

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

Quarterly Technical Progress Report  
April 1, 1997 to June 30, 1997

John N. Harb  
Brigham Young University  
Provo, Utah 84602

Date published- August 7, 1997

PREPARED FOR THE UNITED STATES  
DEPARTMENT OF ENERGY

Contract No. DE-FG22-93PC93226

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

RECEIVED  
DOE/PC/ETC  
APR 14 1997 10:41  
DOE/PC/ETC

### **DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

## **DISCLAIMER**

**Portions of this document may be illegible electronic image products. Images are produced from the best available original document.**

## FOREWORD

This report summarizes technical progress during the fifteenth (April 1, 1997 to June 30, 1997) of a 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. Ewerthon Fonsesca, an undergraduate student in chemical engineering at BYU, also made important technical contributions to this report.

## ABSTRACT

This report describes work performed in the fifteenth quarter of a fundamental study to examine the effect of staged combustion on ash formation and deposition. Efforts this quarter included addition of a new cyclone for improved particle sampling and modification of our existing sampling probe. Particulate samples were collected under a variety of experimental conditions for both coals under investigation. Deposits formed from the Black Thunder coal were also collected.

Particle size and composition from the Pittsburgh #8 ash samples support previously reported results. In addition, our ability to distinguish char/ash associations has been refined and applied to a variety of ash samples from this coal. The results show a clear difference between the behavior of included and excluded pyrite, and provide insight into the extent of pyrite oxidation.

Ash samples from the Black Thunder coal have also been collected and analyzed. Results indicate a significant difference in the particle size of "unclassifiable" particles for ash formed during staged combustion. A difference in composition also appears to be present and is currently under investigation.

Finally, deposits were collected under staged conditions for the Black Thunder coal. Specifically, two deposits were formed under similar conditions and allowed to mature under either reducing or oxidizing conditions in natural gas. Differences between the samples due to curing were noted. In addition, both deposits showed skeletal ash structures which resulted from in-situ burnout of the char after deposition.

## 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<sub>x</sub> emissions from coal-fired units. It is applicable to both advanced combustion systems currently under development (e.g. HITAF) and low NO<sub>x</sub> retrofits for existing units. These low NO<sub>x</sub> 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 fifteenth quarter of a fundamental 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 fifteenth 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

A new cyclone separator was built to facilitate the collection of particulate samples. The old unit was constructed of Teflon and became ineffective due to wear and fouling of the soft material. The new cyclone is fashioned from aluminum. It can be easily disassembled for inspection and cleaning between experiments. In addition, the interior surface has been polished to reduce the amount of material sticking to the sides.

A number of problems related to corrosion of the particulate sampling probe when running under reducing conditions were encountered and solved this quarter. Pitting of the outer shell leading to cooling water leaks was corrected by installing a stainless steel sleeve over the affected part of the probe. Corrosion of the interior sample tube was likewise remedied by the insertion of a sleeve of stainless steel syringe tubing.

### Task 3

Following the improvements and changes documented in Task 2 the last two quarters, the focus of the experimental work was obtaining samples and replicates under the newly-controlled operating conditions. The new cyclone separator was important in this regard because it made it possible to insure that samples were not contaminated from run to run.

The samples and conditions were similar to those we have taken and reported previously. Staged combustion samples were collected with an initial stoichiometric ratio 0.75. Final stoichiometric ratios were in the range 1.04-1.08. For Pittsburgh #8, the total heating rate was 40,000 BTU/hr, with 1.5 lbs/hr coal feed rate. For Black Thunder, samples were taken with coal feed rate 3 lbs/hr and total heating rate 57,000 BTU/hr except for one staged combustion run, which had total heating rate 70,000 BTU/hr. Natural gas was used to preheat and stabilize the flame during all runs.

Two Black Thunder deposit samples were collected this quarter. Both of these samples were collected at the same position, 14 inches below the burner. This corresponds to a location above the staged air injection ports. The tests were conducted at a heating rate of 40,000 BTU/hr



under staged conditions (SR of 0.75). The coal feed rate was 3 lb/hr with the remainder of the heat provided by natural gas, which was necessary for flame stability. It was determined that the effect of oxidizing conditions on deposits could be investigated by growing the deposits under identical conditions and then allowing them to mature under different conditions. Therefore, the deposits were grown for 45 minutes under the above conditions, and then they were allowed to mature with the reactor fired on natural gas. The deposits were matured under either SR=0.75 or SR=1.2 conditions for 3 hours. The temperature of the deposit probe tube surface was maintained at about 350 °C during deposit growth and maturation. Due to a decrease in the incident radiant heat flux, the deposit tube surface temperature dropped when the coal was turned off. Therefore, the heating rate was increased to 55,000 BTU/hr after the coal was turned off to maintain the deposit tube temperature at 350 °C. These samples were then removed from the reactor and cast in epoxy for SEM examination.

