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

Quarterly Technical Progress Report
January 1, 1995 to March 31, 1995

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FOREWORD

This report summarizes technical progress during the sixth quarter (January 1 to March 31, 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. Bret Abbott, 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 sixth quarter of a three-year study was made in two task areas: 1) parametric testing of the target coals, and 2) analysis of samples from the combustion tests. A new microanalysis system was acquired (no cost to DOE) and is now functional, although development of analysis routines for the system is still in progress. This system has significantly increased our analytical throughput and has provided increased reliability. Parametric testing of the Pittsburgh #8 coal (weathered) was initiated this quarter. Initial analytical results from these tests show sulfur release and iron transformations as a function of test conditions and sampling location. A new supply of Pittsburgh #8 coal has been shipped and will be used to contrast behavior between the oxidized (weathered) and unoxidized Pittsburgh fuels. Finally, specific tasks for the next quarter have been identified and reported.

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 sixth 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 sixth quarter. Progress is summarized by task.

Task 1

As mentioned in previous reports, it was necessary to replace our SEM microanalysis system because of a defect in the operating system which the manufacturer has been unable to fix. Our new microanalysis system finally became operational near the end of this quarter. As expected, the new system is much faster and we are now able to analyze a great deal more data in a shorter time. However, we have had to develop new procedures for automated analysis since it was not possible to transfer the old procedures to the new system. Procedures for analyzing the mineral size and composition distributions have been developed and are now in use. Development of the routines for image analysis to determine coal-mineral associations is still in progress.

One of the first analytical results from the new system was the observation that the pyrite in the Pittsburgh #8 coal was partially oxidized (weathered). The rate of oxidation was undoubtedly enhanced when the coal was repulverized to solve our feeding problems. The CCSEM analysis reported previously (4th quarter) showed that a major fraction of the iron in the coal was found in pyrite. In contrast, our most recent analysis of the same coal after repulverization shows iron in an oxidized form. We are now working to determine the extent of the oxidation and if the oxidation occurred in all pyrite particle size ranges. Also, once it is completed, our image analysis routine will be used to examine the relative oxidation of included and excluded particles. Finally, additional samples of a Pittsburgh #8 coal have been acquired and should arrive shortly. These samples will be stored under nitrogen prior to testing. Comparison of the different sets of tests will allow us to contrast the behavior of the weathered and unweathered coals.

Task 2

Only maintenance was performed under this task this quarter.

Task 3

Tests were initiated this quarter as part of the parametric study with the Pittsburgh #8 coal. The tests were conducted at a coal feed rate of 0.91 kg/hr (2 lb/hr) under both staged and conventional conditions. In both cases, about one half of the total heat was supplied by natural gas. In the staged tests, the stoichiometric ratio (SR) above the staged air injection point of the down-fired reactor was 0.65. Overfire air was added 65 cm (26 inches) downstream from the burner to produce a final SR of 1.00. In contrast, all of the combustion air for the unstaged (conventional) test was premixed with the coal and entered the reactor through a premixed burner. The overall SR for the unstaged test was 1.04. Ash samples

were collected at two locations in the reactor for each of the tests, one upstream from the injection point (43 cm from the burner) and one downstream from the injection point (170 cm from the burner).

Note that the stoichiometric ratio of 0.65 is significantly lower than commonly used for low NO_x firing. Use of a laminar flow reactor precludes simulation of the mixing conditions which dominate behavior in large-scale systems. However, the laboratory combustor permits a fundamental study of particles with a narrow range of time-composition-temperature histories. Operating conditions in the laboratory combustor are chosen to approximate conditions experienced by particles in large-scale systems designed for low NO_x combustion. For example, in a utility system equipped with low-NO_x burners, the coal is devolatilized in a low SR zone since only about 10-15% of the total air is fed with the coal. An additional 60-65% is injected coaxially as secondary air, and the remainder of the air is injected at some point above the burner. This staging of the combustion air results in a longer flame. A typical low NO_x burner produces a reducing zone (established by controlling mixing) with a mean residence time of approximately 100-250 milliseconds. The experimental conditions (SR = 0.65) were designed to approximate the reducing conditions experienced by the particle during the initial period.

