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MECHANISMS OF PYRITE OXIDATION TO NON-SLAGGING SPECIES

Quarterly Report for the Period

July 1, 1995 - September 30, 1995

Grant DE-FG22-94PC94205

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THE UNITED STATES DEPARTMENT OF ENERGY

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Submitted by

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

March 1996

**HIGH TEMPERATURE GASDYNAMICS LABORATORY
Mechanical Engineering Department
Stanford University**

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March 1996

High Temperature Gasdynamics Laboratory
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REPORTED BY: **A. E. Jacob Akan-Etuk and Reginald E. Mitchell**

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RESEARCH OBJECTIVES

This document is the fifth quarterly status report on a project that is conducted at the High Temperature Gasdynamics Laboratory at Stanford University, Stanford, California and is concerned with enhancing the transformation of iron pyrite to non-slagging species during staged, low-NO_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_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 July 1 to September 30, 1995. During the quarter, quantitative characterization was completed for the combustion products of pyrite oxidized (at 1500 K) in the 1% and the 12% oxygen level test series.

Pyrite samples that had been oxidized in 12% oxygen for 22 ms and for 109 ms were subjected to X-ray diffraction (XRD) scans suitable for quantitative chemical analysis. These samples were also characterized by scanning electron microscopy (SEM) to identify transformations in particle morphology and observe gradients in particle chemical composition.

All quantitative XRD scans for the 1% oxygen level test series were reduced, and sample compositions were calculated. At 42 ms, the composition was 90 wt% pyrite (FeS_2)-6 wt% pyrrhotite 3T ($\text{Fe}_{0.877}\text{S}$)-4 wt% troilite (FeS). By 52 ms, the pyrrhotite 3T had disappeared, and the sample contained 8 wt% wustite (FeO). Between 77 ms and 146 ms, the pyrite and troilite had completely converted, and magnetite (Fe_3O_4) had formed, reaching 86 wt%.

Quantitative XRD scans were reduced for the 12% oxygen level test series as well. At 22 ms, the obtained composition was 82 wt% pyrite-18 wt% magnetite. By 25 ms, the speciation was 11 wt% wustite and 89 wt% magnetite. With increased reaction time, the wustite converted to magnetite. Complete conversion to magnetite was attained between 36 ms and 109 ms, and the sample composition remained at pure magnetite for up to 146 ms.

These tests indicate that in 1% oxygen, pyrite transforms to magnetite by passing through a well-defined sequence: pyrite, troilite, wustite, and magnetite. The conversion reaches 86 wt% by 146 ms. In 12% oxygen, the troilite-to-wustite and the wustite-to-magnetite transformation steps are so rapid that no troilite or wustite is detected at early residence times in a reactor. Furthermore, in 12% oxygen, 89 wt% conversion is attained by 25 ms.

FINDINGS

Stanford University's pyrite oxidation research program aims to address the need for a more accurate quantitative description of chemical and mass transfer resistances that control pyrite transformation rates during pulverized coal (P. C.) combustion. A model has been formulated, in which pyrite oxidation is depicted as occurring in sequential stages [1]. The overall transformation rate between the stages is expressed in terms of a rate equation containing kinetics and transport parameters.

Combustion experiments have been performed at conditions intended to amplify the effects of intraparticle kinetics parameters. Pyrite particles of 20 μm diameter were oxidized in 1500 K environments at 1% and 12% oxygen levels [2, 3]. Qualitative analysis of the condensed reaction products by X-ray diffraction (XRD) was used to establish the reaction pathway. Subsequently, a scheme for performing quantitative XRD of the pyrite combustion products was effected [4]. This quantitative XRD scheme has still not been utilized to determine the compositions of combustion products obtained thus far in our research program.

Activity during the quarter was focused on the quantitative characterization of the obtained pyrite reaction products (Task 2 of the project plan). Quantitative XRD scans were to be performed. Diffraction patterns were to be reduced and compositions calculated.

