PYRRHOTITE OXIDATION: REACTION RATE, MECHANISM, AND CONTROLLING VARIABLES

Status Report June 30, 1999

Minnesota Department of Natural Resources Division of Minerals Reclamation Section

PYRRHOTITE OXIDATION: REACTION RATE, MECHANISM, AND CONTROLLING VARIABLES

Status Report June 30, 1999

Emmelyn Jakel Kim Lapakko

Minnesota Department of Natural Resources Division of Minerals Reclamation Section

500 Lafayette Road St. Paul, MN 55155-4045 (651) 296-4807

P.O. Box 567 Hibbing, MN 55746 (218) 262-6767

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 Fe₇S₈ to FeS₂ (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.

TABLE OF CONTENTS

INTRODUCTION	1
SCOPE AND OBJECTIVES	2
PYRRHOTITE CRYSTAL STRUCTURE	2
GENERAL DESCRIPTION OF MECHANISM AND REACTION PRODUCTS	2
PYRRHOTITE REACTION RATES	3
RATE CONTROLLING VARIABLES Crystal Structure Trace Constituents pH	4 5 5 5
DIRECTION OF FUTURE WORK	5
REFERENCES	6

LIST OF FIGURES AND TABLES

Figure 1.	Pyrrhotite oxidation takes place through a series of steps	8
Table 1.	Summary of references to pyrrhotite oxidation	9
Table 2.	Rates of pyrrhotite oxidation under environmental conditions that have been reported in the literature vary by several	
	orders of magnitude	11

Appendix 1	Annotated Pyrrhotite Bibliography
Appendix 2	Semi-Annotated Bibliographies for Sulfide Minerals Excluding Pyrrhotite

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.

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; 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 oxidation of pyrite and other sulfide minerals are included in Appendix 2.

PYRRHOTITE CRYSTAL STRUCTURE

Pyrrhotite has a chemical formula of $Fe_{1-x}S$, where $0 \le x \le 0.125$. 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.

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. In the initial step, oxygen partially oxidizes pyrrhotite to form marcasite or pyrite and Fe^{2+} intermediates:

$$2Fe_{x-1}S + (\frac{1}{2}-x)O_2 + (2-4x)H^+ \rightarrow FeS_2 + (1-2x)Fe^{2+} + (1-2x)H_2O$$
(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):

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

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

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

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

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

However, at low pH, Fe³⁺ will remain dissolved and act as an additional pyrrhotite oxidant. This reaction may not proceed to completion, but instead produce elemental sulfur:

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

$$Fe_{1-x}S + (1-x)/2O_2 + 2(1-x)H^+ \rightarrow (1-x)Fe^{2+} + S^0 + (1-x)H_2O$$
(7)

Pratt et al. (1994a) determined the empirical formula of monoclinic pyrrhotite to be $Fe^{II}_{5}Fe^{III}_{2}S_{8}$. 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 O²⁻ and oxidizing either Fe^{II} or S²⁻. Oxygen does not diffuse into the crystal lattice nor does it exchange for S²⁻. 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.

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; 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:

$$[d(SO_4)/dt]_{avg} = (5.97 \text{ x } 10^{-13}) S_T^{0.984} \quad (N = 32, r^2 = 0.801)$$
(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 x 10^{-10} mol/m²/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 x 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 x 10^{-9} mol/m²/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 x 10^{-9} mol/m²/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/m²/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/m²/s and ambient oxygen pressures. The oxidation rate of pure pyrrhotite was 1.3 x 10^{-8} mol/m²/s, approximately one hundred times higher than their measured rate of pure pyrite oxidation.

Janzen (1996) 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/m²/s. The average oxidation rates by dissolved oxygen and ferric iron were 4 x 10^{-9} moles-Po/m²/s and 3.5 x 10^{-8} moles-Po/m²/s, respectively.

RATE CONTROLLING VARIABLES

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.

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.

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 Fe³⁺ 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.

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.

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.

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.

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.



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, sulfurenriched intermediates form in layers between the oxide coating and unreacted pyrrhotite, Fe_7S_8 .

Table 1.Summary of references to pyrrhotite oxidation.

Reference	Structure	Oxidation Rates	Oxidation Products	Mechanisms
Ahmed, SM, 1995, Proc. Conf. Mining and the Environ., Sudbury, ON, 171-80. (#2716)			x	
Ahonen, L et al., 1986, Fundamental and Appl. Biohydrometallurgy, 13-22. (#988)		x		
Ahonen, L; Tuovinen, OH, 1989, Biotech. Lett., 11(5), 331-36. (#2339)			x	
Ahonen, L; Tuovinen, OH, 1991, Appl. & Environ. Microbiol., 57(1), 138-45. (#1122)		x		
Ahonen, L; Tuovinen, OH, 1992, Appl. & Environ. Microbiol., 58(2), 600-06. (#2484)		x		
Banerjee, A, 1976, Indian J. of Chem., 14A, 845-50. (#57)			x	x
Buckley, AN; Woods, R, 1984, Proc. Internat. Symp. On Electrochemsitry in Mineral and Metal Processing, Electrochem. Soc. 286-302 (#2374)		x		:
Bugajski, J; Gamsjager, H, 1982, Monatshefte fur Chemie, 113, 1087-92. (#2895)		x		
Domvile, S et al., 1998, draft paper		x		
Graham, AR, 1969, The Canadian Mineralogist, 10, 4-24. (#2902)	x			
Hamilton, IC; Woods, R, 1981, J. Electroanal. Chem., 118, 327-43. (#59)			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	
Janzen, MP, 1996, MS thesis, U of Waterloo, ON Canada, 175p. (#2788)		х ′	x	x
Jonegewaard, P., 1999, Geologist, EVTAC, Eveleth, MN, personal communication.	x			
Jones, CF et al., 1992, Appl. Surf. Sci. 55, 65-85. (#2907)			x	x
Kissin, SA; Scott, SD, 1979, American Mineralogist, 64, 1306-10.	x			
Kissin, SA; Scott, SD, 1982, Econ. Geol., 77, 1739-54.	x			
Lapakko, KA; Wessels, JN, 1994, 40 th Ann. Meeting Instit. On Lake Superior Geol., 29-30. (#2468)			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.		x		

Reference	Structure	Oxidation Rates	Oxidation Products	Mechanisms
Nicholson, RV; Scharer, JM, 1992, Abstracts of papers of the ACS, 204, #30. (#28)		x		
Nicholson, RV; Scharer, JM, 1994, Environmental Geochemistry of Sulfide Oxidation, Chapter 2. (#987)		x		x
Nickel, EH et al., 1974, Econ. Geol., 69, 93-107. (#62)			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.			x	x
Reimers, GW; Hjelmstad, KE, 1987, US BOM RI 9118, 16p. (#229)			x	
Scott, SD; Both, RA, 1976, Proc. 25 th Internat. Geological Congress, 140-41	x			£
Steger, HF; Desjardins, LE, 1978, Chem. Geol., 23, 225-37. (#64)			x	
Steger, HF, 1977, Talanta, 24, 251-54. (#194)			x	
Steger, HF, 1979, Talanta, 26, 455-60. (#198)			x	
Steger, HF, 1982, Chem. Geol., 35, 281-295. (#199)			x	
Steger, HF, 1982, Geostandards Newsletter, V1(2), 249-55. (#202)			x	
Van Weert, G et al., 1974, CIM Bulletin, 97-103. (#2897)		x		
Xianjian, G; Chunpeng, L, 1991, Chin. J. Met. Sci. Technol., 7, 371-75. (#2837)		X		
Yazawa, A; Eguchi, M, 1962, in Japanese? (#2892)		x		
Yund, RA; Hall, HT, 1969, Econ. Geol., 64, 420-23. (#2893)	x			

.

,

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	
Janzen, MP	MS Thesis, U of Waterloo, 1996	non-oxidative dissolution: DO oxidation: Fe(III) oxidation:	5 x 10 ⁻¹⁰ mol/m ² /s 4 x 10 ⁻⁹ 3.5 x 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 x 10 ⁻¹² mol/g- rock/s 5.7 - 13 x 10 ⁻¹²	
Lapakko, K Antonson, DA	ACS Symposium Series #550	26 °C 58% relative humidity	8.0 x 10 ⁻¹⁰ mol/m ² /s	
Nicholson, RV Scharer, JM	Abstracts of papers 204 th ACS. 1992	controlled T (25°C), P_{02} , A_s , pH, and biotic activity	5 x 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 x 10 ⁻⁹ mol/m ² /s	

APPENDIX 1

Annotated Pyrrhotite Bibliography

- A1.1. Structure
- A1.2. Abiotic Dissolution
- A1.3. Biotic Dissolution
- A1.4. Oxidation Products
- A1.5. Oxidation Mechanism

A1.1. STRUCTURE:

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.

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 $51.40^{\circ} 2\Theta$ (Co K α 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 $\pm 12\%$ 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.

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 Fe₂S₃ product in which linear chains of S_n atoms have a S-S distance similar to elemental sulfur (S₈) but the S(2p) BE is still 0.2-0.6 eV less than S₈. Initially, the acid-reacted surface may be partially 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.

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, $Ag(s)|AgI(s)|Ag_2S(s), S_2(g)$, 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.

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.

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.

Notes from Peter Jongewaard, Geologist, EVTAC

.

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_{s2} 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

A1.2. ABIOTIC 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_{02} , initial surface area of pyrrhotite, pH and biotic activity. The zero-order abiotic rate constant at atmospheric oxygen saturation and 25C was about 5 x 10⁻⁹ mol/m²/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% As₂O₅, and up to 2.6% SiO₂, 3.9% CaO and 10.0% SO₃. 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 SO₄, 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 raw 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 x 10^{-12} mol/g/s; concurrent with the pH decrease, rates for controls increased to 5.7 and 13 x 10^{-12} mol/g/s. The pyrrhotite oxidation rates for the three subaqueous disposal techniques were 1.5, 1.7, and 2.2 x 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 2^{nd} 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 $S([H^{+]} = 0.1, [Na] = 0.9, [ClO_4] = 1.0 \text{ mol/kg})$ 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.

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 leachates. 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.

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 ⁵⁹Fe in sphalerite ($D_{Fe} = 5.6 \times 10^{-4} \exp[-38 +/-2 \text{ kcal/mol/RT}]$, 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.

A1.3. BIOTIC DISSOLUTION:

- Ahonen, Lasse; 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 pyrrhotitechalcopyrite 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.

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.

A1.4. 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, dependent 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.

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, 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.

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.

A1.5. 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 14×10^{-9} mol m⁻²s⁻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 SO₄/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(III). 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 S²⁻ to S⁶⁺.

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 x 10^{-10} , 4 x 10^{-9} , and 3.5 x 10^{-8} moles-Po/m²/s,

respectively.

2909 Pratt, A.R.; Nesbitt, H.W.; Muir, I.J. (1994) Generation of acids from mine waste: Oxidative leaching of pyrrhotite in dilute H₂SO₄ solutions at pH 3.0. Geochim. Cosmochim. Acta 58, 23, 5147-5159.

Abstract. Pyrrhotite (Fe₇S₈) grains 3x3x6 mm were reacted in solutions of H₂SO₄ (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 textrued 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 modelled 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 oxyhdroxide 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.

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 (Fe₇S₈) was leached in air-equilibrated pH 3.0 HCl H₂SO₄ acid mixtures with Cl: SO₄ 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 diffusionlimited 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 reapid 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 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:SO₄ ratios in solution did not appear to have any significant effect on leach rates of iron.

APPENDIX 2

Semi-Annotated Bibliographies for Sulfide Minerals Excluding Pyrrhotite

A2.1. PyriteA2.2. Arsenopyrite

A2.3. Marcasite

A2.4. Miscellaneous

A2.1. PYRITE

<u>Ref#</u> 2

6

Silver, M; Ritcey, GM; Cauley, MP (1985): A lysimeter comparison of the effects of uranium tailings deposition methods on the release of environmental contaminants. Hydrometallurgy 15, 159-172.

Abstract. Results of small lysimeter tests on Elliot Lake U tailings show that pyrite oxidation is decreased when these tailings are deposited by the thickened discharge method or when pyrite is partially removed from these tailings prior to random deposition. Pyrite oxidation is not decreased when these tailings are deposited by the layered sub-aerial method, but is decreased when such tailings are subjected to freezing and thawing. Ra-226 liberation is not decreased sufficiently by any of these disposal methods to permit discharge of effluents in conformation with the accepted federal guidelines of 10 pCi/L. The concentrations of iron-oxidizing bacteria in the lysimeters are 100 to 100,000 fold greater than in an unvvegetated area of the Rio Algom Nordic tailings deposit at Elliot Lake, ON. By deposition of Midweat U tailings (high As-Ni) from northern Saskatchewan in layers the concentrations of arsenic and racdium-226 in the effluent were decreased, but not sufficiently to permit direct discharge of these effluents without further treatment in order to cdonform to the federal guidelines of 0.5 mg/L and 10 pCi/L. Concentrations of Ni in the effluents of these tailings did not exceed the federal guidelines of 0.5 mg/L.

4 Burns, MS (1970): Determination of pyritic sulfur in Australian coals. Fuel 49, 126-133.

Abstract. A thorough investigation into the British Standard method fo the determination of pyritic sulfur has shown that it is not suitable for all Australian coals, and that instead, the direct or non=simultaneous method shoud be adopted. Determinations of the iron which is not extractable with nitric acid, on both the original and demineralized coals, indicate that theis iron is exxentially non-pyritic; consequently size reduction of the sample to -300 BS mesh Is not necessary.

Goldhaber, Martin B (1983): Experimental study of metastable sulfur oxyanion formation during pyrite oxidation at pH 6-9 and 30 degrees C. Am. J. Sci. 283, 193-217.

Abstract. Experimental studies of pyrite oxidation over thepH range 6 to 9 were carreied out at 30°C in 0.1 M KCl under conditions of fixed pH and pO_2 . Rate of addition of base necessary to maintain a fixed pH was monitored. Samples were withdrawn periodically and analyzed for total sulfur in solution, thiosulfate, polythionates sulfite, and sulfide. The results demostrate an increase in rate of hydrogen ion production with increase in pH. Metastable sulfur oxyanions were detected as intermediates in the sulfur oxidation pathway. For short tem (< 2 days) runs, the proportion of these sulfur oxyanions was less sensitive to the length of a run than to the pH of the run. At the lower pH values (6-7), tetrationate and sulfate were the major observed species. As pH is increased, hese ions diminish with respect to thiosulfate and sulfite. The data from this and previous studies are consistent with a pyrite oxidation mechanism whose rate controlling step is a chemical reaction occurring subsequent to the initial adsorption of oxygen to the prytie surface.

8 Luther,GW,III (1987): Pyrite oxidation and reduction: Molecular orbital theory considerations. Geochim. Cosmochim. Acta 51, 3193-3199.

Abstract. It is possible to demonstrate a heterogeneous reaction mechanism for both pyrite oxidation and reduction using a molecular orbital theory approach. The mechanism demonstrates that attachment to the FeS_2 surface by an oxidant or reductant requires that they have a vacant orbital (solution phase) or site (solid phase) to bind the oxidant or reductant to a sulfur from $S_2^{2^2}$ in FeS_2 . The approach thus requires the formation of a

persulfide (disulfide) bridge between the iron in pyrite and the oxidant or the reductant.

The first electron transfer in oxidation occurs from the π^* orbital (HOMO) of the S_2^{2-} in FeS₂ to the π orbital (LUMO) of the oxidant. Electron transfer in reduction occurs from the σ^* orbital (HOMO) of the reductant to the σ^* orbital (LUMO) of the S_2^{2-} in FeS₂. The bridge formation between two metals by a common ligand, and the electron transfer is consistent with an inner sphere type mechanism. In FeS₂, the ligand S_2^{2-} acts as the electron source or sink rather than FeII. The strength of the S-S bond in the persulfido bridge after electron transfer is key to the understanding of FeS₂ oxidation and reduction.

Additional bridges can be formed on the FeS₂ surface during oxidation until the initial oxidation product $S_2O_3^{2^2}$ is produced. The proposed mechanism allows for facile pyrite oxidation by FeIII but not O_2 . This is consistent with experimental observations. The mechanism does not require the formation of a free redical in solution. It does predict the formation of an ion radical on the pyrite surface. The proposed mechanism gives the same initial intermediate (FeS₂O) as recently proposed by Moses et al. (1987), but explains possible surface attachment by an oxidant and subsequent FeS₂ oxidation using a MO theory approach. The proposed surface mechanism is consistent with experimental observations of serveral investigators. The importance of thiosulfate formation and reactivity with FeIII is discussed in light of pyrite oxidation and of previous reports on the presence of thiosulfate in marine porewaters.

10 McKibben,Michael A; Barnes,Hubert L (1986): Oxidation of pyrite in low temperature acidic solutions: Rate laws and surface textures. Geochim. Cosmochim. Acta 50, 1509-1520.

Abstract. Rate laws have been determined for the aqueous oxidation of pyrite by ferric ion, dissolved oxygen and hydrogen peroxide at 30C in dilute, acidi chlorie solutions. Fresh, smooth pyrite grain surfaces were prepared by cleaning prior to experiments. Initial specific surface areas were measured by the multipoint BET technique. Surface textures before and after oxidation were examined by SEM. The initial rate method was used to derive rate laws.

The specific initial rates of oxidation (molpy/cm ² /n	nin) are given by the following rate laws
$R_{sp,Fe3+} = -10^{-9.74} M_{Fe}^{0.5} M_{H+}^{0.5}$	pH= 1-2
$R_{sp,O2} = -10^{-6.77} M_{O2}^{0.5}$	pH= 2-4
$R_{spH2O2} = -10^{-1.46} M_{H2O2}$	pH= 2-4

An activation energy of 56.9 kJ/mol was determined for the oxidation of pyrite by dissolved oxygen from 20 40 C. SEM photomicrographs of cleaned pyrite surfaces indicate that prior to oxidation, substantial intergranular variations in surface texture exist. Reactive surface area is substantially different than total surface area. Oxidation is centered on reactive sites of high excess surface energy such as grain edges and corners, defects, solid and fluid inclusion pits, cleavages and fractures. These reactive sites are both inherited from mineral growth history and applied by grain preparation techniques. The geometry and variation of reactive sites suggests that the comon assumption of a first-order, reproducible dependence of oxidation rates on surface area needs to be tested.

12 Miller, Stuart D (1980): Sulfur and hydrogen ion buffering in pyritic strip-mine spoil. In: Biogeochemistry of ancient and modern environments. (Eds: Ralph, BI; Trudinger, BA; Walter, MR) Springer-Verlag, New York, 537-543.

Summary. This paper examines issues and identifies fundamental geochemical reactions responsible for the bufering of hydrogen and sulfate ions in an acidic strip-mine spoil.

Applications of thermodynamic principles to the soil solution of this pyritic strip-mine spoil successfully identified the existence of a quasi-equilibrium between jarosite and $Fe(OH)_3$. This equilibrium was significant in buffering the acidity and ionic composition of the soil solution in a phytotoxic state which persisted under low oxygen conditions. Therefore, if pyrite oxidation has occurred and the jarosite-Fe(OH)₃ couple has become established, burial of acid material or covering with topsoil to establish vegetation and reduce the supply of oxygen to pyrite crystal surfaces may not prevent acid mine drainage or aquifcer contamination.

It can also be concluded that a pyritic strip-mine spoil may remain acid for many years after reactive pyrite has been oxidized due to jarosite- $Fe(OH)_3$ buffering. This time will depend upon the jarosite content and the climatic and weathering characterisitics the spoil is exposed to.

Moses,CO; Nordstrom,DK; Herman,JS; Mills,AL (1987): Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. Geochim. Cosmochim. Acta 51, 1561-1571.

Abstract. Rates of aqueous, abiotic pyrite oxidation were measured in oxygen saturated and anaerobic FeIII saturated solutions with initial pH from 2 to 9. These studies included analyses of sulfite, thiosulfate, polythionates, and sulfate, and procedures for cleaning oxidation productas from pyrite surfaces were evaluated. Pyrite oxidation in oxygen saturated solutions produced 1) rates that were only slightly dependent on initial pH, 2) linear increases in sulfoxy anions, and 3) thisulfate and polythionates at pH > 3.9. Intermediate sulfoxy anions were observed only at high stirring rates. In anaerobic FeIII saturated solutions, no intermediates were observed ecept traces of sulfite at pH 9. The faster rate of oxidation if FeIII saturated solutions supports a reaction mechanism in which FeIII is the direct oxidant of pyrite in both aerobic and anaerobic systems. The proposal of this mechanism is also supported by theoretical considerations regarding the low probability of a direct reaction between paramagnetic molecular oxygen and diamagnetic pyrite. Results from a study of sphalerite oxidation support the hypothesis that thiosulfate is a key intermediate in sulfate production, regardless of the bonding structure of the sulfide mineral.

Nicholson, RV; Gillham, RW; Reardon, EJ (1988): Pyrite oxidation in carbonate-buffered solution:
 1. Experimental kinetics. Geochim. Cosmochim. Acta 52, 1077-1085.

Abstract. The kinetic behaviour of pyrite oxidation in carbonate-buffered solution was investigated in the laboratory. Oxygen concentration, surface area and T were varied while pH values were limited to the range of 6.7-8.5. The rate experiments were performed on crushed and sieved size-fractions of pyrite that were carefully cleaned and mixed with similar-size silica sand., Oxidation occurred in a moisture-suction device that maintained partially-water saturated conditions. Dilute NaHCO₃ solution and a $CO_2-O_2-N_2$ gas mixture were passed continuously through the pyritic sand. The reaction rates were monitored by sulfate mass balabce in the effluents.

