

(200)

R290

no. 95-389

U.S. GEOLOGICAL SURVEY
RESTON, VA.

JUN 25 1996

SR
LIBRARY

OXIDATION OF PYRITE

By A. Bergholm

(A translation from Swedish)

U.S. GEOLOGICAL SURVEY
Open-File Report 95-389



OXIDATION OF PYRITE

By A. Bergholm

U.S. GEOLOGICAL SURVEY

Open-File Report 95-389

Translated by

Douglas Baxter
University of Umeå
Umeå, Sweden

Edited by

D. Kirk Nordstrom
Jennifer M. DeMonge
U.S. Geological Survey

and

Lars Lövgren
University of Umeå
Umeå, Sweden



Boulder, Colorado

1995

U. S. DEPARTMENT OF THE INTERIOR

BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY

Gordon P. Eaton, Director

For additional information write to:

Chief, Branch of Regional Research
U.S. Geological Survey
Denver Federal Center,
Box 25046, MS-418
Denver, Colorado 80225

Copies of this report can be purchased from:

U.S. Geological Survey
Earth Science Information Center
Open-File Reports Section
Denver Federal Center,
Box 25286, MS 517
Denver, Colorado 80225

CONTENTS

| | Page |
|---|------|
| Preface | vi |
| Oxidation of pyrite by A. Bergholm | 1 |
| Introduction | 1 |
| Different possibilities for the oxidation of pyrite | 1 |
| Wet oxidation | 1 |
| Dry oxidation | 2 |
| Combustion | 2 |
| Previous studies | 2 |
| Wet oxidation | 3 |
| Material | 3 |
| Apparatus | 5 |
| Oxidation of pyrite by oxygen | 6 |
| Results | 7 |
| Oxidation of iron(III) salts in a nitrogen atmosphere | 10 |
| Dry oxidation | 13 |
| Undecomposed pyrite | 13 |
| Undecomposed pyrrhotite | 14 |
| Wet oxidized pyrite | 14 |
| Wet oxidized pyrrhotite | 15 |
| Decomposed sulfide mineral from the Falun Mine | 15 |
| Conclusions | 15 |
| Spontaneous ignition | 15 |
| Wet oxidation | 16 |
| Summary | 17 |
| References | 19 |

ILLUSTRATIONS

| | Page |
|--|------|
| Figure 1. Schematic of the apparatus for studying the oxygen consumption during oxidation of sulfide minerals | 4 |
| Figure 2. Arrangement of the oxidation apparatus | 5 |
| Figure 3. Some typical oxygen consumption curves for the oxidation of pyrite | 6 |
| Figure 4. Oxidation of pyrite by oxygen as a function of time | 9 |
| Figure 5. Permanganate consumption converted to mL O ₂ during oxidation experiments with iron(III) sulfate in a nitrogen atmosphere | 11 |
| Figure 6. Oxidation of pyrite by iron(III) sulfate solution as a function of time | 13 |

TABLES

| | Page |
|--|------|
| Table I. Oxidation of pyrite by oxygen | 7 |
| Table II. Oxidation of pyrite by oxygen, results of the calculations | 8 |
| Table III. Oxidation of pyrite by iron(III) sulfate in a nitrogen atmosphere | 11 |
| Table IV. Oxidation of pyrite by iron(III) sulfate, results of calculations | 12 |
| Table V. Weight change during dry oxidation of pyrite in air | 14 |

CONVERSION FACTORS AND ABBREVIATIONS

| Multiply | By | To obtain |
|---|------------------------|---------------------|
| liter (L) | 0.2642 | gallon (gal) |
| milliliter (mL) | 3.381×10^{-2} | fluid ounce (fl oz) |
| gram (g) | 3.520×10^{-2} | ounce (oz) |
| milligram (mg) | 3.520×10^{-5} | ounce (oz) |
| ton (t) | 1.102 | short ton |
| degree Fahrenheit (°F) = 1.8 x degree Celsius (°C) + 32 | | |

Explanation of abbreviations:

μm (micrometer)
 mmol (millimoles)
 W (Watts)
 h (hour)
 Temp (temperature)
 kcal/h (kilocalories per hour)

PREFACE

While reading and reviewing the literature on pyrite oxidation and the formation of acid mine waters, occasionally reference would be made to a paper by A. Bergholm, that was originally published in Swedish (Bergholm, A., 1955, Oxidation av pyrit, Jernkontorets Annaler, vol. 139, no. 8, pp. 531-549). This paper is unusual in several respects. It presents experimental data on pyrite oxidation for a temperature interval rarely ever reported, i.e. 60-80°C, because it was motivated by the desire to understand the spontaneous combustion of pyrite. The concentrations of Fe(II), and Fe(III), the pH, and the extractable sulfur were measured before and after every experiment and oxygen content was monitored. The pyrite was analyzed for trace metals and examined optically and by X-ray spectrometry. We know of no investigation that reports all of these parameters along with the mass balance results for both wet and dry oxidation of pyrite. These were some of the reasons that encouraged us to translate the paper into English.

A translation was started several years ago by one of us (DKN) but when the offer was made to translate the paper at the University of Umeå, we gratefully accepted. The original format of the paper has been changed slightly to conform with U.S. Geological Survey standards. We hope this translation may be of some value to researchers investigating pyrite oxidation, the spontaneous combustion of pyrite, and the formation of acid mine waters.

The Falun mine, referenced by Bergholm, is the oldest and largest copper mine in Sweden. The deposit was discovered and mined at least one thousand years ago and has been known in Swedish as Stora Kopparberget, or the Great Copper Mountain. It contributed iron ore as well as copper, leading to a major steel industry and a major lumber and paper industry. It was, for a very long time, the economic backbone of Sweden. The mineral deposit was massive and vein sulfides in a high-grade metamorphic country rock. The main sulfide minerals were pyrite, pyrrhotite, and chalcopyrite.

Oxidation of pyrite

by

A. Bergholm

Introduction

In certain sections of the Falun Mine, a relatively rapid decomposition of sulfide ore is occurring, causing oxidation to sulfates or hydrous oxides under the influence of air and water. The oxidation processes are mainly active within the so-called landslide region, that arose during past centuries and consists of more or less crushed and weathered sulfide ore mixed with stones, soil and timber. In this region, oxidation processes result in heat generation of some 600,000 kcal/h, and temperatures in excess of 50°C have been measured. A calculation based on mine water analyses indicates that around 2,000 t sulfide mineral are oxidized each year.

Since sulfide-ore mine fires have frequently occurred abroad, and on several occasions presumably started by spontaneous ignition, it was decided to investigate oxidation processes in the Falun Mine in the beginning of 1954. The principal aim of the study was to answer the following questions:

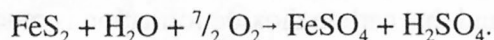
1. Can the current wet oxidation process, which is limited to temperatures below about 100°C, initiate combustion of mine timber or ore?
2. How do temperature, the oxygen content of air, and the mine water concentrations of sulfate and sulfuric acid affect the rate of oxidation?