1.0 TASK 2: PYRITE INTRAPARTICLE KINETICS RESISTANCE

During the quarter, quantitative characterization was completed for the combustion products of pyrite oxidized in the 1% and the 12% oxygen level test series. Pyrite samples that had been oxidized in 12% oxygen for 22 ms and for 109 ms were subjected to X-ray diffraction (XRD) scans suitable for quantitative chemical analysis. These samples were also characterized by scanning electron microscopy (SEM) to identify transformations in particle morphology and observe gradients in particle chemical composition. All quantitative XRD scans for the 1% and the 12% oxygen level test series were analyzed, and sample compositions were calculated.

1.1 Experimental Observations

Pyrite samples that had been oxidized at 12% oxygen level for 22 ms and for 109 ms were subjected to quantitative XRD scans and SEM characterization. Previously, these two samples had undergone qualitative chemical analysis by XRD [2]. Approximately 100 mg of each sample had been ground, placed on a silicon wafer, and bound with nitrocellulose-in-amyl acetate to form an XRD specimen.

This quarter, each specimen was scanned on an X-ray diffractometer (manufactured by Philips) illuminated with Cu $K\alpha$ radiation. The diffractometer was operated without a monochromator. XRD scans were taken for 2θ angles from 40° to 49° , in increments of 0.1° , at hold times of 60 s. The resulting diffraction patterns were plotted by the PC-APD software that accompanies the Philips diffractometer, to yield X-ray counts versus 2θ angle.

Whole particles were characterized for morphology by examining SEM images generated by secondary electrons. The particle shape and roughness were used to determine if the particles had undergone fusion or crystallization. On the other hand, cross-sectioned particles were characterized for phase dispersion by using SEM images generated by backscatter electrons. The atomic number contrast was used to determine if transport processes were sufficiently great, relative to chemical kinetics.

4.5 cm (22 ms) Test

Shown in Figure 1.1 is the XRD pattern of the ash recovered after oxidation in 12% oxygen at 1500K for 22 ms. The diffraction pattern spans a range of 2θ values from 40° to 49° . Cursors mark the most significant peaks identified by the PEAK SEARCH program of the Philips diffractometer's PC-APD software. As usual, a systematic shift of peak positions with respect to tabulated values occurs due to non-ideal instrument alignment.

Figure 1.1 X-ray diffraction pattern of pyrite after reaction at 1500K and 12% oxygen for 22 ms. Present are pyrite (FeS_2 ; P) and magnetite (Fe_3O_4 ; M) peaks.

The sample's constituents had been previously determined to be pyrite (FeS_2) and magnetite (Fe_3O_4) [2], but only those pyrite and magnetite peaks utilized for quantitative calculations are labeled on Figure 1.1. The pyrite peak at 47.2° completely dwarfs the magnetite peak at 42.9° . The pyrite peak possesses a breadth approximately equal to that of the solid sample

used for XRD calibration [4]. The magnetite peak of the reaction products, however, is broader than that of the calibration standard, suggesting that the magnetite had experienced a softening transition during combustion. The absence of troilite and wustite intermediates suggests that the troilite-to-wustite and the wustite-to-magnetite transformation steps are extremely rapid.

Figure 1.2 is a secondary SEM at 1000 X of the oxidized pyrite. The micrograph reveals that almost all of the particles are angular and on the order of 20 μm in size. These partially oxidized particles resemble the feed material used for the study [2], except the oxidized pyrite particles generally exhibit greater micro-roughness. In addition, a few spherical particles are present among the angular ones. The presence of these spherical particles is consistent with previous observations that during oxide formation, pyrite experiences a softening transformation [3]. The spherical particles exhibit crystallites in varying degrees; it is not clear whether these are pure magnetite or magnetite-pyrite mixtures.

Figure 1.2 Secondary scanning electron micrograph at 1000 X magnification of pyrite after oxidation at 1500 K and 12% oxygen for 22 ms.

