MECHANISMS OF PYRITE OXIDATION TO NON-SLAGGING SPECIES

Quarterly Report for the Period
January 1, 1995 - March 31, 1995

Grant DE-FG22-94PC94205

Prepared for
THE UNITED STATES DEPARTMENT OF ENERGY

Margie Kotzalas
Project Manager
Morgantown Energy Technology Center
Morgantown, WV 26507-0880

Submitted by
Mr. A. E. Jacob Akan-Etuk and Professor Reginald E. Mitchell

August 1995

HIGH TEMPERATURE GASDYNAMICS LABORATORY
Mechanical Engineering Department
Stanford University

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August 1995

High Temperature Gasdynamics Laboratory
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RESEARCH OBJECTIVES

This document is the third quarterly status report on a project conducted at the High Temperature Gasdynamics Laboratory at Stanford University, Stanford, California and concerned with enhancing the transformation of iron pyrite to non-slagging species during staged, low-NO\textsubscript{X} pulverized coal (P. C.) combustion. The research project is intended to advance PETC's efforts to improve our technical understanding of the high-temperature chemical and physical processes involved in the utilization of coal. The work focuses on the mechanistic description and rate quantification of the effects of fuel properties and combustion environment on the oxidation of iron pyrite to form the non-slagging species magnetite. The knowledge gained from this work is intended to be incorporated into numerical codes that can be used to formulate anti-slagging strategies involving minimal disturbance of coal combustor performance. This project is to be performed over the three-year period from September 1994 to August 1997.

The project aims to identify the mechanisms of pyrite combustion and to quantify their effects, in order to formulate a general rate expression for the combustion of pyrite that accounts for coal properties as well as furnace conditions. Pyrite is introduced into a P. C. combustor as pure (extraneous) pyrite particles, pyrite cores within carbon shells, and inclusions in carbon matrices. In each case, once oxygen is transported to a pyrite particle's surface, the combustion of the pyrite involves the diffusion of oxygen from the particle's surface to its unreacted core and
reaction of the diffused oxygen with the core. Consequently, a key feature of the program's approach to quantifying pyrite combustion is the sequential formulation of a reaction rate resistance network by isolating and quantifying the rate resistance induced by pyrite intraparticle mass transfer and pyrite intraparticle kinetics mechanisms.

Crucial to the project's methodology is the utilization of feed materials with carefully controlled properties to eliminate the uncertainty inherent in interpreting data obtained with natural coals (a consequence of the heterogeneity of natural coals). Homogeneous materials facilitate the modeling of specific combustion mechanisms without complications of non-uniform chemical composition and morphology.

In general, the project has the following objectives: 1) the characterization of the various mechanisms of intraparticle mass transfer and chemical reaction that control overall pyrite combustion rates and 2) the synthesis of the reaction rate resistances of the various mechanisms into a general rate expression for pyrite combustion. The knowledge gained from this project will be incorporated into numerical codes and utilized to formulate slagging abatement strategies involving the minor adjustment of firing conditions. Ultimately, the benefit of this research program is intended to be an increase in the range of coals compatible with staged, low-NO\textsubscript{X} combustor retrofits.

Following are specific objectives and deliverables associated with the six tasks of the research program:

**Task 1: Production and Characterization of Pyrite Feeds**

*Objective:* to produce and characterize pyrite feed materials of controlled particle size, carbon content, and carbon macroporosity.

*Deliverables:*
- Size-classified samples of pure pyrite particles.
- Size-classified samples of pyrite-laden synthetic bituminous coal particles of controlled macroporosity and mineral content.
- Data on the physical properties of the feed materials: density, porosity, pore size distribution, and total surface area.
- Data on the chemical composition of the feed materials: component species, elemental composition, and proximate matter partitioning.

**Task 2: Pyrite Intraparticle Kinetics Resistance**

*Objective:* to perform combustion tests to quantify the reaction rate resistance introduced by pyrite intraparticle kinetics with respect to particle temperature and oxygen level.