The initial rate of oxidation was found to be a linear function of surface area. The ratedependence on oxygen concentration is non-linear and the data fit a geterogeneous kinetic model in which the surface decomposition reaction, not sorption of oxygen, is the rds. This decomposition model explains the range of linear to nonlinear models reported in the literature when different values of the adsorption constant are applied. The T-dependence follows Arrhenius behaviour with an equivalent activation energy of about 88 kJ/mol in the T range of 3-25C, showing that diffusion was not rate limiting. The oxidation rates of flive pyrite specimens obtained from aroius locales exhibited maximum differences of only about 25%.

16 Taylor,BE; Wheeler,MC; Nordstrom,DK (1984): Stable isotope geochemistry of acid mine drainage: Experimental oxidation of pyrite. Geochim. Cosmochim. Acta 48, 2669-2678.

Abstract. Sulfate and water from experiments in which pyrite was oxidized at a pH of 2.0 were analyzed for sulfur and oxygen stable isotopes. Experiments were conducted under both aerobic and anaerobic sterile conditions, as well as under aerobic conditions in the presence of T. ferrooxidans, to elucidate the pathways of oxidat8on. Oxygen isotope fractionation between sulfate and water varied from +4.0 permil (anaerobic, sterile) to +18.0 permil (aerobic, T. ferrooxidans). The oxygen isotope composition of DO utilized in both comical and microbially mediated oxidation was also determined (+11.4 per mil by T. ferrooxidans, +18.4 permil chemical). Contributions of water derived oxygen and DO to the sulfate produced in the oxidation of pyrite could thus be estimated. Water derived oxygen constituted from 23 to 100% of the oxygen in the sulfate produced in the experiments, and this closely approximates the range of contribution in natural AMD. Oxidation of sulfides in anaerobic, water saturated environments occurs primarily by chemical oxidation pathways, whereas oxidation of sulfidesx in well aerated, unsaturated zone environments occurs dominantyly by microbially mediated pathways.

Wiersma, CL; Rimstidt, JD (1984): Rates of reaction of pyrite and marcasite with ferric iron at pH 2. Geochim. Cosmochim. Acta 48, 85-92.

Abstract. The relative reactivities of pulverized samples (100-200 mesh) of 3 marcasite and 7 pyrite specimens from varoius sources were determined at 25C and pH 2.0 in ferric chloride solutions with initial ferric iron concentrations of 10^{-3} molal. The rate of the reaction was determined by calculating the rate of reduction of aqueous ferric ion from measured redox potentials. The reaction follows the rate law:

 $-dm_{Fe3+}/dt = k(A/M)m_{Fe3+}$

where k is the rate constant and A/M is the surface area of reacting solid to mass of solution ratio. k ranged from 1.0×10^{-4} to 2.7×10^{-4} s⁻¹ +/- 5%, with lower-T early diagenetic pyrite having the smallest rate constants, marcasite intermediate, and pyrite of higher-T hydrothermal and metamorphic origin having the greatest rate constants. Geologically, these small relative differences between the rate constants are not significant, so the fundamental reactivities of marcasite and pyrite are not appreciably different.

The activation energy of the reaction for a hydrothermal pyrite in the 25-50C is 92 kJ/mol. This relatively high activation energy indicates that a surface reation controls the rate over the T range. The BET-measured specific surface area for lower-T/early diagnetic pyrite is an order of magnitude greater than that for pyrite of higher=T origin. consequently, since the lower-T types have a much greater A/M ratio, they appear to be more reactive per unit mass than the higher T types.

Wiese, RG; Powell, MA; Fyfe, WS (1987): Spontaneous formation of hydrated iron sulfates in laboratory samples of pyrite- and marcasite-bearing coals. Chem. Geol. 63, 29-38.

Abstract. Hydrated iron sulfates identified as melanterite, rozenite, szomolnokite and halotrichite have been observed growing on iron sulfides in polished and rough cut surfaces of samples of Ohio and Utah coals stored under normal atmospheric conditions. Melanterite and rozenite are likely the earliest hydrated sulfates to form. Szomolnokite and halotrichite appear to be the most stable sulfates in the samples studied. The formation of halotrichite involves the interaction between the oxidation of sulfies and the breakdown of clays. In many cases the oxidation process occurs below the polished surfaces of the sulfides, and the sulfates are extruded from pores and grain boundaries within and marginal to the sulfide grains. The first stages of sulfate formation may involve development of amorphous sulfate

18
phases that subsequently become crystalline. There appear to be no significant differences between reactivities of pyrite and marcasite with respect to sulfate formation. Porous, or spongy textured sulfides are more prone to oxidation and sulfate formation than are well crystallized sulfides. In addition to conditions of high humidity the presence of clays associated with the sulfides is an important contributory factor in the oxidation of the sulfides. The oxidation of iron sulfides contained in coals and associated strata is the principal cause of acid waters generated by mining activities and of the spontaneous combustion of coal storage piles and mine waste dumps. The environmental impact of these phenomena depends upon reaction kinetics.

Kornicker, William A; Morse, John W (1991): Interactions of divalent cations with the surface of pyrite. Geochim. Cosmochim. Acta 55, 2159-2171.

Abstract. Interactions between pyrite and dissolved Ca, Mn, Co, Ni, Cd, and Zn were studied as a function of pH, ionic strenngth, and adsorbate concentration in NaCl solutions and in seawater. Apparent adsorption constants were calculated using an ion-exchange surface complexation model, and second order rate constants for the sorption of Co, Ni Cd, and Zn were calculated from their uptake kinetics.

Apparent adsorption constants generally varied by less than an order of magnitude, except for Ca which exhibited complex behavior. The appared adsorption constants decreased in the order Co>Cd>Mn>Ni>Ca>Zn. The raning of the apparent adsorption constants does not correlate with the first hydrolysis constants of the adsorbates or the solubility products of their sulfide minerals.

The behavior of the second order forward and reverse rate constants in different solutions indicates that adsorption is more complex than the second order reaction medol described by the ion excahange surface complexation medol. The forward sorption reaction reate constants increased with increasing pH, and decreased with increasing I or initial adsorbate concentration. The reverse sorption reaction rate constants increased with increasing pH or initial adsorbate concentration, and were unaffected by I. The effect of pH on the forward and reverse rate constants may have been due to, respectively, a surface-induced hydrolysis reaction mechanism and a rate limiting step prior to the surface complex-hydrogen ion reaction. The effect of ionic strength on the forward rate constants may have been due to site competition with Na, while the effect of initial adsorbate concentration on the forward and reverse rate constants may have been due to, respectively, the assumption of a constant concentration of surface sites available for reaction and the presence of heterogeneous surface sites.

Morse, John W (1991): Oxidation kinetics of sedimentary pyrite in seawater. Geochim. Cosmochim. Acta 55, 3665-3667.

Abstract. Long-term (weeks to months) experiments were conducted on the oxidation kinetics of sedimentary pyrite in which initially anoxic sediments containing pyrite were suspended in seawater that was kept in equilibrium with the atmosphere. During an initial reaction period the oxidation of pyrite is relatively rapid, with 3% to 18% oxidation occurring in one day. Calculations indicate that this initial rapid rate of oxidation is the result of the oxidation of very fine (<0.3 um) pyrite. Following this initial period of rapid oxidation, the oxidation rate slows, with about 20% oxidation typically occurring during the first week. Only a few percent more of the pyrite is oxidized over months of reaction time. Framboidal pyrite is likely of dominate in this period of oxidation and iron oxide or other coatings may significantly inhibit oxidation kinetics. These results indicate that suspended pyrite can persist in oxic seawater for long periods of time and consequently be transported substantial distances.

20

Sullivan, Patrick J; Yelton, Jennifer L; Reddy, KJ (1988): Solubility relationships of aluminum and iron minerals associated with acid mine drainage. Environmental Geology and Water Sciences 11(3), 283-287.

Abstract. The ability to properly manage the oxidation of pyritec minerals and associated AMD is dependent upon understanding the chemistry of the disposal environment. One accepted disposal method is placing pyritic containing materials in the groundwater environment. The objective of this study was to examine the solubility relationships of Al and Fe minerals associated with pyritic waste disposed in a low leaching aerobic saturated environment. Two eastern oil shales were used in this oxidizing equilibration study, 4.6% pyrite and 1.5% pyrite). Oil shale samples were equilibrated with distilled di water from 1 to 180 days with a 1:1 soild to solution ratio. The suspensions were filtered and the clear filtrates were analyzed for toal cations and anions. Ion activities were calculated from total concentrations. Below pH 6.0, depending upon SO₄ activity, Al solubility was controlled by AlOHSO₄ for both shales. Initially Al solubility for the 4.6% shale showed equilibrium with am. $Al(OH)_{4}$. The pH decrease with time, and Al solubility approached eq with AlOHSO₄. Below pH 6.0, FeIII solubility appeared to be regulated by a basic iron sulfate solid phase with the stoichimetric composition of FeOHSO₄. The results of this study indicate that below pH 6.0, Al and FeIII solubilityes are limited by basic Al and Fe sulfate solid phases. The results from theis study further indicate that the acidity in oil shale waters is produced for the hydcrolysis of Al and FeIII activities in solution. These results indicate a fundamental change in the stoichiometric dequations used to predict acidity from iron sulfide oxidation. The results of this study also indicate that water quality predictions associated with acid mine drainage can be based on fundamental thermodynamic relationships. As a result, waste management decisions can be based on waste-specific/sitespecific test methods.

van Breemen, N (1988): Redox processes of iron and sulfur involved in the formation of acid sulfate soils. Chap. 25. In: Iron in soils and clay minerals. (Eds: Stucki, JW et al.) D. Reidel Publishing Co.,, 825-841.

Summary. This chapter first discusses the formation of pyrite and the conditions where it is formed, then deals with the oxidation of pyrite and its oxidation products. Finally, the formation of nontornite in soil horizons with pyrite oxidation, observed in certain coastal plain soils in Thailand, will be described.

Bryner, LC; Walker, RB; Palmer, R (1967): Some factors influencing the biological and non-biological 55 oxidation of sulfide minerals. Transactions of the Society of Mining Engineers, AIME 238(Mar), 56-65.

Summary. The purpose of this investigation was to further study some of the factors affecting the air oxidation of sulfide minerals. Data obtained from laboratory studies on the effecto ot T, concentration of iron salts, pH and other catalysts on the biological and nonbiological oxidation of sulfide minerals are presented.

The effect of T on the biological oxidation of pyrite and CuII sulfide was studied over the range from 25-75°C. The optimum biological oxidation for pyrite was near 35°C and dropped off to a minimum near 65°C. The optimum for the biological oxidaiton of CuII sulfide was 35°C with a minimum at 55°C, the nonbiological oxidation increased with T for the CuII sulfide.

Iron III is known to be effective in the oxidation of many sulfide minerals. Since it is known that activated carbon is a catalyst in the air oxidation of FeII, it was used to increase the

44

oxidation of FeII in the presence of the mineral. Studies were also made on the biolgical oxidation of sulfide minerals and compared to the non-biological oxidation. The effect of activated carbon was marked on the CuII sulfide and chalcopyrite. This indicates that activated carbon has a surface action effect on the oxidation of the mineral in addition to its effect on the oxidation of FeII. This catalytic action is direct oxidaton of the mineral by absorbed oxyen from the air or catalysis of the oxidation of the mineral by FeIII.

In oxidation of CuII sulfide the bacterial have an optimum FeII concentration of about 0.5 g/L. Studies with carbon also indicate that only a small amount of FeII is needed for efficient oxidation of CuII sulfide. The oxidation of cuprite and copper was studied to determine the effect of FeII and FeIII on the air oxidation of copper. FeII or III act as intermediate catalysts in the air oxidation of copper in dilute sulfuric acid solution. Activated carbon and ironII increased the rate of oxidation of free copper.

The air oxidation of pyrite in 0.1N sufuric acid, with FeI and activated carbon or FeIII was 15 times faster than when the iron salts were absent. FeIII oxidized about 1/3 as much pyrite in the absence of air as it did in the air. In the biological oxidation of sulfide minerals the bacteria catalyze the oxidation of FeII to III, which in turn acts as a catalyst in the oxidation. 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. Pyrites 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.

8 de Haan, Sophie Bierens (1991): A review of the rate of pyrite oxidation in aqueous systems at low temperature. Earth Sci. Rev. 31, 1-10.

Abstract. The thermodynamic stability of pyrite is limited to a narrow range of Eh conditions, but pyrite occurs in almost any geological environment under earth surface conditions. When mine wastes or pyritic shales are exposed to the atmosphere and moteoric water, however, the weathering of pyrite takes place at such a rate that it can cuse pollution and geotechnical problems within a few years. Recent work on pyrite oxidaiton has been aimed at determining which chemical properties of the geological environment affect the rate of pyrite oxidation most and to what extent. Some investigators have leached samples of ground pyrite in the lab under a range of experimental conditions. The observed that the rate of pyrite oxidation depends on the surface area of the sample, on the initial concentration of oxidizing agent and only slightly on the initial pH of the leaching medium. Results were expressed as a rate law which relates these experimental factors to the rate of pyrite oxidation. There is some disagreement between authors about the rate laws obtained. This may be due to changes in the properties of the pyrite surface during the experiments or to unforeseen reactions that are part of the chemical pathway for pyrite oxidation. Mechanisms have been proposed for pyrite oxidation according to theoretical considerations about chemical reactions between solute and solid, magnetic properties of substances and molecular orbital theory.

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

57

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 quantites, particularly in the alkaline solutions. Oxidation of pyrrhotite is strongly inhibited by the surface ferric oxide produced.

Mehta,MP; Murr,LE (1983): Fundamental studies of the contribution of galvanic interaction to acid-bacterial leaching of mixed metal sulfides. Hydrometallurgy 9, 235-256.

Abstract. A systematic study has been made towads understanding the role of galvanic interactions in the leaching of sulfide minerals both in the absence and presence of bacteria. When two sulfide minerals are in contact with each other in an acid-aqueous solution, the mineral lower in the electromotive series dissolves rapidly while the one higher in the series is galvanically protected. To ascertain the magnitude of galvanic interaction when chalcopyrite and pyrie are in contact, potentiodynamic polarization measurements were carried out in 1 M H_2SO_4 and in Bryner and Anderson medium The individual rest potentials of CuFeS₂ and FeS₂ were found to be 0.52 V and 0.63 V (SHE), respectively. The mixed potential of the CuFeS₂:FeS₂ couple was found to be 0.56 V and 0.28 V in 1 M H_2SO_4 and Bryner and Anderson medium respectively. The corrosion current (5 uA/cm²) was calculated from the polarization curves. These results were found to be in agreement with the actual leaching rates of copper from contacting large mineral specimens composing the CuFeS₂/FeS₂ system.

Both powdered samples as well as large mineral specimens of $CuFeS_2$, FeS_2 and ZnS were used to observe the effect of galvanic interactions on the process of leaching. Chalcopyrite and pyrite powders, as pulp mixtures, were leached under a variety of experimental conditions to optimize their ratio and size fraction for efficient metal extration by way of maximum contact with each other. A $CuFeS_2$:FeS₂ ratioof 5:5 (g/g) and size fraction of -200 mesh was found to be the most preferable when leaching was carried out in the presence of T ferrooxidans. The effect of T and thermophilic bacteria on the rate of leaching was also studied. The presence of pyrite in theoptimized quantities considerably enhanced the rate of copper dissolution which was increased by a factor of 2 to 15. Under these experimental conditions, Eh increased from 338 mV to 580 mV while pH dropped from 2.30 to 1.56.

In order to have a definite control of surface area of the ores and a constant contact between two sulfide ores, large crystalline mineral samples of $CuFeS_2$, FeS_2 and ZnS were leached singly as well as in intimate contact (coupled glavanically). This also made it possible to observe the surfaces of the specimens as the leaching proceeded in the presence of galvanic interaction. Coupled $CuFeS_2/FeS_2$, ZnS/FeS_2 and $CuFeS_2/FeS_2/ZnS$ systems showed improved metal dissolution as compared to leaching of single large specimens. SEM observations showed that there were no major changes on pyrite surfaces when in galvanic contact with chalcopyrite and or sphalerite. These observations have been supported by chemical data and by energy dispersive X-ray analysis.

61 Moses,CO; Herman,JS (1991): Pyrite oxidation at circumneutral pH. Geochim. Cosmochim. Acta 55, 471-482.

Abstract. Previous studies of pyrite oxidation kinetics have concentrated primarily on the reaction at low pH, where Fe(III) has been assumed to be the dominant oxidant. Studies at circumneutral pH necessitated by effective pH buffereing in some pyrite oxidation systems, have often implicitly assumed that the dominant oxidant must be DO, owing to the diminished solubility of Fe(III). In fact, Fe(III) is an effective pyrite oxidant at circumneutral pH, but the reaction cannot be sustained in the absence of DE. The purpose

of this experimental study was to ascertain the relative roles of Fe(III) and DO in pyrite oxidation at circumneutral pH.

The rate of pyrite oxidation was first-order with respect to the ratio of surface area to solution volume. Direct determinations of both Fe(II) and Fe(III) demonstrated a dramatic loss of Fe(II) from the solution phase in excess of the loss for which oxidation alone could account. Based on rate data, we have concluded that Fe(II) is adsorbed onto the pyrite surface. Furthermore, Fe(II) is preferred as an adsorbate to Fe(III), which we attribute to both electrostatic and acid-base selectivity. We also found that the rate of pyrite oxidation by either Fe(III) or DO is reduced in the presence of aqueous Fe(II), which leads us to conclude that, under most natural conditions, neither Fe(III) nor DO directly attacks the pyrite surface.

The present evidence suggests a mechanism for pyrite oxidation that involves adsorbed Fe(II) giving up electrons to DO and the resulting Fe(III) rapidly accepting electrons from the pyrite. The adsorbed Fe is, thus, cyclically oxidized and reduced, while it acts as a conduit for electrons traveling from pyrite to DO. Oxygen is transferred from the hydration sphere of the adsorbed Fe to pyrite S. The cycle of adsorbed Fe oxidation and reduction and the successive addition of oxygen to pyrite S continues until a stable sulfoxy species dissociates from the surface. Prior work has shown that sulfoxy species of lower oxidation state than sulfate may accumulate in solution under some circumstances but not under the conditions of the experiments reported here. in these experiments, the rate of sulfate accumulation in solution is proportional to the rate of pyrite oxidation.

Nicholson, RV; Gillham, RW; Reardon, EJ (1990): Pyrite oxidation in carbonate-buffered solution: 2. Rate control by oxide coatings. Geochim. Cosmochim. Acta 54, 395-402.

Abstract. The kinetic behavior of pyrite oxidation in the lab was studied over a period of about 10,000 hrs in reactos through which a carbonate-buffered solution and air $(20\% O_2)$ flowed continuously. Three grain size fractions were monitored. The concentration of sulfate and the mass of the effluent solution were measured periodically to calculate oxidation rates.

The results indicate that the rates of reaction decreased significantly with time. The rates initially exhibited an inverse dependence on grain size (within 400 hrs) then became more linear with the square of the inverse grain size at later times (after (8000 hr) suggesting a surface-layer control of the reaction with time. Surface analysis by XPS revealed the presence of ferric oxide o the pyrite surfaces, and ion boring with AES indicated a layer thickness on the order of 0.6 microns on the 215 micron grains.

The data are represented by a shrinking core model which includes the effects of the surface rate constnat plus the diffusive resistance to oxygen transfer through the accumulating reaction layer as oxidation proceeds. The three grain sizes (representing different specific surface areas) exhibited consistent estimates of the surface rate constant ($k_s = 3.04 \times 10^{-6} \text{ m/h} + /-46\%$) and the diffusion coefficient for oxydent through the oxide layer ($D_s = 1.08 \times 10^{-12} \text{ m}^2/\text{hr} + /-30\%$). The estimated thickness of the oxide layer at the end of the experiment agreed well with the measured value. Osxide accumulation on the pyrite surfaces under neutral pH conditions results in a significant reduction in oxidation rates over time. This behaviour has important implications for the reduction of the rate of release of oxidation products, including H⁺, to environments where sulfide mineral wastes are exposed to the atmosphere.

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

63

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.

65 Thornber, MR (1975): Supergene alteration of sulphides. I. A chemical model based on massive nickel sulphide deposits in Kambalda, Western Australia. Chem. Geol. 15, 1-14.

Abstract. An electrochemical model for the weathering of massive sulfide deposits that have undergone conditions similar to those affecting the Kambalda nickel deposits is presented. Galvanic corrosion due to aeration of the top of the ore body near the water table results in a deep anodic reaction whereby primary sulfides undergo an oxidatiove transition to sulfur rich violarite pyrite ore and also a shallow oxidative anodic reaction where the violarite ptrite ore is oxidized to sulfate and gossanous oxides. Electrons are conducted through the ore from the anode to the cathode where dissolved oxygen radicals are reduced and the corrosion cells are completed by ionic transport through the groundwaters to the anodic regions that can be some 200 m deep in the case of deep weathering processes. The kinetics of the weathering are described in terms of resistance to the flow of corrosion currents in the electrochemical cells. The effect on the model of physical perturbations such as rising and falling water table, faulting, etc. is discussed.

138 Brady, Keith BC; Cravotta, Charles AIII (1992): Acid-base accounting: an improved method of interpreting overburden chemistry to predict quality of coal-mine drainage. Paper presented at the West Virginia Surface Mine Drainage Task Force Symposium, April 8-9, 1992, Morgantown, West Virginia.

