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**COMBUSTION CHARACTERIZATION OF
BENEFICIATED COAL-BASED FUELS**

QUARTERLY REPORT NO. 7 FOR THE PERIOD OCTOBER 1990 TO DECEMBER 1990

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PREPARED FOR

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QUARTERLY REPORT

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INTRODUCTION

The Pittsburgh Energy Technology Center of the U.S. Department of Energy has contracted with Combustion Engineering, Inc. (CE) to perform a three-year project on "Combustion Characterization of Beneficiated Coal-Based Fuels." The beneficiated coals are produced by other contractors under the DOE Coal Preparation Program. Several contractor-developed advanced coal cleaning processes were run at the DOE/EPRI cleaning facility in Homer City, Pennsylvania, to produce 20-ton batches of fuels for shipment to CE's laboratory in Windsor, Connecticut. CE then processed the products into either a coal-water fuel (CWF) or a dry microfine pulverized coal (DMPC) form for combustion testing.

The objectives of this project include: 1) the development of an engineering data base which will provide detailed information on the properties of BCFs influencing combustion, ash deposition, ash erosion, particulate collection, and emissions; and 2) the application of this technical data base to predict the performance and economic impacts of firing the BCFs in various commercial boiler designs.

The technical approach used to develop the technical data includes: bench-scale fuel property, combustion, and ash deposition tests; pilot-scale combustion and ash effects tests; and full-scale combustion tests. Subcontractors to CE to perform parts of the test work are the Massachusetts Institute of Technology (MIT), Physical Science, Inc. Technology Company (PSIT) and the University of North Dakota Energy and Environmental Research Center (UNDEERC).

Twenty fuels will be characterized during the base program: three feed coals, fifteen BCFs, and two conventionally cleaned coals for full-scale tests. Approximately nine BCFs will be in dry microfine pulverized coal (DMPC) form, and six BCFs will be in coal-water fuel (CWF) form. Additional BCFs would be characterized during optional project supplements.

SUMMARY

During the fourth quarter of 1990, the following technical progress was made.

- Calculated the kinetic characteristics of chars from the combustion of microbubble flotation beneficiated products.
- Continued drop tube combustion tests of the spherical oil agglomeration beneficiated products.
- Analyzed the data from three (MIT) pilot-scale combustion tests of the Upper Freeport feed coal.
- Continued analyses of the data from the CE pilot-scale tests of nine fuels.

TASK 1 - FUEL PREPARATION

Beneficiated coals (BCs) and feed coals are acquired from other DOE projects and shipped to CE. These fuels are then processed into either a dry pulverized coal form by CE or a coal-water fuel (CWF) form using OXCE Fuel Company technology. The feed coals are fired as standard grind (70% minus 200 mesh) pulverized coal (PC), while the dry beneficiated fuels are generally dry microfine pulverized coal (DMPC).

Nine twenty-ton batches of test fuel have been produced under the DOE-PETC Coal Preparation program since 1987. These fuels include:

1. Illinois #6 feed coal
2. Pittsburgh #8 feed coal
3. Upper Freeport feed coal
4. Illinois #6 microbubble flotation product
5. Pittsburgh #8 microbubble flotation product
6. Upper Freeport microbubble flotation product
7. Illinois #6 spherical oil agglomeration product
8. Pittsburgh #8 spherical oil agglomeration product
9. Upper Freeport spherical oil agglomeration product

All these fuels were tested in the pilot-scale facility between October 1989 and June, 1990. Bench-scale testing continued throughout 1990. Approximately fifty barrels of each spherical oil agglomeration product (SOAP) were unused and remained in storage.

TASK 2 - BENCH-SCALE TESTS

All test fuels are fully characterized using various standard and advanced analytical techniques. These tests evaluate the impacts of parent coal properties and beneficiation process on the resulting BCF's qualities.

A few selected fuels are tested in a laminar flow drop tube furnace to determine fly ash particle size and chemical composition. Results include mineral matter measurements and modeling of fly ash history.

A swirl-stabilized, entrained flow reactor is used to characterize the surface compositions and the states of ash particles formed during combustion. Deposition rates on a target are determined, and the size and compositions of the deposits from different fuels are compared.

The nine coal and BCF samples received to date have been completely analyzed for: (1) complete chemical analyses; (2) flammability index measurements; (3) weak acid leaching; (4) TGA reactivities and BET surface areas of chars produced in the DTFS-1 (Figure 2.2.1). All these data have been reduced and reported in the Quarterly Report for the Period July-September, 1990.

Work during this quarter focused on completing the analysis of all the DTFS-1 combustion test data obtained from the three MFPs and also completing the DTFS-1 combustion testing of the three SOAPs. The MFP data are reported herein. The analysis of the SOAP data is in progress and results will be reported in the next quarterly report. Fuel analyses done by UNDEERC are shown in Appendix A.

Combustion Kinetic Parameters of MFP Chars

Chars were prepared from the MFPs (See analyses in Table 2.1) in the CE's DTFS-1 (Figure 2.2.1) as depicted in Figure 2.2.2. The effects of temperature and time on the combustion efficiency of these chars in the 1900-2650 °F temperature range and time ranging up to approximately 0.8 sec. are depicted in Figures 2.2.3a - 2.2.5a. These results clearly show a few important things: (1) both temperature and time play a major role in char combustion; (2) these chars are fairly comparable to one another in combustion characteristics and (3) the reproducibility of the DTFS-1 data is quite good (compare T1 with T1R and T4 with T4R cases).

