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**STUDIES IN COAL LIQUEFACTION WITH APPLICATION
TO THE SRC AND RELATED PROCESSES**

Quarterly Report for May—July 1981

By
James A. Guin
Christine W. Curtis
Arthur R. Tarrer

Work Performed Under Contract No. AC22-79ET13397

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U. S. DEPARTMENT OF ENERGY

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STUDIES IN COAL LIQUEFACTION
WITH APPLICATION TO
THE SRC AND RELATED PROCESSES³⁴

Quarterly Report for the
Period May, 1981 - July, 1981

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PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY

Under Contract No. DE-AC01-79ET13397

Objective and Scope

Scope:

The Auburn Coal Conversion Laboratory is engaged in a research program designed to investigate fundamental aspects of the Solvent Refined Coal (SRC) and other closely related coal liquefaction processes. The SRC process provides a method for liquefaction of coal, and removal of sulfur and ash pollutants which would results from direct combustion of the raw coal. If successful, the SRC process will permit the use of high sulfur coals as a boiler fuel, which otherwise could not be used under EPA regulations. This research program seeks to improve the economic attractiveness of the SRC process through the application of chemical engineering techniques.

Objective:

The objective of this research program is to systematically investigate, characterize, and delineate the effects of changes in process operating conditions, equipment configuration, and nature of raw materials upon the kinetics, mechanism, and extent of coal dissolution, heteroatom removal, and hydrogenation in the SRC and closely related processes, for the purpose of providing an increased fundamental understanding of SRC process chemistry as well as guidelines and recommendations leading to economic and technical improvements in SRC technology. The program objectives are being carried out in cooperation with the Southern Services' SRC pilot plant operation at Wilsonville, Alabama, and with the Rust Engineering subsidiary of Wheelabrator-Frye, Inc.

The research program is divided into three major tasks with several sub-tasks within each area. An outline of the program by tasks and subtasks is presented on the following page.

Program Task Outline

Task 1. Mechanistic Studies of Coal Particle Dissolution

- A. Dissolution Behavior as a Function of Coal Characteristics
- B. Effect of Solvent Type and Gas Phase Composition on Particle Dissolution
- C. Direct Visual Observation of In-situ Particle Dissolution

Task 2. Catalysis by Coal Mineral Matter

- A. Process Variable and Kinetics
- B. Characterization of Coal Minerals
- C. Regeneration/Pretreatment of Coal Minerals and Residue
- D. Effect on Individual Species in Coal Liquefaction Products
- E. Continuous Reactor Studies

Task 3. Analytical Support

- A. Fourier Transform Infrared Spectroscopy of Coal and SRC
- B. Energy Dispersive X-Ray Fluorescence of Coal and SRC

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SUMMARY

This report discusses a kinetic investigation of the Fe-S-H₂ system conducted as an outgrowth of current research in the SRC-I (solvent refined coal) process to better understand the effects of naturally occurring iron sulfides in coal hydrogenation and hydrodesulfurization. A total of twelve closed system reactions were carried out in which 48-60 mesh pyrite, in the presence of hydrogen gas, underwent transformation to 1C hexagonal pyrrhotite. Reaction temperatures were 350⁰C and 400⁰C with four sample runs at temperature. Initial pressure of hydrogen gas was 1250 psig (8617 KPa). A comparison of the results for each reaction series was evaluated with time and temperature as variables. The transformation rate of pyrite to pyrrhotite was found to increase over the range of reaction temperatures with the 400⁰C samples showing the greatest amount of transformation per unit time. For the 375⁰C and 400⁰C runs pyrrhotite formation decreased after approximately 15 minutes of reaction time due to (1) reduced availability of pyrite, and (2) resistance to diffusion in the topochemical product layer.

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I. INTRODUCTION

In the SRC-I (solvent refined coal) process, partial beneficiation is achieved by removal of sulfur and sulfur compounds during hydrogenation and hydrodesulfurization. Beneficiation by these processes involves closed system reactions between hydrogen donor solvents, inorganic catalysts and hydrogen gas (Guin and others, 1978, 1979). Current research in these processes is aimed toward (1) reduction of hydrogen consumption, (2) increasing product yield (low sulfur coal), and (3) improvement of selectivity of catalytic reactions involving the removal of sulfur from coal slurry.

Pyrite, a ubiquitous constituent of coal, is currently the subject of detailed investigations with respect to its role in coal catalysis and its potential value in improving selectivity of known, but as yet only empirically understood, reactions (Guin and others, 1978, 1979a,b, 1980; Montano and Granoff, 1980; Padrick and others, 1980). At the high temperature and pressures required for the SRC-I process, pyrite, in the presence of hydrogen, reduces to pyrrhotite (Fe_{1-x}S) via the reaction

The extent of research done on the system Fe-S-H₂ up to the present has been mostly empirical mathematical and chemical modelling, as opposed to actual observation and description of the solid products. However, pyrrhotites of known stoichiometry have been synthesized by reduction of pyrite in the presence of hydrogen gas resulting in a much-needed thermodynamic evaluation of the above reaction (Lambert and others, 1980).

In addition to the small amount of data concerning pyrrhotites produced by hydrogen reduction of pyrite, is the extent of the catalytic role of these compositionally variable synthetic sulfides and the kinetics of phase transformations that are known to take place with increasing temperature (Guin and others, 1980).

The purpose of this study is to define the chemical, physical and morphological transformations occurring over specific physical and time intervals in the system Fe-S-H₂. Descriptions of morphological transformations apply only to changes observed on the surfaces of the reaction products whereas physical transformations denote those that occur within the reaction products. This distinction is convenient in that it reasonably applies to those effects in gas-solid reactions on pellets modelled by Shen and Smith (1965).

This study is relevant because current coal refining techniques must be modified to dispose of or alternately utilize recently recognized, environmentally harmful bulk

and liquid waste products such as sulfur and sulfur compounds. To obtain an economically refined coal for increasing future demands it is imperative that basic and applied research be conducted to define the most efficient method of coal refining.

There are four specific objectives in this study as follows:

1. To qualitatively determine the mineralogical composition of the reacted pyrite samples.
2. To fully quantify mineralogical data for the samples, i.e., determine concentrations of pyrite versus pyrrhotite for each sample as well as changes in iron fraction within synthetic pyrrhotites.
3. To evaluate morphological/physical transformations and determine reaction kinetics based on structure, reaction time and chemical changes.
4. To observe and evaluate physico-chemical or structural anomalies.

II. PREVIOUS INVESTIGATIONS

Coal Beneficiation

Low pressure - high temperature research concerning the kinetics of reduction of pyrite by hydrogen gas was first done by Schwab and Philinis (1947) in which a continuous flow velocity of hydrogen was passed over pyrite grains in a glass vessel. According to their findings, reduction of pyrite did not take place below 500°C, under experimental conditions. Although they found no pyrrhotite polytypes as reaction products, they did succeed in synthesizing essentially pure troilite (FeS).

This hydrogen reduction concept has been revived, although modified in procedure and application, during the past ten years, particularly with respect to the removal of pyritic sulfur in bituminous coals and the evaluation of the catalytic potential of pyrite in coal liquefaction processes (Garg and others, 1979; Guin and others, 1979a,b, 1980; Padrick and others, 1980; Montano and Granoff, 1980).

Pyrite reduction by hydrogen has undergone two distinct branches of industrial evaluation: (1) magnetic separation of pyrrhotite synthesized from pyrite (Liu and Lin, 1976) and, (2) removal of pyritic, sulfate and organic sulfur in the SRC-I process by the addition of hydrogen gas and sulfur

scavenging compounds to a coal-light recycled oil (LRO) slurry (Tarrer and others, 1981). The latter investigators have also succeeded in quantitatively evaluating the catalytic activity of pyrite at coal liquefaction conditions. Synthesis of pyrrhotite polymorphs of various stoichiometric and non-stoichiometric compositions has been carried out by reduction and thermal decomposition of pyrite in experiments employing CO (Lambert and others, 1980) and helium (Richardson, 1972), respectively.

Kinetics

Kinetic modelling theory as applied to symmetrical solids has been presented by Shen and Smith (1965) as an outgrowth of work done by Schwab and Philinis (1947). The models have been effectively applied to other chemical systems (Yannopoulos and Themelis, 1965; Simonsson, 1979), the results of which have been compared with data obtained in the present study.

Crystallography and Sulfide Phase Equilibria

Phase equilibria studies of binary and ternary sulfide systems were initiated to supply knowledge of the physical and chemical constraints that control the deposition of naturally occurring ore deposits. It was hoped that these constraints once quantified, would provide a rational method for the exploration and evaluation of base and precious metal deposits. Of particular relevance to this

study are the works of Kullerud and Yoder (1959), and Arnold (1962), who independently attempted to develop a pyrrhotite geothermometric model based on the relationships between temperature and composition. Although later studies (Carpenter and Desborough, 1964; Froese and Gunter, 1976) indicate interpretive errors in the results of these earlier works, the phase equilibria data remain internally consistent from paper to paper.

