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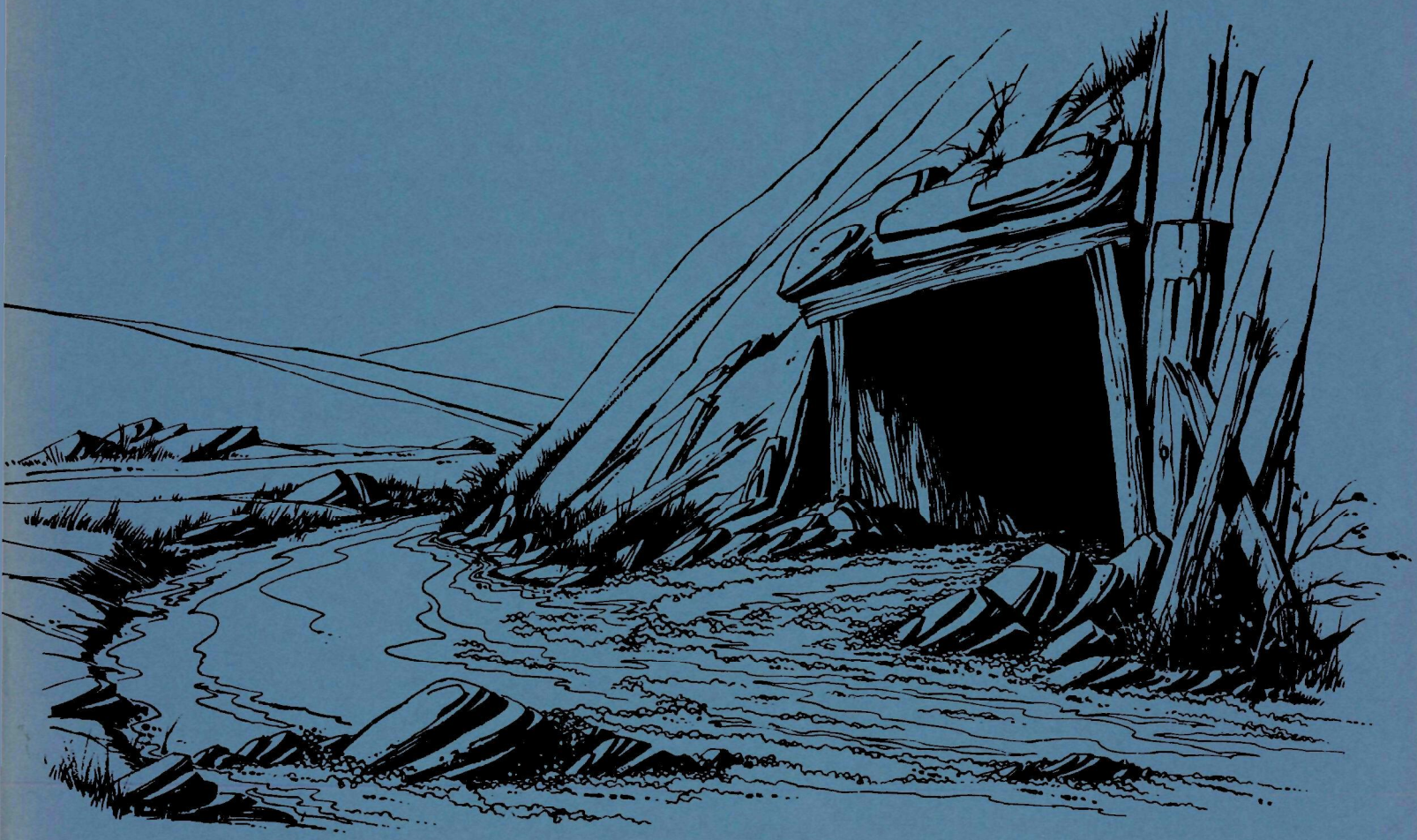
Evaluation of Pyritic Oxidation by Nuclear Methods



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Evaluation of Pyritic Oxidation by Nuclear Methods

by

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for the

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ABSTRACT

EVALUATION OF PYRITIC OXIDATION BY NUCLEAR METHODS

by Robert A. Baker

Laboratory studies demonstrated the feasibility of using the Mössbauer effect and a backscattering mode of detecting 14.4 Kev gamma rays to spectroscopically monitor the oxidation processes taking place on pyrite materials. A cobaltous oxide form of cobalt-57 was the radiation source.

Spectra were obtained of pyritic surfaces under 2 mm of water. Differentiation of nonoxidized and oxidized pyritic surfaces was possible with further separation of the spectra to show individual oxidation product peaks suggesting ferric hydroxide and ferric sulfate.

This report was submitted in fulfillment of Research Grant No. 14010 FII between the Federal Water Pollution Control Administration and the Mellon Institute, Carnegie-Mellon University.

Key Words: Mössbauer effect, backscatter detection, mine drainage, pyrite, iron-57, cobalt-57, iron.

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Section I

CONCLUSIONS

It has been demonstrated in this short feasibility study that the Mössbauer effect, a nuclear resonance absorption phenomenon, may be used in conjunction with a scattering-mode detection system to monitor chemical oxidation of pyritic material.

The technique is sensitive to differences in extra-nuclear electron distributions and permits nondestructive observation of the chemical state being studied. Differences between ferric and ferrous iron and between pyrite and oxidation products are measured.

Spectra of pyritic surfaces were obtained without difficulty when these were covered by a film of water 2 mm in depth.

The spectrographic measurements were favored when the surface of the material being measured was flat and at right angles to the radiation beam. Particles of larger size or highly irregular surfaces are geometrically less favored for analyses.

Oxidized pyritic material gave Mössbauer spectra which could be separated to indicate presence of ferric hydroxide and ferric sulfate.

Oxidation reaction rates with the particular pyrite under study were sufficiently slow so that spectra could be taken over extended periods such as 8 to 24 hours without significant differences in the spectral response. This facilitates long-term scanning and hence the likelihood of detection of low concentrations of reaction products.

Section II

RECOMMENDATIONS

Major effort in this feasibility study was devoted to construction of a backscattering detector and verification that 14.4 Kev gamma rays could be used to monitor the chemical state of pyritic surface through a film of water. It was beyond the scope of the study to quantitatively characterize the response of the analytical system to the various ferrous and ferric compounds known or suspected of being involved in the pyritic oxidation process. The concentration and time of absorption relationships should be established for these compounds.

In future research, a cobalt-57 source of 200 millicuries intensity in the form of cobaltous oxide should be used. This would enhance the analytical efficiency of the system over that with the 100 millicurie source used in the feasibility study.

Once the aforementioned steps have been taken, the system should be applied to a study of the oxidation reactions of pyrites with and without organisms. The nature and rate of formation of the reaction products on the surface should be compared with those existing in the aqueous solution. Comparison of the biologically seeded and nonseeded systems should indicate the nature of the role of the microorganisms in the oxidation process.

Section III

INTRODUCTION

The objective of this research was to demonstrate the feasibility of using the Mössbauer effect and backscattering mode detection of 14.4 Kev gamma rays to spectroscopically monitor pyritic oxidation. Successful demonstration will provide a valuable technique for defining the nature of the oxidation processes. Such knowledge is necessary if practical methods of eliminating or restricting acid mine drainage formation are to evolve.