Different possibilities for the oxidation of pyrite

Pyrite is the major mineral present in the landslide bulk, and so the study was initially devoted to investigations concerning the oxidation of this mineral. Chemically speaking, the oxidation of pyrite includes a large number of sub-processes, as follows:

Wet oxidation

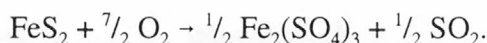
[Oxidation] occurs in the presence of water or aqueous solutions. The upper temperature limit is set by the boiling point of the solutions, that is about 100°C. The following reaction scheme is commonly used:



The iron(II) sulfate formed is eventually further oxidized to iron(III) sulfate.

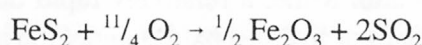
Dry oxidation

[Oxidation] characterized by sulfate production and loss of sulfur dioxide. One of the sub-reactions can, according to Schwab and Philinis (15), be described as:



The reaction proceeds at temperatures up to about 550°C. Below 400°C the reaction is very slow.

Combustion



[Schwab and Philinis (15)].

The reaction is very rapid at temperatures above the iron sulfate decomposition temperature (550-650°C).

A similar division of these reactions has been used by Vertuschkof (18), who distinguishes between hypogene, pseudothermal, and thermal phases.

Previous studies

There are numerous descriptions of self-ignition in sulfide ore mines. Knevitt (7) has described spontaneous ignition in *Broken Hill (South Mine)* 1944 as caused by oxidation of sulfide-containing enrichment deposits, used for landfill, which had come into contact with timber. Spontaneous ignition of crushed ore from Rio Tinto is described by Berggren (2), who states that during the copper leaching process, the ore sometimes catches fire despite the absence of timber or other combustible substances. Vertuschkof (18) has reported mine fires in *Ural (Kalatinski)*, and considers that these fires started through spontaneous ignition. In a report dated 1953 from a British institution "*The Fire Research Station of the Joint Fire Research Organization*" (5), spontaneous ignition of sulfide ore from *Huelva* in Spain is mentioned. The risk for ignition in piles of ground pyrite is considered to be great, particularly if the pyrite is completely dry.

Wet oxidation is a process that ought to occur in all sulfide ore mines or deposits, and yet its course has not been completely delineated. Gottschalk and Buehler (6) have treated small samples of ground sulfide mineral with water at room temperature in an open atmosphere and analyzed the leaching liquids. Bergenfelt (1) has studied the formation of water soluble oxidation products in piles of sulfide mineral stored outdoors. Drakely (4) has investigated the formation of sulfate and sulfur dioxide on treatment of ground pyrite with water vapor and air at a temperature between ambient and 100°C. He has found that carbon dioxide formation is much greater from a mixture of pyrite + coal than from coal alone. The oxidation of iron(II) sulfate solutions, a certain sub-reaction in the decomposition of pyrite in the presence of water, has been studied by numerous research

workers, including Lamb and Elder (10), Kobe and Dickey (9) and Posnjak (13). Bryner and others (21) have shown that sulfur bacteria enhance the rate of pyrite oxidation.

The dry oxidation of pyrite has been the object of numerous studies, of which the following should be mentioned. Neumann and others (11) have, at 200°C, observed favorable heat development on warming in air. Schwab and Philinis (15) have found that the reaction between pyrite and air proceeds slowly and incompletely at 400°C because of sulfate production blocking pores and hindering oxygen introduction. Ogijewski and Karjakin (12) have demonstrated ignition of pure pyrite at 400-450°C in an O₂ atmosphere, and of pyrite + wood chips at 200-230°C. Ryss and others (14) have measured ignition temperatures around 430°C for pure pyrite and 200-300°C for pyrite mixed with wood or charcoal. They consider that timber, hydrolyzed by mine water, is the cause of spontaneous ignition in sulfide ore mines.

From the cited literature it is apparent that, since dry oxidation proceeds so slowly at temperatures between 100 and 200°C, it is difficult to understand how pyrite can reach the temperature necessary to ignite wood or coal. Even more difficult to explain is spontaneous ignition of sulfide ore in the absence of wood, in which case the dry oxidation would need to account for several hundred degrees heating.

In the earliest stages of this investigation, sulfur formation was observed during wet oxidation. The formation of elemental sulfur by decomposition of marcasite is a well known phenomenon. Sulfur production during the decomposition of pyrite has been shown by Wurm (20) and by Dittler (3). Stokes (17) has demonstrated that the oxidation of pyrite by iron(III) salts in strongly acidic solutions yields elemental sulfur, although in lesser quantities than from marcasite. He also makes the statement that: "as is well known, finely powdered pyrite and marcasite on exposure to the air for a short time give free sulfur, which can be detected by extraction with ether...The difficulty is rather to account for the complete oxidation of the sulfur usually occurring in nature."

Wet oxidation

Material

All experiments on the oxidation of pyrite in the presence of water or aqueous solutions were performed with the same mineral sample. This had been cut from solid rock in February 1954 "in the middle of the western wall in room 13 at the 181 m level." Judging from the appearance, it was a piece of very pure pyrite. The following data were obtained on chemical analysis:

| | |
|-------|--------|
| 48.2% | S |
| 41.4% | Fe |
| 4.5% | Zn |
| 1.3% | Pb |
| 0.14% | Cu |
| <hr/> | |
| Total | 95.54% |

The high concentration of zinc was not noticed until after a part of the study had been completed. Microscope analysis of polished surface samples was performed by Dr. Koark (8) who did not find any zinc minerals but observed a few percent magnetite, and traces of chlorite, limonite and pyrrhotite.

Assoc. Prof. Schönberg (16) performed X-ray analysis of the mineral and, apart from pyrite, found magnetite, pyrrhotite and galena at estimated contents of about 2% each. The presence of zinc minerals - zinc blende, wurtzite or zincite - could not be detected, and Schönberg considers that it is most likely that the Zn atom is contained in the FeS_2 lattice.

The oxidation experiments were performed using particles separated by sieving between mesh 100 and 60 DIN, corresponding to an assumed size of 60-100 μm .