A visually observable difference was noted between the sample cured under reducing conditions (SR=0.75) and the one cured under oxidizing conditions (SR=1.2). The sample cured under reducing conditions contained significantly more carbon-rich material near the probe surface than the one cured under oxidizing conditions. The appearance of the material at the deposit surface, however, was similar.

The ash and deposit samples are discussed more fully under Task 4 below. Mechanical breakdowns hampered several attempts to obtain replicate conventional combustion ash samples for both coals. Obtaining these replicates to accompany the replicate staged combustion samples is a top priority for next quarter.

#### **Task 4**

Analyses of samples obtained during the current and previous quarters are reported in this section. Carbon burnout levels of recent Pittsburgh #8 flyash samples are presented in Table 1. As discussed above, replicate conventional combustion samples are lacking. It is readily apparent that the carbon burnout levels of the staged combustion samples are low. Earlier, we reported burnouts for bottom samples on the order of 90% for all conditions. This is in contrast with the recent samples which show burnouts of 75% and 78% for staged combustion fly ash. We believe the difference is due to the unmetered oxygen present in our earlier experiments.

Our new experiments show that staged combustion does affect the rate or extent of char combustion. While samples taken at the top have comparable burnouts, it should be noted that the residence time under staged combustion is larger than that under conventional combustion. Therefore, the combustion in the initial reducing zone proceeds more slowly, as would be expected.

There is also a change in the effect of the final section of the reactor on the char. Under conventional conditions with a relatively short residence time, the char proceeds from 73% to 90% burnout, a difference of 17%. In contrast, average burnouts under staged combustion

changed by only 7%. The oxidizing section of the reactor is unable to compensate for the effects of the reducing section on the char.

**Table 1 Burnouts of Pittsburgh #8 ash samples**

Sample Date	Position	SR = 0.75	SR = 1.04
4-10-97	Top	74	69
4-10-97	Bottom	82	
5-29-97	Top	70	
5-29-97	Bottom	78	
6-4-97	Top		73
6-4-97	Bottom		90
6-9-97	Top	69	
6-9-97	Bottom	75	

The significance of this burnout difference is that char cenospheres, which contain a large fraction of the ash particles, remain intact throughout our staged combustion experiments. Whether this promotes or hinders ash coalescence is an open question. In any case, the staged combustion ash is not "final ash." It is, however, qualitatively consistent with utility experience that staged combustion has higher ash LOI.

Since Black Thunder is much more reactive than Pittsburgh #8, the results in Table 2 indicate nearly complete combustion. The bottom ash under all conditions is essentially a final product. The inconsistency in the unstaged SR = 0.75 middle and bottom samples is likely due to mechanical difficulties with the staged air injectors or the sample probe. This will be investigated next quarter if time permits.

**Table 2 Burnouts of Black Thunder ash samples**

Sample Date	Position	SR = 0.75	SR = 1.04
5-22-97	Top	87	
5-22-97	Bottom	99	
5-23-97	Middle		94
5-23-97	Bottom		98
6-24-97	Bottom	98	
7-17-97	Top	82	
7-17-97	Middle, Unstaged	96	
7-17-97	Bottom, Unstaged	91	

## Black Thunder ash

The weight-averaged particle size distributions of Black Thunder ash particles 15 microns or less in diameter are presented in Figure 1. The effect, if any, of staged combustion on particles in this size region is small. There appears to be a slight shift towards larger particles in the staged samples.

However, a clear effect of staged combustion can be seen if the particle size distribution is limited to only amorphous or "unclassified" particles. These particles comprise 60% to 70% of the total mass of the Black Thunder fly ash but are relatively small compared to quartz and the aluminosilicates. Figure 2 clearly shows that particles formed under staged combustion are *significantly larger* than those formed under conventional conditions. The effect is evident in samples obtained at both firing rates and is therefore not simply a temperature effect. The manifestations of this effect on ash composition are currently under investigation.

