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MECHANISMS OF PYRITE OXIDATION TO NON-SLAGGING SPECIES

Quarterly Report for the Period

January 1, 1996 - March 31, 1996

Grant DE-FG22-94PC94205

Prepared for

THE UNITED STATES DEPARTMENT OF ENERGY

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May 1996

High Temperature Gasdynamics Laboratory
Department of Mechanical Engineering
Stanford University

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RESEARCH OBJECTIVES

This document is the seventh 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 January 1 to March 31, 1996. During the quarter, the effort to characterize experimentally the impact of a carbon matrix on the oxidation of pyrite inclusions continued. The experimental conditions were moved further inside the operating regime in which mass transfer limitations become detectable. The objective was to use the more easily produced ash-free model coal to identify appropriate carbon matrix porosities for pyrite-containing model coal that is to be burned in future tests.

Approximately 6.75 grams of ash-free synthetic model coal was prepared to be utilized in combustion experiments. The model coal was synthesized to have 16% porosity (all of which was due to micropores of less than 0.05 μm diameter). The coal was further processed to yield particles of 75 - 125 μm size class.

The model coal was oxidized in a flow reactor at 1500 K and 12% oxygen. Char was extracted at residence times of 25 ms, 63 ms, and 109 ms. Mass burnoff was determined by gravimetry, particle morphology was characterized by scanning electron microscopy, and particle size distribution was measured with a Coulter Multisizer.

Fractional mass remaining was 0.86 at 25 ms, 0.49 at 63 ms, and 0.46 at 109 ms. Particle morphology became increasingly dominated by sub-micron pores and micron-scale fissures as residence time increased. The size distributions exhibited features consistent with fragmentation at 25 ms, burning at 63 ms, and decelerated burning at 109 ms.

The data indicated that in 12% oxygen at 1500 K, 16%-porosity model coal of 75 - 125 μm particle size class burns more slowly than pyrite of 20 μm particle diameter. For pyrite, fractional mass remaining is only 0.11 at 25 ms. Consequently, mass transfer limitations constitute the main mechanism by which carbon matrix would reduce oxygen flow to pyrite inclusions in 16%-porosity model coal. Furthermore, assessment of all model coal test results obtained to date indicated that mass transfer impedance of oxygen flow grows at a faster than linear rate as macroporosity is reduced.

FINDINGS

In the prevailing model of pyrite combustion, pyrite oxidation during pulverized coal firing occurs at a rate determined by pyrite kinetics and transport parameters [1]. The formulators of the model cite the need for more accurate characterization of the pyrite kinetics and transport parameters, however. They also note the need for further study with respect to the effects of associated carbon.

Stanford University's pyrite oxidation research program aims to provide the needed pyrite kinetics and transport parameters as well as data on the impact of a carbon matrix [2]. Thus far, extraneous pyrite has been oxidized at 1500 K [3, 4] to obtain time-resolved compositions of burning pyrite [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. Last quarter, an effort to determine experimentally the impact of the carbon matrix was launched, as kinetics effects and mass transfer effects were separately investigated using ash-free model coals [6]. It was evinced that for carbon matrix porosities less than 36%, mass transfer effects would diminish expected reactivity of pyrite inclusions.

This quarter, the effort to determine experimentally the impact of a carbon matrix on the oxidation of pyrite inclusions continued. The experimental conditions were moved further inside the operating regime in which mass transfer limitations become detectable. Activity covered two tasks, as low-porosity model coal was prepared (Task 1) and subjected to combustion (Task 5).

1.0 TASK 1: PRODUCTION AND CHARACTERIZATION OF PYRITE FEEDS

During the quarter, 6.75 grams of synthetic model coal suitable for combustion experiments was prepared. The model coal, which was mineral matter-free, was synthesized to have 16% porosity. All of the porosity was distributed as micropores of nominal size less than approximately 0.05 μm . The coal was further processed to yield particles of 75 - 125 μm size class.

The aim of the work performed in this task was to prepare feed materials that amplify the mass transfer limitations 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. 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. Last quarter, it was determined that the initial emphasis of the carbon matrix studies would be placed on decreasing coal porosity to induce mass transfer control of pyrite oxidation [6].

