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MECHANISMS OF PYRITE OXIDATION TO NON-SLAGGING SPECIES

Quarterly Report for the Period

October 1, 1995 - December 31, 1995

Grant DE-FG22-94PC94205

Prepared for

THE UNITED STATES DEPARTMENT OF ENERGY

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

Submitted by

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

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

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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 sixth 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, 1995. During the quarter, an effort was launched to experimentally determine the impact of a carbon matrix on the oxidation of pyrite inclusions. Kinetics effects and mass transfer effects were separately investigated using model coals of different porosities. Operating regimes that highlight each of the preceding two classes of carbon matrix effects were sought.

Synthetic, model coal of 75 - 125 μm size class was oxidized in a flow reactor at 1500 K and 12% oxygen. For each of the two porosities of coal burned, char was recovered at 25 ms, 63 ms, and 109 ms. The chars were subjected to gravimetry to determine the extent of mass burnoff. In addition, the particle size distributions of the chars were measured with a Coulter Multisizer.

A 36%-porosity (20% macroporosity) model coal was used to determine the minimum porosity compatible with carbon matrix kinetics control of available oxygen. The fractional mass remaining was 0.41 at 25 ms, 0.20 at 63 ms, and 0.21 at 109 ms. The size distributions exhibited features consistent with fragmentation at 25 ms, burning at 63 ms, and extinction at 109 ms. For the 36%-porosity char, normalized instantaneous mass was proportional to the 7th power of normalized instantaneous particle diameter. [The power is 3 and ∞ for burning at constant density and constant diameter, respectively.]

Similarly, a 23%-porosity (7% macroporosity) model coal was used to determine the maximum porosity compatible with carbon matrix mass transfer control of available oxygen. The fractional mass remaining for this coal was 0.71 at 25 ms, 0.21 at 63 ms, and 0.19 at 109 ms. The size distributions exhibited features consistent with fragmentation at 25 ms, burning at 63 ms, and greatly reduced burning at 109 ms. Normalized instantaneous mass was proportional to normalized instantaneous particle diameter raised to a power of 4.3.

The finite powers of the mass-diameter correlations indicate that, in 12% oxygen at 1500 K, oxygen does not fully penetrate carbon particles of 75 - 125 μm size class. Since the carbon burns much more slowly than pyrite particles of 20 μm diameter, even at a carbon porosity of 36%, mass transfer limitations would constitute the main mechanism of oxygen reduction by carbon matrix.

FINDINGS

In the prevailing model of pyrite combustion, pyrite oxidation occurs at a rate determined by pyrite kinetics and transport parameters [1]. The formulators of the model note that during pulverized coal (P. C.) combustion, the embedding of pyrite in carbon retards pyrite oxidation. Nevertheless, the reaction impedance of a carbon matrix is not included in the model. The need for further study with respect to the effects of associated carbon is cited.

Stanford University's pyrite oxidation research program aims to quantify the impact of carbon matrix on pyrite transformation rates [2]. The occlusion of pyrite by carbon imposes a transport resistance to oxygen diffusion from the coal particle exterior to pyrite inclusions. Furthermore, the reaction of diffusing oxygen with carbon depletes the oxygen available for pyrite conversion. In the current research program, these kinetics and mass transfer effects of the carbon matrix are distinguished from the reactivity of pyrite inclusions (as well as from one another).

Thus far, extraneous pyrite has been oxidized to evaluate pyrite reactivity [3, 4]. Time-resolved compositions of pyrite burning at 1500 K have been obtained for a wide range of oxygen levels [5]. For 20 μm pyrite particles burning at 1500 K and 12% oxygen, 89 wt% conversion is attained in 25 ms, in the absence of carbon.

This quarter, an effort to experimentally determine the impact of the carbon matrix was launched. Activity covered three tasks, as kinetics effects (Task 4) and mass transfer effects (Task 5) were separately investigated using model coals (Task 1). Operating regimes that highlight each of these two classes of carbon matrix effects were sought.