The combustion efficiency maps given in Figures 2.2.3a - 2.2.5a were used to derive the Arrhenius plots shown in Figures 2.2.3a - 2.2.5b. Least squares fits of the data in Figures 2.2.3a - 2.2.5b were used to derive the apparent activation energies (E) and frequency factors (A) from, respectively, the slopes and intercepts of the $\ln K_s$ vs. $1/T_p$ (where K_s is the surface reaction rate coefficient and T_p is the calculated particle surface temperature) plots. The E and A values were also calculated using measured bulk gas temperatures (i.e., T_g). Results from these calculations are given below. [Note that the values in parentheses were derived using bulk gas temperatures (T_g) and all others were derived using particle surface temperatures (T_p)].

MICROBUBBLE FLOTATION PRODUCT (MFP)	CHAR COMBUSTION KINETIC PARAMETERS	
	E (cal/mole)	A (g/cm ² sec.O ₂ atm.)
Upper Freeport	14415 (14240)	2.15 (2.14)
Pittsburgh #8	12740 (12625)	0.80 (0.79)
Illinois #6	11075 (10930)	0.48 (0.47)

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Figure 2.2.1
Schematic of Combustion engineering's
Drop Tube Furnace System-1 (DTFS-1)

Table 2.1

SELECTED ANALYSES OF TEST FUELS*

QUANTITY	ILLINOIS #6		UPPER FREEPORT		PITTSBURGH #8	
	FEED COAL	MFP	FEED COAL	MFP	FEED COAL	MFP
Proximate (Wt.%)						
Volatile Matter	38.6	40.4	28.1	27.4	38.9	41.6
Fixed Carbon	52.4	55.4	61.2	67.2	51.6	55.1
Ash	9.0	4.2	10.7	5.4	9.5	3.3
HHV, Btu/lb	12675	13185	13615	14525	13025	14030
Ultimate (Wt.%)						
Hydrogen	5.0	4.8	4.7	5.1	5.0	5.4
Carbon	69.3	75.5	76.9	81.3	71.4	77.3
Sulfur	3.0	2.7	1.8	1.3	4.5	3.3
Nitrogen	1.3	1.0	1.3	1.5	1.2	1.4
Oxygen	12.4	11.8	4.6	5.4	8.4	9.3
Ash	9.0	4.2	10.7	5.4	9.5	3.3
Forms of Sulfur (Wt%)						
Pyritic	0.53	0.09	0.49	0.05	1.34	0.05
Sulfate	0.35	0.4	0.55	0.56	0.44	0.51
Organic	2.12	2.2	0.76	0.78	2.72	2.74
Ash Fus. Temps. (RED. ATM)						
IDT	2000	2020	2010	1960	2130	1900
ST	2280	2180	2380	2120	2390	1980
HT	2420	2230	2450	2380	2440	2020
FT	2530	2280	2400	2430	2490	2120
Ash Composition (Wt.%)						
SiO ₂	51.7	42.0	43.8	41.0	39.3	34.1
Al ₂ O ₃	20.7	19.3	24.2	25.1	20.2	22.3
Fe ₂ O ₃	16.9	21.2	18.8	18.1	31.4	27.7
CaO	2.2	3.7	3.1	3.3	3.0	4.6
MgO	0.9	1.4	0.9	1.2	0.8	1.3
Na ₂ O	0.5	2.3	0.3	1.6	0.5	2.2
K ₂ O	2.0	2.3	2.2	2.6	1.5	1.6
TiO ₂	0.8	2.2	0.9	2.0	1.0	1.8
P ₂ O ₅	0	0.1	0.2	0.2	0.1	0.2
SO ₃	2.1	3.4	3.9	3.1	2.1	3.2

MFP = Microbubble Flotation Product

* All analyses are reported on dry basis

Figure 2.2.2

**DROP TUBE FURNACE SYSTEM-1 (DTFS-1) DETERMINATION OF
BCF CHARS' COMBUSTION KINETIC PARAMETERS**

A. DTFS-1 GENERATION OF CHARS

B. DTFS-1 COMBUSTION OF CHARS

FIGURE 2.2.3a DTFS COMBUSTION EFFICIENCY PLOTS OF 325X0 MESH UPPER FREEPORT MICROBUBBLE PRODUCT CHAR

FIGURE 2.2.3b ARRHENIUS PLOTS FOR 325X0 MESH UPPER FREEPORT MICROBUBBLE PRODUCT CHAR COMBUSTION IN THE DTFS

FIGURE 2.2.4a DTFS COMBUSTION EFFICIENCY PLOTS OF 325X0 MESH PITTSBURGH #8 MICROBUBBLE PRODUCT CHAR

FIGURE 2.2.4b ARRHENIUS PLOT FOR 325X0 MESH PITTSBURGH #8 MICROBUBBLE PRODUCT CHAR COMBUSTION IN THE DTFS

FIGURE 2.2.5a DTFS COMBUSTION EFFICIENCY PLOTS OF 325X0 MESH ILLINOIS #6 MICROBUBBLE PRODUCT CHAR

FIGURE 2.2.5b ARRHENIUS PLOT FOR 325X0 MESH ILLINOIS #6 MICROBUBBLE PRODUCT CHAR COMBUSTION IN THE DTFS

The E and A values obtained from this statistical analysis are fairly insensitive to the calculation method used (i.e., particle surface temperature vs. bulk gas temperature), due to the fact that the particle surface temperatures are, in these cases, only slightly higher than the bulk gas temperatures. The kinetic data reported here are quite low but are, in any event, in the range of those found in the CE data bank and in the open literature. These results and their applicability will be discussed in more detail along with the other results from this Task 2 work facet in the topical report under preparation.

MIT Laminar Flow Reactor Tests

Samples collected from the laminar flow reactor (LFR) for the effect of excess air level upon flyash particle size distribution and chemical composition were analyzed by CCSEM and the results obtained are discussed in this Quarterly Progress Report. The combustion conditions maintained in the reactor for the two cases were:

Fuel: Microbubble - Upper Freeport BCF
 Oxygen Mole Percent: 5% and 10%
 Flow reactor temperature: 1750°K

In the study, analysis of the CCSEM data for the two cases indicated that some coagulation/agglomeration of mineral matter takes place during the combustion process. Figure 2.3.1 illustrates that the final flyash particle distribution shifts to larger sizes as compared to the minerals present in the beneficiated coal particles.