When coal mine pyrite, FeS_2, is oxidized in the presence of water, acidity is formed. Acidity is attributed to S_2^{-II} oxidation to sulfate and to Fe(II) oxidation to ferric iron and its hydrolysis.

$$FeS_2(s) + \frac{7}{2}\,O_2 + H_2O \longrightarrow Fe^{+2} + 2SO_4^{-2} + 2H^+$$

Yellow-brown ferric sulfate and ferric hydroxide precipitates which form are known as "yellow-boy" in the colloquial language of the coal industry. The acidity and dissolved salt content impair the quality of the receiving body of water and restrict usefulness of the resource. Hence, the need to prevent these discharges. Despite much study, the understanding of the pyrite oxidation is still incomplete. Singer and Stumm (1968) found that sulfate retards Fe(II) oxidation. Though the oxidation rate is first order with respect to Fe(II) it is slower than in the presence of sulfate. The rate of ferric hydrolysis is linear second-order with respect to Fe(III) and faster in the presence of sulfate. They proposed that in the absence of bacteria the rate determining step is the Fe(II) oxidation. Schematically:

$$FeS_2 \xrightarrow[\text{slow}]{} SO_4^{-2} + Fe(II)$$

and

$$Fe(II) + O_2 \xrightarrow{\text{slow}} Fe(III)$$

$$Fe(III) + FeS_2 \xrightarrow{\text{fast}} Fe(II) + SO_4^{-2}$$

The FE(II) oxidation rate is dependent upon the anionic species under acidic conditions (Huffman and Davidson, 1956). Since the hydroxyl ligand has a strong Fe(III) affinity it was postulated to be a factor in Fe(II) oxidation. The hydrolysis of free Fe(III) is therefore involved in Fe(II) dissolution from the pyrite. Garrels and Thompson (1960) studied pyrite oxidation by iron sulfate and showed that the rate is independent of total Fe(II) ions on the pyritic surface. Oxidation of pyrites to release ferrous and sulfate ions was observed only at sites occupied by ferric ions. This oxidation rate is slow relative to the adsorption process, hence the latter controls.

The specific role of acidophilic chemoautotrophic bacteria in pyritic conversion to acid mine drainage is still undefined. These Fe(II)- and S_2^{-II}-utilizing organisms are active at pH 2 to 4.5 and use carbon dioxide as their carbon source. Since oxidation of FeS_2 may proceed solely by chemical routes the microorganisms are not essential to acid formation. Their role may be: (1) as a direct catalyst to alter the overall chemical reaction rates, or (2) as specific catalytic agents which alter the rate of intermediate reactions and the nature of the resulting by-products but not the overall rate. The microorganisms may remove electrons from surface pyritic iron to start a reaction chain and/or catalyze sulfur oxidation or they may simply increase Fe(III) concentration and hence the Fe(III) to Fe(II) ionic ratio. The ferric ion is reduced to ferrous ion by the pyrite and the pyrite is oxidized to the ferrous ion.

Silverman and Ehrlich (1964) outlined two alternate mechanisms for bacterial conversion of S_2^{-II}. One involves Fe(III) oxidation of pyrites to obtain Fe(II) which the organism oxidizes back to Fe(III). The alternate mechanism is independent of Fe(III) and requires only contact between the bacteria and S_2^{-II}. It is likely that both mechanisms could take place in a given system depending on the nature of the pyritic material. Silverman (1967) further elaborated on the mechanism of the bacterial action and proposed that two mechanisms of bacterial pyrite oxidation operate concurrently. These were termed the direct contact and indirect contact mechanisms. The direct contact mechanism requires physical contact between the bacteria and the pyrite particles. The indirect contact mechanism requires that the bacteria oxidize Fe(II) to the Fe(III) state thereby regenerating the Fe(III) ions required for chemical oxidation of pyrite. During this investigation it was reported that Fe(III) oxidizes pyrite in the absence of bacteria and oxygen. Smith and Shumate (1970) claim that direct oxygen oxidation and Fe(III) oxidation of pyrite are independent processes and that the latter is a chemical analogy of the microbially enhanced pyrite oxidation process.

The role of S_2^{-II} and the ferrous ion is twofold in the metabolism of these bacteria. They supply both the energy and reducing power for carbon dioxide fixation. Dugan and Lungren (1965) have proposed, in the case of the Fe(II), a model to explain the coupling of the energy released from Fe(II) in the form of an electron to the carbon reduction mechanism within the cell. In this model, an initial iron and oxygen complex is oxygenated but not oxidized in the absence of electron transport. Subsequently, this complex reacts with iron oxidase or oxygenase to effect the electron transport. It is not evident from this study whether the complex is formed in solution or on the pyrite surface.

These often unreconcilable reports prompted a pilot plant investigation by this laboratory of the microbiological and chemical aspects of pyritic oxidation. These studies utilized continuous flow, environmentally controlled units to simulate conditions in an actual mine. The results, Baker and Wilshire (1968, 1970), provided quantitative information about the kinetic and hydraulic factors affecting acid mine drainage release. However, the exact nature of the reaction mechanism at the mineral surface was still unknown. It was concluded that a novel analytical procedure would have to be

applied. This is especially true if reactions on the pyritic surface were to be differentiated from those that occur in the aqueous solution at some finite distance from the surface.

It was suggested that the Mössbauer effect, a nuclear resonance absorption phenomena, might provide a means of monitoring pyritic surface reactions. The technique is sensitive to differences in extra-nuclear electron distributions and permits nondestructive observation of the chemical state of the isotope under examination. The difference between ferric and ferrous iron and their oxides, sulfates and sulfides may be observed. Radiation from cobalt-57 source in a known crystal lattice will preferentially be absorbed by iron-57 nuclei. Absorption will only occur when the iron-57 nuclei are incorporated in either a crystal lattice or a sufficiently large molecule to prevent the recoil which occurs when gamma rays are emitted or absorbed by the nuclei. Absorption requires that the energy levels match precisely. Precision of the match may be destroyed by the small amount of energy involved in a Doppler shift produced by velocities on the order of tenths of a mm per second.

Mössbauer effect may be observed by two modes. Usually a transmission mode is used in which the source, absorber and detector are in series. However, the nature of the pyritic material to be studied suggested use of the scattering mode in which the source and detector are on the same side of the sample. Shielding is arranged so that the detector does not respond to a significant fraction of the primary radiation emitted by the source. With the scattering mode detection system, only atoms in a layer approximately 0.01 mm deep on the mineral surface will respond.

The source and absorber are mounted so that their relative velocity may easily be varied in a precisely controlled manner. Resonance absorption is observed at certain discrete velocities depending on the chemical states. If the source and absorbing nuclei are in the same state, resonance absorption will be observed at zero relative velocity. Differences in chemical state are observed as a shift from zero velocity and by quadrupole splitting which is manifest as two peaks. The degree of shifting and splitting expected during the measurement of pyritic surfaces will be indicative of the state of the iron-57.

