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MECHANISMS OF PYRITE OXIDATION TO NON-SLAGGING SPECIES

Quarterly Report for the Period

July 1, 1996 - September 30, 1996

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 1997

MASTER

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

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March 1997

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PROJECT TITLE: **MECHANISMS OF PYRITE OXIDATION TO NON-SLAGGING SPECIES**

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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 ninth 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, 1996. Characterization of intraparticle mass transport limitations during pyrite oxidation was embarked upon. The effort was intended to confirm that intraparticle transport limitations are negligible.

Samples of 20 micron pyrite particles extracted from the flow reactor after oxidation at 1550 K in 1% oxygen level were analyzed. The samples had been extracted after reaction times of 42 ms, 52 ms, 77 ms, and 146 ms. For these samples, the bulk product compositions previously determined by X-ray diffraction analysis consisted of varying proportions of FeS_2 , Fe_{1-x}S , FeO , and Fe_3O_4 . The particles were analyzed to determine if the iron compounds previously identified by bulk X-ray diffraction analysis (XRD) were well mixed within individual particles.

The extracted pyrite particles, epoxied and sectioned, were subjected to a variety of analytical techniques using the microprobe (JEOL 733 Superprobe). Secondary electron and backscatter electron imaging was performed. Iron, sulfur, and oxygen elemental X-ray (K_α) maps were generated. Energy dispersive spectrometry (EDS) was used for qualitative elemental analysis of selected particles. These particles were subsequently subjected to quantitative elemental analysis by wavelength dispersive spectrometry (WDS), using Fe_2O_3 and FeS_2 as standards. During WDS analysis, micron-radius hemispherical volumes bisected by sectioning plane were sampled.

The microprobe analyses of oxidized pyrite showed that, generally, particles could be modeled as well-stirred, having negligible compositional gradients of the scale of the particle radius. In all four samples of pyrite analyzed, there were particle edge effects. Furthermore, there were finger-like projections of different phases in mixed-phase particles. Nevertheless, compositional gradients were of concern only in the 77 ms sample (only those particles of relatively low oxygen level).

FINDINGS

In Srinivasachar and Boni's model [1], pyrite oxidation manifests the pathway

During each transformation step, the reaction rate, $\dot{R}$, is expressed as

$$\dot{R} = \frac{A_p C_{O_2}}{\frac{1}{k_G} + \frac{1}{k_R} + \frac{1}{k_L}},$$

where A_p is the external surface area of the particle, C_{O_2} is the concentration of oxygen in the combustion environment, k_G and k_L are the gas and the liquid mass transfer coefficients, respectively, and k_R is the surface reaction rate constant, which combines the effects of intrinsic reaction and pore diffusion. Srinivasachar and Boni explicitly cited the need for characterization of intraparticle mass transport limitations [1]. In fact, Srinivasachar *et al.* [2] subsequently suggested that several aspects of the model needed revisiting.

In the current research program, time-resolved phase identifications of extraneous pyrite combustion products have been used to determine a pyrite oxidation pathway [3] different from that initially proposed by Srinivasachar and Boni. Tests at 1550 K gas temperature and 1% oxygen level indicate that, after transient thermal decomposition to form $Fe_{0.877}S$, pyrite oxidizes through the pathway

with no evidence of significant fragmentation. Last quarter [4], results of this research program were used to update the model framework of Srinivasachar and Boni. In the updated model, after the initial transient decomposition of pyrite, intraparticle limitations were neglected.

This quarter, characterization of intraparticle mass transport limitations during pyrite oxidation was embarked upon. The effort was intended to confirm that intraparticle transport limitations are negligible. The activity fell under the auspices of Task 3 of the research program.

1.0 TASK 3 PYRITE INTRAPARTICLE MASS TRANSFER RESISTANCE

The main objective of the effort was to confirm that intraparticle transport limitations are negligible during pyrite oxidation at typical pulverized coal firing conditions. Samples of 20 micron pyrite particles extracted from the flow reactor after oxidation at 1550 K in 1% oxygen level were analyzed. Interest was in determining if the iron compounds previously identified by bulk X-ray diffraction analysis (XRD) [3] were well mixed within individual particles.