The equilibrium relations between pyrite and pyrrhotite from 325°C to 743°C were experimentally determined by Arnold (1962). Lower temperature equilibrium relations in this system were later evaluated by Arnold (1969) and Yund and Hall (1969) who carried out experimental determinations up to 290°C and 320°C, respectively.

A direct result of these investigations was the refinement of laboratory procedures related to problems inherent to working with synthetic sulfides, i.e., compositional determinations by x-ray diffraction and polished section preparation techniques. Overviews by Kullerud (1971) and Scott (1974) are valuable guides in experimental methods in sulfide synthesis, many of which have been employed in this study.

A modification of the methods of Arnold (1962) and Kullerud and Yoder (1959) led to the studies of Toulmin and Barton (1964), who made an extensive thermodynamic investigation of the Fe-S system from 325°C to 743°C. This study

related pyrrhotite composition and sulfur fugacity to temperature. Additional contributions directly related to the crystallography of pyrite and pyrrhotite have been offered by Fleet (1968) and Nakazawa and Morimoto (1971).

III. METHODS OF INVESTIGATION

To accommodate the objectives of this study, two analytical methods have been employed: (1) x-ray diffractometry, and (2) reflected light microscopy. Of the four previously outlined objectives, the first two involve x-ray diffraction analyses. Utilizing x-ray diffractometry it is possible to identify the crystalline phases present in a particular sample. An extension of this capability is that quantitative analyses may be performed quickly and accurately. In this respect, x-ray diffraction has provided data to determine the weight fraction of pyrrhotite in a reaction product and the atomic percent iron within the pyrrhotite molecule. A comparison of the results for each series of reactions has been evaluated in terms of time and temperature as variables.

The last two objectives rely primarily on reflected light microscopy. By this method crystalline phases and textures evolved during reaction processes may be observed in detail. In reflected light microscopy the samples are ground and polished so that they may be viewed in cross section. Mineralogical differences are manifested by characteristic colors, reflectance intensities, and textural differences. As a result, it is possible to describe the physical changes displayed in a sample quenched in a

nonequilibrium state. In relating the term "sample" in this discussion to the research topic, a sample of research products actually consists of a population of pyrite grains reacted under constant parameters. The organization of procedures for this study is shown by a flow diagram in figure 1.

Closed System Reaction Equipment

Because the reduction of pyrite by hydrogen gas was to be conducted at high temperatures and pressures, it was necessary to construct closed system reaction vessels for the experiments. A tubing bomb reactor was employed that was equipped with a variable-speed electric motor, a series of agitation components and a small tubing bomb (fig. 2).

Three stainless-steel tubing bombs that average 15.30 ml capacity, were constructed in accordance with parts and size specifications outlined by Guin and others (1979a). Reaction temperatures were maintained in a fluidized sand bath (fig. 2). This device is a vat of fine-grained sand that behaves as a fluid when air is injected under pressure into the vat. Temperature of the fluidized sand bath was adjusted by means of a temperature controller and monitored by reading a thermometer (Techne, Inc., SRI-2). This thermometer is electronically connected to a thermocouple inserted directly into the sand bath.

Figure 1. Flow diagram of investigative procedure.

Figure 2. Reactor system used in pyrite reduction experiments.

Preparation of Reactants

Pyrite from Ambasaquas, Spain was used in the reactions and was obtained from Ward's Natural Science Establishment. The crystals were anhedral hexahedra that averaged 2 cm in diameter and were free of visible adhering matrix. This pyrite is relatively pure (97%) with identifiable impurities being calcite and quartz, as determined by x-ray diffraction.

Preparation of pyrite for reaction involved crushing individual crystals in a steel piston which is struck with a mallet. Further grain size reduction was done by an automatic mortar and pestle. After this operation, the grains were then segregated as to size in U.S. Standard sieve screens with the 48 to 60 mesh fraction set aside for this study. Selection of this grain size range is based on several factors described in a later section on microscopy techniques.

Reaction Procedure

After cleaning, the tubing bombs were charged with 1.0 g of pyrite. For all reaction runs the pyrite fractions were tared to a ± 10 mg deviation from 1.0 g, on a Mettler balance. Table 1 shows the actual weight of pyrite present in each tubing bomb prior to reduction.

Before reaction, each tubing bomb was sealed under atmospheric conditions with Swagelok caps tightened down on both ends. Hydrogen gas was then introduced into the reaction chamber through a small needle valve which is

Table 1
Reaction Parameters

Run	Temp °C	Reaction ₂ Volume (cm ²)	Starting wt of FeS ₂ (g)	Reaction Time (min)	Initial P H ₂	PH ₂ @ T°C * ₂ psig
C01	400	15.15	1.00	5	1250	2822
C02	400	15.35	0.99	15	1250	2822
C03	400	15.33	0.99	30	1250	2822
C15	400	15.15	1.00	60	1250	2822
C05	375	15.35	1.00	5	1250	2717
C06	375	15.33	1.00	15	1250	2717
C07	375	15.35	0.99	30	1250	2717
C14	375	15.15	0.99	60	1250	2717
C16	350	15.15	1.00	5	1250	2612
C08	350	15.15	1.00	15	1250	2612
C09	350	15.35	1.00	30	1250	2612
C10	350	15.33	1.00	60	1250	2612

(*Values calculated from Ideal Gas Law.)

connected by a stainless-steel tube to the reaction chamber. A hydrogen gas cylinder (2000 psi grade) equipped with fine metering valves and reducing unions was used for introduction of the gas into the bombs. Hydrogen was charged into each tubing bomb to 1250 psig (8617 kPa). Repeated pressurizing and bleeding-off of hydrogen gas from a tubing bomb reduced the possibility of any atmospheric gases remaining once final pressurizing was achieved. The needle valve on a bomb was closed, removed from the hydrogen cylinder and capped.

A total of twelve reactions were carried out in the tubing bomb reactor at $350 \pm 2^\circ\text{C}$, $375 \pm 2^\circ\text{C}$ and $400 \pm 2^\circ\text{C}$. Four reactions were run for each temperature increment. Durations for each run at temperature were 5, 15, 30 and 60 minutes. Vertical agitation rates were monitored on a tachometer (fig. 2) and were kept between 600 and 625 cpm. Separate preliminary runs conducted under nearly identical conditions, except for agitation rates, resulted in no difference in product character except for undue additional milling of the pyrites at higher agitation rates.

At the end of each run, the tubing bomb was removed from the supporting equipment and immediately immersed in a cool, stationary water bath to quench the reaction. The reaction products, upon removal from the bombs, were placed in labelled vials and stored in a desiccator jar.

X-Ray Diffraction Analysis

Equipment

X-ray analyses of standards and reaction products were carried out on a Philips Electronic Instruments x-ray diffractometer equipped with a monochromator. The unit is powered by an XRG 3100 generator. The radiation source was a Norelco x-ray tube with a copper target which emits K-alpha radiation of wavelength 1.5418 Å. A complete list of component settings is presented in appendix B. Throughout the study, generator settings remained at 35 KV and 28 MA, with the goniometer head travelling through 1.0 degree 2θ per minute. Recorder chart speed was set to graph 0.5 degree 2θ per minute.

Preparation of Smear Mounts

Prior to x-ray analysis, all samples were ground in an agate mortar to less than 325 mesh. Grinding was done in an acetone slurry to prevent sample loss and to provide a fluid barrier to oxidizing atmosphere (Toulmin and Barton, 1964). After evaporating off the acetone under a fume hood, each sample was immediately transferred to a glass petrographic slide. Approximately 20 mg of powdered sample was required to sufficiently cover a 1x2 cm area, per slide. Two to three drops of 3:1 acetone and shellac were then added to a powdered sample and the mixture smeared to

uniform thickness across the slide. Drying time for the slide mounts was ten minutes.

Construction of Working Curve

A number of standards were used as a basis for quantitative analysis of the reactions products by x-ray diffraction. These standards, consisting of various weight proportions of pyrite mixed with pyrrhotite, were prepared with the intention of constructing a working curve from which the weight fraction of pyrrhotite versus pyrite in a reaction product could be read directly (fig. 3).

Justification for using a working curve rather than comparing the measured ratio of peak heights (intensities) between pyrrhotite and pyrite lies in the fact that these two minerals do not have the same mass absorption properties with respect to x-ray irradiation due to slight differences in density (Cullity, 1978); pyrite having a density of 4.95 g cm^{-3} and pyrrhotite 4.6 g cm^{-3} (Deer, Howie and Zussman, 1966). Hence, the relationship between peak intensity and concentration is not linear.

The external standard method of quantitative analysis has been employed for this phase of the study and is described completely in appendix C. This method was chosen over other x-ray analytical techniques because (1) the working curve compensates for mass absorption effects, and (2) many samples may be analyzed precisely in a short period of time.

Figure 3. Working curve for the determination of weight fraction pyrrhotite in pyrite-pyrrhotite mixture.

