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PYRITE OXIDATIVE DISSOLUTION
RATES, PRODUCTS, AND MECHANISMS

Annotated Bibliography

In Progress
June 30, 1999

Minnesota Department of Natural Resources
Division of Minerals
Reclamation Section

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TABLE OF CONTENTS

PREFACE	1
Table 1. Summary of pyrite oxidation information	2
CRYSTAL STRUCTURE	6
DISSOLUTION RATES	
Abiotic Dissolution Rates	8
Biotic Dissolution Rates	16
OXIDATION PRODUCTS	
Dissolved Oxidation Products	22
Surface Oxidation Products	24
REACTION MECHANISM	
Abiotic Dissolution Mechanism	29
Biotic Dissolution Mechanism	46

PREFACE

The Minnesota Department of Natural Resources, Division of Minerals, has been conducting an ongoing literature review of sulfide oxidation rates and mechanisms. Understanding the relative rates of the oxidation of specific iron sulfide minerals provides a background necessary to evaluate literature regarding current developments relevant to environmental waste management. It also creates a foundation for calculating acid production rates in laboratory dissolution tests on reactive mine waste materials, 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.

This document is intended to serve as a directory of literature found in a database maintained within the Minerals Division Reclamation Section that is most relevant to pyrite, FeS_2 , oxidation under environmental conditions. When available, a database reference number is provided with each citation. It is important to note that an extensive volume of literature has been published on the subject of pyrite oxidation. However, this document does not attempt to address the entire range of information that has been published on pyrite oxidation. Rather, the references listed in this document are meant to provide an overview of the type of information that has been published (Table 1). This document will also serve as an foundation for future literature searches and reviews on the oxidation of pyrite.

Table 1. Summary of pyrite oxidation information contained in the references listed in this document. Reference numbers for the Reclamation Unit's literature database (Papyrus) are shown in parentheses when available.

Reference	Structure	Oxidation Rates	Oxidation Products	Mechanisms
Ahonen, L.; Tuovinen, O.H. 1991. Appl. and Environ. Microbiol., 57, 138-145. (#1122)				x
Ahonen, L.; Tuovinen, O.H. 1994. ACS Symp. 550, 79-89. (#1688)			x	
Andrews, G. 1989. Biotechnology in Minerals and Metal Processing, 87-93. (#2362)				x
Arkesteyn, G.J.M.W. 1980. Plant and Soil, 54, 119-134. (#1124)		x		x
Bailey, L.K.; Peters, E. 1976. Can. Metallurgical Quarterly, 15(4), 333-334. (#178)				x
Banerjee, A.C. 1976. Indian J. of Chem., 14A, 845-850. (#57)			x	
Bergholm, A. 1995. USGS, OFR 95-389.				x
Berry, V.K. et al., 1978. Hydrometallurgy, 3, 309-326. (#2356)			x	x
Blevins, D.W.; Chafin, D.T. 1988. Symp. Mining, Hydrology, Sedimentology, and Reclamation, 53-57. (#224)				x
Borek, S.L. 1992. USBM, Draft Report. (#1177)			x	x
Borek, S.L. 1994. ACS Symp. 550, 45-58. (#1685)			x	
Bronold, M. et al., 1994. Surf. Sci., 314, L931-936.	x			
Bryner, L.C. et al., 1967. Trans. Soc. Mining Eng., AIME, 238, 56-65. (#55)				x
Buehler, H.A.; Gottschalk, V.H. 1910. Econ. Geol., 5, 28-35. (#361)		x		
Chaiken, R.F.; Dalverny, L.E. 1995. USBM, RI 9569. 42p.		x		
Chander, S.; Briceno, A. 1987. Minerals and Metallurgical Processing. 171-176. (#2357)			x	x
Chander, S.; Briceno, A. 1988. Mine Water and Mine Waste, V1. 164-169. (#1436)		x		
Chander, S. et al., 1992. SME Ann. Meeting. (#1729)			x	x
Dalverny, L.E.; Chaiken, R.F. 1992. Environ. Issues and Waste Management in Energy and Minerals Production, 435-443. (#2684)		x		
Dold, B. et al., 1996.				x
Doyle, F.M.; Mirza, A.H. 1990. Mining and Mineral Processing Wastes, 5, 43-51. (#1602)				x
Dubrovsky, N.M. et al., 1984. Can. Geotech. J., 22, 110-128. (#2896)				x

Reference	Structure	Oxidation Rates	Oxidation Products	Mechanisms
Duncan, D.W. et al., 1967. Can. J. Microbiol. 13, 397-403. (#2483)		x		x
Eggleston, C.M. et al., 1996. Am. Mineralogist, 81, 1036-1056.			x	x
Ehlers, E.G.; Stiles, D.V. 1965. Am. Mineralogist, 50, 1457-1461. (#2608)			x	
Evangelou, V.P. 1995. Pyrite Oxidation Chemistry. (#2747)	x	x	x	x
Evangelou, V.P. 1998. Environ. Sci. Tech., 32, 2084-2091. (#2987)		x	x	x
Frost, D.C. et al., 1977. Fuel, 56, 277-280. (#2353)			x	
Garrels, R.M.; Thompson, M.E. 1960. Am. J. Sci., 258(A), 57-67. (#170)			x	x
Goldhaber, M.B. 1983. Am. J. Sci., 283, 193-217. (#6)			x	x
Gottschalk, V.H.; Buehler, H.A. 1912. Econ. Geol., 7, 13-34. (#362)		x		
Gould, W.D. et al., 1989. Biohydrometallurgy, 81-91. (#2557)				x
Guevremont, J.M. et al., 1997. Surf. Sci., 391, 109-124.	x			
Guevremont, J.M. et al., 1998. Environ. Sci. Tech., 32, 3743-3748. (#3162)			x	x
de Haan, S.B., 1991. Earth Sci. Rev., 31, 1-10. (#58)		x		x
Halbert, B.E. et al., 1983. (#583)		x		
Hamilton, I.C.; Woods, R. 1981. J. Electroanal. Chem., 118, 327-343. (#59)			x	
Hammack, R.W. 1985. Symp. on Surf. Mining, Hydrology, Sedimentology, and Reclamation, 139-144. (#225)			x	
Hammack, R.W. 1987. Proc 1987 Nat. Meeting Am. Soc. for Surf. Mining and Reclamation, 289-295. (#2620)				x
Hammack, R.W.; Watzlaf, G.R. 1990. Mining and Reclamation Conf. and Exhibition, 257-264. (#2748)		x		x
Karthe, S. et al., 1993. Appl. Surf. Sci., 72, 157-170.			x	x
Kleinmann, R.L.P. et al., 1981. Mining Eng., 300-305. (#163)				x
Kriegman-King, M.R.; Reinhard, M. 1994. Environ. Sci. Tech., 28, 692-700. (#2271)			x	x
Lapakko, K; Wessels, J.N. 1994. Inst. on Lake Superior Geol. Proc. 40 th Ann. Meeting, 29-30. (#2468)		x		
Li, J. et al., 1992, EPD Congress 1993, 229-244. (#2821)				
Lovgren, L.; Sjoberg, S. 1992. Internat. Mine Waste Management News, 2(2), 11. (#1271)				x
Lowson, R.T. 1982. Chem. Rev., 82, 461-497. (#175)		x	x	x