*Deliverables:*
- A quench probe that can be used to extract particles from a laminar flow reactor at various residence times.
- An X-ray diffraction (XRD) procedure for the quantitative analysis of the solid residue from the combustion of pure pyrite samples.
- Measurements of the gas temperature and oxygen level in the flow reactor for the gaseous conditions to be used in our experiments.
- The results of combustion tests performed using pure pyrite particles to determine the minimum oxygen levels, maximum particle sizes, and appropriate extents of reaction compatible with negligible transport resistance for each stage of pyrite combustion: morphology and composition of reacted pyrite.
- The results of combustion tests performed using pure pyrite particles of small particle size to characterize intraparticle chemical kinetics resistance at various particle temperatures and oxygen levels: particle size distribution, morphology, and composition of reacted pyrite.
- An expression for the reaction rate resistance of the chemical kinetics of pyrite oxidation, including a kinetics rate coefficient expressed in Arrhenius form.

**Task 3: Pyrite Intraparticle Mass Transfer Resistance**

*Objective:* to perform combustion tests to quantify the reaction rate resistance introduced by pyrite intraparticle mass transfer with respect to particle size and temperature.
Deliverables:
- The results of combustion tests using pure pyrite particles of small particle size to characterize intraparticle mass transfer resistance during the decomposition and solid oxidation stages of pyrite oxidation for various particle size classes and particle temperatures: particle size distribution, porosity, pore size distribution, total surface area, morphology, and composition of reacted pyrite.
- An expression for the reaction rate resistance introduced by intraparticle mass transfer during pyrite oxidation.

Task 4: Carbon Matrix Kinetics Effects

Objective: to perform combustion tests to characterize the effects of carbon matrix oxidation kinetics on the overall oxidation rate of pyrite inclusions.

Deliverables:
- A procedure for performing chemical analysis of the solid residue of the combustion of pyrite-laden synthetic coal.
- The results of combustion tests using highly macroporous synthetic coal of small particle size, loaded with small pyrite inclusions to characterize the impact of the carbon chemical kinetics resistance for various particle temperatures: weight loss, morphology, and composition of reacted synthetic coals.
- A description of the effects of carbon matrix chemical kinetics resistance on the oxidation rate of pyrite.

Task 5: Carbon Matrix Mass Transfer Effects

Objective: to perform combustion tests to characterize the effects of carbon matrix mass transfer on the overall oxidation rate of pyrite inclusions.

Deliverables:
- The results of combustion tests using low-macroporosity synthetic coal loaded with small pyrite inclusions to characterize the impact of the carbon matrix mass transfer resistance: weight loss, morphology, and composition of reacted synthetic coals.
- A description of the effects of carbon matrix mass transfer resistance on the oxidation rate of pyrite.
Task 6: Rate Expression Formulation and Validation

**Objective:** to formulate and validate an overall rate expression for pyrite combustion.

**Deliverables:**

- A mathematical expression for the pyrite chemical transformation rate formulated on the basis of reaction resistances of individual mechanisms.
- The results of combustion tests using a natural coal to validate the pyrite combustion rate expression with respect to coal particle size class, coal porosity, pyrite size class, pyrite content, gas temperature, and oxygen level: compositions of reacted coal samples.
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TECHNICAL PROGRESS DURING CURRENT QUARTER

SUMMARY

The information presented constitutes the report for the period January 1 to March 31, 1995. During the quarter, efforts to experimentally characterize the chemical kinetics parameters of pyrite combustion continued. The activities associated with the quarter's efforts involved Tasks 1 and 2 of the research project.

Samples of 20 μm pyrite particles were prepared using sedimentation-wet sieving. The pyrite was subjected to combustion in a flow reactor at 1500 K gas temperature. The pyrite was monitored for changes in morphology and composition as it transformed to magnetite.