1.0 TASK 1: PRODUCTION AND CHARACTERIZATION OF PYRITE FEEDS

The aim of the work performed in this task was to obtain feed materials that amplify the impedances that a carbon matrix imposes on the oxidation of pyrite inclusions. During pulverized coal (P. C.) combustion, oxygen diffuses from a coal particle's surface to the interior. As it diffuses, the oxygen reacts with the coal's carbon matrix. Concurrently, the oxygen reacts with each pyrite inclusion at a rate prescribed by the pyrite reactivity at the local oxygen level.

Oxygen pore diffusion through the carbon matrix becomes the predominant retardant of pyrite oxidation (relative to carbon matrix kinetics and pyrite reactivity) at small pyrite particle size, large coal particle size, and low coal porosity. Carbon oxidation kinetics becomes more rate-controlling at high temperature, small pyrite particle size, small coal particle size, and high coal porosity.

The initial emphasis of the carbon matrix studies was placed on varying coal porosity to switch between carbon matrix kinetics and mass transfer control of pyrite oxidation. The goal was to establish the minimum and maximum coal porosities required for carbon matrix kinetics and mass transfer, respectively, to become rate-controlling. To achieve this goal, homogeneous feed materials are required.

Due to their high degree of intraparticle and interparticle homogeneity, the feed materials selected for the studies consisted of synthetic, model coals. Various investigators such as Senior and Flagan [6] as well as Erickson *et. al.* [7] have established model coals as powerful modeling tools in the investigation of ash transformations. Model coals constitute powerful modeling tools because their mineral matter system, pore structure, and other morphological and chemical characteristics can be precisely defined to facilitate the study of specific issues of interest. Currently, the issue of interest is the impact of coal matrix reduction of available oxygen on the oxidation rate of pyrite inclusions. The objective is not to obtain a numerical rate that will be applied directly without modification to natural coals. Instead, the objective is to formulate an expression for predicting the combustion rate of pyrite-rich fractions when the coal's reactivity, porosity, and particle size are specified.

Because of the great labor required to produce sizable batches of pyrite-containing model coals, the initial combustion experiments were performed using mineral-free model coals. The model coals are produced from the polymerization of furfuryl alcohol with p-toluenesulfonic acid in water, following the procedures described by Senior and Flagan [6]. Carbon black particles (nominally 20 nm in diameter) added during the synthesis procedure form micropores by causing the carbonized furfuryl alcohol matrix to crack around the locations of the carbon black inclusions [8]. Akan-Etuk and Niksa [9] found that the addition of lycopodium plant spores produces monodisperse macropores (nominally 20 μm in diameter) when they vaporize during the thermal curing step of the synthesis procedure.

The model coals produced are ground and size-classified by wet sieving into the size ranges 76 - 89 μm , 90 - 106 μm , and 106 - 125 μm . The proximate and ultimate analyses of the model coal correspond to those of a low-volatile bituminous coal. Helium pycnometry is used to determine the true density of the carbonaceous material and mercury intrusion porosimetry combined with a tap density procedure [10] is used to determine apparent particle densities.

Figures 1.1 and 1.2 show model coal particles of 90-106 μm size class representing a broad range of porosities: 16% and 55%, respectively. For each char, the microporosity is 16%, and macrovoids constitute the remainder of the porosity. Hence, particles of 16% porosity (see Figure 1.1) have no large void volumes within them. The largest intraparticle pores for the 16% porosity chars are nominally 0.05 μm .

Figure 1.1 Secondary scanning electron micrograph of synthetic, model coal of 16% porosity (no macroporosity).

Figure 1.2 Secondary scanning electron micrograph of synthetic, model coal of 55% porosity (39% macroporosity).

2.0 TASK 4: CARBON MATRIX KINETICS EFFECTS

The aim of the work performed for Task 4 was to determine the operating regime that amplifies the impedance that the oxidation kinetics of a carbon matrix imposes on the oxidation of pyrite inclusions. Carbon oxidation kinetics becomes more rate-controlling at high temperature, small pyrite particle size, small coal particle size, and high coal porosity. In this case, the goal was to establish the minimum coal porosity required for carbon matrix kinetics to become rate-controlling of pyrite oxidation.