Reference	Structure	Oxidation Rates	Oxidation Products	Mechanisms
Lowson, R.T. et al., 1991. Proc. 2 nd Internat. Conf. Abatement of Acidic Drainage, V4, 159-172. (1291)				x
Luther, G.W.III 1987. Geochim. Cosmochim. Acta, 51, 3193-3199. (#8)				x
Lyalikova, N.N. 1961. Trudy Instituta Mikrobiologii Akademiya Nauk USSR, 9, 134-143. (#2631)				x
McKay, E.R.; Halpern, J. 1958. Trans. Metallurgical Soc. of AIME, 301-309. (#344)		x	x	x
McKibben, M.A.; Barnes, H.L. 1986. Geochim. Cosmochim. Acta, 50, 1509-1520. (#10)		x	x	
Mehta, M.P.; Murr, L.E. 1983. Hydrometallurgy, 9, 235-256. (#60)				x
Michell, D.; Woods, R. 1978. Aust. J. Chem., 31, 27-34. (#2358)			x	x
Morse, J.W. 1991. Geochim. Cosmochim. Acta, 55, 3665-3667. (#21)			x	
Morth, A.H.; Smith, E.E. 1966. Symp. Fossil Fuels and Environmental Pollution, 10, 83-92. (#248)				x
Moses, C.O. et al., 1987. Geochim. Cosmochim. Acta, 51, 1561-1571. (#13)				x
Moses, C.O.; Herman, J.S. 1991. Geochim. Cosmochim. Acta, 55, 471-482. (#61)				x
Mycroft, J.R. et al., 1990. J. Electroanal. Chem., 292, 139-152.			x	
Nakai, N. 1963. J. of Earth Sci., 11(2), 279-296. (#2488)		x		
Nesbitt, H.W.; Muir, I.J. 1994. Geochim. Cosmochim. Acta, 58, 21, 4667-4679.			x	x
Nicholson, R.V. et al., 1988. Geochim. Cosmochim. Acta, 52, 1077-1085. (#15)		x		x
Nicholson, R.V. et al., 1990. Geochim. Cosmochim. Acta, 54, 395-402. (#63)				x
Nordstrom, D.K. 1982. Acid Sulfate Weathering, 37-56. (#237)				x
Okereke, A.; Stevens, E.S. Jr. 1991. Appl. Environ. Microbiol., 57(4), 1052-1056. (#1123)		x		
Pahlman, J.E.; Reimers, G.W. 1986. USBM, RI 9059. (#227)				x
Pettenkofer, C. et al., 1991. Ber. Bunsenges. Phys. Chem., 95, 5, 560-565.	x			
Pugh, C.E. et al., 1984. Soil Sci., 137, 309-314. (#171)		x		
Reedy, B.J. et al., 1991. Geochim. Cosmochim. Acta, 55, 1609-1614.				x
Riley, J.A. 1985. Acid Water Implications for Mine Abandonment, 12-17. (#1744)				

Reference	Structure	Oxidation Rates	Oxidation Products	Mechanisms
Rimstidt, J.D.; Newcomb, W.D. 1989. Water-Rock Interaction-6, 581-584. (#1080)		x		
Sasaki, K. 1997. Can. Mineralogist, 35, 999-1008.			x	x
Silver, M.; Torma, A.E. 1974. Can. J. Microbiol., 20, 141-147. (#2485)				x
Singer, P.C.; Stumm, W. 1970. Science, 167, 1121-1123. (#246)				x
Smith, E.E. et al., 1969. ACS 13(2), 68-78. (#340)				x
Smith, E.E., Ohio State U., 1-11. (#697)				x
Steger, H.F. 1977. Talanta, 24, 251-254. (#194)			x	
Steger, H.F. 1979. Talanta, 26, 455-460. (#198)			x	
Steger, H.F.; Desjardins, L.E. 1978. Chem. Geol., 23, 225-237. (#64)			x	
Stenhouse, J.F.; Armstrong, W.M. 1952. CIM Bull., 55, 49-53. (#343)				x
Sullivan, P.R. et al., 1988. Environ. Geol. and Water Sci., 11(3), 289-295. (#261)			x	x
Szolnoki, J; Bognar, L. 1964. Acta Geologica, 8 (4), 179-187. (#2489)		x		
Taylor, B.E. et al., 1984. Geochim. Cosmochim. Acta, 48, 2669-2678. (#16)				x
Taylor, B.E. et al., 1984. Nature, 308, 538-541.				x
Temple, K.L.; Delchamps, E.W. 1953. Appl. Microbiol., 1, 255-258. (#169)				x
Van Breemen, N. 1988. Iron in Soils and Clay Minerals, 825-841. (#44)			x	
Walsh, F.; Mitchell, R. 1972. Environ. Sci. Tech., 6(9), 809-812. (#176)				x
Watzlaf, G.R.; Hammack, R.W. 1989. Proc. 9 th Ann. West Virginia Surf. Mine Drainage Task Force Symp. (#215)		x		
Wiersma, C.L.; Rimstidt, J.D., 1984. Geochim. Cosmochim. Acta, 48, 85-92. (#18)		x		
Wiese, R.G. et al., 1987. Chem. Geol., 63, 29-38. (#19)			x	x
Woods, R. et al., 1989. Internat. J. Mineral Processing, 27, 309-326. (#2482)		x	x	
Zheng, C.Q. et al., 1986. Ind. Eng. Chem. Process Des. Dev. 25(1), 308-317. (#173)		x		

CRYSTAL STRUCTURE

Bronold, M.; Tomm, Y.; Jaegermann, W. (1994) Surface states on cubic d-band semiconductor pyrite (FeS_2). *Surface Sci.*, 314, L931-L936.

Abstract. A model for the electronic structure of the (100) surface of the d-band semiconductor pyrite is presented based on ligand field theory. The existence of a new type of surface states at the valence band edge resulting from a symmetry reduction of the Fe coordination sphere is deduced. The model is able to explain the inversion layer observed on n-type crystals as well as surface core level shifts in S 2p photoemission spectra.

Guevremont, J.M.; Strongin, D.R.; Schoonen, M.A.A. (1997) Effects of surface imperfections on the binding of CH_3OH and H_2O on $\text{FeS}_2(100)$: using adsorbed Xe as a probe of mineral surface structure. *Surface Sci.*, 391, 109-124.

Abstract. Studies are presented that investigate the adsorption and binding of CH_3OH and H_2O on the atomically clean (100) crystallographic plane of pyrite, FeS_2 . Temperature programmed desorption suggests that both reactants adsorb molecularly at 90K and desorb thermally between 170 and 400K depending on the surface coverage. Photoemission of adsorbed Xe (PAX) suggests that the surface of pyrite is heterogeneous and contains a significant fraction of defect sites that are believed to be, at least in part, anion vacancy or sulfur-deficient sites. An upper limit of 0.2 is proposed for the fraction of surface sites that are defects on $\text{FeS}_2(100)$. PAX indicates that these defect sites at low adsorbate coverage serve as the exclusive binding sites for H_2O and CH_3OH adsorbate. We speculate on the basis of our ability to interpret PAX data for pyrite, that PAX may be of use for understanding the effect of short range order on adsorbate binding on other complex mineral surfaces. On the basis of high resolution electron energy loss spectroscopy, it is found that some dissociation of the adsorbate occurs on the pyrite. Vibrational data obtained with this technique suggests that Fe-O species result from the adsorbate decomposition. After saturation of the defect sites, further molecular adsorption is accommodated on the less reactive surface that we postulate is largely disulfide, the characteristic structural group of pyrite.

Pettenkofer, C.; Jaegermann, W.; Bronold, M. (1991) Site specific surface interaction of electron donors and acceptors on $\text{FeS}_2(100)$ cleavage planes. *Ber. Bunsenges. Phys. Chem.* 95, 5, 560-565.

Abstract. The interaction of UHV cleaved $\text{FeS}_2(100)$ surfaces with adsorbed H_2O as an electron donor and adsorbed Br_2 as an electron acceptor has been studied with

LEED, LEISS, UPS, and XPS to simulate semiconductor/electrolyte interfaces in UHV. The (100) cleavage plane is characterized by a $c(2 \times 2)$ or $p(\sqrt{2} \times \sqrt{2})R 45^\circ$ LEED pattern which is interpreted in terms of the unreconstructed FeS_2 surface. H_2O is molecularly adsorbed at low temperatures (100K) and desorbs completely at room temperature. LEIS-spectra taken at low coverages (<0.5 ML) suggest a preferential interaction with the Fe sites. Br_2 is ionosorbed at low coverages as well interacting specifically with Fe-sites. It is molecularly adsorbed at higher coverages. The ionosorbed part does not desorb at RT. The behavior of specific adsorption is related to the electronic nature of the band edges which are derived from Fe d-states.

DISSOLUTION RATES

Abiotic Dissolution Rates

Note: Sulfide oxidation rarely occurs abiotically. In this context, “abiotic” refers to studies that did not specifically mention biologic influences on pyrite oxidation.