Analysis of the particle size distributions illustrated in Figure 2.3.2 indicates that the high excess air level (10% O₂) resulted in larger particles than when the oxygen concentration was maintained at 5%.

As for the chemical composition of the flyash samples, it can be seen from Figure 2.3.3 that the Iron Oxide (FeO) compound present in the coal mineral matter was redistributed in the flyash particles for the above two combustion cases primarily in particles which contained FeO in the range of 1 to 30% on a weight basis.

In order to determine the effect of the redistribution of FeO upon flyash, the viscosity of flyash particles and the coal mineral inclusions was determined at 1750°K and at 1250°K using the Watt and Faraday equation

$$\text{Log } \eta = \frac{10^7 \cdot B}{(T-150)^2} + F$$

where η is viscosity in poise

T is the temperature in Kelvin

B, F are constants calculated from the chemical composition of particles.

At 1750°K, which is the flame temperature, Figure 2.3.4 illustrates that all of the coal mineral inclusions have a viscosity below 10⁴ poise, indicating that if the mineral inclusions are close to each other coalescence will take place as suggested by Raask, who determined that the critical viscosity for coalescence is around 10⁴ poise. At 1250°K exit temperature, the fraction of particles with a viscosity lower than 10⁴ poise is higher for the coal mineral matter (30%), compared to the flyash (20%).

BCF mineral and flyash number based size distribution functions

Figure 2.3.1

Figure 2.3.2

Distribution Of FeO Content in BCF Mineral Matter and Fly Ash Samples

Figure 2.3.3

BCF Mineral Matter and Fly Ash
 Viscosity Distribution
 Laminar Flow Reactor Temp. = 1750 K

Figure 2.3.4

TASK 3 - PILOT SCALE TESTING

Combustion experiments are conducted with selected fuels in MIT's Combustion Research Facility (CRF) to characterize the effects of fuel type, beneficiation process, and firing mode upon flame stability, carbon conversion, and gaseous emissions. Combustion tests are also run in CE's Fireside Performance Tests Facility (FPTF) with most of the base project fuels, to evaluate combustion performance, furnace wall slagging, convection pass fouling, fly ash erosion, electrostatic precipitator performance, and emissions. The FPTF results were reported in previous quarterlies.

Fly Ash Collectability

The ESP Pilot facility was modified to improve the accuracy of the test. The modifications included installing current leak detector rings on the electrode power supply insulator, and installing a dedicated data acquisition system. In addition, the ESP was uncoupled from the FPTF gas discharge by installing a bypass gas duct to permit a reduction in gas flow to the ESP. Flow and gas temperature control were improved to maintain closer control of gas conditions entering the ESP.

Computer data analysis routines were modified to take advantage of the new data acquisition capabilities. These routines can also be used to analyze BCF ESP data obtained prior to the modifications. Modifications consist of plotting the specific power consumption vs. time and calculating average values of power and consumption for specific operating periods. Also, the efficiency and migration velocity calculation routines permit the incorporation of particle size distribution into the calculations instead of using mean particle sizes. The preliminary results indicate that power consumption was low. Further analysis will be conducted on all tests.

The analysis of the existing data has been initiated. The completion of the analysis is scheduled for the next quarter.

Pilot-Scale Tests at MIT

In the Combustion Research Facility (CRF) experiments, the effects of atomization quality (secondary vs. normal), and excess air level upon the mineral matter transformation were investigated for the Upper Freeport parent coal and MFP. Two flames which used the beneficiated coal fuel were considered. In the first flame, the oxygen concentration at the exit was 4%. In the second the O₂ concentration at the end of the combustion tunnel was 2.7%. Results showing the effect of excess air level upon the size distribution and chemical composition of the flyash are discussed next.

A comparison of the number based particle size distributions of the flyash samples collected from the two flames with the coal mineral matter size distribution of the BCF is shown in Figure 3.1. The results illustrate that the mean particle size of the flyash is much larger than that of the coal mineral matter, i.e. the former had a mean size of 6.56 μm while the latter had a mean size of 2 μm . Moreover, the variance of the mineral particle size increases by 20 times. This illustrates that a high degree of coalescence between mineral inclusions occurs during the char burnout process. As for the excess air level (see Figure 3.2), it was observed that the flyash particle size distribution did not change as the excess O₂ level was reduced from 4% to 2.7%.

The chemical composition of individual particles was determined using the CCSEM technique. However, only the weight distribution of SiO₂ among flyash particles is discussed here to illustrate the changes in the chemical structure of the mineral inclusions during the combustion of the coal particles. Figure 3.3 illustrates that in the coal, SiO₂ is primarily distributed in mineral inclusions which contain it in the range of 0 to 60% by weight. However, as the coal burns, SiO₂ is redistributed in the flyash particles and ends up in particles that

BCF Mineral Matter and Fly ash
number based sizedistributions
- lognormal approximation -

Figure 3.1

BCF Mineral and Fly ash
number based sizedistribution
lognormal approximation

Figure 3.2

Distribution of SiO_2 content in BCF
mineral matter and fly ash samples

*****	mineral matter	mean=32	st.dev=19
◇◇◇◇◇	fly ash $\text{O}_2=2.4\%$	mean=34	st.dev=16
□□□□□	fly ash $\text{O}_2=4.0\%$	mean=33	st.dev=15

Figure 3.3

contain SiO_2 primarily in the range of 20% to 50%. This observation is thought to be due to the random coalescence of the mineral inclusions during the burnout of individual char particles. It was also observed that reducing the excess air level had no significant effect upon the distribution of chemical compounds present in flyash particles.