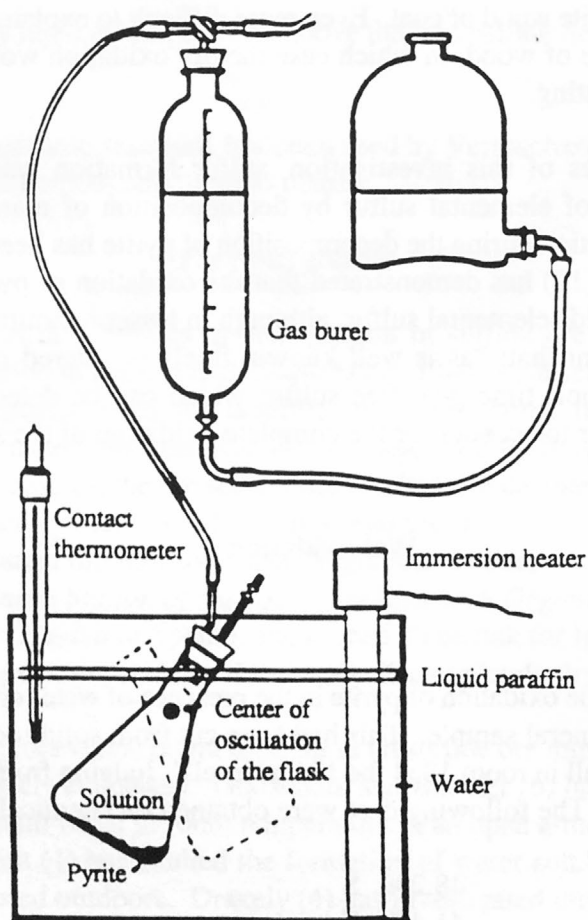


Figure 1. Schematic of the apparatus for studying the oxygen consumption during oxidation of sulfide minerals.

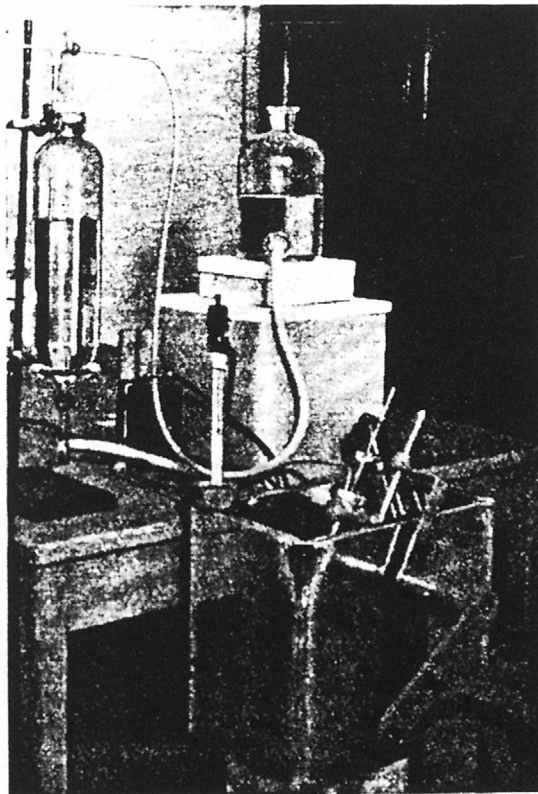


Figure 2. Arrangement of the oxidation apparatus.

Apparatus

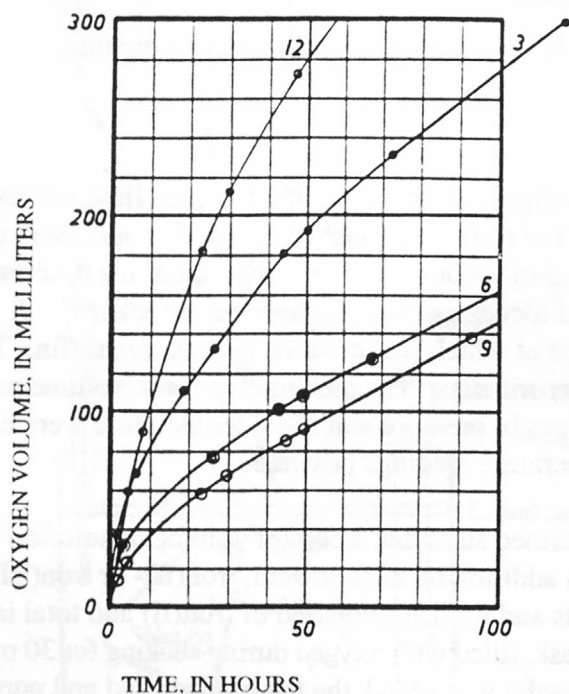
The experimental apparatus (figs. 1-2) consisted of a 1 L glass flask immersed in a thermostat bath and connected to a gas buret. The flask was attached to a shaker arm oscillated through 80° by an electric motor at a rate of 33 oscillations per min. The flask itself served as stirrer in the thermostat bath, which maintained a constant temperature within $\pm 0.2^\circ\text{C}$. A 750 W immersion heater warmed the water, the surface of which was covered by liquid paraffin. The 2.5 L gas buret was calibrated before starting the experiments. The maximum error in volume readings is estimated to be ± 3 mL. Corrections for changes in pressure and room temperature were calculated using the most accurate barometer and temperature readings possible.

The experiments were performed such that a certain volume of solution was prepared from distilled water, in some cases with addition of sulfuric acid, iron(II)- or iron(III)-sulfate. Samples were removed for pH measurements and for determination of iron(II) and total iron concentrations. The solution was poured into the flask, filled with oxygen during shaking for 30 min at a pre-selected temperature. Then 5.00 g pyrite powder was added, the flask was sealed and purged with five times the free gas volume. Volume readings commenced immediately thereafter, the contained gas volume first increasing somewhat (about 20 mL) during heating to the flask's temperature and becoming saturated with water vapor. After a few minutes the volume increase stopped, and the volume and time noted at that point were taken as starting values.

Two experimental series were performed, one to investigate the reaction between oxygen and pyrite, and the other to study the sub-reaction between an iron(III) sulfate solution and pyrite under a nitrogen atmosphere.

Oxidation of pyrite by oxygen

During each experiment 100 mL solution was employed. The briefest experiment lasted for 6.5 h and the longest 167 h. During the experiments the oxygen volume was initially recorded every hour, and then at least twice a day. Figure 3 shows some typical oxygen consumption curves. In cases where the oxidation was performed with relatively low oxygen concentrations, the flask was connected to the gas buret without any preliminary purging. Since consumed oxygen was continually replaced by new oxygen from the buret, the oxygen concentration in the flask remained fairly constant. At the end of the experiment a gas sample was taken for analysis. In cases where the flask was purged with oxygen the analytical results generally showed an oxygen concentration of around 95%. In comparing between the different experiments it should be noted that the oxygen concentration can vary a few percent, despite using the same filling method. On repeated experiments using the same solutions, it was observed that the oxygen consumption curves were always in good agreement.



| | |
|--------------|---|
| Experiment 3 | 100% O ₂ , without addition of iron(II) salt or acid |
| Experiment 6 | 25% O ₂ , without addition of iron(II) salt or acid |
| Experiment 9 | 100% O ₂ , 3.8 g sulfuric acid per liter |
| Experiment 3 | 100% O ₂ , 10 g Fe ²⁺ per liter |

Figure 3. Some typical oxygen consumption curves for the oxidation of pyrite.

The experiments were terminated by cooling the contents of the flask, which were then filtered immediately through a dry glass filter crucible. The solution was analyzed for pH, iron(II) and total iron, whereas the residues on the filter were rinsed with water and dried at 70°C to constant weight. Elemental sulfur was determined in the residue on the filter by extraction with carbon disulfide followed by evaporation and weighing. Weight loss and extract weight were in good agreement. In one case the sulfur extraction was repeated as a check, no additional sulfur being obtained.

