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MECHANISMS OF PYRITE OXIDATION TO NON-SLAGGING SPECIES

Quarterly Report for the Period

April 1, 1995 - June 30, 1995

Grant DE-FG22-94PC94205

Prepared for

THE UNITED STATES DEPARTMENT OF ENERGY

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Submitted by

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

December 1995

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

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December 1995

High Temperature Gasdynamics Laboratory

Department of Mechanical Engineering

Stanford University

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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 fourth 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 April 1 to June 30, 1995. During the quarter, an X-ray diffraction (XRD) scheme was effected for the quantitative characterization of the condensed phase reaction products collected thus far in the pyrite oxidation research project. The activities associated with the quarter's efforts involved Task 2 of the research project's work plan.

A theoretical justification was established for using the intrinsic standard method, the procedure used earlier for quantitative XRD analysis [1], as the basis of a scheme for the quantitative determination of pyrite reaction products. In the theoretical development, instrument-related limitations of the intrinsic standard method were identified. Consequently, the need to verify the ideality of a diffractometer facility before utilizing the previously determined intrinsic standard calibration curves was demonstrated.

Mixtures comprising pyrite, pyrrhotite, wustite, and magnetite were prepared and analyzed in the current project's Philips diffractometer facility to evaluate the existing intrinsic calibration curves. When the pyrrhotite reference was utilized, the errors in the inferred component mass concentrations were typically 1% absolute. The errors increased to 2 - 7 % absolute at pyrrhotite levels below 15 wt%. During the evaluation of the calibration curves, additional data was incorporated to extend the maximum pyrite-magnetite concentration ratio of the calibration curves from 1.28 to 18.07 (thus covering the span of concentration ratios generally encountered).

The calibration curves were then refined to account for the characteristics of reaction products observed in the current project. A scheme for obtaining and utilizing true heights, as opposed to apparent heights, of overlapping magnetite and pyrrhotite diffraction peaks was developed and assessed. Although the use of true peak heights typically reduced errors in inferred concentrations by 2 wt% absolute, it reduced an already acceptable magnetite reading from 4.2 wt% to practically nil (1.7 wt%). Consequently, it was determined that the gains had not been demonstrated to justify the potential losses at low magnetite levels associated with refining the calibration curves to use true peak heights.

A quantitative scheme based on diffraction peak areas, instead of peak heights, was established. The program PEAK SEARCH in the PC-APD software was used to establish standard peak widths for pyrite, pyrrhotite, wustite, and magnetite, which are to be used in calculating effective peak heights for conditions utilized for the data collected thus far.

A calibration scheme for determining the wustite content of pyrite reaction products was effected. The data obtained in the previous work [1] were used to establish a calibration curve, and this calibration curve was evaluated using new samples. Absolute errors in inferred wustite concentration were typically less than 0.9 wt%, except for one sample (8.3%). A second calibration curve was generated using the new samples. The maximum wustite absolute error was reduced to 5.3 wt%, but other errors grew.

From the various attempts, a final calibration scheme was synthesized for the reaction products of the pyrite oxidation program.

FINDINGS

For the pyrite oxidation project, X-ray diffraction analysis (XRD) has been selected as the main analytical technique for the quantitative characterization of the condensed phase reaction products. It was previously demonstrated that XRD constitutes a reliable analytical technique for iron pyrite and its combustion products [1]. When evaluated against samples of known compositions, intrinsic standard XRD calibration curves were typically of greater than 95% accuracy for concentrations as low as 5% (except for wustite).

In the current project, the previously developed XRD scheme has already been utilized for estimation of ash compositions, albeit with modifications. Modifications in procedure consist of the reduction of the severity of particle grinding during sample preparation and the utilization of a different diffractometer facility. Furthermore, the procedure has been applied to samples exhibiting great scatter in pyrrhotite-magnetite concentration ratio, possessing softened constituents, and containing wustite. While these changes in procedure and application do not affect the identification of specimen constituents, they could conceivably invalidate the assignment of concentrations using the calibration curves previously developed. Consequently, a need exists to revisit the intrinsic standard XRD data reduction scheme.

Activity during the quarter was restricted to Task 2 of the project plan and centered about developing a scheme for accurate analysis of XRD data. The first objective of this effort was to assess the validity of the existing calibration curves. The second objective was to modify the calibration curves to account for observations made thus far in the current project. These observations include the scatter of pyrrhotite-magnetite concentration ratios, the softening of iron compounds, and the presence of wustite.