The first series of combustion tests were performed at 1% oxygen in order to achieve a sufficiently low reaction rate to permit the resolution of pyrite oxidation pathways. The oxidation pathway of pyrite at pulverized coal firing temperatures was established to be consistent with the following sequence: $FeS_2 \rightarrow FeS \rightarrow FeO \rightarrow Fe_3O_4$. The advent of FeS in the reaction product corresponded to the appearance of spherical (softened) particles.

The second series of tests were intended to reveal the rate-limiting step of the reaction pathway during combustion in an oxidizing environment (12% oxygen). By 25 ms, all of the FeS2 had been converted to FeO-Fe3O4 (with trace FeS). The FeS and FeO subsequently oxidized to yield a product composition of Fe3O4 (with trace FeO) at 36 ms. Micrographs revealed that for almost all of the particles, the shape had changed from angular to spherical by 25 ms. These experimental observations, when coupled with those in the previous quarterly report, suggested that the rate-limiting step of pyrite combustion changes with the extent of conversion.
FINDINGS

A new model of pyrite oxidation was introduced in a previous quarterly report [1]. The model constitutes an attempt to reconcile incomplete and sometimes contradictory studies in the literature with new observations by the author. In the model, pyrite oxidation is depicted as occurring in the following sequential stages: \( FeS_2 \rightarrow FeS \rightarrow FeS_{\text{melt}} \rightarrow Fe_3O_4 \).

The pyrite oxidation pathway proposed in the new model differs from that of the prevailing model [2]. Srinivasachar and Boni's model was based on the following transformations: \( FeS_2 \rightarrow Fe_{0.877}S \rightarrow Fe - S - O_{\text{melt}} \rightarrow Fe_3O_4 \).

The differences between the proposed reaction pathways lead to an expanded set of potential rate-controlling mechanisms for pyrite oxidation. This in turn increases the uncertainty in predicted particle compositions and fusion temperatures. Consequently, there exists an incentive to definitively establish the pertinent sequence of chemical kinetics processes during pyrite oxidation.

Activity during the quarter centered about the characterization of pyrite oxidation pathways at pulverized coal (P. C.) firing conditions. The first objective of this effort was to identify the reaction pathways, and the second objective was to determine the rate-controlling steps in the pathways. The approach used in performing Tasks 1 and 2 was to investigate pyrite oxidation at operating conditions that permit the resolution of intraparticle kinetics processes. The work performed spanned two tasks, as pyrite samples were prepared (Task 1) and oxidized (Task 2).
1.0 TASK 1: PRODUCTION AND CHARACTERIZATION OF PYRITE FEEDS

The focus of activity in this task was the preparation of feed materials that would permit the resolution of pyrite intraparticle kinetics processes during P. C. combustion. In the last quarterly report, extraneous pyrite of 20 μm particle diameter was deemed a reasonable initial choice of feed materials [3].

In last quarter's report, a sedimentation-wet sieving materials preparation scheme was demonstrated to yield the required batches of 20 μm pyrite particles. X-ray diffraction analysis indicated that the preparation procedure extracts all impurities from the pyrite. In addition, Coulter Multisizer measurements established that the resulting pyrite sample possesses a narrow log-normal size distribution of 19.9 μm median size and 1.2 geometric standard deviation.

1.1 Materials

During the current quarter, grams of pyrite were prepared using the sedimentation-wet sieving procedure. Shown in Figure 2.1 is a scanning electron micrograph of representative particles of the pyrite, at the onset of oxidation. The micrograph affirms previous conclusions that the preparation procedure yields monodisperse particles of 20 μm diameter.
Figure 1.1 Secondary scanning electron micrograph of pyrite at the onset of oxidation.
2.0 TASK 2: PYRITE INTRAPARTICLE KINETICS RESISTANCE

The aim of the work performed under Task 2 was to use the materials prepared in Task 1 to experimentally determine the pyrite intraparticle kinetics mechanisms relevant to pulverized coal (P. C.) combustion. First, the oxidation pathways of pyrite were to be established using time-resolved characterizations of pyrite composition. Second, the rate-governing steps of the oxidation pathways were to be determined at P. C. firing conditions.