Selection of Standards

Selection of pyrite and pyrrhotite for use as standards was based on purity and outward qualities of the minerals. Small, pristine aggregates of both pyrite and pyrrhotite were obtained from the mineral collection at the Auburn University Department of Geology. The naturally occurring pyrite samples used for preparing the standards are from Gilman, Colorado, and were incorporated into the study prior to arrival of the Spanish pyrite. Later qualitative comparison of the two suites by x-ray diffraction analysis showed that they were nearly identical in purity and crystallographic properties.

The naturally occurring 1C hexagonal pyrrhotite aggregate chosen from the collection was analyzed by x-ray diffraction and was found to be essentially pure. The stoichiometric determination of this pyrrhotite was not critical to this preliminary activity in that the measured parameter (diffraction intensity) is dependent on the concentration of a particular phase and not small variations in chemical composition. A similar procedure to that comparing the two pyrite suites was conducted for the collection pyrrhotite versus pure pyrrhotite, synthesized by hydrogen reduction of pyrite in the preliminary runs. Crystallographic characteristics of significance to this study were found to be identical.

Procedure for Preparation of Standards

Using a Mettler balance, weight percentage proportions of the pyrite and pyrrhotite standards were prepared as mixtures (table 2). After taring the weighing paper, pyrrhotite was added to a predetermined weight, the value being within one order of magnitude of the percentage desired; i.e., 1000 mg equals 100 weight percent. After adding pyrite to obtain a total of 100 weight percent pyrite and pyrrhotite, the mixture was again ground in a mortar, as per procedure, to insure homogeneous distribution of the grains and prevent the possibility of a biased sample. Smear mounts were then prepared from each standard.

X-Ray Analysis of Standards

Following x-ray irradiation the mounts were placed in an airtight storage cabinet. The diffractograms were then qualitatively analyzed by comparing each graph to the standard pyrite and pyrrhotite diffractograms. As opposed to peak intensity measurements, the integrated intensity of the pyrrhotite d(102) peak was measured for each standard diffractogram by planimetry. The integrated intensity of a reflection peak is a measure of the unit area under a peak, which with increasing peak intensity also takes on a greater value. Moreover, it is a more precise measurement of intensity than measurement of peak height (Cullity, 1978).

Table 2

Weight Percentage Mixtures of Pyrite and Pyrrhotite
Used in Construction of Working Curve

STDpo	1000 mg po	100 wt% po
STPpo-90	900 mg po	90 wt% po
	+	
	100 mg py	
STDpo-70	700 mg po	70 wt% po
	+	
	300 mg py	
STDpo-50	500 mg po	50 wt% po
	+	
	500 mg py	
STDpo-30	300 mg po	30 wt% po
	+	
	700 mg py	
STDpo-10	100 mg po	10 wt% po
	+	
	900 mg py	
STDpy	1000 mg py	100 wt% py

The integrated intensities of the d(102) peak for each known weight percent pyrrhotite were divided by the integrated intensity of the d(102) peak of standard 100 weight percent pyrrhotite to obtain I_{po}/I_{po_p} , where I_{po} is the integrated intensity of the d(102) pyrrhotite peak in the standard mixtures and I_{po_p} is the integrated intensity of the d(102) peak in the pure pyrrhotite standard. The values of I_{po}/I_{po_p} from each standard diffractogram were then plotted against the corresponding premeasured weight fractions of pyrrhotite in the pyrrhotite and pyrite mixtures for a total of six points on the working curve.

To find the best fit line for the array of data points a linear regression program was employed using a Texas Instruments-59 programmable calculator equipped with a statistics library.

To check the validity of the determinative curve, mass absorption coefficients for each phase were obtained from the "International Tables for X-ray Crystallography, Volume III" and substituted in equation (8), appendix C, along with the weight fractions of the standard pyrite and pyrrhotite. Using the quantities derived from equation (8) a theoretical curve has been superimposed on the experimentally determined curve.

Diffractogram tracings of the standards, as shown in figure 4, clearly show the x-ray diffractometry manifestation of the varying relative abundance of pyrrhotite to

Figure 4. X-ray diffractogram tracings of variable weight percentage mixtures of standard pyrite and pyrrhotite. Dark peaks are pyrrhotite.

pyrite. A notable increase in the d(102) pyrrhotite peak occurs with increasing weight fractions of pyrrhotite. Likewise, the prominent d(311) and d(200) peaks of pyrite noticeably decrease with increasing amounts of pyrrhotite.

Determination of Atomic Percent Iron in Pyrrhotite

Variations in the atomic percentage of iron within the synthetic pyrrhotites over the experimental temperature/time ranges were measured from data obtained from diffractograms of the reaction products. X-ray methods currently used in the measurement of the compositions of sulfide solid solution phases, such as pyrrhotite, have been reviewed by Scott (1974). The particular method of Toulmin and Barton (1964) was used in this part of the study and relies on measurable variations with composition in the d-spacings of the hexagonal pyrrhotite d(102) peak. According to Arnold (1962) the d(102) peak is sensitive to minor changes in unit cell volume, attendant with ionic substitution or elemental depletion by diffusion.

To be consistent with the procedure outlined by Toulmin and Barton (1964), pure halite was used as an internal standard with which the d(220) peak was compared with the d(102) pyrrhotite peak. The d(220) peak, which represents a constant, reliable cell edge reflection, was measured with respect to its Bragg angle as a standard from which the

d(102) pyrrhotite Bragg angle position could be measured (fig. 5).

A small amount of halite was thoroughly mixed with a reaction product sample prior to making a smear mount. During irradiation of a mount, the x-ray goniometer was oscillated at 1.0 degree per minute through two cycles per smear mount. Bragg angle measurement from the diffractograms was done with a 20 division-per-inch engineer's scale which conveniently corresponds to a recorder chart speed of 0.5 degree per minute. Bragg angle measurements of the d(102) peaks were made to 0.05 degree.

After recording the averaged Bragg angle of the d(102) peak for a sample run, the angle value (degrees 2θ) was converted to a corresponding d-spacing value, in angstroms. The d-spacing values were obtained for each Bragg angle from the "International Tables for X-ray Crystallography, Volume III" for Cu-K $_{\alpha}$ radiation. Where d-spacings recorded for a number of samples took on values intermediate to those on the standardized table, mathematical interpolation was necessary.

A determinative (working) curve comparing the d(102) peak of synthetic pyrrhotites of known stoichiometry versus mole fraction iron in the synthetic pyrrhotites was initially constructed by Arnold (1962) and subsequently modified by later investigators; notably Toulmin and Barton (1964), and Yund and Hall (1969). The curve constructed by Toulmin and

Figure 5. X-ray diffractogram tracing showing position of halite (NaCl) d(220) reflection peak relative to - pyrrhotite d(102) reflection peak.

Barton (1964) has been accepted by most experimentalists and has been incorporated in concept in this study.

For the sake of precision the d-spacing values were substituted into Yund and Hall's (1969) equation:

$$Y = 45.212 + 72.86 (d_{102} - 2.0400) + 311.5 (d_{102} - 2.0400)^2.$$

In this equation Y is the composition of hexagonal pyrrhotite in atomic percent iron and d_{102} is the d-spacing value (Å) of pyrrhotite derived from the diffractograms of the product runs. This equation in effect describes the curve of Toulmin and Barton (1964).

Microscopy

Equipment

The optical equipment used for this study was a Leitz/Wetzlar Ortholux II binocular polarizing microscope equipped with reflected light optics and oil immersion lenses. A camera mount on the microscope permitted photomicrography of the product grains with a Leica M-3 35 mm camera. Photography was done at 320x and 500x (oil immersion objectives) under reflected light. The type of film used was Kodak Panatomic-x, ASA 32 and was developed with Microdol X developer at manufacturer's specifications.

Sample Preparation

Preliminary procedure for microscopic examination of the reaction products involved making cold-set plastic pellet mounts for the grains which would serve both to preserve the samples and to stabilize the grains for grinding and polishing. The pellets were made by mixing 40 drops of Buehler Castoglas resin hardener in 50 ml Buehler Castoglas resin. The mixture was poured into 2.5 cm diameter bakelite form rings and allowed to harden for several hours. This amount of Castoglas filled three form rings at a time.

An electric drill with a 0.25 inch (6.3 mm) bit was used to bore three 5 mm deep wells per pellet. Approximately 0.1 g of three different samples was then placed in a well and filled with a new batch of Castoglas. After hardening overnight, the pellet mounts were ground manually with a series of continuously fining abrasives from 600 grit (Buehler Metallography paper) to 0.25 μm (Buehler Metadi diamond compound). This simple technique for making polished grain mounts was modified after Kullerud (1971).

Analytical Procedure

Point counts were done on each sample to determine the volume percentages of pyrite versus pyrrhotite. The standard reference for point count theory and applications used in this study was Hutchison (1974). Statistical

deviation in point count ratios for the two phases was found to be negligible after counting 300 points pyrite plus pyrrhotite, per sample. Thus, this value was taken to be the optimum grain population that would be statistically meaningful.

