite, traditionally $Fe_{1-x}S$, $0 \le x \le 0.125$, the Fe-deficienc6y is attributable to Fe-vacancies in an amount dependent on T and f_{S_2} of formation. The charge is not compensated by Fe^{3+}. The Mössbauer spectra of Fe_7S_8 show no sign of Fe^{3+} even at 4.2K.

Fe-Fe interactions are significant in pyrrhotite and yield partial metallic bonding character. Fe-Fe and S-S distances are significantly shorter than the sums of the ionic radii:
> Fe-S: 2.4 - 2.6 Å
> S-S: 3.45 Å
> Fe-Fe: 2.9Å

3409   Scott, S.D.; Both, R.A. (1976): Sulphide petrology of the Broken Hill region, New South Wales, Australia. 25th Proc. Internat. Geological Congress. 140-141.

Abstract only. ...The mineralogy of the pyrrhotites is complex. Alteration has produced rims of secondary Monoclinic pyrrhotite along fractures and grain boundaries of most samples. Cores of such grains, where very iron-rich, contain exsolved lamellae of troilite in a "hexagonal" pyrrhotite host (actually a low-temperature superstructure). Some replaced grains consist entirely of secondary Monoclinic pyrrhotite, pyrite or marcasite. Compositions of the "hexagonal" phase in the cores of altered pyrrhotites lie in the narrow range 47.2 to 47.8 at % Fe and are compatible with low-temperature phase relations in the Fe-S system. Because of this pervasive retrograde alteration, most of the pyrrhotites do not provide information on a_{FeS} during prograde metamorphism. Exceptions are three samples from No. 3

Lens in the granulite facies which on textural and compositional grounds do not appear to be altered.

3021. Jones, Colin F; LeCount,Sean; Smart,Roger StC; White,Timothy J (1985): Compositional and structural alteration of pyrrhotite surfaces in solution: XPS and XRD studies. Applied Surface Science 55(1, 2 January), 65-85.
[ALTERATION; COMPOSITION; HYDROXIDE; IRON; METAL SULFIDES; PYRRHOTITE; SPECIATION; STRUCTURE; SURFACE REACTIONS; XPS; XRD]

A1.2. Pyrrhotite Oxidative Dissolution

A1.2.1.   Abiotic Pyrrhotite Dissolution

28   Nicholson,RV; Scharer,JM (1992): Laboratory investigation of the controls on the rate of pyrrhotite oxidation. Abstracts of Papers 204 (American Chemical Society, 23 August, Ed: American Chemical Society), 30-GEOC.

Abstract only. Pyrrhotite is a significant component of waste rock and tailings at several sulfide mining operations worldwide. The purpose of this study was to identify the critical parameters controlling the oxidation of pyrrhotite that would allow the modeling of reaction rates and resulting water quality in the field.

The oxidation experiments were conducted in continuous-flow fluidized bed reactors with the ability to control T, P_{O2}, initial surface area of pyrrhotite, pH and biotic activity. The zero-order abiotic rate constant at atmospheric oxygen saturation and 25C was about 5×10^{-9} mol/m^2/s or about a factor of 10 greater than that observed for the oxidation of pyrite under similar conditions. The Arrhenius activation energy was 44.7 kJ/mol, ten to forth kJ less than comparable values reported for pyrite, yet large enough to indicate independence of diffusion controls during the oxidation reaction. Preliminary results also indicate a dependence on $[H^+]^{0.5}$ with higher rates at lower pH values. The iron to sulfate molar ratio of unity observed in the experiments suggested that intermediate forms of sulfur products other than sulfate were not important at non-biologic reaction rates. Kinetic experiments to study the galvanic effect on pyrite oxidation and others with mixed *Thiobacillus* cultures are in progress.

57   Banerjee,Anil C (1976): Mechanism of oxidation and thermal decomposition of iron sulphides. Indian J. of Chemistry 14A, 845-850.

Abstract. Thermoanalytical techniques (DTA and DTG), chemical, and XRD methods have been combined to study the courses of oxidation and thermal decomposition of synthetic iron pyrites and pyrrhotite. Pyrite is oxidized directly to ferrous sulfate, and no intermediate pyrrhotite is formed. Interaction of pyrites and ferrous sulfate, and decomposition of ferrous sulfate to normal and basic ferric sulfates are the other important reactions in the oxidation. Ferrous sulfate is the major oxidation product even in pure oxygen and abundant supply of air.

346   Rivett,LS; Oko,UM (1971): Tailings disposal, generation of acidity from pyrrhotite and limestone neutralization of wastewater at Falconbridge's Onaping Mines. The Canadian Mining and Metallurgical (CIM) Bulletin, 108-113.

Abstract. The dissolution process of sulfur from pyrrhotite, accelerated in an alkaline environment, is typical of that of other metal sulfides...

1292   Jambor,JL; Blowes,DW (1991): Mineralogical study of low-sulfide, high carbonate, arsenic bearing tailings from the Delnite Minesite, Timmins Area, Ontario. In: Proc. 2nd International Conference on the Abatement of Acidic Drainage. Vol. 4. (Ed: MEND Program) Quebec Mining Association, Ottawa, 173-197.

Abstract. The Delnite mine near Timmins, ON. The gold occurred in carbonate-rich quartz veins containing 3-5 wt% sulfides consisting mainly of pyrite with lesser amounts of pyrrhotite and small amounts of arsenopyrite. Oxidation of the tailings has discolored only the uppermost 60 - 100 cm, wherein the partial alteration of sulfides indicates that pyrrhotite has been the most susceptible to attack. Electron-microprobe analyses have shown that alteration rims on sulfides are highly variable in composition; the rims contain up to 18.8 wt% As_2O_5, and up to 2.6% SiO_2, 3.9% CaO and 10.0% SO_3. X-ray powder patterns indicate that the rims consist of goethite. No crystalline arsenate mineral was detected. The acid generated by oxidation of the sulfides is buffered by reaction with the carbonate-rich components of the tailings, thereby releasing Ca to form gypsum.

1492   Kwong,YT John; Ferguson,Keith D (1990): Water chemistry and oxidation mineralogy at Mount Washington - Implication to acid generation and metal leaching. In: Acid mine drainage: Designing for closure. (Presented at GAC/MAC Joint Annual Meeting in Vancouver, May 16-18) (Eds: Gadsby,John W; Malick,James A; Day,Stephen J) BiTech Publishers Ltd., Vancouver, BC, 217-230.

Abstract. The reclamation of the abandoned minesite at Mt Washington near Courtenay, BC in 1988 and 1989 offered a unique opportunity to study the distribution of minerals in conjunction with water chemistry to elucidate the geochemical parameters controlling the acid generation and metal leaching processes. A preliminary assessment of the data indicates that the reactivity of sulfide minerals at the site is in the order of marcasite> pyrrhotite> chalcopyrite> pyrite= arsenopyrite. The oxidation of sulfides involves formation of intermediate alteration products including native sulfur. The acid generation and metal leaching occur in two stages: (i) mineral-water interactions during dry summer and winter periods giving rise to a concentrated solution in vugs and in films of water adhered to the mineral grains; and, (ii) flushing and dissolution of secondary minerals during spring freshet and fall

rains. Of the two elements of most concern at the site, arsenic is immobilized under mildly acidic and neutral conditions due to the formation of highly insoluble secondary minerals (scorodite and an unknown copper arsenate mineral) but copper is more readily transported because of increased solubility of the observed secondary minerals (malachite, chalcoalumite and brochantite) with acidity.

