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**INVESTIGATION OF MINERAL TRANSFORMATIONS AND ASH
DEPOSITION DURING STAGED COMBUSTION**

Quarterly Technical Progress Report
July 1, 1995 to September 30, 1995

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FOREWORD

This report summarizes technical progress during the eighth quarter (July 1, 1995 to September 30, 1995) 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 Neal Adair and Peter Slater. Syndi Nettles, Eyas Hmouz, and Rachel Newsom, undergraduate students in chemical engineering at BYU, also made important technical contributions to this report.

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ABSTRACT

Progress during the eighth quarter of a three-year study was made in three task areas: 1) analysis of coals, 3) parametric testing of the target coals, and 4) analysis of samples from the combustion tests. Routines for automated analysis of coal and mineral associations were completed and are now functional on our new ISIS system. Work on data processing which led to the development of a new means of interpreting composition information from the SEM was also completed during the quarter. This work is expected to yield substantial benefits in understanding the ash transformations during combustion. Several additional ash and deposit samples were collected this quarter. Deposition results have been explained qualitatively and samples has been mounted for quantitative analysis. A detailed characterization of mixing and coalescence was performed during the quarter. Results indicate that combustion under staged conditions does not change the chemistry of the final ash produced. Specifically, both iron and potassium distributions in long residence time ashes did not change as a function of combustion conditions. Some differences were observed in the potassium distribution at shorter residence times. There was also a difference in the size distribution of particles formed during staged combustion. The nature and significance of these differences are still under investigation. Some of these results were presented at the International Coal Conference, Oviedo, Spain in September, and a manuscript documenting the results will be submitted for publication in the near future.

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 NO_x emissions from coal-fired units. It is applicable to both advanced combustion systems currently under development (e.g. HITAF) and low NO_x retrofits for existing units. These low NO_x 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 eighth 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 eighth quarter. Progress is summarized by task.

Task 1

Recent work on coal characterization has focused on the development of a new means of interpreting composition information which may yield substantial benefits in understanding the ash transformations during combustion. In CCSEM, particles classified as "unknown" are typically ignored in the interpretation of the results simply because no aggregate information pertaining to them is available; all that is known is that they do not fit into the known phase classifications. This is a significant drawback since the unknown particles comprise a significant fraction of the total particles in a typical analysis and can account for appreciable quantities of important elements such as iron. An algebraic interpretation of the phase classification criteria used to interpret compositions allows the use of quadratic programming to classify the unknown particles based on the closeness of the unknown compositions to known phases. The technique can thus identify new "pseudo-phases" which can then be used to track mineral transformations. A paper detailing the technique and initial results has been submitted for presentation at the March meeting of the American Chemical Society in New Orleans.

Progress has also been made in converting to the Link ISIS microanalytical system. Routines for the analysis of coal and mineral associations (AMCA) are now complete and functional. The first set of associations data from the new microscope system for the Pittsburgh #8 coal has been collected. These data will be reported when more corroborative data is available.

Work is also in progress on the development of methods for examining intimate associations of minerals (e.g. pyrite inclusions in quartz, etc). Manual work with the online analysis routines discussed last quarter has shown that such particles are present in the coal and that quantifying them may play a role in understanding the composition of the ash.

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 test has been largely completed, although improvements to current probe designs are under consideration.

Task 3

During this quarter, additional ash and deposit samples were collected for the DOE Pittsburgh #8 coal. Experiments were performed at two different firing rates under both staged (SR=0.75 before downstream air injection) and conventional (SR=1.04) conditions. Thus, a total of four different tests were conducted. For the low firing rate tests, 1.5 lb/hr (17,850 BTU/hr) of coal was fed under SR=1.04 conditions, while 2 lb/hr (23,800 BTU/hr) was fed under SR=0.75 conditions. The total rate of energy (BTU/hr) was the same for both types of firing conditions (40,500 BTU/hr). However, a larger percentage of natural gas was needed to stabilize the flame at SR=1.04 than at SR=0.75. The coal feed rates for the high heating rate tests (80,500 BTU/hr)

were twice those used for the low firing rate tests.