1.0 TASK 2: PYRITE INTRAPARTICLE KINETICS RESISTANCE

In earlier work, XRD was utilized for chemical analysis of iron pyrite and its combustion products [1]. Samples containing pyrite (FeS_2), pyrrhotite (Fe_{1-x}S), wustite (FeO), magnetite (Fe_3O_4), and hematite (Fe_2O_3) were utilized to establish calibration curves having pyrrhotite and magnetite as reference standards. When evaluated against samples of known compositions, these "intrinsic standard" calibration curves were typically of greater than 95% accuracy for concentrations as low as 5%. [For wustite, the scatter was too great for a calibration curve of acceptable accuracy to be calculated.]

In an XRD pattern, the intensity of diffracted X-rays ($\text{Cu K}\alpha$ in our case) is plotted versus 2θ , the diffraction angle. The positions and relative heights of intensity peaks identify specific minerals, and the absolute peak heights determine mass concentrations when referenced to calibration standards.

Three methods are conventionally used for quantitative XRD analysis: the external standard method, the direct comparison method, and the internal standard method. The external standard method uses the diffraction peak heights of a pure component as a reference and is suitable for only binary-phase mixtures. The direct comparison method relies on theoretically calculated reference peak heights. The internal standard method references with respect to peaks from a foreign material added in known quantities to the sample of interest. These conventional XRD quantitative methods are inherently unsuitable for the analysis of multiphase iron products of pyrite combustion, however. The external standard method and the direct comparison method are highly susceptible to changes in sample properties (such as grain size) and diffractometer settings. The internal standard method, on the other hand, often suffers from irresolvable peak overlap introduced by the addition of the internal standard.

To overcome the limitations of the conventional quantitative schemes, an intrinsic standard method was developed in earlier work [1]. In this method, the diffraction peak of a mixture component is used as the reference. The concentration of each of the other phases in the mixture is determined relative to that of the reference constituent using an empirical calibration curve. The concentration of the reference constituent is obtained by difference.

The objective of this quarter's effort was to verify and, if necessary, modify this procedure to obtain a widely applicable XRD data reduction scheme. After a theoretical analysis was rendered, laboratory characterizations were performed. First, the calibration curves developed in the earlier work were evaluated using new samples prepared and analyzed on a Philips XRD facility instead of the previously used Huber XRD facility. Second, the impact of the overlap of magnetite and pyrrhotite diffraction peaks was investigated. Third, a quantitative scheme based on peak area instead of peak height was explored. Fourth, a calibration scheme for determining the wustite content of samples was sought.

1.1 Evaluation of Calibration Curves

In earlier work, intrinsic standard calibration curves were established for quantitative analysis of condensed phase products of pyrite combustion [1]. Samples containing uncorrelated amounts of pyrite, pyrrhotite, wustite, magnetite, and hematite were utilized to establish calibration curves having pyrrhotite and magnetite as reference standards. These sample constituents were selected because (based largely on equilibrium considerations) the major expected products of pyrite combustion are pyrrhotite and magnetite as well as pyrite, wustite, and hematite to a lesser extent [2]. Pyrrhotite and magnetite were specified as the reference species because at least one of these two species is always expected to be present in the product mixture.

Calibration curves for pyrite, pyrrhotite, magnetite, and hematite are shown in Figure 1.1. These curves are graphed on log axes to facilitate the perception of their accuracy over a wide range of concentrations. The three solid curves represent calibrations with respect to pyrrhotite, whereas the three dotted curves are based on a magnetite reference standard. Each of these calibration curves possesses a linear correlation coefficient that supersedes 99%.

Intensity versus concentration data previously obtained for wustite are shown in Figure 1.2. The open circles are data normalized with respect to pyrrhotite, and the filled squares use a magnetite reference. The correlation is not as good as it is for the other species, even over the reduced range of concentrations. Thus, a calibration curve had not been established from this data.

Figure 1.1 Intrinsic standard calibration curves for X-ray diffraction analysis of pyrite derivatives. Shown are curves for pyrrhotite (square), pyrite (triangle), hematite (circle), and magnetite (diamond) relative to pyrrhotite (solid curves) and magnetite (dotted curves).