1716   Robl,Thomas L (1994): Iron sulfide oxidation: Impact on chemistry of leachates from natural and pyrolyzed organic-rich shales. Chap. 35. In: Environmental geochemistry of sulfide oxidation. (ACS Symposium Series 550; Symposium at 204th National Meeting of the ACS, Washington, DC, Aug. 23-28) (Eds: Alpers,Charles N; Blowes,David W) American Chemical Society, Washington, DC, 574-592.

Abstract. Retorted and raw Devonian oil shales were placed in large field lysimeters and allowed to weather for a period of 1300 days. The shales were composed of iron sulfides and silicates (quartz, illite, chlorite and kaolinite). Retorting induced the dehydroxylation and decrystallization of kaolinite and illite and converted part of the pyrite to pyrrhotite. The leachates generated in the field lysimeters were highly acidic (pH 2.5 to 3.5) with high concentrations of SO_4, Mg and Fe (1000 to 10,000 ppm); Al, Zn, Na, Ca, K (100-1000 ppm); Ni and Mn (10-100 ppm). The concentrations of most of the elements in the raw-shale leachates were a function of the rate of acid generation. The matrix of the retorted shale was more reactive than the rew shale. Elemental release was transport controlled, with the exception of Ca, which appeared to be near equilibrium with respect to gypsum.

2374   Buckley,AN; Woods,R (1984): An x-ray photoelectron spectroscopic investigation of the surface oxidation of sulfide minerals. In: Proceedings of the international symposium on electrochemistry in mineral and metal processing. (Eds: Richardson,PE; Srinivasan,S; Woods,R) The Electrochemical Society,, 286-302.

Abstract: XPS spectroscopy has been used to identify the products of surface oxidation of galena, bornite, chalcopyrite and pyrrhotite. In these studies, fresh fracture surfaces were exposed to air, immersed in air-saturated acid or alkaline solutions, or treated with dilute hydrogen peroxide. For each mineral, the initial oxidation reaction involved removal of a metal component from the surface leaving a sulfide with the same sulfur lattice as the original mineral. The metal atoms removed in the oxidation process formed a hydroxy-oxide when the mineral was exposed to air or treated with basic solutions whereas they formed soluble ions in acid media. The sulfide oxidation product resulting from the removal of metal atoms can be a metal-deficient sulfide with a composition outside the range of established, stable phases. At the higher potentials reached when hydrogen peroxide was present, elemental sulfur and sulfate were produced.

2719 Lapakko,Kim A (1994): Subaqueous disposal of mine waste: Laboratory investigation. In: Proceedings International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acidic Drainage. (Pittsburgh, PA, April 24-29, 1994) (:),, 270-278.

Abstract: Lab experiments were conducted for 120 weeks to examine the effect of three different subaqueous disposal techniques on the oxidation of sulfide minerals present in the Virginia Fm hornfels rock containing about 14 wt % pyrrhotite... The pH of drainage from the two controls... ranged from 3.7 to 4.2 during the initial 100 weeks, then decreased rapidly to 3.2 at 120 weeks. During the first 100 weeks the sulfate release averaged roughly 2.0×10^{-12} mol/g/s; concurrent with the pH decrease, rates for controls increased to 5.7 and 13×10^{-12} mol/g/s. The pyrrhotite oxidation rates for the three subaqueous disposal techniques were 1.5, 1.7, and 2.2×10^{-12} mol/g/s. With the exception of some initial rapid sulfate release from rock that was not pretreated, these rates were relatively constant over the course of the experiment. The rates observed in the lab were used, in conjunction with existing knowledge on oxygen transport, to determine rates of acid production for subaqueous disposal of similar mine waste in an open pit.

2821 Li,Jun; Zhu,Ximeng; Wadsworth,Milton E (1992): Raman spectroscopy of natural and oxidized metal sulfides. In: EPD Congress 1993. (Denver, CO, February 21-25, 1993) (Ed: Hager,JP) The Minerals, Metals & Materials Society,, 229-244.

Abstract. Several metal sulfides were examined in-situ by Raman spectroscopy before and after anodic oxidation. Results obtained for chalcocite, chalcopyrite, covellite, galena, pyrrhotite and pyrite electrodes are presented. Under appropriate conditions, sulfur was detected after a potential was applied to the mineral electrodes for a threshold period of time. For all the minerals, application of a negative potential on the oxidized mineral reduced the surface product and the sulfur peaks disappeared from the observed spectra. For those minerals containing sulfur as $S_2^=$ in the crystal lattice, polysulfides were identified as oxidation intermediates.

2836 Linge,HG (1995): Anodic oxidation of pyrrhotite in simulated CIP liquors. Minerals Engineering 8, 795-806.

Abstract: Natural pyrrhotite can be oxidized in alkali at 25 C at potentials above -0.2V.

2837 Xianjian,GUO; Chunpeng,LIU (1991): Kinetics of mineralogical phase transformation of the Ni-bearing pyrrhotite oxidized with steam at elevated temperature. Chin. J. Met. Sci. Tech. 7, 371-375.

Abstract: Oxidation kinetics and mineralogical phase transformations of Ni-bearing pyrrhotite oxidized with steam was investigated. The kinetics data were fitted in with a mathematical model of mixed control of chemical reaction at the interface and diffusion of steam through product layer. The equations of specific rate constant and effective diffusion coefficient functional to the temperature derived from experimental data are:

$$logk = (-10190/T) + 7.099$$
$$logD_e = (-2725/T) + 3.833$$

from which the E_A of both the chemical reaction and the diffusion calculated are 194.8 kJ/mol and 52.0 kJ/mol, respectively.

2892 Yazawa, A; Eguchi, M. (1962): Study on the dissolution rate of pyrrhotite in aqueous sulfuric acid. IN JAPANESE?

Abstract. In the absence of oxidizing conditions, the rate of dissolution of pyrrhotite with aqueous sulfuric acid was studied in the concentration rage 0.25 to 1 M and in the temperature range of 30 to 80C. The reaction products were hydrogen sulfide and dissolved iron, and the progress of the reaction was followed by an analysis of dissolved iron content in the solution.

Under the condition of vigorous agitation to eliminate diffusion control of the reaction, the following results were obtained: i) The rate of dissolution with the lapse of reaction time showed the 2nd order relation to the concentration of suspended pyrrhotite in the solution. ii) The initial rate of dissolution was directly proportional to the total surface area of suspended pyrrhotite. iii) The rate of dissolution was proportional to the sulfuric acid concentration. iv) The activation energy of the reaction was 13.2 kcal/mol. Overall dissolution rate may be expressed by the following:

$$-d[FeS]/dt = Z\, e^{-EA/RT}\, A_{FeS}\, [H_2SO_4]$$

2895 Bugajski, J.; Gamsjager, H. (1982) The kinetics of the dissolution of monoclinic pyrrhotite in aqueous acidic solutions. Monatshefte fur Chemie 113, 1087-1092.

