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INVESTIGATION OF MINERAL TRANSFORMATIONS AND ASH DEPOSITION DURING STAGED COMBUSTION

Quarterly Technical Progress Report
January 1, 1996 to March 31, 1996

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FOREWORD

This report summarizes technical progress during the tenth quarter (January 1, 1996 to March 31, 1996) of a three-year study conducted for the Department of Energy (DOE) under Contract No. DE-FG22-93PC93226. The principal investigator for this work was Dr. John N. Harb; Mr. James Hickerson was the technical representative for DOE.

The technical work reported for this quarter was performed by graduate students Peter Slater and Neal Adair. Syndi Anderson, Eyas Hmouz, John Dobbs, and Rachel Newsom, undergraduate students in chemical engineering at BYU, also made important technical contributions to this report.

DISCLAIMER

ABSTRACT

Progress during the tenth quarter of a three-year study of ash formation and deposition was made in several areas. One of the key contributions this quarter was the development of an algorithm to distinguish between ash particles that are associated with char particles (included) and ash particles which are excluded. This algorithm was used to determine the extent to which pyrite transformations are influenced by whether the pyrite grains are included or excluded. The results indicate that pyrite oxidation is slower for included pyrite grains.

Replicate experiments were also performed for the Pittsburgh #8 coal (washed) under both staged and conventional conditions. An objective of these experiments was to validate the effect of staged combustion on the size distribution of ash particles as reported for the previous quarter. Analysis of the new samples and repeat analyses of previous samples showed no significant difference in the ash particle size for samples collected at stoichiometric ratios of 0.75 (before the stage) and 1.04. The number of points in the new analyses was considerably higher than in previous analyses, resulting in greater confidence. The similarity in the ash composition for samples collected under staged and conventional conditions was also verified this quarter with replicate samples and analyses. The net result is that staged combustion does not appear to have a significant impact on either ash size or composition for the Pittsburgh #8 coal.

Finally, numerical simulations of the temperature distribution in the laboratory combustor were performed and evaluated. Also, a paper documenting the classification algorithm developed last quarter was presented at the March ACS meeting in New Orleans and published in the ACS Division of Fuel Chemistry Preprints.

OBJECTIVES AND SCOPE

A. Background

A thorough understanding of the fundamental processes which govern the mineral behavior is essential to the development of tools to predict and manage ash deposition. The purpose of the current project is to perform a fundamental study of mineral transformations and ash deposition during staged combustion of pulverized coal. Staging of combustion air is a strategy used to reduce NOx emissions from coal-fired units. It is applicable to both advanced combustion systems currently under development (e.g. HITAF) and low NOx retrofits for existing units. These low NOx combustion strategies produce fuel rich or reducing conditions in the lower furnace. Therefore, the combustion history of the coal particles is significantly changed from that experienced under normal combustion conditions. A carefully designed experimental study is needed to examine the effects of altered combustion conditions on mineral matter release, fly ash formation, particle stickiness and deposit formation. This project uses state-of-the-art analytical equipment and a well-characterized laboratory combustor to address this need.

B. Objectives

This report describes work in the tenth quarter of a fundamental, three-year study of mineral transformations and ash deposition during staged combustion. The objectives of this project are:

1) Creation of an experimental database which documents the behavior of inorganic constituents during staged combustion under well-defined conditions,

2) Identification of key mineral species or reactions which may be problematic,

3) Development of increased understanding and insight into the mechanisms which control ash formation and deposition.

C. Research Task Summary

Task 1: Select specific coals, prepare the coals for use in the laboratory combustor, and perform a detailed characterization of samples from the prepared coals.

Task 2: Prepare and test reactor facilities and sampling probes for use in the proposed experiments.

Task 3: Conduct a parametric study of mineral transformations and particle stickiness during staged combustion by performing a series of tests at a variety of conditions and collecting both particulate and deposit samples for each of the tests.

Task 4: Analyze particulate samples collected in Task 3 in order to determine the size, shape, and composition of the particles. Also, examine particle stickiness by analyzing the composition (bulk and local) and morphology of deposits collected as part of Task 3.

Task 5: Design and perform additional tests based on the results of Tasks 3 and 4 in order to define mechanisms, identify critical conditions, etc.

PROGRESS REPORT

This section of the report describes progress made during the tenth quarter. Progress is summarized by task.

Task 1

As mentioned above, the purpose of this task was to select specific coals, prepare the coals for use in the laboratory combustor, and perform a detailed characterization of samples from the prepared coals. This task has been largely completed and no additional work on this task was performed during the quarter.