The grain size range used (48 to 60 mesh) proved most convenient to work with as observations could be made well within the optical capabilities of the microscope while also providing a large population of product grains to count and describe.

The mean differential reflectivity between pyrite and pyrrhotite is 15 percent, pyrrhotite being less reflectant than pyrite (Stanton, 1972). This difference in reflectivity is easily distinguished by the eye and was a main differentiating parameter between pyrite and pyrrhotite. Pyrite and pyrrhotite show different colors in reflected light, pyrrhotite being slightly pink or bronze as opposed to the brassy yellow of pyrite.

References used for determination and evaluation of crystalline textures were Stanton and Gorman (1968), Spry (1969) and Stanton (1972).

IV. RESULTS

Crystallography

The reaction products analyzed by x-ray diffraction yielded proportions of coexisting pyrite and pyrrhotite. Under all reaction conditions the type of synthesized pyrrhotite conformed to the $1\bar{C}$ hexagonal polymorph having approximate unit cell dimensions $a = 3.45 \text{ \AA}$ and $c = 5.75 \text{ \AA}$, with respect to the NiAs derivative structure (Nakazawa and Morimoto, 1971). The atomic percent iron in pyrrhotite was found to range from 47.88 to 48.44, which lies within the compositional range of the $1\bar{C}$ polymorph (Nakazawa and Morimoto, 1971). As shown in figure 6, these phases plot within the $1\bar{C}$ hexagonal pyrrhotite thermal stability field of the Fe-S system.

Physical Chemistry

Conversion FeS_2 to Fe_{1-x}S

The percentage conversion of pyrite to pyrrhotite during the reactions is presented as a function of reaction time in figure 7. With increasing reaction time the amount of pyrrhotite produced by reduction of pyrite in hydrogen increases. Since the thermal conversion rate curves do not overlap, they show that an increase in temperature

Figure 6. T-X phase diagram showing position of synthetic pyrrhotite in the divariant 1C hexagonal pyrrhotite stability field. Modified from Arnold (1962) and Scott (1974).

Figure 7. Kinetic diagram showing rate of pyrrhotite production during reaction time at temperature.

accelerates the reaction rate. For example, at 400°C after five minutes of reaction time (C01), nearly 50 weight (and volume) percent of the pyrite has transformed to pyrrhotite as opposed to only ten percent for the same reaction time at 350°C (C16).

The rate curves show a variability in the degree of inflection with respect to each other. The pyrite reduced at 350°C transformed to pyrrhotite at nearly a steady rate, whereas those reduced at 375°C and 400°C show a decrease in pyrrhotite production within the first 15 minutes of reaction (fig. 7).

Table 3 shows a comparison of x-ray diffraction and point count determinations with respect to percentage conversion to pyrrhotite. The two data sets correlate to a reasonable degree with discrepancies mainly due to slight differences in density between the two phases and x-ray unit calibration changes caused by atmospheric fluctuations. The percentage pyrrhotite determined by point counts has been plotted on figure 7 and the rate curves adjusted to average point count and x-ray data.

Variation in X_{FeS} and V_{po}

Pyrrhotite production during reaction was accompanied by enrichment of the iron fraction in pyrrhotite (fig. 8). This effect is clearly thermal in nature being manifested as increasing initial iron fractions for each reaction

Table 3

Comparison of Percentage Conversion of Pyrite to
Pyrrhotite as Determined by X-ray Diffraction
and Microscopic Point Counts

Run	Temp. °C	% Po, x-ray	% Po, point count
C16	350	10	8
C08	350	20	38
C09	350	67	62
C10	350	84	87
C05	375	22	28
C06	375	50	51
C07	375	62	63
C14	375	89	86
C01	400	46	50
C02	400	67	67
C03	400	86	80
C15	400	96	87

Figure 8. Variation in X_{FeS} pyrrhotite with time at temperature.

temperature. Similar to the conversion rate curves, the mole fraction FeS variation diagrams show a region of maximum inflection after about 15 minutes reaction time, beyond which the rate of iron enrichment decreases. To maintain consistency of definition between this study and previous works, the hypothetical component FeS in Fe_{1-x}S is taken as

$$X_{\text{FeS}} = \left(\frac{\text{Fe}/(\text{Fe}+\text{S})}{\text{S}/(\text{Fe}+\text{S})} \right) = \frac{\text{Fe}}{\text{S}} = 1-x$$

the numerical quantity of which is equal to the atomic fraction iron in the pyrrhotite molecule (1-x), if rendered as Fe_{1-x}S .

As a consequence of apparent iron enrichment, there were measurable changes in the molar volumes of the pyrrhotites. Using the regression line calculated by Froese and Gunter (1976) (fig. 9) it was possible to determine the molar volumes of pyrrhotite for each reaction product since X_{FeS} for the pyrrhotite has been determined. Table 4 shows X_{FeS} in pyrrhotite as determined by x-ray diffraction for each sample run, and their corresponding molar volumes extrapolated from figure 9. To show changes in molar volume of pyrrhotite as a function of reaction time a variation diagram was constructed for each reaction temperature. These diagrams are shown in figure 10.

Figure 9. Regression line of Froese and Gunter (1976) showing relation between X_{FeS} and molar volume of pyrrhotite. Data points represent lattice parameters of Fleet (1968).

Table 4. Calculated Hypothetical Component FeS in Synthetic Pyrrhotites and Corresponding Molar Volumes
 Calculated from $V = 14.458 + 3.740 X_{\text{FeS}}$ of Figure 9. V_{FeS} , troilite = $18.20 \text{ cm}^3 \text{ mol}^{-1}$ and V_{FeS_2} , pyrite = $23.94 \text{ cm}^3 \text{ mol}^{-1}$ (Robie and others, 1979).

Run	Temp °C	X FeS	Molar Volume (V) $\text{cm}^3 \text{ mol}^{-1}$
C16	350	.9560	18.0334
C08	350	.9622	18.0566
C09	350	.9660	18.0700
C10	350	.9666	18.0730
C05	375	.9580	18.0410
C06	375	.9640	18.0633
C07	375	.9644	18.0648
C14	375	.9644	18.0648
C01	400	.9600	18.0484
C02	400	.9644	18.0633
C03	400	.9666	18.0730
C15	400	.9688	18.0813

Figure 10. Variation in molar volume of pyrrhotite as a function of reaction time.

Stoichiometry and Consumption of H_2

Using the reaction parameters listed in table 1 and the X_{FeS} in $Fe_{1-x}S$ values obtained from each run (fig. 8), it is possible to calculate the theoretical percentage hydrogen consumed during reaction time for each run at temperature. The resulting relation is

$$\begin{aligned} & \% H_2 \text{ consumed} \\ &= \frac{8.35(10^{-3})R \left[\frac{2(X_{FeS}) - 1}{X_{FeS}} \right]}{5.32(10^{-2})} \times 100 \end{aligned}$$

where the quantity $8.35(10^{-3})$ is the moles of pyrite prior to reaction as calculated in appendix E, R is the fractional conversion of pyrite to pyrrhotite (fig. 7) and $5.32(10^{-2})$ is the moles of H_2 prior to reaction, also calculated in appendix E.

The stoichiometric determination of hydrogen consumption was calculated bearing the following assumptions: (1) all S liberated by the theoretical half-reaction $FeS_2 \rightarrow FeS + S$ bonded with available H_2 in the system, (2) the half-reaction $H_2 + S \rightarrow H_2S$ is nonreversible in the system.

These assumptions are justified in that no sulfur or sulfur compounds were found during analyses of the reaction products and, in addition, figure 8 shows a generally continuous decrease in sulfur with respect to iron in pyrrhotite.

Table 5 shows the results of the stoichiometric calculations for each run with respect to fractional conversion pyrite to pyrrhotite (R), X_{FeS} and mole % H_2 consumed by reaction.

Figure 11 shows the theoretical percentage hydrogen consumed during reaction versus reaction time for each temperature. Note that only 12.4 to 14.6 percent of the total hydrogen was consumed over each temperature range even after 60 minutes reaction time. Therefore, hydrogen consumption is a function of the fractional conversion of pyrite to pyrrhotite (R) and X_{FeS} (x) which may be expressed

$$\text{H}_2 \text{ cons.} = f(R, x).$$

Microstructures

General Physical and Morphological Variation

Photomicrographs were taken of polished mounts of the reaction products and are selectively presented in figure 12. With increasing reaction duration at temperature this figure shows that pyrrhotite formation increases and is manifested by pyrrhotite replacing pyrite concentrically around a continuously shrinking pyrite core. At higher temperature

Table 5
Stoichiometric Variables Used in Calculation
of Percentage of H₂ Consumed

Run	Temp °C	R	X _{FeS}	Mole % H ₂ Consumed ²
C16	350	0.10	.9560	1.50
C08	350	0.33	.9622	4.97
C09	350	0.60	.9660	9.0
C10	350	0.82	.9666	12.4
C05	375	0.24	.9580	3.6
C06	375	0.48	.9640	7.25
C07	375	0.66	.9644	9.97
C14	375	0.85	.9644	12.8
C01	400	0.47	.9600	7.0
C02	400	0.67	.9644	10.12
C03	400	0.83	.9666	12.57
C15	400	0.96	.9688	14.58

Figure 11. Theoretical hydrogen consumption as a function of reaction time.