To determine if carbon matrix kinetics effects were more dominant than mass transfer limitations, changes in time-resolved particle mass and size were monitored. First, in the limit of infinite carbon matrix resistance, a coal particle burns as a shrinking core. In that case, fractional mass remaining (m/m_0) is proportional to the third power of the fraction initial particle diameter (d/d_0). On the other hand, if the carbon matrix offers no impedance to oxygen supply to inclusions, the coal particle burns at constant diameter. In this scenario, fractional mass remaining is proportional to the infinite power of the fraction initial particle diameter. Finally, in the case of size reduction by fragmentation only, the proportionality is to the zero power.

Moreover, when carbon matrix kinetics imposes a greater restriction on oxygen availability than carbon matrix mass transfer, the coal particle burns more quickly than pyrite does under the same conditions. For pyrite burning at 1500 K and 12% oxygen, 89 wt% conversion is attained in 25 ms [5].

2.1 Experimental

Materials

Mineral-free model coal was used for the experiments. The coal used was of 36% porosity (distributed as 16% microporosity and 20% macroporosity). Three different size classes were combined to yield a 75-125 μm size class.

Shown in Figure 2.1 is the cumulative number distribution of the coal feed obtained with the Coulter Multisizer (see description below). Approximately 15,000 particles were measured to derive the size distribution. The size distribution exhibits an initially steep increase in the 5.8 μm to 15 μm range. Subsequently, the distribution tapers off until approximately 75 μm , which corresponds to the lower bound of the sieves used to size-classify the coal. This point marks the beginning of the steepest portion of the size distribution curve as the cumulative number rises from 63% at 75 μm to 99% at 116 μm . For the size distribution in the figure, the number median diameter is 20 μm .

Figure 2.1 Initial cumulative number distribution of 36%-porosity model coal.

Flow Reactor

The coal was burned in the same entrained flow reactor used for oxidation of extraneous pyrite [3]. The flow reactor is similar in design to that used in coal char oxidation studies by Mitchell *et. al.* [10]. Pulverized fuel particles are fed by a syringe and entrained by a nitrogen stream into the base of a flat flame burner. The atmospheric-pressure comprises an array of

diffusion flamelets fueled by $\text{CH}_4\text{-H}_2\text{-O}_2\text{-N}_2$ mixtures that can be adjusted to provide homogeneous post-flame environments in the temperature range 1250 K to 2000 K. Oxygen concentrations can be adjusted from trace amounts (ppm level) to approximately 21 mole%. The entrained particles are injected along the reactor centerline, transported across the flame, and discharged into a test section at loadings that do not appreciably affect the post-flame temperature or oxygen concentration. The test section consists of a 5 x 5 cm square quartz chimney of 50 cm length that provides residence times of up to almost 200 ms.

At selected residence times, the reacting particles were extracted by a helium quench probe. The reactor enables sampling at various residence times, as the burner-test section assembly is movable in the vertical direction (while the sampling probe remains fixed). Once the extracted reaction products are quenched, they are transported to a filter assembly, where particulates are removed and gaseous products are passed to a moisture drop-out tube.

The reactor was operated to provide a combustion environment of 12% oxygen. The average centerline temperature was 1500 K. Partially reacted chars were extracted from the reactor at heights corresponding to residence times of 25 ms, 63 ms, and 109 ms.

Analysis

The partially reacted char particles were characterized for burnoff and particle size distributions. Burnoff was determined by measuring the mass of recovered char using a Mettler AE240 balance.