Task 2

The purpose of this task was to prepare and test reactor facilities and sampling probes for use in the current experimental program. This testing has been largely completed, although improvements and maintenance work continue. For example, it appears that it may be necessary to recast the insulation on the reactor walls during the next quarter.

Task 3

During this quarter, replicate ash samples were collected for the Pittsburgh #8 coal at stoichiometric ratios of 0.75 (before downstream air injection) and 1.04. A total of six ash samples were collected at different residence times (heights) in the reactor. These samples will be used to verify findings on the particle size and composition distributions reported previously. Duplicate samples were needed in order to make the results suitable for publication. Analysis of these samples is described under Task 4 below. A deposit sample for the same coal was also collected.

To date, we have been unable to determine gas temperatures in the combustor. Instead, measured wall temperatures have been used to characterize the reactor temperature. We had originally intended to measure the gas temperatures optically. However, this does not currently seem feasible for both technical and practical reasons. As an alternative, numerical simulations of the combustor have been performed using the commercial program Fluent. These simulations were performed for the combustor fired on natural gas; the measured wall temperatures were used as input to the program.

The rate at which gases cool in the reactor and the magnitude of radial temperature gradients are the principal concerns related to reactor temperature. Cooling is an issue because of the combustor's high surface area-to-volume ratio and our desire to keep the reactor exit temperature above 1200° C (1473K). Severe radial gradients would lead to particles with a wide distribution of time-temperature histories. For sampling purposes, we would like to keep that distribution as narrow as possible.

The reactor was modeled under gas-fired conditions to simplify the calculations and avoid the necessity of simulating the combustion chemistry and reaction rates. The flame was not simulated; instead the reaction products and adiabatic flame temperature determined by an equilibrium calculation (NASA Lewis) were used as input to the Fluent code. This approach is valid since methane combustion takes place in a thin flame of millimeter thickness which is insignificant compared to the length of the reactor. The simulations shown in this report correspond to methane combustion at a stoichiometric ratio of 0.75, which is a limiting case. The reactor is hotter when it is fired with methane at stoichiometric ratio 1.04. When the reactor is fired with coal, the heat release takes place over a larger volume, elongating the region of high temperature. Thus if the temperature constraints are satisfied under gas firing stoichiometric ratio 0.75, we believe that they will also be satisfied under any other operating conditions we expect to use.

The temperature field calculated by Fluent is shown in Fig. 1, with temperatures reported in Kelvin. The centerline temperature remains above 1500K throughout the reactor. Also the flame has the expected shape and size, validating the modeling approach. The centerline temperature profile is plotted in Fig. 2. The temperature falls linearly down the length of the reactor, but remains high enough to satisfy our constraints. Radial profiles at various positions in the reactor are plotted in Fig. 3. The vertical line at approximately 0.055 indicates the radius of the burner. Near the burner (Z = 0.0767 m), the profile is nearly flat over most of the reactor diameter. This is consistent with the burner geometry and gas flow patterns. Farther from the burner, radial gradients exist, but do not fall sharply inside the burner radius, where we collect our samples.

These modeling results indicate neither of the concerns discussed above will be a problem in typical reactor operation. Temperatures throughout the reactor are high enough to allow us to realistically simulate boiler ash formation.

Task 4

The principal contributions made during the quarter were performed as part of this task. These contributions included another important analytical advance which is described in the paragraphs which follow. In addition, replicate ash samples from the Pittsburgh #8 coal were collected in order to validate observations made from previous samples taken under similar conditions. Finally, an initial analysis of deposits from the Pittsburgh coal is reported.

Behavior of included and excluded pyrite

As mentioned in previous reports, we have focused much of our attention on the combustion behavior of pyrite. Differences in the amount of sulfur release, an indicator of the extent of pyrite transformation, were observed in short residence time samples obtained under different initial stoichiometries (SR = 0.65, 0.75, 1.04). These differences seemed to disappear at longer residence times. The short residence time samples contained a great deal of unburned carbon which was not present in the long residence samples. One question we asked was if there was a carbon effect on the release of sulfur from pyrite particles. Specifically, do included pyrite particles combust at a different rate than excluded particles?