10 McKibben, M.A.; Barnes, H.L. (1986) Oxidation of pyrite in low temperature acidic solutions: Rate laws and surface textures. *Geochim. et 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 30 °C in dilute, acidic chloride 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 (mol pyrite cm⁻² min⁻¹) are given by the following rate laws:

$$R_{\text{sp,Fe}^{3+}} = - 10^{-9.74} [\text{Fe}^{3+}]^{0.5} [\text{H}^+]^{-0.5} \quad (\text{pH 1-2})$$

$$R_{\text{sp,Fe}^{3+}} = - 10^{-6.77} [\text{O}_2]^{0.5} \quad (\text{pH 2-4})$$

$$R_{\text{sp,Fe}^{3+}} = - 10^{-1.43} [\text{H}_2\text{O}_2] \quad (\text{pH 2-4})$$

An activation energy of 56.9 ± 7.5 kJ/mol was determined for the oxidation of pyrite by dissolved oxygen from 20 - 40 °C. HPLC analyses indicated that only minor amounts of polythionates are detectable as products of oxidation by oxygen below pH 4; the major sulfur product is sulfate. Ferric ion and sulfate are the only detectable products of pyrite oxidation by hydrogen peroxide. Hydrogen peroxide is consumed by catalytic decomposition nearly as fast as it is by pyrite oxidation.

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 common assumption of a first-order, reproducible dependence of oxidation rates on surface area needs to be tested.

15 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 behavior 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 CO₂-O₂-N₂ gas mixture were passed continuously through the pyritic sand. The reaction rates were monitored by sulfate mass balance in the effluents.

The initial rate of oxidation was found to be a linear function of surface area. The rate-dependence on oxygen concentration is non-linear and the data fit a heterogeneous kinetic model in which the surface decomposition reaction, not sorption of oxygen, is the rate determining step. 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 behavior 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 five pyrite specimens obtained from various locales exhibited maximum differences of only about 25%.

18 Wiersma, C.L.; Rimstidt, J.D. (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 various sources were determined at 25 °C 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 oxidation-reduction potentials. The reaction follows the rate law:

$$-d[\text{Fe}^{3+}]/dt = k(A/M)[\text{Fe}^{3+}]$$

where [Fe³⁺] is the molal concentration of uncomplexed ferric iron, k is the rate constant and A/M is the surface area of reacting solid to mass of solution ratio. The measured rate constants, k, range from 1.0 x 10⁻⁴ to 2.7 x 10⁻⁴ sec⁻¹ ± 5%, with lower-temperature/ early diagenetic pyrite having the smallest rate constants, marcasite intermediate, and pyrite of higher-temperature 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 temperature interval of 25 to 50 °C is 92 kJ/mol. This relatively high activation energy indicates that a surface reaction controls the rate over this temperature range. The BET-measured specific surface area for lower-temperature origin. Consequently, since the lower-temperature types have a much greater A/M ratio, they appear to be more reactive per unit mass than the higher temperature types.

58 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 meteoric water, however, the weathering of pyrite takes place at such a rate that it can cause pollution and geotechnical problems within a few years. Recent work on pyrite oxidation 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. They 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.

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 $\text{FeS}_2 + 14 \text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$. 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 constant 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:

$$r_{\text{FeS}_2} = k_1 - k_2[\text{FeII}]^{0.5}[\text{FeIII}]^{0.5} / 1/[\text{FeIII}]^{0.5} + k_3 + k_4[\text{FeII/FeIII}]^{0.5}$$

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:

$$r_{\text{FeS}_2} = k'K_1'(\text{Fe}^{3+}) / [1 + K_1'(\text{Fe}^{3+}) + K_2'(\text{Fe}^{2+}) + K_3'(\text{Fe}^{3+})(\text{HSO}_4^-)]^{1.5}$$

- 344 McKay, E.R.; Halpern, J. (1958) A kinetic study of the oxidation of pyrite in aqueous suspension. Transactions of the Metallurgical Society of AIME., 301-309.

Abstract. A kinetic study of the oxidation of pyrite in aqueous suspension by molecular oxygen, at temperatures 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 temperatures 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.

- 361 Buehler, H.A.; Gottschalk, V.H. (1910) Oxidation of sulphides. Econ. Geol., 5, 28-35.

Summary. Experiments show not only a measurable oxidation for most sulphides treated, but also indicate that pyrite or marcasite, when mixed with other sulphides, causes a much more rapid oxidation of the second sulphide... that fine grinding affects the rate of oxidation.

- 362 Gottschalk, V.H.; Buehler, H.A. (1912) Oxidation of sulphides. Econ. Geol., 7, 13-34.

Summary... 1) confirmed our observations on the increased solubility of sulphides, 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 electrochemical 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.

583 Halbert, B.E.; Scharer, J.M.; Knapp, R.A.; Gorber, D.M. (1983) Determination of acid generation rates in pyritic mine tailings.

Measured sulfide oxidation rates in "pyritic" tailings. Supposedly "pyritic" meant mixed pyrite and pyrrhotite. Experiments were run at 6 and 21 °C and pH 3 and 7. Sulfate generation rates ranged from 7.12×10^{-3} to 1.17 mol/kg tailings/month. Activation energies ranged from 1.07 to 2.56×10^4 cal/mol.

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 values for the rate constant and reaction order when the data were analyzed in terms of reaction rates versus ferric iron concentrations. The rate law that fits these results best is:

$$dn_{\text{FeIII}}/dt = 3.63 \times 10^{-5} A m_{\text{FeIII}}^{0.7}$$

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 batch and plug flow experiments to hypothesized integrated rate equations gave ambiguous results.

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 results 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.

2357 Chander, S; Briceno, A (1987): Kinetics of pyrite oxidation. *Minerals and Metallurgical Processing* (August), 171-176.

Abstract. The properties of surface films on pyrite have been studied through electrochemical techniques of cyclic voltammetry and AC impedance measurements. The characteristics of the surface films depend on the conditions of oxidation and the source of pyrite. At potentials near 0.0 V, some pyrites have large values of polarization resistance, shown a certain degree of passivity. Some pyrites show more passivation than others, however. On oxidation, metastable phases of $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ form that transform to more stable phases on aging. The growth of surface films near the corrosion potential of pyrite follows linear kinetics that is attributed to a chemical (or an electrochemical) reaction as the rate determining step. The surface film is considered to be a hydroxide or an oxide because it is hydrophilic. This study has also demonstrated that AC impedance measurements can be used to study the growth characteristics of films at mineral/solution interfaces.

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

Summary of abstract. Ten tailings samples were collected from operating North American gold mines. The samples were quite fine, with 47 to 97% of each sample occurring in the -270 mesh fraction and 26 to 91% in the -500 mesh fraction. The total sulfur contents, an indicator of acid production potential, ranged from 0.1 to 7.63%. Most of the sulfur was associated with pyrite and pyrrhotite, with iron sulfide minerals constituting 0.58 to 13.6% of each sample.

A wet-dry cycle dissolution test was conducted on the tailings. A relationship between sulfate release rates and solid-phase sulfur content of the samples was determined by regression analysis. samples which were inconsistent with the relationship defined, as well as some "typical" samples, were analyzed for specific surface area and surface morphology. The anomalous sulfate release rates were

apparently due to differences in pyrite specific surface area resulting from variations in pyrite particle size and morphology. There was no apparent evidence suggesting that something other than the pyrite surface area was controlling the rates of pyrite oxidation.

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.

Abstract. The sulfur-II/sulfur-0 system has been studied in basic solutions at gold, galena, pyrite, and chalcopyrite surfaces using the rotating ring disc electrode technique. Polysulfide ions have been identified as intermediates in the system. The relative rates of the formation and further reactions of polysulfides vary from one surface to another. The fraction of the disc current that results in dissolved polysulfide ions during the initial stages of sulfur-II oxidation, increased in the order: gold \approx pyrite < chalcopyrite < galena. The reaction of sulfur-II with air at the mineral surfaces has been investigated by measuring open circuit potentials. The relevance of these studies to the depressant action of sulfur-II species for sulfide mineral flotation is discussed.

2684 Dalverny, L.E.; Chaiken, R.F. (1992) Leaching of pyrite from coal wastes in a trickle-bed reactor. *Environmental Issues and Waste Management in Energy and Minerals Production*, Balkema, Rotterdam, 435-443.