Task 4

Burnout data for samples collected at both 43 cm and 170 cm downstream from the burner are shown in Table 1 for both conventional firing and staged combustion. The particle residence time at a given sampling location for the staged combustion case was longer than the residence time at the same location under conventional firing due to lower flow rates in the upper section of the combustor under staged conditions. The burnouts were considerably lower for the staged experiments, in spite of the longer residence times. Low burnouts were expected since the combined amount of coal volatiles and natural gas was sufficient to consume the oxygen in the upper portion of the combustor before the staged-air inlet.

Sample	Burnout
Staged, Top (43 cm)	67%
Staged, Bottom (107 cm)	74%
Conventional, Top (43 cm)	86%
Conventional, Bottom (107cm)	91%

The four samples collected under Task 3 were also analyzed using a JSM840A electron microscope and the new Link ISIS microanalytical system. Samples were mounted in epoxy, sectioned, polished and carbon-coated. Automated analyses were used to collect data from 2000 to 6000 inorganic particles, depending on the time available for analysis and the density of the particles in the sample. Due to the current status of our CCSEM routines

which are being developed from scratch for the new system, only inorganic particles (minerals/ash) were analyzed and no quantitative analysis of organic/inorganic associations was performed. Also, only a single magnification was used (500X). At this magnification there was a paucity of data from large particles. Consequently, *the results discussed below apply only to small particles less than 15 μm* . The number of particles in this small size range was large enough that we feel confident of the results.

Sulfur release was examined as a function of firing conditions and sampling location. Figures 1 and 2 show the frequency percent of inorganic particles as a function of their sulfur content (mole percent). The mineral phases in the coal which contained the largest proportion of sulfur were the iron sulfide/sulfate phases. Only 15 to 20% of the coal minerals had a sulfur content above 5 mole%. Fig. 1 shows partial release of the sulfur above the stage when firing under staged conditions. A significant number of particles remain in the mid-sulfur range (10-40 mole% sulfur). However, the high sulfur containing particles are no longer present. Considerably more sulfur was released after the stage (bottom). In contrast to the staged combustion results, Fig. 2 indicates that the sulfur was released much earlier when firing under conventional conditions (SR = 1.04), even though the residence times were shorter than those of the staged experiments because of increased gas flows in the top section of the combustor.

The release of sulfur from iron containing particles is illustrated in Fig. 3. Note the group of particles in the coal whose composition is approximately 50 mole% sulfur and 50 mole % iron, corresponding to oxidized pyrite. The particles lose sulfur in the combustor and their compositions shift down and to the right as shown on the figure. The rate of sulfur release varies from particle to particle as evidenced by the distribution of sulfur in the partially oxidized particles. The difference in the release rate is expected to be a function of particle size and may also depend on whether the individual mineral grains are included or excluded.

Figure 4 provides a summary of phases determined for the sampling positions before (Top) and after (Bottom) the staged air inlet during the experiments performed under staged conditions. Although many of the phases were similar, there are a couple of noticeable differences. In particular, the amount of iron oxide is considerably higher in the bottom (after staged air inlet) sample. In contrast, the amount of partially oxidized iron/sulfur (FeS Intermediate) and the amount of an aluminosilicate/iron sulfide blend are significantly higher in the top sample taken before the staged air inlet. It is not clear whether the blend phase is an actual blend or an intimate association of small aluminosilicate and iron sulfide inclusions. It appears, however, that iron is transferred from the blend phase to the oxide phase. This conclusion is further supported by Fig. 5 which shows the weight percent of iron in each of the specified phases. The movement of iron from the FeS intermediate and the Al-Si_Fe-S_blend to the iron oxide phase is clearly seen in this figure. The nature of these transformations as well as transformations of the large inorganic particles will be examined as part of continuing work on this contract.