The extracted pyrite particles, epoxied and sectioned, were subjected to a variety of analytical techniques using the microprobe (JEOL 733 Superprobe). Secondary electron and backscatter electron imaging was performed. Iron, sulfur, and oxygen elemental X-ray (K_{α}) maps were generated. Energy dispersive spectrometry (EDS) was used for qualitative elemental analysis of selected particles. These particles were subsequently subjected to quantitative elemental analysis by wavelength dispersive spectrometry (WDS), using Fe_2O_3 and FeS_2 as standards. During WDS analysis, micron-radius hemispherical volumes bisected by sectioning plane were sampled.

Depicted in the following sections are characterizations of four samples of 20 micron pyrite oxidized at 1550 K and 1% oxygen level [3]. The samples had been extracted after residence times of 42 ms, 52 ms, 77 ms, and 146 ms. For these samples, the bulk product compositions previously determined by X-ray diffraction analysis consisted of varying proportions of FeS_2 , Fe_{1-x}S , FeO , and Fe_3O_4 .

1.1 Results: 1% O_2 , 1550 K, 42 ms

The bulk composition previously determined by XRD for the 42 ms-reaction pyrite sample was FeS_2 with small quantities of $\text{Fe}_{0.877}\text{S}$ and nearly stoichiometric FeS . Many backscatter-imaged SEMs were obtained for this sample. The true size and shape of the particles were distorted because of image optimization for contrast. Obtaining good contrast was deemed more important than obtaining accurate shape, because brightness correlates with weight-averaged atomic number.

Shown in Figure 1A is a typical backscatter-imaged SEM of sectioned particles. Labeled are points on which quantitative WDS elemental analyses were performed. From the brightness, it may be inferred that round particles possess a greater average atomic number than angular ones. While there are internal pockets of low brightness, noticeable shading within particles is restricted to particle edges (a common artifact of an SEM). Furthermore, the different luminosity zones are mixed in an in orderly fashion. In effect, gradients in intraparticle brightness on the scale of the particle radius are not significant.

Figure 1A. Backscatter scanning electron micrograph of 20 micron-diameter pyrite after reaction at 1550 K and 1% oxygen for 42 ms.

An iron X-ray map is presented in Figure 1B. Particle shapes are different from those in Figure 1A, since X-rays originate from a greater depth than do backscatter electrons. Round particles, due to their higher volumetric concentration of iron atoms, appear brighter than angular particles. Intraparticle gradients in intensity are perceptible only in the particle in the upper right corner (next to point 8 of Figure 1A), however. The image is degraded because the particle lies deep within the epoxy. Therefore, the dullness of the left side may be due to the particle's comprising two attached particles. In general, the iron appears well-dispersed within particles.

Figure 1B. Iron X-ray map of 20 micron-diameter pyrite after reaction at 1550 K and 1% oxygen for 42 ms.

A sulfur distribution map is shown in Figure 1C. In this image, angular particles are brighter than spherical ones, in contrast with the iron map of Figure 1B. The only significantly non-uniform particle is the angular one in the upper-right corner. As in Figure 1B, the left side of this particle is somewhat darker than the right side. Again, intraparticle uniformity in intensity is evident in most particles.

Figure 1C. Sulfur X-ray map of 20 micron-diameter pyrite after reaction at 1550 K and 1% oxygen for 42 ms.

Presented in Figure 1D is an oxygen map, and the map indicates that there is significantly more oxygen in the epoxy than in the particles. Although angular particles are completely dark, the round particles exhibit evidence of a minor oxygen content. (The oxygen may be due to adsorption or vacancy occupation.) Consistently anomalous, the left side of the particle in the upper-right corner of the picture contains even greater oxygen than the epoxy. With the exception of this particle, intraparticle gradients in composition are not noticeable.

Figure 1D. Oxygen X-ray map of 20 micron-diameter pyrite after reaction at 1550 K and 1% oxygen for 42 ms.