Abstract. Bureau of Mines researchers used a large countercurrent trickle-bed column reactor to obtain data on the chemical and transport processes controlling the leaching of pyrite from coal wastes. The acrylic plastic cylinder, 182.9 cm high 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 three-phase system contained stationary solid coal preparation plant waste, downward flowing lixiviant, and upward flowing air and gaseous reaction products. The longest duration experiment continued about nine 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/g pyrite/ hour, as based on the initial pyrite content. The rate of pyrite oxidation approached zero at about 140 days.

2748 Hammack, R.W.; Watzlaf, G.R. (1990) The effect of oxygen on pyrite oxidation. Mining and Reclamation Conference and Exhibition, Charleston, WV, 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 Å, 2) 5 g quantities of pyrite in small columns, and 3) 175 kg quantities 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%, the reaction rate was proportional to oxygen partial pressures.

Chaiken, R.F.; Dalverny, L.E. (1995) Leaching of pyrite from coal waste: Results of a diagnostic study. USBM Report of Investigations, RI 9569. 42p.

Abstract... conducted an experimental and theoretical study of coupled chemical kinetic and mass transport processes during leaching of pyrite from coal in a counterflow, "tickle-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 Fe³⁺) 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. Maximum 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. An adsorption-desorption model of solids leaching, which considers the role of heterogeneous porosity in solids leaching, was used to describe time-dependent leaching rates.

Biotic Dissolution Rates

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 non-inoculated treatments at 20% oxygen, compared with 0% oxygen., and was approx. ninefold greater for the same treatments inoculated with *T. ferrooxidans*.

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.

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 effect 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 columns 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 another 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% of 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 active 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.

1123 Okereke, Amechi; Stevens, Edward S Jr (1991): Kinetics of iron oxidation by *Thiobacillus ferrooxidans*. *Applied and Environmental Microbiology* 57(4), 1052-1056.

Abstract. A statistical relationship between the rate of ferric ion production by a strain of *T. ferrooxidans* and various levels of cell concentration, FeII concentration, Na concentration and temperature was studied by a direct colorimetric method at 304 nm. The relationship was linear (90 to 93%), cross-product (3 to 4%), and quadratic (1 to 2%). The levels of cell concentration and FeII concentration and their respective interactions with one another and the other factors had the most significant effects on the regression models. The solution of the quadratic response surface for optimum oxidation was a saddle point, and the predicted critical levels of temperature, cell concentrations, FeII concentration, and Na concentration ranged between -6 and 2 °C, 0.43 and 0.62 mg/ml, 72 and 233 mM, and 29.6 mM, respectively.

1124 Arkesteyn, GJM (1980): Pyrite oxidation in acid sulphate soils: The role of microorganisms. *Plant and Soil* 54, 119-134.

Summary. A study has been made of microbial processes in the oxidation of pyrite in acid sulfate soil material. Such soils are formed during aeration of marine muds rich in pyrite. Bacteria of the type of *Thiobacillus ferrooxidans* are mainly responsible for the oxidation of pyrite, causing a pronounced acidification of the soil. However, because *T. ferrooxidans* function optimally at pH values below 4.0, its activity cannot explain the initial pH drop from approximately neutral to about 4. This was shown to be a non-biological process, in which bacteria play an insignificant part. Although *T. thioparus* and *T. thiooxidans* were isolated from the acidifying soil, they did not stimulate oxidation of FeS₂, but utilized reduced sulfur compounds, which are formed during the non-biological oxidation of FeS₂.

Ethylene-oxide sterilized and dry sterilized soil inoculated with pure cultures or mixtures of various thiobacilli or with freshly sampled acid sulfate soil did not acidify faster than sterile blanks. *T. thiooxidans*, *T. thioparus*, *T. intermedius*, and *T. perometabolis* increased from about 10⁴ to 10⁵ cells/ml in media with FeS₂ as energy source. However, FeS₂ oxidation in the inoculated media was not faster than in sterile blanks.

Attempts to isolate microorganisms other than *t. ferrooxidans*, like Metallogenium or *Leptospirillum ferrooxidans*, which might also be involved in the oxidation of FeS₂ were not successful. Addition of CaCO₃ to the soil prevented acidification but did not stop non-biological oxidation of FeS₂.

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.

Abstract. The bacterial leaching of a low-grade chalcopyrite waste rock in a lixiviant containing thermophilic, *Sulfolobus*-like microorganisms at 60 °C and a lixiviant containing *Thiobacillus ferrooxidans* at 28 °C has been compared with the leaching in sterile lixiviant in terms of copper solubilized in elapsed time and the conversion of FeII to FeIII. Bacterial action has been shown to drastically increase the ratio of FeIII/FeII with elapsed time of leaching. Direct observations of the associated pyrite and chalcopyrite surface corrosion, utilizing scanning electron microscopy, showed that during the leaching of these sulfides as separate, non-contacting phases, the pyrite corroded more rapidly than the chalcopyrite in both sterile and inoculated media. This effect was more pronounced at elevated temperature and in the presence of bacteria. When the pyrite and chalcopyrite were in contact, the resulting galvanic interaction caused the chalcopyrite to corrode more rapidly than the pyrite, which was effectively passivated. The leaching of chalcopyrite is thereby enhanced in contact with pyrite. This effect is accelerated in the presence of bacteria. The corrosion of chalcopyrite was also markedly enhanced as a result of the oxidation of elemental sulfur (formed during the reaction) to sulfuric acid. This reaction was also accelerated by bacterial catalysis. The important implications of the enhanced chalcopyrite corrosion by galvanic interaction in the leaching of low-grade chalcopyrite waste and other galvanic-contact regimes involving metal sulfides are identified and discussed.

2362 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.

Abstract. Experiment shows that the microbial degradation of pyrite does not necessarily proceed stoichiometrically. Under some condition sulfur is oxidized preferentially leaving something approaching iron in composition; under others, the pyrite is converted almost to element sulfur. A kinetic model for the process based on three elementary biochemical reactions can explain these observations. The diffusion of sulfur along grain boundaries and dislocations in the solid pyrite uncouples the oxidation rates of sulfur and iron from the requirements of stoichiometry. This mechanism also explains qualitatively why bacteria adsorb preferentially at dislocation sites on pyrite surfaces, why they form "pits" at these sites, and why amorphous pyrite is more readily degraded than pure crystals. The rate-limiting step for pyrite oxidation is discussed.

2483 Duncan, DW; Landesman, J; Walden, CC (1967): Role of *Thiobacillus ferrooxidans* in the oxidation of sulfide minerals. Can. J. Microbiol. 13, 397-403.

Abstract. Selective inhibitors of iron and sulfide oxidation, sodium azide and N-ethyl-maleimide respectively, were used to demonstrate that washed cell suspensions of *T. ferrooxidans* attacked both insoluble ferrous iron and sulfide during the oxidation of chalcopyrite and pyrite. The oxidation of the two substrates occurred simultaneously and independently but the relative rates depended on how the cells were grown. When chalcopyrite-grown cells were used to oxidize chalcopyrite, 68-74% of the oxygen uptake was the result of sulfide oxidation and 25-30% the result of iron oxidation. With pyrite, all the oxygen uptake was due to sulfide oxidation. When iron-grown cells were used to oxidize chalcopyrite, two rates resulted. During the initial rapid rate, 80-90% of the oxygen uptake was due to iron oxidation, but during the second slower rate, the result duplicated those found with chalcopyrite-grown cells. Iron-grown cells oxidized pyrite at a constant and more rapid rate than chalcopyrite-grown cells. The faster rate was due to iron oxidation; since only 20-30% of the total oxygen uptake was due to sulfide oxidation.

2485 Silver, Marvin; Torma, Arpad E (1974): Oxidation of metal sulfides by *Thiobacillus ferrooxidans* grown on different substrates. Can. J. Microbiol. 20, 141-147.

Abstract. *T. ferrooxidans*, grown on either ferrous sulfate, lead sulfide concentrate, or chalcopyrite concentrate demonstrated oxygen uptake and CO₂ fixation in the presence of ferrous sulfate, chalcopyrite ore, pyrite ore, and red antimony trisulfide. Lead sulfide-grown cells could oxidize lead sulfide ore and galena, using the energy obtained for CO₂ fixation. All three cell types could oxidize nickel sulfide, but could not fix CO₂ in the presence of this substrate. The solubilization of metals from the substrates and the crystallographic changes in the insoluble residues are reported.