Use of the Mössbauer effect and the backscattering detection mode to monitor reactions at the pyritic surface, though theoretically possible, had not been previously demonstrated. Of particular concern was the practicality of making measurements through an aqueous film and the relative time intervals for significant oxidative reaction vs. requisite exposure time necessary to obtain spectra. It was proposed to use krypton-methane filled proportional counters to detect resonantly-scattered 14.4 Kev photons as the optimum approach to intrinsic detection sensitivity. This system was selected in preference to alternates of detection of conversion electrons or detection of 6.5 Kev x-rays. The efficiency of the 14.4 Kev system was expected to be greater because of the lower nonresonance effect. Clarification of these points was the objective of this feasibility study.

Section IV

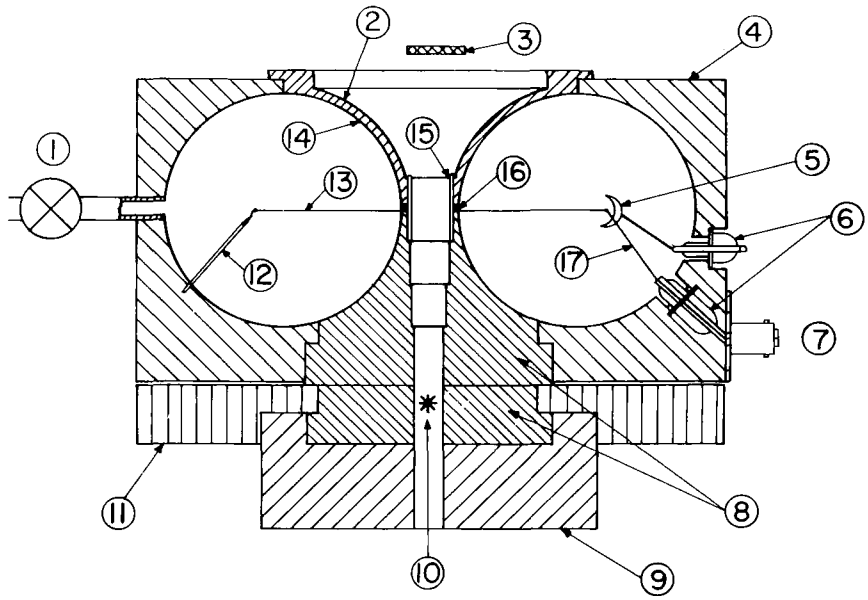
EXPERIMENTAL EQUIPMENT

Major effort was devoted to manufacturing, assembling and improving the backscattering detector system. The basis of this work was a detector developed under sponsorship of the U. S. Atomic Energy Commission. (Chow, et al., 1969.) The design of this prototype unit was modified to maximize signal to noise ratio by increasing shielding; improving detector resolution; and optimizing the geometry of the physical system.

Improved detector shielding reduces the count rate caused by high energy radiation coming directly from the source. This reduces the background counting rate and improves the signal to noise ratio. The reduced background count rate for a given source intensity also permits use of a more intense source without loss of counter resolution. Geometric optimization maximizes exposure to direct radiation without sacrificing efficiency of measuring the scattered photons. The following design innovations were made: (a) a circular anode replaced the eight-cornered design of the prototype; (b) thinner anode supports were made of quartz; (c) a guard electrode was added at the lead-in to compensate for field distortion; (d) a window was used which completed rather than truncated the toroidal shape of the detector active volume.

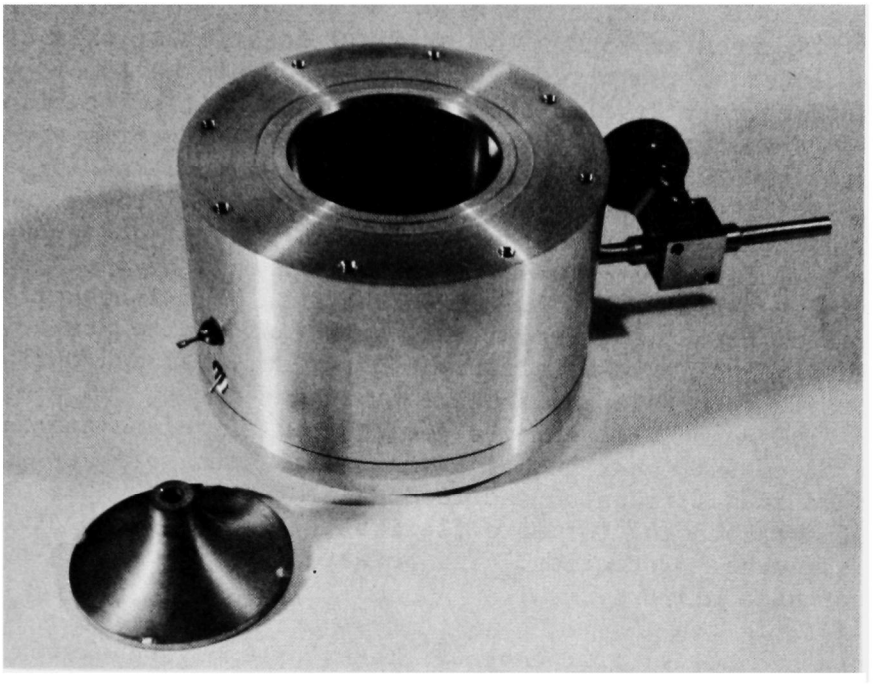
Figure 1 depicts the cross-sectional view of the detector and identifies the parts. Figure 2 shows two views of the detector in an early stage of assembly. The detector wall encloses a toroidal volume and consists of an aluminum body for the outermost part of the toroid, a tantalum shield for the inner quarten (nearest the source, and an aluminum-coated polypropylene window for the inner quarter) nearest the sample. The joints, between the tantalum and the aluminum, and between the polypropylene and the aluminum, are sealed with epoxy cement as are the lead-in supports for the anode and guard and the gas inlet tubing. The joint between the window and the tantalum shield is provided with a rubber o-ring and an aluminum sleeve and is sealed with a silicone compound. Earlier attempts to seal the latter joint with a rigid epoxy failed because pressure-vacuum cycling during detector filling caused the thin window to flex and crack the seal. An aluminum clamping plate holds the tantalum shield in place (bolts not shown) and another thin plate (1/8" thick - not shown) clamps the window edge to the detector body. The evaporated aluminum window coating was applied by vacuum deposition and was shown to make electrical contact with the body of the detector.

Ecosil - Manufactured by Emerson & Company, Incorporated, Canton, Massachusetts.