Further evidence of great intraparticle mixing is provided by numerous quantitative WDS analyses, some of which are contained in Table 1A. Shown are normalized atomic ratios of iron, sulfur, and oxygen for sampling positions numbered in Figure 1A. These measurements indicate that angular particles are FeS_2 and round particles are $\text{FeS}_{0.80}\text{O}_{0.24}$ (omitting the low-weight total point 7, $\text{FeS}_{0.82}\text{O}_{0.24}$) More importantly, the measurements establish that intraparticle variations in atomic ratio are less than $\pm 5\%$ (except particle 6 - 7's oxygen ratio, which is $\pm 15\%$).

Table 1A WDS Analyses of Pyrite after Reaction at 1550 K and 1% Oxygen for 42 ms
(see Figure 1A for sampling positions)

<u>Position</u>	<u>Fe</u>	<u>S</u>	<u>O</u>
1	1.000	2.054	0.004
2	1.000	2.016	0.000
3	1.000	2.034	0.000
4	1.000	2.004	0.000
5	1.000	1.992	0.000
6	1.000	0.773	0.286
7*	1.000	0.727	0.212
8	1.000	0.828	0.237
9	1.000	0.827	0.229
10	1.000	0.842	0.216

* Low weight total, 91.58%.

Other WDS data, when used in conjunction with their corresponding backscatter SEMs also suggest a high degree of intraparticle mixedness. Shown in Table 1B are WDS analyses for non-angular particles (angular particles are always FeS_2), some of which are contained in the SEM of Figure 1E. Among the non-angular particles, even particle-to-particle variations are small. With the exception of the crescent, the particles can be characterized as $\text{FeS}_{0.98}\text{O}_{0.12}$. Variations in sulfur ratio and oxygen ratio are $\pm 1.5\%$ and $\pm 12.6\%$, respectively.

Table 1B WDS Analyses of Pyrite after Reaction at 1550 K and 1% Oxygen for 42 ms
(see Figure 1E for sampling positions)

<u>Particle</u>	<u>Fe</u>	<u>S</u>	<u>O</u>
Semi-Plastic (5)	1.000	0.966	0.138
Nodule (4)	1.000	0.995	0.107
Crescent (6)	1.000	0.842	0.240
Mesosphere	1.000	0.971	0.112
Sphere	1.000	0.986	0.137

Figure 1E. Backscatter scanning electron micrograph of 20 micron-diameter pyrite after reaction at 1550 K and 1% oxygen for 42 ms.

1.2 Results: 1% O₂, 1550 K, 52 ms

Previous XRD of 52 ms-reaction pyrite sample detected FeS₂ and nearly stoichiometric FeS, with small quantities of nearly stoichiometric FeO. Shown in Figure 2A is one of several backscatter SEMs of sectioned particles. Angular and semi-plastic particles are duller than round particles. Within particles, dark spots due to focusing effects and macrovoids are evident. The SEM suggests that radius-scale intraparticle gradients in composition are not substantial.

Figure 2A. Backscatter scanning electron micrograph of 20 micron-diameter pyrite after reaction at 1550 K and 1% oxygen for 52 ms.

The iron map of the pyrite particles is presented in Figure 2B. There is slightly greater iron concentration in the round particles than in the angular and semi-plastic particles. Within the resolution of the map, there does not appear to be significant radius-scale intraparticle gradients in iron content.

Figure 2B. Iron X-ray map of 20 micron-diameter pyrite after reaction at 1550 K and 1% oxygen for 52 ms.

The sulfur map of Figure 2C indicates that there exists an interparticle variation in sulfur content. The angular and semi-plastic particles have a high sulfur content. The round particles range from intermediate to low brightness. The particles of low brightness appear spotty, perhaps indicative of mixture of sulfur-containing and non-sulfurous grains. Other than edge effects, radius-scale intraparticle gradients are not detectable.

Figure 2C. Sulfur X-ray map of 20 micron-diameter pyrite after reaction at 1550 K and 1% oxygen for 52 ms.

Figure 2D is the oxygen X-ray map after 52 ms of reaction, and it contains particles which exhibit substantially greater oxygen content than the epoxy background. Angular particles (points 1, 2, 3, 4, 5, 6 in Figure 2A) are oxygen-deficient. Semi-plastic particles show a deficit (points 3 and 4) as well as a high oxygen level (point 11). Generally, high oxygen level is associated with round particles (9, 10, 12), but there is a hollow shell next to point 7 (barely visible in Figure 2A) that also exhibits high oxygen level. Although angular particles are uniformly low in oxygen content, the intraparticle dispersion of oxygen in non-angular particles is difficult to discern.