Figure 1.2 Wustite concentration versus X-ray diffraction intensity, normalized with respect to pyrrhotite (circle) and magnetite (square).

1.1.1 Theoretical Basis of Intrinsic Standard Method

During the current quarter, a theoretical basis for an intrinsic standard calibration was established. The starting point for deriving the theoretical basis was the equation for the X-ray diffraction intensity of a polycrystalline material. From Bish and Howard [3], $I_{\alpha,hkl}$, the integrated diffraction intensity from the hkl plane of constituent α , is given by

$$I_{\alpha,hkl} = \frac{1}{2\mu_m} KR_{\alpha,hkl} C_{\alpha}$$

with

$$K = \left[\frac{I_0 A \lambda^3}{32 \pi r} \right] \left[\frac{\mu_0 e^2}{4 \pi m} \right]^2$$

and

$$R_{hkl} = \left[\frac{1}{V^2} \right] \left[|F|^2 p \left(\frac{1 + \cos^2 2\theta \cos^2 2\theta_m}{\sin^2 \theta \cos \theta} \right) e^{-2M} \right]_{hkl},$$

where μ_m is the linear absorption coefficient of the mixture, K is a factor dependent only on diffractometer conditions, R is a factor dependent on the material properties of the sample (and the diffraction angle of any diffracted-beam monochromator used), and C_{α} is the volume fraction of phase α . Also, I_0 is the intensity of the incident beam, A is the cross-sectional area of the incident beam, λ is the wavelength of the incident beam, r is the radius of the diffractometer circle, μ_0 is the permeability of free space, e is the charge of an electron, m is the mass of an electron, V is the volume of a unit cell, F is the structure factor, p is the multiplicity factor, θ is the Bragg angle, and θ_m is the diffraction angle of the diffracted-beam monochromator crystal.

When normalized to the intensity from the $h_2 k_2 l_2$ plane of the reference constituent ($I_{R,h_2 k_2 l_2}$), the intensity from the hkl plane of constituent α ($I_{\alpha,hkl}$), becomes

$$\frac{I_{\alpha,hkl}}{I_{R,h_2 k_2 l_2}} = \frac{\left[\frac{1}{V^2} |F|^2 p \left(\frac{1 + \cos^2 2\theta \cos^2 2\theta_m}{\sin^2 \theta \cos \theta} \right) e^{-2M} \right]_{\alpha,hkl} \frac{\rho_R W_{\alpha}}{\rho_{\alpha} W_R}}{\left[\frac{1}{V^2} |F|^2 p \left(\frac{1 + \cos^2 2\theta \cos^2 2\theta_m}{\sin^2 \theta \cos \theta} \right) e^{-2M} \right]_{R,h_2 k_2 l_2}}$$

where ρ is density and W is weight fraction. The normalized intensity is, theoretically, independent of diffractometer parameters (if no diffracted-beam monochromator is used or if the monochromator diffraction angle is 0°) and is linearly proportional to the normalized mass concentrations. Nevertheless, because of possible differences in incident beam wavelength, extent of drift in incident beam strength during an analysis, diffracted-beam monochromator angle, and detector response, the normalized intensities may vary slightly with XRD diffraction facility. Consequently, it is useful to empirically verify the numerical value of the normalized intensities each time a new XRD facility is used.

1.1.2 X-Ray Diffraction Measurements

During this reporting period, the intrinsic standard calibration curves were evaluated against 100 mg mixtures that contained known amounts of pyrite, pyrrhotite, magnetite, and wustite. The mixtures were prepared to cover the range of estimated compositions of pyrite oxidation products observed to date in the pyrite oxidation project. They were subjected to less grinding than previous calibration standards [1] and analyzed on a different type of diffraction facility. A diffractometer manufactured by Philips was utilized, and it produces XRD patterns of a much lower signal-to-noise ratio than the one used previously, manufactured by Huber. [Consequently, the Philips was run without the signal-depressing monochromator that had been positioned at a diffraction angle (θ_m) of 13.3° to filter out iron fluorescence in the Huber.] The obtained diffraction patterns were analyzed for baseline and peak height with different software from that used previously.