Summary. This paper establishes a useful relation between the contents of sulfur and carbonate in coal bearing rocks that can be used to predict whether post mining discharge water will be acidic or alkaline. Methods of ABA data interpretation, by use of stoichiometric equivalence factors of 31.25 and 62.5 to compute MPA and NNP, are compared with water quality data from mine site field studies.

Although an improved method of interpreting overburden chemistry to predict the quality of coal mine drainage has been demonstrated, additional work is needed to perfect ABA methods and interpretations...The use of multiple tools and the computation of MPA by multiplying % total SD by a factor of 62.5 as propsed by Cravotta et al. (1990) improve the accuracy of predicting the quality of mine drainage water, primarily as a result of reducing the error "predicted alkaline was acidic."

163 Kleinmann, RLP; Crerar, DA; Pacelli, RR (1981): Biogeochemistry of acid mine drainage and a method to control acid formation. Mining Engineering (March), 300-305.

Abstract. T. ferrooxidants are of prime importance in the formation of acid drainage from pyritec material. Above pH 4.5, T ferrooxidans increases initial acidification; below pH 4.5, it allows acidification to continue by oxidizing FeII. Below a pH of approximately 2.5, the acitivity of FeIII is significant and results in steady-state cycling between oxidation of pyrite by FeIII and bacterial oxidation of FeII. Lab and field tests demonstrate that inhibition of T. ferroxidans by controlled release of anionic detergents can inexpensively reduce pyrite oxidation and acid formation.

Temple, Kenneth L; Delchamps, Earsie W (1953): Autotrophic bacteria and the formation of acid in 169

bituminous coal mines. Applied Microbiology 1, 255-258.

Summary. T. thiooxidans increases the acid formation from certain types of the pyritic concretions in coal known as 'sulfur balls,' as well as from marcasite. T. ferrooxidans increases the acid formed from museum grade pyrite of fine particle size as well as from 'sulfur balls.' A general mechanism for acid formation in coal mines is proposed.

170 Garrels, RM; Thompson, ME (1960): Oxidation of pyrite by iron sulfate solutions. Am. J. Sci. 258(A), 57-67.

Abstract. The rate of oxidation of pyrite specimens from three localities was measured in acid iron sulfate solutions. The rate of reduction of ferric ion in these solutions is considered to be a measure of the rate of oxidation of the pyrite. The overall oxidation reaction, in the range 100% to 0.1% m_{Fe+++} is in accord with the classical reaction:

 $\text{FeS}_2 + 8\text{H}_2\text{O} = 14 \text{ Fe}^{+++} \rightarrow 15\text{Fe}^{++} + 2\text{SO}_4^{=} + 16\text{H}^+.$

The average rate of reduction from 100% m_{Fe+++} to 50% m_{Fe+++} is constant for pyrite from a given locality, and differences in the average rates between specimens from different localities could not be related to minor compositional variations of the solutions or of the pyrites. The pH did not affect rate in the tested range, pH 0 to Ph 2. The instantaneous rate of reduction of ferric ion diminishes with decrease in the ferric-ferrous ratio; it is postulated that instantaneous rate is controlled by differential absorption of ferric and ferrous ions on the pyrite surface, and is proportional to the fraction of pyrite surface occupied by ferric ion.

171 Pugh,CE; Hossner,LR; Dixon,JB (1984): Oxidation rate of iron sulfides as affected by surface area, morphology, oxygen concentration, and autotrophic bacteria. Soil Science 137(5, May), 309-314.

Abstract. This study sought to determine the relationship between surface area and rate of oxidation of Fe sulfides (pyrite and marcasite) separated from Texas lignite. We evaluated the reaction kinetics with respect to Fe sulfide morphology and particle size. The oxygen concentration and the presence of autotrophic Fe and S oxidizing bacteria on the rate of oxidation were also evaluated.

The formation of sulfate from Fe sulfide was selected to measure the rate of oxidation. Relative reaction rates for different morphological forms of Fe sulfide were: marcasite > framboidal pyrite > massive pyrite. The rate of oxidation of marcasite was much higher than for pyrite at an equivalent surface area. As the surface area of pyrite doubled, reaction rate increased by a factor of 1.5. Sulfate production at optimum reaction conditions in this experiment of the 5 to 2 um fraction was twice that of the 50 to 20 um fraction. Reaction rate was approx. five fold greater for noninoculated treatments at 20% oxygen, compared with 0% oxygen., and was approx. ninefold greater for the same treatments inoculated with T. ferrooxidans.

172 Erickson, Patricia M; Ladwig, Kenneth J; Kleinmann, LP (1985): Acid mine drainage from inactive eastern coal operations. Environmental Geochemistry and Health 7, 16-25.

Abstract. This paper reports on several field studies intended to determine the location of pyrite oxidation zones and migration pathways of oxidation products at inactive spoil and refuse sites. Oxygen required for pyrite oxidation is believed to be provided in the gaseous state from the atmosphere. Therefore, the oxygen concentration in unsaturated mine waste should provide an estimate of the weathering tendency in the local environment. We are currently monitoring gas composition in refuse and spoil at six sites. Barren refuse appeared to be oxygenated (>2%O₂) in a shallow zone extending less than 1 m below the surface during most of the year. Preliminary data from coal spoil showed that oxygen can be

available throughout the unsaturated thickness, even at a revegetated site. Gas composition varied vertically and laterally at a single site and also appeared to show seasonal dependence.

Hydrologic factors are also important in acid production and transport. Discharge monitoring alone does not adequately describe the mass transport of acid products through the spoil. For example, at one reclaimed mine the mean sulfate content in six monitoring wells ranged from 24% to 240% of the mean concentration at the discharge point. Sources of recharge and relative flow rates determine the contribution of a particular zone to overall discharge quality.

These basic studies of acid production and transport indicate some shortcomings of standard reclamation practices at certain sites. This information will be used to develop alternative abatement technology designed to mitgate acid production at the source.

173 Zheng, Chang Qiong; Allen, Charles C; Bautista, Renato G (1986): Kinetic study of the oxidation of pyrite in aqueous ferric sulfate. Ind. Eng. Chem. Process Des. Dev. 25(1), 308-317.

Abstract. The oxidation of pyrite in aqueous ferric sulfate is given by the chemical reaction $FeS_2 + 14 Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$. It was found that the reaction was kinetically limited and the oxidation rate for the pyrite depended on the total iron concentration and on the ratio of ferric to ferrous ions under constnat acid concentration. The experimental data were found to best fit the Hougen-Watson dual site adsorption model for total FeIII and total FeII ions with the rate expression given by

 $r_{\text{FeS2}} = k_1 - k_2 [\text{FeII}]^{0.5} [\text{FeIII}]^{0.5} / 1 / [\text{FeIII}]^{0.5} + k_3 + k_4 [\text{FeII}/\text{FeIII}]^{0.5}$

It was also found that the rate of pyrite oxidation depended on the free ferric, free ferrous, and bisulfate ions when the sulfate concentration is varied. The experimental data could be represented by a Hougen-Watson simple adsorption irreversible reaction model for FeIII, FeII and HSO₄ ions with the rate expression given by

 $r_{FeS2} = k'K_1'(Fe^{3+}) / [1+K_1'(Fe^{3+})+K_2'(Fe^{2+})+K_3'(Fe^{3+})(HSO_4)]^{1.5}$

175 Lowson, Richard T (1982): Aqueous oxidation of pyrite by molecular oxygen. Chemical Reviews 82(5, October), 461-497.

Abbr. Summary. The chemistry and physics of iron disulfide were reviewed with reference to the aqueous oxidation of pyrite by molecular oxygen. Morphology and crystal structure influence the reaction rate in the following order: euhedral pyrite < framboidal pyrite < marcasite. Three reaction paths have been identified vor the aqueous oxidation of pyrite by molecular oxygen, bacterial, chemical, and electrochemical. The bacterial path was not discussed. The chemical oxidation path is a sequence of three steps: i) the oxidation of pyrite by molecular oxygen to sulfate and FeII, ii) the oxidation of FeII by molecular oxygen to FeIII, and iii) the oxidation of pyrite by FeIII to sulfate and FeII. The activation energy of approx. 60 kJ/mol indicates a chemical rather than a physical rate-determining step. A number of reaction mechanisms have been proposed; these include the formation of an adsorbed oxygen species, formation of thio intermediates, and an electrochemical sequence. Evidence has been presented for all of these mechanisms.

176 Walsh, Fraser; Mitchell, Ralph (1972): A pH-dependent succession of iron bacteria. Environ. Sci. Technol. 6(9), 809-812.

Abstract. The role of an acid tolerant, filamentous iron bacterium in a succession of pH dependent events affecting the rate of iron oxidation is identified. This organism significantly catalyzes iron oxidation in the pH range of 4.5-3.5. At pH greater than 4.5,

abiotic iron oxidation proceeds rapidly. At pH less than 3.5, T. ferrooxidans significantly catalyzes iron oxidation. The activity of the filamentous iron bacteria in this succession of events may directly affect the rate of acidity production in coal mine waters.

178 Bailey,LK; Peters,E (1976): Decomposition of pyrite in acids by pressure leaching and anodization: the case for an electrochemical mechanism. Canadian Metallurgical Ouarterly 15(4), 333-344.

Abstract. The oxygen pressure leaching of pyrite has been studied with regard to reaction mechanism by ¹⁸O tracer tests, electrochemical simulation and actual leaching experiments over the following range of variables: T, 85 - 130 °C; P, 0 - 976 psi O₂; and acid concentration 0.01 - 3 M H_2SO_4 . The dissolution mechanism has been found to be electrochemical and is a potentiostatically controlled steady state between sulfate forming and elemental sulfur forming anodic reactions:

 $FeS_2 + 8H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^-$ 1.

 $FeS_2 + - Fe^{2+} + 2S + 2e^{-}$

Ferric ions are produced primarily by a slow homogeneous reaction:

 $4Fe^{2+} + O_2 + 4H^+ - 4Fe^{3+} + 2H_2O$

The cathodic reaction initially involves the reduction of oxygen:

 $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

2.

This reaction is supplemented by cathodic reduction of ferric ions after these have buit up to a significant concentration. The electrochemical model has been cited to explain the effect of oxygen pressure on the system and acid production or consumption by pryite during leaching.

179 Biegler, T; Swift, DA (1979): Anodic behaviour of pyrite in acid solutions. Electrochimica Acta 24, 415-420.

Abstrat. In acid solution, pyrite gives reproducible anodic current voltage curves with Tafel slopes 95 \pm 10 mV. There is no influence of pyrite semiconducting properties on the kinetics of the anode process. This process, as determined by coulometry at constant potential and product analysis, is a combination of the reactions

 $FeS_2 + 8H_2O \rightarrow Fe^{3+} + 2SO_4^{2-} + 16H^+ + 15e^ FeS_2 \rightarrow Fe^{3+} + 2S + 3e^-$

The sulfate route dominates over the potential range accessible at ambient temperature, and the sulfate yield increases lineraly with potential. Data from other sources suggest that sulfate yield at fixed potential may be independent of T. Evidence from studies of the electrochemical behavior of sulfur and its compounds leads to the conclusion that elemental sulfur is not an intermediate in the sulfate route. A mechanism for sulfate formation involving adsorbed oxygen containing intermediates is postulated and the kinetics analyzed under Temkin adsorption conditions. The Tafel slope and pH dependence suggest that the second electron transfer step is rate-determining.

184 Mishra,KK; Osseo-Asare,K (1988): Electrodeposition of $H\{++\}$ on oxide layers at pyrite (FeS $\{-2\}$) surfaces. J. Electrochem. Soc. 135(8), 1898-1901.

Abstract. The electrochemical behavior of pyrte has been studied in 1 mol dm³ HClO₄ solution in the potential range of -350-300mV (SCE). Reversible surface processes are observed in this potential region. The electrochemical i-V behavior is found to be dependent upon the amount of surface oxide below a monolayer that is present and on the pH. These surface processes are attributed to the electroadsorption/desorption of H⁺ on a surface oxide layer.

185 Mishra,KK; Osseo-Asare,K (1988): Aspects of the interfacial electrochemistry of semiconductor

pyrite (FeS{-2}). J. Electrochem. Soc. 135(10), 2502-2509.

Abstract. The electrochemical oxidation of pyrite has been studied using CV, EDX and AES techniques. CV's reveal one anodic peak and two cathodic peaks on the return sweep. These peaks are attibuted to the electroadsorption/desorption of OH groups on pyrite surfaces. It is proposed that the electrocatalytic electroadsorption of OH groups on pyrite is due to the presence of Fe 3d electrons in the upper portion of the valence band. Thus, OH ions are oxidized by holes on Fe 3d states in the first step. These groups are transferred to S_2^2 sites in the second step. Surface analysis reveals preferential release of FeII from the pyrite lattice. A mechanism for the anodic dissolution of pyrite is proposed, according to which S is not an intermediate product, but is rather a stable end product which forms due to the decomposition of thiosulfate. The proposed mechanism is consistent with the observations reported by previous investigators.

- 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.
- 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.
- 202 Steger,HF (1982): The rejection of RU-1 due to ambient oxidation. Geostandards Newsletter 6(2), 249-255.
- 215 Watzlaf, George R; Hammack, Richard W (1989): The effect of oxygen, iron-oxidizing bacteria, and leaching frequency on pyrite oxidation. In: Proceedings of the Ninth Annual West Virginia Surface Mine Drainage Task Force Symposium. (Eds: West Virginia Surface Mine Drainage Task Force; West Virginia Mining & Reclamation Association) West Virginia Surface Mine Drainage Task Force and West Virginia Mining & Reclamation Association, Morgantown, West Virginia,.

Abstract. The major objective of this study was to examine the rate of pyrite oxidation in column leaching tests and to relate these results to commonly used field abatement techniques. Specific objectives included determining the evfect of oxygen, leaching frequency, and weathering on the biotic oxidation rate as well as the effect of oxygen on the abiotic rate. Pyrite oxidation was studied under various conditions using small (40 cm x 2.54 cm ID) and large (1.92 m x 0.29 m ID) column leaching tests. The small c olumns contained 5 g of pyrite mixed with 100 g of inert silica sand. The large columns were filled with 175 kg of unweathered pyritic shale containing 3.5% S. In the small column experiments, biotic oxidation of pyrite was faster than abiotic oxidation at all levels of oxygen tested with the largest difference occurring at the lowest oxygen level tested (0.5%). Biotic oxidation of pyrite at applied oxygen levels of 0.5, 1, 5, and 10% measured 12.9, 15.2, 13.2 and 16 mg SO₄/day, respectively. Abiotic oxidation rates of 1.9, 8.3, 11, and 14.8 mg SO4/day were observed for columns exposed to 0.5, 5, 9.6, and 14.5% oxygen. This suggests that unless the bacteria are inhibited, pyrite oxidation proceeds at approximately the same rate at any oxygen level above 0.5%. In the large column experiments, pyrite oxidation, based on sulfate release, was calculated at 18.2 gSO₄/day for unsaturated leaching. After the material was saturated with water, the rate of pyrite oxidation resulting from biweekly flushings with oxygenated water was reduced to 0.7 g SO₄/day. In anouther test, comparison of water quality of leachates from fresh material to weathered (26% less S) material showed no differences in release rates of sulfate (14.4 - 13.1 g/day), iron (4.26 -4.20 g/day), or aluminum (0.29 - 0.27 g/day). Release rates for Mn, Ca, Mg, and Na were reduced by weathering to values 12.6, 23.2, 4.3 and 56.2% pf the values from the fresh leaching tests, respectively. Partial pressures of CO₂ were reduced from between 0.8 and 3.2 to 0.01 and 0.4. Weathering caused oxygen to penetrate deeper into the material inferring the downward movement of the acitve pyrite oxidation zone with time.

Additionally, four different leaching schedules were tested: 1 L every day, 7 L every 7 days, 14 L every 14 days, and 21 L every 21 days. The results indicated that leaching frequency did not have a significant effect on any water quality parameter or on pore gas composition.

224 Blevins, Dale W; Chafin, Daniele T (1988): Determination of chemical processes in coal mine spoil in west-central Missouri using sulfur and oxygen isotopes. In: 1988 Symposium on Mining, Hydrology, Sedimentology and Reclamation. (Ed: University of Kentucky) University of Kentucky, Lexington, Kentucky, 53-57.

Abstract. Iron disulfide and gypsum are common constituents of the unmined coal bearing rocks of the Pennsylvanian age in MO. Consequently, the two most probable sources of dissolved sulfate in mine spoil are the oxidation of iron disulfides and dissolution of gypsum. The δ^{34} S values of iron disulfide and gypsum were too similar to identify the source of sulfur in the dissolved sulfate. Oxygen isotopes in dissolved sulfate were used to determine whether ferric iron or dissolved oxygen was the principal oxidizer of iron disulfides in the acidic spoil of the study area. When ferric iron is the principal oxidizer, sulfate oxygen comes entirely from the water molecule. However, when oxygen is the principal oxidizer, atmospheric oxygen theoretically contributes 87.5% of the sulfate oxygen and water contributes the remaining. The δ^{18} O values of meteoric water ranged from -5.8 to +4.4 permil and averaged +0.4 permil., which is similar to δ^{18} O values in dissolved sulfate that ranged from -1.95 to +3.75 permil and averaged -0.06 permil, indicating ferric iron is the principal oxidizer of iron disulfides. The δ^{18} O values fro sulfate oxygen in the gupsum samples ranged from -0.7 to +15.8 per mil and averaged 5.8 permil, which is substantially heavier than that of water or dissolved sulfate. These data also indicate that dissolution of gypsum is a smaller source of dissolved sulfate than iron disulfide oxidation.

Hammack, Richard W (1985): The relationship between the thermal activity of pyrite and the rate of acid generation. In: 1985 Symposium on Surface Mining, Hydrology, Sedimentology, and Reclamation. (Ed: University of Kentucky) University of Kentucky, Lexington, Kentucky, 139-144.

Abstract. An evolved gas analysis technique that provides a quick and simple determination of pyrite reactivity has been developed by the USBOM. This method employs a furnace for the programmed heating of overburden samples in an oxidizing atmosphere. The evolution of sulfur dioxide is monitored by an infrared analyzer and recorded simultaneously with the sample termperature. Pyrite oxidizes to sulfur dioxde and hematite at sample temperatures ranging from 150-550 C. Pyrite displaying "normal" reactivity ignites at T>300C, whereas pyrite displaying "aberrant" reactivity ignites at T< 200C.

Seven of 25 overburden samples examined in this study contained pyrite that ignited at T> 200C. All seven samples containing "aberrant pyrite" reulted in significantly higher leachate conductivities in humidity cell weathering tests. Evolved gas analysis (EGA) thus can identify material that may significantly affect water quality. Wen used in conjunction with ABA, EGA provides a better prediction of resultant water quality than does ABA alone.

"Aberrant" and "normal" pyrite concentrates were examined by XPS, XRD, and EGA to determine the cause of the anomalous reactivity and the apparent dependence of this reactivity on the "freshness" of the sample. XPS revealed that significantly more iron disulfide is present within 30 angstroms of the surface of "aberrant pyrite". More stable forms exhibited coatings of sulfate salts and iron oxides that inhibited reactivity.

226 Lai,RW; Diehl,JR; Hammack,RW; Khan,SUM (1989): Comparative study of the surface properties and the reactivity of coal pyrite and mineral pyrite. In: Society of Mining Engineers. (Ed: Society of Mining Engineers) Society of Mining Engineers, Littleton, Colorado, 1-13.

Abstract. Cyclic voltammetry, flotation response, evolved gas analysis, and XPS were employed to evaluate the major differences in the surface property and surface reactivity of coal pyrite and mineral pyrite. Surface properties of pyrite were evaluated in terms of flotation response in the presence of both an anionic fluorosurfactant and sodium hydrosulfide. The carge transfer adsorption and oxidation potential of sodium hydrosulfide were evaluated using CV. Cuurent voltage dependence indicated that the coal pyrite behaved as an n-type semiconductor and that the mineral pyrite acted as a p-type semiconductor. Drastic differences in the flotation response have been observed between the coal pyrite and the mineral pyrite. Significant differences in the CV's at pyrite surfaces of these two sources were also observed. Measurements by XPS and EGA were used to determine the oxidation products and the rate of oxidation of the coal pyrite and the mineral pyrite surfaces.

227 Pahlman, JE; Reimers, GW (1986): Thermal gravimetric analysis of pyrite oxidation at low temperature. Bureau of Mines: Report of Investigations 9059, 1-12.

Abstract. Spontaneous oxidation and combustion of sulfides and resultant fires are serious problems in underground mines. The US BOM has conducted fundamental TGA research to determine the mechanisms and factors governing the rate of low-T pyrite oxidation, and to identify possible inhibitors to spontaneous oxidation and combustion. The mechanism of low-T pyrite oxidation was found to be topochemical, meaning that the oxidation process is controlled by the chemical reaction at the interface between pyrite and iron sulfate. An activation energy of 8.9 kcal/mor pyrite was obtained for oxidation of -500 mesh pyrite in an atmosphere of 60 vol pct water vapor and 40 vol pct O_2 . Water vapor content of the atmosphere was found to be the critical factor in the rate of spontaneous oxidation. The rate of pyrite oxidation is also greatly affected by the particle size of pyrite. Pyrite oxidation rate increased drastically for particles less than 40 um. RT pyrophoric behavior was observed for freshly ground unoxidized pyrite (55% at -5 um) upon exposure to air. Addition of water adsorbing materials such as activated alumina decreased the rate of pyrite oxidation.