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 oxidation 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 S³² during oxidation of both sulfur and pyrite. Mixed culture experiments in the lab are shown to be necessary, in order to clarify 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 autotrophic 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 passage of bacteria on sulfide ores as well as the greater initial population of bacteria had a positive effect on the rate of oxidation. 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 those parts of the lattice where elements have different ionic radii can be easily attacked by microorganisms.

OXIDATION PRODUCTS

Dissolved Oxidation Products

- 6 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 the pH range 6 to 9 were carried 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 demonstrate 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), tetrathionate and sulfate were the major observed species. As pH is increased, these 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 pyrite surface.

- 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.

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 sulfides 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 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.

- 44 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 nontronite in soil horizons with pyrite oxidation, observed in certain coastal plain soils in Thailand, will be described.

- 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.

- 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-

phananthranoline 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 phanthranoline complex produced in these two determinations is a function of the original Fe(III) concentration and of time.

Surface Oxidation Products

- 21 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 μm) 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 to 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.

- 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. 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.

- 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.

- 225 Hammack, R.W. (1985) The relationship between the thermal activity of pyrite and the rate of acid generation. Symp. on Surface Mining, Hydrology, Sedimentology, and Reclamation, University of Kentucky, Lexington, KY, Dec 9-13, 139-144.

Summary. A coating of oxidation products composed of sulfate salts and iron oxides, determined by XPS, was responsible for the observed decreases in reactivity with time after crushing. The reactivity of pyrite can be partially restored by rinsing the sample with dilute HCl which removes the oxidation products.

- 2271 Kriegman-King, M.R.; Reinhard, M. (1994) Transformation of carbon tetrachloride by pyrite in aqueous solution. Environ. Sci. Technol. 28, 692-700.

Summary. Surface oxidation products were analyzed using XPS and STM. After five weeks of aerobic reaction, FeOOH began to form on the pyrite surface. Sulfur largely remained as pyrite, however some evidence of polysulfides and elemental sulfur was observed. FeII was depleted in the near surface of the pyrite lattice. They concluded that FeII was leached while the S lattice remained intact.

- 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 spectroscopic 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 measurements for the three surface preparations.

2608 Ehlers, E.G.; Stiles, D.V. (1965) Melanterite-rozenite equilibrium. *Am. Mineralogist*, 50, 1457-1461.

Summary. Samples of altered pyrite were collected from an abandoned mine dump in the upper reaches of Sandy Run in Brown Township, Vinton County, Ohio, as part of a study dealing with the oxidation of iron sulfides. The pyrite samples were encrusted with either masses of pale green fibers, extremely white powder, or a mixture of both. The fibrous material was determined by XRD to be mixtures of melanterite, rozenite, $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$, and halotrichite $(\text{Mg,Fe})\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$.

Karthe, S.; Szargan, R.; Suoninen, E. (1993) Oxidation of pyrite surfaces: a photoelectron spectroscopic study. *Appl. Surf. Sci.*, 72, 157-170.

Abstract. Surfaces of pyrite differently prepared in situ and ex situ have been studied before and after contact to air and air-saturated aqueous solutions of $4 \leq \text{pH} \leq 10$ by means of photoelectron spectroscopy. Pyrite surfaces fractured or scraped in situ revealed FeS-like species concentrated in the surface region. Preparation (polishing, grinding, powdering and prolonged oxidation in air mainly resulted in basic iron sulfate and iron oxide/hydroxide. A promoting effect of an increased surface roughness due to the preparation was observed for the formation of iron oxide/hydroxide compared with sulfate in contrast to the natural oxidation process. Oxidation in air also led to sulfur-rich species identified as iron-deficient regions below monolayer coverage. Similar regions were present at ground surfaces exposed to air-saturated solution of pH 4 and 5. In near-neutral to alkaline solution mainly iron hydroxyoxide is formed in the layer thickness of which was estimated in the range of 0.5 mm (pH 5) to 1.7 mm (pH 10).

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 were placed 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 rozenite) 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.

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, viz. covellite, jarosites, and S⁰, 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.

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 done 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 S_{2p} 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 pyrite 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.

Mycroft, J.R.; Bancroft, G.M.; McIntyre, N.S.; Lorimer, J.W.; Hill, I.R. (1990) Detection of sulphur and polysulphides on electrochemically oxidized pyrite surfaces by X-ray photoelectron spectroscopy and Raman spectroscopy. *J. Electroanal. Chem.* 292, 139-152.

Abstract. The electrochemical oxidation of pyrite surfaces in near-neutral aqueous chloride solutions has been investigated using XPS and Raman spectroscopy in conjunction with electrochemical techniques. The surface oxidation products of pyrite, between 600 and 700 mV (SCE), have been identified by Raman spectroscopy as polysulfides and elemental sulfur.

OXIDATION MECHANISM

Abiotic Dissolution Mechanism

Note: Sulfide oxidation rarely occurs abiotically. In this context, "abiotic" refers to studies that did not specifically mention biologic influences on pyrite oxidation.

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-} 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 FeS_2 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 FeS_2 . The bridge formation between two metals by a common ligand, and The electron transfer is consistent with an inner sphere type mechanism. In FeS_2 , 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 FeS_2 oxidation and reduction.

Additional bridges can be formed on The FeS_2 surface during oxidation until The initial oxidation product $\text{S}_2\text{O}_3^{2-}$ 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 radical in solution. It does predict The formation of an ion radical on The pyrite surface. The proposed mechanism gives The same initial intermediate (FeS_2O) as recently proposed by Moses et al. (1987), but explains possible surface attachment by an oxidant and subsequent FeS_2 oxidation using a MO theory approach. The proposed surface mechanism is consistent with experimental observations of several 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.

13 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 products 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) thiosulfate 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 except traces of sulfite at pH 9. The faster rate of oxidation in 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.

60 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 towards 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 pyrite are in contact, potentiodynamic polarization measurements were carried out in 1 M H₂SO₄ 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 H₂SO₄ and Bryner and Anderson medium respectively. The corrosion current (5 μ A/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 CuFeS₂, FeS₂ 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

extraction by way of maximum contact with each other. A $\text{CuFeS}_2:\text{FeS}_2$ ratio of 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 The optimized 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 galvanically). This also made it possible to observe The surfaces of The specimens as The leaching proceeded in The presence of galvanic interaction. Coupled $\text{CuFeS}_2/\text{FeS}_2$, ZnS/FeS_2 and $\text{CuFeS}_2/\text{FeS}_2/\text{ZnS}$ 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 buffering 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 DO. 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.

63 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.

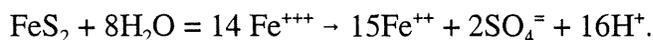
Abstract. The kinetic behavior of pyrite oxidation in The lab was studied over a period of about 10,000 hrs in reactors through which a carbonate-buffered solution and air (20% O₂) flowed continuously. Three grain size fractions were monitored. The concentration of sulfate and The mass of The effluent 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 constant 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 ($k_s = 3.04 \times 10^{-6}$ m/h +/- 46%) and the diffusion coefficient for oxidant through The oxide layer ($D_s = 1.08 \times 10^{-12}$ m²/hr +/- 30%). The estimated thickness of The oxide layer at The end of The experiment agreed well with The measured value. Oxide accumulation on The pyrite surfaces under neutral pH conditions results in a significant reduction in oxidation rates over time. This behavior 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.

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% $m_{\text{Fe}^{+++}}$ is in accord with The classical reaction:



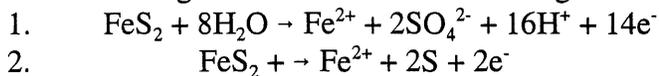
The average rate of reduction from 100% $m_{\text{Fe}^{+++}}$ to 50% $m_{\text{Fe}^{+++}}$ is constant for pyrite from a given locality, and differences in The average rates between specimens from different localities could not be related to minor compositional variations of The solutions or of The pyrites. 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.

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

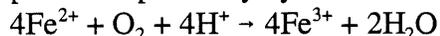
Abbr. Summary. The chemistry and physics of iron disulfide were reviewed with reference to The aqueous oxidation of pyrite by molecular oxygen. Morphology and crystal structure influence The reaction rate in The following order: euhedral pyrite < framboidal pyrite < marcasite. Three reaction paths have been identified for 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.