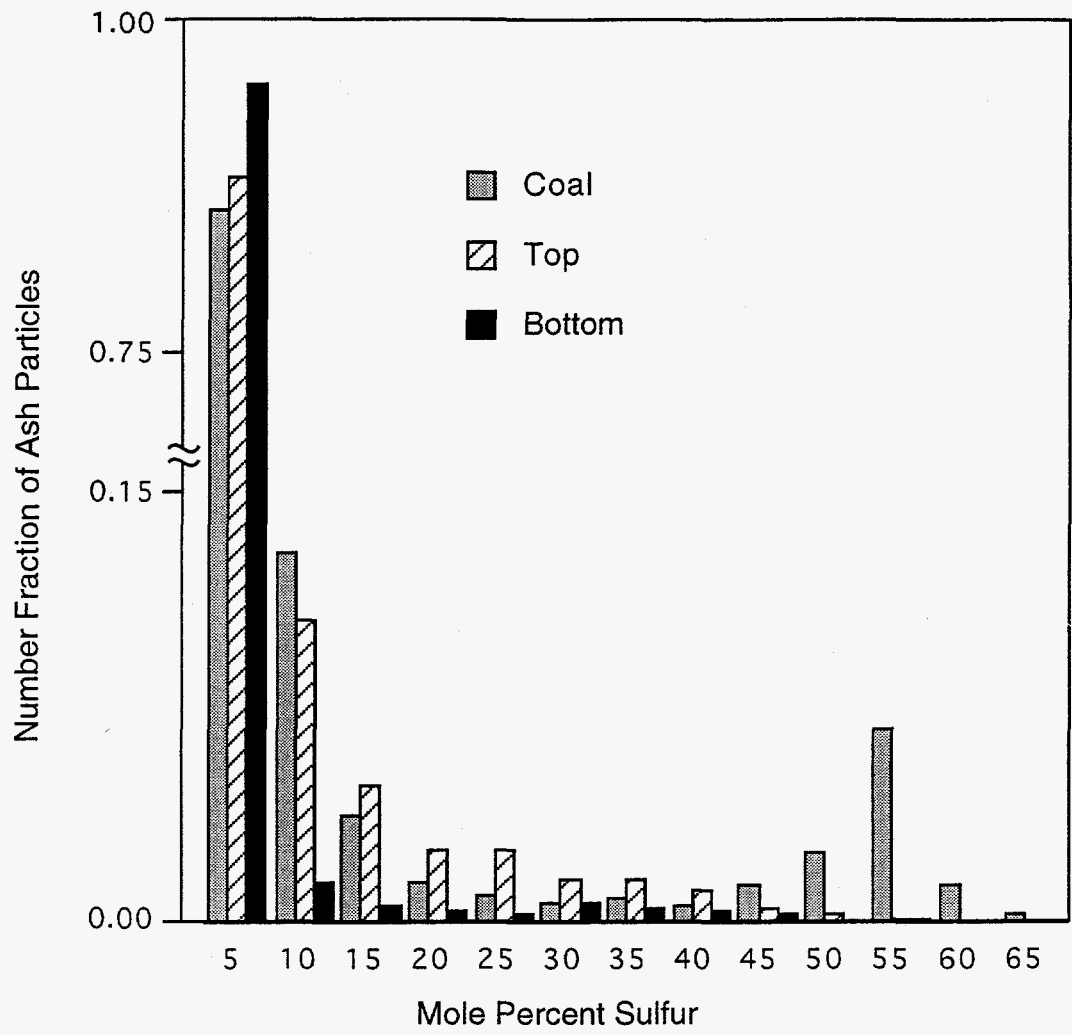


Figure 1. Distribution of sulfur in staged samples.