237 Nordstrom, Darrell Kirk (1982): Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. Chap. 3. In: Acid Sulfate Weathering. (:) Soil Science Society of America, Madison, WI, 37-56.

Abstract. The oxidation of pyrite in aqueous systems is a complex biogeochemical process involving several redox reactions and microbial catalysis. This paper reviews the kinetic data on pyrite oxidation, compares available data on the inorganic vs. microbial oxidative mechanisms and describes the occurrence of mineral products resuting from pyrite oxidation. Although oxygen is the overall oxidant, kinetic data suggests that ferric iron is the direct oxidant in acid systems and that temperature, pH, surface area, and the presence of iron and sulfur oxidizing bacteria can greatly affect the rate of reaction. The vast amount of literature on the microbial and geochemical investigations on this subject have limited usefulness for understanding natural systems. Additional research is needed on the hydrologic, geologic and microbiologic characteristics of field sites where oxidation occurs. The acid water resulting from pyrite oxidation may precipitate a large suite of soluble and insoluble iron minerals depending on pH, degree of oxidation, moisture content, and solution composition.

246 Singer, Philip C; Stumm, Werner (1970): Acidic mine drainage: The rate-determining step. Science 167, 1121-1123.

Abstract. The rate-determining step in the oxidation of iron pyrite and the formation of acidity in strams associated with coal and copper mines is the oxidation of ferrous iron. Effective pollution abatement necessitates controlling this reaction.

248 Morth,AH; Smith,Edwin E (1966): Kinetics of the sulfide-to-sulfate reaction. In: Symposium on Fossil Fuels and Environmental Pollution. Vol. 10. (151st National Meeting: American Chemical Society, Division of Fuel Chemistry) (Ed: American Chemical Society) American Chemical Society and Division of Water, Air, and Waste Chemistry, Washington DC, 83-92.

Objective: the attempt to define kinetics of the rate-determining mechanism and the role of oxygen and water in the kinetics of chemical pyrite oxidation

- 261 Sullivan, Patrick J; Yelton, Jennifer L (1988): Iron sulfide oxidation and the chemistry of acid generation. Environmental Geology and Water Sciences 11(3), 289-295.
- 271 Kolling, Martin (1990): Modellierung geochemischer prozesse im sickerwasser und grundwasser. Beispier: Die pyritverwitterung und das problem saurer grubenwasser. Ph.D. Dissertation, Universitat Bremen. 136 p.
- 285 Rickard, DT (1969): The chemistry of iron sulphide formation at low temperatures. Chap. 4. In: Unknown. (Ed: Unknown) Vald. Pedersens Bogtrykkeri, Copenhagen, Denmark, 67-95.
- 291 Shumate,Kenesaw S; Smith,EE; Ricca,Vincent T; Clark,Gordon M (1976): Resources Allocation to Optimize Mining Pollution Control. (Contract No. 68-10-0724: EPA-600/2-76-112) Industrial Environmental Research Laboratory, Office of Research and Development and U.S. Environmental Protection Agency, Cincinnati, OH.
- 339 Shumate,KS; Smith,EE; Brant,RA (1969): A model for pyritic systems. American Chemical Society 13(2), 50-58.

The purpose of this paper is to present a model for the conceptualization of pyritic systems. The model draws principally on the type of descriptive framework commonly used in chemical engineering systems and is neither new nor controversial. Rather it is merely a restatement, in the context of pyritic systems, of the fundamental principles which describe virtually any reaction system. The model is intended to identify and provide a framework for integration of the numerous factors which determine the rate of acid release from any type of pyritic system associated with mining activity. It is hoped that this model will spark an increased level of critical discussion among those persons associated with acid mine drainage.

340 Smith, EE; Svanks, K; Halko, E (1969): Aerobic-anaerobic oxidation of pyrite. American Chemical Society 13(2), 68-78.

Abstract. There are two general approaches to control AMD: treatment of mine effluent or prevention or abatement of the sulfide oxidation which is responsible. This paper describes one phase of a basic study on the kinetics and mechanism of pyrite oxidation, a study which has provided information necessary to the analysis and evaluation of methods for abatement of AMD at its source. This study was made to clarify the machanism by which bacteria catalyze the oxidation of pyrite by using what is assumed to be a chemically analogous system. The regime of bacterial influence are described in terms of conditions at the reaction site. Bacterial-enhanced oxidation rates are compared to rates in a chemical system and the independence of the two mechanisms demonstrated.

342 Lorenz, Walter C; Stephan, Robert W (1969): Oxidation of pyrite associate with coal mines. Acid? Mine Drainage in Appalachia 2, C-D-1--C-D-21. 343 Stenhouse, James F; Armstrong, WM (1952): Aqueous oxidation of pyrite. The Canadian Mining and Metallurgical (CIM) Bulletin 55(January), 49-53.

Abstract. The aqueous oxidation of pyrite in caustic solutions under oxygen pressure was investigated by measuring the effect of reaction variables on oxygen consumption by the reactions. From the results of this investigation, a model for the process has been proposed. In this model, sulfur diffuses as a positive ion through an oxide layer which forms on the sulfide particles and is then oxidized to sulfate ion. Iron is oxidized by substitutional diffusion of oxygen atoms into the oxide layer. The effect of most reaction variables on the rate of oxygen consumption can be explained with this model.

344 McKay,DR; Halpern,J (1958): A kinetic study of the oxidation of pyrite in aqueous suspension. Transactions of the Metallurgical Society of AIME (June), 301-308.

Abstract. A kinetic study of the oxidation of pyrite in aqueous suspension by molecular oxygen, at T between 100 and 130°C, is described. The overall rate of oxidation is proportional to the pyrite surface area and to the oxygen partial pressure, and is independent of the composition of the solution. However, the latter is important in determining the distribution of products. High T and low acidities favor the formation of sulfuric acid while the opposite conditions are conducive to the production of elemental sulfur. The reactions involved and their mechanisms are discussed.

- 345 Subramanian,KN; Stratigakos,ES; Jennings,PH (1972): Hydrometallurgical processing of pyrrhotite. Canadian Metallurgical Quarterly 11(2), 425-433.
- 348 Kennedy, T; Sturman, BT (1975): Oxidation of iron (II) sulphide. J. Thermal Anal. 8, 329-337.
- 349 Downes,KW; Bruce,RW (1955): Recovery of elemental sulphur from pyrite and pyrrhotite. The Canadian Mining and Metallurgical (CIM) Bulletin 58(March), 127-132.
- 356 Biegler, T; Rand, DAJ; Woods, R (1975): Oxygen reduction on sulphide minerals: Part I. Kinetics and mechanism at rotated pyrite electrodes. Electroanalytical Chemistry and Interfacial Electrochemistry 60, 151-162.
- 361 Buehler,HA; Gottschalk,VH (1910): Oxidation of sulphides. Economic Geology 5, 28-35.

Experiments show that not only a measurable oxidation for moste sulfides treated, but also indicate that pyrite or marcasite, when mixed with other sulfides, causes a much more rapid oxidation o the second sulfide. We find, for instnace that sphalerite, galena, covellite, and enargite are oxidize from 8 to 20 times faster in the presence of an equal amount of pyrite or marcasite than when treated alone under the same conditions.

362 Gottschalk,VH; Buehler,HA (1912): Oxidation of sulphides. Economic Geology 7, 13-34.

Showed that 1) confirmed observations on the increased solubility of sulfides, in the presence of marcasite or pyrite; 2) shown that there is a complementary protection from oxidation of the pyrite or marcasite; 3) shown that there exists a difference of electro-motive force between the various natural minerals and arranged a number of these in a series analogous to the electro-chemical series of the metals; 4) shown that the minerals, when in contact and moistened, act as batteries; 5) indicated that such contact may be an important factor in the general process of oxidation of the natural minerals.

410 Trexler, Bryson D; Ralston, Dale R; Renison, William; Williams, Roy E (1974): The hydrology of an acid mine problem. Water Resources Problems Related to Mining (June), 32-40.

- 429 Wentz, Dennis A (1974): Effect of Mine Drainage on the Quality of Streams in Colorado. (Circular No. 21) Colorado Water Conservation Board, Colorado Water Resources, Denver, CO. 118 pages.
- 440 Erickson,Patricia M; Hammack,Richard W; Kleinmann,Robert LP (1800): Prediction of acid drainage potential in advance of mining. In: Control of Acid Mine Drainage: Proceedings of a Technology Transfer Seminar. (IC #9027) (Ed: Staff,Bureau of Mines) U.S. Department of the Interior, Bureau of Mines, Unknown, 3-11.
- Krothe, Noel C; Edkins, John E; Schubert, Jeffrey P (1980): Leaching of metals and trace elements from sulfide-bearing coal waste in Southwestern Illinois. In: Symposium on Surface Mining, Hydrology, Sedimentology, and Reclamation. (December 1-5) (Ed: Unknown) University of Kentucky, Lexington, Kentucky, 455.
- 448 Banaszak, Konrad J (1981): Predicted changes in the mineralogy of spoil as a function of net neutralization potential and rate of flushing. In: Symposium on Surface Mining, Hydrology, Sedimentology, and Reclamation. (December 7-11) (Ed: Unknown) University of Kentucky, Lexington, Kentucky, 459.
- 489 Bhumbla,DK; Singh,RN; Keefer,RF (1990): Retardation of pyrite oxidation by massive fly ash application to mine spoils. In: Proceedings of the 1990 Mining and Reclamation Conference and Exhibition. Vol. 2. (Eds: Skousen,Jeff; Sencindiver,John; Samuel,Dave) Unknown, Unknown, 469.
- 500 Aplan, FF (1993): Coal properties dictate coal flotation strategies. Mining Engineering 45(1, January), 83-96.
- 512 Morrison, JL; Scheetz, BE; Strickler, DW; Williams, EG; Rose, AW; Davis, A; Parizek, RR (1990): Predicting the occurrence of acid mine drainage in the Alleghenian coal-bearing strata of western Pennsylvania; An assessment by simulated weathering (leaching) experiments and overburden characterization. In: Recent Advances in Coal Geochemistry: Geological Society of America Special Paper 248. (Eds: Chyi, LL; Chou, CL) Geological Society of America, Unknown, 87-99.
- 520 Caruccio,FT (1800): Characterization of strip-mine drainage by pyrite grain size and chemical quality of existing groundwater. In: Ecology and Reclamation of Devastated Land. Vol. 1. (Eds: Hutnik,Russell J; Davis,Grant) Gordon and Breach, New York, 193-225.
- 558 Lutwick, Gerald D (1986): An Unsolicitied Proposal to Develop a Rapid Method of Determining Net Acidity in Rock Quarries. Nova Scotia Research Foundation Corporation, Dartmouth, Nova Scotia, Canada. 7 pages.
- 559 Lutwick, Gerald D (1986): Mineral Composition and Acid Consuming Potential of Nova Scotia Shales. Nova Scotia Research Foundation Corporation, Dartmouth, Nova Scotia, Canada. 32 pages.
- 575 Renton, John J; Stiller, Alfred H; Rymer, Thomas E (1985): Evaluation of the acid producing potential of toxic rock materials. In: Stopping Acid Mine Drainage: A New Approach. (Ed: Unknown) West Virginia Geological and Economic Survey, Morgantown, 7-12.
- 583 Halbert, BE; Scharer, JM; Knapp, RA; Gorber, DM (1983): Determination of Acid Generation Rates in Pyritic Mine Tailings. SENES Consultants Limited, Toronto, Ontario.

Summary. The case study discussed in this paper is concerned with the assessment of acid generation in pyritic tailings from a base metal mine in the subarctice region of Canada. A series of lab-scale studies were performed to determine the biotic rate of pyritic sulfur oxidation. Rates and activation energies appear in table 2 (page 6).

- Hansen, BJ (1979): Mine and Concentrator Waste Characterization Studies for the Crandon Project. 584 Exxon Minerals Company, U.S.A, Unknown. 45 plus appendix pages.
- Burt, Ronald A; Caruccio, Frank T (1986): The effect of limestone treatments on the rate of acid 626 generation from pyritic mine gangue. Environmental Geochemistry and Health 8(3), 71-78.
- O'Hagan, Mike; Caruccio, Frank T (1986): The Effect of Admixed Limestone on the Rates of Pyrite 627 Oxidation in Low, Medium, and High Sulfur Rocks. In: 1986 National Symposium on Mining, Hydrology, Sedimentology, and Reclamation. (Symposium held December 8-11, 1986) (Ed: University of Kentucky) University of Kentucky, Lexington, Kentucky, 155.

Abstract. To simulate conditions within an admixed gob pile or reclaimed backfill, the following leaching experiment was conducted. Three different rock types, and alkaline shale $(S_T = 0.25\%)$ a non-alkaline shale $(S_T = 1.07\%)$ and a preparation plant refuse $(S_T = 4.40\%)$ were admixed with varying weight percentages of limestone. Limestone was admixed at rates of 1, 2, 3, and 5 wt% for each rock type. The experiment consisted of 16 samples; 4 controls and 12 admixed samples. The admixed samples and controls were analyzed for a variety of whole rock parameters. The samples were placed in inert PVC columns and leached for 12 weeks, followed by an 8 week hiatus followed by a second stage of 4 weekly leachings. Leachates were analyzed for pH, SC, alkalinity, SO₄, Fe, Ca, and MG, and confirmatory tests for the presence of T. ferrooxidans.

Leachates produced by the alkaline shale were neutral to alkaline. This is attributed to a low S content, a hugh intrinsic neutralization potential before admixing, and the absence of T. ferrooxidans. Admixed limestone served to augment the preexisting neutralization potential of these samples.

The medium S, non-calcerous shale produced leachates ranging from acid to neutral/slightly acid to alkaline. Leachates from the control sample contained moderate levels of Fe while leachate emanating from the admixed samples contained no iron. During the second leaching stage of the experiment, leachates from the columns with 1-2% limestone became acid in nature, as the limestone declined in effectiveness and pyrite oxidation went from an inorganic to organic admixed limestne, all of the samples tested positive for T. ferrooxidans. Admixed limestone was effective in neutralizing oxidation products and delaying the onset of acidification in the medium S samples.

The high S rock samples produced highly acid, Fe-rich leachates during the course of the experiment. Admixed limestone accounted for a slight difference in acidity and Fe levels as compared to the control sample. Theis differece is probably the result of processes including neutralizsation and precipitation of acidity and Fe by reaction with limestone, consumption of acidity as the result of destruction of alumino-silicates and consequent neomineralization of alumnum as beohmite clay and alunite, and the formation of gypsum. All of the samples tested positive for T. ferrooxidans.

628 Geidel, Gwendelyn (1979): Alkaline and acid production potential of overburden material: The rate of release. Reclamation Review 2, 101-107.

Abstract. The quality of coal mine drainage is a function of the balance between the acid and alkalined production potentials. The acidity is derived primarily from the oxidation of pyrite and the subsequent hydrolysis of the weathering products. Alkalinity is produced by the dissolution reaction between calcium carbonate and water. The kinetics of both systems

are markedly different and the concentrations of acidity or alkalinity are time dependent.

Simulated weathering tests of acid and alkaline producing rocks showed that the rates of reactions of the two systems were different. The amount of acidity released was proportional to the time interval between flushings. This is possibly explained by the continued oxidation of pyrite through time. The degree of accumulation of weathering products which are readily soluble in water, is correlative with the degree of acidity released at the time the sample is rinsed with water.

Alkalinity production, however, is limited by the solubility of calcium carbonate in water which at a given P_{CO2} has a maximum neutralizing potential. Simulated weathering tests indicated that the amount of alkalinity produced at various flushing intervals was similar. These data suggest that the time interval between flushing is critical to the prevention of acidic drainages in strip mines that contain potentially neutralizing material.

- 691 Peters, E; Majima, H (1800): Electrochemical reactions of pyrite in acid perchlorate solutions. Canadian Metallurgical Quarterly 7(3), 111-117.
- 697 Smith, EE; Svanks, K; Shumate, K (1800): Sulfide to sulfate reaction studies. In: Unknown. (:),, 1-11.
- 699 Morth,AH; Smith,EE; Shumate,KS (1800): Pyritic systems: A mathematical model. In: Unknown. (:),, 132-137.

Researchers at OSU have begon a systematic analysis of mine drainage to coordinate information and ideas from diverse fields. The object of this analysis is to develop a mathematical model of pyritic systems. A useful model must quantitatively relate the physical and chemical parameters of apyritic systems to the rate of pollution discharge across the boundaries of the system. Suc a model would accurately predict long term effects of mining operation, abatement procedures, and other conditions imposed on the system. Of equal importances i the ability to predict surges and peak flows of acid.

Development of the mathematical model depends on identifying what is known and what must be evaluated in the system. The best and simplest starting point in the pyritic oxidation system is kinetic relationships estimated solely from the physical-chemical parameter of the system. Calculated kinetic data can then be compared with experimentally determined values to give a direct, independent check on the validity of the physical model. The model will be checked and refined using pyritic systems now under study.

The final area of concern is the technique of comparing "micro" laboratory data with "macro" natural systems. A natural system is not just many identical micro systems placed side by side but rather a collage of differend micro systems.

- 720 Ramadorai,G; Mishra,RK (1988): Roasting of arsenical gold and silver-bearing minerals. Chap. 2. In: Proc. 1988 TMS Annual Meeting and Exhibition: Arsenic Metallurgy--Fundamentals and Applications Symposium. (Symposium held at Pheonix, AZ, January 25-29) (Eds: Reddy,RG; Hendrix,JL; Queneau,PB) The Metallurgical Society, Inc., Warrendale, PA, 161.
- 721 Stefanakis,M; Hassapis,D; Demetriades,D; Kontopoulos,A (1988): Dearsenifying roasting and gold extraction from a refractory pyrite concentrate. Chap. 2. In: Proc. 1988 TMS Annual Meeting and Exhibition: Arsenic Metallurgy--Fundamentals and Applications Symposium. (Symposium held at Pheonix, AZ, January 25-29) (Eds: Reddy,RG; Hendrix,JL; Queneau,PB) The Metallurgical Society, Inc., Warrendale,PA, 173.
- 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.

817 Harries, JR; Ritchie, AIM (1986): The impact of rehabilitation measures on the physicochemical conditions within mine wastes undergoing pyritic oxidation. Chap. 7. 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, 341-351.

Abstract. Bacterially catalyzed oxidation of pyritic material in mine wastes can be a major source of pollution. There is therefore considerable interest in cost-effective methods of reducing the oxidation rate to acceptable levels. Two waste rock dumps which are such pollution sources have been studied. Rehabilitation measures designed to reduce the influx of air and water to the wastes have been implemented on one of the waste dumps.

Temperatures started to fall significantly in those parts of the dump where previously the oxidation rate was high within about a month of rehabilitation. Oxygen levels fell even more dramatically. In parts of the dump where previously there was thought to be little oxidation and where oxygen levels were less than 1%, T also dropped indicating that oxidation was indeed occurring. In the other dump there is a large region where oxidation rates are high and clearly controlled by the rate of supply of oxygen. In other areas of this dump the oxygen levels are relatively constant at depths greater than 3 m from the surface but at the low level of about 0.03-0.05%. It is of considerable practical interest whether or not pollutants are generated in such areas by bacterially catalyzed processes.

- 819 Frenay, Jean; Michiels, Thierry; Ek, Cornelle (1986): Kinetics aspects in bioleaching of complex pyritic ores. Chap. 10. 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, 473-475.
- 823 Maylotte,DH; Spiro,CL; Lobos,JH; Holmes,DS (1986): A study of thiobacillus ferrooxidans penetration depth into lump coal using x-ray computed tomography. Chap. 10. 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, 483.
- 825 Ferguson, KD (1986): Static and kinetic methods to predict acid mine drainage. Chap. 10. 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, 486-488.
- 933 Harries, JR; Ritchie, AIM (1981): The use of temperature profiles to estimate the pyritic oxidation rate in a waste rock dump from an opencut mine. Water, Air, and Soil Pollution 15, 405-423.

Abstract. T distributions were measured in a dump of waste rock from an old opencut U mining operation in the Northern Territory of Autralia. The 20 yr old dump contained pyritic material, averaging about 3% S, which is known to be oxidizing. T ranged from 32-37 °C for most of the dump, but ranged up to 56 in one region. The temperature distrubutions were used to evaluate the heat source distrubutions which identify oxidation sites and are a direct measure o rates of oxidation within the dump.

Oxidation occurred in the top 5 m of the dump and at some sites down to 15 m from the

surface. Oxidation rates at the deep sites did not change over the 8 month period from the end of one wet season to the beginning of the next.

Harries, JR; Ritchie, AIM (1987): The effect of rehabilitation on the rate of oxidation of pyrite in a mine waste rock dump. Environmental Geochemistry and Health 9(2), 27-36.

Abstract. T profiles within a mine wate rock dump undergoing pyritic oxidation have been used to estimate the rate of oxidation and the sites where oxidation was occurring. The waste rock dump is located at the abandoned Rum Jungle mine site in NOrthern Australia and was a major source of pollution to the local river system. The dump was rehabilitated in 1983-84 by reshaping to reduce erosion and covering with clay and soil to reduce infiltration of water.

Heat source distributions were derived from T profiles measured in the dump. The oxidation of pyritic material is the main cause of heat i nthe dump, hence the rate and location of oxidation can be obtained from the distrubution of heat sources. A comparison of the heat source distributions before and after rehabilitation showed that rehabilitation greatly reduced or stopped the oxidation of pyrite in the dump.

935 Daniel, JA; Harries, JR; Ritchie, AIM (1980): Temperature distributions in an overburden dump undergoing pyritic oxidaton. In: Biogeochemistry of Ancient and Modern Environments. (Eds: Trudinger, PA; Walter, MR; Ralph, BJ) Springer-Verlag, Berlin Heidelberg NY, 630-636.