Due to their high degree of intraparticle and interparticle homogeneity, the feed materials selected for the studies consisted of synthetic model coals. Because of the great labor required to produce sizable batches of pyrite-containing model coals, mineral-free model coals were specified for initial combustion experiments. Once appropriate carbon matrix porosities are identified, pyrite-containing model coals may be synthesized and subjected to combustion tests. Last quarter, it was observed that coal of 23% porosity burns in a manner consistent with noticeable carbon matrix mass transfer effects [6].

To increase the carbon matrix mass transfer effects, this quarter the porosity of utilized model coal was reduced to 16%. The model coal was produced from the polymerization of furfuryl alcohol with p-toluenesulfonic acid in water, following the procedures described by Senior and Flagan [7]. 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]. Previously, lycopodium plant spores were also

added, as 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. This quarter, the lycopodium was omitted and all of the porosity was distributed as micropores of nominal size less than approximately 0.05 μm .

The model coal produced was ground by hand using a ceramic mortar and pestle. Grinding was performed until visual inspection suggested that particle size had been reduced to P. C. size range. The ground coal was transferred into a plastic vial for storage using filter paper.

Ground coal was subjected to preliminary size classification through dry sieving for 75 - 125 μm size class. Sieves of 125 μm , 106 μm , 90 μm , and 75 μm mesh sizes were stacked and fitted on an electrical sieve shaker. One gram of ground coal was spread on the top sieve, and the sieve shaker was operated for 5 to 10 minutes. Oversized material was reground and sieved again. This was repeated until very little material was left on the 125 μm sieve. The sieve shaker was operated for an additional 15 minutes to discharge fines through the 75 μm sieve. Coal particles retained by the different screens were mixed together.

The dry sieved coal particles were further size-classified by wet sieving to remove fines. A suspension was formed using 1 g of coal and one l L of water. Approximately 250 ml of suspension was poured into a beaker and ultrasonicated for 5 minutes to separate coagulating particles. The suspension was then poured through a sieve of 38 μm mesh size, and fines were discharged through the screen. After the 1 L suspension was completely exhausted, coal retained by the screen was further washed with water until fines could no longer be removed.

After the coal had been wet sieved, it was transferred onto filter paper and dried. The coal was placed in an oven at 50 C and purged with nitrogen. The duration of drying was 8 - 10 hours.

Figure 1.1 is a scanning electron micrograph (SEM) showing a representative sample of the production coal particles. The SEM is of 100X magnification, and the scale bar corresponds to 300 μm . The particles in the SEM are angular and irregularly shaped (similar to natural P. C.),

Figure 1.1 Secondary scanning electron micrograph at 100X magnification of synthetic, model coal of 16% porosity (0% macroporosity).

with projected-area particle size hovering around 70 - 100 μm . Unlike natural coal, the model coal exhibits a high degree of uniformity in particle shape, size, and roughness, thereby making model coal more suitable for fundamental model development studies.

In Figure 1.2, the coal is presented at higher magnification, in order to resolve its topographic features. Figure 1.2 is a SEM of a particle at a magnification of 600X; the scale bar corresponds to 50 μm . Although the coal particle appears smooth at micron-scale (other than a few specks of carbon black), roughness is evident at a scale 1 or 2 orders of magnitude smaller. The observed scale of surface roughness is consistent with mercury porosimetry characterization, which indicates that the largest pores for 16%-porosity coal are nominally 0.05 μm .

Figure 1.2 Secondary scanning electron micrograph at 600X magnification of synthetic, model coal of 16% porosity (0% macroporosity).

2.0 TASK 5: CARBON MATRIX MASS TRANSFER EFFECTS

For Task 5, the objective of the work was to characterize the burning behavior of model coal under operating conditions that amplify the mass transfer impedance that a carbon matrix imposes on the oxidation of pyrite inclusions. Carbon matrix mass transfer becomes more rate-controlling at low coal porosities. Experiments performed last quarter suggested that carbon matrix mass transfer effects are detectable at 23% porosity. This quarter, coal of lower porosity (16%) was burned, in order to make mass transfer limitations even more significant.