In the last quarterly report, an entrained flow reactor was presented as the core facility for obtaining desired pyrite combustion parameters [3]. In the flow reactor, pulverized fuel particles are fed by a syringe and entrained by a nitrogen stream into the base of a flat flame burner. When operated at gas condition #4 (CH$_4$ - 1.34 l/min, H$_2$ - 7.30 l/min, N$_2$ = 38.2 l/min, O$_2$ = 13.1 l/min), the reactor attains an average gas temperature of 1500 K and oxygen level of 12%.

Following combustion experiments, solid residues captured by a quench probe are analyzed by X-ray diffraction analysis (XRD). In addition, scanning electron microscopy (SEM) is performed for observation of gradients in particle chemical composition and identification of pyrite phase changes such as melting or softening.

2.1 Studies

Two studies were performed in order to attain the two objectives of this task and thereby characterize the pyrite kinetics mechanisms relevant to P. C. combustion. In both studies, the relative impact of kinetics was magnified by reducing the reactor gas temperature to 1500 K, the lower end of the industrially-relevant temperature range.

The first study established the oxidation pathways of pyrite in a series of four tests intended to monitor the complete progress of pyrite oxidation to magnetite. For this study, a sufficiently low reaction rate was required to resolve the reaction intermediates. On the other hand, the gas temperature had to lie in the range typical of a P. C. furnace, to access all pertinent high-activation energy transitions. Consequently, gas condition #5 (CH$_4$ - 1.34 l/min, H$_2$ - 7.30 l/min, N$_2$ =
44.3 l/min, O₂ = 6.9 l/min) was defined this quarter, to provide the same gas temperature profile as gas condition #4, but reduced oxygen level, 1%. [The gas temperature profile is maintained the same by keeping the same adiabatic flame temperature, methane flow rate, hydrogen flow rate, and sum of nitrogen and oxygen flow rates.]

In the second study, the rate-governing steps of the oxidation pathways were determined for a selected P. C. firing condition. This study was performed at 12% oxygen level, to further magnify the impact of kinetics in the likely event of oxidation mechanisms of reaction orders less than one. Two tests were performed this quarter, and the results were combined with those obtained previously [3].

In both studies, lower bounds on the required residence times were estimated by using the diffusion-limited reaction rate for a 20 μm pyrite particle oxidizing at 1500 K. For the reaction

\[ FeS_2 + \nu O_2 \rightarrow \text{products}, \]

the diffusion-limited reaction time, \( \tau \), is

\[ \tau = \frac{\nu n_{FeS_2}}{\pi d^2 J_{O_2}}, \]

with \( J_{O_2} = \frac{2 \delta C_{O_2}}{d} \),

where \( n_{FeS_2} \) is moles of FeS₂, \( d \) is particle diameter, \( J_{O_2} \) is molar flux of oxygen, \( \delta \) is diffusion coefficient of oxygen, and \( C_{O_2} \) is molar concentration of oxygen. For a 20 μm pyrite particle oxidizing at 1500 K, the reaction time is 55.7 ms and 4.6 ms for 1% and 12% oxygen levels, respectively, when \( \nu \) equals 1.

The pyrite was expected to burn significantly more slowly than at its diffusion-limited rate. On the other hand, the particle temperature was expected to exceed the gas temperature due to exothermic reactions. An accurate estimation of the required residence time could only be made after the oxidation kinetics of pyrite had been sufficiently characterized.
2.1.1 Oxidation Pathway Identification

8.89 cm (42 ms) Test

The aim of the first test was to determine the initiation reaction for the pyrite oxidation process. A pyrite particle ignites at a height of approximately 1.25 cm (7 ms) in the test section. The pyrite burns heterogeneously as a glowing orange particle until it is quenched by the sampling probe. In this test, the probe was positioned at a height corresponding to 35 ms of particle oxidation. Even if the oxidation proceeds at its diffusion-limited rate, at least 28 ms would be required for the complete decomposition of FeS$_2$ by the reaction $FeS_2 + \frac{1}{2}O_2 \rightarrow FeS + SO$.