Abstract. Using the rotating disc method, the rates of dissolution of natural monoclinic pyrrhotite, $FeS_{1.14}$, in oxygen-free aqueous solutions S([H^{+}] = 0.1, [Na] = 0.9, [ClO_4] = 1.0 mol/kg) were determined. In the T range of 40 - 90 C. the

dissolution reaction occurs under kinetic control; the activation energy being 14 +/- 1 kcal/mol (59 +/- 5 kJ/mol).

2897   Van Weert, G.; Mah, K.; Piret, N.L. (1974) Hydrochloric acid leaching of nickeliferous pyrrhotites from the Sudbury District. CIM Bulletin, January.

Abstract. Results of experimental work on HCl leaching of nickeliferous pyrrhotites from the Sudbury district are described. Leach T (60-90C), Cl (6-8 N), excess acid (15-55%) and residence time (<3 hrs) were all chosen to be compatible with industrial practice. Iron dissolutions varied from 87-98%, and H_2S yield was, at maximum, 83% of the sulfur in the feed to the leach. The effects of acid addition rate and leach temperature on rate and degree of iron nickel and impurity dissolution are described. The formation of nickel-bearing marcasite at 90C is reported. Leach incubation is discussed and a mechanism proposed.

3020. Elberling,B; Nicholson,RV; Reardon,EJ; Tibbs,P (1994): Evaluation of sulphide oxidation rates: A laboratory study comparing oxygen fluxes and rates of oxidation product release. Canadian Geotechnical Journal 31(3, June), 375-383.
       [COLUMN TEST; COVER; DISPOSAL; LABORATORY; METAL SULFIDES; MITIGATION; MODEL; OXIDATION; OXYGEN; PYRRHOTITE; REACTION RATES; SOURCE CONTROL; SUBAQUEOUS; TAILINGS]

3404   Mizuta, T.; Scott, S.D. (1997) Kinetics of iron depletion near pyrrhotite and chalcopyrite inclusions in sphalerite: The sphalerite speedometer. Econ. Geol. 92, 772-783.

Abstract.   The textures and chemical compositions of sphalerite containing chalcopyrite and pyrrhotite inclusions from some skarns, together with experimental data on diffusivity, have permitted rates of exsolution and cooling histories of the skarns to be calculated. These calculations are based upon Fe depletion profiles obtained by electron microprobe transverses across those portions of sphalerite grains that are adjacent to chalcopyrite lamellae and pyrrhotite laths. The lamellae and laths occur within and along grain boundaries and polysynthetic twin planes in the host sphalerite. In addition, the samples contain 2 to 10 um chalcopyrite blebs that do not have the appearance of chalcopyrite disease textures.

Two types of iron depletion profiles are observed in iron-rich sphalerite near sulfide inclusions; one type indicates a slight decrease in the Fe contents adjacent to chalcopyrite blebs, the other exhibits a larger Fe depletion (e.g., 3-6 mole %FeS over 70 um) near chalcopyrite lamellae and pyrrhotite laths.

Experimentally determined tracer diffusion rates of ^{59}Fe in sphalerite ($D_{Fe} = 5.6 \times 10^{-4}$ exp[-38 +/- 2 kcal/mol/RT], with a pyrrhotite + pyrite buffer) have been applied as

a test to determine if Fe depletion can be explained by the simple cooling histories of the skarns. If all the sulfide inclusions are assumed to have been originally dissolved in Cu-bearing sphalerite at a higher T, the duration for isothermal precipitation of a chalcopyrite bleb from a sphalerite sphere of 50 um radius is calculated to be ca. 870 m.y. at 400C, the estimated T at which such a process may have taken place. Because of the slow Fe diffusivity in sphalerite, this time is unreasonably long, exceeding the geologic age (Mesozoic) of the deposits under consideration, so exsolution of chalcopyrite blebs from homogenous sphalerite is unlikely. In contrast, Fe-rich sphalerite attending the exsolution of pyrrhotite laths in response to decreasing temperature and rising sulfur fugacity. The measured profiles near pyrrhotite laths have been simulated by finite difference approximations to Fick's diffusion equation. For an exsolution process starting at 350C and with a cooling rate of 0.5C/1000yr, the observed Fe depletion profiles would have been frozen in within 210,000 yr and with a closure T estimated to be 245C.

3405 Domvile, S.; Li, M.; Sollner, D.; Nesbitt, W. (1998?) Investigation of weathering behavior of mine tailings under laboratory-simulated disposal conditions. Draft.

Abstract. 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 analysis conducted on the solid residues. Samples of pure pyrrhotite and arsenopyrite were analyzed using XPS and 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, ARD is initiated when rock is blasted, sulfide sulfur is oxidized to di and poly sulfides prior to forming sulfates, and significantly more sulfate is produced upon exposure to aqueous environments than to air.

3769. Lapakko,Kim A (1994): Comparison of Duluth Complex rock dissolution in the laboratory and field. In: International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acidic Drainage. Vol. 1. (Pittsburgh, PA, April 24-29, 1994) (:),, 419-428.
    [INCOMPLETE; AMD; CASE STUDY; DULUTH COMPLEX; FIELD; LABORATORY; MINE WASTE CHARACTERIZATION; MINE WASTE MANAGEMENT; MINNESOTA; OXIDATION; PYRRHOTITE; REACTION RATES]

3770. Lapakko,Kim A; Wessels,Jennifer N (1995): Release of acid from hydrothermal quartz-carbonate hosted gold-mine tailings. In: Sudbury '95 Conference on Mining and the Environment. Vol. 1. (Sudbury, Ontario, May 28-June 1, 1995) (:),, .

[INCOMPLETE; ACIDIC; AMD; GOLD; KINETICS; MINE WASTE CHARACTERIZATION; MINE WASTE MANAGEMENT; OXIDATION; PREDICTION; PYRITE; PYRRHOTITE; REACTION RATES; TAILINGS]

Veglio, F.; Belochini, F.; Nardini, A.; Toro, L. (2000) Bioleaching of a pyrrhotite ore by a sulfooxidans strain: kinetic analysis. Chem. Eng. Sci., 55, 783-795.

Abstract: A kinetic study of the batch leaching of a pyrrhotite ore by a sulfooxidans strain is reported in this work. A mathematical model consistent with experimental data is developed, which takes into account both direct and indirect mechanism. The development has been performed from a separate study of microorganisms' adsorption on the solid surface and of chemical leaching of pyrrhotite by ferric iron. The representative equations of these phenomena (Langmuir equation and a kinetic model with variable activation energy, respectively) have been combined with material balances of total iron, ferric iron and biomass. The final model consists of a system of three ordinary differential equations, where he independent variable is time and the dependent variables are total iron, ferric iron and adsorbed bacteria, and the reaction rate constant of ferrous iron oxidation, k. These parameters were estimated by curve fitting using experimental data and estimated values are in agreement with values found in the literature.