Ash samples were collected at three locations for each of the four operating conditions to provide a total of twelve different samples. The sampling locations were 1) directly above the staged air inlet (33 cm from the burner), 2) below the staged air inlet (81 cm from the burner), and 3) at the bottom of the reactor (180 cm from the burner). Under staged conditions, overfire air was added 65 cm downstream from the burner to produce a final SR of 1.04. The sampling locations were chosen to provide insight into the mechanisms which control ash transformations. Most of the ash was collected in a cyclone designed to capture 50% of particles with an aerodynamic diameter of 2 μm . The balance of the particles were collected on an in-line filter with a pore size of 0.8 μm . Over 90% of the particulate was collected in the cyclone in a typical run.

Deposits were also collected at each of the four operating conditions at a single sampling point located 33 cm from the burner. The deposits collected at the low firing rate closely resembled those previously reported at a coal feed rate of 2 lb/hr. At this firing rate, the SR=0.75 deposit was grey/orange and ashlike on the surface after 45 minutes of sample collection. Near the tube, however, the particles did not burn out completely after impacting on the surface. Therefore, a significant amount of carbon was present in the deposit adjacent to the tube, resulting in a deposit which was only loosely attached to the tube. Less deposition was observed at SR=1.04, but the deposit was more highly sintered. Additionally, the deposit was more firmly attached to the tube than the SR=0.75 deposit. It was expected that the higher firing rates would result in higher deposition rates and greater levels of sintering in the deposits at both SRs due to the higher temperatures. However, the deposits were smaller and contained more carbon than those collected at the low firing rate. This observation suggests that the dominating factor in these deposition experiments may have been the incident velocity of the particles. Molten particles were observed on deposits formed near the edges of the deposition probe where the velocities were significantly lower. However, the velocities in the center of the probe apparently precluded the formation of a substantial deposit.

Three additional deposits were collected at SR=1.04 conditions in an attempt to quantify the velocity effect. The firing rates of coal and gas for these runs were 45,000 BTU/hr (1.75 lb/hr), 49,000 BTU/hr (2 lb/hr), and 59,000 BTU/hr (2.25 lb/hr). While all of these deposits were similar to the deposit formed at the low firing rate (1.5 lb/hr), the deposit height decreased with increasing firing rate. None of these deposits appeared to contain a significant amount of carbon. Similar runs for SR=0.75 are now in progress.

Task 4

The scanning electron microscope was used to analyze ash samples from the Pittsburgh #8 DOE coal collected at different residence times under two different types of firing conditions. Both manual and automated analyses were performed to examine particle morphology and mineral transformations. Automated analyses were performed on particulate samples collected in the cyclone. A small amount of material was also collected on in-line filters downstream of the cyclone. These filter samples did not provide enough material to perform automated analyses using our current sample preparation procedures. Therefore, only manual SEM examination of the filter samples was performed.

Figure 1 is a representative secondary electron image of the char and ash from the SR 1.04 filter. Spherical ash particles with diameter 1-2 microns are the dominant features seen. The broken remnants of char cenospheres are also observed, but in far less abundant numbers than the ash particles.

Figure 2 is a corresponding image from the SR 0.75 sample. While ash is seen, it is far less abundant than it is in the SR 1.04 sample. Specifically, the 1-2 μ m ash particles are not the dominant feature in this sample. The char also appears in the form of larger cenosphere remnants. The samples have similar burnouts (94% and 92%), so the differences observed may be attributed to the mixing/coalescence phenomena discussed below.

Automated analysis of the samples was performed using a JSM 840A electron microscope and a Link ISIS microanalytical system. Samples were mounted in wax, cast into epoxy plugs, sectioned, polished and carbon-coated. Data were collected from 7,000 to 13,000 inorganic particles per sample, depending on the time available for analysis and the density of the particles in the sample. Sample analysis was performed at two magnifications. Since the primary goal this quarter was to investigate mixing, only results relevant to that topic will be reported here.

If the ash is considered on a particle-by-particle basis, then the effect of the combustion conditions on both the elemental composition and size of the particles can be examined. It may also be possible to examine shape at a later date to provide insight into the mechanisms which govern coalescence and fragmentation. Figure 3 is a number frequency histogram of the distribution of iron in the parent Pittsburgh #8 coal. Since a large number of bins were used for resolution, the data have been presented as a continuum plot instead of in the more typical bar chart format. Two distinct types of iron-bearing particles are seen. Pyrite particles, which account for 45% of the iron in the coal, give rise to the small peak centered at 47%. The relatively large number of silicate particles which contain iron as a minor constituent are responsible for the peak near the left edge of the graph. There are also a small number of iron oxide particles which should appear at 100% iron since oxygen was not considered, but are not visible due to scaling. Also note that 38% (by number) of the mineral particles in the coal contained little or no iron.