X-ray diffraction analysis (XRD) was performed on the recovered ash to determine its bulk composition. In this and every other XRD analysis discussed in this report, two patterns were obtained. The first was a quick scan spanning a broad range of 2θ diffraction angle, from 20 degrees to 70 degrees, for a positive identification of constituent species. The second was a slower scan spanning a narrow range of 2θ from 40 degrees to 49 degrees, for a better estimate of the relative amounts of the constituent species.

Shown in Figure 2.1 is the diffraction pattern of the recovered ash, and a systematic shift of peak positions occurs due to instrument alignment. The peaks at 46.7 degrees, 43.3 degrees, and 42.6 degrees are due to pyrite (FeS$_2$), pyrrhotite 3T (Fe$_{0.877}$S), and a second form of pyrrhotite, respectively. The second pyrrhotite's peak is only slightly shifted from that of perfectly stoichiometric troilite, FeS (after instrument alignment is accounted for). The peak also appears approximately 50% broader than the pyrrhotite 3T peak, indicating a softening transition. From Akan-Etuk's calibration curve for pyrite:pyrrhotite [4], the ash composition was estimated to be 84 wt% pyrite, 10 wt% pyrrhotite 3T, and 6 wt% troilite. Thus the onset of oxidation was attributed to be either of the following transitions: $FeS_2 \rightarrow FeS$ or $FeS_2 \rightarrow Fe_{0.877}S$.

The particle structure of the oxidized pyrite was characterized by scanning electron microscopy (SEM). Figure 2.2 is a secondary SEM at 1000 X, and it reveals that almost all of the particles are angular and on the order of 20 μm. A few particles are spherical, however, and their diameters are approximately 15 microns. The micrograph in Figure 2.1 confirms that prior to oxide formation, pyrite experiences a softening transformation.
Figure 2.1 X-ray diffraction pattern of pyrite after reaction at 1500K and 1% oxygen for 42 ms. Present are pyrite (P), pyrrhotite 3T (Ph), and troilite (T) peaks.

Figure 2.2 Secondary scanning electron micrograph at 1000 X magnification of pyrite after oxidation at 1500 K and 1% oxygen for 42 ms.
11.43 cm (52 ms) Test

This test was intended to investigate the later stages of pyrite decomposition. The residence time, 52 ms, was specified to correspond to 45 ms of oxidation. Complete decomposition requires at least 56 ms of oxidation, if it proceeds by the reaction $\text{FeS}_2 + O_2 \rightarrow \text{FeS} + \text{SO}_2$. [It was shown in the 42 ms test that decomposition occurs more slowly than at the diffusion-limited rate of $\text{FeS}_2 + \frac{1}{2}O_2 \rightarrow \text{FeS} + \text{SO}_2$.]

Figure 2.3 is the XRD pattern of the recovered ash (sulfur aerosols were also recovered). Present on the diffraction pattern are peaks attributable to pyrite, troilite, as well as an iron oxide (at 41.3 degrees). The iron oxide peak is only slightly shifted from that of perfectly-stoichiometric wustite, FeO. Almost completely absent is the pyrrhotite 3T peak observed at 42 ms reaction time; the troilite peak is approximately 1.5 times its previous width (i.e., more softened)- equal to the wustite peak's width. The relative concentrations assigned to the identified species using Akan-Etuk's calibration curves were approximately 60 wt% pyrite, 30 wt% troilite, and 30 wt% wustite. The appearance of wustite suggested that the second step in the oxidation pathway is $\text{FeS} \rightarrow \text{FeO}$.

![Figure 2.3 X-ray diffraction pattern of pyrite after reaction at 1500K and 1% oxygen for 52 ms. Present are pyrite (P), troilite (T), and wustite (W) peaks.](image-url)
The structure of the oxidized particles was characterized using micrographs, and example of which is shown in Figure 2.4. The particles in the micrograph exhibit a variety of shapes. Present are angular, spherical, and highly irregular particles of approximately 20 μm size. There are also a few spherical particles of 5 μm diameter.