A1.2.2.   Biotic Pyrrhotite Dissolution

812   Lasse,Ahonen; Hiltunen,Paula; Tuovinen,Olli H (1986): The role of pyrrhotite and pyrite in the bacterial leaching of chalcopyrite ores. Chap. 1. In: Fundamental and Applied Biohydrometallurgy: Proc. 6th International Symposium on Biohydrometallurgy in Vancouver, BC, Canada, August 21-24, 1985. (Eds: Lawrence,Richard W; Branion,Richard MR; Ebner,Hans G) Elsevier, Amsterdam-Oxford-New York-Tokyo, 13-22.

813   Miller,PC; Huberts,R; Livesey-Goldblatt,E (1986): The semicontinuous bacterial agitated leaching of nickel sulphide material. Chap. 1. In: Fundamental and Applied Biohydrometallurgy. (Proc. 6th International Symposium on Biohydrometallurgy in Vancouver, BC, Canada, August 21-24, 1985) (Eds: Lawrence,Richard W; Branion,Richard MR; Ebner,Hans G) Elsevier, Amsterdam, 23-42.

988   Ahonen,Lasse; Hiltunen,Paula; Tuovinen,Olli H (1986): The role of pyrrhotite and pyrite in the bacterial leaching of chalcopyrite ores. In: Fundamental and Applied Biohydrometallurgy. (Proc. 6th International Symposium on Biohydrometallurgy, Vancouver, BC, Canada, August 21-24, 1985) (Eds: Lawrence,Richard W; Branion,Richard MR; Ebner,Hans G) Elsevier, Amsterdam, 13-22.

Abstract: Comparison of the leaching behavior of a pyrite-chalcopyrite sample and a pyrrhotite-chalcopyrite sample revealed considerable differences due to the different mineralogical composition. Bacterial leaching rate and reaction stoichiometry of purified mineral fractions were studied and compared with the copper ore leaching data. Copper dissolution from pyrite-chalcopyrite was faster than that from pyrrhotite-chalcopyrite or from pure chalcopyrite, suggesting a galvanic coupling effect in the pyrite-chalcopyrite mixture. During the oxidation of pyrrhotite, elemental sulfur was observed as a reaction intermediate forming a rim around pyrrhotite particles. Elemental sulfur was not detected in the oxidation of pyrite.

1122   Ahonen,Lasse; Tuovinen,Olli H (1991): Temperature effects on bacterial leaching of sulfide minerals in shake flask experiments. Applied and Environmental Microbiology 57(1, January), 138-145.

Abstract. The microbiological leaching of a sulfide ore samples was investigated in shake flask experiments. The ore sample contained pyrite, pyrrhotite, pentlandite, sphalerite, and chalcopyrite as the main sulfide minerals. The tests were performed at eight different temps (4-37C). The primary data were used for rate constant calculations, based on kinetic equations underlying two simplified models of leaching, i.e., a shrinking particle model and a shrinking core model. The rate constants thus derived were further used for the calculation of activation energy values for some of the sulfide minerals present in the ore sample. The chalcopyrite leaching rates were strongly influenced by the interaction of T, pH, and Eh. Pyrite and Sphalerite leaching could be explained with the shrinking particle model. The data on pyrrhotite leaching displayed good fit with the shrinking core model. Activation energies calculated from the rate of constants suggested that the rate-limiting steps were different for the sulfide minerals examined; they could be attributed to a chemical or biochemical reaction rather than to diffusion control.

1688 Ahonen,Lasse; Tuovinen,Olli H (1994): Solid-phase alteration and iron transformation in column bioleaching of a complex sulfide ore. Chap. 7. In: Environmental geochemistry of sulfide oxidation. (ACS Symposium Series 550; Symposium at 204th National Meeting of the ACS, Washington, DC, Aug. 23-28) (Eds: Alpers,Charles N; Blowes,David W) American Chemical Society, Washington, DC, 79-89.

Abstract. The objective of the work was to characterize solid-phase changes and Fe(III) precipitation during biological leaching of a sulfide ore which contained chalcopyrite, pentlandite, pyrite, pyrrhotite, and sphalerite. The leaching experiments were carried out using bench-scale column reactors which were inoculated with acidophilic Fe and S-oxidizing thiobacilli. Experimental factors included inoculation, pH, T, flood and trickle leaching, aeration, particle size, and mineralogical composition. Secondary solid phases, covellite, jarosites, and elemental S, were detected in biologically active columns. Dissolved ferric iron data were pooled from all experiments and compared with solubility curves calculated for jarosites and ferric hydroxides. The data suggested that ferric-iron solubility was controlled by jarosites.

1689 Bhatti,Tariq M; Bigham,Jerry M; Vuorinen,Antti; Tuovinen,Olli H (1994): Alteration of mica and feldspar associated with the microbiological oxidation of pyrrhotite and pyrite. Chap. 8. In: Environmental geochemistry of sulfide oxidation. (ACS Symposium Series 550; Symposium at 204th National Meeting of the ACS, Washington, DC, Aug. 23-28) (Eds: Alpers,Charles N; Blowes,David W) American Chemical Society, Washington, DC, 90-105.

Abstract. This work examines mineralogical changes during the bacterial leaching of a black-schist ore material. A mixed culture of acidophilic iron and sulfur oxidizing thiobacilli was used in shake flasks containing acid media and finely ground black schist. The main sulfide phases were pyrrhotite and pyrite, with lesser amounts of sphalerite, pentlandite, and chalcopyrite. The solubilization of Cu, Ni, and Zn was enhanced in inoculated suspensions. The major Si-containing phases were quartz, mica (phlogopite), and feldspars (primarily anorthite, and microcline). Pyrrhotite was oxidized faster than pyrite and was associated with elemental S accumulation. The accumulation was transient in inoculated systems because of eventual bacterial oxidation of elemental S. Formation of K-bearing jarosite, resulting from the bacterial oxidation of Fe sulfides, was coupled with mica alteration to vermiculite. Chemical dissolution also occurred parallel with structural alteration of the mica phase. The results suggested that jarosite was a sink for K released during mica weathering. Jarosite and vermiculite were not detected under comparable abiotic leaching conditions. Gypsum was produced after 100 days, presumably because of the release of Ca from anorthite.

2484   Ahonen,Lasse; Tuovinen,Olli H (1992): Bacterial oxidation of sulfide minerals in column leaching experiments at suboptimal temperatures. Applied and Environmental Microbiology 58, 600-606.

Abstract. The purpose of the work was to quantitatively characterize temperature effects on the bacterial leaching of sulfide ore material containing several sulfide minerals. The leaching was tested at 8 different T in the range of 4 to 37C. The experimental technique was based on column leaching of a coarsely ground (particle diameter, 0.59 to 5 mm) ore sample. The experimental data were used for kinetic analysis of chalcopyrite, sphalerite, and pyrrhotite oxidation. Chalcopyrite yielded the highest (73 kJ/mol) and pyrrhotite yielded the lowest (25 kJ/mol) activation energies.   Especially with pyrrhotite, diffusion contributed to rate limitation. Arrhenius plots were also linear for the reciprocals of lag periods and for increases of redox potentials (dmV/dt). Mass balance analysis based on total S in leach residue was in agreement with the highest rate of leaching at 37 and 28 C. The presence of elemental S in leach residues was attributed to pyrrhotite oxidation.