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

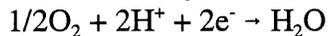
Abstract. The oxygen pressure leaching of pyrite has been studied with regard to reaction mechanism by ^{18}O tracer tests, electrochemical simulation and actual leaching experiments over The following range of variables: T, 85 - 130 °C; P, 0 - 976 psi O_2 ; and acid concentration 0.01 - 3 M H_2SO_4 . 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:



Ferric ions are produced primarily by a slow homogeneous reaction:



The cathodic reaction initially involves The reduction of oxygen:



This reaction is supplemented by cathodic reduction of ferric ions after these have built 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 pyrite during leaching.

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 $\delta^{34}\text{S}$ 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 $\delta^{18}\text{O}$ values of meteoric water ranged from -5.8 to +4.4 permil and averaged +0.4 permil., which is similar to $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ values fro sulfate oxygen in The gypsum 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.

- 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 USBM 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 O₂. Water vapor content of The atmosphere was found to be The critical factor in The rate of spontaneous oxidation of pyrite, with a water vapor content greater than oxygen resulted in negligible 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 resulting 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 steams 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; Reddy, K.J. (1988): Iron sulfide oxidation and The chemistry of acid generation. *Environmental Geology and Water Sciences* 11(3), 289-295.

Abstract. Acid mine drainage produced from The oxidation of iron sulfides often contains elevated levels of dissolved Al, Fe, and SO_4 and low pH. Understanding The interactions of these elements associated with acid mine drainage is necessary for proper solid waste management planning. Two eastern oil shales were leached using humidity cell methods. This study used a Now Albany Shale (4.6% pyrite) and a Chattanooga Shale (1.5% pyrite). The leachates from The humidity cells were filtered and The filtrates were analyzed for total concentrations of cations and anions. After correcting for significant solution species and complexes, ion activities were calculated from total concentrations. The results show that The activities of FeIII, FeII, Al and SO_4 increased due to The oxidation of pyrite. Furthermore, The oxidation of pyrite resulted in a decreased pH and an increased $\text{pe} + \text{pH}$. The FeIII and FeII activities appeared to be controlled by amorphous $\text{Fe}(\text{OH})_3$ solid phase above a pH of 6.0 and below $\text{pe} + \text{pH}$ 11.0. The FeIII, FeII and SO_4 activities reached saturation with respect to FeOHSO_4 solid phase between pH 3.0 and 6.0 and below $\text{pe} + \text{pH}$ 11.0. Below a pH of 3.0 and above a $\text{pe} + \text{pH}$ of 11.0, FeII, FeIII, and SO_4 are supported by $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solid phase. Above a pH of 6.0, The Al activity showed an equilibrium with amorphous $\text{Al}(\text{OH})_3$ solid phase. Below pH 6.0, Al and SO_4 activities are regulated by The AlOHSO_4 solid phase, irrespective of The $\text{pe} + \text{pH}$. The results of this study suggest that under oxidizing conditions with low to high leaching potential, activities of Al and Fe can be predicted on The basis of secondary mineral formation over a wide range of pH and redox. As a result, The

long-term chemistry associated with disposal environments can be largely predicted (including trace elements).

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.

697 Smith, E.E.; Svanks, K.; Shumate, K. (xxxx) Sulfide to sulfate reaction studies. Ohio State University, Columbus, OH. 1-11.

Summary. Based on present knowledge, a possible mechanism involved in The sulfide to sulfate reaction may be described as follows: 1) The final electron transfer is through The reduction of a ferric ion species adsorbed on a "reactive site" of pyrite. 2) The ferric species may be adsorbed as a ferric ion from a solution of high Eh or as a ferrous ion; The adsorbed ferrous ion is then catalytically oxidized to ferric by oxygen adsorbed on The active site formed by The ferrous ion. 3) Under laboratory conditions used, The rate limiting step is The surface electron transfer reaction.

In oxidation by ferric ions, rates are determined by concentration and ferric/ferrous ratio. Since adsorption of ferrous ions is much greater than ferric, rates increase rapidly as The ferric/ferrous ratio approaches infinity.

Aerobic oxidation rates are much higher than The corresponding anaerobic rate at The same ferric/ferrous ratio, and orders of magnitude higher than can be accounted for by chemical oxidation of ferrous ions in solution, thus leading to The conclusion that solution reactions are insignificant in a purely chemical system. It is possible that The ferric/ferrous ratio can be increased by microbial action to The point that The ferric/ferrous ratio is rate determining in an aerobic system. The possibility increases as The oxygen concentration decreases.

Neither The nature of The "reaction sites" nor a description of The adsorbed ferrous and ferric species are known. Qualitatively, it appears that The reactive sites for

aerobic and anaerobic oxidation are different, since The aerobic rate is independent of iron in solution. A higher order of bond strength for The regenerative ferrous ion is necessary than that for The ferrous ion produced by reduction of ferric ions.

1177 Borek, Sandra L (1992): The Effect of Humidity on Pyrite Oxidation (DRAFT). U.S. Department of The Interior, Bureau of Mines, Pittsburgh, PA.

Abstract. Pyrite is an iron disulfide mineral commonly associated with coal and adjacent strata. When water and oxygen react with pyrite, iron, sulfate, and acidity are produced. At certain humidities, some pyrites may be able to utilize water vapor in The humid air and weather. The rates of oxidation and weathering products differ among and between pyrites in different relative humidity situations. In this experiment, six different types of pyrite were placed in four humidity controlled chambers (34-79% RH) and analyzed by Mossbauer spectroscopy after approximately 30, 60, 90, 120, 150, 200, and 250 days. Hematite was present in The samples of one pyrite after 90 days in all experimental humidity conditions. Ferrous sulfates (melanterite and rozenite) were detected in three samples after 30 days in high relative humidity conditions, and after 90 days in mid- to high relative humidity conditions. Two samples did not display significant weathering over time in any relative humidity. By using The humidity chamber/Mossbauer method, The contribution of humidity to pyrite oxidation can be monitored.

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.

1291 Lawson, 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.

Abstract. Pyrite was oxidized under $^{18}O_2$ gas in $H_2^{16}O$ solutions with and without added ferric ion. The product sulfate was analyzed by vibrational spectroscopy to determine The relative amounts of sulfate isotopomers formed. At $70^\circ C$ and pH 1 with no added FeIII The majority of The sulfate formed was that which derived all four oxygen atoms from water, but significant amounts of other isotopomers which derive one or two oxygen atoms from molecular oxygen were observed. The reverse experiment using $^{16}O_2$ gas in $H_2^{18}O$ produced a mirror image in product isotopomer composition. Addition of FeIII at The commencement of The reaction reduced The amount of $S^{16}O_2^{18}O_2$ observed in The product. The relative concentrations of isotopomers were found to vary with pH and temperature. The results indicate a

progressive change in mechanism as The system generates products and that FeIII is directly involved in The oxidation process.

1602 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.

Abstract. Pyrite is one of The most problematic components of The waste from mining and mineral processing operations. When oxidized in The presence of water, pyrite releases acid, dissolved iron, sulfate, and heat. All of these can be highly deleterious. Unfortunately, The rate of pyrite oxidation is difficult to predict, and hence allow for in The design of waste management facilities. The rate varies according to The oxidant; dissolved ferric ions can accelerate oxidation by orders of magnitude, compared to oxidation by atmospheric oxygen alone. naturally occurring, acidophilic, chomolithotrophic bacteria markedly increase The rate of pyrite oxidation. Nevertheless, none of these effects can account completely for The significant variations in reactivity observed for pyrites from different sources. Work done to relate The reactivity to The semiconducting characteristics of ore pyrite samples from different sources is reported here. Samples were chemically characterized by electron microprobe and atomic absorption spectrophotometry. The semiconducting properties were determined from Hall effect measurements. The electrochemical behavior was determined by rest potential measurements and cyclic voltammetry studies of single crystals. The results indicate that The electrochemical behavior is correlated to some extent with The composition and electrical properties, but is dominated by The preceding electrochemical history. This suggests that caution should be exercised in using electrochemical studies to predict The rate of acid and heavy metals release from pyritic wastes.

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.