The distribution shown in Fig. 3 is expected to change due to transformations and coalescence during combustion. For example, the number fraction of particles which contain little or no iron would decrease due to mixing and coalescence with iron containing particles. Pyrite particles which mix with silicate minerals would increase the number fraction of iron containing particles on the left-hand side of the figure. In contrast, pyrite particles which did not mix with other minerals would show up on the right side of the diagram as iron oxide. In either case, the pyrite peak in the middle should disappear. Therefore, a diagram such as that shown in Fig. 3 can be used for both coal minerals and ash to quantify the extent of ash mixing.

Both short residence time (collected 33 cm from the burner) and long residence time (collected 180 cm from the burner) samples at staged (SR=0.75) and conventional (SR=1.04) firing conditions are compared in the results which follow. Note that the burnout of the samples at each sampling location was approximately equal.

Iron distribution data from ash samples taken at the two residence times are shown in Fig. 4, along with the coal data. The dramatic decrease in the fraction of iron-free particles from 38% to about 15% is strong evidence that mixing has taken place during combustion. Given that there is not a large difference between the short and long residence time data, it appears that much of the change occurs quickly. The small pyrite peak at 47% iron in the coal data is no longer present in the ash, consistent with rapid pyrite oxidation. The appearance of the small iron peak near 100% iron indicates that at least a portion of the pyrite does not interact with other minerals. This observation is consistent with our studies of coal/mineral associations which show that a significant fraction of the pyrite is not available for mixing. The increase in the number of iron-containing particles is due to coalescence of iron-free particles with iron-bearing clays and with a fraction of the pyrite particles which are found in association with other minerals.

Comparison of the results from ash collected at SR=1.04 with those from the staged combustion test (SR=0.75) indicates that staged combustion appears to have little or no effect on the distribution of iron in the ash. Both data sets indicate approximately the same amount of mixing and a similar distribution of the iron in the final ash.

Potassium distribution data for the same samples are presented in Fig. 5. Here, the residence time and firing conditions are both seen to affect the distribution. The potassium in the coal is found in clays, and not in minerals which contain high concentrations of potassium. Therefore, there are no peaks in the coal data similar to the pyrite peak observed for iron, and there is no significant formation of a potassium oxide phase. Rather, the clay minerals containing 10-20% potassium are the source of material for mixing. (Note that the horizontal axis has been truncated at 25 wt% potassium; there are essentially no particles to the right of that point.) The difference in shape between the short and long residence time curves implies that two mixing and coalescence mechanisms are at work, and that one operates on a much shorter time scale than the other. The short residence time curve in the SR 1.04 sample is different from that in the SR 0.75 sample, indicating that stoichiometry has an effect on the faster mixing mechanism, although the final ash is not affected. In fact, no significant difference was seen in the distribution of the final ash when the two sets of data are plotted on the same figure.

A difference due to stoichiometry is also evident in the frequency distribution of the long residence time ash particle size (Fig. 6). The SR 0.75 ash is clearly larger than the SR 1.04 ash. This implies more coalescence, and may provide an explanation for the differences seen in the filter sample. The small SR 0.75 ash particles may be absent because they have combined to form larger ash particles.

In summary, combustion under staged conditions does not appear to change the chemistry of the final ash. Specifically, both the iron and potassium distributions in the final ash did not change as a function of combustion conditions. However, there was a difference in the size distribution of particles formed during staged combustion. The nature and significance of this difference is still under investigation. Some of these results were presented at the International Coal Conference, Oviedo, Spain in September, and a manuscript documenting these results will be submitted for publication in the near future.

D. Plans for the Next Quarter

1. Continue development of CCSEM routines to permit association analysis on coal and char. Coal analyses are now possible; development of the char procedure is still in progress.
2. Perform SEMPC analysis of the first set of deposit samples.
3. Examine particle size effects in particulate samples.
4. Prepare at least one publication documenting our results.