To determine the extent to which carbon matrix mass transfer limitations were more dominant than kinetics effects, changes in time-resolved particle mass and size were monitored. When carbon matrix mass transfer imposes a greater restriction on oxygen flow than carbon matrix kinetics, coal particles burn more slowly than pyrite does under the same conditions. For 20 μm pyrite particles burning at 1500 K and 12% oxygen, 89 wt% conversion is attained in 25 ms [5]. During the quarter, the burning rate of ash-free model coal was assessed relative to that of pyrite, in order to identify appropriate carbon matrix porosities for pyrite-containing model coal that is to be burned in future tests.

2.1 Experimental

The feed material for this study was the mineral-free model coal described in Section 1.0. Recall, the coal was synthesized to possess 16% porosity (distributed as micropores of less than 0.05 μm size) and size-classified to 75 - 125 μm .

The size distribution of the coal feed was measured using the Coulter Multisizer. For this and all other measurements presented in this report, a 280 μm orifice tube was used. The 280 μm orifice provides a measurement range of 5.6 μm to 168 μm . In addition, the Multisizer was programmed for 256 size bins, to yield a resolution of 1.4%. The sample size used in all measurements was approximately 20,000 particles.

Shown in Figure 2.1 is the cumulative number distribution of the coal feed obtained with the Coulter Multisizer. The size distribution exhibits features consistent with the existence of three distinct size ranges: 1) a gradual increase from 5.8 μm to 15 μm ; 2) a tapering off until approximately 75 μm , the lower mesh size used to size-classify the coal; 3) a step increase as the cumulative number rises from 45% at 75 μm to 99% at 115 μm . For the size distribution in the figure, the number median diameter is 78 μm .

Figure 2.1 Initial cumulative number distribution of 16%-porosity model coal.

The coal was burned in the entrained flow reactor used previously for oxidation of model coal [6] and extraneous pyrite [3, 4]. In the flow reactor, pulverized fuel particles are fed by a syringe and entrained by a nitrogen stream into the base of a flat flame burner. 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. At selected residence times, the reacting particles are extracted by a helium quench probe.

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. The partially reacted char particles were characterized for burnoff, morphology, and size distribution. Burnoff was determined by measuring the mass of recovered char using a Mettler AE240 balance. Morphology was characterized through secondary electron micrographs obtained with a HITACHI S-2500 scanning electron microscope. Size distribution was measured using a Coulter Multisizer.

2.2 Results

Combustion tests corresponding to three different residence times were performed with the 16%-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. Approximately 1 cm downstream (5 ms later), the flame recedes, and the model coal burns heterogeneously as a glowing orange particle. Unlike macroporous model coal, 16%-porosity coal does not exhibit much particle extinction between 10 cm and 25 cm height (60 ms and 100 ms).

Scanning electron micrographs (SEMs) of chars recovered after reaction for 25 ms, 63 ms, and 109 ms are presented in Figures 2.2 and 2.3; 2.5 and 2.6; and 2.8 and 2.9; respectively. For each residence time, a low magnification is used to determine the dispersion of features, while a high magnification is used for topographic characterization of selected particles. The SEMs reveal that particles increasingly exhibit fissures and surfaces become rougher as oxidation progresses.

Cumulative number distributions of chars recovered after 25 ms, 63 ms, and 109 ms are also shown, in Figures 2.4, 2.7, and 2.10, respectively. In general, each size distribution exhibits three distinct ranges: $-15\text{ }\mu\text{m}$, $15 - 75\text{ }\mu\text{m}$, and $+75\text{ }\mu\text{m}$. Overall, the $-15\text{ }\mu\text{m}$ portion of the distribution becomes steeper as oxidation progresses, while the $+75\text{ }\mu\text{m}$ portion becomes less steep. Observed changes in number distribution are generally consistent with a reduction in particle size to lower values with increased burning.