One of the key contributions this quarter was the development of an algorithm to distinguish between ash particles that are associated with char particles (included) and ash particles which are excluded. We have been making a similar distinction for minerals in coal particles for several years (Yu 1992, Richards 1994). However, the algorithm uses continuity to match minerals with coal particles, which are not porous, and is not applicable to analyses of the porous cenospheric chars. The problem is illustrated in Fig. 4, a BSE micrograph of a cross-section containing char and ash particles. The large cenospheric char particle at lower left in the image contains a number of ash particles within its walls. These may or may not have continuity with the char walls. There are also two particles in the interior of the cenosphere, which clearly do not have continuity. All of the these particles should be considered as included, but since they cannot be assumed to have continuity, they would not be correctly identified.

A new algorithm was designed to match ash particles to char without using continuity. A region surrounding a given char particle is identified by determing the vertices of a rectangle or box which is just large enough to enclose the particle. All ash particles whose centers fall within a box are identified as included. The remainder are identified as excluded. This is clearly an approximation since ash particles not associated with the char may be inadvertently included in the box. It is unlikely, however, that ash particles which are actually "included" would be inappropriately identified as "excluded." Therefore, even though the algorithm is approximate, any differences between included and excluded ash particles would be real and would represent a conservative estimate of actual differences.

The new algorithm was used to determine if char/ash association (included/excluded) affects the sulfur release from pyrite particles under strongly reducing conditions (SR = 0.65). We limit our report to particles which were either iron oxide or iron sulfide (Fe + S ≥ 80 mole percent), and to particles with diameters less than or equal to 15 microns, since large particles do not typically occur as inclusions. The sulfur distributions for included and excluded particles are presented in Figs. 5 and 6, respectively.

The first apparent difference is the amount of fully oxidized pyrite, i.e. iron oxide. This is found in the lowest bin, which accounts for 41% of the excluded mineral area but only 22% of the included mineral area. Other differences are seen in the height and location of the partially oxidized pyrite peaks. The included particle pyrrhotite peak (Fig. 5) is centered at about 50 mole percent sulfur, whereas the excluded pyrrhotite peak (Fig. 6) is centered at about 45 mole percent sulfur. The area fraction of the peaks is also different, 60% included vs. 33% excluded. Note also that some relatively high sulfur included particles are found, but virtually no high sulfur excluded particles are evident. The excluded pyrrhotite peak ends quite abruptly on the high sulfur side.

These results show that sulfur release from pyrite is affected by whether the pyrite mineral grains are included or excluded. The practical implications of this observation are under investigation and will be considered in a future report. Also, the ability to distinguish included and excluded ash particles should permit tracking of composition changes which occur because of coalescence.

Particle Size Distribution

We previously reported that Pittsburgh #8 produced a slightly larger ash when burned under staged combustion conditions. A number of steps were taken this quarter to validate this result. Additional samples were collected under similar conditions. Also, the previous samples were reanalyzed to insure that no systematic differences in the analysis procedure would bias the results. In addition, a large number of points was analyzed to improve the statistical validity of the results. Finally, the basis for reporting particle size distributions was changed from a number basis to an area to provide more appropriate weighting of the results for different particle sizes.

The cumulative particle size distributions shown in Fig. 7 represents the average of two samples under each firing condition. The number of points in the analyses ranged from 6,000 to over 26,000. No significant difference in the particle size distributions at stoichiometric conditions of 0.75 (before stage) and 1.04 is apparent. Good reproducibility was observed for samples taken several months apart.

Replicate analyses of composition were also performed and found to agree with previously reported results. Hence, we are left with the following conclusions for the Pittsburgh #8 coal fired under staged conditions: 1) there is no significant difference in the composition of the ashes from the staged and conventional combustion experiments, and 2) there is no significant difference in the size of the ash formed during staged combustion. Therefore, differences in deposition rates in utility boilers operating under low-NOx conditions cannot be attributed to differences in the ash composition or PSD, since no such differences exist.

Our conclusion that PSD is unaffected by staged combustion is in apparent conflict with that of Boole et al., who found (Fig. 8) that the PSD of Pittsburgh #8 ash increased with decreasing stoichiometric ratio under reducing conditions. This discrepancy can explained by noting that the residence time in the reducing zone under staged combustion is on the order of a few hundred milliseconds whereas the total reducing residence time in the results reported by Boole et al. was 1.5 seconds. Reducing conditions may indeed lead to more coalescence and hence larger particles. However, in staged combustion the particles do not experience reducing conditions long enough to produce an observable effect.

Deposit Sample

A Pittsburgh #8 deposit sample was cast in epoxy, cross-sectioned, polished and examined in the SEM. Figure 9 is a backscattered image of the cross-section collected at 100X. The surface of the deposit probe is shown as the bright area across the bottom of the image. The gray and white material above it is the deposit. Since the deposit particles are much larger than fly ash grains and heterogeneous, it is evident that the deposit has sintered to some extent, although not completely. Discrete fly ash particles can no longer be discerned. Given our concern about temperatures and heat fluxes in the reactor, we are very pleased to find that we are able to grow sintered deposits.