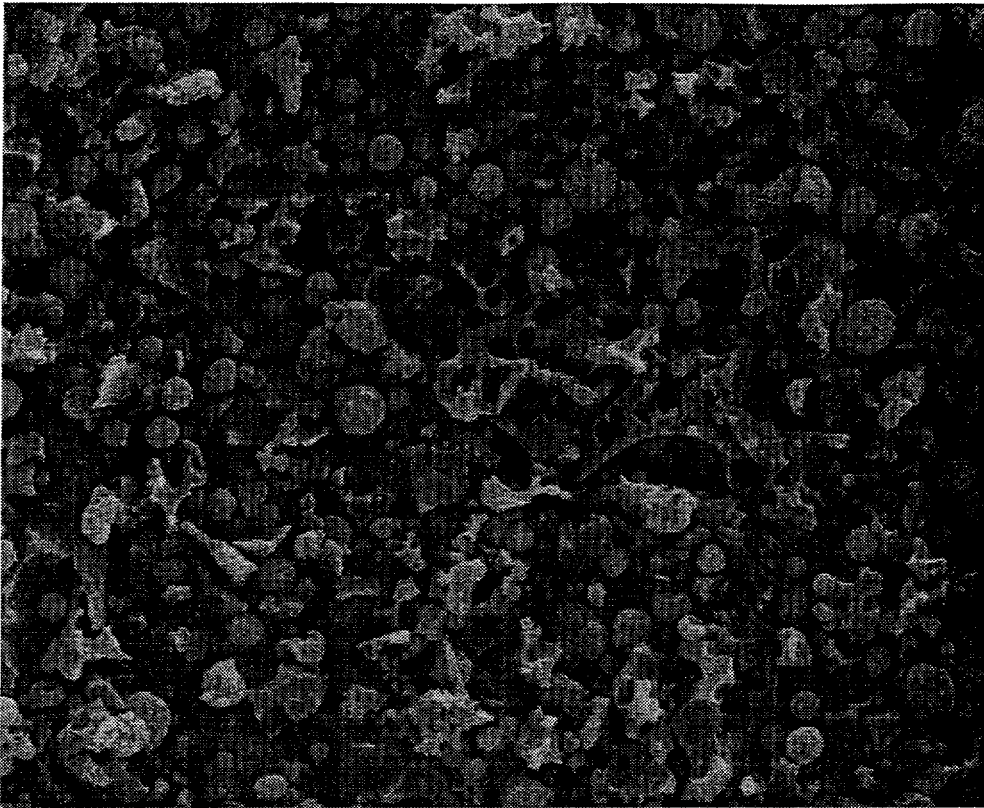


Figure 1. Secondary Electron Image of SR=1.04 Filter Sample