We have seen previously that distributions of both the viscosity and size of mineral matter change during char burnout. It has been also observed that the viscosity distribution of flyash particles has a smaller standard deviation than that of the mineral matter due to the random redistribution of chemical compounds during the process of mineral matter coalescence. Some increase in the mean size and standard deviation of mineral matter was also observed. In the following we give more evidence on these changes.

A comparison of the mass-based viscosity distributions of the BCF mineral matter and the flyash calculated for a temperature of 1750°K is plotted in Figure 3.4. The flyash was produced by burning the BCF in the laminar flow reactor (LFR) in a gas stream of 1750°K and containing 5% O_2 . A slight narrowing of the flyash viscosity distribution can be seen relative to that of the BCF mineral matter, probably due to some coalescence of the randomly distributed mineral particles in the coal into a more homogeneous material in the flyash. The standard deviation of the flyash viscosity distribution remains, however, quite large.

The BCF was burned also in the MIT Combustion Research Facility in the form of coal-water fuel (CWF). The mass based viscosity distribution of the flyash calculated at 1750°K is given in Figure 3.5. The flyash was produced in CRF experiments in which the unheated CWF was atomized by pressurized air and burned giving 3% O_2 in the stack. The viscosity distribution of the LFR flyash is also plotted in Figure 3.5 for comparison. The narrowing of the viscosity distribution of the CWF flyash compared to that produced in the LFR indicates more mineral matter coalescence during CWF combustion (especially under conditions of unheated slurry atomization). The number based cumulative size distributions of the BCF mineral matter, of the flyash of the pulverized BCF burned in the LFR at 1750°K and 5% O_2 in the oxidizing gas stream, and of the flyash produced by burning the BCF in coal-water fuel form in the CRF with 3% O_2 in the stack are plotted in Figure 3.6.

There is a small increase in the flyash size relative to that of the coal mineral matter when burned in the LFR, but a larger increase in flyash size resulted from the CWF combustion. This latter increase in the flyash size is most likely due to the agglomeration of several coal particles in the finely atomized coal water fuel droplets producing thereby larger char particles for burn-out in the CWF flame. Comparison of the BCF coal particle size distribution plotted in Figure 3.7 lends further support to the above explanation.

Viscosity Distribution

Figure 3.4

Viscosity Distribution

Figure 3.5

Figure 3.6

Size Distributions

Figure 3.7

TASK 4 - SCALE-UP TESTS

The purpose of the scale-up tests is to verify that the results obtained from tests done at bench-and pilot-scales in Tasks 2 and 3 can be used to provide reasonable estimates of the performance effects when firing BCFs in commercial-scale boilers. Two beneficiated fuels will be fired in either a small utility boiler or a full-scale test furnace.

The only activities in this task were discussions on fuel procurement, alternative test facility selection, and scheduling. Recommendations were submitted to the DOE to run the tests in CE's Boiler Simulation Furnace, a 50×10^6 Btu/hr unit that models full-scale boilers.

TASK 5 - TECHNICAL-ECONOMIC EVALUATIONS

The results of bench-scale, pilot-scale, and scale-up tests (Tasks 2, 3, and 4) are used to predict the performance of three commercial boilers. The boilers include: a 560MW coal-designed utility unit; a 600MW oil-designed utility unit; and an 80,000 lb/hr oil designed, shop assembled industrial unit. Eight of the base project BCFs will be used in models of each unit to calculate performance.

No activity was scheduled for Task 5 during this quarter.

WORK PLANNED FOR NEXT QUARTER

- Continue standard bench-scale tests.
- Continue drop tube furnace tests at CE and UNDEERC.
- Analyze data from pilot-scale combustion tests and ash deposition tests.
- Continue preparations for the scale-up tests.
- Write draft topical summary report including results to date from the testing of the nine fuels.

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APPENDIX

UNDEERC SUPPORT OF THE COMBUSTION CHARACTERIZATION OF BENEFICIATED COAL-BASED FUELS PROJECT

1.0 INTRODUCTION

The University of North Dakota Energy and Environmental Research Center (EERC) is providing analytical and data interpretation support for the BCF project. All solid fuels are being analyzed by computer-controlled scanning electron microscopy (CCSEM) under Task 2 to determine the types and size distributions of the discrete mineral particles present in each fuel. The fuels are also being fractionated by specific gravity into four fractions: <1.4, 1.4x2.5, 2.5x2.9, and >2.9. Ash content, ash composition, and fusion temperatures for each specific gravity fraction are to be determined. In addition, fly ash from each solid fuel will be generated in a drop-tube furnace system. Each fly ash sample will be sized by Malvern (laser diffraction), analyzed by ESCA-Auger for surface composition, x-ray fluorescence (XRF) for composition, x-ray diffraction (XRD) for crystalline phases and quantitative quartz determinations, and CCSEM to quantitatively determine the types and size distributions of the inorganic particles in the ash. Also included under Task 2 is analytical support for the PSI drop-tube work. This support will include CCSEM, ESCA-Auger, and SEM-EDX analyses of three fly ashes and several submicron fume substrates.

The EERC involvement in Task 3 consists of a number of different analyses of samples produced during combustion testing of the parent and beneficiated fuels in the Combustion Engineering Fireside Performance Test Facility (FPTF). The specific analyses are summarized in Table 1.

2.0 TASK 2 RESULTS AND DISCUSSION

2.1 Fuel Analyses

2.1.1 CCSEM

CCSEM in conjunction with image analysis of the Pittsburgh No. 8 spherical oil agglomeration product (SOAP) was completed during this quarter. This completes the CCSEM and image analyses of the original suite of nine fuels. Table 2 is a summary of the PARTCHAR output for the CCSEM analyses of the Pittsburgh No. 8 parent coal. The definitions of the different particle types and general discussion of the format used for the data are described in the July through September 1990 quarterly technical progress report.