Shown in Figures 1.3 to 1.6 are the XRD patterns of the four samples prepared. To reduce the XRD analysis time, but still scan the relevant diffraction peaks and also produce a discernible background, the XRD patterns were specified to span a range of 2θ from 41° to 49° (as opposed to the previous range of 38° to 51°). Figures 1.3 and 1.4, the XRD patterns of Samples 1 and 2, respectively, exhibit peaks from all three constituents of those particular samples: pyrite, pyrrhotite, and wustite. Figure 1.5, the XRD pattern of Sample 3 accurately reflects the presence of pyrrhotite, wustite, and magnetite as the sample's components. Figure 1.6 contains the peaks of pyrite, pyrrhotite, and wustite (the magnetite peak is not resolvable), which were among the constituents of Sample 4. In each figure, cursors mark the most significant peaks identified by the PEAK SEARCH program of the Philips diffractometer's PC-APD software (described below).

Figure 1.3 X-ray diffraction pattern of calibration standard Sample 1, containing pyrite (FeS_2 ; P), pyrrhotite (Fe_{1-x}S ; Ph), and wustite (FeO ; W).

Figure 1.4 X-ray diffraction pattern of calibration standard Sample 2, containing pyrite (FeS_2 ; P), pyrrhotite (Fe_{1-x}S ; Ph), and wustite (FeO ; W).

Figure 1.5 X-ray diffraction pattern of calibration standard Sample 3, containing pyrrhotite (Fe_{1-x}S ; Ph), wustite (FeO ; W), and magnetite (Fe_3O_4 ; M).

Figure 1.6 X-ray diffraction pattern of calibration standard Sample 4, containing pyrite (FeS_2 ; P), pyrrhotite (Fe_{1-x}S ; Ph), wustite (FeO ; W), and magnetite (Fe_3O_4 ; M).

The PEAK SEARCH program was used to obtain diffraction intensities from the XRD patterns in Figures 1.3 to 1.6. The program locates the peaks in an XRD pattern by detecting the minima from the second derivative of the diffractogram [4]. Output from the program includes background intensities, peak locations, net peak heights, and peak widths.

For each sample, the diffraction intensity of each constituent was normalized with respect to the pyrrhotite intensity and used in the calibration curves previously determined. Shown in Table 1.1 is a comparison of inferred versus actual concentrations of Samples 1 to 4 using calibration curves for pyrrhotite as the reference constituent. In calculating the tabulated concentrations of pyrite, pyrrhotite, and magnetite, the actual value of the wustite concentration was used. Errors in inferred concentrations are less than 1% absolute when the pyrrhotite content is greater than approximately 15 wt%. At lower pyrrhotite concentrations, the absolute errors in concentration rise to the 2 - 7% range.

Table 1.1 Inferred Compositions of non-Wustite Component of Mixtures Using
Intrinsic Standard Calibration Curves

Sample ID.	<u>Pyrite (wt%)</u>		<u>Pyrrhotite (wt%)</u>		<u>Magnetite(wt%)</u>	
	<u>Actual</u>	<u>Inferred</u>	<u>Actual</u>	<u>Inferred</u>	<u>Actual</u>	<u>Inferred</u>
1	38.1	37.2	26.6	27.5	0	0
2	20.6	21.2	45.3	44.7	0	0
3	0	0	11.7	14.0	73.0	68.7
4	83.9	76.5	7.0	11.0	4.6	8.0

The errors at low pyrrhotite levels are primarily due to errors in the inferred pyrrhotite content. This raises the possibility that these errors are merely an artifact of incomplete blending of constituents during the preparation of the synthetic mixtures. Such species segregation is not

expected to be encountered when pyrite combustion products are analyzed, however. The comparison suggests that the calibration curves derived in previous work produce acceptable results for most situations of interest.

It should be noted that the mixture labeled Sample 4 in Table 1.1 was prepared to possess a higher pyrite-magnetite ratio than that spanned by the existing calibration curve. For Sample 4, the pyrite-magnetite concentration ratio was specified at 18.07, and this concentration ratio yielded an intensity ratio of 10.19. The existing curve was bounded by a pyrite-magnetite concentration ratio of 1.28 and an intensity ratio of 1.62. The measurement of Sample 4 was coupled with a previously unused datum from earlier work (concentration ratio of 3.026 and intensity ratio of 3.724) to generate a new calibration curve. The new calibration curve for pyrite referenced to be used for intensity ratios greater than 1.62.