Blowes, D.W.; Jambor, J.L. (1990) The pore-water geochemistry and the mineralogy of the vadose zone of sulfide tailings, Waite Amulet, Quebec, Canada. Appl. Geochem., 5, 327-346.

A1.3. Pyrrhotite Oxidation Products

59   Hamilton,IC; Woods,R (1981): An investigation of surface oxidation of pyrite and pyrrhotite by linear potential sweep voltammetry. J. Electroanal. Chem. 118, 327-343.

Abstract. The products of surface oxidation of pyrite and pyrrhotite have been determined from analysis of linear potential sweep voltammograms. Pyrite oxidizes to both sulfur and sulfate. The formation of sulfur is restricted to the order of a monolayer at pH 9.2 and 13, but significant yield occurs at pH 4.6. The proportion of sulfate formed increases rapidly with increase in potential. Sulfur is the major product of pyrrhotite oxidation at pH 4.6, 9.2, and 13. Sulfate is also formed in significant quantities, particularly in the alkaline solutions. Oxidation of pyrrhotite is strongly inhibited by the surface ferric oxide produced.

62   Nickel,EH; Ross,JR; Thornber,MR (1974): The supergene alteration of pyrrhotite pentlandite ore at Kambalda, Western Australia. Economic Geology 69, 93-107.

Abstract. The mineralogical and chemical changes that occur as a result of the supergene alteration of massive pyrrhotite-pentlandite ore at Kambalda are described in detail. In the lowermost Transition Zone, pentlandite is progressively replaced by violarite, accompanied by the release of iron and nickel. This nickel reacts with the pyrrhotite, converting some of it to a second type of violarite. When the pentlandite has been completely replaced, the pyrrhotite is dissolved and the iron and sulfur, together with some Mi and sulfur species derived from the Oxide Zone, are redeposited as nickel-rich pyrite and marcasite. The new assemblage of violarite-pyrite/marcasite remains stable throughout a considerable part of the supergene profile, here called the Violarite-Pyrite Zone. The violarite becomes richer in Ni toward the top of this zone, presumably through exchange with the Ni-rich solutions migrating downward from the overlying Oxide Zone. The base of the Oxide Zone coincides approximately with the water table and marks the point where atmospheric oxygen has access to the sulfides. Here violarite appears to be unstable and is replaced by nickel carbonates and iron oxides over a vertical interval of one to two meters. Pyrite and marcasite are oxidized to goethite, although relict pyrite and marcasite may persist upwards, in decreasing abundance, through much of the Oxide Zone.

The supergene process can be explained in terms of an electrochemical model in which the driving force is the gradient in oxidation potential resulting from access of atmospheric oxygen to the suboutcrop of massive sulfides. Cathodic reduction of oxygen at the water table results in anodic oxidation of sulfides at depth and upward conduction of electrons. Above the water table, where the sulfides are no longer protected by cathodic reactions, they decompose, releasing nickel and ionic sulfur

species that are transported downwards by aqueous solutions and redeposited, resulting in secondary enrichment below.

64   Steger,HF; Desjardins,LE (1978): Oxidation of sulphide minerals, 4. Pyrite, chalcopyrite and pyrrhotite. Chem. Geol. 23, 225-237.

Abstract. Samples of pyrite, chalcopyrite and pyrrhotite were subjected to 52C and 68% relative humidity in air for periods of up to four weeks. The resultant oxidation products were analyzed for metal and the various possible surface-bearing products such as sulfate, etc. It was concluded that pyrite and chalcopyrite are initially oxidized to ferrous or a combination of ferrous and cuprous thiosulfates which undergo further oxidation to ferric or ferric and cupric sulfates. In addition to this thiosulfate-sulfate oxidation, pyrrhotite undergoes a much more rapid oxidation to goethite and elemental S.

194   Steger,HF (1977): Oxidation of sulphide minerals--I: Determination of ferrous and ferric iron in samples of pyrrhotite, pyrite and chalcopyrite. Talanta 24, 251-254.

Abstract. A method has been developed for determining small amounts of both ferrous and ferric iron in oxidized samples of pyrrhotite, pyrite and chalcopyrite. The oxidized iron is selectively dissolved in 10M phosphoric acid under reflux and can be determined with the accuracy generally accepted in chemical phase analysis.

198   Steger,HF (1979): Oxidation of sulphide minerals--VI: Ferrous and ferric iron in the water-soluble oxidation products of iron sulphide minerals. Talanta 26, 455-460.

Abstract. A pseudo-kinetic method has been developed for determining the ferrous and ferric iron in the water-soluble oxidation products of pyrrhotite, pyrite and chalcopyrite, and ores and concentrates containing them. Two determinations are required for each material. In one, the total iron is determined with 1,10-phenathroline after reduction to Fe(II). In the other, the reduction of Fe(III) is retarded by complexation with fluoride. The difference in the amount of ferrous phananthranoline complex produced in these two determinations is a function of the original Fe(III) concentration and of time.

199   Steger,HF (1982): Oxidation of Sulfide Minerals--VII: Effect of temperature and relative humidity on the oxidation of pyrrhotite. Chem. Geol. 35, 281-295.

Abstract. Samples of pyrrhotite have been oxidized at 50, 43, 35, and 28C with 62% relative humidity; and at 50C with 75, 55, 50, 37% RH, for periods up to 7 days. The results indicate that the oxidation proceeds by a sequence of reactions to give $FeSO_4$, $Fe(OH)(SO_4)*xH_2O$ and ultimately ferric oxide and elemental sulfur. The formation of ferric oxide obeys the parabolic rate law at all values of temperature and RH. The reflectance spectral study of the oxidize samples of pyrrhotite indicates that an undefined ferrous-ferric sulfate is formed as an intermediate in the oxidation of $FeSO_4$ to $Fe(OH)(SO_4)*xH_2O$.

202   Steger,HF (1982): The rejection of RU-1 due to ambient oxidation. Geostandards Newsletter 6(2), 249-255.

The history of a zinc-copper sulfide ore, RU-1, is presented to show quantitatively the serious effects of ambient oxidation on unprotected samples that led to its rejection for continued use as a reference material. It is shown that pyrrhotite, sphalerite and chalcopyrite are much more susceptible to oxidation than is pyrite, the major constituent. The preparation of another sample, RU-2, from the same ore body verifies that oxidation also occurs to an appreciable extent during the preparation stages.

229   Reimers,GW; Hjelmstad,KE (1987): Analysis of the oxidation of chalcopyrite, chalcocite, galena, pyrrhotite, marcasite, and arsenopyrite. Bureau of Mines: Report of Investigations 9118, 1-16.

Abstract. Conditions in the underground mine environment can cause self-heating of sulfide ores as a result of exothermic oxidation reactions, which may result in mine fires. This USBOM report describes thermal analyses of finely ground chalcopyrite, chalcocite, galena, pyrrhotite, marcasite, and arsenopyrite, to characterize their responses under oxidizing conditions. TGA and DTA were used, in the temperature range 100 to 500C.

.   ..Moisture in the oxidizing atmosphere lowered the ignition point of marcasite and arsenopyrite but not that of pyrrhotite. All the sulfides exhibited exothermic behavior at T< ignition point.