NO	DESCRIPTION
1	High Vacuum Valve
2	Polypropylene Window
3	Typical Sample Location
4	Aluminum Body
5	Grid for Guard Voltage
6	Stupakoff Seals
7	Connector for Preamplifier
8	Tantalum Shield
9	Lead Shield
10	Typical Source Location
11	Clamping Plate (bolts not shown)
12	Quartz Support Rod (one of seven)
13	0.001" dia. Wire Anode (3" diameter circle)
14	Evaporated Aluminum Coating
15	Aluminum Tube Insert
16	"O" Ring
17	Lead to Anode

Figure 1. Assembly of Mössbauer Scattering Proportional Counter



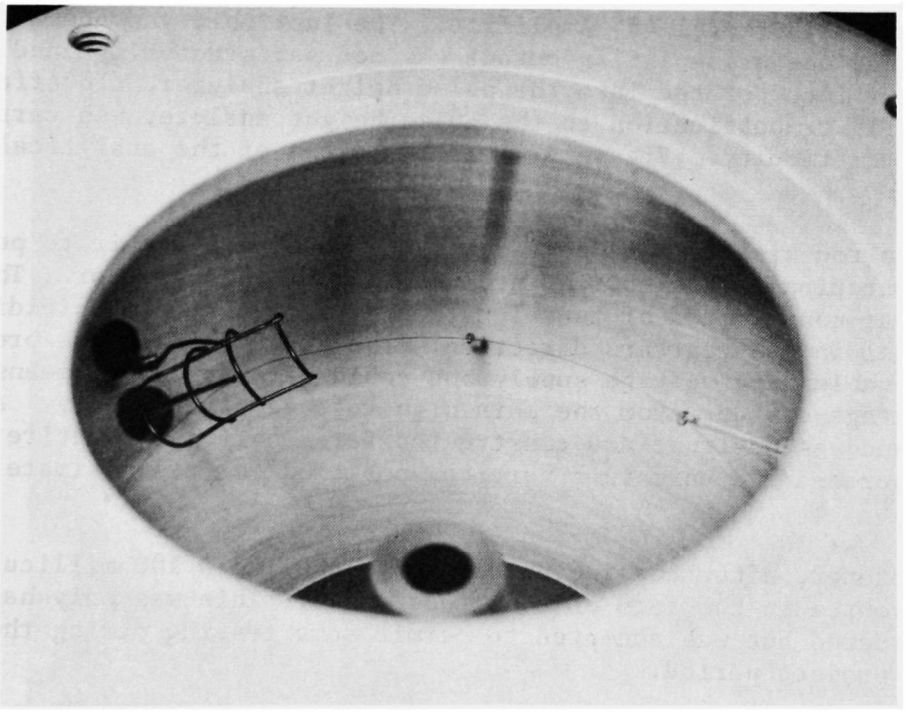


Figure 2. Mossbauer Detector During Assembly - Two Views

The anode is a 0.001" diameter Neutroloy[2] wire and is supported at eight points along its circular form. The original location of this circular anode at the center of the circular cross-section of the toroid was found to yield unsatisfactory resolution. Optimization of its location led to the present 3" diameter circle. Seven of the anode supports are 1 mm diameter quartz rods which are thinned down at the ends and formed into loops through which the wire passes. The lower ends of these rods are epoxy-cemented into holes in the detector body. The eighth support is a .010" O.D. stainless steel tube into which the ends of the anode pass. This stainless steel tube is soldered to the tube of a stupakoff seal which is cemented into the detector body. The anode wire passes through this tube and is finally soldered at the outer end. An appropriate fitting is provided to make the electrical connection to the preamplifier (see below). The guard electrode is constructed of welded tantalum wire and is soldered to the inner end of a solid-wire stupakoff seal (see Figure 2). Additional tantalum and lead shielding is provided at the source end of the detector for more flexibility in source location as well as for personnel protection. The detector is filled with a 90% krypton-10% methane mixture.

The electronic components of the spectrometer assembly consisted of: (a) Nuclear Science Industries Model MM-60 Mössbauer Effect Spectrometer; (b) Northern Scientific Model NS-600 pulse height analyzer; (c) John Fluke Model 412 B High Voltage Power Supply; (d) ORTEC Model 109 PC Preamplifier; (e) ORTEC Model 485 Amplifier. The last unit was added when it was found that the preamplifier output was not satisfactorily handled by the amplifier incorporated into the pulse height analyzer. Interfacing, including slight modification to the pulse height analyzer was carried out without difficulty. Figure 3 gives two views of the analytical assembly.

An extension rod was designed to fit the Mössbauer drive unit to permit deeper penetration of the source into the back of the detector. This extension was constructed of tantalum to provide additional shielding for personnel in the rearward direction. The guard voltage was provided by an adjustable high voltage supply but could be provided by means of a fixed voltage divider from the main high voltage power supply. A support stand was designed and constructed for mounting the entire sample-detector-source-drive unit in a vertical position for its ultimate application.

The manufacturer, after considerable delay, supplied a 100 millicurie cobalt-57 source in the form of cobaltous oxide. This was only half the strength ordered but was accepted to permit some testing during the brief nine-month project period.

When the source was first placed in position within the detector central hole, an unexpectedly high background was obtained. After considerable study of this effect, it was ascertained that the source, though well within the specifications for radiochemical purity, contained significant concentrations of cobalt-56 and cobalt-58 and a small amount of cobalt-60.

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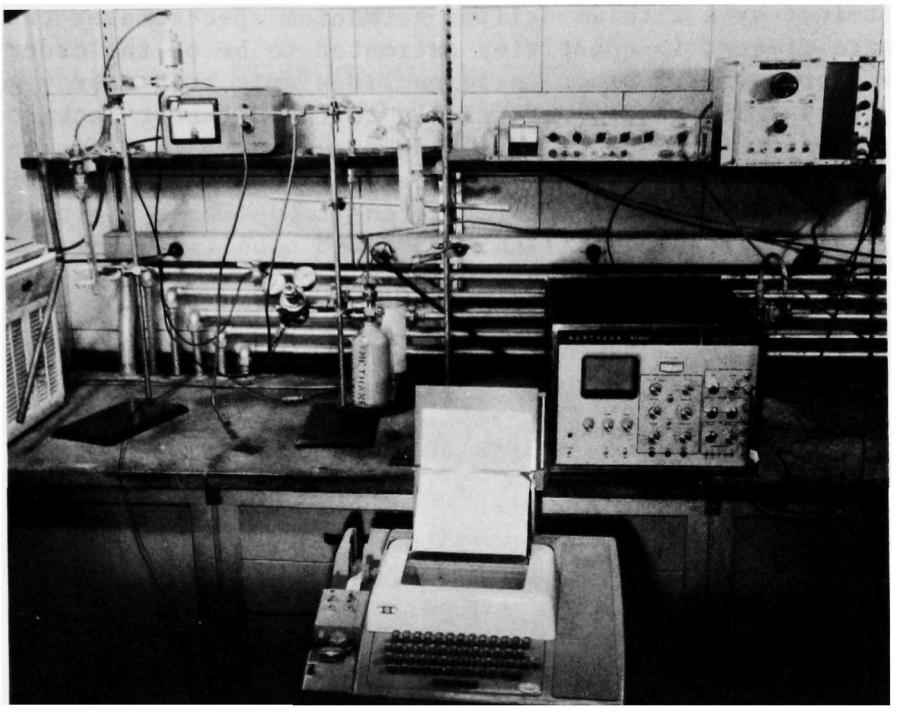
[2] Molecu-Wire Corporation, Wall Township, New Jersey.