The size distributions of the chars were measured using the Coulter Multisizer. Essentially, the Multisizer consists of two electrodes (one of which lies within an orifice tube) immersed in an electrolyte through which a small current flows. The sample to be counted and sized is placed in the electrolyte, on one side of the orifice. When a particle passes through the orifice, the resistance between the electrodes momentarily increases, which induces a voltage pulse whose amplitude is proportional to the particle volume. The Multisizer calculates and reports the diameter of a sphere of equivalent volume to the particle.

For the measurements in this report, a 280 μm orifice tube was used, thereby providing a measurement range of 5.6 μm to 168 μm . In addition, the Multisizer was setup for 256 size bins, to yield a resolution of 1.4%. The sample size was approximately 20,000 particles per measurement (except for the distribution in Figure 2.1 that was derived from 15,000 particles).

2.2 Results

Three combustion tests, corresponding to three different residence times, were performed with the 36%-porosity coal. Upon injection into the reactor, a model coal particle devolatilizes and becomes engulfed by a luminous yellow flame at a height of approximately 1.9 cm (10 ms) in the test section. A few centimeters downstream (approximately 10 ms later), the flame recedes, and the model coal burns heterogeneously as a glowing orange particle. Between 10 cm and 25 cm height (60 ms to 100 ms), depending on the particle's size, the model coal begins to gradually extinguish.

Shown in Figures 2.2 to 2.4 are the cumulative number distributions of char captured after reaction for 25 ms, 63 ms, and 109 ms, respectively. In general, each size distribution exhibits three distinct zones: $-15\ \mu\text{m}$, $15 - 75\ \mu\text{m}$, and $+75\ \mu\text{m}$. The $-15\ \mu\text{m}$ portion of the distribution curve becomes monotonically steeper with time. Furthermore, the 99% point is reached at progressively lower particle sizes. There is an overall shift of particles to lower sizes as char oxidation progresses.

With respect to the size distribution of the coal feed, the size distribution at 25 ms (Figure 2.2) exhibits a great shift of particles from the $+75\ \mu\text{m}$ range to the $15 - 75\ \mu\text{m}$ range. [See Figure 2.1 for the size distribution of the coal feed.] The median size is 15 μm , as opposed to 20 μm for the coal feed. Since many particles extracted at this residence time (25 ms) were extracted during their devolatilization phase, it is plausible that the observed size shift was due to particle fragmentation associated with heatup and rapid evolution of volatiles. Further evidence to support this hypothesis is the fact that the macropores in the feed coal were approximately 20 μm , consequently the minimum fragment size generated from these macropores would be on the order of 20 μm . For this test, the fractional mass remaining was 0.41.

Figure 2.2 Cumulative number distribution of 36%-porosity model coal after reaction at 1500 K and 12% oxygen for 25 ms.

Figure 2.3 is the size distribution of char after 63 ms, and it reveals that continued burning depletes the $+75\ \mu\text{m}$ slightly, augments the $50 - 75\ \mu\text{m}$ subrange greatly, does not affect the $30 - 50\ \mu\text{m}$ subrange, depletes the $20 - 30\ \mu\text{m}$ subrange greatly, and augments the $-20\ \mu\text{m}$ range. The increased augmentation in the $15 - 75\ \mu\text{m}$ range with increasing diameter is consistent with Zone II or Zone III burning, in which the specific burning rate decreases with size. The augmentation of the fines could be due to a shift to constant diameter burning at small sizes, or extinction due to increased particle specific surface area available for cooling, or rapid preferential fragmentation. In this test, the median size was $14\ \mu\text{m}$, and the fractional mass remaining was 0.20.

As seen in Figure 2.4, the size distribution after 109 ms, there is a subtle change from the trend observed at 63 ms (Figure 2.3). While the $+75\ \mu\text{m}$ range continues to be depleted, the $-15\ \mu\text{m}$ range stabilizes and the $15 - 75\ \mu\text{m}$ range is slightly augmented (except the $30 - 50\ \mu\text{m}$ subrange is slightly depleted). This pattern is consistent with particle extinction, which was visually observed between 60 ms and 100 ms. Fines cool off faster than large particles, and therefore exhibit a lower burning rate. For this test, the median size was $13.8\ \mu\text{m}$, and the fractional mass remaining was 0.21. The insignificant change in fractional mass remaining is consistent with extinction.