## Pittsburgh #8 Ash

The effect of staged combustion on included and excluded pyrite particles was investigated using our char/ash associations algorithm on the recent Pittsburgh #8 ash samples. The char/ash associations algorithm was originally described in the report for the tenth quarter. At that time, the algorithm identified the "included" region surrounding a cenospheric char particle with rectangles. The algorithm now identifies included regions by determining the convex hulls of cenospheric ash particles, as illustrated in Figure 3. This improvement reduces the size of the included regions and thus enhances the algorithm's segregation of included and excluded ash particles.

For purposes of this investigation, pyritic particles were defined as those whose oxygen-free mole fractions of iron and sulfur accounted for 80% or more of the total, i.e.  $Fe + S \geq 80$ . For each pyritic particle, an extent of reaction for pyrite conversion to iron oxide was calculated by assuming that the particle began as iron sulfide ( $FeS_2$ ):

$$\xi = 1 - \frac{S}{2Fe}$$

$\xi$  is bounded by zero below and one above. The parent pyrite has  $\xi = 0$  and iron oxide has  $\xi = 1$ .

Four samples were analyzed: short and long residence times under both staged and conventional conditions. In quarter ten, we showed that for a  $SR = 0.65$  short residence time sample, included pyrite particles were less oxidized than excluded particles. Figure 4, which shows the distributions of  $\xi$  for included and excluded particles in each sample, indicates that there is a difference between included and excluded particles under all conditions examined.

Samples obtained under conventional combustion have lower residence time than samples collected at the same position under staged combustion. Thus it is reasonable to find more unreacted pyrite in the top conventional sample than in the top staged sample. Comparison of the "top" sample included and excluded graphs shows for both stoichiometric ratios shows that the included particles do contain more unreacted pyrite than the excluded particles, as expected.

The differences between included and excluded particles can also be seen in the mean values of  $\xi$  (Table 3). The greater extent of oxidation of the excluded particles is evident. A particularly interesting feature is the difference between the means of the included and excluded particles, which is constant except for the staged short residence time sample. This greater difference at the low SR suggests that staged combustion does affect included pyrite oxidation in the initial reducing zone. However, the effect is short-lived, as included particles continue to oxidize and reach the same extent as in conventional combustion by the end of the reactor.

**Table 3 Mean  $\xi$  of included and excluded particles**

	Included	Excluded	Difference
SR = 1.0 Top	0.64	0.71	0.07
SR = 1.0 Bottom	0.86	0.92	0.06
SR = 0.75 Top	0.65	0.91	0.26
SR = 0.75 Bottom	0.89	0.96	0.07

### Deposit

The Black Thunder deposits collected during the quarter were analyzed as part of this task. SEMPC analyses of these samples showed enrichment of  $\text{SiO}_2$  in the deposit relative to the ASTM bulk oxide composition of the ash. It is believed that this enrichment is due to the effects of inertia which favors the impaction of the larger ash and char particles. Small particles, which are enriched in calcium, tend to follow the gas streamlines.

As mentioned previously (see Task 3), experiments were designed to determine the effect of exposure to reducing conditions on the morphology and composition of the deposits. To initiate this study, deposits were formed under reducing conditions and then "cured" in a natural gas flame at a stoichiometric ratio of either 0.75 or 1.2. The deposit cured at SR=0.75 had a black carbon-rich layer adjacent to the tube surface. Microscopic examination of this layer showed the presence of char particles in the deposit similar to the particles collected at the same location in the reactor. The outside of the deposit showed relatively little carbon, although the morphology of the ash reflected that of the char particles. It is believed that this structure resulted from in-situ oxidation of the char after deposition to leave a lacy ash skeleton (Fig. 5). The sample cured at SR=1.2 showed relatively little carbon and was similar to the outer layer of the sample cured at SR=0.75.

Independent of the curing conditions, both deposits formed under reducing conditions were significantly different than deposits formed from a similar coal (also Black Thunder) under oxidizing conditions (Richards, 1994). The deposits collected in this earlier study consisted of spherical ash particles (Fig. 6) and hence had a morphology which was very different than that shown in Fig. 5. The vast difference in morphology due to the large extent of carbon burnout in deposits formed under reducing conditions is expected to affect the strength and sintering behavior of the deposits.

## **References**

Richards, G.H., Ph.D. Dissertation, Brigham Young University, 1994.