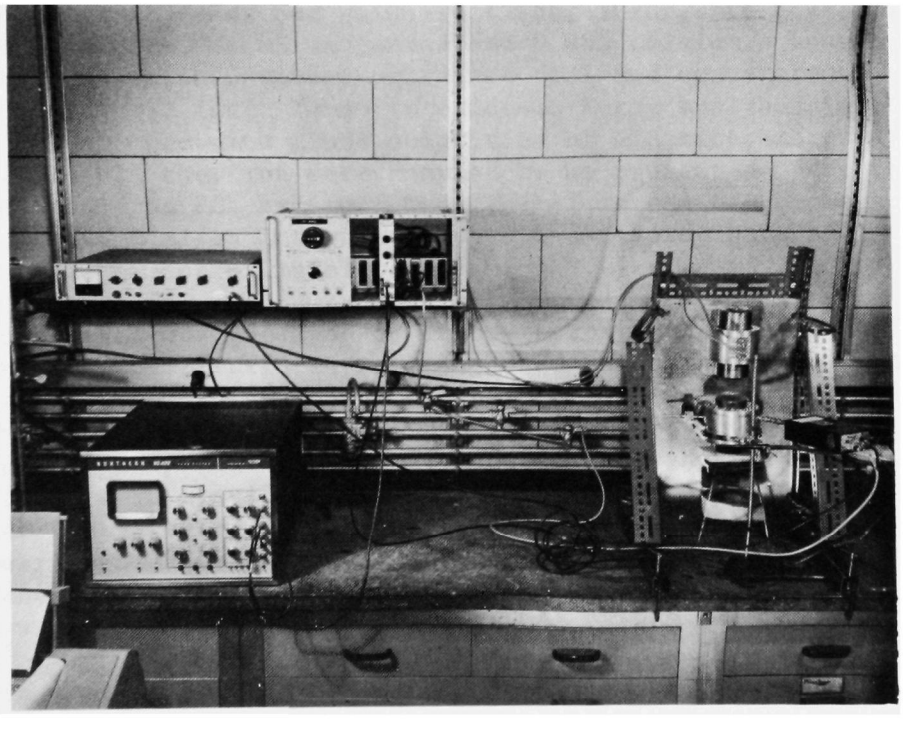


Figure 3. Experimental Equipment - Two Views

It was determined by a lithium-drifted germanium spectrometer that cobalt-56 and 58 were present in quantities estimated to be of the order of hundreds of microcuries. Since these nuclides emit high energy gamma rays (~800 Kev), they contribute substantially to the detector background at low energies despite the source shielding provided. [In addition, 0.2% branch in the decay of cobalt-57 itself also yields gamma-radiation of high energy (~690 Kev) and of similar intensity.] These isotopic impurities are unavoidable in freshly prepared cobalt-57. As time passes, their concentrations relative to cobalt-57 will decrease since the half lives of cobalt-56 and cobalt-58 are 77 and 72 days, respectively. (The longer-lived cobalt-60 present is more than a factor of ten lower in concentration.)

Section V

EXPERIMENTAL PROCEDURE

Samples were mounted beneath the vertically-oriented Mössbauer unit and as close as possible to the detector window. Radiation counts were measured over specific time intervals. At the conclusion of the absorption period, the counts were transferred from the multi-channel analyzer to tape and printed format via a NS 102, Teletype Series 33 page-printer and tape-punch. The data were then analyzed by an IBM 360 computer. A plot tape was produced and used in conjunction with a Calcomp Plotter to prepare the final absorption spectra.

Detector response characteristics were evaluated by monitoring with a 310 stainless steel natural absorber, 2" x 2" x 0.01".

Ferric hydroxide was prepared for spectroscopic analysis by reacting a ferric chloride solution with sodium hydroxide, filtering the precipitate through a 0.1μ filter and placing the dried precipitate on a watch glass. Ferric sulfate was a reagent grade laboratory supply. This was also placed in a watch glass prior to analysis.

The pyritic samples used in this study were obtained from Shawville, Pennsylvania and have been used in previous pilot plant investigations in this laboratory. Baker and Wilshire (1968, 1970). It contains 45% iron, 0.05% magnesium, 0.26% manganese and 0.08% calcium. Loss on ignition is 27.8% which includes entrained coal and conversion of carbonates or other anionic forms to oxides. X-ray analyses indicate content of 90% or more with minor quantities of siderite, marcasite and quartz. If all the iron were assumed to be present as FeS_2 then the material would be 98% pyrite. The mineral is a microporous solid with at least 0.036 ml/gm internal voids. These voids have an internal specific surface of approximately 1 m^2/gm.

The pyritic mineral was received as lumps approximately three to five inches in size. Outer surfaces were rejected and the material was prepared either by crushing or by cutting of cross-sectional slabs with a carborundum disc to obtain a flat surface. The crushed material was screened and only the 3.5 to 7 mesh particles were retained for testing. These were sterilized for at least 24 hours in an atmosphere of carboxide (10% ethylene oxide and 90% carbon dioxide) prior to use. The slabs were approximately three inches in diameter and 0.5-inches thick. These were heat sterilized for three days at 112°C, after which the surfaces were polished to remove residual oxides before use.

The pyritic slabs were checked for uniformity of spectral response over their cross-sectional area. Holes were drilled at approximately 90° in the sides of the slabs. Small glass rods were affixed in these holes and one was colored red to provide a point of reference. Mössbauer spectra were obtained at various points in each quadrant of the surface area and compared. No differences were found so that only one Mössbauer spectrum taken at the center of the pyritic slab is presented in this report. Spectra were obtained of the dry slab and when the surface was submerged beneath 2 mm of water.

The reacted pyritic particulates which were spectroscopically examined had undergone oxidation for 87 days in a horizontal, packed-bed pilot plant. The continuously flowing unit was seeded with a ternary mixture of chemoautotrophic organisms (*Ferrobacillus ferrooxidans*, *Ferrobacillus sulfooxidans* and *Thiobacillus thiooxidans*). Thus, the pyrite had been subjected to biologically promoted oxidation. The initially yellow-gray colored pyrite surfaces were covered by a typical reddish-brown reaction product at the end of the test period. These particles were packed into a shallow plastic plate for analysis. Details of the horizontal reactor pilot plant studies have previously been published. Baker and Wilshire (1968, 1970).

Section VI

RESULTS

The quality of the cobaltous oxide source was checked with a lithium-drifted germanium spectrometer for 690 Kev gamma rays and an x-ray proportional counter for 14.4 Kev activity. Self-absorption was compared with a Co^{57} on chromium source of known high quality. Table I. There is a smaller loss of 14.4 Kev radiation, through self-absorption, with the cobaltous oxide source than with the more conventional cobalt on chromium source.

TABLE I

Evaluation of Cobalt-57 Source Quality

Co^{57} Source	Energy Level, Kev	Relative Count Rate	Ratio
On Chromium	14.4	27,701	0.38
Cobaltous Oxide		71,538	
On Chromium	690	4,200	0.58
Cobaltous Oxide		7,215	

The prototype and redesigned detectors were compared using the cobaltous oxide source and a 310 stainless steel reference. Single peak spectra were obtained. Figures 4 and 5. The prototype detector spectrum was made over 17.5 hours and that of the redesigned detector over 3.2 hours. Table II. The difference in peak position, 1.07 vs 1.09, is insignificant. The approximately 20% greater peak amplitude of the spectrum with the redesigned detector is significant. At comparable exposure time the deviation in peak position, amplitude and width would be smaller with the redesigned detector. Mechanical difficulties with the seals were not corrected until the end of this feasibility study. The tests described in the subsequent paragraphs were made with the prototype detector. These analytical results would have been enhanced if time had permitted testing with the redesigned detector.