Results

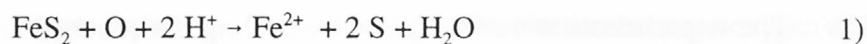
The conditions and primary data from the oxidation experiments are presented in table I.

Table I. Oxidation of pyrite by oxygen.

| No. | Date | Time h | Experimental conditions | | | | | | | | Primary Results | | |
|-----|-------|--------|-------------------------|---------------------|--------|-------|------------------|--------------|------------------|--------------|-----------------------------|---------|----------------------------|
| | | | Temp °C | O ₂ % | pH | | Fe ²⁺ | | Fe ³⁺ | | Oxygen consumptio nmL | S mg | Weight reductio n mg |
| | | | | | before | after | before g/L | after g/L | before g/L | after g/L | | | |
| 1 | 11/11 | 6.5 | 70 | 100 | 7 | 3.0 | 0 | 0.13 | 0 | 0 | 64 | 71 | -32 |
| 2 | 1/12 | 20.3 | 70 | 100 | 7 | 2.5 | 0 | 0.27 | 0 | 0 | 115 | 84 | -25 |
| 3 | 27/10 | 116.5 | 70 | 100 | 7 | 1.9 | 0 | 0.81 | 0 | 0.04 | 308 | 145 | 137 |
| 4 | 13/11 | 166.7 | 70 | 100 | 7 | 2.0 | 0 | 0.80 | 0 | 0.04 | 382 | 168 | 256 |
| 5 | 19/11 | 26.3 | 70 | 21 | 7 | 3.0 | 0 | 0.13 | 0 | 0 | 74 | 71 | -27 |
| 6 | 30/11 | 67.0 | 70 | 25 | 7 | 2.6 | 0 | 0.30 | 0 | 0 | 128 | 87 | 14 |
| 7 | 11/12 | 76.0 | 60 | 100 | 7 | 2.7 | 0 | 0.22 | 0 | 0 | 150 | 94 | 63 |
| 8 | 3/12 | 46.5 | 80 | 100 | 7 | 2.1 | 0 | 0.45 | 0 | 0 | 221 | 132 | 125 |
| 9 | 25/11 | 93.0 | 70 | 100 | 1.3 | 2.2 | 0 | 0.80 | 0 | 0.05 | 137 | 143 | 155 |
| 10 | 8/10 | 143.0 | 60 | 100 | 1.3 | 2.3 | 0 | 1.15 | 0 | 0.05 | 140 | 133 | 154 |
| 11 | 29/11 | 49.5 | 70 | 100 | 2.8 | 2.5 | 0 | 0.36 | 0 | 0 | 176 | 111 | 80 |
| 12 | 23/11 | 47.0 | 70 | 100 | 3.4 | 1.6 | 9.80 | 3.70 | 0.1 | 1.65 | 272 | 252 | -770 |
| 13 | 15/12 | 63.8 | 70 | 100 | 3.3 | 1.9 | 4.90 | 2.22 | 0 | 0.12 | 210 | 209 | -290 |
| 14 | 18/10 | 92.6 | 70 | 100 | 1.2 | 1.6 | 0 | 3.80 | 4.00 | 2.53 | 296 | 282 | 386 |
| 15 | 22/10 | 116.0 | 70 | 25 | 1.2 | 1.7 | 0 | 5.00 | 4.10 | 1.08 | 109 | 212 | 410 |
| 16 | 14/10 | 89.3 | 60 | 100 | 1.4 | 1.7 | 0 | 3.98 | 4.09 | 2.16 | 167 | 229 | 520 |
| 17 | 2/11 | 95.5 | 60 | 100 | 0.7 | 1.3 | 0 | 3.99 | 4.00 | 2.49 | 199 | 252 | 601 |

Footnote: The reported oxygen volumes are corrected for variations in room temperature and pressure. Twenty-five mL corresponds to 1 mmol O₂.

The data presented in table I have been used to calculate sulfur production and sulfur oxidation according to the reactions



In the calculations consideration has been made for the oxygen volume consumed by iron(III) ion formation and for the effect of iron(III) ions on pyrite. The results of the calculations are given in table II.

Table II. Oxidation of pyrite by oxygen, results of the calculations.

| No. | Time h | Temp °C | O ₂ % | Solution | S formation mg/S | S oxidation | | FeS ₂ decomposition mg | Relative reaction rate | |
|-----|-----------|------------|---------------------|-----------------------------|------------------------|-------------|----|---|------------------------|-------------|
| | | | | | | mg/S | % | | S | S oxidation |
| 1 | 6.5 | 70 | 100 | water | 102 | 31 | 30 | 191 | 1 | 1 |
| 2 | 20.3 | 70 | 100 | water | 148 | 64 | 43 | 277 | 1 | 1 |
| 3 | 116.5 | 70 | 100 | water | 333 | 188 | 56 | 623 | 1 | 1 |
| 4 | 166.7 | 70 | 100 | water | 401 | 233 | 58 | 750 | 1 | 1 |
| 5 | 26.3 | 70 | 21 | water | 108 | 37 | 34 | 202 | 0.30 | 0.30 |
| 6 | 67.0 | 70 | 25 | water | 160 | 73 | 46 | 299 | 0.39 | 0.40 |
| 7 | 76.0 | 60 | 100 | water | 181 | 87 | 48 | 338 | 0.45 | 0.47 |
| 8 | 46.5 | 80 | 100 | water | 258 | 126 | 49 | 482 | 1.6 | 1.4 |
| 9 | 93.0 | 70 | 100 | pH 1.3 | 214 | 71 | 33 | 400 | 0.54 | 0.36 |
| 10 | 143.0 | 60 | 100 | pH 1.3 | 211 | 78 | 37 | 395 | 0.34 | 0.20 |
| 11 | 49.5 | 70 | 100 | pH 2.8 | 212 | 101 | 48 | 396 | 1.0 | 0.93 |
| 12 | 47.0 | 70 | 100 | Fe ²⁺ : 10 | 332 | 80 | 24 | 620 | 2.5 | 0.68 |
| 13 | 63.8 | 70 | 100 | Fe ²⁺ : 5 | 286 | 77 | 27 | 535 | 1.4 | 0.45 |
| 14 | 92.6 | 70 | 100 | Fe ³⁺ : 4 | 450 | 168 | 37 | 842 | >2.2 | 1.8 |
| 15 | 116.0 | 70 | 25 | Fe ³⁺ : 4 | 283 | 71 | 25 | 529 | 0.75 | 0.2 |
| 16 | 89.3 | 60 | 100 | Fe ³⁺ : 4 | 329 | 100 | 30 | 615 | 1.3 | 0.5 |
| 17 | 95.5 | 60 | 100 | Fe ³⁺ : 4 pH 0.7 | 368 | 116 | 32 | 688 | 0.95 | 0.68 |

Figure 4 is based on the results of experiments 1-4, where the uppermost curve illustrates the formation of sulfur as a function of time, and the second curve the oxidation of the sulfur formed. From the curves it can be seen that sulfur formation is initially very fast, but the rate then decreases. The same tendency is apparent for sulfur oxidation, although the initial rate is considerably lower. The difference between the two upper curves gives the amount of residual sulfur, shown by the bottom curve. If it is assumed that the curves become linear, it can be calculated that the fraction of released pyrite-sulfur which is oxidized to sulfate asymptotically approaching the value of 65% (compare corresponding column in table II).