1.2 Magnetite-Pyrrhotite Peak Overlap

The impact of overlap of the peaks of the two calibration reference species pyrrhotite and magnetite was investigated. The two peaks slightly overlap due to instrument broadening associated with the widening of diffractometer slits on the Philips XRD facility. The overlap could conceivably become significant when the selected reference peak is much less than the other reference peak. For instance, the pyrite-pyrrhotite intensity ratio decreases if the magnetite content is increased, due to overlap of the magnetite and pyrrhotite peaks. Thus, the overlap induces a scatter when the amounts of non-reference sample constituents are inferred.

A scheme was developed for resolving the pyrrhotite and magnetite peaks from each other. Recall, Figure 1.5 is the XRD pattern of a mixture containing pyrrhotite, wustite, and magnetite. Overlap of the pyrrhotite and magnetite peaks is evident; hence, the apparent peak height of each species is greater than the true peak height.

A peak at position $(2\theta)_0$ of height I_0 having an arbitrary lineshape

$$f[2\theta - (2\theta)_0]$$

imparts a fraction of its peak height α to the intensity at position $(2\theta)_1$. In mathematical terms,

$$\alpha I_0 = I_0 f[(2\theta)_1 - (2\theta)_0].$$

If it is assumed that the two overlapping peaks have the same lineshape, the apparent peak height at $(2\theta)_1$, I'_1 , is related to the two true peak heights (I_0 and I_1) by the following relation:

$$I'_1 = I_1 + \alpha I_0.$$

With such an equation for each of the two overlapping peaks, the solution for the true peak height at position $(2\theta)_1$ is

$$I_1 = \frac{I'_1 - \alpha I'_0}{1 - \alpha^2}.$$

Determination of the extent of overlap exclusively from theory requires knowledge of the lineshape of each peak (for instance, Gaussian or Cauchy). In the absence of the functional forms of the line shapes of the pyrrhotite and magnetite peaks, an empirical determination of the extent of peak overlap was embarked upon. To determine α , the fraction of the pyrrhotite peak that is contributed to the signal level at the diffraction angle of magnetite, two samples containing pyrrhotite but no magnetite were analyzed by XRD. The obtained values of α were 14.9% and 17.9%, and α was assigned the average value, 16.4%. Thus the true pyrrhotite and magnetite levels were determined to be the following:

$$I_{pyrrhotite,true} = 1.028 I_{pyrrhotite,apparent} - 0.1685 I_{magnetite,apparent}$$

$$I_{magnetite,true} = 1.028 I_{magnetite,apparent} - 0.1685 I_{pyrrhotite,apparent}$$

The XRD intensities of Samples 3 and 4 were recalculated using the above formulas to obtain true peak heights. Shown in Table 1.2 are the compositions inferred by applying the true peak heights in the calibration curves. For comparison, also shown are compositions obtained by using the apparent peak heights. The use of true peak height reduces the errors for Sample 3 by approximately 2 wt% absolute, but does not improve Sample 4's analysis as consistently. In fact, Sample 4's inferred magnetite concentration becomes close to nil due to the use of true heights.

Table 1.2 Comparison of Inferred Compositions of non-Wustite Component of Mixtures Using True and Apparent Peak Heights in Intrinsic Standard Calibration Curves

<u>Species</u>	<u>Measurement</u>	<u>Composition (wt%)</u>	
		<u>(Sample 3)</u>	<u>(Sample 4)</u>
Pyrite	Actual	0	83.9
	Apparent Peak Height	0	76.5
	True Peak Height	0	82.2
Pyrrhotite	Actual	11.7	7.0
	Apparent Peak Height	14.0	11.0
	True Peak Height	12.0	11.6
Magnetite	Actual	73.0	4.6
	Apparent Peak Height	68.7	8.0
	True Peak Height	70.7	1.7

Basically, no conclusion could be drawn regarding any significant gains from the utilization of true peak heights. The marginal improvements obtained for most of the constituents would tend to favor the use of true peak heights. The poor result that the true peak height yielded for Sample 4's magnetite content could be attributed to the low magnetite signal level in that sample. In any case, use of true peak height does not greatly improve the already reasonable calculation of compositions. This may be due to the fact that in the establishment of the calibration curves, the pyrrhotite-magnetite peak overlap was close enough to the overlap observed with the current project's diffractometer facility. It was determined that the gains had not been demonstrated to justify the potential losses at low magnetite levels associated with the use of true peak heights.