Abstract. The mechanism of oxidation of sulfur in pyrite is a function of The rate and driving force for oxidation. New evidence is presented in this article to show that at moderate potentials, a sulfur-rich hydrophobic layer is formed. Under ordinary conditions, The sulfur layer is covered with a layer of iron oxides, hydroxides, sulfate or oxy-sulfide ions. Under these conditions, pyrite is hydrophilic. In The presence of iron-chelating agents or iron sequestering ions, iron layer might not form. Under these conditions, sulfur-layer is exposed and pyritic might become

hydrophobic. Stronger oxidizing conditions decompose The sulfur-layer, thereby making The surface hydrophilic.

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.

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.

Abstract. An x-ray photoelectron spectrometer was used to monitor The abiotic oxidation of pyrite under unsaturated conditions. Results of this study indicated that reclamation to inhibit acid production in The unsaturated zone should be directed towards reducing The relative humidity within pyritic zones. Reducing oxygen in The unsaturated zone resulted in reduced acid production only if The oxygen partial pressure was sustained below 10%.

2747 Evangelou, VP (1995): Pyrite Oxidation Chemistry. Lewis Publishers, Boca Raton, FL. 304 pages.

Features. 1) Includes a review on solution and surface chemistry of minerals, including acid drainage production and control, 2) Discusses The molecular and surface properties of pyrite and how such properties influence kinetics of pyrite oxidation, 3) Discusses The role of microorganisms in pyrite oxidation, 4) Examines The advancement and potential application of pyrite microencapsulation in coal waste, and 5) Gathers scientific knowledge on pyrite and acid mine drainage, evaluates it, and uses it as a springboard to new and improved control technologies.

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.

2896 Dubrovsky, N.M.; Cherry, J.A.; Reardon, E.J.; Vivyurka, A.J. (1984): Geochemical evolution of inactive pyritic 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 hydrochemical zonation has developed in which infiltration water from rain and snow has resulted in an upper zone of low-pH water with high concentrations of sulfate, 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 process 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 pyrite in 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 aluminum 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 amounts 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 hundred years. A long-term potential for acid and iron production is also shown by 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.

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 electroneutrality and pH considerations, however, The pyrite surface FeII coordinates OH. We proposed that this surface FeII OH when in The presence 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 CO₂ 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 -FeIIIHCO₃ complex whereas a second potential mechanism involved formation of a pyrite surface carboxylic acid group complex [-Fe(II)SSCOOFe(II)]. We hypothesized that these pyrite surface -CO₂ complexes could promote abiotic oxidation of pyrite by accelerating The abiotic oxidation of FeII. Iron III would oxidize The disulfide (-S₂) by accepting its electrons. Using a miscible displacement technique, oxidation of FeS₂ with H₂O₂ 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 FeS₂. Furthermore, The data show that FeS₂ oxidation kinetics were more dependent on HCO₃⁻ but were less dependent on H₂O₂ for The range of HCO₃ and H₂O₂ concentrations tested.

3162 Guevremont, J.M.; Bebie, J.; Elsetinow, A.R.; Strongin, D.R.; Schoonen, M.A. (1998) Reactivity of The (100) plane of pyrite in oxidizing gaseous and aqueous environments: effects of surface imperfections. *Environ. Sci. Technol.*, 32, 3743-3748.

Abstract. The oxidation induced degradation of pyrite in mine tailing piles is of significant interest, since The resulting production of sulfuric acid has a severe detrimental impact on The surrounding environment. Hence, there has been much effort to understand The mechanism of pyrite oxidation. Much of The information concerned with The surface reactivity of pyrite, however, has been inferred from macroscopic observations during aqueous studies. Here, we directly investigated model FeS₂ (100) surfaces after exposure to well defined oxidizing environments, with XPS, to evaluate The mechanism of pyrite oxidation at a microscopic level. Our studies showed that, in The pure H₂O vapor environment, oxidation was spatially limited to non-stoichiometric or sulfur deficient surface sites. Results further suggested that thiosulfate was a long lived intermediate that ultimately converted to

sulfate on The pyrite surface in this environment. Significant oxidation of The disulfide group of $\text{FeS}_2(100)$ only occurred if O_2 was present along with H_2O vapor. It is proposed that O_2 adsorption on The stoichiometric region of $\text{FeS}_2(100)$ resulted in The formation of Fe^{3+} sites that facilitated The dissociation of H_2O and The oxidation of The disulfide group.

Reedy, B.J.; Beatie, J.K.; Lowson, R.T. (1991) A vibrational spectroscopic ^{18}O tracer study of pyrite oxidation. *Geochim. Cosmochim. Acta*, 55, 1609-1614.

Abstract. Pyrite was oxidized under $^{18}\text{O}_2$ gas in H_2^{16}O solutions, with and without added ferric ion, and The sulfate produced was analyzed by vibrational spectroscopy to determine The relative amounts of sulfate isotopomers ($\text{S}^{16}\text{O}_n^{18}\text{O}_{4-n}$) formed. At 70°C and pH 1, with no added Fe^{3+} , The majority of The sulfate formed was that which derived all four oxygen atoms from water, but significant amounts of two other isotopomers, $\text{S}^{16}\text{O}_3^{18}\text{O}$ and $\text{S}^{16}\text{O}_2^{18}\text{O}_2$, which derive one or two oxygen atoms from molecular oxygen were observed. When Fe^{3+} was added at The start under identical conditions, no $\text{S}^{16}\text{O}_2^{18}\text{O}_2$ was observed. The major isotopomer formed was still S^{16}O_4 , with $\text{S}^{16}\text{O}_3^{18}\text{O}$ present as a minor product. Experiments which were performed at initial pH 7 yielded similar results, as did others performed at 20°C , although The amounts of The minor isotopomers formed vary with temperature. All of The results were confirmed by performing identical experiments with The source of The oxygen isotopes reversed, that is by oxidizing pyrite under air in H_2^{18}O solutions and obtaining The same products in isotopic reverse.

Nesbitt, H.W.; Muir, I.J. (1994) X-ray photoelectron spectroscopic study of a pristine pyrite surface reacted with water vapor and air. *Geochim. Cosmochim. Acta*, 58, 4667-4679.

Abstract. Pristine pyrite fracture surfaces, exposed for 7 h to water vapor at low pressure (10^{-5} Pa), display no change to their Fe(2p) or S(2p) XPS spectrum, but oxygen deposition occurs as H_2O , OH^- , and O^{2-} (74, 19, and 7%, respectively). An additional 24 h exposure to air (80% humidity) causes The proportions of oxygen species to change dramatically, with OH and O increasing to 55 and 25%, and H_2O decreasing to 20%. These changes are accompanied by development of a broad FeIII peak of The Fe(2p) spectrum, produced by oxidation of FeII to FeIII and formation of FeIII oxyhydroxide surface species. There is, however, no sulfate peak developed in The S(2p) spectrum during The 24 h exposure to air. The XPS data demonstrate that formation of FeIII oxyhydroxides precedes sulfate formation, hence rates of redox reactions producing sulfate or other oxygen-bearing S species are initially slower than redox reactions leading to The formation of FeIII oxyhydroxide surface species.

Exposure to air for an additional 9 days produces no appreciable change to The O(1s) or Fe(2p) spectrum, but small amounts of sulfate are observed in The S(2p) spectrum.

After production of sulfate species, FeIII sulfate salts probably form at The surface of pyrite by reaction of sulfate with previously formed FeIII oxyhydroxides.

The Fe(2p_{3/2}) spectrum of the vacuum fractured pyrite surface reveals a high energy tail on the major FeII peak. the tail may result from the metallic character of Fe in pyrite. The binding energy and shape of the tail, however, are accurately predicted from S-bonded FeIII spectral peaks observed in the pyrrhotite Fe(2p) spectrum; consequently, the presence of FeIII bonded to sulfur in the near surface of pyrite is another reasonable explanation for the tail.

Disulfide, monosulfide, and polysulfide are present on the vacuum fractured pyrite surface at 85, 10, and 5% respectively. Monosulfide decreases and disulfide increases proportionately during the first 24 h exposure to air. After a total of 10 days exposure, monosulfide decreases to half its original value, polysulfide increases appreciable, and sulfate and thiosulfate are present at 1.8 and 2.3% respectively. There is little change to disulfide content during the entire experiment.