## **D. Plans for next quarter**

1. Obtain replicate conventional ash samples for both coals
2. Obtain Black Thunder deposit samples under conventional conditions and longer residence times
3. Begin the collection of Pittsburgh #8 deposit samples
4. Complete the analysis of the current deposit samples and begin analysis of collected deposits

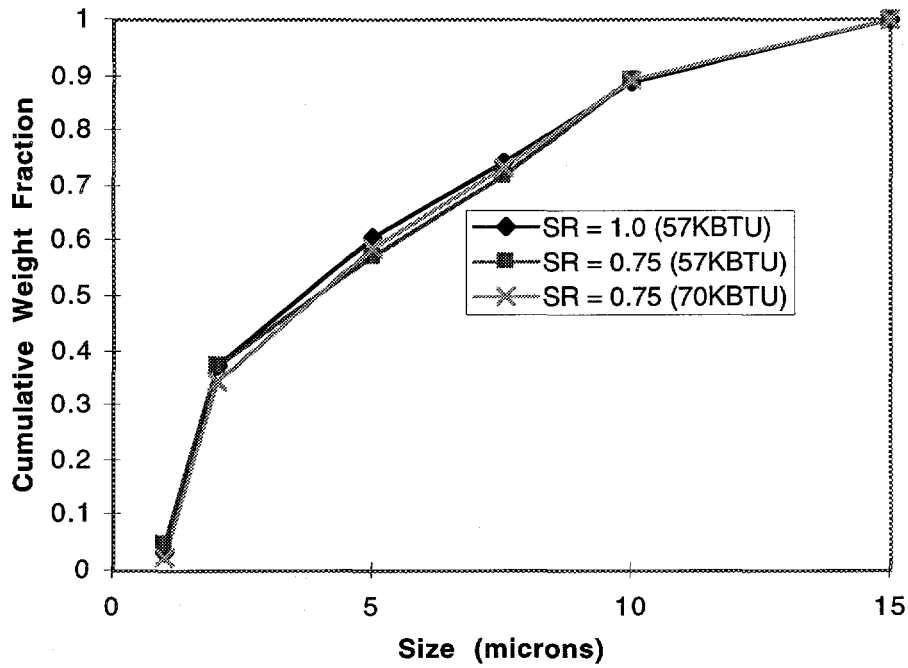


Figure 1 Particle size distribution of Black Thunder ash

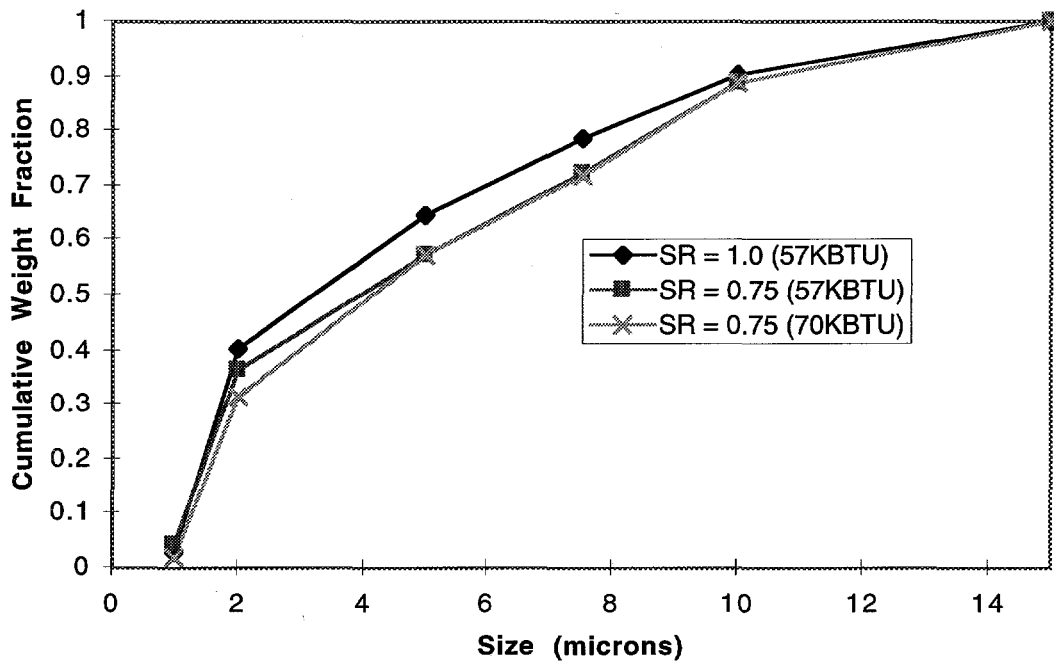
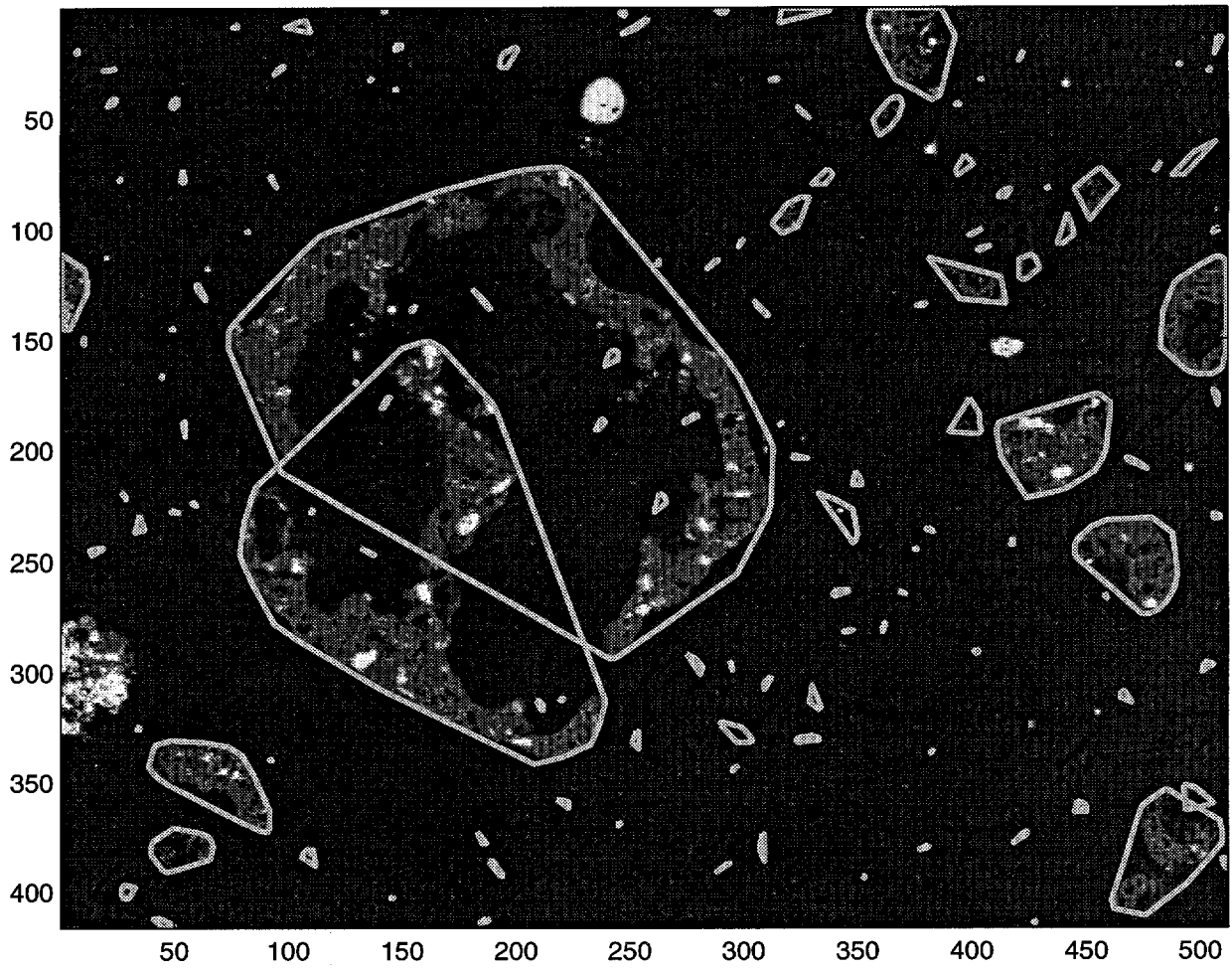
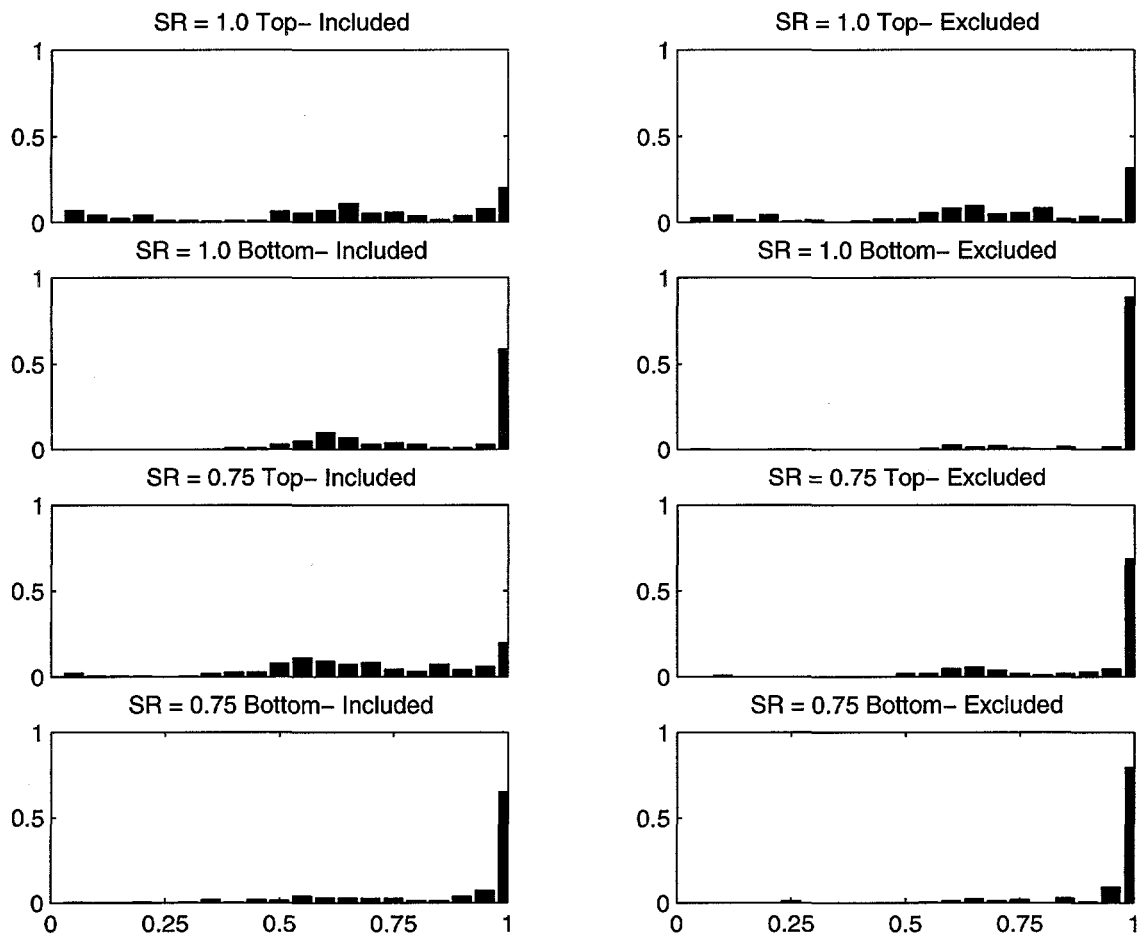