References

Boole, L. E., et al., Fundamental Study of Ash Formation and Deposition: Effect of Reducing Stoichiometry, Final Report - DOE Contract No. DE-AC22-93PC92190, 1995.
Richards, G.H., Ph.D. Dissertation, Brigham Young University, 1994.
Yu, H., M.S. Thesis, Brigham Young University, 1992.

D. Plans for the Next Quarter

1. Determine the differences, if any, between the transformations of included and excluded mineral particles during staged combustion.
2. Analyze Black Thunder ash samples and determine the effect of staged combustion on ash formation. Analyses will be similar to those used for the Pittsburgh #8 coal.
3. Collect and analyze deposit samples from both the Black Thunder and Pittsburgh #8 coals and quantify the effects of staged combustion on deposit formation.
4. Prepare two manuscripts for peer-reviewed publication and submit them.

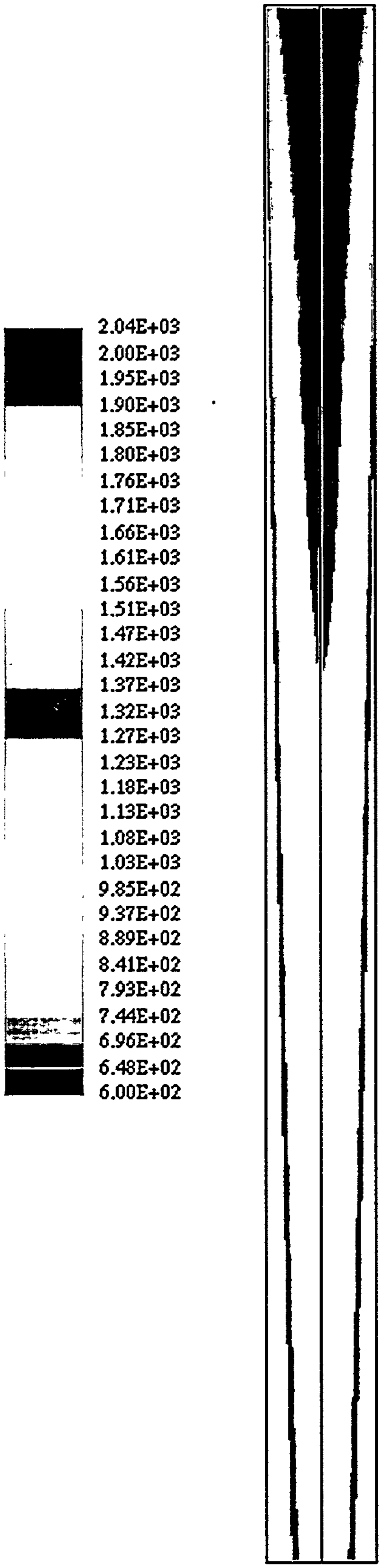

Figure 1. Modeled reactor temperature profile

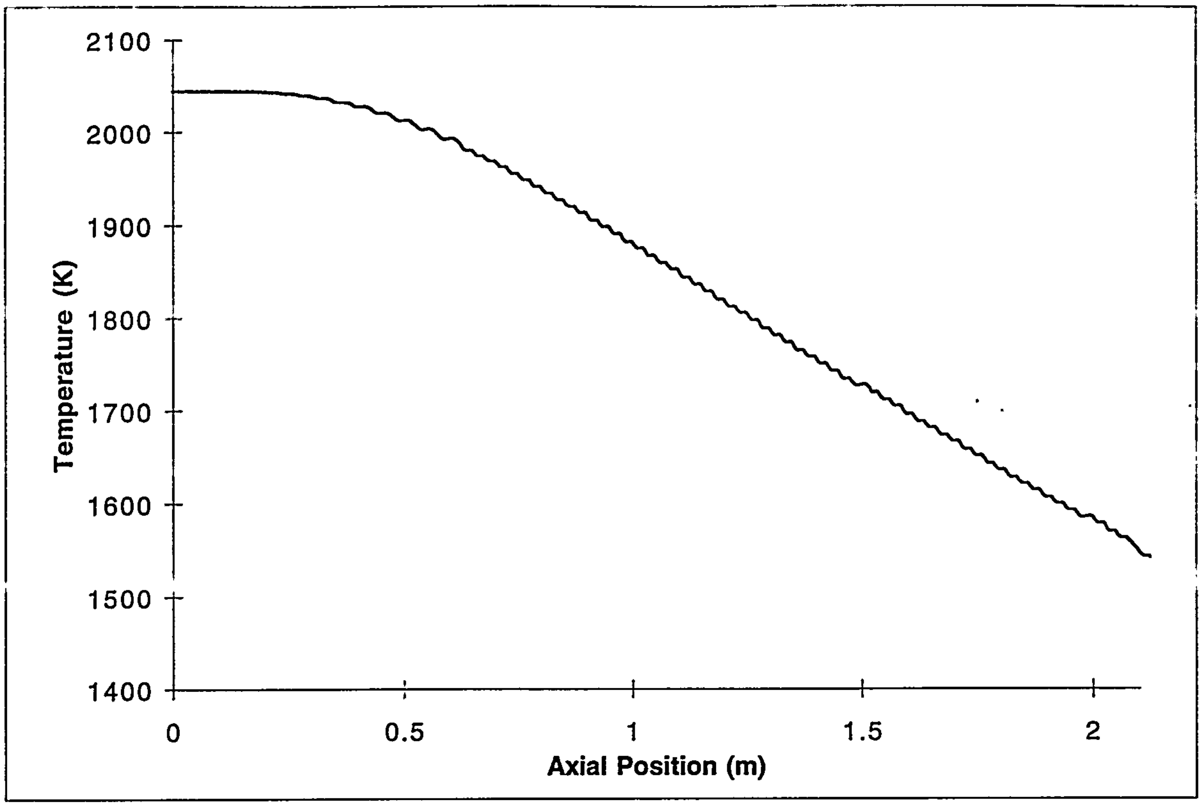

Figure 2. Axial centerline temperature profile

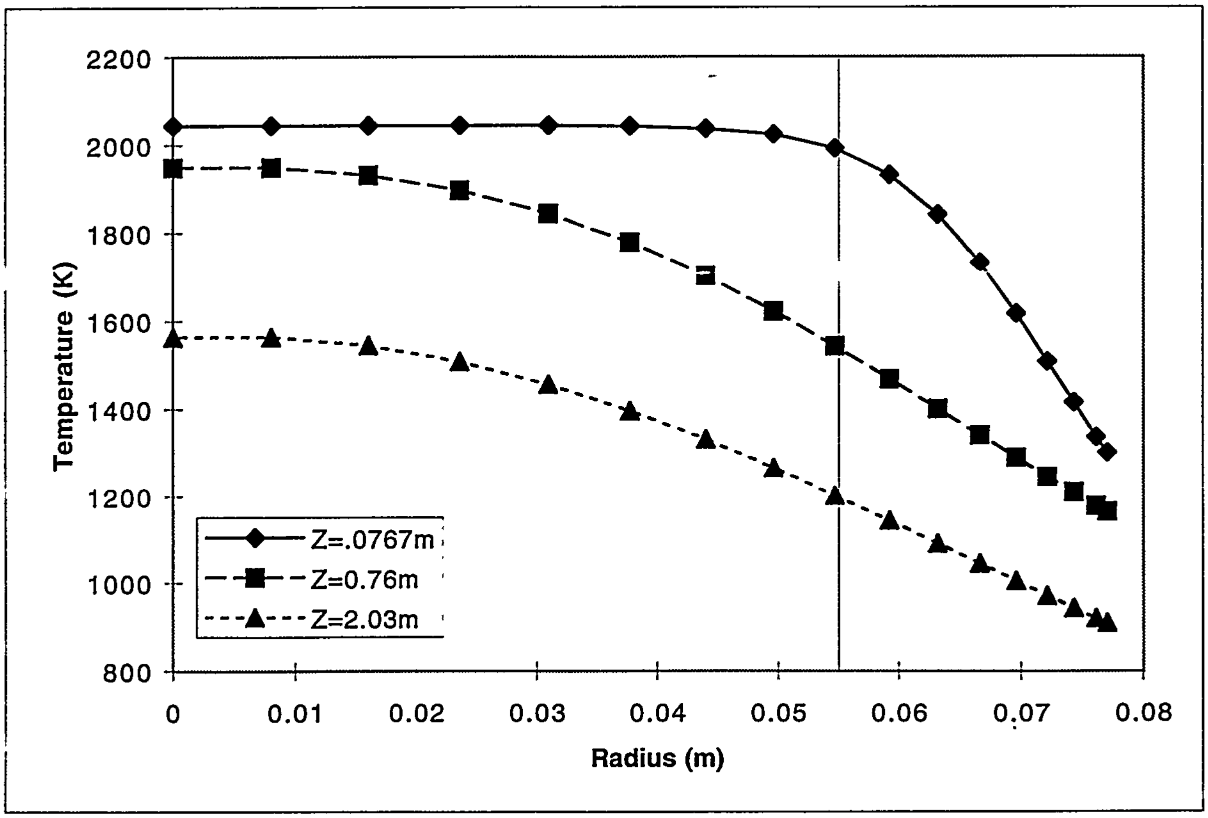

Figure 3. Radial temperature profile

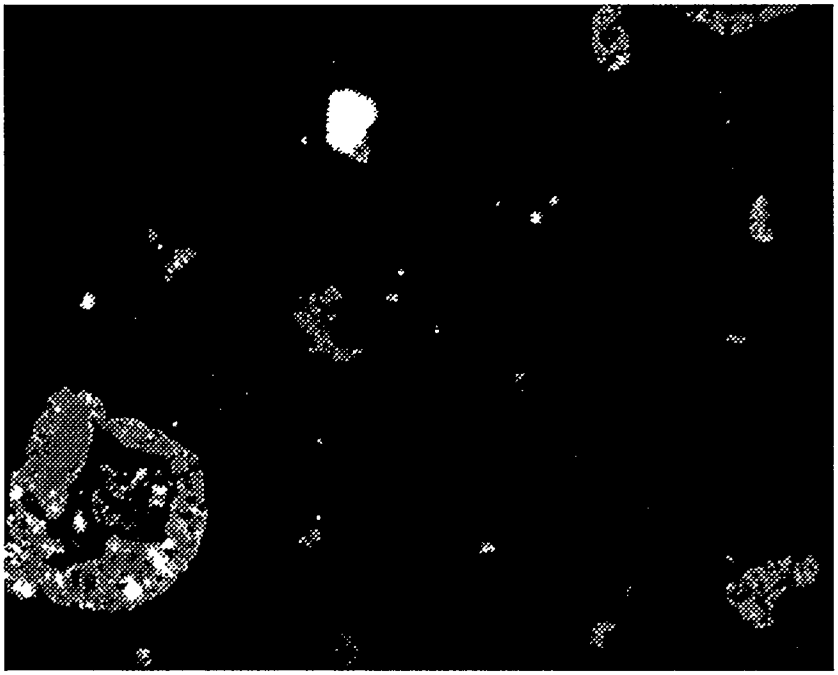

Figure 4. Cross section of Char and Ash Sample, BSE Image (250X)