It has proved possible to produce heat source distributions as a function of depth from the surface of White's overburden heap by analyzing measurements of the T distributions in it. It is reasonable to associate the heat sources with the heat released in the oxidation of pyrites. The analysis has shown that significant pyritic oxidation occurs at depths of 10 m or greater in some parts of the heap. The analysis also shows that there is significant pyritic oxidation in the top 4 to 5 m in all parts of the heap. Estimates of heat input to the surface from insolation and better measurements of temperature changes near the surface will allow better estimates to be made of heat sources in the top 1 to 2 m.

- 970 Watkin, EM; Watkin, J (1983): Inhibiting pyrite oxidation can lower reclamation costs. Canadian Mining Journal 104(12, December), 29-31.
- 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.
- 993 Le Roux, NW; Wakerley, DS (1980): The leaching of sulfide ores by a thermophilic bacterium. In: Biogeochemistry of Ancient and Modern Environments. (Proc. 4th International Symposium on Environmental Biogeochemistry (ISEB) and Conference on Biogeochemistry in Relation to the Mining Industry and Environmental Pollution (Leaching Conference) in Canberra, Australia, 26 August-4 September 1979.) (Eds: Trudinger, PA; Walter, MR; Ralph, BJ) Springer-Verlag, Berlin-Heidelberg-New York, 451-457.
- 997 Tuovinen,OH; Hoffman,MR; Panda,FA; Tsuchiya,HM (1980): Inhibition by pyrite of bacterial iron oxidation activity. In: Biogeochemistry of Ancient and Modern Environments. (Proc. 4th International Symposium on Environmental Biogeochemistry (ISEB) and Conference on Biogeochemistry in Relation to the Mining Industry and Environmental Pollution (Leaching Conference) in Canberra, Australia, 26 August-4 September 1979.) (Eds: Trudinger, PA; Walter, MR; Ralph, BJ) Springer-Verlag, Berlin, 529-536.

- 999 Le Roux,NW; Dacey,PW; Temple,KL (1980): The microbial role in pyrite oxidation at alkaline ph in coal mine spoil. In: Biogeochemistry of Ancient and Modern Environments. (Proc. 4th International Symposium on Environmental Biogeochemistry (ISEB) and Conference on Biogeochemistry in Relation to the Mining Industry and Environmental Pollution (Leaching Conference) in Canberra, Australia, 26 August-4 September 1979.) (Eds: Trudinger,PA; Walter,MR; Ralph,BJ) Springer-Verlag, Berlin, 515-520.
- 1000 Temple, Kenneth L; Koehler, WA (1954): Drainage from bituminous coal mines. Engineering Experiment Station Research Bulletin (25), 3-35.
- 1001 Backes,CA; Pulford,ID; Duncan,HJ (1987): Studies on the oxidation of pyrite in colliery spoil. II. Inhibition of the oxidation by amendment treatments. Reclamation and Revegetation Research 6, 1-11.
- 1059 Bloch, J (1989): Sedimentation and early sulfide diagenesis of the Harmon Member (Peace River Formation), Western Canada. In: Water-Rock Interaction WRI-6. (Proc. 6th International Symposium, Malvern, UK) (Ed: Miles, Douglas L) A.A.Balkema, Rotterdam, Netherlands, 87-90.
- 1080 Rimstidt, J Donald; Newcomb, William D (1989): A comparison of pyrite oxidation rates in batch, mixed flow, and plug flow reactors. In: Water-Rock Interaction WRI-6. (Proc. 6th International Symposium, Malvern, UK) (Ed: Miles, Douglas L) A.A.Balkema; Rotterdam, Netherlands, 581-584.

Abstract. The oxidation of pyrite by ferric iron, a process involving as many as eight intermediate steps, is typical of many complex mineral/solution reactions. The reaction is very far from equilibrium so there is no significant back reaction. Furthermore, the rate of the reaction depends on the concentration of ferric iron raised to a fractional power. It is important to determine the reaction order of such complex reactions. A comparison of the three fundamentally different experiment types (batch, plug, and mixed flow reactors) showed that all give comparable alues for the rate constant and reaction order wheen the data were analyzed in terms of reaction rates versu7s ferric iron concentrations. The rate law that fits these results best is

$dn_{\text{FeIII}}/dt = 3.63 \text{ x } 10^{-5} \text{ A } \text{m}^{0.7}_{\text{FeIII}}$

This differential rate law can be integrated to predict the concentration versus time data from the batch and plug flow reactor experiments. On the other hand, fitting concentration versus time data for the atch and plug flow experiments to hypothesized integrated rate equations gave ambiguous results.

- 1091 Ammons, JT; Coburn, CB Jr; Shelton, PA (1800): An application of acid-base accounting for highway construction in east Tennessee. In: Unknown. (Ed: Unknown) Unknown, Unknown, 265-269.
- 1092 Mirza, Abbas H; Herrera, Miguel N; Doyle, Fiona M (1800): Characterization of pyrite-bearing materials by chemical oxidation. In: Unknown. (Ed: Unknown) Unknown, Unknown.
- Harrar, Norman J (1800): Solvent effects of certain organic acids upon oxides of iron. In: Unknown.
 (Ed: Unknown) Unknown, 50-61.
- 1119 Ferris, FG; Tazaki, K; Fyfe, WS (1989): Iron oxides in acid mine drainage environments and their association with bacteria. Chem. Geol. 74, 321-330.
- 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, pyrhotite, pentlandite, sphalerite, and chalcopyrite as the main sulfide ninerals. The tests were performed at eight different temps

(4-37C). The primary data were used for rate constant calculations, based on kinetic equations underlyig 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 explanied 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.

- 1123 Okereke, Amechi; Stevens, Edward S Jr (1991): Kinetics of iron oxidation by thiobacillus ferrooxidans. Applied and Environmental Microbiology 57(4), 1052-1056.
- 1124 Arkesteyn,GJMW (1980): Pyrite oxidation in acid sulphate soils: The role of microorganisms. Plant and Soil 54, 119-134.
- 1125 Reedy,Brian J; Beattie,James K; Lowson,Richard T (1990): Determination of sulphate isotopomers by vibrational spectroscopy. Spectrochimica Acta 46A(10), 1513-1519.
- 1135 Stefanakis,M; Hassapis,J; Demetriades,D; Kontopoulos,A (1988): Dearsenifying roasting and gold extraction from a refractory pyrite concentrate. In: Proc. 1988 TMS Annual Meeting and Exhibition: Arsenic Metallurgy--Fundamentals and Applications Symposium, Phoenix, AZ, January 25-29. (Eds: Reddy,R; Hendrix,JL; Queneau,PB) The Metallurgical Society, Inc., Warrendale, PA, 173.
- 1137 Lawrence, Richard W; Branion, Richard MR; Ebner, Hans G (1986): Fundamental and Applied Biohydrometallurgy. (Proc. 6th International Symposium on Biohydrometallurgy, Vancouver, BC, Canada, August 21-24, 1985) Elsevier, Amsterdam.
- 1140 Norris, PR; Parrott, L (1986): High temperature, mineral concentrate dissolution with Sulfolobus. 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, 355-365.
- 1143 Livesey-Goldblatt,Eric (1986): Bacterial leaching of gold, uranium, pyrite bearing compacted mine tailing slimes. 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, 89-96.
- 1177 Borek, Sandra L (1992): The Effect of Humidity on Pyrite Oxidation (DRAFT). U.S. Department of the Interior, Bureau of Mines, Pittsburgh, PA.
- 1181 Hinkle, Kenneth R (1984): Project Summary: Reclamation of Toxic Mine Waste Utilizing Sewage Sludge: Contrary Creek Demonstration Project, Addendum Report. (S2-84-016) U.S. Envrionmental Protection Agency, Municipal Environmental Research Laboratory, Cincinnati, OH. 4 pages.
- 1182 Hinkle, Kenneth (1982): Project Summary: Reclamation of Toxic Mine Waste Utilizing Sewage Sludge-Contrary Creek Demonstration. U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, OH. 4 pages.
- 1206 Ziemkiewicz, PF (1990): Advances in the prediction and control of acid mine drainage. Presented at 1990 Mining and Reclamation Conference and Exhibition, Charleston, West Virginia, April 23-26. p. 51-54.

- 1208 O'Shay, Tracey; Hossner, LR; Dixon, JB (1990): A modified hydrogen peroxide oxidation method for determination of potential acidity in pyritic overburden. J. Environ. Qual. 19, 778-782.
- 1209 Finkelman,Robert B; Giffin,David E (1986): Hydrogen peroxide oxidation: An improved method for rapidly assessing acid-generating potential of sediments and sedimentary rocks. Reclamation and Revegetation Research 5, 521-534.
- 1216 Batarseh, Kareem I; Swaney, Glenn P; Stiller, Alfred H (1989): A mathematical model for heterogeneous reactions with a moving boundary. AIChE Journal 35(4), 625-634.
- 1218 Per Age Beck, Veritas (1991): Acid mine drainage abatement in Norway. International Mine Waste Management News 1(3, October), 4-12.
- 1236 Wentz, Dennis A (1974): Stream quality in relation to mine drainage in Colorado. Water Resources Problems Related to Mining Unknown(June), 158-173. (Proc. No. 18)
- 1241 Brady, Keith BC; Smith, Michael W (1990): Pyritic sulfur analyses for coal overburden: Differences between laboratories. In: 1990 National Symposium on Mining. (:) University of Kentucky, Unknown, 53-58. (Lexington, KY, May 14-18, 1990)
- 1247 Wildeman, Thomas (1800): Drainage from coal mines: Chemistry and environmental problems. In: Summary of Literature Regarding AMD Control Technologies. (Ed: Terry I. Mudder Environmental Services Ltd.) Times Limited, Redmond, WA, Unknown.
- 1271 Lovgren, Lars; Sjoberg, Staffan (1992): Chemical speciation, solubilities and solid phase: Relations during weathering of sulphide-minerals. International Mine Waste Management News 2(2), 11.
- 1275 Huerta-Diaz, Miguel A; Carignan, Richard; Tessier, Andre (1993): Measurement of trace metals associated with acid volatile sulfides and pyrite in organic freshwater sediments. Environ. Sci. Technol. 27(12, November), 2367-2372.
- Liseth, Paul (1991): Abatement measures for the acid mine drainage at Skorovas Mine, Norway. In:
 Proc. 2nd International Conference on the Abatement of Acidic Drainage. Vol. 4. (Ed: MEND
 Program) Quebec Mining Association, Ottawa, 43-68.
- 1291 Lowson, Richard T; Reedy, Brian J; Beattie, James K (1991): An {+18}O{-2} tracer study of pyritic oxidation. In: Proc. 2nd International Conference on the Abatement of Acidic Drainage. Vol. 4. (Ed: MEND Program) Quebec Mining Association, Ottawa, 159-172.
- 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.
- 1294 Skousen, JG (1991): Cooperative efforts in solving and problems: The Surface Mine Drainage Task Force and the AMD Technical Advisory Committee. In: Proc. 2nd International Conference on the Abatement of Acidic Drainage. Vol. 4. (Ed: MEND Program) Quebec Mining Association, Ottawa, 229-234.
- 1316 Bennett, John W (1991): Measurements of the transport of oxygen into two rehabilitated waste rock dumps. In: Proc. 2nd International Conference on the Abatement of Acidic Drainage. Vol. 3. (Ed: MEND Program) Quebec Mining Association, Ottawa, 289-298.
- 1346 Jaynes, DB (1991): Modeling acid mine drainage from reclaimed coal stripmines. In: Proc. 2nd

International Conference on the Abatement of Acidic Drainage. Vol. 2. (Ed: MEND Program) Quebec Mining Association, Ottawa, 191-209.

- 1347 Scharer, JM; Garga, V; Smith, R; Halbert, BE (1991): Use of steady state models for assessing acid generation in pyritic mine tailings. In: Proc. 2nd International Conference on the Abatement of Acidic Drainage. Vol. 2. (Ed: MEND Program) Quebec Mining Association, Ottawa, 211-229.
- 1353 Ahmed, SM (1991): Electrochemical and surface chemical methods for the prevention of the atmospheric oxidation of sulphide tailings. In: Proc. 2nd International Conference on the Abatement of Acidic Drainage. Vol. 2. (Ed: MEND Program) Quebec Mining Association, Ottawa, 305-319.
- Yanful, Ernest K; St-Arnaud, Luc C (1991): The Waite Amulet hydrogeochemical evaluation. In: Proc.
 2nd International Conference on the Abatement of Acidic Drainage. Vol. 1. (Ed: MEND Program)
 Quebec Mining Association, Ottawa, 91-114.
- 1390 Kalin,M; Smith,MP (1991): Biological amelioration of acidic seepage streams. In: Proc. 2nd International Conference on the Abatement of Acidic Drainage. Vol. 1. (Ed: MEND Program) Quebec Mining Association, Ottawa, 355-368.
- 1391 Blenkinsopp,SA; Herman,DC; Costerton,JW (1991): The use of biofilm bacteria to exclude oxygen form acidogenic mine tailings. In: Proc. 2nd International Conference on the Abatement of Acidic Drainage. Vol. 1. (Ed: MEND Program) Quebec Mining Association, Ottawa, 369-377.
- Ritcey,GM (1991): Deep water disposal of pyritic tailings a simulation for acid prediction. In: Proc.
 2nd International Conference on the Abatement of Acidic Drainage. Vol. 1. (Ed: MEND Program)
 Quebec Mining Association, Ottawa, 421-442.
- 1417 Morin, Kevin A (1993): Rates of sulfide oxidation in submerged environments: Implications for subaqueous disposal. In: Proc. 17th Annual British Columbia Mine Reclamation Symposium: Mine Reclamation "Building Confidence". (Ed: Sponsored by: Mining Association of British Columbia) The Ministry of Energy, Mines and Petroleum Resources, British Columbia, 235-247.

Abstract. The placement of sulfide bearing tailings and rock in submerged environments has long been recognized as a primary technique for control of acid drainage, and recent field investigations provide further evidence of its success. However, subaqueous disposal does not automatically ensure that acid generation is completely halted. In fact, there are reasons why acid generation might not cease in a submerged environment.

Recent experimental data from a generic experiment and from the proposed Cinola Gold Project are reviewed to 1) obtain rates of pyrite oxidation under submerged conditons and 2) show that ferric iron apparently does not oxidize pyrite in the absence of DO. The rates are then used to estimate consumption of DO along groundwater flowpaths and to determine a first order rate relationship between reaction rate and DO for calculations of DO diffusion. Three relatively simple examples show how to apply the concepts and equations. One example for oxygen diffusion shows that, for constant values of porosity and pyrite content, tailings will generate more acidity than coarse rock because of the steeper oxygen gradients within the tailings. The major conclusions drawn from this work are that site specific conditions dominate in determining the eventual water chemistry and that environmental (hydrogeological) conditions of the disposal site should be well defined. In this way, the site specific rates and concentrations can be determined and, if necessary, details of the subaqueous disposal can be refined for optimum performance.

1424 Murray, Eric W; Goudey, S Paul; McCready, Ron GL; Salley, Joe (1988): Laboratory and field testing of a salt-supplemented clay cap as an impermeable seal over pyritic slates. In: Mine drainage and

surface mine reclamation. Vol. 1: Mine water and mine waste. (Ed: Bureau of Mines) U.S. Department of the Interior, Pittsburgh, 52-58.

- Backes, CA; Pulford, ID; Duncan, HJ (1988): Treatments to combat pyrite oxidation in coal mine spoil.
 In: Mine drainage and surface mine reclamation. (Ed: Bureau of Mines) U.S. Department of the Interior, Pittsburgh, 91-96.
- 1436 Chander,S; Briceno,A (1988): The rate of oxidation of pyrites from coal and ore sources An AC impedance study. In: Mine drainage and surface mine reclamation. Vol. 1: Mine water and mine waste. (Ed: Bureau of Mines) U.S. Department of the Interior, Pittsburgh, 164-169.

Abstract. The rate of oxidation of pyrites from coal and mineral sources has been determined using a new technique of AC impedance spectroscopy. In this technique the impedance of the pyrite/solution interface is measured as a function of frequency from which the charge transfer resistance can be calculated. From the charge transfer resistance the rate of oxidation is calculated using the Stern-Geary equation. The resuts show that the rate of oxidation of the pyrite sample from a coal source is substantially greater than the corresponding rate of oxidation of the pyrite sample from an ore source. The charge transfer resistance of the ore pyrite increases with the extent of oxidation whereas the coal pyrite showed now such increase. In the case of ore pyrite the surface film acts as a passivating layer and retards the rate of oxidation. The formation of a protective film on coal pyrite is not observed.

- 1439 Ammons, JT; Shelton, PA (1988): A comparison of results from acid-base accounting versus potential acidity measured by the peroxide oxidation of weathered and unweathered soils containing pyrite. In: Mine drainage and surface mine reclamation. Vol. 1: Mine water and mine waste. (Ed: Bureau of Mines) U.S. Department of the Interior, Pittsburgh, 206-209.
- Hedin,Robert S; Hyman,David M; Hammack,Richard W (1988): Implications of sulfate-reduction and pyrite formation processes for water quality in a constructed wetland: Preliminary observations. In: Mine drainage and surface mine reclamation. Vol. 1: Mine water and mine waste. (Ed: Bureau of Mines) U.S. Department of the Interior, Pittsburgh, 382-388.
- 1473 Wicks, CM; Herman, JS; Mills, AL; Schubert, JP (1988): Iron monosulfide and pyrite formation in sediments of lakes that receive acid mine drainage. In: Mine drainage and surface mine reclamation. Vol. 1: Mine water and mine waste. (Ed: Bureau of Mines) U.S. Department of the Interior, Pittsburgh, 402.
- 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.
- Byerly,Don W (1990): Guidelines for handling excavated acid-production material. 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, 109-131. (N)
- 1503 Dave,Nand K; Lim,Tjoe P; Vivyurka,Albert J; Bihari,Biman; Kay,David A (1990): Development of wet barriers on pyritic uranium tailings Elliot Lake, Ontario: Phase I. 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, 295-310.
- 1504 Collin, Marie; Rasmuson, Anders (1990): Mathematical modelling of water and oxygen transport in

layered soil covers for deposits of pyritic mine tailings. 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, 311-333. (N)

- Dave,Nand K; Lim,Tjoe P; Chakravatti,Jawahar L (1990): Hydrogeochemical evolution of an experimental thickened tailings pile of pyritic uranium tailings. 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, 335-351. (N)
- 1525 McCready,RGL (1987): A review of the physical, chemical and biological measures to prevent acid mine drainage: An application to the pyritic Halifax shales. In: Proc. acid mine drainage seminar/workshop. (Seminar held in Halifax, Nova Scotia, March 23-26) (Ed: Environment Canada) Environment Canada, Ottawa, 333-355.
- Doolittle,JJ; Frisbee,NM; Hossner,LR (1992): Evaluation of acid/base accounting techniques used in surface-mine reclamation. In: Achieving land use potential through reclamation. (ASSMR9-92) (Ed: American Society for Surface Mining and Reclamation) American Society for Surface Mining and Reclamation, WV, 68-76.
- 1544 Watzlaf, George R (1992): Pyrite oxidation in saturated and unsaturated coal waste. In: Achieving land use potential through reclamation. (ASSMR9-92) (Ed: American Society for Surface Mining and Reclamation) American Society for Surface Mining and Reclamation, WV, 191-205.
- 1564 Nielsen, Kai (1988): Mining in Norway. Chap. 1. In: Proc. International Conference on Control of Environmental Problems from Metal Mines. (Program excursion map and schedule in back of book) (Eds: State Pollution Control Authority; Federation of Norwegian Industries) State Pollution Control Authority, Norway, 10 p.
- 1568 Aanes, Karl Jan (1988): Environmental impact of pyrite mining and dressing on a mountain stream in Norway. Chap. 5. In: Proc. International Conference on Control of Environmental Problems from Metal Mines. (Eds: State Pollution Control Authority; Federation of Norwegian Industries) State Pollution Control Authority, Norway, 17pages.
- 1590 Rasmuson, Anders; Collin, Marie (1988): Mathematical modelling of water and oxygen transport in layered soil covers for deposits of pyritic mine tailings. Chap. 28. In: Proc. International Conference on Control of Environmental Problems from Metal Mines. (Eds: State Pollution Control Authority; Federation of Norwegian Industries) State Pollution Control Authority, Norway, 32pages.
- 1593 Byerly, Don W (1988): Using pyritic rock with high acid potential in road construction. Chap. 31. In: Proc. International Conference on Control of Environmental Problems from Metal Mines. (Eds: State Pollution Control Authority; Federation of Norwegian Industries) State Pollution Control Authority, Norway, 12pages.
- Doyle, Fiona M; Mirza, Abbas H (1990): Understanding the mechanisms and kinetics of acid and heavy metal release from pyritic wastes. Chap. 6. In: Mining and mineral processing wastes. (Proc. Western Regional Symposium on Mining & Mineral Processing Wastes) (Ed: Doyle, Fiona M) Soc. for Mining, Metallurgy, and Exploration, Inc., Littleton, CO, 43-51.
- 1607 Ziemkiewicz,PF; Stiller,AH; Rymer,TE; Hart,WM (1990): Advances in the prediction and control of acid mine drainage. Chap. 12. In: Mining and mineral processing wastes. (Proc. Western Regional Symposium on Mining and Mineral Processing Wastes, Berkeley, CA, May 30-June 1) (Ed: Doyle,Fiona M) Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO, 93-101.