25-ms Test

After 25 ms in the flow reactor, changes in char characteristics were evident. In Figure 2.2 is a SEM at 100X magnification (scale bar of 300 μm) of char particles. The particles appear more polydisperse than the feed materials of Figure 1.1. There is now a greater number of small particles. These fines may have originated from thermal fragmentation of feed materials. Evidence in support of the fragmentation hypothesis is the existence of particles with major fissures. Since most of the cleaving particles are still as angular and smooth as the feed materials, it is plausible that the cleavage originated from thermal stresses more so than volatiles evolution or oxidation.

Figure 2.2 Secondary scanning electron micrograph at 100X magnification of 16%-porosity model coal after oxidation at 1500 K and 12% oxygen for 25 ms.

Another contributor to polydispersion is the presence of particles exhibiting greater micro-roughness than the feed materials. The roughness appears to be pores (perhaps due to oxygen attack), but at this magnification not much can be inferred regarding the pores. In general, despite the fragmentation and pore formation, particle features are similar to those of the feed coal. [There is not much evidence of plastic deformation such as swelling or blow holes.]

Figure 2.3 provides the higher magnification required to resolve the changes detected in char after 25 ms of reaction. The SEM in Figure 2.3 is of 300X magnification with a scale bar of 100 μm . Evident are smooth particles that are indistinguishable from the coal feed. Also apparent, in the lower-left quadrant of the micrograph, is a smooth particle with a deep fissure. The fissure is approximately 3 μm wide, extending deep into the particle interior and spanning the breadth of the particle. Another new particle structure is the porous type evident in the upper-left corner of the micrograph. The roughness associated with porosity is of micron scale; there are no macrovoids.

Figure 2.3 Secondary scanning electron micrograph at 300X magnification of 16%-porosity model coal after oxidation at 1500 K and 12% oxygen for 25 ms.

With respect to the size distribution of the coal feed, the size distribution at 25 ms (Figure 2.4) exhibits a great shift of particles from the +75 μm range to the lower size ranges. While the -15 μm range exhibits an increase in particles, the greatest increase occurs in the 15 - 60 μm

Figure 2.4 Cumulative number distribution of 16%-porosity model coal after reaction at 1500 K and 12% oxygen for 25 ms.

subrange. [See Figure 2.1 for the size distribution of the coal feed.] The median particle size decreases from 78 μm to 14 μm , and the 99% cumulative point recedes from 115 μm down to 92 μm .

Since many particles extracted at this residence time (25 ms) were extracted during or immediately subsequent to their devolatilization phase, it is plausible that the observed size shift was due to particle fragmentation associated with heatup and rapid evolution of volatiles. The fragmentation hypothesis is supported by the observation that the extent of augmentation of the 15 - 60 μm subrange of the particle size distribution does not change with diameter. Furthermore, for this test, the fractional mass remaining was 0.86, which corresponds to very little burnoff.

The transformations evident at 25 ms became more pronounced at 63 ms. The SEM in Figure 2.5 displays recovered char particles at 100X magnification (scale bar of 300 μm). Over half of the particles exhibit the fissures observed in Figure 2.2. Moreover, most particles possess a multiplicity of fissures, and these fissures are often thicker than those observed at 25 ms. The curvature of the fissures is also greater, and short, semi-circular fissures can be observed.

Figure 2.5 Secondary scanning electron micrograph at 100X magnification of 16%-porosity model coal after oxidation at 1500 K and 12% oxygen for 63 ms.

In Figure 2.5, particle surfaces appear only somewhat more porous than at 25 ms, but SEMs of higher magnification confirm that the prevalence and length-scale of porosity are greater. Even in Figure 2.5, particles with 5 μm craters are discernible, however. [It is worth noting that despite the increase in fissures and pores, there is still no evidence of plasticity.]

Figure 2.6 provides greater resolution of the char features just described. Figure 2.6 is a micrograph at 600X magnification (scale bar of 50 μm) of a representative char particle. The particle is clearly porous, with pores coalescing to form circular pores of all diameters up to 2 μm . Also evident are fissures, whose sharp demarcations imply that the fissures are not the product of pore coalescence.

Figure 2.6 Secondary scanning electron micrograph at 600X magnification of 16%-porosity model coal after oxidation at 1500 K and 12% oxygen for 63 ms.