The most abundant particle type in the Pittsburgh No. 8 parent fuel is listed as unclassified because the particles that fell into that definition had compositions which did not match those of the defined categories. Most of the particles were silica-rich aluminosilicates or sulfur-rich iron sulfides that did not match given definitions. In addition, many of the particles appeared to be combinations of these aluminosilicates and iron sulfides. In addition to the unclassified particles, other aluminosilicates and iron sulfides made up the bulk of the inorganic particles with diameters between 1 and 100 μm . Approximately 25% of the inorganic particles were larger than 10 μm .

TABLE 1
EERC ANALYSES OF FPTF SAMPLES

<u>Sample</u>	<u>Composition</u>	<u>Fusion</u>	<u>SEMP</u>	<u>CCSEM</u>	<u>XRD</u>	<u>ESCA</u>
In-Flame Solids						
Waterwall	X			X	X	X
Furnace Outlet	X			X	X	X
Waterwall Deposits						
T1						
Inner Layer	X	X		X	X	X
Outer Layer	X	X	X		X	X
Waterwall Deposits						
T2						
Inner Layer	X	X			X	
Outer Layer	X	X			X	
Superheater Deposits						
T1						
Inner Layer	X	X	X		X	X
Outer Layer	X	X	X		X	X
Superheater Deposits						
T2						
Inner Layer	X	X			X	
Outer Layer	X	X			X	
Fly Ash	X	X		X	X	X
Bottom Ash	X	X				

Table 3 gives the CCSEM data for the Pittsburgh No. 8 MFP fuel. As was true for the parent coal, approximately one-third of the inorganic particles did not fit one of the defined categories. In general, the particles were silica-rich aluminosilicates that contained some potassium, calcium, and iron. In general, the proportion of potassium decreased, and calcium increased as particle size dropped. In the 1- to 2.2- μm -size range, the concentration of sulfur was relatively high, although it was not always associated with high-iron particles. More likely, the high-sulfur values were due to interference from organically associated sulfur. In comparison to the inorganic particles in the parent coal, the inorganic particles in the MFP fuel were generally smaller with only 10% of the particles greater than 10 μm in diameter. The overall size reduction was caused primarily by the comminution of pyrite grains during processing to make the MFP fuel. In addition to comminution during processing, the pyrite was partially oxidized to form particles with compositions similar to pyrrhotite, oxidized pyrrhotite (lower sulfur), and iron oxide. The relative concentration of these high-iron particles was reduced only slightly with the MFP process, showing that they were not preferentially removed. In contrast, there is an apparent preferential removal of aluminosilicate particles in the 1-100- μm range. However, the ash composition did not show a reduction in aluminum, so the apparent reduction in aluminosilicate particles is most likely caused by a size reduction to less than

TABLE 2

PARTCHAR SUMMARY OF THE CCSEM DATA FOR THE PITTSBURGH NO. 8 PARENT COAL

Summary of Parameters

Total Mineral Area Analyzed at High Mag.	=	5,742.0 μm^2
Normalized Area Analyzed at High Mag.	=	141,710.8 μm^2
Total Mineral Area Analyzed at Low Mag.	=	45,140.2 μm^2
Number of Frames at High Mag.	=	7
Number of Frames at Low Mag.	=	8
Total Number of Points Analyzed	=	1,188
Number of Points Under Threshold	=	12

Weight Percent on a Mineral Basis

	1.0 to 2.2	2.2 to 4.6	4.6 to 10.0	10.0 to 22.0	22.0 to 46.0	46.0 to 100.0	Totals
Quartz	1.1	2.1	2.2	.8	.5	.0	6.7
Iron Oxide	.0	.0	.0	.0	.0	.0	.0
Periclase	.0	.0	.0	.0	.0	.0	.0
Rutile	.1	.1	.0	.0	.0	.0	.2
Alumina	.0	.0	.0	.1	.0	.0	.1
Calcite	.0	.0	.0	.1	.0	.0	.1
Dolomite	.0	.0	.0	.0	.0	.0	.0
Ankerite	.0	.0	.0	.0	.0	.0	.0
Kaolinite	1.4	4.3	2.6	1.8	.2	.0	10.2
Montmorillonite	.2	.7	.2	.6	.2	.0	1.9
K Al-Silicate	.5	1.1	.6	.8	.3	.0	3.3
Fe Al-Silicate	.0	.1	.0	.0	.0	.0	.1
Ca Al-Silicate	.4	.2	.0	.0	.0	.0	.6
Na Al-Silicate	.0	.0	.0	.0	.0	.0	.0
Aluminosilicate	.1	.0	.0	.0	.0	.0	.1
Mixed Al-Silica	.0	.0	.0	.0	.0	.0	.0
Fe Silicate	.0	.0	.0	.0	.0	.0	.0
Ca Silicate	.0	.0	.0	.0	.0	.0	.0
Ca Aluminate	.0	.0	.0	.0	.0	.0	.0
Pyrite	3.8	7.9	7.9	6.5	5.1	1.9	33.1
Pyrrhotite	.2	.3	.0	.5	.0	.0	1.0
Oxidized Pyrrhotite	.0	.0	.0	.0	.0	.0	.0
Gypsum	.1	.6	.0	.5	2.4	.0	3.6
Barite	.0	.0	.0	.0	.0	.0	.0
Apatite	.0	.0	.0	.0	.0	.0	.0
Ca Al-P	.0	.0	.0	.0	.0	.0	.0
KCl	.0	.0	.0	.0	.0	.0	.0
Gypsum/Barite	.0	.0	.0	.0	.0	.0	.0
Gypsum/Al-Silicate	.3	.3	.2	.0	.0	.0	.0
Si-Rich	.1	.4	.5	.0	.0	.0	.0
Ca-Rich	.0	.0	.0	.0	.0	.0	.0
Ca-Si Rich	.0	.0	.0	.0	.0	.0	.0
Unclassified	8.6	17.4	6.7	3.5	1.1	.0	37.4
Totals	17.0	35.5	20.8	15.0	9.7	1.9	100.0

