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Mechanisms of Pyrite Oxidation to Non-Slagging Species

**Quarterly Report
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**By:
A.E. Jacob Akan-Etuk
Reginald E. Mitchell**

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U.S. Department of Energy
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Federal Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

RECEIVED

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By
Stanford University
High Temperature Gasdynamics Laboratory
Mechanical Engineering Department
Stanford, California 94305

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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

Phone: 415-725-2015

RESEARCH OBJECTIVES

This document is the tenth 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 October 1 to December 31, 1996. Numerical encoding of a pyrite combustion model was embarked upon. The effort was intended to lead to predictive capabilities with respect to pyrite composition during pulverized coal firing.

Many subroutines were written of a FORTRAN computer program to track the fate of a pyrite particle by integrating time-dependent differential equations for species, momentum, and energy conservation. Inputs to the program include fuel-related properties such as particle size and composition, as well as properties of the reactor environment such as oxygen level, temperature, gas velocity, and a set of initial and final positions. With some of the program inputs used as initial conditions, the pyrite particle's differential equations of species, momentum, and energy conservation are integrated with respect to time using ODERT, a Runge-Kutta variable-step ODE solver. Each time ODERT has integrated to a specified terminal position, an output is generated comprising particle composition, size, and temperature.

The encoding of the computer program is still ongoing. Subsequent debugging should be facilitated by the modular nature of the program structure.

FINDINGS

In the current research program, time-resolved phase identifications of extraneous pyrite combustion products have been used to determine a pyrite oxidation pathway [1] different from that contained in the prevailing model of pyrite combustion, Srinivasachar and Boni's [2]. Tests at 1550 K gas temperature and 1% oxygen level indicate that, after transient thermal decomposition to form $\text{Fe}_{0.877}\text{S}$, pyrite oxidizes through the pathway

with no evidence of significant fragmentation. The results of this research program were used to update the model framework of Srinivasachar and Boni and formulate a new model [3].

This quarter, numerical encoding of a pyrite combustion model was embarked upon. The effort was intended to lead to predictive capabilities with respect to pyrite composition during pulverized coal firing. The activity fell under the auspices of Task 6 of the research program.

1.0 TASK 6 RATE EXPRESSION FORMULATION AND VALIDATION

1.1 Results

The main objective of the effort was to write a computer program that would lead to predictive capabilities with respect to pyrite composition during pulverized coal firing. Numerical encoding of a pyrite combustion model was embarked upon in the FORTRAN programming language.

Many subroutines were written to track the fate of a pyrite particle by integrating time-dependent differential equations for species, momentum, and energy conservation. At all times, rate of change of each intraparticle species is obtained by explicitly accounting for reaction rate resistances associated with reaction kinetics as well as mass transport. The particle trajectory for a vertically moving particle is provided by solving for the momentum balance between the gravitational and drag forces acting on the particle. The particle vertical position is obtained by integrating particle velocity with respect to time. Instantaneous particle temperature is obtained by ascribing rate of change of particle temperature to the net effect of chemical reaction, convection, and radiation.

Inputs to the program are user-specified to be either by file or by hand. These inputs include fuel-related properties such as particle size and composition. Also included are properties of the reactor environment such as oxygen level, temperature, gas velocity, and a set of initial and final positions.

With some of the program inputs used as initial conditions, the pyrite particle's differential equations of species, momentum, and energy conservation are integrated with respect to time using ODERT, a Runge-Kutta variable-step ODE solver developed by Gordon [4]. The subroutine ODERT integrates from an initial time, t_i , to a final time, t_f . ODERT calls on other subroutines to advance the solution and to interpolate the solution and its derivative. To advance the solution, a divided difference formula, along with local extrapolation is used. The order and step size are adjusted to control the local error per unit step. After each step, another subroutine is used to

check that the particle position has not reached the current terminal position in the reactor. If the particle position reaches the specified terminal position before the time equals t_f , the integration is completed for that position.

Each time ODERT has integrated to a specified terminal position, an output is generated. The output includes particle composition, size, and temperature.

1.2 Conclusions

The encoding of the computer program is still ongoing. Subsequent debugging should be facilitated by the modular nature of the program structure.

PLANS FOR NEXT QUARTER

Next quarter's emphasis will be placed on completing the numerical encoding of the pyrite combustion model and 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 January 1 to March 31, 1997 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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