TABLE II

Comparison of Prototype and Redesigned Detectors Spectral Analyses

	Position, mm/sec		Relative Absorption		Width[c], mm/sec		
Detector	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ	Area
Prototype[a]	-1.095	0.009	0.025	0.001	0.310	0.013	0.024
Redesigned[b]	-1.069	0.021	0.029	0.002	0.297	0.030	0.027

[a] 17.5 hour scan

[b] 3.2 hour scan

$\bar{X}$, mean

σ, standard deviation

[c] half peak width at half maximum

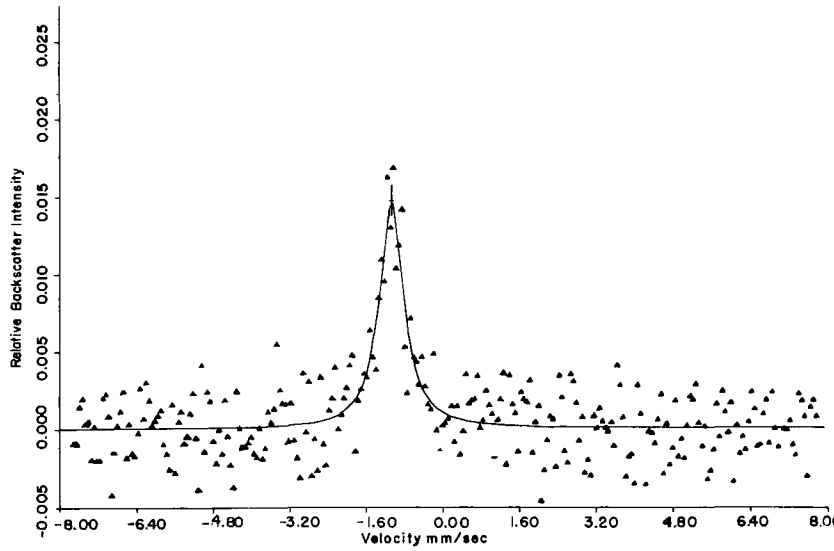


Figure 4. Spectrum of Stainless Steel Made with Prototype Backscattering Detector

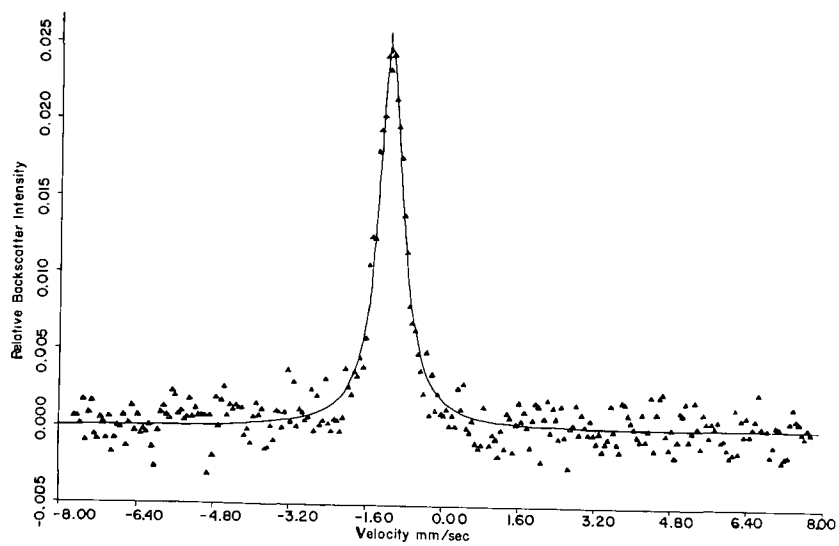


Figure 5. Spectrum of Stainless Steel Made with Redesigned Backscattering Detector

Oxidation products which might be expected on the surface of the pyritic mineral include ferric hydroxide and ferric sulfate. The Mössbauer spectra of these compounds were measured with a velocity range of ±10 mm/sec. The ferric hydroxide, Figure 6, was prepared by adding NaOH to a saturated ferric chloride solution, filtering the resulting hydroxide and measuring the absorption spectra of the precipitate for 13.75 hours. The ferric sulfate, Figure 7, was reagent grade chemical or unspecified water of hydration measured for 9.0 hours. These compounds were placed in watch glasses for spectral analyses. Each of the spectra actually consists of two peaks, although that for sulfate, Figure 7, may appear as a single peak. The overall width is too great for a single peak. Two peaks, representing the quadrupole splitting, are present. Table III. The ferric hydroxide preparation method precluded pure compound formation. The Mössbauer spectral characteristics for ferric sulfate were compared with literature values. The main doublet, Figure 7, is centered at +0.41 mm/sec relative to iron metal. Fluck, et al., (1963), reported a position of +0.101 relative to cobalt-57 diffused into platinum. Their ferric sulfate had seven waters of hydration. Some variation may be expected if the water of hydration differs. The experimental value for the quadrupole splitting is 0.29 mm/sec vs their reported value of 0.28 mm/sec. Thus the experimental results agree very well with those cited by Fluck, et al.

TABLE III

Mössbauer Spectra of Ferric Hydroxide and Ferric Sulfate-Peak Analyses

Compound	Position, mm/sec		Relative Absorption		Width[c], mm/sec		Area
	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ	
Ferric Hydroxide[a]	-0.981	0.015	0.013	0.001	0.239	0.025	0.010
	-0.320	0.016	0.015	0.001	0.290	0.024	0.014
Ferric Sulfate[b]	-0.730	0.029	0.016	0.004	0.191	0.041	0.010
	-0.444	0.038	0.022	0.004	0.270	0.028	0.018