Figure 12. Photomicrograph composite showing the topochemical expression of pyrrhotite rimming pyrite and the effect of temperature on reaction kinetics.

(400°C), there is a greater volume of pyrrhotite produced during the shorter reaction times than at a lower temperature (350°C).

Because pyrite has no cleavage the grains of each sample are largely anhedral. In figure 12, C16 is representative of the morphology of essentially unreacted pyrite. In the more reacted grains the original external morphology of a grain is preserved even after a large portion of a grain has been transformed to pyrrhotite (C10, figure 12). In addition, the unreacted pyrite core takes on the approximate physical expression of its original morphology prior to hydrogen reduction.

Pyrrhotite Texture

Within the pyrrhotite phase of a reaction product there consistently appears the development of porosity. Figure 13 is a photomicrograph showing the detail of the pores. These pores radiate perpendicularly from near or at, the pyrite-pyrrhotite phase boundary and extend toward the exterior of the grain as fine, interconnecting, cylindrical tubules. The degree of pore development appears consistent from sample to sample.

During the 375°C and 400°C runs, unique v-shaped structures developed that could not be identified in the 350°C sample runs. Figure 14 shows an example of this structure. This development was more commonly observed in

Figure 13. Porous texture development in the pyrrhotite layer (15 min, 400°C).

Figure 14. Anomalous structural development
(15 min., 400°C).

the 400°C sample runs and did not appear to preferentially attack any particular grain shape, e.g., lathe-like or semi-spherical.

Under polarized light, the pyrrhotite showed some degree of bireflectance (anisotropy). However, due to complex development of the porous fabric, the crystallographic orientation of pyrrhotite around a pyrite core could not be determined.

Pyrite-Pyrrhotite Phase Boundary

Figure 15 shows a representative phase boundary between pyrite and pyrrhotite for a single product grain in which the pyrrhotite penetrates the pyrite as a somewhat linear continuum of small, scalloped embayments. Porosity is weakly developed to nonexistent along the grain boundary. According to Stanton (1972) this texture conforms to simple solid state massive replacement of pyrite by pyrrhotite. Analogous textures have been described by Arnold (1962) in which pyrite rims pyrrhotite as the replacement phase. However, these experiments were done in evacuated glass vessels in which the sulfides were allowed to equilibrate for several days, diminishing the possibility of pore development.

Figure 15. Phase boundary between pyrite and pyrrhotite (30 min, 350°C).

V. DISCUSSION AND CONCLUSIONS

Thermochemistry

In the Fe-S-H₂ system the pyrite to pyrrhotite transformation is accomplished by thermal decomposition of pyrite in which hydrogen acts as a scavenger bonding with sulfur. To proceed at a measurable rate, elevated temperatures must be applied to the system to initiate this endothermic reaction. For example, an approximation of the heat of reaction for this system at 350°C (623.15 K) may be calculated considering the end-members of the Fe-S subsystem. For the reaction

where FeS is the stoichiometric phase troilite, we have from the data of Robie and others (1979)

$$\begin{aligned} \Delta H_{623\text{K}}^{\text{rxn}} &= (\Delta H_{\text{FeS}}^{\text{tr}} + \Delta H_{\text{H}_2\text{S}}^{\text{g}}) - (\Delta H_{\text{FeS}_2}^{\text{py}} + \Delta H_{\text{H}_2}^{\text{g}}) \\ &\approx 7.5 \text{ J mol}^{-1} \text{ K}^{-1}. \end{aligned}$$

By the experiments of Schwab and Philinis (1947), reduction of pyrite in an ambient hydrogen atmosphere did

not take place below 500°C. However, the results of the present study demonstrate that this reaction does proceed at a measurable rate below this temperature (fig. 7); and, by the above argument, thermal energy is required for reaction. What may be considered a lower limit for this reaction to proceed was given as 250°C by Padrick and others (1980).

On the basis of atomic percentage iron, the pyrrhotites synthesized in the present study plot within the pyrrhotite thermal stability field of figure 6. In nearly all the reaction products pyrrhotite was found coexisting with pyrite (fig. 12). This relationship suggests that the reaction products were quenched in a nonequilibrium state. This is additionally supported by the development of scalloped phase boundaries between pyrite and pyrrhotite (fig. 15) which, according to Spry (1969, p. 24), is indicative of a mobile reaction front quenched in a nonequilibrium state.

Kinetics

Rate Determining Factors

The morphological and physical result of pyrite reduction by hydrogen gas conforms to what is variously termed the "topochemical" (Pepper and others, 1976; Yen and others, 1978) or the "unreacted shrinking core" model (Shen and Smith, 1965; Simonsson, 1979). The net effect, as shown in

figure 12, is the concentric, free growth of the metasome (replacing phase) around, and at the expense of, the host phase (Stanton, 1972, p. 264).

As pointed out in chapter III of this study, the rate of pyrrhotite (metasome) production is initially rapid. This is particularly evident in the 375°C and 400°C sample runs (fig. 7). At these temperatures 50 to 70 percent of the pyrite has transformed to pyrrhotite after only 15 minutes reaction time. After approximately five minutes reaction time, pyrrhotite formation continuously decreased. This effect may be due to a number of rate limiting/determining factors. According to the Shen and Smith (1965) topochemical kinetics study, the rate-determining factors are: (1) heat transfer and diffusion resistances in the gas layer surrounding the grains, (2) heat transfer and diffusion resistances over the diameter of the product layer, and (3) shrinkage of the core (restricted availability of a reactant). Within this particular model is an assumption of bidirectional diffusion in which a gaseous reactant diffuses through the product layer to a reaction site as a gaseous product counterdiffuser through the product layer.

Because of the small grain-sizes of pyrite employed in the present study and the effect of agitation on the system during reaction, heat transfer and diffusional resistances in the gas layer surrounding the grains are taken to be minor and warrant no further consideration.

The Shen and Smith (1965) rate determining factors are mainly applicable to an open, ambient system. Because the present study involves closed system reactions an additional factor, the effect of gas mixing, must be taken into consideration. Therefore, the primary rate determining factors to be evaluated in this study are: (1) the effects of gas mixing, (2) resistance to diffusion in the product (pyrrhotite) layer, and (3) the restricted availability of a reactant (pyrite). With these factors defined, it subsequently becomes necessary to evaluate the system with respect to that factor, or combination of factors, which contribute the most significant constraint on reaction rates.

Effects of Gas Mixing

As shown in figure 11, the percentage hydrogen consumed by the reaction increases with increasing temperature and reaction time. A comparison of this figure with figure 7 indicates that hydrogen consumption is coincident with pyrrhotite production (S liberation from reacted pyrite). In the system, hydrogen is consumed in the reaction, evolving H_2S . At any time during a reaction the gases present in a tubing bomb consist of a variable mixture of H_2S and unreacted H_2 . Assuming that H_2S and hydrogen behave as a perfect gas under the reaction conditions of this study,

we may calculate the theoretical partial pressure of H_2S (P_{H_2S}) at a specific reaction condition as given by

$$P_{H_2S} = \epsilon P_t$$

where ϵ is the fraction H_2 consumed by reaction and P_t is the total pressure of the system, at temperature. The H_2 fraction is derived from decimal equivalents of those values in figure 11. This approach is not unwarranted in that it has been previously applied to the Fe-S- H_2 system by Lambert and others (1980). For example, in figure 7, sample run C15 was reacted at $400^\circ C$ for one hour. The partial pressure H_2S existing under these conditions is given by

$$\begin{aligned} P_{H_2S} &= .133 \left[(1250 \text{ psig}) \left(\frac{698.15K}{298.15K} \right) \right] \\ &= 389 \text{ psig} \end{aligned}$$

In the context of the effects of gas mixing as a rate limiting factor, the partial pressure of H_2S , as shown above, remains small in relation to the total pressure of the system (2927 psig) and would likely have little effect in altering the reaction rates. It has been suggested by Lambert and others (1980) that H_2 and H_2S may not behave

ideally under coal liquefaction conditions and, therefore, the reaction conditions of this study. Because the theoretical partial pressure H_2S is shown to be a very small quantity even under the most extreme reaction conditions of this study, it was deemed unnecessary to empirically treat H_2S and H_2 as non-ideal gases.

Diffusional Resistance of Pyrrhotite

The topochemical character of the reduced pyrite (fig. 12) requires mobility of products and reactants on the atomic level relative to the scale of a grain and its proximal atmosphere. This effect conforms to thermally induced phase transformations by diffusion, as discussed by Burke (1965, p. 93).