347   Ingraham,TR; Parsons,HW; Cabri,LJ (1972): Leaching of pyrrhotite with hydrochloric acid. Canadian Metallurgical Quarterly 11(2), 407-411.

Abstract.   When nonstoichiometric pyrrhotite is leached under nonoxidizing conditions in warm aqueous solutions containing HCl, both H_2S and S are formed. The amount of sulfur is proportional to the nonstoichiometry of the pyrrhotite. The leaching reaction is rapid but, when minimum conditions of acidity and/or T are not met, the sulfur coating becomes protective and the reaction ceases. When the reaction is begun rapidly, all of the acid or all of the pyrrhotite will be consumed, depending upon which is in excess.

2339   Ahonen,Lasse; Tuovinen,Olli H (1989): Effect of temperature on the microbiological leaching of sulfide ore material in percolates containing chalcopyrite, pentlandite, sphalerite, and pyrrhotite as main minerals. Biotechnology Letters 11(5), 331-336.

Abstract. Microbiological leaching of complex sulfide ore material was evaluated in percolators at 4, 10, and 20C. The onset of leaching was associated with an increase in redox potential and an decrease in pH. Copper from chalcopyrite was leached at a slow rate at each test temperature compared with the leaching of zinc from sphalerite and nickel from pentlandite.

2468   Lapakko,K; Wessels,JN (1994): Release of acid and trace metals from quartz-carbonate hosted gold mine tailings. In: Institute on Lake Superior Geology Proceedings, 40th Annual Meeting. Vol. 40, part 1. (Eds: Bornhorst,TJ; McDowell,S Douglas) Michigan Technological University, Houghton, MI, 29-30.

Abstract. nonferrous experiments.

2716   Ahmed,Syed M (1995): Chemistry of pyrrhotite hardpan formation. In: Sudbury '95, Conference on Mining and the Environment, Sudbury, Ontario, May 28th - June 1st. 2nd ed. (:) Springer-Verlag, New York, 171-180.

Abstract. Hardpans formed naturally in pyrrhotite-rich tailings at the mine disposal sites, normally consist of FeS grains cemented in lepidocrocite and goethite structures of iron oxyhydrates. It was possible to make high density, pyrrhotite hardpans with the same structure on a small scale, by electrochemical treatment of pyrrhotite rich tailings. Attempts to make such structures surface chemically, resulted in two distinct types of hardpans depending on the experimental conditions. A reddish brown variety was formed as an outer layer in the fully oxidizing zone and a gray colored variety formed in a reduced state with ferrous iron, in the non

oxidizing zone. Several other forms of hardpans with intermediate oxidation states were also identified. The gray and the fully oxidized forms of hardpans, if dense, are stable in air. All other hardpans with FeS partly exposed, get readily hydrolyzed in contact with water, producing iron hydroxides and acid. The electrochemically formed hardpan, however, was an exception in stability. Pyrite hardpans are rare in occurrence and different in structure. The chemistry of hardpan formation and structures have been discussed and the possibility of using such formations in the prevention of sulfide oxidation and the acid drainage has been examined.

2887   Buckley,AN; Woods,R (1985): X-ray photoelectron spectroscopy of oxidized pyrrhotite surfaces: Exposure to aqueous solutions. Applications of Surface Science 20(4, Feb-Mar), 472-480.
[AMMONIA; AQUEOUS CHEMISTRY; LABORATORY; METAL SULFIDES; OXIDATION; PEROXIDE; PYRRHOTITE; SPECTROSCOPY; SURFACE CHARACTERISTICS; SURFACE REACTIONS; XPS]

2888   Buckley,AN; Woods,R (1985): X-ray photoelectron spectroscopy of oxidized pyrrhotite surfaces: I. Exposure to air. Applications of Surface Science 22/23(May), 280-287.
[IRON; LABORATORY; LOW TEMP; METAL SULFIDES; OXIDATION; OXIDES; PYRRHOTITE; SPECTROSCOPY; SURFACE CHARACTERISTICS; SURFACE REACTIONS; XPS]

2891   Hodgson, M.; Agar, G.E. (19??): An electrochemical investigation into the natural flotability of pyrrhotite.

Abstract.   The electrochemical reactions of the pyrrhotite surface have been investigated using single mineral crystal and particulate electrode techniques. using CV procedures, a series of reactions was postulated to describe the oxidation reactions which progressively take place on the pyrrhotite surface. Major products were found to be $Fe(OH)_3$, and S.

A1.4. Pyrrhotite Oxidation Mechanism

987 Nicholson,Ronald V; Scharer,Jeno M (1994): Laboratory studies of pyrrhotite oxidation kinetics. Chap. 2. In: Environmental geochemistry of sulfide oxidation. (ACS Symposium Series 550; Symposium at 204th National Meeting of the ACS, Washington, DC, Aug. 23-28) (Eds: Alpers,Charles N; Blowes,David W) American Chemical Society, Washington, DC, 14-30.

Abstract: A pneumatically mixed flow-through reactor was used to study the oxidation kinetics of pyrite and pyrrhotite. Experiments were conducted at pH values of 2, 3, 4, and 6 with temperatures controlled at 10, 22, and 33 C. A grain-size fraction with an average particle diameter of 105 microns was used in all experiments.

The rates of pyrrhotite oxidation ranged from 6 to 14 x 10^{-9} molm^{-2}s^{-1} at 22 C for solution pH values of 2 to 6. Although the rates were not strongly pH-dependent, minimum values were observed for pH values of 3-4. Experimental activation energies were approximately 50 kJ/mol at pH values of 2 and 4, but in excess of 100 kJ/mol at pH 6. The molar ratio of SO_4/Fe in the reactor effluent varied from 0.93 at pH 2 to 0.76 at pH 6, suggesting a preferential retention of sulfur on the pyrrhotite solids with increasing pH. The rates of pyrrhotite oxidation at atmospheric concentrations of oxygen and at 22 C were on the order of 100 x those measured for pyrite. The iron deficiency in pyrrhotite is considered the major factor for these high rates.

2334 Pratt,AR; Muir,IL; Nesbitt,HW (1994): X-ray photoelectron and Auger electron spectroscopic studies of pyrrhotite and mechanism of air oxidation. Geochim. Cosmochim. Acta 58(2), 827-841.

Abstract: Pyrrhotite fractured under high vacuum and reacted with air for 6.5 and 50 hrs was analyzed using XPS and AES. XPS iron data from fresh surfaces indicate 32% Fe(III) and 68% Fe(II), both bonded to sulfur. The result agrees closely with stoichiometry which suggests 29% Fe(III) in the pyrrhotite studied. This is the first spectroscopic evidence to indicate Fe(III) in pyrrhotite. Sulfur is present primarily as monosulfide, with minor amounts of disuilfide and polysulfide.

XPS examination of 6.5 hr air-oxidized surfaces indicates 58% Fe(III) and 42% Fe(II). Fe(III) is bonded to oxygen and most Fe(II) remains bonded to sulfur. XPS iron and oxygen data suggest a Fe(III) oxyhydroxide to be the species forming. Sulfur spectra demonstrate a rage of oxidation states from S^{2-} to S^{6+}.