The relative reaction rates given in the final two columns in table II have been calculated as follows. The time for a certain sulfur formation and sulfur oxidation has been read from fig. 4. These times have been divided by the actual time. For example, in experiment 6, 160 mg sulfur was formed after 25 h according to fig. 4. Therefore the relative reaction rate becomes $25/67 = 0.39$. The term relative reaction rate has been introduced in order to obtain a measure of how much a deviation from standard conditions (70°C , 100% O_2 without addition of iron salts or sulfuric acid) will affect the reaction rate.

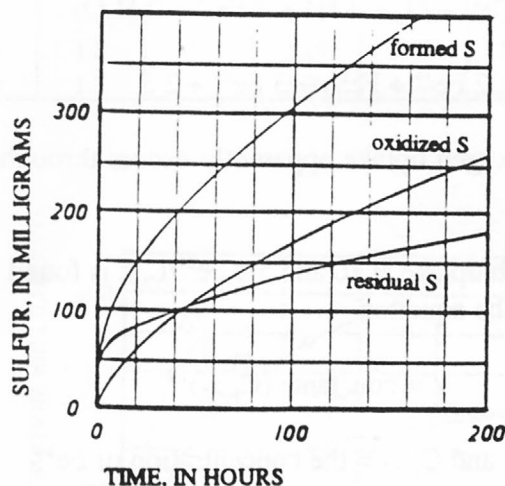
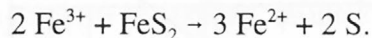
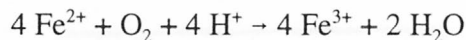


Figure 4. Oxidation of pyrite by oxygen as a function of time.

From table II (experiments 5-6) it can be seen that the rates of both reactions are approximately proportional to the oxygen concentration. Experiments 7-8 show that the reaction rate increases rapidly with increasing temperature, despite the fact that an increased temperature also results in an increased concentration of water vapor and therefore also a reduced oxygen pressure. With correction for this secondary effect, the reaction rates for sulfur formation and oxidation become 0.39 and 0.40, respectively, in experiment 7 and 2.1 and 1.80, respectively, in experiment 8. Consequently, the rate of sulfur formation is slightly more than doubled by a 10°C temperature rise, whereas sulfur oxidation is somewhat less temperature dependent. Experiments 9-11 show that sulfuric acid inhibits both reactions, but sulfur oxidation is most affected. As little as 0.1 g/L sulfuric acid addition reduced sulfur oxidation and therefore decreased the total oxygen consumption markedly.

From experiments 12-13 it is seen that iron(II) salts increase sulfur formation (pyrite decomposition) but inhibit sulfur oxidation. Experiments 14-17 are more difficult to analyze, since an additional reaction, namely reduction of iron(III) to iron(II), comes into the picture. During these experiments it could be concluded that within a few hours iron(III) sulfate was reduced to iron(II) sulfate, as seen by a change in the color of the solution. The reaction between pyrite and iron(III) salts in a nitrogen atmosphere has been studied separately and is discussed below.

Two experiments on the oxidation of iron(II) sulfate solutions by oxygen at 70°C (pH about 3) without addition of pyrite have been made in the same apparatus. It was seen that the oxygen consumption was 6.0 mL/h, when the solutions iron(II) ion concentration was 10 g/L (as Fe²⁺) and 2.0 mL/h at 5 g Fe²⁺/L. In corresponding experiments in the presence of pyrite, the average oxygen consumption during the first five hours was 14 mL/h at 9.80 g Fe²⁺/L and about 7 mL/h at 4.9 g Fe²⁺/L. From these experiments it can be seen that the oxygen uptake partly occurs according to the scheme:



A major portion of the oxygen uptake apparently occurs through direct reaction between pyrite and oxygen.

If one compares the oxygen uptake at 10 and 5 g Fe²⁺/L, it is found that the values obtained, 6.0 and 2.0, respectively, satisfy the equation

$$V = \text{constant} \cdot (C_{\text{Fe}^{2+}})^{1.6}$$

where V = oxygen uptake (mL/h) and C_{Fe²⁺} = the concentration of Fe²⁺.

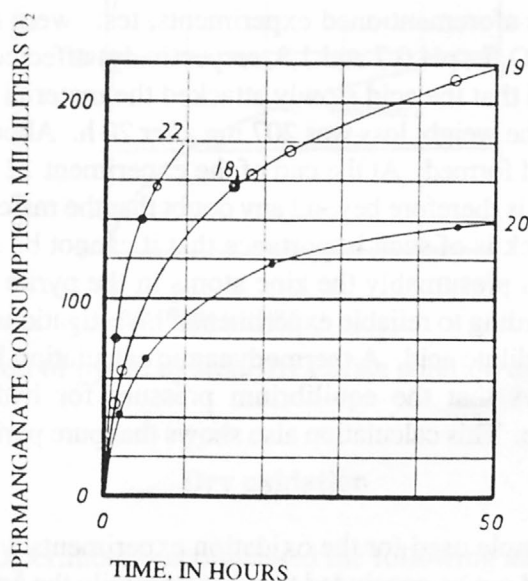
Such a correlation seems reasonable considering that the reaction between oxygen and iron(II) sulfate in solution is bimolecular with respect to Fe²⁺ [Lamb and Elder (10)] but is inhibited by the slow diffusional process at the phase interface.

Oxidation by iron(III) salts in a nitrogen atmosphere

These experiments were performed using the same apparatus and with the same amount of pyrite (5 g) as in the experiments with oxygen. The original volume of solution was, however, greater, specifically 500 mL. The course of reaction was followed by titrating 5 mL samples, withdrawn using a pipette, after the shaker motor was stopped and the pyrite ore had settled out. After each sampling the flask was refilled with nitrogen. The reaction conditions and primary data are given in table III and the results of the calculations in table IV. In table III the iron(III) ion consumption has been recalculated to a corresponding amount of oxygen to simplify comparison with the experiments using oxygen. Some typical curves for iron(III) ion consumption converted to oxygen are shown in fig. 5.