1.3 Peak Broadening

The XRD patterns obtained thus far in the pyrite oxidation project have occasionally contained broad peaks, as reacting pyrite particles sometimes experience softening transformations. When the crystallite size of a sample constituent falls below 0.2 μm , the XRD peak height decreases and peak width increases, while peak area is preserved. Since in the previous work calibration curves were based on peak height, an effective peak height had to be defined to account for peak broadening in pyrite samples subjected to combustion.

The effective peak height is easily defined by invoking peak area conservation principles. If the standard conditions of a species are defined as the conditions (including extent of melting) that the species experiences during the preparation and analysis of a calibration standard, its peak area, A_{std} , is then expressed as

$$A_{std} \equiv (\Delta 2\theta)_{std} I_{std} ,$$

where $\Delta 2\theta$ and I are peak width and peak height, respectively, and subscript *std* refers to standard conditions. If the peak is broadened by constituent softening, its area is preserved and the following relation is observed:

$$(\Delta 2\theta)I = A = A_{std} \equiv (\Delta 2\theta)_{std} I_{std} .$$

Thus the effective peak height, the height that would be measured under standard conditions, is

$$I_{std} = \frac{\Delta 2\theta}{(\Delta 2\theta)_{std}} I .$$

The only remaining issue is the definition of standard peak widths for the desired diffractometer settings. [The reaction product analysis must then be performed at the same diffractometer settings to ensure that peaks are not changed by narrowing slit widths, etc.]

The assignment of standard peak widths was attempted using the PEAK SEARCH program on the XRD patterns of Samples 1 - 4. Listed in Table 1.3 are the peak widths obtained. Some of the peaks could not be identified by the program (even after numerous perturbations of program parameters) due to the low values of net peak heights. Even those peaks that were identified were not completely reproducible in their widths. The variability in peak widths was attributed to a combination of inherent pattern smoothening errors and width round-off errors. The round-off errors stem from the 0.1° resolution of the peak widths.

Table 1.3 X-Ray Diffraction Peak Widths (in Degrees 2θ) of Mixture Components Obtained Using PEAK SEARCH Program

Sample ID.	<u>Pyrite</u>	<u>Pyrrhotite</u>	<u>Wustite</u>	<u>Magnetite</u>
1	0.3	0.4	0.3	Not Applicable
2	0.3	0.4	0.4	Not Applicable
3	Not Applicable	Undetected	0.4	0.2
4	0.4	0.4	0.3	Undetected

A more sophisticated peak fitting program in the Philips PC-APD software package was used to recalculate peak widths from the diffraction patterns of Samples 1 - 4. PROFILE FIT is a program that is claimed to render accurate determination of background, peak position, peak intensity, and peak width [4]. The program utilizes a model that employs twelve parameters to fit each peak in a diffraction pattern, based on user-supplied initial estimates of peak positions and heights. The fit is performed using a Marquardt non-linear least squares algorithm and terminates when the difference in the Chi-square values of successive iterations becomes less than 0.001. Program outputs include positions, heights, and widths for up to eight peaks.

The XRD patterns for Samples 1 - 4 were analyzed with PROFILE FIT, and it was discovered that the results were sensitive to the initial estimates in peak positions and background shape. For instance, when Sample 1's XRD pattern was analyzed, differences in the initial estimates of the pyrite peak position had a dramatic effect on the final result for the pyrite peak. In one case, the pyrite peak location and width were 46.975° and 0.0417°, respectively, and in another attempt, the location and width were 47.103° and 0.211°, respectively. Similarly, a 10% increase in the initial background estimate caused a clearly visible peak to disappear from the fitted pattern. Consequently, it was determined that to use PROFILE FIT, the PEAK SEARCH program must first be used to provide initial estimates of peak locations.

Shown in Table 1.4 are the peak widths generated by PROFILE FIT, in comparison with widths previously supplied by PEAK SEARCH. The peak widths from PROFILE FIT and PEAK SEARCH are labeled "A" and "B", respectively. Sample 3's pyrrhotite and Sample 4's magnetite peaks were undetected by the PEAK SEARCH program. For those two peaks, the initial estimates used in PROFILE FIT were obtained by inspection of the raw data file. In general, the data in Table 1.4 indicates that the variability in the new set of peak widths obtained from PROFILE FIT is much greater. Such failure of available peak area-fitting software to provide consistent results had prompted the use of XRD instead of Mossbauer analysis and the foundation of the XRD scheme on peak heights rather than peak areas.