Two explanations are offered for the presence of the three S species on the vacuum fractured pyrite surfaces. Approximately 5% of S is present as polysulfide and 10% as monosulfide. This 1:2 ratio is obtained is some disulfide is “disproportionate” to polysulfide and monosulfide where, on average, four atoms of S are included in the polysulfide species. An alternative explanation includes ferric iron; if present, it may give rise to complex charge compensation involving “disproportionation” of disulfide to monosulfide (for charge balance) and polysulfide.

Eggleston, C.M.; Ehrhardt, J.J.; Stumm, W. (1996) Surface structural controls on pyrite oxidation kinetics: An XPS-UPS, STM, and modeling study. *Am. Mineralogist*, 81, 1036-1056.

Summary. X-ray and UV photoelectron spectroscopy and STM were used to observe the initial oxidation of pyrite surfaces in air. The results show the growth of oxide-like oxidation products, with minor contributions from sulfate. UPS shows a decrease in the density of electronic states in the uppermost valance band of pyrite, corresponding to oxidation of surface Fe²⁺. This allows reliable interpretation of STM images, which show that initial surface oxidation of Fe²⁺ proceeds by growth of oxidized patches. The borders of oxidized patches contain small segments oriented in the (110) and (100) directions. STM of as-received pyrite cube surfaces, oxidized in air for years, also show the importance of the (110) crystallographic directions, on the surface, in controlling reaction progress.

An oxidation mechanism consistent with the XPS, UPS STM and Monte Carlo results is proposed. The rate constant for electron transfer from surface exposed pyrite Fe²⁺ to O₂ is small. Electron transfer is more rapid from pyrite Fe²⁺ to Fe³⁺

present on the surface as an oxidation product, such as in the patches we observed. Fe^{2+} in oxide is a better reductant than Fe^{2+} in pyrite, so electron transfer to O_2 from the oxide is also fast. However, this two-step mechanism is faster overall only if electron transfer to the surface oxide patches is irreversible (e.g. because of S_2 oxidation or electron hopping within the surface oxide patches). Cycling of Fe between II and III forms, particularly along borders between oxidized and unoxidized areas, is thus a key feature of the pyrite oxidation mechanism. An understanding of the surface electronic and band structure aids definition of the redox potentials of electrons in various surface states. Rates of electron transfer from these states to O_2 are estimated using a kinetic theory of elementary heterogeneous electron transfer.

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 above, 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 inhomogeneous 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 sulfides 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 "unspecified" adsorption (surface) on the FeIII hydroxides and/or of sulfide precipitation. 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.

Bergholm, A. (1995) Oxidation of pyrite. U.S. Geological Survey, OFR 95-389, 20p.

Partial Summary. The experiments on the wet oxidation of pyrite have shown that the reaction between the mineral and oxygen is partly a direct process, and partly proceeds via oxidation of FeII ions in solution and the subsequent turnover between FeIII and the mineral. This turnover has been studied in a particular series of experiments. The reaction pathway through FeII-FeIII ions is of little importance except in acidic solutions (pH <3) with an iron concentration of at least 2 g/L.

During wet oxidation the effects of the conditions are:

- 1) the reaction rate is approximately proportional to the oxygen concentration
- 2) the reaction rate doubles on increasing the temperature by 10°C
- 3) the reaction is severely inhibited by acid (pH<3)
- 4) the reaction is favored by iron salts.

In general, the major part of the sulfur in pyrite is converted to elemental sulfur during wet oxidation, while a minor part is converted to sulfate. In acidic solutions and in the presence of iron salts, a larger fraction of the decomposed pyrite is converted to sulfur than would otherwise occur. The sulfur produced remains on the mineral surface and inhibits further reaction. This explains the reduced rate of reaction with increasing time.

Biotic Dissolution Mechanisms

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 oxidation. 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 chemical 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 sulfides in well aerated, unsaturated zone environments occurs dominantly by microbially mediated pathways.

55 Bryner, LC; Walker, RB; Palmer, R (1967): Some factors influencing the biological and non-biological 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 effect of 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 oxidation 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 oxidation of FeII in the presence of the mineral. Studies were also made on the biological 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 oxidation of the mineral by absorbed oxygen 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 iron II increased the rate of oxidation of free copper.

The air oxidation of pyrite in 0.1N sulfuric 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.

- 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. ferrooxidans* are of prime importance in the formation of acid drainage from pyritic 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 activity 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. ferrooxidans* by controlled release of anionic detergents can inexpensively reduce pyrite oxidation and acid formation.

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

- 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 resulting 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.

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

Summary. 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 mechanism 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.

Anaerobic oxidation rate of pyrite is determined by the ferric/ferrous ratio and total iron concentration in solution. The adsorption equilibrium constant for ferrous ions on pyrite is much greater than ferric ions. At least for the three different pyrite samples examined, the reactivity is inversely related to the ratio of the adsorption constants, ferrous to ferric.

Aerobic oxidation rate is a function of oxygen concentration at the reaction site. It is not affected by the presence of either ferric or ferrous ions nor the total iron concentration. Since the two rates are also independent, it appears that different "reactive sites" are involved in aerobic and anaerobic oxidation.

The aerobic and anaerobic rates are approximately equal for sulfur ball pyrite when 70% of the iron in solution is in the ferric state and the solution is in equilibrium with air of 21% oxygen. Since such a high ferric/ferrous ratio is only possible in a microbial system in a natural environment, oxidation by ferric ions (anaerobic oxidation) can be significant only in bacteria-catalyzed systems. the oxidation regime can be determined from oxygen and iron concentrations and the ferric/ferrous ratio at the reaction site. Note that the effluent water cannot be used to determine these factors since this water is in no way representative of the water in contact with the "reactive sites."

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.

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 Hole Wyoming, August 13-18, 1989. (Eds: Salley, Joseph; McCready, Ron GL; Wichlacz, Paul L) CANMET, Ottawa, 81-91.

Abstract. The isotopic composition of sulfate produced during the oxidation of four sulfide minerals by two environmental isolates of *Thiobacillus ferrooxidans* was determined. The substrates were pyrite, sphalerite, chalcopyrite, and pentlandite. The bacterial oxidation of each of these minerals was carried out in water of varying initial ^{18}O compositions, and samples for sulfate analysis were collected at appropriate time intervals. Insignificant sulfur isotope selectivity was observed during bacterial oxidation, but the ^{18}O composition of the sulfate was dependent upon that of the water. Since the sulfur oxidizing system of *T. ferrooxidans* has previously been shown to be a true oxygenase, the incorporation of oxygen from the water into sulfate is probably due to rapid ^{18}O exchange between water and reactive sulfur intermediates.

2631 Lyalikova, NN (1961): Bacteria in the oxidation of sulfide ores. Trudy Instituta Mikrobiologii Akademiiy Nauk USSR 9, 134-143.

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

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 10^9 cells) of *T. ferrooxidans*. In the range of $600\text{-}200\text{ cm}^{-1}$, 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 poorly 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 density 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 exhausted. Ammoniojarosite subsequently was formed. In the sterilized control, precursors were less readily formed, and jarosite formed. There was no evidence for direct involvement of bacteria in the formation of jarosite. The changes 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.

Taylor, B.E.; Wheeler, M.C.; Nordstrom, D.K. (1984) Isotope composition of sulphate in acid mine drainage as measure of bacterial oxidation. *Nature*, 308, 538-541.

Abstract. The formation of acid waters by oxidation of pyrite-bearing ore deposits, mine tailings piles, and coal measures is a complex biogeochemical process and is a serious environmental problem. We have studied the oxygen and sulphur isotope geochemistry of sulfides, sulfur, and sulfate and water in the field and in experiments to identify sources of oxygen and reaction mechanisms of sulfate formation. Here we report that the oxygen isotope composition of sulfate in acid mine drainage shows a large variation due to differing proportions of atmospheric- and water-derived oxygen from both chemical and bacterially-mediated oxidation. ^{18}O -enrichment of sulfate results from pyrite oxidation facilitated by *Thiobacillus ferrooxidans* in aerated environments. Oxygen isotope analysis may therefore be useful in monitoring the effectiveness of abatement programs designed to inhibit bacterial oxidation. Sulfur isotopes show no significant fractionation between pyrite and sulfate, indicating the quantitative insignificance of intermediate oxidation states of sulfur under acid conditions.