Shown in Figure 1.3 are reacted pyrite particles that had been epoxied and polished. These sectioned particles were imaged by backscatter SEM, in order to facilitate the perception of atomic number contrast. Among the angular particles in the micrograph, minimal variation of brightness is observed. Similarly, the round particles exhibit negligible contrast. Hence, the micrographs suggest that intraparticle transport processes are sufficiently great to thoroughly mix reacted material as it is being formed. The discernible evidence supports the view that pyrite transformation is limited by chemical kinetics under the conditions of the test.

Figure 1.3 Backscatter scanning electron micrograph at 1000 X magnification of pyrite after oxidation at 1500 K and 12% oxygen for 22 ms.

27 cm (109 ms) Test

Figure 1.4 is the XRD pattern of the condensed-phase product of pyrite oxidation in 12% oxygen at 1500 K for 109 ms. The only peak present on the diffraction pattern is located at 42.9° ,

and it belongs to magnetite. Completely absent are peaks due to intermediates such as pyrrhotite and wustite. The magnetite peak is narrower than that obtained after 22 ms of reaction, but it is still broader than the diffraction peak of the calibration standard [4]. This intermediate value of the magnetite peak width suggests a crystallization phase transition yet to be completed.

Figure 1.4 X-ray diffraction pattern of pyrite after reaction at 1500K and 12% oxygen for 109 ms. Present is a magnetite (Fe₃O₄; M) peak only.

The structure of the fully oxidized particles was characterized using SEMs generated by secondary electrons, and example of which is shown in Figure 1.5. All of the particles in the micrograph are spherical (except for one in the lower left hand corner) and on the order of 20 μm in size. Crystallites no longer feature as prominently as they did after 22 ms of reaction (see Figure 1.2). The decrease in crystallites may be due to sintering of the crystallites subsequent to the

completion of magnetite formation. Alternatively, the crystallites may have been iron pyrite restructured during softening.

Figure 1.5 Secondary scanning electron micrograph at 1000 X magnification of pyrite after oxidation at 1500 K and 12% oxygen for 109 ms.

Figure 1.6 is a backscatter SEM of sectioned particles of fully oxidized pyrite. Texture is more evident than in the partially oxidized particles in Figure 1.3. Radial gradients in brightness are not evident other than what appears to be a few voids on the periphery of the particles.

Figure 1.6 Backscatter scanning electron micrograph at 1000 X magnification of pyrite after oxidation at 1500 K and 12% oxygen for 109 ms.

1.2 Quantitative Results

Data from the entire set of quantitative XRD scans were reduced to calculate iron speciation for the 1% oxygen and 12% oxygen test series. Peaks were identified on the diffraction patterns using the PEAK SEARCH program of the PC-APD software. Each peak height was multiplied by the ratio of its width to the calibration standard's width, and standardized peak heights were obtained. These standardized heights were used as inputs to the intrinsic standard calibration curves, after normalization with respect to reference lines of calibration standards (Fe_{1-x}S and Fe_3O_4). The concentration of each of the other phases in the mixture was determined relative to those of the reference constituents.

1% Oxygen Test Series

Depicted in Figures 1.7 to 1.10 are the compositions of the condensed phase products of iron pyrite after combustion at 1500K in 1% oxygen environment. Figures 1.7 to 1.10 provide iron speciation data after 42 ms, 52 ms, 77 ms, and 146 ms, respectively. In each figure, the weight fractions of the pyrite (FeS_2), troilite (FeS), wustite (FeO), and magnetite (Fe_3O_4) components are depicted in histogram form. These four species (and a small amount of pyrrhotite 3T at 42 ms) were the only ones observed in the XRD analyses quantified in this report.

Figure 1.7 suggests that the phase partition in pyrite ash is 90 wt% pyrite-10 wt% troilite at 42 ms. More precisely, the "troilite" in this particular figure is defined to comprise 4 wt% stoichiometric troilite and 6 wt% off-stoichiometric pyrrhotite 3T. [This is the only analysis that revealed the presence of pyrrhotite 3T.] Furthermore, in this figure, no wustite or magnetite is evident.