- 1611 Stewart,Bill M; Lambeth,Robert H; Williams,Barbara C (1990): Effects of pyritic tailings in an abandoned impoundment on downgradient groundwater quality. Chap. 16. In: Mining and mineral processing wastes. (Proc. Western Regional Symposium on Mining and Mineral Processing Wastes, Berkeley, CA, May 30-June 1) (Ed: Doyle,Fiona M) Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO, 133-143.
- 1658 Mirza, Abbas H; Herrera, Miguel N; Doyle, Fiona A (1992): Characterization of pyrite-bearing materials by chemical oxidation. Chap. 17. In: Emerging process technologies for a cleaner environment. (Proc. Symposium on Emerging Process Technologies for a Cleaner Environment, February 24-27, Phoenix, Arizona) (Eds: Chander, S; Richardson, PE; El-Shall, H) Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO, 121-129.
- 1659 Chander,S; Zhou,R (1992): Effect of organic additives on acid generation from pyrite waste. Chap. 18. In: Emerging process technologies for a cleaner environment. (Proc. Symposium on Emerging Process Technologies for a Cleaner Environment, February 24-27, Phoenix, Arizona) (Eds: Chander,S; Richardson,PE; El-Shall,H) Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO, 131-139.
- 1685 Borek, Sandra L (1994): Effect of humidity on pyrite oxidation. Chap. 3. 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, 45-58.

Abstract. The amounts of weathering products formed during abiotic chemical pyrite oxidation was dependent on relative humidity and time. Six pyrites wereplaced under four relative humidities (34%,50%, 70%, 79%). These samples were periodically analyzed using Mossbauer spectroscopy to determine the types and amounts of weathering products formed. Hematite was present in Waldo pyrite samples after 30 days in all experimental humidity conditions. Ferrous sulfates (melanterite and rozentie) were detected in the three sedimentary pyrites after 30 days in 79% RH and after 90 days in 50, 70 and 79%RH conditions. Two hydrothermal pyrites displayed no significant weathering over time in any RH.

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 FeIII ppt'n 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, vis. covellite, jarosites, and 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. The environmental impact of pollutants generated by the oxidation of pyrite in mine wastes involves a number of processes which have very different characteristic timescales. In the first instance water quality estimates require the convolution of pollutant generation in water transport through the wastes followed by convolution with water transport through the aquifer underlying the wastes. As a significant fraction of the wastes may be unsaturated, transit times may be two orders of magnitude greater than those in the saturated aquifer. Such a difference requires care in interpreting the impact of rehabilitation measures. The pollution generation rate within the wastes also depends on a number of interacting processes with greatly differing timescales. For example oxidation rates of pyrite under optimiz conditions are typically three orders of magnitude greater than 'high' oxidation rates measured in wastes. In this paper these various rates and the influence that they have on the overall environmental impact is discussed. Data on some important mechanisms is sparse and some indication is given as to how this situation may be rectified.

1690 Ritchie, AIM (1994): Rates of mechanisms that govern pollutant generation from pyritic wastes. Chap.
9. 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, 108-122.

Abstract. The environmental impact of pollutants generated by the oxidation of pyrite in mine wastes involves a num ber of processes which have very different characteristic timescales. In the first instance water quality estimates require the convolution of pollutant generation in and water transport through the wast3s followed by convolution with water transport through the aquifer underlying the wastes. As a significant fraction of the wastes may be unsaturated, transit times may be two orders of magnitude greater than those in the saturated aquifer. Such a difference requires care in interpreting the impact of rehabilitation measures. The pollution generation rate within the wastes also depends on a number of interacting processes with greatly differeng timescales. For example oxidation rates of pyrite under optimized conditions are typically three orders of magnitude greater than 'high' oxidation rates measured in wastes. In this paper these various rates and the influence that they have on the overall environmental impact is discussed. Data on some important mechanisms is sparse and some indication is given as to how htis situation may be rectified.

1692 Scharer, Jeno M; Nicholson, Ronald V; Halbert, Bruce; Snodgrass, William J (1994): A computer program to assess acid generation in pyritic tailings. Chap. 11. 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, 132-152.

Abstract. A computer program known as Reactive Tailings Assessment Program (RATAP) was developed to assist in predicting acid generation and major hydrogeochemical events brought about by the chemical and microbiological oxidation of sulfide minerals. The objective of the program is the application of fundamental kinetic and physical knowledge to field conditions for simulating the rate of acid production with time, simulating porewater quality in space and time.

The kinetics of the abiotic and biological oxidations are key components of the program. The primary variables include the composition of the sulfide minerals, the specific surface area, the partial pressure of oxygen, the temperature and the pH. In addition, biological reaction rates depend on the sorption equilibrium of the bacteria on the sulfide surface, the moisture content, and the availability of CO_2 and other macronutrients.

The tailings soil profile is subdivided into layers comprising the unsaturated zone, the capillary fringe, and the saturated zone. Acid productio occurs primarily in the unsaturated zone. A major control on the acid generation rate is the diffusive vflux of oxygen in the pore space of the unsaturated zone. The diffusion coefficient, in turn is related to the moisture content in a given zone.

Computations are carried out at monthly time steps. The program can be run in a dterministic or probablilistic manner. For probablilistic assessment, and additional module known as RanSIM is utilized for the allocation of distributed parameter values. The program has been employed successfully to simulated field data at several tailings sites.

1699 Fuge,Ron; Pearce,Fiona M; Pearce,Nicholas JG; Perkins,William T (1994): Acid mine drainage in Wales and influence of ochre precipitation on water chemistry. Chap. 18. 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, 261-274.

Abstract. A long history of metalliferous mining has left Wales with a legacy of abandoned mines and attendant spoil tips which are continuing sources of environmental contamination. Several of these old mines are sources of highly polluted acid drainage resulting from the oxidative weathering of pyrite and marcasite. The AMD which containes elevatied levels of many elements is characterized by red-brown ppt of ochre on stream beds and in lakes intercepting the drainage. Ppt of ochre has a marked influenc on the chemistry of these acid waters with many elements concentrated in the ochre.

1701 Morse, John W (1994): Release of toxic metals via oxidation of authigenic pyrite in resuspended sediments. Chap. 20. 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, 289-297.

Abstract. During early diagenesis in anoxic sediments many reactive trace metals are coprecipitated with authigenic pyrite. Metals of potential environmental concern, such as As and Hg, can have in excess of 80% of their reactive fraction incorporated into authigenic pyrite within the top 10 cm of many sediments. Resuspension of sediment into overlying oxic waters can result in the oxidation of pyrite leading to release of the coprcipitated metals. Experimental studies indicate that from about 20% to 50% of the pyrite can oxidize in a day. The loss of trace metals from the pyrite fraction relative to pyrite Fe is highly variable during the oxidation reaction, but generally is close to or greater than that of pyrite Fe.

1704 Cravotta III,CA (1994): Secondary iron-sulfate minerals as sources of sulfate and acidity. Chap. 23.
 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, 345-364.

Abstract. Despite negligible concentrations of DO in ground water, concentrations of sulfate and acidity increae with depth along paths of ground water flow from the water table in mine spoil through underlying bedrock at a reclaimed surface coal mine in the bituminous field of western Pennsylvania. This trend can result from the oxidation of pyrite in the unsaturated zone, transport of oxidation products, and additional oxidation in the saturated zone. Pyrite can be oxidized by DO or by FeIII in the absense of DO. In acidic water, FeIII is more soluble than oxygen. Iron sulfate hydrates, including romerite, copiapite, and coquimbite, are associated with pyrite in coal from the mine. These soluble salts can form on the surface of oxidizing pyrite in unsaturated mine spoil, coal and overburden, and can dissolve in ground water thereby releasing sulfate and FeIII. Subsequent oxidation of pyritic sulfur by FeIII and (or) hydrolysis of FeIII will produce acid under water saturated conditions, even if oxygen is not present in the system.

Hammack,Richard W (1994): Evolved-gas analysis: A method of determining pyrite, marcasite, and alkaline-earth carbonates. Chap. 28. 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, 431-444.

Abstract. An evolved-gas analysis technique has been developed for the simultaneous determination of pyrite and alkaline-earth carbonates in geologic materials. The technique can also be used to estmate oxidation rates for coal pyrite and therefore may improve the prediction of acid discharges resulting from mining activity.

Huang,Xiao; Evangelou, VP (1994): Suppression of pyrite oxidation rate by phosphate addition. Chap.
 34. 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, 562-573.

Abstract. Pyrite produces highly acidic drainage water when exposed to the atmosphere. Current acidic drainage remediation technologies are not long lasting or cost effective. In this study we demonstrate that a ferric phosphate coating can form on pyrite surfaces when contacted with a solution of KH_2PO_4 and H_2O_2 . This ferric phosphate coating was shown to inhibit pyrite oxidation.

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 ehydroxylation and decrystallization of kaolinite and illite and converted part of the pyrite to pyrrhotite. The leachates generated in the field lysimeters were highly acidic and with high concentrations of sulfate , Mg, Fe, Al, Zn, Na, Ca, K Ni and Mn. 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 raw shale. Elemental release was transport controlled, with the exception of Ca, which appeared to be near equilibrium with respect to gypsum.

- 1723 Erickson, Patricia M; Campion, Peter SA (1982): Reducing oxidation of pyrite through selective reclamation practices. In: 1982 Symposium on surface mining, hydrology, sedimentology, and reclamation. (University of Kentucky, Lexington, KY, December 5-10) (Eds: Graves, Donald H; DeVore, R William) University of Kentucky, Lexington, KY, 97-102.
- 1729 Chander,S; Briceno,A; Pang,J (1992): On the mechanism of sulfur oxidation in pyrite. (Presented at 1992 SME Annual Meeting, Phoenix, AZ, Feb. 24-27; Preprint Number 92240) Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO.
- 1744 Riley, JA (1985): The chemistry of pyrite oxidation. In: Acid water implications for mine

abandonment, Coeur D'Alene mining district, Idaho. (Research report submitted to Mineral Industry Waste Treatment and Recovery Generic Center, USBM, Washington, DC) (Ed: Riley, John A) Riley, John A, Moscow, Idaho, 12-17.

- 1759 Daniel,JA; Harries,JR; Ritchie,AIM (1980): Water movement caused by monsoonal rainfall in an overburden dump undergoing pyritic oxidation. In: Biogeochemistry of ancient and modern environments. (Proc. 4th International Symposium on Environmental Biogeochemistry and Conference on Biogeochemistry in Relation to the Mining Industry and Environmental Pollution, Canberra, Australia, Aug 26-Sept 4, 1979) (Eds: Trudinger,PA; Walter,MR) Springer-Verlag, Berlin, 623-629.
- 1852 Rickard, David T (1970): The origin of framboids. In: Unknown. (Ed: Unknown) Unknown, Unknown, 269-293.
- 1865 Tyler, Stanley A; Barghoorn, Elso S (1963): Ambient pyrite grains in precambrian cherts. Am. J. Sci. 261(5), 424-432.
- 1926 Hinkle, Kenneth R (1984): Reclamation of toxic mine waste utilizing sewage sludge: Contrary creek demonstration project Addendum Report. U.S. Department of Commerce, Cincinnati,OH.
- 1932 Fuller, Richard H; Shay, Johnevan M; Ferreira, Rodger F; Hoffman, Ray J (1978): An evaluation of problems arising from acid mine drainage in the vicinity of Shasta Lake, Shasta County, California. (Water-Resources Investigations 78-32) U.S. Geological Survey, Menlo Park, CA. 39 pages.
- 2271 Kriegman-King, Michelle R; Reinhard, M (1994): Transformation of carbon tetrachloride by pyrite in aqueous solution. Environ. Sci. Technol. 28, 692-700.

Abstract. The reactivity of CCl_4 with pyrite was investigated by measuring the CCl_4 transformation rates and products under aerobic and anaerobic conditions. Under all reaction conditions, >90% of the CCl_4 was transformed within 12-36 days in the presence of 1.2-1.4 m²/L pyrite at 25°C. A zero order dependence on the CCl_4 concentration supports a surface controlled reaction mechanism wherein the rate of reaction depends on the absorbed CCl_4 concentration. In aerobic systems >70% of the CCl_4 was transformed to CO_2 whereas in a fresh ground/anaerobic pyrite system approximately 50% of the CCl_4 was transformed to $CHCl_3$. XPS of the reacted pyrite showed that an FeOOH coating formed on the surface under aerobic conditions. Under all reaction conditions, the pyrite surface was depleted of ferrous iron.

2296 Pantelis,G; Ritchie,AIM (1992): Rate-limiting factors in dump leaching of pyritic ores. Appl. Math. Modelling 16(October), 553-560.

Abstract. A model describing the oxidation of mining heaps containing pyrite was presented in an earlier paper and applied to cylindrical heaps. Special attention was given to the interaction of macroscopic transport with the microscopic particle kinetics. We reexamine the model using the more realistic truncated cone geometries. It is seen that while macroscopic transport is still the major rate-limiting factor, the overall behavior of the heap oxidation is significantly different from that shown in previous studies using the simple cylindrical heap geometry. Water infiltration, which was omitted in the earlier model, is included, and the impact of the irrigation rate on the oxidation rate of the heap is examined.

- 2297 Cathles,LM; Apps,JA (1975): A model of the dump leaching process that incorporates oxygen balance, heat balance, and air convection. Metallurgical Transactions B 6B(December), 617-624.
- 2298 Davis, GB; Ritchie, AIM (1987): A model of oxidation of pyritic mine wastes: part 3: import of

particle size distribution. Appl. Math. Modelling 11(December), 417-422.

- Horita, Hiromitsu (1971): Electrical properties of natural pyrite between 1.3 and 700{+0}K. Japan. J. Appl. Phys. 10, 1478-1479.
- 2346 Ennaoui,A; Fiechter,S; Jaegermann,W; Tributsch,H (1986): Photoelectrochemistry of highly quantum efficient single-crystalline n-FeS{-2} (pyrite). J. Electrochem. Soc. 33(1, January), 97-106.
- 2347 Marinace, John C (1954): Some electrical properties of natural crystals of iron pyrite. Physical Review 96(3, November), 593-.
- 2348 Sasaki, Akira (1955): On the electrical conduction of pyrite. Mineralogical Journal 1(5), 290-302.
- 2349 Horita, Hiromitsu (1973): Some semiconducting properties of natural pyrite. Japan. J. Appl. Phys. 12(4), 617-618.
- 2350 Jaegermann,W; Tributsch,H(1983): Photoelectrochemical reactions of FeS{-2} (pyrite) with H{-2}O and reducing agents. Journal of Applied Electrochemistry 13, 743-750.
- 2353 Frost, David C; Leeder, W Ross; Tapping, Robert L; Wallbank, Barry (1977): An XPS study of the oxidation of pyrite and pyrites in coal. Fuel 56(July), 277-280.

Abstract. XPS was used to study mineral, synthetic and coal associated pyrites, oxidized for various time intervals at low T with humid air or oxygen. This was doen to find out if XPS could detect, monitor and clarify pyrite surface oxidative changes that influence surface dependent coal cleaning methods such as froth flotation, and could provide a means of directly analyzing coal sulfur, by determining if oxidizing conditions existed which would effectively eliminate the surface pyrite whose XPS peak may occur at the same energy as the organic sulfur peak of coal. The conditions of study were as follows: a mineral and two coals containing pyrite were exposed to air at 24°C and 33% RH up to 600 hr; and the two mineral and a synthetic pyrite were exposed to oxygen at 100% RH and 55°C for up to 300 hr and at 72°C for 25 hr. The results indicated that the XPS S2p pyrite peak at 169 eV and the surface oxidation product peaks at 163 eV could be detected and followed with XPS, although no conclusions could be made about the oxidation mechanism. The pryite XPS peak became small compared to that of its oxidation products when the synthetic and mineral pyrites were exposed to 55°C oxygen at 100% RH for 300 hr. These conditions may prove useful in trying to determine directly the organic sulfur in coal.

- Ogunsola,Olumbunmi M; Osseo-Asare,Kwadwo (1986): The electrochemical behavior of coal pyrite
 Effects of mineral source and composition. Fuel 65, 811-815.
- 2355 Mishra, KK; Osseo-Asare, K (1987): Photodissolution of coal pyrite. Fuel 66, 1161-1162.
- 2356 Berry, VK; Murr, LE; Hiskey, JB (1978): Galvanic interaction between chalcopyrite and pyrite during bacterial leaching of low-grade waste. Hydrometallurgy 3, 309-326.
- 2357 Chander,S; Briceno,A (1987): Kinetics of pyrite oxidation. Minerals and Metallurgical Processing (August), 171-176.
- 2358 Michell, Donald; Woods, Ronald (1978): Analysis of oxidized layers on pyrite surfaces by X-ray emission spectroscopy and cyclic voltammetry. Aust. J. Chem. 31, 27-34.

Abstract. X-ray emission spectroscopicc analysis of the surface of pyrite has demonstrated the presence of an oxygen containing layer. Differences between the quantity of oxygen

detected after grinding the pyrite on 600 grade silicon carbide paper and polishing to the 10 um or 0.25 um diamond stage are considered to be due to differences in surface roughness. Triangular potential sweep voltammograms display current peaks which have been identified with the oxidation and reduction of the oxide layer between iron II and iron III valence states. The quantities of oxide on the surface determined from the charge passed on a potential sweep correlate with the X-ray emission measurments for the three surface preparations.

- 2359 Lalvani, Shashi B; Shami, M (1987): Passivation of pyrite oxidation with metal cations. Journal of Materials Science 22, 3503-3507.
- 2361 Esposito, MC; Chander, S; Aplan, FF (1987): Characterization of pyrite from coal sources. In: AIME Annual Meeting, February 1987, Cenver, CO. (Ed: Unknown) Unknown, Unknown, 475-493.
- Andrews, Graham (1989): An examination of the kinetics of bacterial pyrite decomposition. Chap. 12.
 In: Biotechnology in minerals and metal processing. (Eds: Sheiner, BJ; Doyle, FM; Kawatra, SK)
 Society of Mining Engineers, Inc., Littleton, CO, 87-93.
- 2363 Caruccio, Frank T (1970): The quantification of reactive pyrite by grain size. In: Symposium on coal mine drainage research. (Ed: Unknown) CMD Research Symposium, Monroeville, PA, 123-131.

During the 2nd symposium on coal mine drainage research it was shown that in a biuminous coal field of Pennsylvania ther wer four types of mine drainages produced by various strate of the Allegheny Group. The concentration of acidity produced could be effedtively neutralized by the alkalinity generated by a layer of crushed limestne. Hence, within the limits discussed above it should be possible to develop an ameliorative technique whereby certain types of mine drainages could be neutralized by incorporating a limestone layer in the top of the backfill cover. Although the method outoined can be used to evaluate reacftive pyrite a need still exists to incorporate the permeability of the stratum in order to obtain a more rigorous method of predictin acid production. Permeability of the host rock was found to be an oxidation rate controlling factor and should be considered as a parameter in the evaluation. Another facet of this study was the observation that stable pyrite, when pulverized to particles 2-5 um, did not oxidize. This suggests that the framboidal pyrite is mineralogically different from the stable pyrite. TYHe exact nature of the chemical difference between reactive and inert pyrite warrants further study.

- 2365 Hiskey, JB; Pritzker, MD (1988): Electrochemical behavior of pyrite in sulfuric acid solutions containing silver ions. Journal of Applied Electrochemistry 18, 484-490.
- 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.
- 2471 Ziemkiewicz, Paul F; Skousen, Jeffrey G (1992): Prevention of acid mine drainage by alkaline addition. Green Lands 22, 42-51.
- 2482 Woods,R; Constable,DC; Hamilton,IC (1989): A rotating ring disc electrode study of the oxidation of sulfur(-II) species on gold and sulfide minerals. International Journal of Mineral Processing 27, 309-326.
- 2483 Duncan,DW; Landesman,J; Walden,CC (1967): Role of Thiobacillus ferrooixdans in the oxidation of sulfide minerals. Can. J. Microbiol. 13, 397-403.

- 2485 Silver, Marvin; Torma, Arpad E (1974): Oxidation of metal sulfides by {IThiobacillus ferrooxidans} grwon on different substrates. Can. J. Microbiol. 20, 141-147.
- 2488 Nakai, Nobuyuki (1963): Biochemical oxidation of sulfur and sulfide minerals by mixed cultures, and the behaviors of stable sulfur isotopes. Journal of Earth Science 11(2), 279-296.

Abstract. Isotopic and quantitative results obtained from the biochemical oxidation of elementary S and sulfides to sulfate are reported in this paper. For this purpose, mixed culture techniques have been devised to simulate naturally occurring biochemical reactions.

Oxidation experiments on elementary S, pyrite, marcasite and zinc sulfide have been carried out at 30°C, with bottom muds from lakes for bacterial source and an aqueous medium containing only inorganic salts. The results indicate that the low T oxidation of S compounds to sulfate takes place predominantly by biochemical processes, and the order of biochemical oxdation is ZnS> marcasite> elementary S>pyrite. The order of oxidation is estimated from the relative oxidation rates. Calcium carbonate in the aqueous medium apparently accelerates the oxidation.

Analysis of stable isotopes indicates that the sulfate produced is slightly enriched in S^{32} during oxidation of both sulfur and pyrite. Mixed culture experiments in the lab are shown to be necessary, in order to claify the fundamental processes of biochemical reactions.

2489 Szolnoki, J; Bognar, L (1964): Experiments on the biogenic oxidation of some sulphide ores. Acta Geologica 8(1-4), 179-187.