Figure 2.7 is the size distribution of char after 63 ms, and it reveals that continued burning depletes the $+75 \mu\text{m}$ range slightly, augments the 60 - 75 μm subrange slightly, does not affect the 40 - 60 μm subrange, depletes the 15 - 40 μm subrange greatly, and augments the $-15 \mu\text{m}$ range greatly. The decreasing depletion with increasing diameter in the 15 - 75 μm range is consistent with Zone II and Zone III burning, in which the specific burning rate decreases with size. The

Figure 2.7 Cumulative number distribution of 16%-porosity model coal after reaction at 1500 K and 12% oxygen for 63 ms.

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 13.1 μm , and the fractional mass remaining was 0.49.

109-ms Test

Results from the 109-ms test differed little from 63-ms test results. Figure 2.8, a micrograph at 100X with a scale bar of 300 μm , reveals that after 109 ms, particle size and shape are the same as after 63 ms (Figure 2.5). The only perceptible differences are a slight thickening of fissures and a small increase in the proportion of porous particles.

Figure 2.8 Secondary scanning electron micrograph at 100X magnification of 16%-porosity model coal after oxidation at 1500 K and 12% oxygen for 109 ms.

Figure 2.9 is a micrograph at 600X (scale bar of 50 μm), and it shows that char surface is highly porous. Pore sizes are still typically sub-micron, and coalesced pores remain as circles of approximately 2 μm diameter. Also evident are semi-circular fissures of approximately 25 μm diameter. The inside surfaces of these fissures are also porous.

As seen in Figure 2.10, the char size distribution obtained after 109 ms was quite similar to the size distribution obtained after 63 ms (Figure 2.7). Furthermore, the fractional mass remaining after 109 ms was 0.46, almost the same as the 0.49 value obtained after 63 ms. The minuscule change in fractional mass remaining is consistent with a diminished burning rate.

Figure 2.9 Secondary scanning electron micrograph at 600X magnification of 16%-porosity model coal after oxidation at 1500 K and 12% oxygen for 109 ms.

Figure 2.10 Cumulative number distribution of 16%-porosity model coal after reaction at 1500 K and 12% oxygen for 109 ms.

2.3 Discussion

Reduction of oxygen flow attributable to mass transfer (relative to kinetics) can be inferred from the burning rate. When carbon matrix mass transfer imposes a greater restriction on oxygen flow than carbon matrix kinetics, the coal particle burns more slowly than pyrite does under the same conditions. [Mass transfer effects of coal are defined to include the additional impedance to boundary layer diffusion induced by the larger coal particle size.] 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 combustion tests of 16%-porosity model coal, conversion was only 14% after 25 ms. Even after 109 ms, conversion was only 54% and seemed to stabilize. The low burning rate of model coal relative to that of pyrite implies that mass transfer restrictions would constitute a greater impediment (than kinetics limitations) for oxygen flow to pyrite inclusions.

Assessment of all model coal test results obtained to date [6] indicates that mass transfer impedance of oxygen flow grows at a faster than linear rate as macroporosity is reduced. The change in burning rate when going from 16% porosity to 23% porosity is much greater than the corresponding change as porosity is increased from 23% to 36%. For instance, after 63 ms of combustion, fractional mass remaining is 0.49, 0.21, and 0.20 for coal porosities of 16%, 23%, and 36%, respectively. Consequently, when attempting to resolve carbon matrix kinetics effects from carbon matrix mass transfer effects it is more expedient to include model coals from the lower end of the porosity scale.

CONCLUSIONS

The data indicate that in 12% oxygen at 1500 K, 16%-porosity ash-free model coal of 75 - 125 μm particle size class burns in a fashion consistent with fragmentation at 25 ms, oxidation at 63 ms, and decelerated oxidation at 109 ms. Because the coal burns more slowly than pyrite of 20 μm particle diameter, mass transfer limitations would constitute the main mechanism of oxygen reduction by carbon matrix for 16%-porosity model coal with pyrite inclusions. Furthermore, assessment of all model coal test results obtained to date indicates that mass transfer impedance of oxygen flow grows at a faster than linear rate as macroporosity is reduced.

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 April 1 to June 30, 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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