From the theoretical half reaction for the decomposition of pyrite to pyrrhotite, sulfur is liberated and subsequently bonds in mass balance with hydrogen gas. Although this concept has been shown to be convenient for stoichiometric calculation, the actual mechanism by which pyrite reduction by hydrogen occurs must await later consideration. Regardless of the composition of the reaction products escaping from a reaction site, a certain amount of diffusional resistance afforded by a continuously thickening product layer would be expected. However, a large diffusional resistance as a rate-determining factor on the production of pyrrhotite (fig. 7) and consequent hydrogen

consumption (fig. 11) appears diminished as indicated by the molar volume changes and microstructural development within pyrrhotite.

As shown in figure 9, changes in the molar volume of pyrrhotite are a function of the X_{FeS} pyrrhotite component. Since X_{FeS} is variable with temperature (fig. 8), changes in the molar volume of pyrrhotite are coincident with changes in temperature (fig. 10). It will be noted from this figure and the data in table 4 that the molar volumes of pyrrhotite increase with temperature and that there is a general levelling-off of the rate of volume change with reaction duration. However, pyrite has a standard molar volume of 23.940 cm^3 (Robie and others, 1979) which is approximately 25 percent greater than the statistical mean of the pyrrhotite molar volumes of table 4.

In a manner analogous to stress-induced lattice distortion in metals (Stanton and Gorman, 1968) the molar volume differential in the pyrite to pyrrhotite transformation may cause lattice distortion in the pyrrhotite phase. This strained state is the result of compression, tension or twisting (Stanton and Gorman, 1968). Such a phenomenon could account for the randomness of optical anisotropy in pyrrhotite as described in chapter IV.

In this context, it seems reasonable that the development of porous microstructures is controlled by a net volume loss in the pyrrhotite phase. A similar explanation for

porosity development has been given by Pepper and others (1976) with respect to the thermally induced hematite-magnetite transformation. In turn, by the geometry of these pores (chapter IV), they would likely function in a capacity that enhances the reaction since diffusion occurs at a greater rate along a surface (lattice defect) than in a volume of crystalline matter (Vernon, 1975, p. 81).

By this argument, resistance to diffusion in the pyrrhotite product layer may exist due to an increased distance through which the reaction products must diffuse, but is likely not the sole constraint in determining reaction rate. Figure 16 demonstrates that diffusion control (resistance) in the pyrrhotite layer is not per se rate determining in that there is not a linear dependence of conversion rate of a sphere with time.

Restricted Availability of a Reactant

As observed by Yannopoulos and Themelis (1965) from experiments on the topochemical reduction of ferrous chloride (FeCl_2) by hydrogen, the reduction rate at a specific unit area reaction interface remains constant under isothermal conditions. Because their mathematical proofs are consistent with those of Shen and Smith (1965) for topochemical situations, this hypothesis is most likely the case for the physical results of figure 15 of the present study. In addition, Yannopoulos and Themelis (1965) noted that the

Figure 16. Diffusion control test plot where R is fractional conversion pyrite to pyrrhotite. After Levenspiel (1962).

generation of reaction products at the surface of a particle (short reaction times) does not remain constant with increasing reaction duration, but decreases as the reaction interface advances toward the center of a particle. The net effect is that the reaction rate is constant but the generation of reaction products decreases as the reaction interface advances due to a continuously decreasing reaction surface area.

Since the conversion rate curves of figure 7 of this study qualitatively agree with the kinetic results of Schwab and Philinis (1947, fig. 3), it is feasible that the restricted availability of FeS_2 , due to its decreasing surface area, is a rate-determining factor. The curves in figure 7 also compare with the general results of Yannopoulos and Themelis (1965, fig. 4).

Figure 17 demonstrates that the restricted availability of a reactant (shrinking core) is not in itself a rate determining factor, provided that the reaction products are roughly spherical. However, the shrinking core and the diffusional resistance afforded by the pyrrhotite product layer may collectively constitute the primary rate determining factors in this system.

Reaction Mechanism

The structural changes found to occur in the reduction of pyrite by hydrogen are a result of diffusional phenomenon.

Figure 17. Area control test plot where R is fraction conversion pyrite to pyrrhotite. After Levenspiel (1962).

By the model of Shen and Smith (1965) H_2 reacts directly with FeS_2 to produce $Fe_{1-x}S$ and H_2S ($450^\circ C$ to $495^\circ C$). This requires that hydrogen initially reacts with a pyrite particle surface, carrying out the pyrrhotite transformation, and then diffusing back through the pyrrhotite product layer as H_2S . Generally analogous topochemical diffusion mechanisms involving gas-solid reactions have been offered by Yen and others (1978) concerning the sulfidation of dolomite, and by Yannopoulos and Themelis (1965) on the reduction of ferrous chloride by hydrogen.

An alternate hypothesis has been offered by Padrick and others (1980) in which the reduction of pyrite by hydrogen ($250^\circ C$) takes place by a two step mechanism

where the reduction of FeS_2 in the presence of hydrogen is governed by solid-state diffusion of sulfur to a particle surface and removed by hydrogen. In this study there was evidently no attempt to observe the microstructures in the reaction products.

In figure 8 of the present study it may be noted that X_{FeS} generally increases with reaction time. Each reaction temperature shows a respective increase in X_{FeS} over the same initial reaction times (five minute points). If the

variation trend curve for each temperature is projected back to the X_{FeS} axis, it may be seen that at the first pyrrhotite composition to be formed at a time very close to $t=0$ each pyrrhotite formed at this time will yield a unique composition for the three temperatures of reaction. This suggests that, regardless of reaction time, pyrrhotite of a unique composition is formed at the reaction site in a particle. By the trend of the variation curves in figure 8, this in turn, demonstrates that sulfur is continuously depleted in the thickening pyrrhotite layer during reaction, and that the data points in figure 8 represent the average of a range of pyrrhotite compositions in the product layer. This concept is illustrated in figure 18.

On the x-ray diffractograms the probability of variable pyrrhotite composition within a particle is demonstrated by a slight broadening, or shouldering, of the $d(102)$ pyrrhotite peak below the peak apex. This distance could not be used to determine the variability of composition because it exceeded the limits of the measurement method employed.

Another approach may be taken concerning this phenomenon with respect to thermochemistry. It was demonstrated in chapter IV that the reaction products were quenched preserving a nonequilibrium state relative to an individual particle. However, if we assume that pyrrhotite of a unique composition exists at the reaction site over reaction duration (fig. 16), this indicates that pyrrhotite of this

Figure 18. Hypothetical compositional variation of pyrrhotite within a particle over time at temperature. X_{FeS} values are those from sample runs at 400°C .

composition is in thermal equilibrium with the temperature existing at the reaction site. Because the pyrite-pyrrhotite transformation has been demonstrated to be an endothermic reaction, the temperature existing at the reaction site may be less than the temperature imposed on the total system. With increasing reaction time this would require a temperature gradient across the radius of the pyrrhotite layer of a particle which decreases from the exterior particle boundary inward toward the reaction site. The net effect is continuous depletion of pyrrhotite in sulfur as it attempts to equilibrate with respect to the temperature existing at some point in the product layer. At this point the temperature would be intermediate between the temperature imposed on the total system and the reaction site at the pyrite-pyrrhotite phase boundary. This is justified in that less heat would be required for the transformation of a lower X_{FeS} pyrrhotite to a higher X_{FeS} pyrrhotite than from pyrite to pyrrhotite. However, the grain size of the reaction products and the very slight temperature difference across the radius preclude this phenomena as a constraint on the system.

The pyrite-pyrrhotite phase boundary is predominantly a solid-solid type boundary (figs. 13 and 15). These structures indicate the lack of evolution of a gaseous phase at the reaction site as porous texture is nonuniform and poorly developed, to nonexistent over the continuation

of the phase boundary. At the magnification used in this aspect of the study (500x) this cannot definitely be proven.

In light of a concentrically variable composition of pyrrhotite in the product layer of a particle coincident with changes in molar volume, it is feasible that the transformation could be accomplished by either bidirectional diffusion processes or the two-step mechanism. It has been shown that hydrogen accelerates the transformation rate (Guin and others, 1980), but this is not necessarily definitive. The exact mechanism by which the pyrite-pyrrhotite transformation takes place awaits investigation on a much smaller scale than the approach taken in this study.

Other Observations

Figure 14 shows the development of an anomalous structure. In three dimensions this feature would morphologically approach the particle structure illustrated by Guin and others (1980, fig. 3). This structure has not been previously described nor its significance postulated. It may be the result of contraction due to volume loss in the pyrrhotite in the pyrite-pyrrhotite transformation.

In figure 8 of this study the variation in X_{FeS} with reaction time curve at 375°C does not yield consistent results with the lower and high temperature curves. Since x-ray diffraction was used in the determination of X_{FeS} ,

the depth of x-ray penetration may have influenced these results. However, separate analyses yielded the same curve. Two tubing bomb runs were done at 375°C and one hour with little variation in results. This seeming inconsistency may be a graphical manifestation of the pyrrhotite in the reaction products reaching a composition that is near equilibrium with respect to the surrounding temperature.