Table III. Oxidation of pyrite by iron(III) sulfate in a nitrogen atmosphere.

| No. | Date | Time h | Experimental Conditions | | | | | | Primary results | | |
|-----|-------|--------|-------------------------|--------------|------------------|--------------|------------------|--------------|--|---------|-----------------------------|
| | | | Temp °C | pH before | Fe ²⁺ | | Fe ³⁺ | | Fe ³⁺ consumption n ml O ₂ | S mg | Weight loss reduction |
| | | | | | before g/L | after g/L | before g/L | after g/L | | | |
| 18 | 10/12 | 15.8 | 60 | 0.7 | 0.02 | 3.03 | 8.13 | 5.55 | 167 | 223 | 559 |
| 19 | 27/9 | 44.5 | 60 | 0.7 | 0.02 | 4.13 | 7.95 | 4.35 | 215 | 258 | 599 |
| 20 | 23/9 | 23.5 | 60 | 0.7 | 0 | 2.65 | 3.98 | 1.73 | 137 | 207 | 574 |
| 21 | 30/9 | 43 | 60 | 1.3 | 0 | 3.20 | 4.01 | 1.35 | 167 | 247 | 528 |
| 22 | 4/10 | 6.3 | 80 | 1.3 | 0 | 3.00 | 4.04 | 1.50 | 157 | 231 | 522 |



Experiment 19 (18) 60°C, 6.2 g Fe³⁺/L
Experiment 20 60°C, 2.9 g Fe³⁺/L
Experiment 22 80°C, 2.8 g Fe³⁺/L

Figure 5. Permanganate consumption converted to mL O₂ during oxidation experiments with iron(III) sulfate in a nitrogen atmosphere.

The last two columns in table IV have been calculated in an analogous fashion to the values in table II. The course of the degradation is seen in fig. 6. If one compares this figure with fig. 4 it is found that the oxidation by iron(III) salts is initially very rapid, but the rate soon decreases. Sulfur oxidation is less pronounced than in an oxygen atmosphere. From fig. 6 it has been calculated that the oxidation would amount to 39 % after extensive treatment.

Table IV. Oxidation of pyrite by iron(III) sulfate, results of calculations.

| No. | Temp °C | pH | Fe ³⁺ g/L | S formation mg S | S oxidation | | Pyrite decomposition mg | Relative reaction rate | |
|-----|------------|-----|-------------------------|------------------------|-------------|----|-------------------------------|------------------------|------|
| | | | | | mg S | % | | S | S |
| 18 | 60 | 0.7 | 6.8 | 286 | 63 | 22 | 535 | 1 | 1 |
| 19 | 60 | 0.7 | 6.2 | 354 | 96 | 27 | 660 | 1 | 1 |
| 20 | 60 | 0.7 | 2.9 | 261 | 54 | 21 | 490 | 0.49 | 0.49 |
| 21 | 60 | 1.3 | 2.7 | 313 | 66 | 21 | 590 | 0.57 | 0.41 |
| 22 | 80 | 1.3 | 2.8 | 293 | 62 | 21 | 550 | 2.8 | 2.5 |

Footnote: Column 4 gives the mean value of the iron(III) ion concentration before and after the experiment.

In connection with the aforementioned experiments, tests were made to study how dilute sulfuric acid (17 and 3.8 g H₂SO₄/L; pH 0.7 and 1.3, respectively) affected the pyrite mineral under consideration. It was observed that the acid slowly attacked the material while releasing hydrogen sulfide. At 60°C and pH 1.3, the weight loss was 207 mg after 20 h. About 50 mL hydrogen sulfide and 21 mg elemental sulfur had formed. At the end of the experiment 12 mg Zn²⁺ and 140 mg Fe²⁺ were present in the solution. It is therefore beyond any doubt that the material was attacked by dilute sulfuric acid, and that the attack is of such importance that it cannot be confined to the content of pyrrhotite and magnetite. It is presumably the zinc atoms in the pyrite lattice (see above) which facilitate the acid attack. According to reliable experimental investigations [Stokes (17)], pure pyrite is completely resistant against dilute acid. A thermodynamic calculation based on Wunderlich (19) entropy data for pyrite shows that the equilibrium pressure for hydrogen sulfide should be approximately 10⁻¹⁰ atmosphere. This calculation also shows that pure pyrite is not attacked by dilute sulfuric acid.

Although the pyrite sample used for the oxidation experiments was clearly slowly attacked by dilute sulfuric acid, it should not be concluded that it is primarily the acid which attacks the pyrite with the concurrent evolution of hydrogen sulfide, which is then oxidized to sulfur. Had that been the case then the oxidation would have proceeded more rapidly the lower the pH-value, whereas the experiments demonstrate the opposite relationship. No smell of hydrogen sulfide was noticed during the first minutes of the oxidation experiments except under acid treatment.

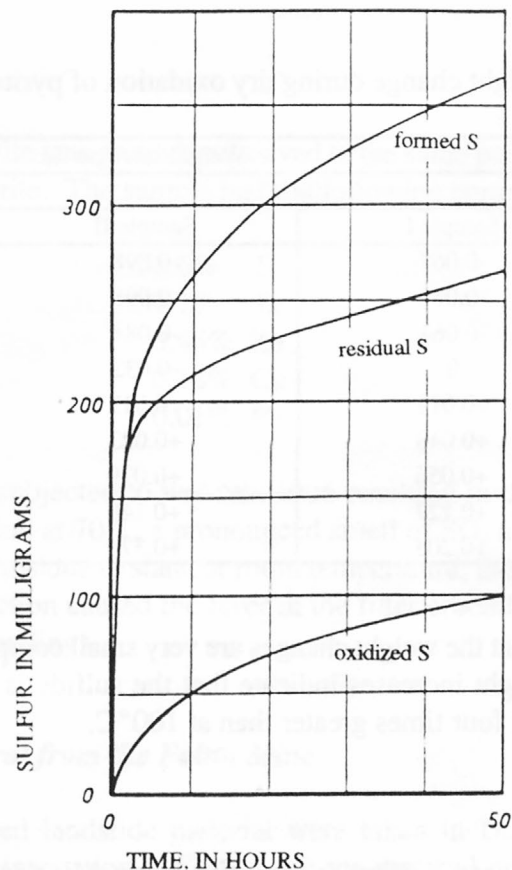


Figure 6. Oxidation of pyrite by iron(III) sulfate solution as a function of time.

Dry oxidation

The dry oxidation experiments encompassed the following materials:

- Undecomposed pyrite
- Undecomposed pyrrhotite
- Wet oxidized pyrite
- Wet oxidized pyrrhotite
- Samples of decomposed sulfide ore from the Falun Mine.

Undecomposed pyrite

A portion of the same mineral sample as used in the wet oxidation experiments was ground and sieved to yield particles of 0.5 - 1 mm. About 25 g was weighed onto a flat dish of 5 cm diameter. The dish was placed in a drying oven held at constant temperature. Every second day the dish was weighed. In every experiment there was an initial weight loss followed by an increase in weight. One series of experiments was performed at 100°C and another at 150°C. The weight changes are seen in table V.