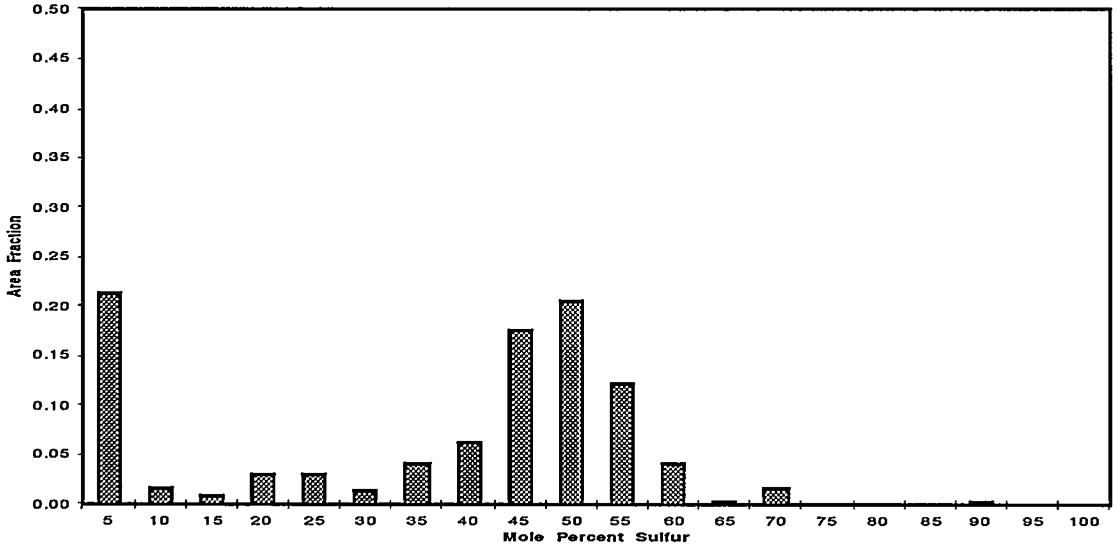

Fig. 5 Sulfur Distribution in Included Particles

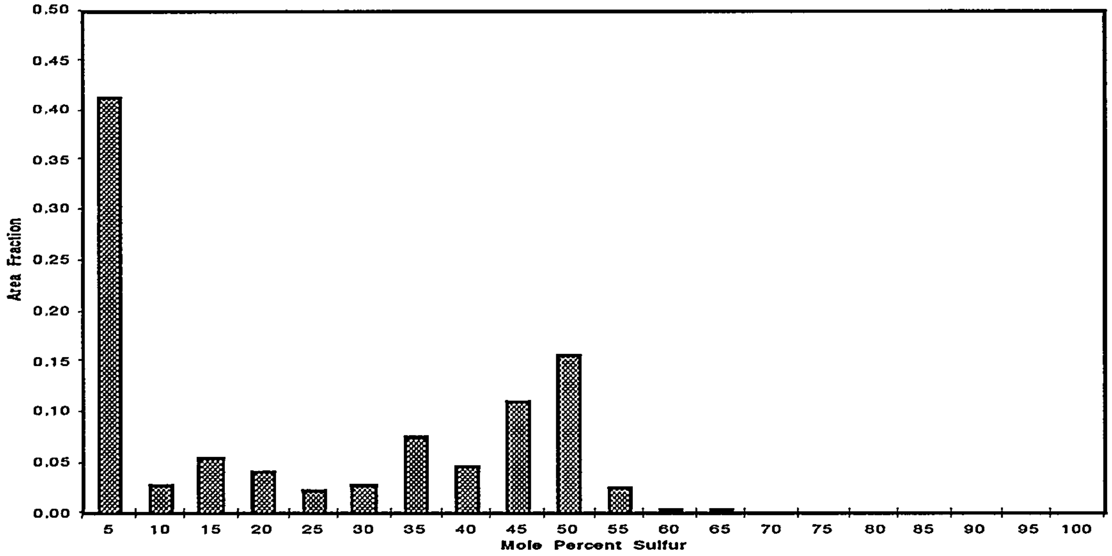

Fig. 6 Sulfur Distribution in Excluded Particles

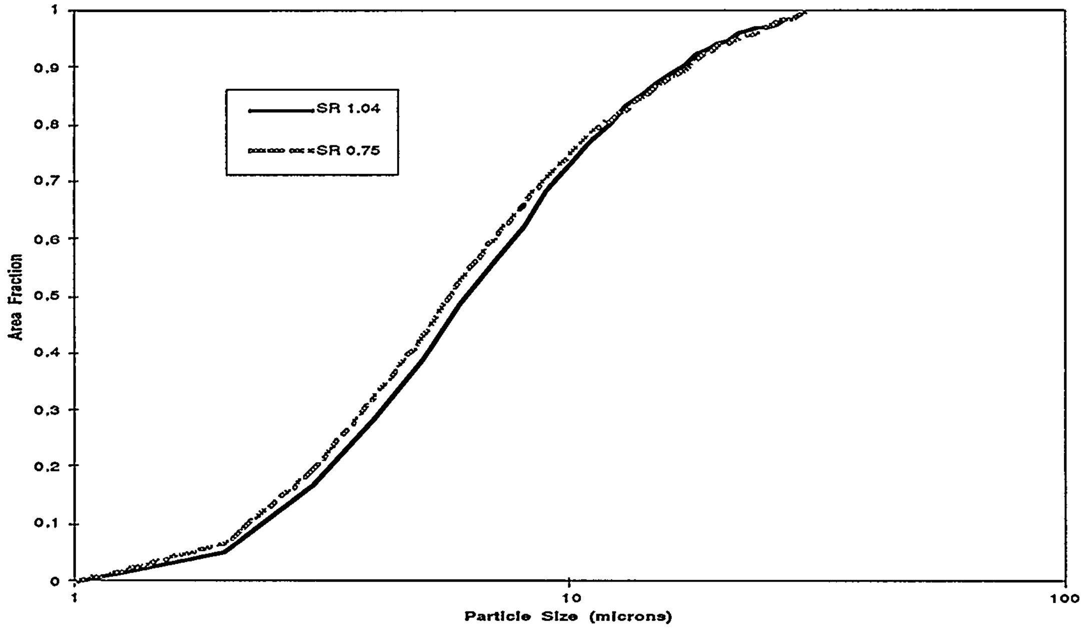