TABLE 3

PARTCHAR SUMMARY OF THE CCSEM DATA FOR THE PITTSBURGH NO. 8 MFP FUEL

Summary of Parameters

Total Mineral Area Analyzed at High Mag.	=	5,115.5 μm^2
Normalized Area Analyzed at High Mag.	=	170,722.2 μm^2
Total Mineral Area Analyzed at Low Mag.	=	17,400.5 μm^2
Number of Frames at High Mag.	=	11
Number of Frames at Low Mag.	=	17
Total Number of Points Analyzed	=	988
Number of Points Under Threshold	=	137

Weight Percent on a Mineral Basis

	1.0 to 2.2	2.2 to 4.6	4.6 to 10.0	10.0 to 22.0	22.0 to 46.0	46.0 to 100.0	Totals
Quartz	1.0	8.0	5.1	.8	.3	.0	15.2
Iron Oxide	.1	1.4	.0	.1	.4	.0	2.0
Periclase	.0	.0	.0	.0	.0	.0	.0
Rutile	.1	.3	.0	.0	.0	.0	.4
Alumina	.0	.1	.0	1.2	1.2	.0	2.6
Calcite	.0	.0	.0	.0	.0	.0	.0
Dolomite	.0	.0	.0	.0	.0	.0	.0
Ankerite	.0	.0	.0	.0	.0	.0	.0
Kaolinite	.0	.0	.0	.1	.0	.0	.1
Montmorillonite	.2	.4	1.2	.0	.0	.0	1.7
K Al-Silicate	.2	2.1	.3	.2	.4	.0	3.3
Fe Al-Silicate	.2	.7	.3	.0	.0	.0	1.1
Ca Al-Silicate	.0	.1	.4	.0	.0	.0	.5
Na Al-Silicate	.0	.0	.0	.0	.0	.0	.0
Aluminosilicate	.0	1.1	1.3	.0	.0	.0	2.4
Mixed Al-Silica	.1	1.2	.0	.0	.0	.0	1.2
Fe Silicate	.0	.0	.0	.0	.0	.0	.0
Ca Silicate	.0	.1	1.2	.0	.0	.0	1.3
Ca Aluminate	.0	.0	.0	.0	.0	.0	.0
Pyrite	3.0	3.3	4.1	1.2	.9	.0	12.5
Pyrrhotite	1.3	1.9	1.2	.0	.0	.0	4.4
Oxidized Pyrrhotite	1.2	1.0	6.6	.1	.0	.0	8.9
Gypsum	.5	.8	.7	1.5	1.0	.0	4.5
Barite	.0	.0	.0	.0	.0	.0	.0
Apatite	.0	.0	.0	.0	.0	.0	.0
Aa Al-P	.0	.0	.0	.0	.0	.0	.0
KCl	.0	.0	.0	.0	.0	.0	.0
Gypsum/Barite	.0	.0	.0	.0	.0	.0	.0
Gypsum/Al-Silicate	.6	.4	.0	.0	.0	.0	1.0
Si-Rich	.9	.7	.5	.0	.0	.0	2.2
Ca-Rich	.1	.0	.0	.0	.0	.0	.1
Ca-Si Rich	.0	.0	.0	.0	.0	.0	.0
Unclassified	11.6	17.0	5.8	.3	.0	.0	34.6
Totals	21.1	40.6	28.4	5.4	4.4	.0	100.0

1- μ m-diameter, making them undetected by CCSEM. The relative increase in quartz is most likely due to a related phenomena. Since the relative concentration of silicon in the coal ash is reduced by the MFP process, the apparent increase in quartz detected by CCSEM is likely related to the overall size reduction of the other mineral matter to the undetectable submicron range. As reported in the July through September 1990 quarterly technical progress report, this same phenomenon was observed in the MFP processing of the Illinois No. 6 and Upper Freeport coals.

Table 4 gives the CCSEM data for the Pittsburgh No. 8 SOAP fuel. The overall inorganic particle-size distribution shows that SOAP processing reduces the size of the remaining mineral matter even more than the MFP process. The size shift is similar to that seen for the Upper Freeport fuels, but did not occur for the Illinois No. 6 fuels. Unlike MFP processing, the SOAP process did not promote oxidation of pyrite or cause an apparent removal of aluminosilicates through size reduction to less than 1 micron, nor did SOAP processing cause these phenomena to occur in the Illinois No. 6 and Upper Freeport coals. The SOAP process was particularly successful in removing, from the Pittsburgh No. 8 parent fuel, the complex aluminosilicates that fell into the unclassified category in the coal analysis. The unclassified particles remaining in the SOAP fuel were either silica-rich aluminosilicates or sulfur-rich iron sulfides that did not match one of the defined categories.

2.1.2 Image Analysis of Inorganic Particles

One measure of the efficiency of a coal-cleaning process is its ability to remove mineral grains that are not associated with coal particles. Removal of these excluded mineral grains results only in ash reduction with no loss of calorific value. Image analysis of the inorganic particles in each of the fuels was used to determine the effectiveness of the cleaning processes used in this project. Since the image analysis is performed in conjunction with CCSEM analysis, the data can be used to determine the inorganic-species-specific efficiency at removing the excluded mineral grains. Approximately 400 of the particles analyzed by CCSEM were manually classified as included, excluded, or unsure. Approximately one-half of the particles were selected from the 1-10- μ m-diameter inorganic particles, and one-half from the 10-100- μ m particles. The image analysis was made difficult by the relatively small size of the inorganic particles in the cleaned coals. Because of the relatively poor resolution of backscatter electron imaging, many of the inorganic particles could not definitively be classified as included or excluded and so were classified as unsure. Only the particle types that made up at least 2.5% of the area of the 400 particles analyzed were included in the output.