Abstract. Literature reveals that some chemosynthetic authotrophic sulfur bacteria are able to intensify the oxidation of sulfide ores. The oxidizing effect of T. ferrooxidans on pyrite, chalcopyrite and sphalerite was studied. Each sulfide ore attacked by T ferrooxidans was found to be oxidized to a greater degree than that noticed in the sterile control sample the total time duration remaining the same in both the cases. Preliminary pasage of bacteria on sulfide ores as weel as the greater initial population of bacteria had a positive effect on the rate of ioxidation. The natural minerals examined were of polymineral nature, so that, besides the essential elements, the associated ones were also dissolved in considerable quantities. For this reason, it may be presumed that thos parts of the lattice where elements have different ionic radii can be easily attacked by microorganisms.

- 2530 Harris, DC (1986): Mineralogy and geochemistry of the main Hemlo Gold Deposit, Hemlo, Ontario, Canada. In: Proceedings of Gold 86 Symposium. (:),, 297-310.
- 2547 Cook,Nigel J; Chryssoulis,Stephen L (1990): Concentrations of "invisible gold" in the common sulfides. Canadian Mineralogist 28, 1-16.
- 2557 Gould,WD; McCready,RGL; Rajan,S; Krouse,HR (1989): Stable isotope composition of sulphate produced during bacterial oxidation of various metal sulphides. In: Biohydrometallurgy: Proceedings of the International Symposium held at Jackson Holw Wyoming, August 13-18, 1989. (Eds: Salley,Joseph; McCready,Ron GL; Wichlacz,Paul L) CANMET, Ottawa, 81-91.
- 2599 Skousen, Jeff; Hilton, Tiff; Faulkner, Ben (1996): Overview of acid mine drainage treatment with chemicals. Green Lands 26(4), 36-45.
- 2608 Ehlers, Ernest G; Stiles, David V (1965): Melanterite-rosenite equilibrium. American Mineralogist 50(September), 1457-1461.
- 2612 Caruccio, Frank T; Geidel, Gwendelyn; Sewell, John M (1976): The character of drainage as a function

of the occurence of framboidal pyrite and ground water quality in Eastern Kentucky. In: Sixth Symposium on Coal Mine Drainage Research. (Ed: Bituminous Coal Research) National Coal Association, Washington, D.C., 1-16.

- 2620 Hammack,Richard W (1987): Pyrite oxidation under unsaturated conditions, Part I: Abiotic oxidation. In: Proceedings of 1987 National Meeting of American Society for Surface Mining and Reclamation and Fourth Biennial Symposium on Surface Mining and Reclamation on the Great Plains. (Report No. 8704) (Ed: Montana State University Reclamation Research Unit),, 289-295.
- 2631 Lyalikova,NN (1961): Bacteria in the oxidation of sulfide ores. Trudy Instituta Mikrobiologii Akademiya Nauk SSSR 9, 134-143.

<Thiobacillus ferrooxidans was found to play a great role in the oxidation of pyrite ore in the Degtiar and Krasnoural beds. The fact that the bacteria was found in the waters of the inflamable district of the Krasnoural bed suggested that it might participate in the initial stages in the self heating of the ore.>

- 2662 Schuring, J; Kolling, M; Sculz, HD (1997): The potential formation of acid mine drainage in pyrite-bearing hard-coal tailings under water-saturated conditions: An experimental approach. Environmental Geology 31(1-2), 59-65.
- 2684 Dalverny, LE; Chaiken, RF (1992): Leaching of pyrite from coal wastes in a trickle bed reactor. In: Environmental Issues and Waste Management in Energy and Minerals Production. (Ed: Singhal, et al) Balkema, Rotterdam, 435-444.

Abstract. USBOM researchers used a large countercurrent trickle-bed column reactor to obtain data on the hemical and transport processes controlling the leaching of pyrite from coal wastes. The acrylic plastic cylinder, 182.9 cm hygh by 30.5 cm diameter, contained probes along the length of the cylinder for measuring temperature and pressure and sampling solids, liquids, and gases as a function of time. The vertical 3-phase system contained stationalry solid coal preparation plant waste, downward flowing lixiviant,mand upward flowing air and gaseous reaction products. The longest duration experiment continued about nne months. Analyses indicated a correlation between hydrocarbon gas desorption and oxygen consumption. The maximum rate of pyrite oxidation (at day 35) was about 0.2 mg SO₄ per g pyrite per hour, as based on the initial pyrite content. The rate of pyrite oxidation approached zero at about 140 days.

- 2707 Caruccio,FT; Geidel,G; Bradham,WS (1991): Accelerated pyrite oxidation/enhanced alkalinity couple to reduce acid mine drainage. Bureau of Mines, US Department of the Interior, .
- 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.
- 2740 Butt, CRM; Zeeggers, H(Eds.) (1992): Regolith Exploration Geochemistry in Tropical and Subtropical Terrains. Vol. 4. Elsevier, Amsterdam.

Chapter II.1: The mechanisms of sulfide oxidation and gossan formation. The wide variety of supergene sulfide minerals that have been reported are an interim step on the way to gossan formation and help retain ore and pathfinder metals. Their forms and fabrics are varied; they may grow from solution with their own crystal morphology constrained by the particular solution channels-or they may replace primary minerals and be a step in the preservation of the primary texture, for example violarite developing from pyrrhotite, pentlandite or millerite. The fabrics of most secondary sulfide minerals have now been

documented in the literature, and in most cases the geochemical processes involved can be understood and used as an aid in gossan evaluation.

Careful evaluation using sensitive chemical analysis techniques, coupled wih the unravelling of the mineralogy by optical microscopy and electron-optical techniques can be most rewarding if this is coupled with an understanding of the processes by which these gossans could have formed. Modern electyron microprobes and analytical SEM that can determine the trace element contents of individual gossan minerals are extremely valuable in this regard. Such an understanding is the first step in comprehending the gossanous material encountered in exploration so that a true assessment can be made of the parent material. The complexities of gossan-forming processes are such that the Fe content, the mass of the sulfide body and the pH of the solutions involved are the major controls on the fate of the chemical elements mobilized during weathering. Subsequent physical and chemical reworking of the gossan material can cause considerable changes and many of the principles outlined in this chapter are also relevant to understanding these processes.

- 2747 Evangelou, VP (1995): Pyrite Oxidation Chemistry. Lewis Publishers, Boca Raton, FL. 304 pages.
- 2748 Hammack,Richard W; Watzlaf,George R (1990): The effect of oxygen on pyrite oxidation. In: Proceedings 1990 Mining and Reclamation Conference and Exhibition. (Charleston, West Virginia, April 23-26, 1990) 257-264.

Abstract. The oxygen dependence of abiotic and biotic pyrite oxidation was examined on three scales: 1) pyrite surfaces to a depth of 20 A, 2) 5 g quantities of pyrite in small columns, and 3) 175 kg quantites of pyritic shale in large columns. Results of these studies indicated that the initial abiotic oxidation of fresh pyrite surfaces was independent of oxygen partial pressures above 10% (0-order rxn) and was proportional to oxygen partial pressures below 10% (1st order rxn). However, the rates of abiotic oxidation measured in small columns were proportional to oxygen partial pressures between atmospheric and 5%. Small column and large column results indicated that with bacteria present, the rate of pyrite oxidation was independent of oxygen partial pressures down to 1%. Below 1% oxygen, the reaction rate was proportional to oxygen partial pressures (1st order). The oxygen impermeab le and oxygen consumptive barriers other than water that are econimically feasible at present are not capable of maintaining oxygen levels below 1%. Therefore, no reduction in the rate of pyrite oxidation would be realized using these techniques unless bacteria were inhibited. The bes method for limiting pyrite oxidation was to place pyritic material below a permanent water table. Results of large column experiments indicated that a 96% reduction in pyrite oxidation could be realized by inundating the pyritic material. Results of large column tests corroborated previous work by other researchers that indicated leaching frequency had no effect on pyrite oxidation and total sulfate load.

- 2784 Huggins, FE; Huffman, GP; Lin, MC (1983): Observations on low-temperature oxidation of minerals in bituminous coals. International Journal of Coal Geology 3, 157-182.
- 2791 Brickett,LA; Hammack,RW; Edenborn,HM (1995): Comparison of methods used to inhibit bacterial activity in sulfide ore bioleaching studies. Hydrometallurgy 39, 293-305.
- 2794 Walton-Day, Katherine; Kimball, BA; Yager, TJ (1994): The effects of remediation of mine drainage in the Upper Arkansas River near Leadville, CO. 1994 Fall Meeting, 237.
- 2795 Kempton, JH; Goode, D; Atkins, D; Nicholson, A; Travers, CL; Davis, AO (1994): A Monte Carlo model for predicting water quality in mine pit lakes. 1994 Fall Meeting, 238.

- 2813 Kleinmann,Robert LP (1990): At-source control of acid mine drainage. In: Acid Mine Water in Pyritic Environments. (Lisboa, Portugal, September, 16-19, 1990) (:),, 85-96.
- 2821 Li,Jun; Zhu,Ximeng; Wadsworth,Milton E (1992): Raman spectroscopy of natural and oxidized netal sulfides. In: EPD Congress 1993. (Denver, CO, February 21-25, 1993) (Ed: Hager,JP) The Minerals, Metals & Materials Society, 229-244.
- 2835 Smart,RStC (1991): Surface layers in base metal sulphide flotation. Minerals Engineering 4, 891-909.
- 2869 Doolittle, J.J.; Hossner, L.R. (1987): Pyrite oxidation in a minespoil environment: a lysimeter study. Billings Symp on Western Surface Mining and Reclamation and the 4th Annual Meeting, Am. Soc. for Surface Mining and Reclamation. March 17-10. Billings MT. pg 269-275.

Abstract. The oxidation of pyrite and the effects of its products on a minesoil containing excess NP was investigated. An anoxic Teas lignite overburden with 0.8% pyrite and 1.6% carbonates (predominantly dolomite) was packed into 0.7 m^3 lysimeters and leached monthly with 63.5 mm of di rainwater for 12 months. The leachantes coming from the lysimeters started at a pH of 8.5 and gradually decreased to a pH of 7.0. The minesoil started at a pH of 8.3 and decreased to pH 6.5 by the end of 12 months. Potential acidity determinations indicate that 50% of the initial pyrite had oxidized; howerver, the release of acidity was sufficiently slow for the inherent neutralizing materials to consume the acidity and maintain a moderate pH. The sulfuric acid and dolomite interactions led to a significant increase in extractable Ca and Mg with time and the formation of a SO₄ bulge in the lower half of the lysimeters. The relatively slow pyrite oxidation observed in this project is attributed to the low surface areas of the pyrite particles present and the relatively high pH maintained by the dolomite.

2896 Dubrovsky, N.M.; Cherry, J.A.; Reardon, E.J.; Vivyurka, A.J. (1984): Geochemical evolution ofc inactive pyrtic tailings in the Elliot Lake uranium district. Can. Geotech. J. 22, 110-128.

Abstract. Geochemical data obtained between 1979 and 1983 from a network of piezometer nests and cores from three inactive U tailings impoundments in the Elliot Lake district indicate that oxidation of pyrite taking place in the shallow part of the zone above the water table is causing the chemistry of the pore water above and below the water table to change. A two-layer hycdrochemical zonation has developed in which infiltartion water from rain and snow has resulted in an upper zone of low-pH water with high concentrations of fulfate, iron and heavy metals. This zone is gradually expanding downward at rates generally between 0.2 and 2 m/yr, causing displacement of the original mill precess water, which has neutral pH and low concentrations of heavy metals. High concentrations of FeIII at shallow depth in the zone above the water table indicate that ferric iron is an important oxidizer of pyritein the presence of free oxygen.

The pe of the groundwaters is controlled by the ferric-ferrous redox couple, and trends in the data indicate iron solubility control by siderite at high pH, by ferric hydroxide at moderate to slightly acid pH values, and possibly by jarosite at low pH. Al solubility controls are complex, and precipitation of amorphous aluminum hydroxide, allophane and basic alumninum sulfates may occur over different pH ranges. Transport of low-pH conditions is retarded relative to the rate of groundwater flow in the tailings, because of the buffering effect of small amou8nts of carbonate minerals added during tailings neutralization; primary aluminosilicates such as sericite; and secondary aluminum hydroxides.

Field data show that the flux of dissolved iron from the vadose zone to the groundwater zone in the Nordic Main tailings has been decreasing in recent years. However, mass balance
calculations indicate a potential for the generation of high-Fe groundwater for several decades to several hyndred years. A long-term potential for acid and iron production is also shown be data from two tailings impoundments that have been inactive 8-10 years longer than the Nordic Main area. Presently only a small portion of the Nordic Main and West Arm tailings areas has become acidic through the entire tailings thickness; however, under existing infiltration conditions more extensive acidification will occur.

Sasaki, K. (1997): Raman study of the microbially mediated dissolution of pyrite by Thiobacillus ferrooxidans. Can. Mineralogist. 35, 999-1008.

Abstract. Raman spectroscopy was applied to the microbially mediated dissolution of pyrite by high density (more than 10⁹ cells) of T. ferrooxidans. In the range of 600-200 cm⁻¹, peaks corresponding to secondary minerals such as elemental sulfur and jarosite were observed in addition to those of pyrite. Small amounts of elemental sulfur and pooryly crystalline jarosite were detected by Raman spectroscopy, but are undetectable by XRD and FTIR. Ammoniojarosite was predominantly formed in microbially mediated dissolution of pyrite with a high densit of cells, whereas jarosite was formed in the sterilized control. This finding is probably ultimately due to the much greater amount of jarosite precursors (FeIII sulfate complexes) formed by the bacterial oxidation of iron. Initially, and in both cases, the kinetically favored jarosite appeared, but in the presence of bacteria, there was so much precursor present that the available K was axhausted. Ammoniojarosite subsequaently was formed. In the sterilized control, precursors were less readilty formed, and jarosite formed. There was no evidence for direct involvement of bacteria in the formation of jarosite. The canges in mineral compositions are correlated with those in the solutions. Raman spectroscopy was used to follow compositional changes in minerals during the microbially mediated dissolution of pyrite.

Dold, B.; Eppinger, K.J.; Kolling, M. (1996): Pyrite oxidation and the associated geochemical processes in tailings in the Atacama Desert/ Chile: The influence of man controlled water input after disuse.

Abstract. This paper reports the results of a study of two tailings, under desert conditions in the III. Region of Chile. Both tailings received significant amounts of man controlled water from the hill side abovve, after operation had ceased. Sampling was undertaken with a soil sampling equipment up to a depth of 8 m. The samples were analyzed by XRD and ICP-MS. Sampling observation in the field showed a zonation inverse, known in humid climates zones, in which the oxidation zone lies above an accumulation zone and a basal primary zone. In the studied tailings the stratigraphic column changes from a homogenous primary zone at the top, to an inhomogenous zone with intercalations of oxidized layers, to a very homogenous oxidation zone at 5-8 m depth. The pH changes from 7-8 to 4 and the grain size from fine sandy to clayey between the primary and the oxidation zone. These zones are directly related to the water level in the tailings. XRD analysis has confirmed that sufides such as pyrite are only present in the primary zone; whereas gypsum and jarosite are present in the oxidation zone. The latter indicate the influence of sulfate rich gypsum and jarosite are present in the oxidation zone. The latter indicate the influence of sulfate rich acid solutions, resulting from the oxidation of pyrite (AMD). The element distribution indicates also a sulfide oxidation zone. The distribution of environmentally unhealthy heavy metals shows an accumulation at the uppermost parts of the oxidation zone, as a result of "unspecifiec" adsorption (surface) on the FeIII hydroxides and/or of sulfide precipitaiton.

Below in the homogenous oxidation zone, heavy metal distribution is also homogenous and the metal contents are much higher than in the primary zone, which indicates a "specified" adsorption (incorporation in the crystal system, stable at low pH) and a geochemical equilibrium. The results show clearly that the geochemical processes in the studied tailings are directly related to the man controlled water input. The detected processes are related to pyrite oxidation and show a strong mobilization of all types of elements. The distribution of elements is interpreted to indicate an upwards migrating oxidation zone, characterized by the precipitation of FeIII hydroxides from FeII, metal rich solutions, and a water flow confined to the top of the oxidation zone.

Chaiken, R.F.; Dalverny, L.E. (1995) Leaching pyrite from coal waste: results of diagnostic study. US Bureau of Mines RI 9569. 42p.

Abstract. The USBOM conducted an experimental and theoretical study of coupled chemical kinetic and mass transport processes during leaching of pyrite from coal in a counterflow, "trickle-bed" column reactor. Spatial and temporal data on reactant and product concentrations were used as solutions to appropriate continuity equations, which in turn define chemical kinetic reaction rates. Data from four 180 by 30 cm column leaching experiments using coal, coal waste, and air-water and air-FeCl₃ lixiviants have been analyzed. The rate of leaching was found to be diffusion limited (probably by FeIII) and not controlled by bacterial action. Rates of pyrite oxidation were found to vary with elapsed time (80 to 225 days) and followed a bell shaped curve, sometimes with a delay before start of reaction. Max rates of reaction ranged from 3 to 10 mmol/d/L for coal waste and 0.4 mmol/d.L for coal. Reaction was 30 to 80% complete, probably due to precipitation of product salts (e.g., jarosites(, which impede transport of oxidant through the coal. And adsorption-desorption model of solids leaching, which considers the role of heterogeneous porosity in solids leaching, was used to describe time-dependent leaching rates.

2987 Evangelou, V.P.; Seta, A.K.; Holt, A. (1998): Potential role of bicarbonate during pyrite oxidation. ES&T, 32, 2084-2091.

Abstract. According to Frontier molecular orbital theory, the surface exposed sulfur atom of pyrite possesses an unshared electron pair which produces a slightly negatively charged pyrite surface that can attract cations such as FeII. Because of surface electronutrality and pH considerations, however, the pyrite surface FeII coordinates OH. We proposed that this surface FeIIOH when in the resence of CO₂ is converted to -FeCO₃ or -FeHCO₃, depending on pH. In this study, using FTIR we demonstrated that such complexes form on the surface of pyrite and continue to persist even after a significant fraction of the surface FeII was oxidized to FeIII. FTIR spectra also showed the presence of two carbonyl absorption bands (1682 and 1653 cm⁻¹) on the surface of pyrite upon exposure to CO_2 which suggested that pyrite surface carbonate complexes existed in two different surface chemical environments, pointing out two potential mechanisms of pyrite surface-CO₂ interactions. One potential mechanism involved formation of a pyrite surface -FeIIHCO₃ complex whereas a second potential mechanism involved formation of a pyrite surface carboxylic acid group comples [-Fe(II)SSCOOFe(II)]. We hypothesized that these pyrite surface -CO₂ complexes could promote abiotic oxidaiton of pyrite by accelerating the abiotic oxidation of FeII. Iron III would oxidize the disulfide $(-S_2)$ by accepting its electrons. Using a miscible displacement technique, oxidation of FeS₂ with H_2O_2 was carried out in the absence or presence of 10 or 100 mM NaHCO₃. The data show that 100 mM NaHCO₃ significantly increased the oxidation rate of FeS_2 . Furthermore, the data show that FeS_2 oxidation kinetics were more dependent on HCO₃ but were less dependent on H_2O_2 for the range of HCO₃ and H_2O_2 concentrations tested.

A2.2. ARSENOPYRITE

Ref#

- 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.
- 706 Beattie, MJV; Ismay, Arnaldo (1990): Applying the redox process to arsenical concentrates. JOM, 31-35.
- 708 Li,GM; Zhang,HE; Usui,S (1991): Adsorption of copper ions on oxidized arsenopyrite--water interfaces. (Presented at 1991 SME Annual Meeting on 25-28 February in Denver, CO) Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO. (Preprint Number 91-9)
- 715 Hiskey, JB; Sanchez, V (1988): An electrochemical study of the surface oxidation of arsenopyrite in alkaline media. In: Proc. 1988 TMS Annual Meeting and Exhibition: Arsenic Metallurgy--Fundamentals and Applications Symposium. (Symposium held in Phoenix, AZ, January 25-29) (Eds: Reddy, RG; Hendrix, JS; Queneau, PB) The Metallurgical Society, Inc., Warrendale, PA, 59-73.
- 720 Ramadorai,G; Mishra,RK (1988): Roasting of arsenical gold and silver-bearing minerals. Chap. 2. In: Proc. 1988 TMS Annual Meeting and Exhibition: Arsenic Metallurgy--Fundamentals and Applications Symposium. (Symposium held at Pheonix, AZ, January 25-29) (Eds: Reddy,RG; Hendrix,JL; Queneau,PB) The Metallurgical Society, Inc., Warrendale, PA, 161.
- 721 Stefanakis,M; Hassapis,D; Demetriades,D; Kontopoulos,A (1988): Dearsenifying roasting and gold extraction from a refractory pyrite concentrate. Chap. 2. In: Proc. 1988 TMS Annual Meeting and Exhibition: Arsenic Metallurgy--Fundamentals and Applications Symposium. (Symposium held at Pheonix, AZ, January 25-29) (Eds: Reddy,RG; Hendrix,JL; Queneau,PB) The Metallurgical Society, Inc., Warrendale,PA, 173.
- 722 Lawrence, RW; Marchant, PB (1988): Biochemical pretreatment in arsenical gold ore processing. Chap. 2. In: Proc. 1988 TMS Annual Meeting and Exhibition: Arsenic Metallurgy--Fundamentals and Applications Symposium. (Symposium held at Phoenix, AZ, January 25-29) (Eds: Reddy, RG; Hendrix, JL; Queneau, PB) The Metallurgical Society, Inc., Warrendale, PA, 199, 207, 209.
- 1134 Reddy,RG; Hendrix,JL; Queneau,PB (Eds.) (1988): Proc. 1988 TMS Annual Meeting and Exhibition: Arsenic Metallurgy--Fundamentals and Applications Symposium. (Symposium held in Phoenix, AZ, January 25-29) The Metallurgical Society, Inc., Warrendale, PA.
- 1135 Stefanakis,M; Hassapis,J; Demetriades,D; Kontopoulos,A (1988): Dearsenifying roasting and gold extraction from a refractory pyrite concentrate. In: Proc. 1988 TMS Annual Meeting and Exhibition: Arsenic Metallurgy--Fundamentals and Applications Symposium, Phoenix, AZ, January 25-29. (Eds: Reddy,R; Hendrix,JL; Queneau,PB) The Metallurgical Society, Inc., Warrendale, PA, 173.
- 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.
- 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.