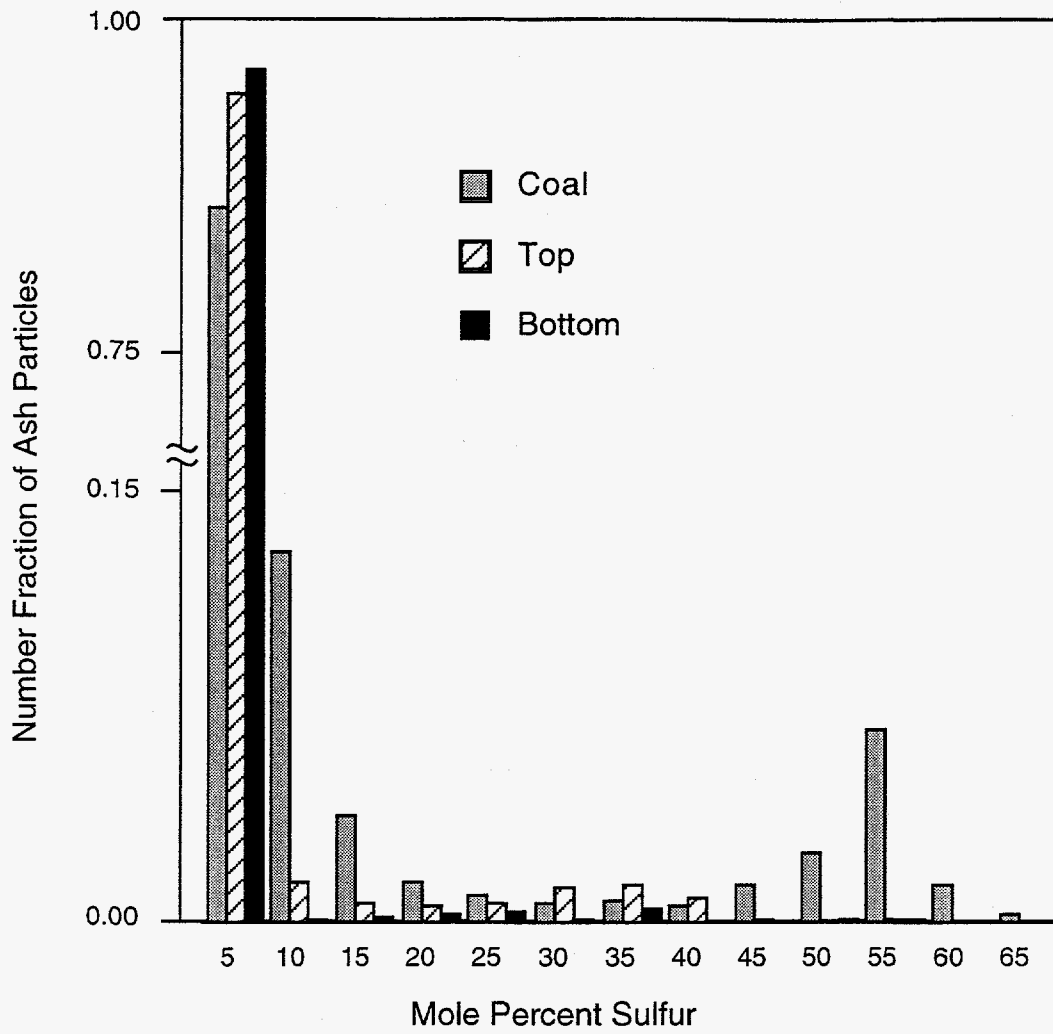


Figure 2. Distribution of sulfur in conventional samples.