VI. SUGGESTIONS FOR FURTHER STUDY

It has been suggested by Guin and others (1978) that the catalytic activity of metal sulfides in hydrogenation and desulfurization is related to defects in their crystal lattice. As discussed by Froese and Gunter (1976), lattice defects are commonly associated with pyrrhotite as point lattice vacancies that are responsible for compositional variations. Catalytic activity associated with these processes may be enhanced by the presence of pyrrhotite. The results and methods of this study may be applied in the capacity that the catalytic activity of pyrrhotite of a unique composition might be evaluated since these experiments were carried out under conditions similar to those applied in the SRC-I process.

The effects of particle size on the mechanism as well as rate of reaction need to be defined for this system in future work. Although Shen and Smith (1965) presented data concerning the effects of particle size in pyrite reduction experiments, they afforded no detailed explanation. Padrick and others (1980) briefly mention that particle size may affect reaction rate, but likewise failed to pursue a detailed investigation. Guin and others (1980) have

investigated the effect of pyrite particle size on the rate of benzothiophene hydrogenolysis.

An orthohombic polymorph of pyrite, marcasite, is another naturally occurring sulfide common to sedimentary rocks such as coal. Even though its occurrence is rare in these rock types it may warrant some degree of consideration in that the reduction of FeS_2 that occurs under coal liquefaction conditions may yield variable catalytic activities based on the crystallographic properties of pyrite, marcasite and pyrrhotite.

VII. SUMMARY OF CONCLUSIONS

The reduction of pyrite by hydrogen gas between $350 \pm 2^\circ\text{C}$ and $400 \pm 2^\circ\text{C}$ was shown to be endothermic by the approximate reaction

forming pyrrhotites of X_{FeS} component .9560 to .9688. In all cases the synthetic polymorph conformed to 1C hexagonal pyrrhotite. Based on the works of Padrick and others (1980), 250°C may be considered a lower limit for this reaction to proceed at a measurable rate.

Of the rate determining factors evaluated in this study, the restricted availability of pyrite due to decreasing surface available for reaction and the diffusional resistance in the pyrrhotite (product) layer are deemed the most influential constraints on the system. The partial pressure of H_2S has been shown to be minor and is unlikely to affect the reaction rate of the system over the temperature range of these experiments.

The physical expression of the phase boundaries shown in figures 13 and 15, based on observations of a large population of grains from each series of runs, may plausibly develop by means of bidirectional diffusion of H_2 and H_2S ,

or solid state diffusion of sulfur from the reaction site to the particle exterior. The results and interpretations offered in this study are inconclusive in this respect.

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APPENDICES

APPENDIX A
PROCEDURE FOR TREATING PYRITE IN
HYDROCHLORIC ACID

To remove calcite (CaCO_3) and surface oxides from the sized grains it was necessary to treat the pyrite in hot hydrochloric acid. Pyrite is not soluble in HCl.

Approximately 3g of sized (48-60 mesh) pyrite were placed in a 500 ml Erlenmeyer flask. Hydrochloric acid (2:3 HCl and H_2O) was then added to the flask. After placing a watch glass on top of the flask, the mixture was placed on a hot plate located under a fume hood. The mixture was allowed to boil for 15 minutes.

After cooling, the contents of the flask were decanted through a vacuum filtration apparatus to retrieve the pyrites. Number 50 (Mallinkrodt) filter paper was used. After the filtrate had passed through the pyrite, it was washed thoroughly with distilled water. The pyrite residue and the filter paper were then placed in a 500 ml beaker, covered with a culture dish and placed in a vacuum oven to dry overnight. Temperature of the oven was 100°C .

APPENDIX B
INSTRUMENT SETTINGS FOR X-RAY DIFFRACTOMETER

<u>Type Unit and Function</u>	<u>Setting</u>
Philips Electronic Instruments XRG 3100	
X-ray Generator	
kilovolts (KV)	35
milliamps (MA)	28
Philips Electronic Instruments Monochromator/ Diffractionmeter	
Step scanning	off
Line	off
Deg. 2 θ /min	1°
Driven shaft gear	40
Motor shaft gear	80
Philips Electronic Instruments Modular Data Measuring System	
3010 Dual high voltage supply	
Scintillation Detector -(KV)	.8
Proportional Detector	off
3020 Linear amplifier	
Gain	256
Input select sum.	scint.
3031 Pulse height selector	
Baseline	2
Window	5
Baseline control	internal
Mode	differential
Clock signal	off
3050 Linear ratemeter	
Range	5K
Range multiplication	x1
Time constant (seconds)	2
% Suppression	0
Audio	off
3060 Scaler/Timer	
multiplier	1
Time: count	10:10 ⁴

APPENDIX C
EXTERNAL STANDARD METHOD OF CHEMICAL
ANALYSIS BY X-RAY DIFFRACTOMETRY

Quantitative analysis by x-ray diffraction is based on the fact that the integrated intensity of reflection peaks of a particular phase in a mixture of phases depends on the concentration of that phase in the mixture (Cullity, 1978). In this study, pyrite and pyrrhotite are considered as two distinct phases composing a mixture. If the presence of one phase is greater than the other, the corresponding integrated peak intensities of that mineral will be greater than those of the less abundant phase with intensities proportional to the concentration in the sample. The following proof has been modified after Cullity (1978) to apply to this study.

The relation between diffraction intensity and the concentration of phase α in a multiphase mixture is

$$I_{\alpha} = \frac{Kc_{\alpha}}{\mu_m} \quad (1)$$

where K is a constant derived from the diffraction intensity equation of Cullity (1978), c_{α} is the volume fraction of α in the sample mixture and μ_m is the linear absorption coefficient.* I_{α} is the integrated intensity of the diffraction peak of phase α obtained from the diffractogram.

*The linear absorption coefficient is an index of that fraction of Cu-K α radiation absorbed by an element, the value of which is unique for each element. Coefficients for inorganic compounds are simply the average of the coefficients for the bonded species.

The concentration of α may be found from the ratio $I_\alpha/I_{\alpha p}$ where sub-p denotes the pure phase.

The external standard method relates the mass absorption coefficients, densities and weight fractions of the phases in a mixture to obtain the concentrations of the phases under study.[†] Once the concentration is obtained for one phase (in a two phase mixture), the concentration of the remaining phase may be found with a further step in basic calculation.

To express linear absorption in terms of concentration we have

$$\frac{\mu_m}{\rho_m} = \omega_\alpha \left(\frac{\mu_\alpha}{\rho_\alpha} \right) + \omega_\beta \left(\frac{\mu_\beta}{\rho_\beta} \right) \quad (2)$$

where ω is the weight fraction and ρ is the density of phases α and β . The sub-m denotes the statistical averages of the values of mass absorption coefficients and densities, respectively for the two phase mixture.

If a unit volume of a mixture is taken into consideration, its weight is ρ_m and the weight of contained α is $\omega_\alpha \rho_m / \rho_\alpha$. This quantity is equal to c_α , or the concentration of α in terms of volume fraction. A similar expression may be used for c_β .

[†]The mass absorption coefficient is simply the quotient of the linear absorption coefficient of an element or compound and its corresponding density (μ/ρ).

Since a relationship between concentration, density and weight fraction has been defined, equation (2) may be written

$$\begin{aligned}\mu_m &= c_\alpha \mu_\alpha + c_\beta \mu_\beta = c_\alpha \mu_\alpha + (1-c_\alpha) \mu_\beta \\ &= c_\alpha (\mu_\alpha - \mu_\beta) + \mu_\beta.\end{aligned}\quad (3)$$

Therefore,

$$I_\alpha = \frac{Kc_\alpha}{c_\alpha (\mu_\alpha - \mu_\beta) + \mu_\beta} \quad (4)$$

Equation (4) relates the integrated intensity of the diffraction line from one phase to the volume fraction of that phase and the mass absorption coefficients of both phases. To change the volume fraction to a weight basis, we consider unit mass: the volume of α is $\omega_\alpha/\rho_\alpha$ and the volume of β is ω_β/ρ_β . Hence,

$$c_\alpha = \frac{\omega_\alpha/\rho_\alpha}{\omega_\alpha/\rho_\alpha + \omega_\beta/\rho_\beta} = \frac{\omega_\alpha/\rho_\alpha}{\omega_\alpha(1/\rho_\alpha - 1/\rho_\beta) + 1/\rho_\beta} \quad (5)$$

Substituting equation (5) in equation (4) we get

$$I_\alpha = \frac{K\omega_\alpha}{\rho_\alpha [\omega_\alpha (\mu_\alpha/\rho_\alpha - \mu_\beta/\rho_\beta)] + \mu_\beta/\rho_\beta} \quad (6)$$

For the pure phase α , equation (4) becomes

$$I_{\alpha p} = \frac{K}{\mu_\alpha} \quad (7)$$

To eliminate the unknown constant K and to provide the external standard (pure phase) ratio, equation (4) is divided by equation (7) which gives

$$\frac{I_{\alpha}}{I_{\alpha p}} = \frac{\omega_{\alpha}(\mu_{\alpha}/\rho_{\alpha})}{\omega_{\alpha}(\mu_{\alpha}/\rho_{\alpha} - \mu_{\beta}/\rho_{\beta}) + \mu_{\beta}/\rho_{\beta}} \quad (8)$$

Equation (8) provides a means of quantitative analysis of a two phase mixture, such as pyrite and pyrrhotite, provided that the mass absorption coefficients are known for each phase.