![Secondary scanning electron micrograph at 1000 X magnification of pyrite after oxidation at 1500 K and 1% oxygen for 52 ms.](image)

**Figure 2.4** Secondary scanning electron micrograph at 1000 X magnification of pyrite after oxidation at 1500 K and 1% oxygen for 52 ms.

**17.78 cm (77 ms) Test**

The aim of this test was to resolve whether the later stages of troilite oxidation lead to the formation of magnetite, an amorphous melt, or some other intermediate species. Pyrite particles were subjected to reaction for 77 ms. Sulfur aerosols were observed, but only ash was recovered and subjected to XRD. The diffraction pattern is displayed in Figure 2.5, and it indicates that the ash constituents were pyrite, troilite, and wustite. The wustite peak width remains unchanged but
the troilite width is decreased from its 52 ms value. The observation of only pyrite, wustite, and troilite in this experiment reinforced the previous inference that the second step of pyrite oxidation is \( \text{FeS} \rightarrow \text{FeO} \). Furthermore, the absence of pyrrhotite 3T in this test and the 52 ms test was consistent with the view that \( \text{FeS}_2 \rightarrow \text{FeS} \) is a more significant decomposition mechanism than \( \text{FeS}_2 \rightarrow \text{Fe}_{0.877}\text{S} \).

The concentrations of the ash constituents were assigned. The ash composition was approximately 24 wt% pyrite, 36 wt% troilite, and 40 wt% wustite.

![Figure 2.5 X-ray diffraction pattern of pyrite after reaction at 1500K and 1% oxygen for 77 ms. Present are pyrite (P), troilite (T), and wustite (W) peaks.](image)

A micrograph of the oxidation products is shown in Figure 2.6. Although over 80% of the particles are spherical, there are still noticeable interparticle variations. Some of the objects that contribute to the heterogeneity in the micrograph are actually pieces of the cracked shells of spherical particles, however. In most particles, the crystallites are quite evident.
36.83 cm (146 ms) Test

The focus of this test was magnetite formation. In the experiment, the reaction time was specified at 146 ms. Ash and a significant amount of sulfur aerosols were captured.

The XRD pattern of the ash is presented in Figure 2.7. From the diffraction pattern, it is evident that all of the troilite had been oxidized and that only wustite and magnetite were present in the particles. The wustite peak is narrower than it was previously, but the magnetite peak is much broader than any peak heretofore observed. Furthermore, the approximate compositions of the ash was established to be 23 wt% wustite and 77 wt% magnetite. This test established that magnetite is formed through the transition $FeO \rightarrow Fe_3O_4$.

Micrographs of the reacted pyrite indicated that after 146 ms of reaction, the particle structure had become more homogeneous. The SEM in Figure 2.8 establishes that almost all of the pyrite particles had become softened. Some particles exhibit 5 µm craters on their surfaces which sometimes contain spherical nodules. The crystallites in the particles are very noticeable.
Figure 2.7  X-ray diffraction pattern of pyrite after reaction at 1500K and 1% oxygen for 146 ms. Present are wustite (W) and magnetite (M) peaks.

Figure 2.8  Secondary scanning electron micrograph at 1000 X magnification of pyrite after oxidation at 1500 K and 1% oxygen for 146 ms.
2.1.2 Rate-Controlling Kinetics

5.08 cm (25 ms) Test

In Section 2.1.1, support is given for the following pyrite oxidation pathway: $FeS_2 \rightarrow FeS \rightarrow FeO \rightarrow Fe_3O_4$. The current test was performed to determine if any intermediates could ever be observed when pyrite oxidizes in a 12% oxygen environment. During oxidation, a pyrite particle ignites and becomes engulfed by a luminous yellow flame at a height of approximately 1.25 cm (3 ms) in the test section. At 4.4 cm (22 ms), the flame recedes, and the pyrite burns heterogeneously as a glowing orange particle until it is quenched by the sampling probe. In the previous quarterly report, it was seen that in a 12% oxygen environment, the ash composition was approximately 8% magnetite-pyrite by 22 ms and 100% magnetite by 109 ms.