Figure 2.3 Cumulative number distribution of 36%-porosity model coal after reaction at 1500 K and 12% oxygen for 63 ms.

Figure 2.4 Cumulative number distribution of 36%-porosity model coal after reaction at 1500 K and 12% oxygen for 109 ms.

2.3 Discussion

To determine if the carbon matrix would pose a significant impedance to oxygen supply to pyrite inclusions, the relationship between fractional mass remaining and fraction initial particle diameter can be examined for the preceding tests. Recall, in the limit of high carbon matrix resistance, a coal particle burns as a shrinking core, and fractional mass remaining is proportional to the cube of fraction initial particle diameter.

More generally, particle mass and diameter are related by the following power-law expression:

$$\frac{m}{m_0} = C \left(\frac{d}{d_0} \right)^\alpha,$$

where m is particle mass, C is a constant, d is particle diameter, and α is reaction mode parameter; subscript 0 denotes initial value. The reaction mode parameter, α , equals ∞ for constant diameter burning, 3 for shrinking core burning, and 0 for fragmentation without burning. To obtain α from experimental data, the natural log of the preceding power-law expression,

$$\ln \left(\frac{m}{m_0} \right) = \ln C + \alpha \ln \left(\frac{d}{d_0} \right)$$

can be subjected to least squares fit.

Figure 2.5 shows the least squares fit obtained by subjecting the data obtained from the previously described tests to the log-log relation above. Plotted is the natural log (negative) of fractional mass remaining versus the natural log (negative) of the volume mean diameter. The volume mean diameter is normalized with respect to the initial value for the coal feed. The least squares fit of the data is represented as a solid line. Also shown is a dotted line corresponding to shrinking core burning. On this type of plot, the y-axis and the x-axis correspond to constant diameter burning and pure fragmentation, respectively. The obtained value of the reaction mode parameter α is 7.0, which is intermediate with respect to the constant diameter and shrinking core values. It may be concluded that the carbon matrix of 36%-porosity model coal would offer observable impedance to the supply of oxygen to pyrite inclusions.

Figure 2.5 Volume mean diameter versus fractional mass remaining for 36%-porosity model coal after reaction at 1500 K and 12% oxygen.

The amount of the reduction of available oxygen due to kinetics as opposed to mass transfer can be deduced from the burning rate. When carbon matrix kinetics imposes a greater restriction on oxygen availability than carbon matrix mass transfer, the coal particle burns more quickly than pyrite does under the same conditions. For pyrite of 20 μm diameter burning at 1500 K and 12% oxygen, 89 wt% conversion is attained in 25 ms [5]. In the preceding model coal tests, conversion is only 80% after 53 ms and seems to stabilize. This suggests that mass transfer restrictions would constitute a greater impediment to oxygen availability for pyrite inclusions. [Mass transfer effects of coal are defined to include the additional impedance to boundary layer diffusion induced by the larger coal particle size.] When the first 10 ms for particle heatup is factored in, mass transfer appears even more restrictive of oxygen availability.

3.0 TASK 5: CARBON MATRIX MASS TRANSFER EFFECTS

For Task 5, the objective of the work was to determine the operating regime that amplifies the mass transfer impedance that a carbon matrix imposes on the oxidation of pyrite inclusions. Carbon matrix mass transfer becomes more rate-controlling at small pyrite particle size, large coal particle size, and low coal porosity. In this Task, the goal was to establish the maximum coal porosity compatible with rate control of pyrite oxidation by carbon matrix mass transfer effects.