The included/excluded data for the Illinois No. 6 parent and MFP fuels were reported in the February through April 1990 quarterly technical progress report. Table 5 lists the data for the Illinois No. 6 SOAP fuel. Compared to the parent coal, the SOAP contains much less excluded mineral matter, implying that the SOAP process, unlike the MFP process, was effective at removing the excluded mineral matter from the coal.

Figures 1 and 2 illustrate the differences in the amount of excluded inorganic particles in the Upper Freeport and Pittsburgh No. 8 parent and cleaned fuels. For the purposes of these graphs, the weights of the particles

TABLE 4

PARTCHAR SUMMARY OF THE CCSEM DATA FOR THE PITTSBURGH NO. 8 SOAP FUEL

Summary of Parameters

Total Mineral Area Analyzed at High Mag.	=	5,281.8 μm^2
Normalized Area Analyzed at High Mag.	=	593,110.8 μm^2
Total Mineral Area Analyzed at Low Mag.	=	45,966.0 μm^2
Number of Frames at High Mag.	=	5
Number of Frames at Low Mag.	=	26
Total Number of Points Analyzed	=	1,126
Number of Points Under Threshold	=	16

Weight Percent on a Mineral Basis

	1.0 to 2.2	2.2 to 4.6	4.6 to 10.0	10.0 to 22.0	22.0 to 46.0	46.0 to 100.0	Totals
Quartz	2.2	12.9	4.6	.1	.2	.0	19.9
Iron Oxide	.1	.0	.7	.1	.1	1.0	2.0
Periclase	.0	.0	.0	.0	.1	.0	.1
Rutile	.2	.5	.0	.0	.0	.0	.7
Alumina	.0	.1	.8	.0	.0	.0	.9
Calcite	.0	.2	.0	.0	.1	.0	.4
Dolomite	.0	.0	.0	.0	.1	.0	.2
Ankerite	.0	.0	.0	.0	.0	.0	.0
Kaolinite	3.0	4.9	1.0	.1	.1	.0	9.0
Montmorillonite	.7	.5	.0	.1	.0	.0	1.3
K Al-Silicate	1.0	2.0	.0	.2	.0	.0	3.2
Fe Al-Silicate	.2	.1	.0	.0	.0	.0	.3
Ca Al-Silicate	.1	.2	.0	.1	.0	.0	.3
Na Al-Silicate	.0	.1	.0	.0	.0	.6	.8
Aluminosilicate	.2	.1	.4	.0	.0	.0	.7
Mixed Al-Silica	.1	.1	.0	.0	.0	.0	.3
Fe Silicate	.0	.0	.0	.0	.0	.0	.0
Ca Silicate	.0	.0	.0	.0	.0	.0	.0
Ca Aluminate	.0	.0	.0	.0	.1	.0	.1
Pyrite	7.9	27.3	5.6	.2	.3	.4	41.6
Pyrrhotite	.0	.0	.0	.0	.0	.0	.0
Oxidized Pyrrhotite	.1	1.0	.0	.0	.0	.0	1.1
Gypsum	1.1	1.9	.6	.6	.4	.0	4.5
Barite	.0	.0	.0	.0	.0	.0	.0
Apatite	.0	.0	.0	.0	.0	.0	.0
Ca Al-P	.0	.0	.0	.0	.0	.0	.0
KCl	.0	.0	.0	.0	.0	.0	.0
Gypsum/Barite	.0	.0	.0	.0	.0	.0	.0
Gypsum/Al-Silicate	.1	.2	.0	.0	.0	.0	.3
Si-Rich	.3	.7	.6	.0	.0	.0	1.6
Ca-Rich	.0	.1	.0	.0	.0	.0	.1
Ca-Si Rich	.0	.0	.0	.0	.0	.0	.0
Unclassified	3.9	4.6	.6	.7	.9	.0	10.7
Total	21.2	57.4	14.8	2.3	2.4	2.0	100.0

TABLE 5

THE ASSOCIATIONS OF THE INORGANIC PARTICLES DETECTED IN CCSEM
ANALYSIS OF THE ILLINOIS NO. 6 SOAP FUEL, WEIGHT PERCENT

<u>Phase</u>	<u>% Included</u>	<u>% Excluded</u>	<u>% Unsure</u>
Quartz	44	6	50
K-Al-Silicate	79	21	0
Aluminosilicate	100	0	0
Pyrite	50	15	35
Pyrrhotite	100	0	0
Gypsum	99	1	0
Unclassified	98	2	0

Figure 1. The associations of the inorganic particles detected in CCSEM analysis of the Upper Freeport parent and cleaned fuels.

Figure 2. The associations of the inorganic particles detected in CCSEM analysis of the Pittsburgh No. 8 parent and cleaned fuels.

classified as unsure in association were split evenly among the excluded and included particles. Figure 1 shows that in the Upper Freeport parent coal all of the kaolinite and montmorillonite was included within coal particles, whereas significant portions of the more complex aluminosilicates and other inorganic types were excluded from the coal particles and so should have been more easily cleaned from the coal. However, only the excluded aluminosilicate and, to a certain extent, quartz and gypsum particles were preferentially removed by cleaning the Upper Freeport coal. The other excluded minerals were not preferentially removed by cleaning, and in some cases the processing of the coal actually liberated some of the inorganic particles so that the amount of excluded mineral matter increased. Both the MFP and SOAP processing behaved similarly in their efficiency at removing the excluded mineral matter from the Upper Freeport coal.