Figure 2D. Oxygen X-ray map of 20 micron-diameter pyrite after reaction at 1550 K and 1% oxygen for 52 ms.

Many WDS measurements were made, and Table 2A contains the WDS results for the points shown in Figure 2A. For those particles with only one WDS sampling point, intraparticle uniformity can be inferred by using WDS data in conjunction with backscatter SEMs and X-ray maps. Evidently, the interparticle variation in composition is greater than that observed after 42 ms of reaction. There are now particles of lower sulfur and correspondingly high oxygen levels. There is even an FeS₂ particle with excess sulfur (or iron deficit)- point 6; it should be noted that the weight total for this particle, 95.04%, is significantly lower than that of the next worst FeS₂ particle, 97.08%.

Table 2A WDS Analysis of Pyrite after Reaction at 1550 K and 1% Oxygen for 52 ms
(see Figure 2A for sampling positions)

<u>Position</u>	<u>Fe</u>	<u>S</u>	<u>O</u>
1	1.000	2.013	0.004
2	1.000	2.032	0.018
3	1.000	2.016	0.000
4	1.000	2.020	0.019
5	1.000	2.023	0.000
6	1.000	2.126	0.028
7	1.000	0.825	0.241
8	1.000	0.813	0.221
9	1.000	0.363	0.734
10*	1.000	0.285	0.823
11	1.000	0.691	0.389
12**	1.000	0.541	0.908
13***	1.000	0.834	0.316
14	1.000	0.801	0.288

* Low weight total, 94.42%.

** Low weight total, 94.60%.

*** Low weight total, 92.44%.

Despite the particle-to-particle variations, intraparticle differences in compositions are relatively minor for the particles in Table 2A. As usual, angular particles are all stoichiometric FeS_2 , with the exception of point 6. Point 6, shown by its secondary electron-imaged micrograph to be angular, has the anomalous stoichiometry of $\text{FeS}_{2.13}\text{O}_{0.03}$. Such a stoichiometry would raise sulfur variation in angular particles to $\pm 3\%$. For spherical particles, intraparticle variations in atomic ratios are less than $\pm 5\%$.

Tabulated in Table 2B are additional WDS analyses further demonstrating intraparticle uniformity. Shown are pairs of measurements for each of six particles from Figure 2E. The particles span a broad range of morphologies. As usual, each angular particle is extremely reproducible in composition, (one angular particle is $\text{FeS}_{1.25}\text{O}_{0.16}$). The compositional variation for non-angular particles is typically $\pm 3\%$ in sulfur ratio and on the order of $\pm 5\%$ in oxygen ratio. The largest variation is only $\pm 9.7\%$, for the oblate particle.

Table 2B WDS Analysis of Pyrite after Reaction at 1550 K and 1% Oxygen for 52 ms

<u>Particle</u>	<u>Fe</u>	<u>S</u>	<u>O</u>
Angular (1)	1.000	2.024	0.000
	1.000	2.028	0.014
Angular (2) *	1.000	1.254	0.160
	**	1.252	0.154
Oblate (3)	1.000	1.008	0.070
	1.000	1.021	0.085
Nodule (4)	1.000	0.894	0.132
	1.000	0.939	0.125
Crescent (5)***	1.000	0.437	0.646
	1.000	0.465	0.687
Mesosphere (6)	1.000	0.901	0.155
	1.000	0.847	0.181

* Low weight total, 85.80%.

** Low weight total, 88.56%.

*** Low weight total, 94.79%.

Figure 2E. Backscatter scanning electron micrograph of 20 micron-diameter pyrite after reaction at 1550 K and 1% oxygen for 52 ms.

1.3 Results: 1% O₂, 1550 K, 77 ms

XRD of pyrite after 77 ms of reaction detected nearly stoichiometric FeS and nearly stoichiometric FeO. SEM, EDS, and WDS analyses were also performed, but no X-ray maps were generated. The backscatter SEM of a large selection of particles is presented in Figure 3. The SEM contains primarily spherical and crescent particles. There are also semi-plastic particles, individually (points 1 and 2), as well as in a dark cluster within a cenosphere (lower right corner).