Table 1.4 Comparison of X-Ray Diffraction Peak Widths (in Degrees 2 θ) of Mixture Components Obtained Using PROFILE FIT (A) versus PEAK SEARCH (B)

Sample ID.	<u>Pyrite</u>		<u>Pyrrhotite</u>		<u>Wustite</u>		<u>Magnetite</u>	
	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>
1	0.211	0.3	0.484	0.4	0.390	0.3	N/A*	N/A
2	0.280	0.3	0.429	0.4	0.060	0.4	N/A	N/A
3	N/A	N/A	2.809	U**	0.412	0.4	0.546	0.2
4	0.302	0.4	0.558	0.4	0.247	0.3	0.035	U

* N/A signifies not applicable

** U signifies undetected by program

It was concluded that the peak widths generated by PEAK SEARCH constituted a more reliable basis for a calibration scheme than those generated by PROFILE FIT. The peak width values listed in Table 1.3 were averaged for each species, except magnetite, and adopted as the standard widths for the sample analysis conditions of the project. For magnetite, since only one peak width value was available, inspection of the raw data file for Sample 3 was performed to determine the full width at half maximum. Because of peak asymmetry (see Figure 1.5), values of 0.105 and 0.255 were obtained for the left and right half-widths, respectively. The hand-calculated right half-width was judged to be in error, due to the influence of the adjacent pyrrhotite peak. The accepted standard peak widths are presented in Table 1.5.

Table 1.5 Standard X-Ray Diffraction Peak Widths (in Degrees 2θ)
Using PEAK SEARCH

<u>Species</u>	<u>Peak Width</u>
Pyrite	0.333
Pyrrhotite	0.400
Wustite	0.350
Magnetite	0.210

1.4 Wustite Calibration

The XRD patterns of pyrite combustion products obtained thus far in the pyrite oxidation project have exhibited relatively large wustite peaks [5]. Wustite has been shown to constitute a reaction intermediate in the transformation of pyrite to magnetite. In order to meet the objectives of this project, a calibration curve for determining the wustite content of pyrite reaction products was sought.

The first attempt to establish a wustite calibration curve consisted of subjecting previously obtained wustite data to least squares fit, and determining if, despite the scatter, the wustite content of Samples 1 - 4 could be reasonably predicted. A linear least squares fit of normalized concentrations versus normalized intensities was performed. Shown in Figure 1.7 is a plot of the data for both the pyrrhotite (circle) and magnetite (square) reference. The resulting equations for concentration (c) as a function of intensity (I) were, for wustite referenced to pyrrhotite,

$$0.0121 + 1.75I \quad 0.0604 < I < 0.7846$$

$$0.0695 < c < 1.4242,$$

and for wustite referenced to magnetite,

$$0.0500 + 0.433I \quad 0.1109 < I < 0.8648$$

$$0.0617 < c < 0.5000.$$

Figure 1.7 Linear least-squares fit of previously obtained wustite data.

Table 1.6 contains the inferred wustite content of Samples 1 - 4 obtained from the preceding pyrrhotite-referenced calibration curve. Although the pyrrhotite-referenced wustite intensity value of Sample 1, 1.03, lay beyond the 0.78 maximum value of the preceding curve, the curve was used nonetheless. Existing intrinsic standard calibration curves were used to calculate the concentrations of the other species in the table: pyrite, pyrrhotite, and magnetite. Peak heights used to evaluate the calibration curves were those obtained from the simple PEAK SEARCH program. In general, the inferred wustite concentration exhibits remarkably good agreement with the true concentration. Absolute errors in calculated wustite content range from 0.1 wt% to 0.9 wt%, except for that of Sample 1, which is 8.3%. Errors in the concentrations of the other species are generally within reasonable ranges. Not tabulated are compositions obtained using the magnetite reference, and these were as accurate as those generated from the pyrrhotite reference.