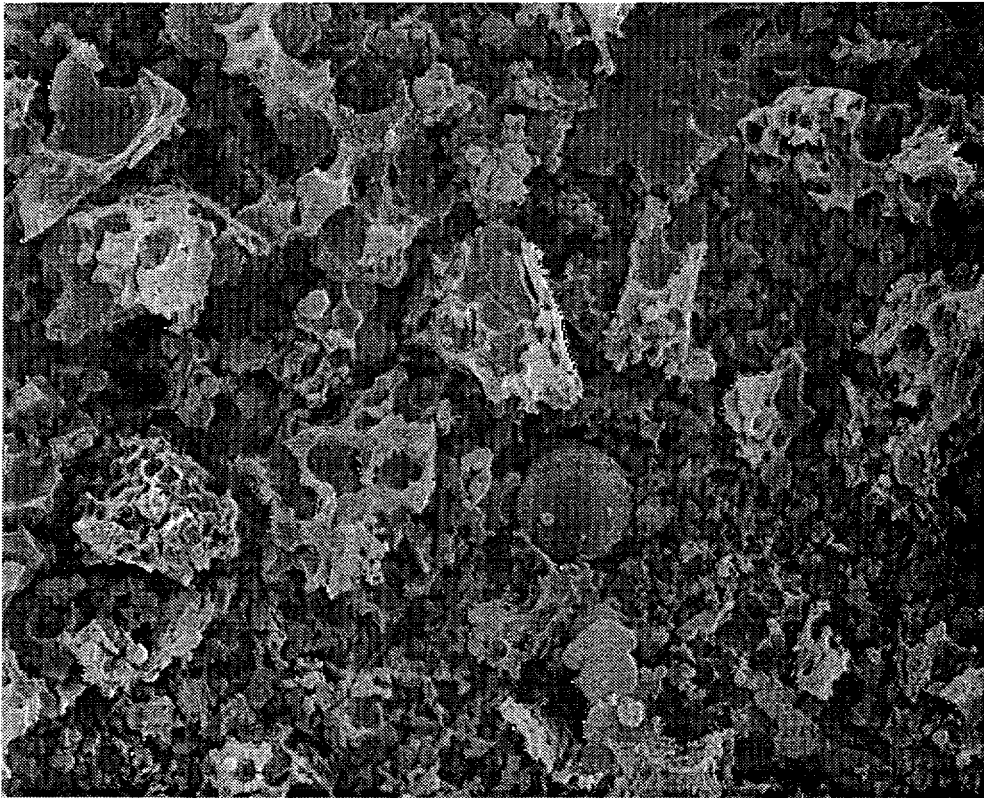


Figure 2. Secondary Electron Image of SR=0.75 Filter Sample



Figure 3. Parent Coal Iron