The micrograph of Figure 3 clearly shows the existence of multiple phases within particles. Dark (low atomic number) finger-like patches are interspersed in a bright matrix. Edge effects (dark patches) are prominent in the brightest particles. Generally, the radius-scale intraparticle structure shows no preference of radial position as the dark, finger-like patches grow, however. Consequently, this SEM can be interpreted as implying that particles become well mixed internally as more of the lower atomic number phase is formed.

Figure 3. Backscatter scanning electron micrograph of 20 micron-diameter pyrite after reaction at 1550 K and 1% oxygen for 77 ms.

Tabulated in Table 3 are elemental compositions for points labeled in Figure 3. The variation in sulfur atomic ratio ranges from $\pm 0.5\%$ to $\pm 5\%$, except for points 3 - 4. For points 3 - 4, the variation is as high as $\pm 36\%$, possibly because of point 4's relatively low weight total of 93.53%. Oxygen variation typically ranges from $\pm 0.2\%$ to $\pm 13\%$. For three particles, the variation is 22%, 32%, and 33%. The measurements in Table 3 establish that intraparticle variations in compositions are somewhat larger after 77 ms of reaction than at earlier times.

Table 3 WDS Analysis of Pyrite after Reaction at 1550 K and 1% Oxygen for 77 ms
(see Figure 3 for sampling positions)

<u>Position</u>	<u>Fe</u>	<u>S</u>	<u>O</u>	<u>Weight Total* (%)</u>
1	1.000	1.004	0.101	
2	1.000	0.982	0.200	
3	1.000	0.154	1.050	
4	1.000	0.072	1.190	93.53
5	1.000	0.290	0.934	
6	1.000	0.359	0.875	
7	1.000	0.772	0.313	
8	1.000	0.807	0.357	
9	1.000	0.778	0.322	
10	1.000	0.908	0.155	
11	1.000	0.931	0.161	94.90
12	1.000	0.864	0.203	
13	1.000	0.850	0.173	94.79
14	1.000	0.722	0.673	
15	1.000	0.696	0.515	
16	1.000	0.570	0.591	
17	1.000	0.568	0.575	
18	1.000	0.548	0.570	
19	1.000	0.726	0.550	
20	1.000	0.733	0.435	

* Low weight totals only.

Table 3 (cont) WDS Analysis of Pyrite after Reaction at 1550 K and 1% Oxygen for 77 ms

<u>Position</u>	<u>Fe</u>	<u>S</u>	<u>O</u>	<u>Weight Total* (%)</u>
21	1.000	0.775	0.687	
22	1.000	0.117	1.066	
23	1.000	0.124	0.944	94.68
24	1.000	0.131	1.150	93.70
25	1.000	0.794	0.334	
26	1.000	0.804	0.290	
27	1.000	0.806	0.299	
28	1.000	0.578	0.601	
29	1.000	0.553	0.578	93.96
30	1.000	0.543	0.495	94.99
31	1.000	0.788	0.378	
32	1.000	0.254	0.934	
33	1.000	0.232	0.880	
34	1.000	0.988	0.092	
35	1.000	0.994	0.079	
36	1.000	0.945	0.154	94.62
37	1.000	0.696	0.461	
38	1.000	0.704	0.463	
39	1.000	0.001	1.287	
40	1.000	0.714	0.356	
41	1.000	0.728	0.386	
42	1.000	0.746	0.417	
43	1.000	0.878	0.182	
44	1.000	0.870	0.181	
45	1.000	0.869	0.235	
46	1.000	0.769	0.296	
47	1.000	0.760	0.307	
48	1.000	0.823	0.385	93.04
49	1.000	0.376	0.756	
50	1.000	0.365	0.821	

1.4 Results: 1% O₂, 1550 K, 146 ms

Previous XRD of a pyrite sample after 146 ms of reaction detected Fe₃O₄ and nearly stoichiometric FeO (with a small amount of unreacted FeS₂ due to momentary experimental excursion). One of the backscatter SEMs obtained for sectioned particles is presented in Figure 4A. (The dark spherical regions are cavities in the epoxy.) Generally, the particles appear more mixed internally than those of Figure 3A, although dark, finger-like patches are still discernible.