- 1684 Rimstidt, J Donald; Chermak, John A; Gagen, Patrick M (1994): Rates of reaction of galena, sphalerite, chalcopyrite, and arsenopyrite with Fe(III) in acidic solutions. Chap. 1. 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, 2-13.
- 1706 Kwong, YTJ; Van Stempvoort, DR (1994): Attenuation of acid rock drainage in a natural wetland system. Chap. 25. 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, 382-392.
- 2408 Piantone, Patrice; Wu, Xin; Touray, Jean-Claude (1994): Zoned hydrothermal alteration and genesis of the gold deposit at Le Chatelet (French Massif Central). Economic Geology 89, 757-777.
- 2486 Komnitsas,C; Pooley,FD (1990): Bacterial oxidation of an arsenical gold sulphide concentrate from Olympias, Greece. Minerals Engineering 3, 295-306.
- 2487 Komnitsas,C; Pooley,FD (1991): Optimization of the bacterial oxidation of an arsenical gold sulphide concentrate from Olympias, Greece. Minerals Engineering 4, 1297-1303.
- 2547 Cook,Nigel J; Chryssoulis,Stephen L (1990): Concentrations of "invisible gold" in the common sulfides. Canadian Mineralogist 28, 1-16.
- 2553 Bhakta,P; Langhans Jr., JW; Lei, KPV (1989): Alkaline oxidative leaching of gold-bearing arsenopyrite ores. (RI 9258) Bureau of Mines, Pittsburgh, PA. 12 pages.

A2.3. MARCASITE

<u>Ref#</u>

- 18 Wiersma, CL; Rimstidt, JD (1984): Rates of reaction of pyrite and marcasite with ferric iron at pH 2. Geochim. Cosmochim. Acta 48, 85-92.
- 19 Wiese,RG; Powell,MA; Fyfe,WS (1987): Spontaneous formation of hydrated iron sulfates in laboratory samples of pyrite- and marcasite-bearing coals. Chem. Geol. 63, 29-38.
- 169 Temple,Kenneth L; Delchamps,Earsie W (1953): Autotrophic bacteria and the formation of acid in bituminous coal mines. Applied Microbiology 1, 255-258.
- 171 Pugh,CE; Hossner,LR; Dixon,JB (1984): Oxidation rate of iron sulfides as affected by surface area, morphology, oxygen concentration, and autotrophic bacteria. Soil Science 137(5, May), 309-314.
- 175 Lowson, Richard T (1982): Aqueous oxidation of pyrite by molecular oxygen. Chemical Reviews 82(5, October), 461-497.
- 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.
- 361 Buehler,HA; Gottschalk,VH (1910): Oxidation of sulphides. Economic Geology 5, 28-35.
- 362 Gottschalk,VH; Buehler,HA (1912): Oxidation of sulphides. Economic Geology 7, 13-34.
- 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.
- 1699 Fuge,Ron; Pearce,Fiona M; Pearce,Nicholas JG; Perkins,William T (1994): Acid mine drainage in Wales and influence of ochre precipitation on water chemistry. Chap. 18. 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, 261-274.
- 1706 Kwong,YTJ; Van Stempvoort,DR (1994): Attenuation of acid rock drainage in a natural wetland system. Chap. 25. 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, 382-392.
- 1709 Hammack,Richard W (1994): Evolved-gas analysis: A method of determining pyrite, marcasite, and alkaline-earth carbonates. Chap. 28. 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, 431-444.
- 2488 Nakai,Nobuyuki (1963): Biochemical oxidation of sulfur and sulfide minerals by mixed cultures, and the behaviors of stable sulfur isotopes. Journal of Earth Science 11(2), 279-296.

A2.4. MISCELLANEOUS

<u>Ref#</u>

- 26 Brady,Patrick V; Walther,John V (1989): Silicate dissolution rates as a function of pH and temperature. Abstracts with Programs 21(6, Ed: Geological Society of America), 101.
- 27 Mast, M Alisa; Drever, James I (1986): Effect of organic chelates on the dissolution rate of oligoclase. Abstracts with Programs 18(6, Ed: Geological Society of America), 685.
- Grandstaff, DE (1986): The dissolution rate of forsteritic olivine from Hawaiian beach sand. Chap.
 In: Rates of Chemical Weathering of Rocks and Minerals. (Ed: Colman, Steven M) Academic Press, Inc., Orlando, 41-59.
- 33 Mast, M Alisa; Drever, James I (1987): The effect of oxalate on the dissolution rates of oligoclase and tremolite. Geochim. Cosmochim. Acta 51(9), 2559-2568.
- Hurd,David C; Fraley,Charles; Fugate,James K (1979): Silica apparent solubilities and rates of dissolution and precipitation: For ca. 25 common minerals at 1-2 degrees C, pH 7.5-8.5 in seawater. Chap. 21. In: Chemical modeling in aqueous systems: speciation, sorption, solubility, and kinetics. (Ed: American Chemical Society) Washington: The Society, Washington, 413-445.
- 39 Casey, William H; Westrich, Henry R (1992): Control of dissolution rates of orthosilicate minerals by divalent metal-oxygen bonds. Nature 355(6356, 9 Jan), 157-159.
- 40 Rose,NM (1991): Dissolution rates of prehnite, epidote, and albite. Geochim. Cosmochim. Acta 55(11), 3273-3286.
- 41 Brady, Patrick V; Walther, John V (1989): Controls on silicate dissolution rates in neutral and basic pH solutions at 25 degrees C. Geochim. Cosmochim. Acta 53(11), 2823-2830.
- 53 Schweda, P (1989): Kinetics of alkali feldspar dissolution at low temperature. In: Water-rock interaction WRI-6: Proceedings of the 6th international symposium, Malvern, UK. Vol. 6. (Ed: Miles, Douglas L) A. A. Balkema Publishers, Balkema, Rotterdam, 609-612.
- 68 Wadsworth, ME (1984): Heterogeneous rate processes in the leaching of base metal sulfides. In: Hydrometallurgical Process Fundamentals. (Ed: Bautista, RG) Plenum Press, New York, 41-76.
- 100 Casey, William H; Westrich, Henry R; Arnold, George W (1988): Mechanisms of feldspar dissolution in acid solutions. Chem. Geol. 70(1-2), 77.
- 103 Talman,SJ; Nesbitt,HW (1988): Dissolution of populations of ultrafine grains with applications to feldspars. Geochim. Cosmochim. Acta 52(6), 1467-1471.
- 118 Fleer, VN; White, WB (1982): The dissolution kinetics of alkaline earth feldspars. EOS, Transactions, American Geophysical Union 63(45, 9 November), 1136.
- 128 Donaldson, CH (1986): Mineral dissolution rates in a superheated basalt melt. Materials Science Forum 7, 267-274.
- 131 Blum, AE; Lasaga, Antonio C (1986): Forsterite Dissolution Kinetics. EOS, Transactions, American Geophysical Union 67(44), 1278-1279.
- 140 Donaldson, CH (1984): Crystal dissolution rates in a basaltic melt. Progress in experimental petrology (NERC) 6, 174-175.
- 201 Steger,HF (1976): The stability of the certified reference ores MP-1 KC-1 and SU-1 towards air oxidation. Talanta 23, 643-648.

- 242 Lerman, A; MacKenzie, FT; Bricker, OP (1975): Rates of dissolution of aluminosilicates in seawater. Earth and Planetary Science Letters 25, 82-88.
- 263 Casey, William H; Westrich, Henry R (1991): Dissolution rates of plagioclase at pH = 2 and 3. American Mineralogist 76(1-2), 211-217.
- 268 Petrovic,Radomir; Berner,Robert A; Goldhaber,Martin B (1976): Rate control in dissolution of alkali feldspars--I. Study of residual feldspar grains by X-ray photoelectron spectroscopy. Geochim. Cosmochim. Acta 40, 537-548.
- 290 Madsen,BW; Groves,RD (1975): Using Oxygen to Reactivate a Nearly Dormant Copper Sulfide Leach. (Report of Investigations 8056) US Government Printing Office: U.S. Department of the Interior. US Bureau of Mines, Pittsburgh, PA. 9 pages.
- Holdren, George R Jr; Adams, John E (1982): Parabolic dissolution kinetics of silicate minerals: An artifact of nonequilibrium precipitation processes? Geology 10, 186-190.
- 298 Aagaard,Per; Helgeson,Harold C (1977): Thermodynamic and kinetic constraints on the dissolution of feldspars. 1977 Annual Meeting of the Geological Society of America and Associated Societies, Seattle, Washington, 873.
- 303 Sjoberg, EL (1976): A fundamental equation for calcite dissolution kinetics. Geochim. Cosmochim. Acta 40, 441-447.
- 310 Grandstaff,DE (1980): The dissolution rate of forsteritic olivine from Hawaiian beach sand. In: 3rd International Symposium on Water-Rock Interaction. (Ed: Water-Rock Interaction International) International Associate of Geochemistry and Cosmochemistry and Alberta Research Council, Edmonton, Canada, 72-74.
- 312 Casey, William H (1991): On the relative dissolution rates of some oxide and orthosilicate minerals. J. Colloid Interface Sci. 146(2, 15 October), 586-589.
- 313 Eriksson, Erik (1982): On the rate of dissolution of olivine in aqueous solutions. Vatten 38, 409-415.
- Roman, RJ; Benner, BR (1973): Dissolution of copper concentrates. Minerals Sci. Engng 5(1), 3-24.
- 331 Vizsolyi,A; Veltman,H; Warren,IH; Mackiw,VN (1967): Copper and elemental sulphur from chalcopyrite by pressure leaching. Journal of Metals, 52-59.
- 332 Dutrizac, JE; MacDonald, RJC (1971): Effect of sodium chloride on the dissolution of chalcopyrite under simulated dump leaching conditions. Metallurgical Transactions 2(August), 2310-2312.
- 333 Dutrizac, JE (1982): Ferric ion leaching of chalcopyrites from different localities. Metallurgical Transactions B 13B(September), 303-309.
- 366 Pankow, James Frederick (1979): The dissolution rates and mechanisms of tetragonal ferrous sulfide (mackinawite) in anoxic aqueous systems. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA. 148 p.
- 544 Dayal,Ramesh (1977): Kinetics of silica sorption and clay dissolution reactions at 1 and 670 atm. Geochim. Cosmochim. Acta 41, 135-141.
- 546 Majima,H; Peters,E (1966): Oxidation rate of sulfide minerals by aqueous oxidation at elevated

temperatures. Transactions of the Metallurgical Society of AIME 236(October), 1409-1413.

- 587 Rauch, Henry W; White, William B (1977): Dissolution kinetics of carbonate rocks 1. Effects of lithology on dissolution rate. Water Resources Research 13(2, April), 381-394.
- 589 Yang,Z; Smith,RW (1987): The reaction of calcite with dilute fluoride solutions. Water Resources Related to Mining and Energy -- Preparing for the Future Unknown(November), 427-438.
- Wichlacz,Paul L; Unz,Richard F (1986): A model of ferrous iron oxidation for attached bacteria.
 Chap. 10. 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, 479-480.
- 1074 Milke,MW; Small,MJ (1989): A modelling approach for estimating long-term and seasonal calcium carbonate dissolution rates. In: Water-Rock Interaction WRI-6. (Proc. 6th International Symposium, Malvern, UK) (Ed: Miles,Douglas L) A.A.Balkema, Rotterdam, Netherlands, 487-490.
- 1079 Richards, Hugh G; Savage, David (1989): Rate of plagioclase dissolution in the Camborne School of Mines experimental hot dry rock geothermal system, Rosemanowes, Cornwall. In: Water-Rock Interaction WRI-6. (Proc. 6th International Symposium, Malvern, UK) (Ed: Miles, Douglas L) A.A.Balkema, Rotterdam, Netherlands, 577-580.
- 1086 Wehrli,B (1989): Surface structure and mineral dissolution kinetics: A Monte Carlo study. In: Water-Rock Interaction WRI-6. (Proc. 6th International Symposium, Malvern, UK) (Ed: Miles,Douglas L) A.A.Balkema, Rotterdam, Netherlands, 751-753.
- 1098 Casey, William H; Westrich, Henry R; Arnold, George W (1988): Surface chemistry of labradorite felspar reacted with aqueous solutions at pH = 2, 3, and 12. Geochim. Cosmochim. Acta 52, 2795-2807.
- 1717 Lapakko,Kim A; Antonson,David A (1994): Oxidation of sulfide minerals present in Duluth complex
 rock. Chap. 36. 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, 593-607.
- 1846 Nicholson, Ronald V (1992): A review of models to predict acid generation rates in sulphide waste rock at mine sites. Presented to International Workshop on Waste Rock Modelling Sponsored by the Mine Environment Neutral Drainage Program, Sept. 29 Oct. 1, Toronto, Canada.
- Lapakko,Kim; Eger,Paul (1980): Mechanisms and rates of leaching from Duluth Gabbro Waste Rock.
 (Presented at SME-AIME Fall Meeting and Exhibit, Minneapolis, MN, October 22-24; Preprint Number 80-367) Society of Mining Engineers of AIME, Littleton, CO.
- 2315 Biber, Madeleine V; Stumm, Werner (1994): A {Iin situ} ATR-FTIR study: The surface coordination of salicylic acid on aluminum and iron (III) oxide. Environ. Sci. Technol. 28(5), 763-768.
- 2352 Eadington, P (1969): Oxidation of lead sulfide in aqueous suspensions. Trans. Instn Min. Metall. 78, C74-C82.
- 2360 Lacey, DT; Lawson, F (1970): Kinetics of liquid-phase oxidation of acid ferrous sulfate by the bacterium {IThiobacillius ferrooxidans}. Biotechnology and Bioengineering 12, 29-50.
- 2389 Szecsody, James E; Zachara, John M; Bruckhart, Patrick L (1994): Adsorption-dissolution reactions

affecting the distribution and stability of Co{+II}EDTA in iron oxide-coated sand. Environ. Sci. Technol. 28(9), 1706-1719.

- 2390 Heaton, Julia S; Engstrom, Royce C (1994): {IIn situ} atomic force microscopy study of the differential dissolution of fayalite and magnetite. Environ. Sci. Technol. 28(9), 1747-1754.
- 2397 Lancia,A; Musmarra,D; Pepe,F; Volpiceli,G (1991): Conentration profiles in the dissolution film in the calcium carbonate dissolution process. Chemical Engineering Science 46(10), 2507-2512.
- 2398 Gage, Cynthia L; Rochelle, Gary T (1992): Limestone dissolution in flue gas scrubbing: Effect of sulfite. J Air Waste Manage. Assoc. 42, 926-935.
- Plummer,Neil L; Wigley,TML (1976): The dissolution of calcite in CO{-2}-saturated solutions at 25 {+0}C and 1 atmosphere total pressure. Geochim. Cosmochim. Acta 40, 191-202.
- 2411 Schott, Jacques; Berner, Robert A; Sjoberg, E Lennart (1981): Mechanism of pyroxene and amphibole weathering -- I. Experimental studies of iron-free minerals. Geochim. Cosmochim. Acta 45, 2123-2135.
- 2412 Wogelius, Roy A; Walther, John V (1992): Olivine dissolution kinetics at near-surface conditions. Chem. Geol. 97, 101-112.
- 2413 Hochella, Michael F Jr; Ponader, HB; Turner, AM; Harris, DW (1988): The complexity of mineral dissolution as viewed by high resolution scanning Auger microscopy: Labradorite under hydrothermal conditions. Geochim. Cosmochim. Acta 52, 385-394.
- 2414 Knauss, Kevin G; Nguyen, Son N; Weed, Homer C (1993): Diopside dissolution kinetics as a function of pH, CO{-2}, temperature, and time. Geochim. Cosmochim. Acta 57, 285-294.
- 2415 Hellmann,Roland; Eggleston,Carrick M; Hochella,Michael F Jr; Crerar,David A (1990): The formation of leached layers on albite surfaces during dissolution under hydrothermal conditions. Geochim. Cosmochim. Acta 54, 1267-1281.
- 2416 Eggleston, Carrick M; Hochella, Michael F Jr; Parks, George A (1989): Sample preparation and aging effects on the dissolution rate and surface composition of diopside. Geochim. Cosmochim. Acta 53, 797-804.
- 2417 Bales,Roger C; Morgan,James J (1985): Dissolution kinetics of chrysotile at pH 7 to 10. Geochim. Cosmochim. Acta 49, 2280-2288.
- 2418 Bruyère, Vivianne IE; Blesa, Miguel A (1985): Acidic and reductive dissolution of magnetite in aqueous sulfuric acid. J. Electroanal. Chem. 182, 141-156.
- 2420 Casey, William H; Banfield, Jillian F; Westrich, Henry R; McLaughlin, Linda (1993): What do dissolution experiments tell us about natural weathering? Chem. Geol. 105, 1-15.
- 2470 Rusin,P; Cassells,J; Quintana,L; Arnold,R; Chrisman,N (1995): Elimination of toxic factors in leachate to enhance biooxidation of sulfide ores. Mining Engineering 47(2), 173-177.
- 2478 Buisman, Cees; Ijspeert, Peter; Janssen, Albert; Lettinga, Gatze (1990): Kinetics of chemical and biological sulphide oxidation in aqueous solutions. Water Research 24, 667-671.

Abstract. A new equation for the non-catalyzed sulfide chemical oxidation rate in a phosphate buffered system at pH 8.0 and 25°C is found. Our experiments show that the reaction order wrt the oxygen concentration, n, depends on the sulfide concentration. The following equation is proposed:

$R_i = k [S]^m [O]^{nlog[S]} (mg/l h).$

The values for the constants m, n, k were found to be 0.41, 0.39 and 0.57, respectively. The biological oxidation rate in cell suspensions from a bioreactor, also measured in a phosphate buffered system at pH 8.0 and 25°C, was found to be a factor 75 faster than the chemical non-catalyzed oxidation rate at sulfide concentrations around 10 mg/l. At higher sulfide concentrations this difference becomes less, e.g. at 100 mg/l the biological oxidation rate is only 7 times faster than the chemical oxidation rate. The two cell suspensions used in the experiments behave quite differently towards the suflide concentration. Cell suspension 1 (taken from a reactor operated at a sulfide concentration of 7 mg/l) exerts its maximal oxidation rate (230 mg/l h) at a sulfide concentration of 10 mg/l. Cell suspension 2 (taken from a reactor operated at a sulfide concentration of 150 mg/l. The total oxidation rate (chemical and biological) of cell suspension 2 at 150 mg/l is 210 mg/l h (of hwich only 5% is chemical). Cell suspension 1 shows severe substrate inhibition at sulfide concentrations around 150 mg/l h (of hwich only 5% is chemical). Cell suspension 1 shows no sulfide inhibition up to a sulfide c oncentration of 600 mg/l.

- 2479 Danielewiski,M; Mrowec,S; Stoklosa,A (1982): Sulfidation of iron at high temperatures and diffusion kinetics in ferrous sulfide. Oxidation of Metals 17(1/2), 77-97.
- 2497 Wilmot, PD; Cadee, K; Katinic, JJ; Kavanagh, BV (1988): Kinetics of sulfide oxidation by dissolved oxygen. J. Water Pollut. Control Fed. 60, 1264-1270.
- 2519 Ma,Qi Ying; Logan,Terry J; Traina,Samuel J (1995): Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. Environ. Sci. Technol. 29, 1118-1126.
- 2591 Brantley, SL; Stillings, L (1996): Feldspar dissolution at 25 C and low ph. Am. J. Sci. 296(February), 101-127.
- 2635 Kehinde-Phillips, Olusegun Omolaja (1982): Causes and inhibition of low-temperature aqueous oxidation of sulfide ores at Lockerby Mine, Ontario. Masters Thesis, Laurentian University, Ontario.
- 2651 Schott, Jacques; Petit, Jean-Claude (1987): New evidence for the mechanisms of dissolution of silicate minerals. In: Aquatic Surface Chemistry. (Ed: Stumm, W) John Wiley and Sons, New York, 293-315.
- 2723 St-Arnaud,Luc C; Yanful,Ernest K (1993): Water covers for the decommissioning of sulphidic mine tailings impoundments: Mattabi mines case study. In: Proceedings CIM Conference of Metallurgists/Advances in Environmental Protection for Metallurgical Industries. (:),, .
- 2731 Kalinowski,Birgitta E; Schweda,Peter (1996): Kinetics of muscovite, phlogopite, and biotite dissolution and alteration at pH 1-4, room temperature. Geochim. Cosmochim. Acta 60(3), 367-385.
- 2732 Malmstrom, Maria; Banwart, Steven (1997): Biotite dissolution at 25 C: The pH dependence of dissolution rate and stoichiometry. Geochim. Cosmochim. Acta 60(3), 2779-2799.