Figure 1.7 Condensed phase product of oxidation of 20 μm extraneous pyrite at 1500 K and 1% oxygen for 42 ms.

The subsequent three figures illustrate that iron cascades from pyrite to troilite to wustite, and finally, to magnetite. Figure 1.8 shows that after 52 ms, the sample composition is 39 wt%

pyrite-53 wt% troilite-8 wt% wustite. In Figure 1.9, it is evident that troilite oxidizes relatively quickly, for the system constituents become 26 wt% pyrite, 30 wt% troilite, and 44 wt% wustite after 77 ms. The pyrite and troilite disappear, and by 146 ms (Figure 1.10), the obtained speciation is 14 wt% wustite and 86 wt% magnetite.

Figure 1.8 Condensed phase product of oxidation of 20 μm extraneous pyrite at 1500 K and 1% oxygen for 52 ms.

Figure 1.9 Condensed phase product of oxidation of 20 μm extraneous pyrite at 1500 K and 1% oxygen for 77 ms.

Figure 1.10 Condensed phase product of oxidation of 20 μm extraneous pyrite at 1500 K and 1% oxygen for 146 ms.

12% Oxygen Test Series

The temporal evolution of condensed-phase speciation within pyrite burned at 1500 K in 12% oxygen is depicted in Figures 1.11 to 1.15. The residence times covered by these five figures are 22 ms, 25 ms, 36 ms, 109 ms, and 146 ms, respectively. Although the figure legends refer to pyrite (FeS_2), troilite (FeS), wustite (FeO), and magnetite (Fe_3O_4) as potential sample constituents, troilite is not evident in the 12% oxygen test series. In contrast, magnetite is present in every analysis of this test series.

The histograms of Figures 1.11 to 1.15 suggest that iron is shuttled from pyrite to wustite to magnetite during oxidation. From Figure 1.11, it is seen that at 22 ms, the constituents of pyrite ash are pyrite (82 wt%) and magnetite (18 wt%). The absence of troilite and wustite intermediates suggests that the troilite-to-wustite and the wustite-to-magnetite transformation steps are extremely rapid. At 25 ms (Figure 1.12), the pyrite is consumed and the reaction product becomes 11 wt% wustite-in-magnetite. Figure 1.13 reveals that an additional 11 ms of oxidation decreases the wustite content of the binary mixture to 7 wt%. By 109 ms (see Figure 1.14), only magnetite is present in the condensed-phase reaction product. Even after 146 ms, the product composition remains at magnetite, as seen in Figure 1.15.

Figure 1.11 Condensed phase product of oxidation of 20 μm extraneous pyrite at 1500 K and 12% oxygen for 22 ms.

Figure 1.12 Condensed phase product of oxidation of 20 μm extraneous pyrite at 1500 K and 12% oxygen for 25 ms.

Figure 1.13 Condensed phase product of oxidation of 20 μm extraneous pyrite at 1500 K and 12% oxygen for 36 ms.

Figure 1.14 Condensed phase product of oxidation of 20 μm extraneous pyrite at 1500 K and 12% oxygen for 109 ms.

Figure 1.15 Condensed phase product of oxidation of 20 μm extraneous pyrite at 1500 K and 12% oxygen for 146 ms.

PLANS FOR NEXT QUARTER

Next quarter's emphasis 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 and 6. Following is a description of the planned activities for the October 1 to December 31, 1995 reporting period:

Task 2: Pyrite Intraparticle Kinetics Resistance

- Intraparticle reaction resistance will be calculated from obtained composition data using the numerical model to be implemented (Task 6).

Task 6: Rate Expression Formulation and Validation

- A numerical model will be implemented to describe pertinent species, momentum, and energy balances during pyrite oxidation.

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