The approach adopted in Task 5 was analogous to the one used in Task 4. To determine if carbon matrix mass transfer limitations were more dominant than kinetics effects, changes in time-resolved particle mass and size were monitored. Recall, in the limit of high carbon matrix resistance, a coal particle burns as a shrinking core. In that case, fractional mass remaining (m/m_0) is proportional to the third power of the fraction initial particle diameter (d/d_0). Furthermore, when carbon matrix mass transfer imposes a greater restriction on oxygen availability than carbon matrix kinetics, the coal particle burns more slowly than pyrite does under the same conditions. For pyrite burning at 1500K and 12% oxygen, 89 wt% conversion is attained in 25 ms [5].

3.1 Experimental

The feed material for this study was model coal of 23% porosity (distributed as 16% microporosity and 8% macroporosity) size-classified to 75-125 μm . Shown in Figure 3.1 is the cumulative number distribution of the coal feed. The size distribution exhibits the same features as that of the 36%-porosity coal of Figure 2.1: an initially steep increase in -15 μm range, slow increase in 15 - 75 μm range, and extremely steep increase in the +75 μm range. The current size distribution has substantially fewer fines, as the -15 μm range is less steep (33% cumulative, as opposed to 45%) and the +75 μm range is steeper (48% of the particles, as opposed to 37%). Furthermore, the number median diameter is 42 μm , as opposed to the previous value of 20 μm .

Figure 3.1 Initial cumulative number distribution of 23%-porosity model coal.

The remaining aspects of the experimental procedure are as described in Section 2. The reactor was operated to provide a combustion environment of 1500 K and 12% oxygen. Partially reacted chars were extracted from the reactor at heights corresponding to residence times of 25 ms, 63 ms, and 109 ms. The partially reacted char particles were characterized for burnoff and size distribution. Burnoff was determined by measuring the mass of recovered char using a Mettler AE240 balance. The size distributions of the chars were measured using the Coulter Multisizer.

3.2 Results

The burning behavior of the 23%-porosity coal was similar to that of the 36%-porosity coal described in Section 2. After an initial steep decline, fractional mass remaining stabilized at approximately 0.20 by 25 ms. Furthermore, the cumulative number distributions of the char exhibited the same distinct ranges: -15μm, 15 - 75 μm, +75 μm. These cumulative number distributions are depicted in Figures 3.2 to 3.4 for the 25 ms, 63 ms, and 109 ms tests, respectively.

Figure 3.2 is the number cumulative distribution of the char extracted after 25 ms of reaction. As usual, the $+75\text{ }\mu\text{m}$ range exhibits depletion with respect to the coal feed. There is substantial augmentation of the $20 - 75\text{ }\mu\text{m}$ subrange, while the $15 - 20\text{ }\mu\text{m}$ subrange remains unaffected. Finally, the $-15\text{ }\mu\text{m}$ range is augmented. Recall, great augmentation of the $15 - 75\text{ }\mu\text{m}$ size range was observed for the 36%-porosity char at the same condition (Figure 2.2). The conclusion was that either particles are fragmenting or there is a gradual change from shrinking-core burning to constant-diameter burning with decreasing size. For the size distribution shown, the median diameter is $25\text{ }\mu\text{m}$.

Figure 3.2 Cumulative number distribution of 23%-porosity model coal after reaction at 1500 K and 12% oxygen for 25 ms.

For this test, the fractional mass remaining was 0.71, which corresponds to a burning rate of 50% of that of the 36%-porosity char. The calculated area due to macroporosity (since the pores are spherical) is 35% of that of the 36%-porosity char. There appears to be a correlation between burning rate and open surface area (*i.e.*, macrovoids). Of course, other porosities must be evaluated before any definitive statements can be made.

For char extracted at 63 ms of residence time, the size distribution is presented in Figure 3.3. Perhaps the most striking feature is the great augmentation of $<20\ \mu\text{m}$ particles, with respect to the char recovered after 25 ms. The percentage of particles of less than $20\ \mu\text{m}$ diameter increases from 47% to 60%. In the $20 - 75\ \mu\text{m}$ range, however, there is no significant change in the distribution. The median size for this distribution is $14\ \mu\text{m}$, and the fractional mass remaining is 0.21.