Distribution by Number Frequency

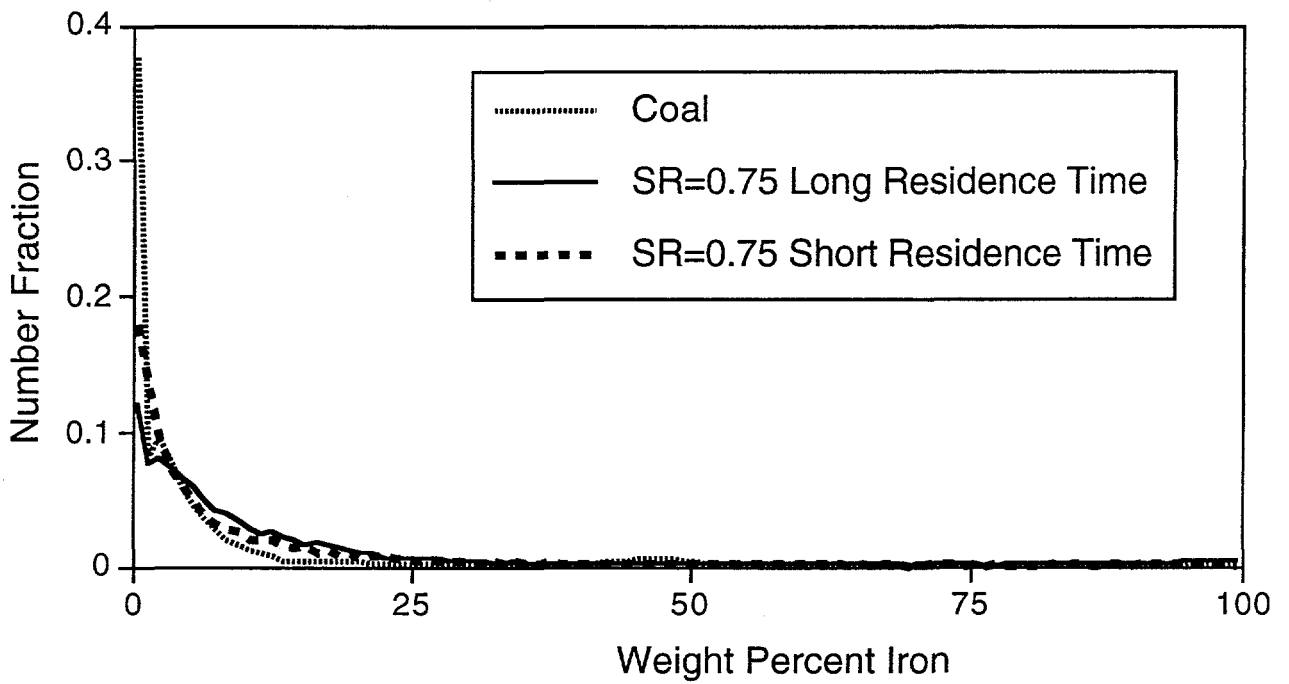
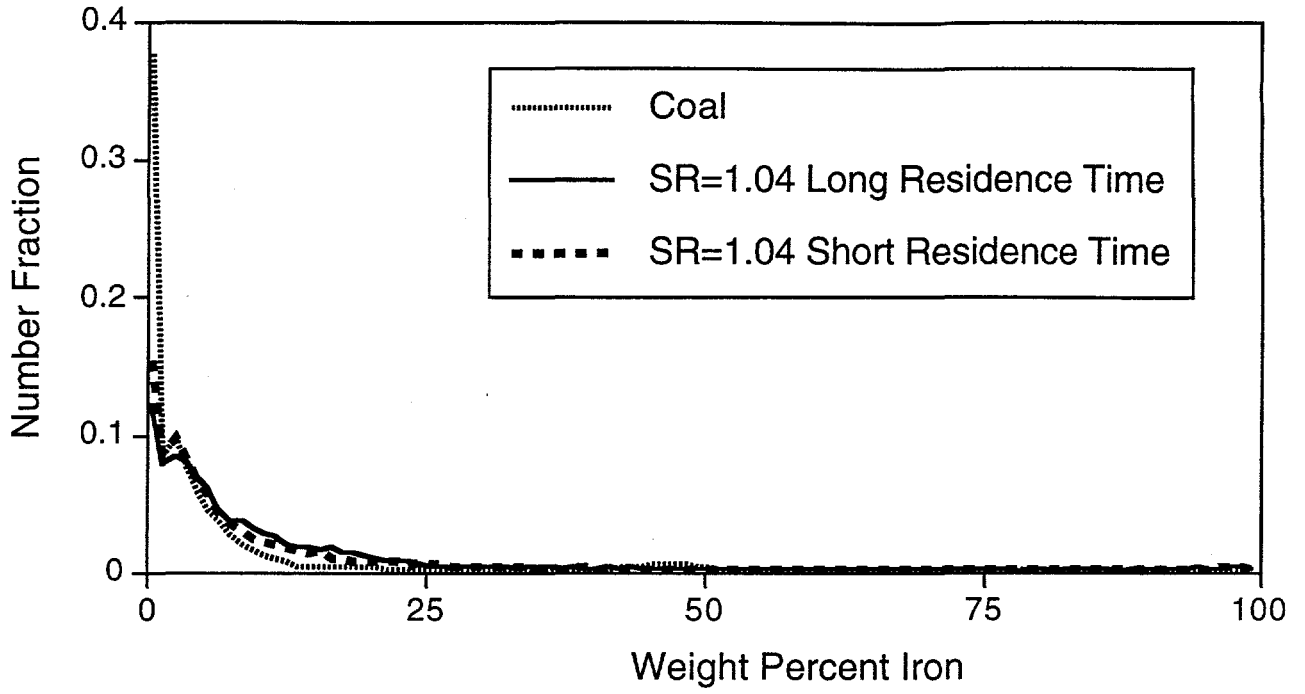