APPENDIX D

CALCULATION OF THEORETICAL CURVE FOR I_{po}/I_{pop} VERSUS
WEIGHT FRACTION PYRRHOTITE

Symbols:

phase α ; pyrrhotite

phase β ; pyrite

I_{α} ; integrated intensity of α in a two phase mixture

$I_{\alpha p}$; integrated intensity of pure phase α

ω_{α} ; weight fraction of phase α

μ/ρ ; mass absorption coefficient (cm^2g^{-1})

μ ; linear absorption coefficient ($4 \times 10^{-7} \text{m Kg C}^{-2}$)

ρ ; density of a phase (g cm^{-3})

p_o ; pyrrhotite (in mixture)

$p_o p$; pyrrhotite (pure phase)

If I_{p_o} is taken as I_{α} and $I_{p_o p}$ is taken as $I_{\alpha p}$ we have

$$\frac{I_{\alpha}}{I_{\alpha p}} = \frac{\omega_{\alpha}(\mu_{\alpha}/\rho_{\alpha})}{\omega_{\alpha}(\mu_{\alpha}/\rho_{\alpha} - \mu_{\beta}/\rho_{\beta}) + \mu_{\beta}/\rho_{\beta}}$$

To solve the equation for $I_{p_o}/I_{p_o p}$ all that is needed are the quantities $\mu_{\alpha}/\rho_{\beta}$ and μ_{β}/ρ_{β} . The mass absorption coefficients have been obtained for Fe and S from "Volume 3 International Tables for X-Ray Crystallography." The mass absorption coefficient for a compound is

$$\frac{\mu}{\rho} = \omega_1\left(\frac{\mu}{\rho}\right)_1 + \omega_2\left(\frac{\mu}{\rho}\right)_2 \quad (9)$$

where the subscripts 1 and 2 denote the elements that make up the compound. The weight fraction of an element in the compound is indicated by ω .

Table 1

Calculation of $\frac{\mu}{\rho}$ FeS₂ and $\frac{\mu}{\rho}$ Fe_{0.95}S

For FeS₂: atomic weight Fe=55.847
atomic weight S₂=64.128

$\frac{\mu}{\rho}$ for Fe with Cu-K_α radiation,
λ = 1.542Å: 304.40 cm² g⁻¹

$\frac{\mu}{\rho}$ FeS₂ = .4654(304.40)
+ .5345(92.530)
= 191.124 cm² g⁻¹

$\frac{\mu}{\rho}$ for S with Cu-K_α radiation,
λ = 1.542Å: 92.53 cm² g⁻¹

For Fe_{0.95}S (synthetic 1C pyrrhotite, JCPDS):

atomic weight Fe_{0.95}=53.054
atomic weight S =32.064

$\frac{\mu}{\rho}$ Fe_{0.95}S = .6232(304.40)
+ .3766(92.530)
= 224.546 cm² g⁻¹

Table 2

Calculated Theoretical Values for I_{po}/I_{pop}

Given:

$$\text{po } 10 \text{ wt\%, } \frac{I_{po}}{I_{pop}} = \frac{0.1(224.546)}{0.1[(224.546) - (191.124)] + 191.124} = 0.1154$$

$$\text{po } 30 \text{ wt\%, } \frac{I_{po}}{I_{pop}} = \frac{0.3(224.546)}{0.3[(224.546) - (191.124)] + 191.124} = 0.3348$$

$$\text{po } 50 \text{ wt\%, } \frac{I_{po}}{I_{pop}} = \frac{0.5(224.546)}{0.5[(224.546) - (191.124)] + 191.124} = 0.5402$$

$$\text{po } 70 \text{ wt\%, } \frac{I_{po}}{I_{pop}} = \frac{0.7(224.546)}{0.7[(224.546) - (191.124)] + 191.124} = 0.7327$$

$$\text{po } 90 \text{ wt\%, } \frac{I_{po}}{I_{pop}} = \frac{0.9(224.546)}{0.9[(224.546) - (191.124)] + 191.124} = 0.9132$$

$$\text{po } 0.5 \text{ wt\%, } \frac{I_{po}}{I_{pop}} = \frac{0.05(224.546)}{0.05[(224.546) - (191.129)] + 191.124} = 0.0582$$

APPENDIX E
STOICHIOMETRIC DETERMINATION OF H_2 CONSUMPTION

The initial hydrogen concentration in each tubing bomb prior to reaction is given by the Ideal Gas Law of the form

$$n = \frac{PV}{RT} \quad (1)$$

From Table 1 the average tubing bomb volume is 15.3 cm^3 ($15.3 \times 10^{-6} \text{ m}^3$) and pressure is 1250 psig H_2 ($86,175 \times 10^2 \text{ Pa}$). Each temperature must be given as degrees Kelvin and the gas constant is given as $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$. Thus, equation (1) takes the form

$$\begin{aligned} n_{\text{H}_{2\text{o}}} &= 86,175(10^2) \text{ Pa} [15.3(10^6) \text{ m}^3] \left(\frac{\text{Kmol}}{8.314 \text{ J}} \right) \left(\frac{1}{298.15 \text{ K}} \right) \\ &= 5.32(10^{-2}) \end{aligned}$$

The quantity $n_{\text{H}_{2\text{o}}} = 5.32(10^{-2})$ is taken to remain constant throughout calculations.

The initial amount of pyrite, normalized to 1.0 g is given by

$$\begin{aligned} n_{\text{FeS}_{2\text{o}}} &= \text{vol lg FeS}_2 \text{ cm}^3 \times \text{density FeS}_2 \text{ g cm}^{-3} \left(\frac{1 \text{ mol FeS}_2}{\text{gfw FeS}_2} \right) \\ &= .202 \text{ cm}^3 \left(\frac{4.95 \text{ g}}{\text{cm}} \right) \left(\frac{1 \text{ mol FeS}_2}{119.8} \right) \\ &= 0.35(10^{-3}) \end{aligned} \quad (3)$$

The quantity $n_{\text{FeS}_{2\text{o}}}$ is likewise taken to remain constant throughout calculations.

With these constants defined we may proceed in calculating the mole percent H_2 consumed in each run which proceeds by the reaction

where the numerical value for $1-x$ (X_{FeS}) is derived from figure 8. Thus, for a given reaction the mole percent H_2 consumed is given by

$$\% \text{H}_2 \text{ cons} = \frac{n\text{FeS}_{2_o} (R) \left[\frac{2(X_{\text{FeS}})^{-1}}{X_{\text{FeS}}} \right]}{n\text{H}_{2_o}} \times 100 \quad (5)$$

where $n\text{FeS}_{2_o}$ and $n\text{H}_{2_o}$ are the constants defined in equations (2) and (3). The variables R and X_{FeS} are then substituted into the equation. R is the fractional conversion of pyrite to pyrrhotite and is the decimal equivalent of the percent conversion values shown in figure 7. The final form of the equation with respect to parameters involved in this study is

$$\% \text{H}_2 \text{ cons} = \frac{8.35(10^3)(R) \left[\frac{2(X_{\text{FeS}})^{-1}}{X_{\text{FeS}}} \right]}{5.32(10^{-2})} \times 100 \quad (6)$$

$$X_{S_2} \text{ in } FeS_{2f} = \text{fraction } FeS_{2f} \times (.202 \text{ cm}^3) \times 4.95 \text{ g cm}^{-3} \\ \times \left(\frac{1 \text{ mole } FeS_2}{119.8} \right) \times 0.5 \quad (7)$$

Equation (6) may now be solved for each reaction run by substituting those values obtained from Equations (5) and (7), and X_{S_2} in $nFeS_{2o}$ derived from Equation (3).

By assumption (1), chapter IV, in order to find the amount of hydrogen remaining after a reaction, we have from Equations (2) and (6)

$$nH_{2f} = nH_{2o} - nS_{lib} \quad (8)$$

the quantity of which, when subtracted from the initial hydrogen concentration will give the moles of hydrogen consumed by reaction with S_{lib} to produce H_2S

$$nH_2 \text{ cons} = nH_{2o} - nH_{2f} \quad (9)$$

Expressed as mole percentage hydrogen consumed by a reaction, Equation (9) becomes

$$\% H_2 \text{ cons} = \left(\frac{nH_{2o} - nH_{2f}}{nH_{2o}} \right) \times 100 \quad (10)$$