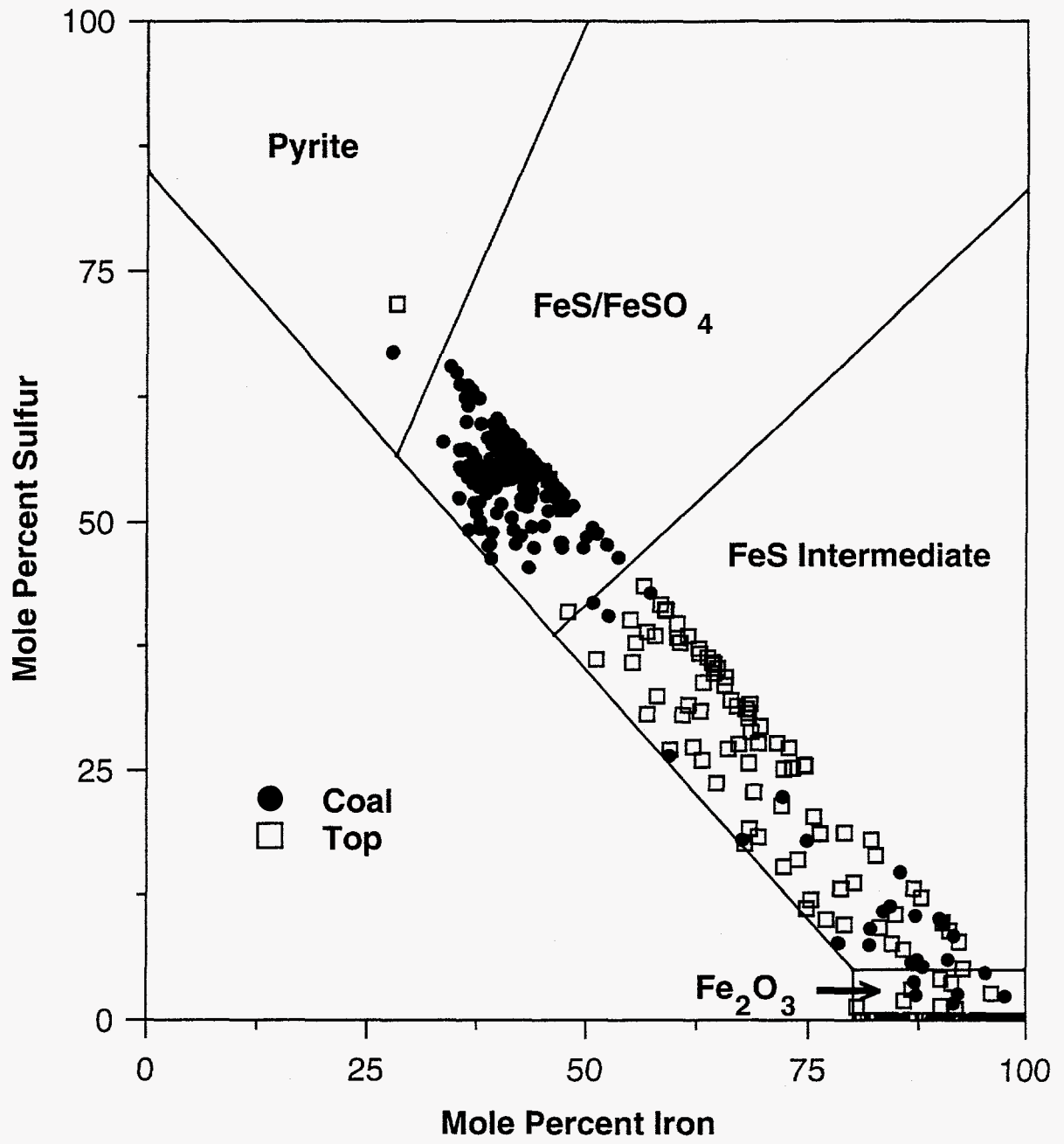


Figure 3. Release of sulfur from iron-containing particles