Table V. Weight change during dry oxidation of pyrite in air.

| Day | Weight increase ‰ | | | |
|-----|-------------------|-----------|----------|-----------|
| | 100°C | | 150°C | |
| | Sample I | Sample II | Sample I | Sample II |
| 1 | -0.067 | -0.098 | -0.043 | -0.037 |
| 2 | -0.067 | -0.098 | +0.047 | +0.046 |
| 3 | -0.064 | -0.084 | +0.098 | +0.083 |
| 5 | 0 | -0.032 | +0.098 | +0.083 |
| 7 | +0.011 | +0.019 | +0.145 | +0.124 |
| 10 | +0.049 | +0.023 | +0.252 | +0.216 |
| 15 | +0.056 | +0.079 | +0.428 | +0.340 |
| 21 | +0.127 | +0.140 | +0.804 | +0.651 |
| 28 | +0.205 | +0.379 | +1.279 | +0.996 |

From table V it is seen that the weight changes are very small compared with those measured during wet oxidation. The weight increases indicate that the sulfide is converted to sulfate. At 150°C the reaction rate is about four times greater than at 100°C.

Undecomposed pyrrhotite

A sample of undecomposed pyrrhotite from the Falun Mine was crushed, magnetically separated and sieved. Twenty-five g of particle size 0.5 - 1 mm was placed in a drying oven at 150°C under the same conditions as described above for the pyrite samples. No continuous weight change could be detected. After 27 days the weight losses amounted to 0.015 and 0.012‰ for the two replicates.

Wet oxidized pyrite

The residues from a wet oxidation experiment, performed according to the same conditions as number 13 (table I), were separated using a glass filter crucible, washed and dried at about 70°C to constant weight. The temperature in the drying oven was then raised to 95°C and the crucible covered with a watch glass. After one hour the sample was removed, and on lifting the lid the smell of sulfur dioxide was noted. The weight loss was 5‰. The experiment continued at 100°C and the smell of sulfur dioxide became stronger although the weight loss proceeded much more slowly. Finally the temperature was raised to about 120°C, whereupon the sulfur dioxide smell became very strong and the weight loss more rapid.

From these results it must be concluded that the sulfur formed during the wet oxidation reacted with air at 95°C, and that the reaction at this temperature is much faster than oxidation of dry pyrite at 150°C.

Wet oxidized pyrrhotite

A sample of pyrrhotite was ground and seived to the same particle size (60 - 100 μm) as used for the wet oxidation of pyrite. The sample had the following composition:

| | |
|-------|----|
| 56.6% | S |
| 37.1% | Fe |
| 0.45% | Zn |
| 0.18% | Cu |
| 0.01% | Pb |

A 5 g sample was subjected to wet oxidation resulting in the formation of 1 g elemental sulfur. On drying the residue at 70°C a pronounced smell of SO_2 and possibly of H_2S was noted. Even after allowing the dry residue to stand at room temperature, the smell indicated the formation of sulfur dioxide. The reaction caused the layer in the filter crucible to maintain a notably higher temperature than the surroundings.

Decomposed sulfide mineral from the Falun Mine

Samples of so-called landslide material were taken in December 1954 from "Överort, opposite room 8." Visual inspection indicated that the material consisted of roughly equivalent amounts of limonite and sulfide mineral, as well as a fair amount of quartz particles. The three samples were dried at room temperature, crushed in a mortar, seived and mixed. The seive mesh was 1 mm, although most of the crushed sample was much more fine-grained than 1mm. Five g of the prepared sample was leached in an open vessel with 100 mL water for 30 min at about 50°C. The solid residue was separated by filtration, dried and weighed. During washing 100 mg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was released. The weight loss was 140 mg. On extraction with carbon disulfide 2.9 % sulfur was released, after which the sample contained 34.8 % sulfur bound as sulfides or insoluble sulfate.

Another portion of the pretreated sample was heated to 100°C, whereupon a distinct smell of sulfur dioxide was noted.

At this point it should be mentioned that a sample taken from a pile of iron sulfide stored outdoors for many months had an elemental sulfur concentration of 4.4 %.

Conclusions

Spontaneous ignition

These laboratory experiments have clearly demonstrated that pyrite, in the presence of water and oxygen (air), decomposes yielding elemental sulfur and more or less hydrated oxides and sulfate. The major part of the pyritic sulfur is converted to elemental sulfur, and a lesser fraction to sulfate.

The sulfur is very fine-grained and reacts, even when dry, with atmospheric oxygen at temperatures below 100°C.

From the results it can be considered proven that wet oxidation, having a maximal reaction rate at around 90°C, can initiate a dry combustion of the sulfur formed during the wet oxidation. Adiabatic combustion of 1 % sulfur with an equivalent amount of air is calculated to produce a temperature increase of about 150°C. Even a very modest formation of sulfur with subsequent dry combustion can therefore lead to such a high temperature that pyrite itself, and in particular wood or coal, is ignited.

The more fine-grained the material and the larger the pile collected, the greater is the risk for spontaneous ignition, since the heat developed cannot be dispersed as rapidly as it is produced. It is probably fortunate for relatively favorable heat dispersion that pyrite fires are, nevertheless, rather unusual.

The risk for spontaneous ignition is greater with pyrrhotite than with pyrite. This can be explained by the fact that wet oxidation occurs more rapidly and produces more elemental sulfur.

At least 1% elemental sulfur production is probably required in order for pyrite to spontaneously ignite. At 20°C and a particle size of 60 - 100 µm, wet oxidation in air requires at least 20 days to reach this sulfur concentration. At 40°C it takes no more than 5 days and at 80°C a few hours are sufficient. Pyrite which has been wetted under a relatively brief period and then dried should not be able to spontaneously ignite, as the oxidation rate of dry pyrite is very slow.

Wet oxidation

Wet oxidation of pyrite by oxygen, and particularly by iron(III) salts is very rapid until a certain amount of the oxidant has been consumed, after which there is a pronounced decrease in the reaction rate. All the experiments indicate that the elemental sulfur formed presents the major hindrance. Specifically, the oxidizing agent must diffuse through the sulfur layer, which increases in thickness while the reaction is proceeding. During oxidation by iron(III) sulfate in a nitrogen atmosphere, no sulfur was seen in solution and in the experiments with oxygen only small amounts of sulfur rose to the surface.

All the wet oxidation experiments used 5 g pyrite. Assuming that all the particles were cubic of 0.075 mm edge, it can be calculated that the total sample surface area was 0.13 m². Corrosion of 100 mg pyrite corresponds to a layer thickness of about 0.2 µm. Since the unit cell length of pyrite is 0.0005 µm, then apparently a 400 molecule thick layer has decomposed within a couple of hours after the start of the experiment. It is clear that the inhibiting sulfur layer is relatively porous.

The hypothesis of a reaction inhibiting sulfur layer is in agreement with the observation that the reaction rate is proportional to oxygen partial pressure and the iron(III) ion concentration. The effect of temperature can partly be explained by the increasing rate of diffusion.