Fig. 7 Particle Size Distributions of Pittsburgh #8 Ash at Long Residence Time

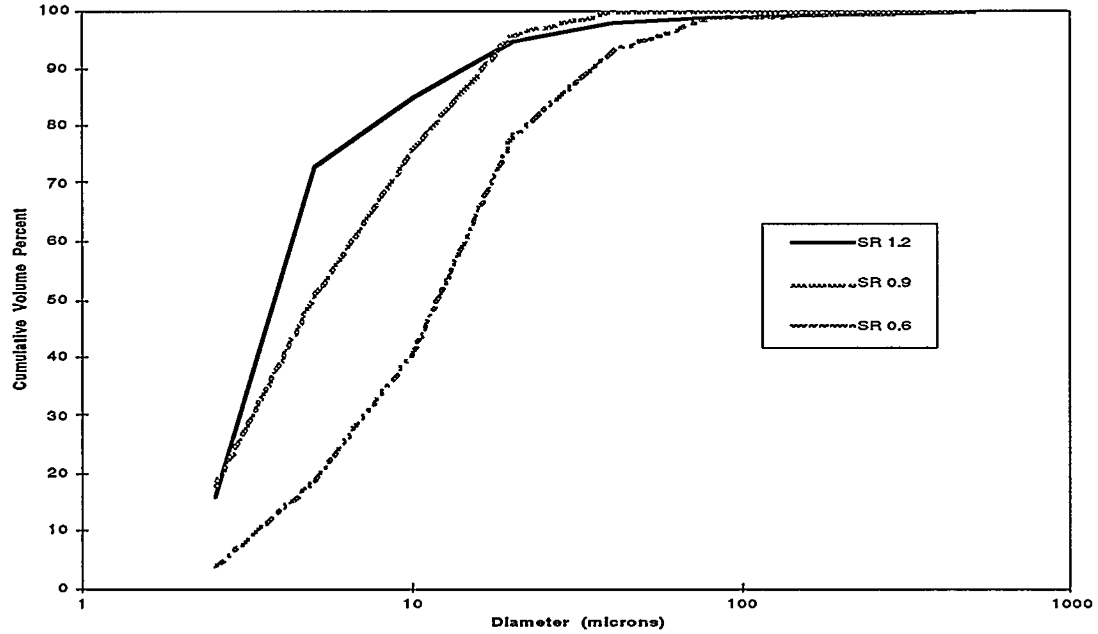

Fig. 8. PSD of Pittsburgh #8 Ash as a function of Stoichiometric Ratio (Boole et. al. 1995)

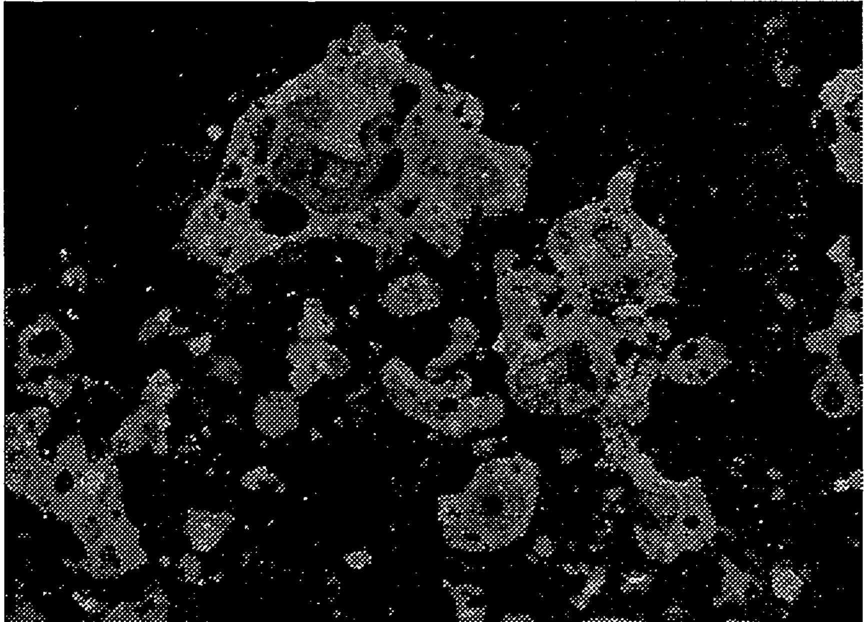

Fig 9. BSE image of Pittsburgh #8 Deposit (100X)