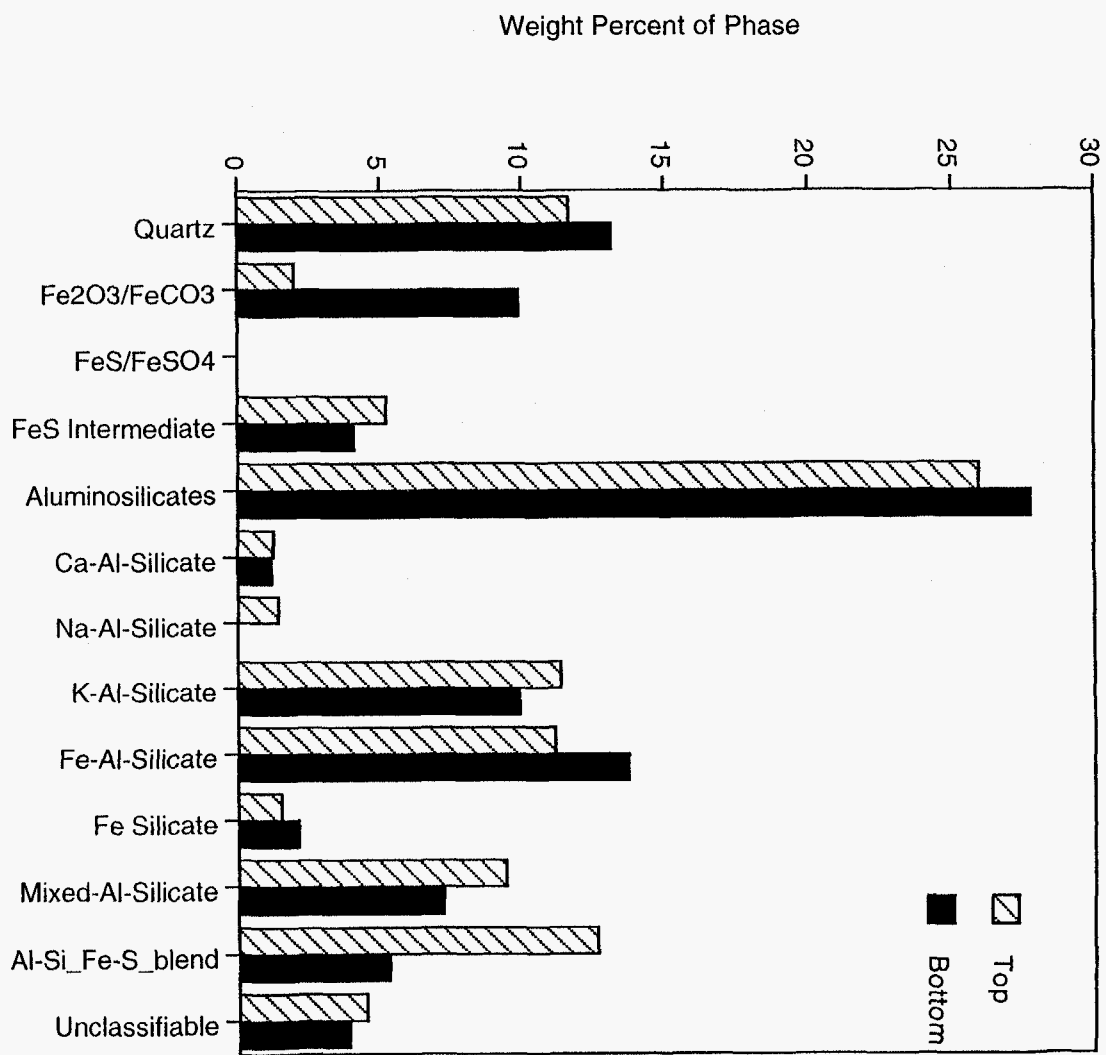


Figure 4. Distribution of inorganic material among the phase classifications.