AES compositional depth profiles of air-oxidized surfaces display three compositional zones. After 50 hrs of air oxidation the outermost layer is less than 10A, oxygen-rich, and sulfur depleted. Immediately below the O-rich layer exists and Fe-deficient, S-rich layer that displays a continuous, gradual decrease in S/Fe from the O-rich zone to that of the unaltered pyrrhotite.

Compositional zones develop by electron and iron migration towards the oxidized surface. Molecular oxygen initially taken onto the surface is reduced to O^{2-} probably by electron transfer from the pyrrhotite interior, and is facilitated by rapid electron exchange between Fe(III) and Fe(II) of the bulk solid. Vacancies inherent to nonstoichiometric pyrrhotite probably promote diffusion of iron to the surface resulting in the formation of iron oxyhydroxide species.

2788   Janzen,Michael Paul (1996): Role of ferric iron, trace metal content, and crystal structure on pyrrhotite oxidation. master Thesis, University of Waterloo, Waterloo, Ontario. 175 p.

Partial Abstract: A lab study on the dissolution of pyrrhotite was conducted to quantify differences in oxidation behaviors among 12 pyrrhotite samples of different crystalline structure and trace metal content, and acquire kinetic data to determine reaction mechanisms. Three processes involving pyrrhotite dissolution were investigated; non-oxidative dissolution, oxidation by DO, and oxidation by Fe(III). The mean dissolution rates were 5×10^{-10}, 4×10^{-9}, and 3.5×10^{-8} moles-Po/m^2/s, respectively.

2901   Orlova,TA; Stupnikov,VM; Krestan,AL (1988): Mechanism of oxidative dissolution of sulfides. Zhurnal Prikladnoi Khimii 61(10), 2172-2177.
        [DISSOLUTION; ELECTROCHEMISTRY; LABORATORY; LEACHING; MECHANISM; METAL SULFIDES; MINERAL DISSOLUTION; MINERALOGY; OXIDATION; PRESSURE; PYRRHOTITE; SULFIDE; SURFACE REACTIONS]

2909   Pratt, A.R.; Nesbitt, H.W.; Muir, I.J. (1994) Generation of acids from mine waste: Oxidative leaching of pyrrhotite in dilute H_2SO_4 solutions at pH 3.0. Geochim. Cosmochim. Acta 58, 23, 5147-5159.

Abstract. Pyrrhotite (Fe_7S_8) grains 3x3x6 mm were reacted in solutions of H_2SO_4 (pH 3.0) for eight hours and analyzed using SEM, AES and XPS. SEM images of reacted surfaces display an array of reaction textures, which are interpreted to represent a five-stage paragenetic alteration sequence. Leached pyrrhotite surfaces are initially featureless. Surfaces leached more extensively develop a mottled felty

texture. Subsequent drying of reacted surfaces causes dehydration, producing cracked, tiled surfaces. Prolonged drying intensifies the effects of desiccation, producing rubbly texture. The rubble is readily spalled, exposing smooth underlayers.

AES and XPS data collected for the first four textured surfaces indicate primarily Fe-oxyhydroxide reaction products. AES depth profiles show that S varies antipathetically with oxygen. AES analysis of the last textured surface detect only Fe and S, with S significantly enriched over Fe. XPS and modeled AES data show the last textured regions are mainly ferric iron bonded to disulfide and or polysulfide species.

The accumulation of S in the underlayer is accomplished by preferential migration of Fe to the overlying oxyhydroxide layer to the pyrrhotite surface, thus, promoting spallation.

Spalling of Fe(III) oxyhydroxides is promoted in waste rock dumps and tailings situated above the water table by periodic wetting, drying, and desiccation of the oxyhydroxide layer. These circumstances may, in turn, lead to high concentrations of suspended Fe-oxyhydroxide in tailings ponds during flooding and in ponds where there are dramatic seasonal overturns of lake or pond water. Exposure by spalling of S-rich sublayers to aqueous solutions is an effective means for producing sulfuric acid-rich mine waste runoff, and of producing periodic flushes of sulfuric acid-rich drainage waters.

3402 Pratt, A.R.; Nesbitt, H.W. (1997) Pyrrhotite leaching in acid mixtures of HCl and H_2SO_4. Am. J. of Science, 297, 807-828.

Abstract: Pyrrhotite (Fe_7S_8) was leached in air-equilibrated pH 3.0 HCl H_2SO_4 acid mixtures with Cl: SO_4 ratios of 1:0, 3:1, 1:1, 1:3 and 0:1. AES depth profiles and XPS analyses of reacted surfaces were consistent with several compositional layers including a surface coating of Fe(III) oxyhydroxide, an underlying zone of sulfur enrichment which decreased in sulfur content with depth, and finally unaltered pyrrhotite. Leaching experiments showed that iron concentrations increased linearly in solution as a function of the square-root of time. This relationship was indicative of a diffusion-limited reaction. Sulfate concentrations increased rapidly to 1.0 ppm within the first few minutes of reaction, then remained unchanged over the duration of the experiment. These results demonstrate that sulfate release was a rapid one time event in the earliest stages of pyrrhotite dissolution.

Pyrrhotite leaching in acid solutions proceeded via the diffusion of iron to the mineral surface. With the removal of iron from the pyrrhotite structure, polysulfide replaced

monosulfide as the dominant sulfur species. Fe(III) oxyhydroxide was determined to be the product of reaction between oxygen and iron species at the surface. Pyrrhotite surfaces reacted in solutions containing the greater sulfate concentrations were found to have the thickest Fe(III) oxyhydroxide layers. In contrast, surfaces reacted with solutions containing appreciable chloride developed sulfur-rich near surfaces with an overlying thin veneer of Fe(III) oxyhydroxide. Results of the study suggest that chloride inhibited the formation of surface Fe(III) oxyhydroxides and promoted the development of sulfur-rich sublayers. $Cl:SO_4$ ratios in solution did not appear to have any significant effect on leach rates of iron.

3048 Buckley,AN; Hamilton,IC; Woods,R (1988): Studies of the surface oxidation of pyrite and pyrrhotite using x-ray photoelectron spectroscopy and linear potential sweep voltammetry. In: Proceedings International Symposium on Electrochemistry in Mineral and Metal Processing. 2nd ed. (:),, 234-246.
       [INCOMPLETE; METAL SULFIDES; OXIDATION; PYRITE; PYRRHOTITE; SURFACE CHARACTERISTICS; SURFACE REACTIONS; VOLTAMMETRY; XPS]

3383 Knipe,SW; Mycroft,JR; Pratt,AR; Nesbitt,HW; Bancroft,GM (1995): X-ray photoelectron spectroscopy study of water adsorption on iron sulfide minerals. Geochim. Cosmochim. Acta 59, 1079-1090.
       [ADSORPTION; AQUEOUS CHEMISTRY; HYDROXYL; IRON; OXIDATION; OXYGEN; PYRITE; PYRRHOTITE; SPECTROSCOPY; SULFIDE; SURFACE REACTIONS; XPS]

3403 Yakhontova,LK (1983): New data on natural oxidation of pyrrhotite. Moscow University Geology Bulletin 38, 41-44.
       [OXIDATION; PYRRHOTITE]