Figure 4. Iron Distribution in Coal and Ash

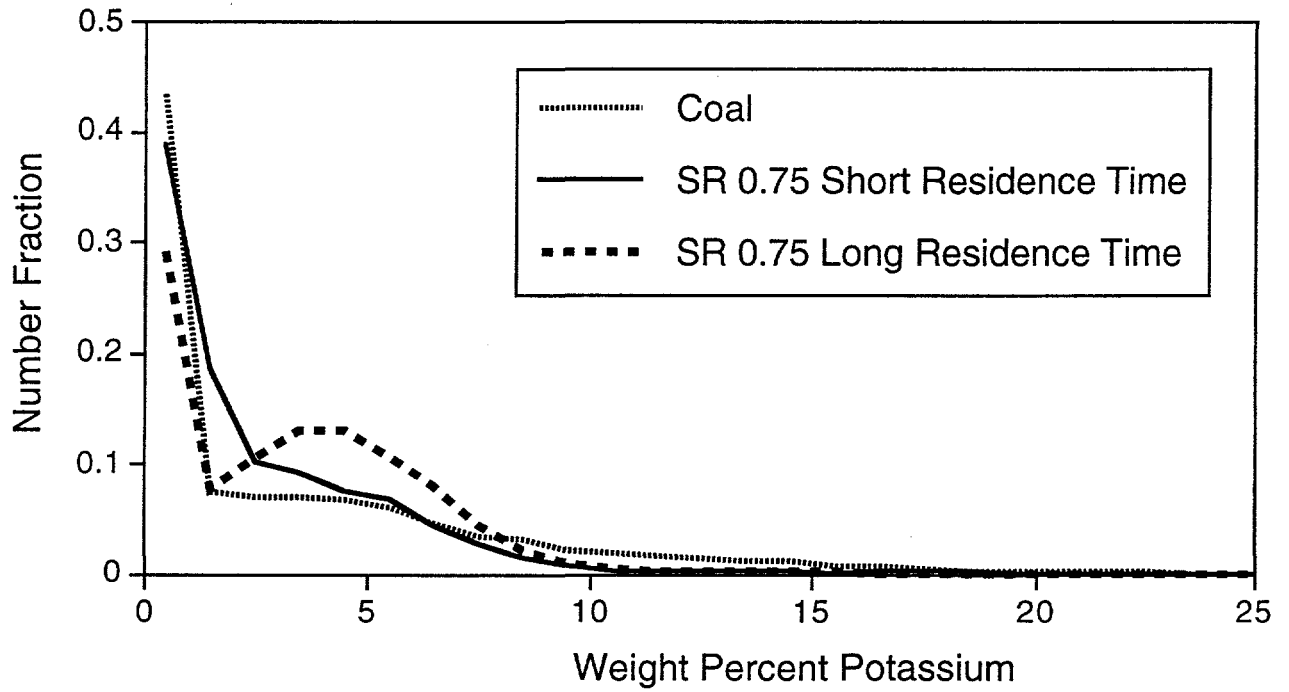
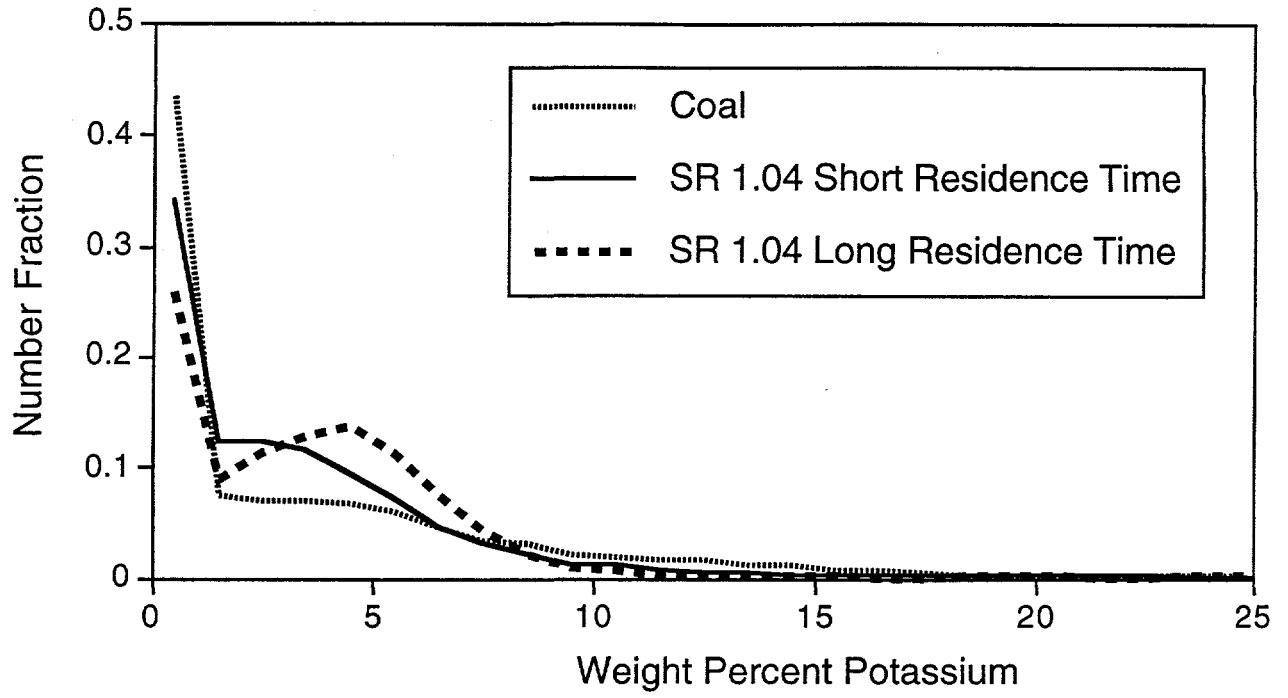