Table 1.6 Inferred Compositions of Mixtures Using Intrinsic Standard Calibration Curves and Least Squares Fit of Previous Wustite Data

Sample ID.	<u>Wustite (wt%)</u>		<u>Pyrite (wt%)</u>		<u>Pyrrhotite (wt%)</u>		<u>Magnetite (wt%)</u>	
	<u>Actual</u>	<u>Inferred</u>	<u>Actual</u>	<u>Inferred</u>	<u>Actual</u>	<u>Inferred</u>	<u>Actual</u>	<u>Inferred</u>
1	35.2	43.5	38.1	32.5	26.6	24.0	0	0
2	34.1	33.2	20.6	21.5	45.3	45.3	0	0
3	17.3	17.4	0	0	11.7	14.0	73.0	68.6
4	4.5	4.6	83.9	76.5	7.0	11.0	4.6	8.0

Due to the great error in the calculated wustite content of Sample 1, an alternative calibration curve was sought. It was hypothesized that wustite was especially sensitive to sample preparation and that a more careful repetition of the calibration procedure was required. Consequently, peak height data from Samples 1 - 4 were used to establish new calibration curves

for wustite, referenced to pyrrhotite and magnetite. Shown in Figure 1.8 is a plot of the two calibration curves, along with the data used to generate the curves. The circles and squares represent data normalized to pyrrhotite and wustite, respectively. The pyrrhotite-referenced data exhibits much greater scatter than desired, but the magnetite-referenced data is difficult to assess due to its paucity. The calibration equations were, for wustite referenced to pyrrhotite,

$$0.475 + 1.09I \quad 0.2311 < I < 1.0302$$

$$0.6433 < c < 1.7815,$$

and, for wustite referenced to magnetite,

$$-0.528 + 1.59I \quad 0.4824 < I < 0.9424$$

$$0.2372 < c < 0.9670.$$

Figure 1.8 Linear least-squares fit of new wustite data.

The wustite calibration curves of Figure 1.8 were combined with the calibration curves for pyrite, pyrrhotite, and magnetite, and used to calculate the compositions of Samples 1 - 4. The calculated weight fractions are tabulated in Table 1.7. The new wustite curve is seen to reduce the absolute error in Sample 1's wustite concentration from 8.3 wt% (see Table 1.5) to 5.3 wt%. On the other hand, the new curve is observed to increase Sample 4's error from 0.1 wt% to 3.2 wt%. It was evident that the new wustite curve produced mixed results. Nevertheless, the magnitude of errors observed were determined to be unacceptable, considering that the samples being tested were the ones used to generate the calibration curves.

Table 1.7 Inferred Compositions of Mixtures Using Intrinsic Standard Calibration Curves and Least Squares Fit of New Wustite Data

Sample ID.	<u>Wustite (wt%)</u>		<u>Pyrite (wt%)</u>		<u>Pyrrhotite(wt%)</u>		<u>Magnetite (wt%)</u>	
	<u>Actual</u>	<u>Inferred</u>	<u>Actual</u>	<u>Inferred</u>	<u>Actual</u>	<u>Inferred</u>	<u>Actual</u>	<u>Inferred</u>
1	35.2	40.5	38.1	34.2	26.6	25.3	0	0
2	34.1	38.6	20.6	19.8	45.3	41.6	0	0
3	17.3	17.4	0	0	11.7	14.0	73.0	68.6
4	4.5	7.7	83.9	74.0	7.0	10.6	4.6	7.7

In general, the fit of the old wustite calibration data leads to a more reliable determination of sample composition. The errors in Sample 1 are due to the fact that the old calibration data were being linearly extrapolated. Consequently, for pyrrhotite-referenced wustite intensities beyond approximately 0.75, the new wustite calibration curve should be used.

1.5 Final Calibration Scheme

A final calibration scheme was derived by combining the results of the previous sections. XRD scans are to be taken from 2θ angle of 41° to 49° . Peaks are identified on the resulting diffraction pattern using the PEAK SEARCH program of the PC-APD software. Output peak heights are width-compensated by using the standard widths to calculate effective heights. These standard heights are used as inputs in the intrinsic standard calibration curves previously determined. For high wustite levels, the new wustite calibration curve should be used.

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. Following is a description of the planned activities for the July 1 to September 30, 1995 reporting period:

Task 2: Pyrite Intraparticle Kinetics Resistance

- The samples of pyrite combustion products collected thus far will be subjected to quantitative X-ray diffraction analysis, and intraparticle reaction resistance will be calculated from the data.

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