Oxidation of pyrite in acidic solution by oxygen proceeds partially directly, and partially via oxidation of iron(II) to iron(III) ions, which can then be reduced by the pyrite surface. At pH-values above 3, the iron(III) ion concentration ought to be so low that the latter reaction pathway is of no consequence.

With the hypothesis of a reaction inhibiting sulfur layer as the starting point, it can be predicted that different sulfide minerals will be attacked at different rates depending on the structure of the sulfur layer. It is natural that the high sulfur content of pyrite leads to slower attack than for pyrrhotite, zinc blende or chalcopyrite. It should be pointed out that all sulfide minerals are unstable, thermodynamically speaking, under oxygen attack.

Finally, it should be mentioned that the average rate of pyrite decomposition (70°C, 100 % O₂-pure water) during the first 10 h is about 0.2 g per m² per h, that is comparable to metallic corrosion.

Summary

The aims of the present investigation have been to study the reaction between pyrite and oxygen in the presence of water or aqueous solutions, and to clarify the possibility and mechanism of spontaneous ignition. The oxidation of pyrite has been classified as follows:

| | |
|----------------|---------------------------------------|
| Wet oxidation: | below 100°C, in the presence of water |
| Dry oxidation: | 100 - 550°C, limited rate |
| Combustion: | above 550°C, rapid. |

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 iron(II) ions in solution and the subsequent turnover between iron(III) ions and the mineral. This turnover has been studied in a particular series of experiments. The reaction pathway through iron(II) - iron(III) 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:

| | |
|-------------------|---|
| the reaction rate | is approximately proportional to the oxygen concentration |
| the reaction rate | doubles on increasing the temperature by 10°C |
| the reaction | is severely inhibited by acid (pH < 3) |
| 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.

The experiments performed on the *dry oxidation* of undecomposed pyrite and pyrrhotite have shown that the oxidation rate at 150°C is negligible for the former and zero for the latter. However, the same minerals were rapidly oxidized after brief treatment with water and oxygen. The fine-grained sulfur produced during wet oxidation rapidly reacts with atmospheric oxygen below 100°C.

There can be no doubt that the dry oxidation of sulfur may lead to large temperature rises and subsequent initiation of pyrite combustion providing that heat dispersion is limited. If wood or some other combustible substance is present, initiation is facilitated because a temperature rise of about 100°C is then sufficient to cause ignition. Therefore the risk for spontaneous ignition is much greater in a stockpile or mine in the presence of wood.

Pyrite which has only been subjected to water for a short period at low temperature (< 20 days at 20°C) should not be able to spontaneously ignite if stored dry. The same should hold for pyrrhotite providing that the contact with water has been limited to about one day at 20°C. These data, which are of course only approximate, are valid for a particle size of 50 to 100 µm. For coarse-grained material longer times can be tolerated.

The risk for spontaneous ignition in piles of sulfide minerals ought to be minimized by ensuring that the wet oxidation process is not permitted to raise the temperature to more than about 50°C. The method used for cooling, once this temperature has been reached, depends on the circumstances.

References

1. Bergenfelt, Sean, 1952, Investigations on the decomposition action of sulfide minerals and sulfide ores: *Jernkontorets Annaler*, v. 136, p. 429-438.
2. Berggren, Olof, 1931, The sulfide deposits at Rio Tinto: *Teknisk Tidskrift*, v. 61B, p. 1-13.
3. Dittler, E., 1917, Adsorption of sulfuric acid by ferric hydroxide and formation of colloidal sulfur and sulfides: *Kolloid Zeitschrift*, v. 21, p. 27-28.
4. Drakely, T. J., 1916, The influence of iron pyrites on the oxidation of coal: *Journal of the Chemical Society, London*, v. 109, p. 723-733.
5. Fire Research Station of the Joint Fire Research Organization, Report 1953, Ref. In *Chemical Age* 71, (1954), Aug., 281 p.
6. Gottschalk, V. H. and Buehler, H. A., 1912, Oxidation of sulfides II: *Economic Geology*, v. 7, p. 14-34.
7. Knevitt, L. T., 1946, Further notes on underground mine fire prevention at the South Mine, Broken Hill: *Australasian Institute of Mining and Metallurgy*, v. 142, p. 127-150.
8. Koark, H., Private communication.
9. Kobe, K. A. and Dickey, W., 1945, Oxidation of FeSO_4 solutions with O_2 : *Industrial and Engineering Chemistry*, v. 37, p. 429-431.
10. Lamb, A. B. and Elder, L. W., 1931, The electromotive activation of oxygen: *Journal of the American Chemical Society*, v. 23, p. 137-163.
11. Neumann, Bernhard, Walther, Lanome, and Köhler, Gotthard, 1931, The chemical processes taking place in oxidizing, sulfatizing, and chlorinating roasting. I. Oxidation of the sulfides of copper, iron, zinc, lead, and silver with dry air: *Archiv für Erzbergbau Erzaufbereitung und Metallhüttenwesen*, v. 1, p. 55-82.
12. Ogijewski, W. M. and Karjakin, Yu. V., 1937, The tendency of pyrite ores to spontaneous ignition: *Tsvetnye Metally*, no. 1, p. 24-29.
13. Posnjak, E., 1926, Acceleration of rate of oxidation of ferrous iron in presence of copper, and its application to the "heap leaching" process: *American Institute of Mining and Metallurgical Engineers*, no. 1615D, 10 p.

14. Ryss, I. G., Zhuravleva, T. G., Perevezentsev, I. G., and Sabinina, L. E., 1937, Laboratory investigation of causes of fires from spontaneous combustion in pyrite mines: *Tsvetnye Metally*, no. 9, p. 21-44.
15. Schwab, G. M. and Philinis, J., 1947, Reactions of iron pyrite: Its thermal decomposition, reduction, and air oxidation: *Journal of the American Chemical Society*, v. 69, p. 2588-2596.
16. Schönberg, N., Private communication
17. Stokes H. N., 1901, On pyrite and marcasite: *U.S. Geological Survey Bulletin* 186, 50 p.
18. Vertuschkof, G. N., 1940, Subterranean pyrite combustion: *Soviet Geology*, p. 48-56.
19. Wunderlich, G., 1952, Thermodynamics of the decomposition of pyrites: *Zeitschrift für Elektrochemie*, v. 56, p. 218-223.
20. Wurm, V. A., 1927, Ueber ein größeres Schwefelvorkommen als Neubildung in der Zementationszone der Schwefelkieslagerstätte von Pfaffenreuth bei Waldsassen in Bayern: *Zeitschrift für praktische Geologie*, v. 35, p. 129-144.
21. Bryner, L. C., Beck, J. V., Davis, D. B., and Wilson, D. G., 1954, Microorganisms in leaching sulfide minerals: *Industry and Engineering Chemistry*, v. 46, p. 2587-2592.

USGS LIBRARY - RESTON



3 1818 00236940 1