Figure 5. Potassium Distribution in Coal and Ash

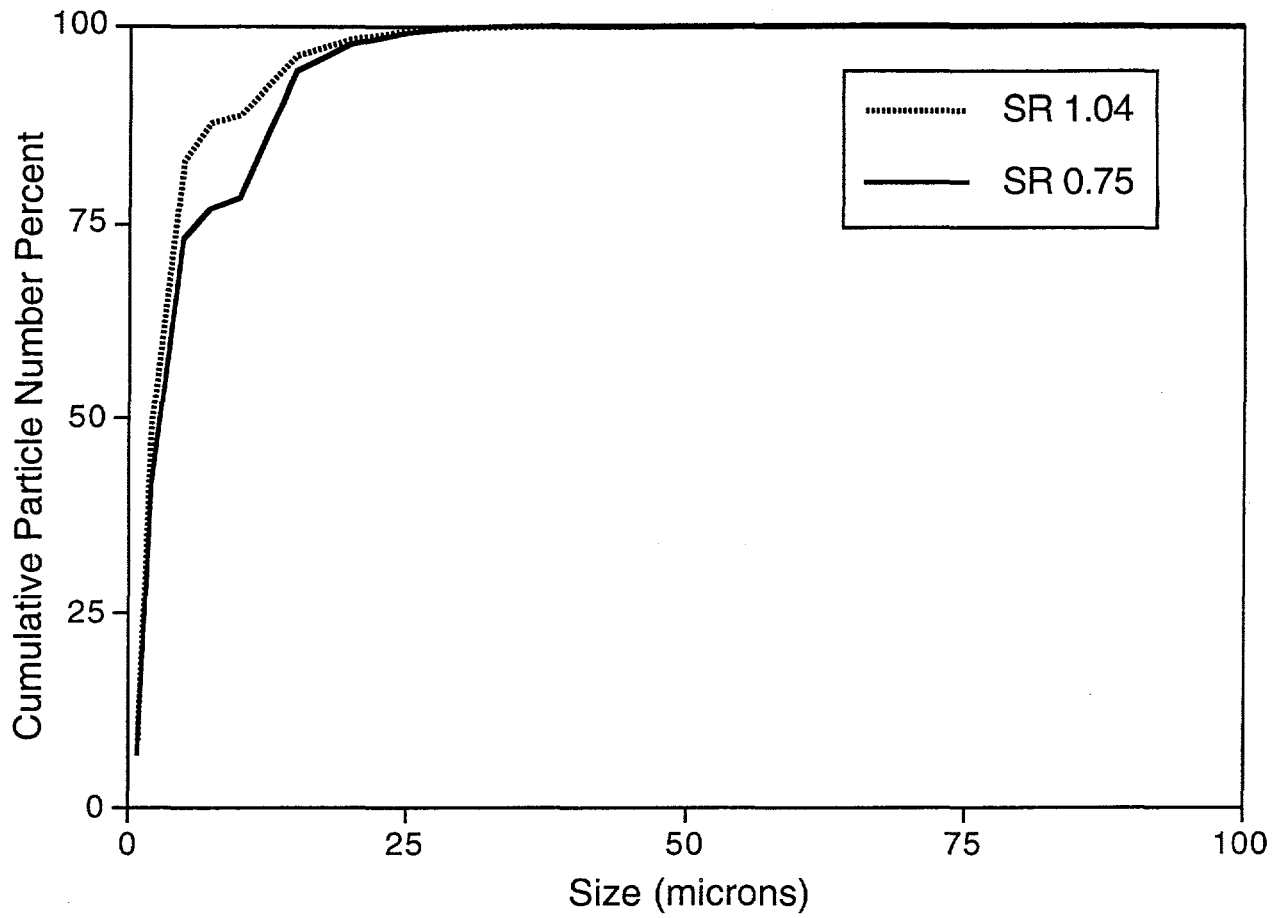


Figure 6. Particle Size Distribution of Long Residence Time Ash