Figure 4A. Backscatter scanning electron micrograph of 20 micron-diameter pyrite after reaction at 1550 K and 1% oxygen for 146 ms.

Elemental X-ray maps were obtained for particles in the triangular region formed by points 4, 5, and 11. The iron map of Figure 4B indicates that despite interparticle differences, within each particle, there are no radial gradients in iron content. Spherical particles have noticeably higher iron levels than other particles. Within the same particle, however, even cores and shells exhibit the same intensity. Nevertheless, it should be noted that spherical particles exhibit patches that correspond to different grain types.

Figure 4B. Iron X-ray map of 20 micron-diameter after reaction at 1550 K and 1% oxygen for 146 ms.

Figure 4C is the sulfur map of the triangular region, and it suggests that although interparticle variations are prominent, there is adequate mixing within each particle, on the scale of particle radius. Angular particles and some spherical particles have noticeable levels of sulfur, but spherical core-and-shells and some spherical particles are devoid of sulfur. At point 5 (see Figure 4A for reference), sulfur is associated with a dendritic structure emanating from the particle center. Nevertheless, on the scale of the particle radius, the particle may be considered thoroughly mixed.

Figure 4C. Sulfur X-ray map of 20 micron-diameter after reaction at 1550 K and 1% oxygen for 146 ms.

Because the oxygen map in Figure 4D is almost an inversion of the sulfur map, it also is interpreted as suggesting that intraparticle mixing is thorough. The greatest deviation from the oxygen-sulfur inversion principle occurs at point 5, which has high levels of both sulfur and oxygen. Oxygen appears more uniformly distributed than the sulfur at point 5, although the oxygen level is slightly higher at the particle edges. Again, radius-scale intraparticle gradients appear negligible.

Figure 4D. Oxygen X-ray map of 20 micron-diameter pyrite after reaction at 1550 K and 1% oxygen for 146 ms.

Table 4 contains the WDS analyses for the points in Figure 4A. Points 7 and 8 are the core and shell, respectively, of the same particle. Both points are devoid of sulfur, and the difference in their oxygen ratios is only $\pm 1\%$. In general, the analyses in Table 4 do not permit direct evaluation of intraparticle compositional variation, but they can be used indirectly. By examining Figures 4A - D in conjunction with the analyses, a correlation can be made between intensity and composition, thus enabling a determination of the extent of intraparticle mixedness. Generally, particles are more mixed internally after 146 ms than after 77 ms of reaction (although variability of sulfur level, is high for 146 ms particles having sulfur levels on the order of 0.01 and below).

Table 4 WDS Analysis of Pyrite after Reaction at 1550 K and 1% Oxygen for 146 ms
(see Figure 4A for sampling positions)

<u>Position</u>	<u>Fe</u>	<u>S</u>	<u>O</u>	<u>Weight Total* (%)</u>
1	1.000	2.079	0.031	
2	1.000	2.032	0.030	
3	1.000	2.020	0.014	
4	1.000	1.199	0.108	84.60
5	1.000	0.265	0.898	89.51
6	1.000	0.076	1.038	93.01
7	1.000	0.001	1.197	89.75
8	1.000	0.002	1.170	84.64
9	1.000	0.016	1.358	
10	1.000	0.002	1.307	92.77
11	1.000	0.064	1.291	90.93
12	1.000	0.164	0.932	93.50
13	1.000	0.220	0.974	92.53
14	1.000	0.001	0.385	73.24
14 (again)	1.000	0.001	0.319	70.91

* Low weight totals only.

1.5 Conclusions

The microprobe analyses of oxidized pyrite showed that, generally, particles could be modeled as well-stirred, having negligible compositional gradients of the scale of the particle radius. In all four samples of pyrite analyzed, there were particle edge effects. Furthermore, there were finger-like projections of different phases in mixed-phase particles. Nevertheless, compositional gradients were of concern only in the 77 ms sample (only those particles of relatively low oxygen level).

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, 1996 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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