In this test, the probe was positioned at a height corresponding to 25 ms of residence time. Even if oxidation proceeds at the fastest conceivable rate, i.e. the diffusion-limited rate of the reaction $FeS_2 + \frac{2}{3}O_2 \rightarrow \frac{1}{3}Fe_3O_4 + S_2$, at least 3 ms is required for complete conversion. Since a residence time of 22 ms yielded only 8% magnetite in the previous quarter, it was treated as the starting point of oxide formation.

Sulfur aerosols and ash were captured. XRD was performed on the recovered ash to determine its bulk composition, and the diffraction pattern is shown in Figure 2.9. The diffraction pattern reveals that an intermediate could be observed, for the peaks at 41.9 degrees and 42.9 degrees are due to wustite and magnetite, respectively. The ash composition was estimated to be 15 wt% wustite-magnetite.

The particle structure of the oxidized pyrite was characterized by SEM. Figure 2.10 is a secondary SEM at 1000 X, and it reveals that almost all of the particles are spherical and on the order of 20 μm. A few particles appear to be segregating into pairs of 10 μm particles. Crystallites are quite apparent in most particles.
Figure 2.9 X-ray diffraction pattern of pyrite after reaction at 1500K and 12% oxygen for 25 ms. Present are wustite (W) and magnetite (M) peaks.

Figure 2.10 Secondary scanning electron micrograph at 1000 X magnification of pyrite after oxidation at 1500 K and 12% oxygen for 25 ms.
The pyrite oxidation pathway described in Section 2.1.1 was used to infer the rate-limiting kinetics. During last quarter's 22 ms test, only pyrite and magnetite were observed, and this suggested that the $\text{FeS}_2 \rightarrow \text{FeS}$ transition was rate-limiting. In the present test, it appears that 3 ms later the $\text{FeO} \rightarrow \text{Fe}_3\text{O}_4$ became rate-limiting, as FeO was the only magnetite precursor observed.

**7.62 cm (36 ms) Test**

This test was designed for investigating the final stages of magnetite formation. In the experiment, the residence time was specified at 36 ms. The ash was captured and characterized by XRD. The obtained diffraction pattern is presented in Figure 2.11. From the diffraction pattern, it is evident that only wustite and magnetite were present in the particles. Furthermore the approximate composition of the ash was established to be 6 wt% wustite and 94 wt% magnetite.

![Figure 2.11 X-ray diffraction pattern of pyrite after reaction at 1500K and 12% oxygen for 36 ms. Present are wustite (W) and magnetite (M) peaks.](image)
A micrograph of the oxidation products is shown in Figure 2.12. Approximately 95% of the particles are perfect spheres. Several particles appear to be undergoing the self-segregation transformation. Practically all particles exhibit crystallites.

Figure 2.12 Secondary scanning electron micrograph at 1000 X magnification of pyrite after oxidation at 1500 K and 12% oxygen for 36 ms.
PLANS FOR NEXT QUARTER

Next quarter's focus will be placed on the quantitative characterization of the reaction rate resistance introduced by intraparticle kinetics during the oxidation of iron pyrite. The activities to support this aim will span Tasks 2. Following is a description of the planned activities for the April 1 to June 30, 1995 reporting period:

Task 2: Pyrite Intraparticle Kinetics Resistance

- The development of an X-ray diffraction (XRD) procedure for the quantitative analysis of the solid product of pyrite oxidation will be effected. The aim is to obtain a scheme that can quantify the expected phases at concentrations down to 5 wt% with accuracy of at least 95% relative.
- Intraparticle kinetics resistance will be inferred from those data points corresponding to conditions that induce negligible transport reaction resistance.
REFERENCES