3530 Blowes,DW; Jambor,JL (Eds.) (1994): Short Course Handbook on Environmental Geochemistry of Sulfide Mine-Wastes. Vol. 22. (Waterloo, Ontario, May 1994) (Short Course Handbook.) Mineralogic Association of Canada, Ontario, Canada. 438 pages.
       [ADSORPTION; AMD; ARSENOPYRITE; BACTERIA; BIOCHEMISTRY; BIOLOGICAL; BORNITE; CHALCOPYRITE; CONTAMINATION; ENVIRONMENT; GALENA; GEOCHEMISTRY; GROUNDWATER; HYDROLOGY; MECHANISM; MINE WASTE; MINE WASTE CHARACTERIZATION; MINE WASTE MANAGEMENT; MINERALOGY; MODEL; MONITORING; OXIDATION; PENTLANDITE; PROCEEDINGS; PYRITE; PYRRHOTITE; REACTION RATES; SATURATION; SPHALERITE; SULFIDE; SURFACE REACTIONS; TAILINGS; TEMPERATURE; TRACE METAL CHEMISTRY; TRANSPORT]

3534   Nicholson,Ronald V (1994): Iron-sulfide oxidation mechanisms: Laboratory studies. Chap. 6. In: Short Course Handbook on Environmental Geochemistry of Sulfide Mine-Wastes. Vol. 22. (Waterloo, Ontario, May 1994) (Eds: Jambor,JL; Blowes,DW) (Short Course Handbook.) Mineralogical Society of Canada, Ontario, Canada, 163-183.
        [ENVIRONMENT; IRON; LABORATORY; MECHANISM; METAL SULFIDES; OXIDATION; PREDICTION; PYRITE; PYRRHOTITE; REACTION RATES; SULFIDE]

3858   Burns,Roger G; Vaughan,David J; England,Katherine ER (1991): Spectroscopic investigations of oxidized pyrrhotite surfaces. Abstracts with Programs - Geological Society of America 23, A146.
        [ACIDIC; AES; GOETHITE; JAROSITE; LABORATORY; MECHANISM; OXIDATION; PYRITE; PYRRHOTITE; SPECTROSCOPY; SURFACE CHARACTERISTICS; SURFACE REACTIONS; TEMPERATURE; XPS]

3941   Thomas, J.E.; Jones, C.F.; Skinner, W.M.; Smart, R. St.C (1998) The role of surface sulfur species in the inhibition of pyrrhotite dissolution in acid conditions. Geochim. Cosmochim. Acta, 62, 9, 1555-1565.

        Abstract. Pyrrhotite, in anoxic acidic conditions, exhibits an induction period before rapid dissolution occurs. The length of the induction period is controlled by the amount of surface oxidation products on the mineral surface, acid strength, and temperature. During the induction period there is slow release of iron but little or no production of H_2S. The induction period is best described as a period of inhibited dissolution, before the onset of H_2S production and increased rate of iron release of at least two orders of magnitude. XPS analysis of the acid-reacted surface shows the progress of the dissolution.

        Four stages of dissolution have been identified. (1) The immediate dissolution of an outermost layer of oxidized iron oxyhydroxide species and oxysulfur species. (2) Inhibited, diffusion limited dissolution during an induction period due to iron diffusion through the metal-deficient layer and oxidative dissolution of the polysulfide species. (3) Rapid, acid-consuming reaction of monosulfide species under nonoxidative or reductive conditions with production of H_2S. (4) Inhibited dissolution due to reoxidation of the sulfide surface by oxidizing solution species (i.e. FeIII, residual oxygen) to produce polysulfide, elemental sulfur, and oxysulfur species.

        Dissolving synthetic pyrrhotite in similar, but aerated, acidic conditions, results in inhibited dissolution characterized by a lower rate of Fe release, minimal release of sulfate and no release of H_2S. The XPS sulfur (S2p) spectrum shows sulfate and a form of elemental sulfur on the reacted surface. Only the first two stages of

dissolution occur. The second stage differs in this case in that there is a plentiful supply of oxidizing species (O_2).

Two reaction mechanisms are proposed for the dissolution of the iron sulfide lattice of pyrrhotite in acidic conditions. The mechanisms are oxidative and nonoxidative dissolution. Two distinct activation energies are associated with the two regimes. A lower activation energy corresponds to inhibited dissolution with no production of H_2S. A $t^{1/2}$ rate law describes dissolution in air saturated solutions and supports diffusion controlled dissolution under these conditions. A higher activation energy corresponds to rapid dissolution with H_2S production. The mechanism of dissolution is determined by the state of the surface, particularly the sulfur species.

3942   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. Fourth International Conference on Acid Rock Drainage, Vancouver, BC, Canada, June 1997, 401-415.

Abstract. A laboratory study on the dissolution of pyrrhotite and an investigation of pyrrhotite and an investigation of pyrrhotite surface area was conducted to quantify differences in oxidation behaviors among twelve pyrrhotite samples of different crystalline structure and trace metal content, and acquire kinetic data to determine reaction mechanisms.

Three processes involving pyrrhotite dissolution were investigated: non-oxidative dissolution, oxidation by dissolved oxygen, and oxidation by ferric iron. Different rates of reaction were obtained from different pyrrhotite samples. Crystallographic type and trace metal content do not appear to consistently affect oxidation rates by either oxygen or ferric iron. Surface area of pyrrhotite appears to be the most influential variable affecting oxidation rates of pyrrhotite. SEM photographs reveal that fractures along cleavage planes and surface roughness are the reasons that the pyrrhotite samples have surface areas 6-40 times greater than the theoretical geometric specific surface area. Preferential oxidation appears to occur at areas of high strain on the pyrrhotite surface. Pyrrhotite BED specific surface areas are variable among pyrrhotite samples. In granular material such as tailings, surface area may be influenced by the method of size reduction.

APPENDIX 2

Additional Pyrrhotite Citations

A2.1. Mineral Processing

23.   Cheng,Xuan (1991): Effects of Pulp Potentials and Chalcopyrite-Pyrrhotite Interaction on Flotation Separation. Master of Science Thesis, University of Minnesota. 118 p.
  [CHALCOPYRITE; ELECTROCHEMISTRY; FLOTATION; METAL SULFIDES; MINERAL DISSOLUTION; OXIDATION; PYRRHOTITE; STRUCTURE; SURFACE CHARACTERISTICS]

45.   Pavlica,Jovo Jovo (1974): Electrochemistry of pyrrhotite in flotation. Master of Science Thesis, University of Minnesota. 112 p.
  [ACIDIC; ELECTROCHEMISTRY; FLOTATION; METAL SULFIDES; MINERAL DISSOLUTION; MITIGATION; PYRRHOTITE; TREATMENT]

46.   Iwasaki,Iwao (1953): Flotation Characteristics of Pyrrhotite. Master of Science Thesis, University of Minnesota. 62 p.

  [ACIDIC; ELECTROCHEMISTRY; METAL SULFIDES; MINERAL DISSOLUTION; MITIGATION; OXIDATION; PYRRHOTITE; STRUCTURE; TREATMENT]

72.   Coghill,WH (1918): Flotation of chalcopyrite in chalcopyrite-pyrrhotite ores of southern Oregon. Government Printing Office, Washington, DC. 13 pages.
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