[a] 13.75 hour scan

[b] 9.0 hour scan

$\bar{X}$, mean

σ, standard deviation

[c] half peak width at half maximum

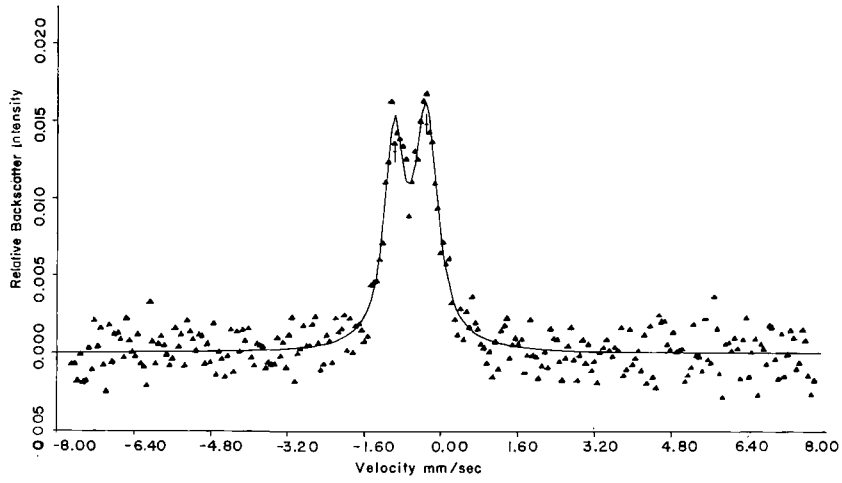


Figure 6. Spectrum of Ferric Hydroxide

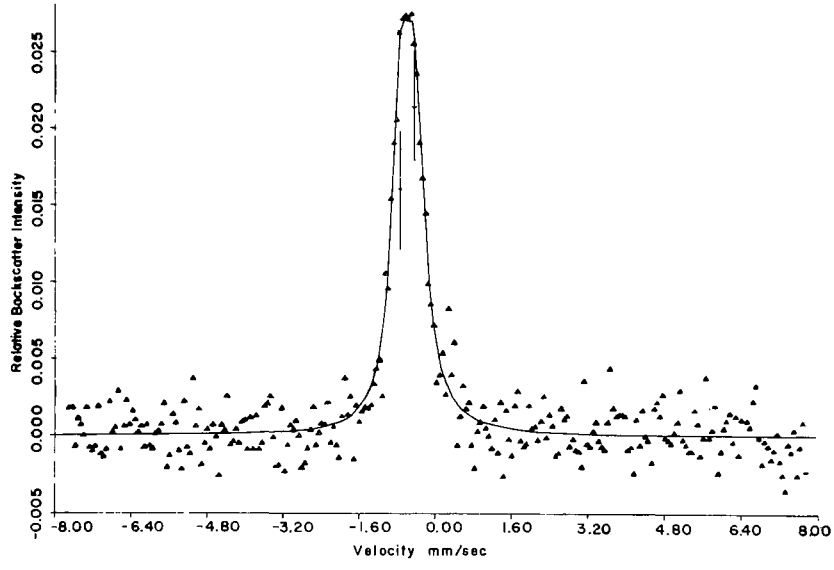


Figure 7. Spectrum of Ferric Sulfate

A basic question involved in this feasibility study was determination of the effectiveness of obtaining backscattering radiation spectra when the pyritic mineral surface was under a water film. In the original research proposal it was expected that oxidation processes would be monitored through 0.5 mm depth of water. In this feasibility study the water depth over a pyritic slab was set at 2 mm. Success in measuring spectra at this condition would assure success with thinner water films on the mineral surface. Spectra of the dry pyritic slab and of the slab through the water film are presented in Figures 8 and 9, respectively. The analyses of the double peak spectra are given in Table IV. The dry slab was monitored for 17 hours and the wetted slab for 55 hours. Loss in peak amplitude is approximately 50%. This would be reduced considerably with thinner water films. An important finding is that backscattering radiation can be measured through the aqueous layer.

TABLE IV

Mössbauer Spectra of Dry and Wetted Pyrite-Peak Analyses
Water Film 2 mm Thick

	Position, mm/sec		Relative Absorption		Width[c], mm/sec		
Condition	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ	Area
Dry[a]	-0.995	0.006	0.028	0.001	0.215	0.009	0.019
	-0.378	0.006	0.028	0.001	0.215	0.009	0.019
Wet[b]	-1.004	0.006	0.014	0.000	0.213	0.010	0.009
	-0.377	0.006	0.015	0.000	0.196	0.009	0.009

[a] 17 hour scan

[b] 55 hour scan

$\bar{X}$, mean

σ, standard deviation

[c] half peak width at half maximum

The Mössbauer spectrum of the dry pyritic slab was compared with the pyritic peak values reported by Fluck, et al. (1963). The main doublet is centered at -0.995 mm/sec or +0.31 mm/sec relative to iron metal. Quadrupole splitting is 0.62 mm/sec. Literature values are +0.32 mm/sec and 0.62 mm/sec. Agreement is excellent.

Pilot plant studies of the microbiological factor in acid mine drainage (Baker and Wilshire, 1968, 1970) utilized 3.5 to 7 mesh pyritic particles. Figure 10 is the Mössbauer spectrum of this material. This sample was