Figure 2 shows that the overall distribution of mineral matter in the Pittsburgh No. 8 parent coal among included and excluded particles is very similar to the distribution in the Upper Freeport parent coal. As was true for the Upper Freeport coal, the MFP-cleaning process did not preferentially remove excluded mineral matter in favor of included. As was also true for the Pittsburgh No. 8 coal, the SOAP process liberated most of the mineral grains from the coal, but did not preferentially remove them. However, the effect was much more pronounced for the Pittsburgh No. 8 than for the Upper Freeport fuels.

2.2 Drop-Tube Furnace Testing

2.2.1 Fly Ash Production

Drop-tube furnace combustion of Illinois No. 6 SOAP, Upper Freeport MFP and SOAP, and Pittsburgh No. 8 MFP and SOAP fuels to form fly ash under controlled conditions was completed this quarter. This completed the drop-tube furnace combustion of the initial suite of nine fuels. The combustion conditions are listed in Table 6. The ashes have been submitted for laboratory analysis.

2.2.2 Surface Analysis of Drop-Tube Furnace Fly Ash

An initial investigation of the surface composition of the drop-tube furnace fly ashes of the Illinois No. 6 parent and MFP, Upper Freeport parent, and Pittsburgh No. 8 parent fuels was completed. Depth profiles were obtained by etching the ash by intermittently sputtering argon ions and analyzing the etched surfaces. Two types of analyses were used: secondary ion mass spectrometry (SIMS) and Auger electron spectrometry. The samples were prepared by spreading a thin layer of ash over carbon-coated double-stick tape. A magnification of 500x was used, and the argon beam was rastered over the entire field so that large numbers of ash particles could be analyzed in order to provide an average depth profile.

The surface layers of all of the ashes were contaminated with carbon so the samples had to be etched for approximately 10 minutes before an "initial" composition could be obtained. Because of poor signal to noise ratios in the data, only broad conclusions about variations in composition with depth in the ash could be obtained. They are as follows:

- Illinois No. 6 Parent - Minor variations except for iron which increased concentration with depth.
- Illinois No. 6 MFP - The average composition of the surface of the MFP ash was higher in sodium and sulfur than the parent coal ash, although the concentrations could not be quantified. The concentrations of both iron and potassium increased with depth.
- Upper Freeport Parent - The concentrations of calcium and potassium increased with depth. Iron also increased initially, but then leveled off.
- Pittsburgh No. 8 Parent - The concentration of iron increased with depth.

The poor signal to noise ratios in the Auger electron signals were caused by problems associated with electron beam rastering and sample charging. Beam rastering is the process of focusing the beam to a small spot at the surface of the samples, then sweeping the beam back and forth over a relatively large area. For example, when analyzing the Auger electron signal from the drop-tube furnace fly ash, the electron beam was rastered in a manner known as TV mode which is the standard U.S. TV scan rate of 535 lines/frame,

TABLE 6
DROP-TUBE FURNACE OPERATING CONDITIONS FOR FLY ASH PRODUCTION

COAL	ILLINOIS #6 SOAP	UPPER FREEPORT MFP	UPPER FREEPORT SOAP	PITTSBURGH #8 MFP	PITTSBURGH #8 SOAP
Gas Flow Rates (L/min)					
Primary air	0.8	0.8	0.8	0.8	0.8
Secondary air	3.2	3.2	3.2	3.2	3.2
Quench Gas	3.0	3.0	3.0	3.0	3.0
Vacuum	7.2	7.0	7.1	7.0	7.0
Temperatures (°C)					
Injector	amb	amb	amb	amb	amb
Secondary air	1143	1142	1143	1141	1140
Furnace 1 Upper (wall)*	1535	1538	1538	1538	1539
Furnace 1 Lower (wall)*	1532	1513	1517	1509	1508
Avg. Coal Feed Rate (g/min)	0.093	0.161	0.078	0.182	0.069
Avg. Ash Collected/Fed	0.8978	0.8568	0.9056	0.6895	0.7443
Residence Time (sec)	1.2	1.2	1.2	1.2	1.2

* Gas temperature is approximately 30 degrees lower than wall temperature.

30 frames/sec., and 63 microseconds/line. The spot size was roughly 10 microns to achieve large beam current for more signal. The area of the sample scan was usually 40,000 square microns as this was thought to be a representative area. However, rastering the electron beam produced noise due to background fluctuations as a result of variations in signal intensity. The variations were caused by surface topography and local changes in composition. Variations in cross section in particles of different composition imposed sawtooth noise on the background as the beam scanned across them. Therefore, instead of rastering a small spot across the sample, it was decided to try defocusing the electron beam to create a large spot that covered the entire analysis area.

A comparison of the Auger electron surveys of fly ash using rastered and nonrastered (defocused spot) electron beams showed a much better relative signal to noise ratio in the nonscanned samples. Reduction in sample charging was also observed, presumably because of the reduced current density in the defocused beam. Also, because of the reduced current density, damage to the sample from exposure to the electron beam should be reduced as well. In the spot mode, spot sizes can be automatically varied roughly from 0.05 to 10 microns and manually defocused from 10 microns to perhaps 1 mm. A spot size of approximately 200 microns will be used in future analyses, as this was the representative area previously used. The spot sizes are measured on the TV monitor, with a ruler, as depressions in an adhesive material on the back of copper tape. This material is easily damaged by the beam and appears to melt or otherwise decompose wherever the beam has been for a relatively short time. Disadvantages due to defocusing may be increased analysis time which could result in sample contamination due to increased reactivity with the ambient. Also, careful alignment of the beam is necessary so the beam will not spiral out of the area of interest when defocused.

In addition to modifications to the analysis procedure, a new technique of sample preparation has shown, in initial tests, to reduce sample charging. This involves the use of conductive carbon adhesive tape available from Structure Probe Incorporated. Carbon-coated copper adhesive tape was used in the past for sample preparation.

2.3 Analysis of PSIT Drop-Tube Furnace Samples

Thirteen drop-tube furnace fly ash and deposit samples were received from PSIT and submitted for analysis.

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