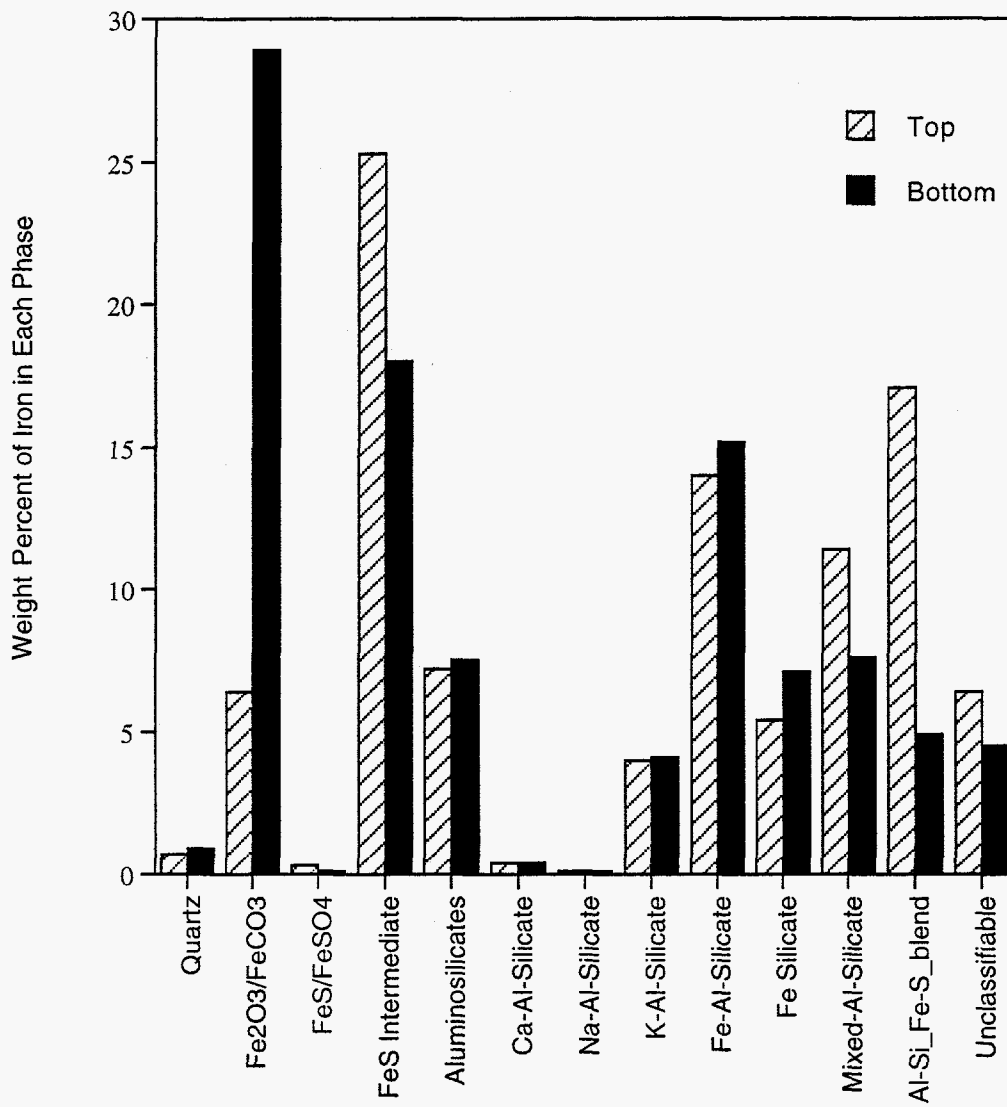


Figure 5. Distribution of Iron in staged samples.

D. Plans for the Next Quarter

1. Perform combustion tests on the new Pittsburgh #8 coal and compare the behavior of the oxidized and unoxidized iron phases under similar conditions.
2. Complete development of CCSEM routines to permit association analysis and analysis at multiple magnifications.
3. Analyze the new Pittsburgh #8 coal on the SEM.
4. Perform analysis on large particles for the samples described in this report.
5. Complete parametric testing for particulate samples on both the Black Thunder and Pittsburgh coals.
6. Test the deposition probe design and use the probe to obtain a deposit from either the Pittsburgh coal or the Black Thunder coal.