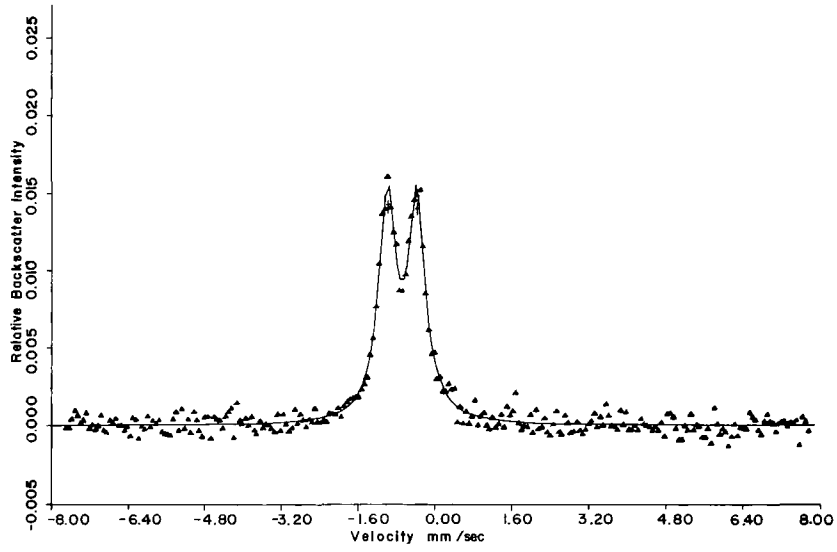


Figure 8. Spectrum of Dry Pyrite Slab

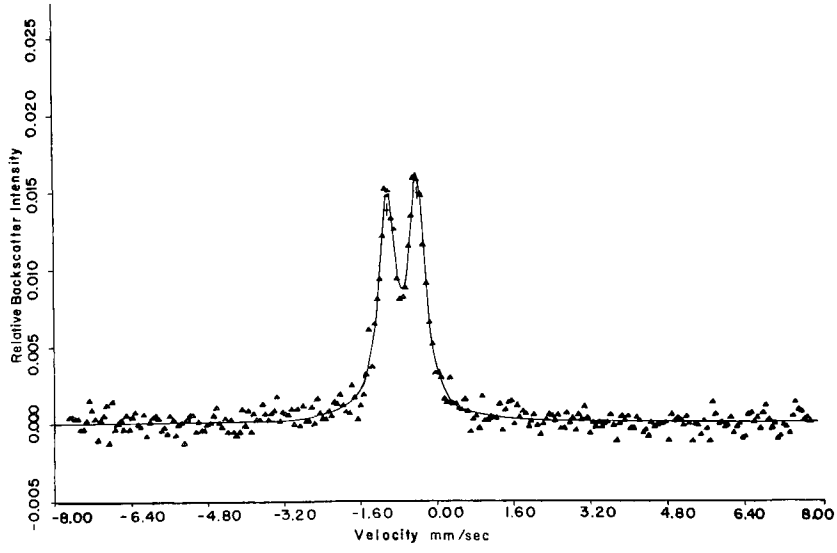


Figure 9. Spectrum of Pyrite Slab Under 2 mm of Water

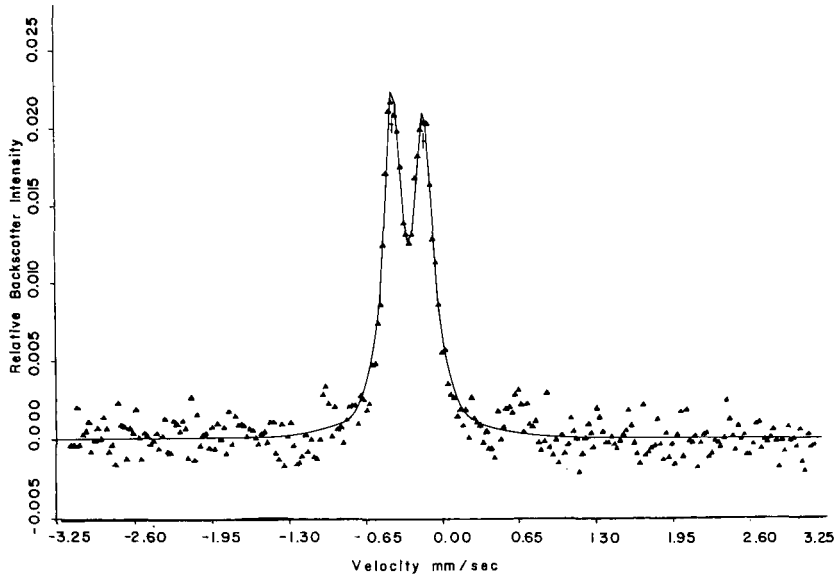


Figure 10. Spectrum of Unreacted Pyrite Particles

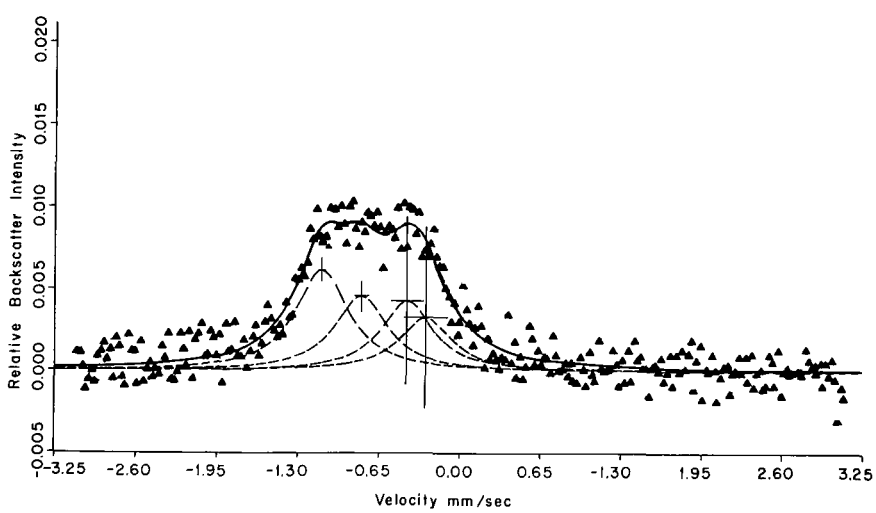


Figure 11. Spectrum of Biologically and Chemically Reacted Pyrite Particles

not freshly ground so that some chemical alteration of the pyritic surface may have occurred during storage. There are two peaks whose position and relative absorption characteristics are summarized in Table V. The main doublet is centered at -1.022 mm/sec (+0.30 mm/sec relative to iron metal) and has quadrupole splitting of 0.65 mm/sec. The values differ somewhat from those of the freshly prepared dry pyritic slab, Table IV, probably reflecting the effect of surface oxidation and the presence of some reaction products. Of greater consequence is the loss of relative absorption when the pyritic mineral was in particulate form rather than as a flat surface. The loss is approximately 33% (0.028 vs 0.020 relative absorption). This reflects the unfavorable geometry involved in applying backscattering detection to an irregular rather than planar surface. In subsequent research the latter configuration is to be preferred.

Figure 11 is the Mössbauer spectrum of the particulate pyritic form after biologically promoted oxidation in a continuous pilot plant for 87 days. The particulates were coated with typical yellow-brown reaction products. The spectral analysis is based on four peaks. Table V.

TABLE V

Mössbauer Spectra of Unreacted and Oxidized Pyrite-
Peak Analyses

	Position, mm/sec		Related Absorption		Width[c], mm/sec		
Condition	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ	Area
Unreacted[a]	-1.022	0.007	0.020	0.001	0.211	0.012	0.014
	-0.373	0.008	0.019	0.001	0.236	0.013	0.014
Oxidized[b]	-1.119	0.031	0.006	0.001	0.258	0.021	0.005
	-0.800	0.057	0.005	0.001	0.258	0.021	0.004
	-0.434	0.131	0.004	0.005	0.258	0.021	0.004
	-0.279	0.177	0.003	0.006	0.258	0.021	0.003

[a] 23.5 hour scan

[b] 24.0 hour scan

$\bar{X}$, mean

σ, standard deviation

[c] half peak width at half maximum

Comparison of this spectrum with those of the unreacted pyrite and the expected ferric reaction products suggests that a composite of all these components is present. The middle pair of peaks most nearly approximate the ferric sulfate and the outer peaks the pyrite. Shift in peak positions is most likely attributable to presence of other reaction products such

as the hydroxide. Detailed analyses of the oxidation processes and their reaction products will require further study. The major finding is the successful demonstration of the application of the Mössbauer effect-backscattering detection experimental technique to the problem of monitoring pyritic surface oxidation. Spectra of this pyritic material exposed to an oxidizing aqueous media for several days showed no significant differences from those of unreacted mineral. Oxidation reaction rates were sufficiently slow so that radiation scans could be taken over extended periods such as 8 to 24 hours without significant differences in spectral response at the beginning and end of the period. This facilitates long-term scanning and hence the likelihood of detection of low concentrations of reaction products.

Section VII

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During this investigation, Drs. Paul A. Flinn and B. Keisch of Carnegie-Mellon University provided technical guidance regarding the Mossbauer and detector systems. Albert G. Wilshire conducted the tests.

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Section VIII

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Section IX

GLOSSARY

Chemoautroph - An organism which utilizes carbon dioxide as sole source of carbon to obtain energy required for metabolism by oxidation of inorganic sources.

Kev - Thousand electron-volts of energy. One electron-volt is approximately 1.6×10^{-12} ergs.

Mössbauer Effect - An effect, discovered by R. Mössbauer, in which by restricting the recoil of radioactive atoms emitting low-energy gamma rays, the full energy of the gamma ray is available for use in the study of the resonant absorption thereof.

Toroidal - Doughnut-shaped.

Quadrupole Splitting - The splitting of nuclear energy states effected by the extra-nuclear electrons of the atom.

BIBLIOGRAPHIC: Carnegie-Mellon University, Mellon Institute
Evaluation of Pyritic Oxidation by Nuclear Methods, Publication No. 14010 FII

ACCESSION NO:

KEY WORDS:

Mossbauer Effect
Backscatter Detection
Mine Drainage
Pyrite
Iron-57
Cobalt-57

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Spectra were obtained of pyritic surfaces under 2 mm of water. Differentiation of nonoxidized and oxidized pyritic surfaces was possible with further separation of the spectra to show individual oxidation product peaks suggesting ferric hydroxide and ferric sulfate.

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23 Descriptors (Starred First)

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*Mossbauer effect, *Backscatter detection, Pyrite, Iron-57, Cobalt-57

27 Abstract

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