Figure 3.3 Cumulative number distribution of 23%-porosity model coal after reaction at 1500 K and 12% oxygen for 63 ms.

Finally, at 109 ms, the char displays a size distribution consistent with minor burning (as opposed to the 36%-porosity char that showed signs of extinction). The $10 - 20\ \mu\text{m}$ subrange exhibits minor depletion, the $20 - 40\ \mu\text{m}$ subrange is steady, and the $40 - 75\ \mu\text{m}$ subrange is augmented with respect to the size distribution of char after 63 ms. More interestingly, the 99% cumulative diameter decreases from $89\ \mu\text{m}$ to $81\ \mu\text{m}$; for the 36%-porosity char, the decrease was only from $80\ \mu\text{m}$ to $77\ \mu\text{m}$. Furthermore, in this case the fractional mass remaining drops from 0.21 to 0.19; for the 23%-porosity char, it had not decreased any further.

Figure 3.4 Cumulative number distribution of 23%-porosity model coal after reaction at 1500 K and 12% oxygen for 109 ms.

3.3 Discussion

To determine if the carbon matrix of 23% porosity would pose a significant resistance to oxygen availability for pyrite inclusions, the log of fractional mass remaining is plotted versus the log of volume mean particle diameter in Figure 3.5 for the preceding tests. The volume mean diameter is normalized to that of the coal feed. The solid line is the least squares fit of the data and its slope provides a value of 7.0 for α , the reaction mode parameter. The dotted line corresponds to shrinking core burning, and evidently the data for the 23%-porosity coal lies much closer to this line than the data for the 36%-porosity coal did (Figure 2.5).

The data suggests that the carbon matrix of 23%-porosity model coal would severely restrict the supply of oxygen to pyrite inclusions. That the impedance of the carbon increases as porosity decreases stands to reason.

Figure 3.5 Volume mean diameter versus fractional mass remaining for 23%-porosity model coal after reaction at 1500 K and 12% oxygen.

The amount of the reduction of available oxygen due to mass transfer (as opposed to kinetics) can be deduced from the burning rate. When carbon matrix mass transfer imposes a greater restriction on oxygen availability than carbon matrix kinetics, the coal particle burns more slowly than pyrite does under the same conditions. For 20 μm -diameter pyrite burning at 1500 K and 12% oxygen, 89 wt% conversion is attained in 25 ms [5]. With 23%-porosity model coal, conversion is only 79% after 53 ms and seems to stabilize. This suggests that for model coal of 23% porosity, mass transfer restrictions would constitute a greater impediment to oxygen availability for pyrite inclusions. [Mass transfer effects of coal are defined to include the additional impedance to boundary layer diffusion induced by the larger coal particle size.] When the first 10 ms for particle heatup is factored in, mass transfer appears even more restrictive of oxygen availability.

CONCLUSIONS

The two preceding studies suggest a direction for further investigation of the effects of associated carbon on pyrite oxidation rates. The finite powers of obtained mass-diameter correlations indicate that, in 12% oxygen at 1500 K, oxygen does not fully penetrate model coal particles of 75 - 125 μm size class. It may be deduced that the carbon matrix of model coal would decrease the oxidation rate of pyrite inclusions. Consequently, model coals constitute appropriate feed materials for combustion tests intended to elucidate the retarding effects of associated carbon on pyrite oxidation.

From the two model coal studies conducted, retardation of pyrite oxidation by carbon matrix would be due to mass transfer limitations, at the two coal porosities used (23% and 36%). Both coals burn more slowly than pyrite particles of 20 μm diameter, therefore the kinetics of carbon-oxygen reactions would not induce a significant depletion of oxygen supply to -20 μm pyrite inclusions. For kinetics to become more significant than mass transfer, model coal of much higher porosity or smaller diameter is required.

It may be concluded that 23%-porosity model coal is of sufficiently low porosity to be used in studying the effects of carbon matrix transport limitations. Coals of porosities much higher than 36% should be used when investigating carbon matrix kinetics effects.

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 January 1 to March 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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