Figure 2 Particle size distribution of unclassified Black Thunder ash

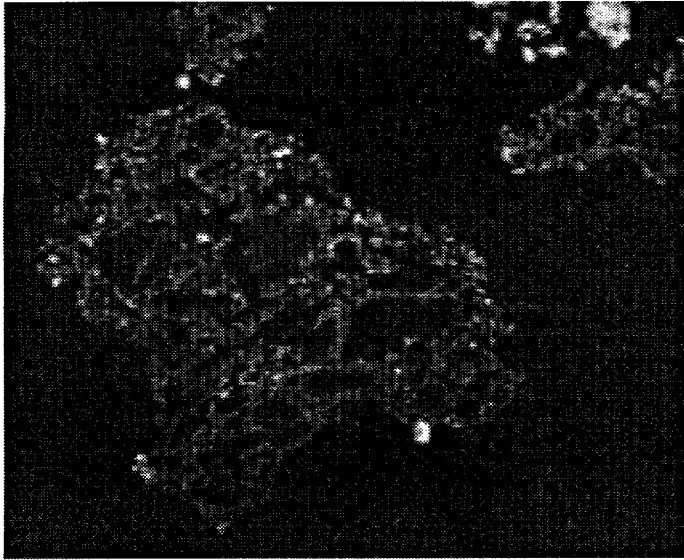


**Figure 3 Convex hulls around cenosperic char particles**

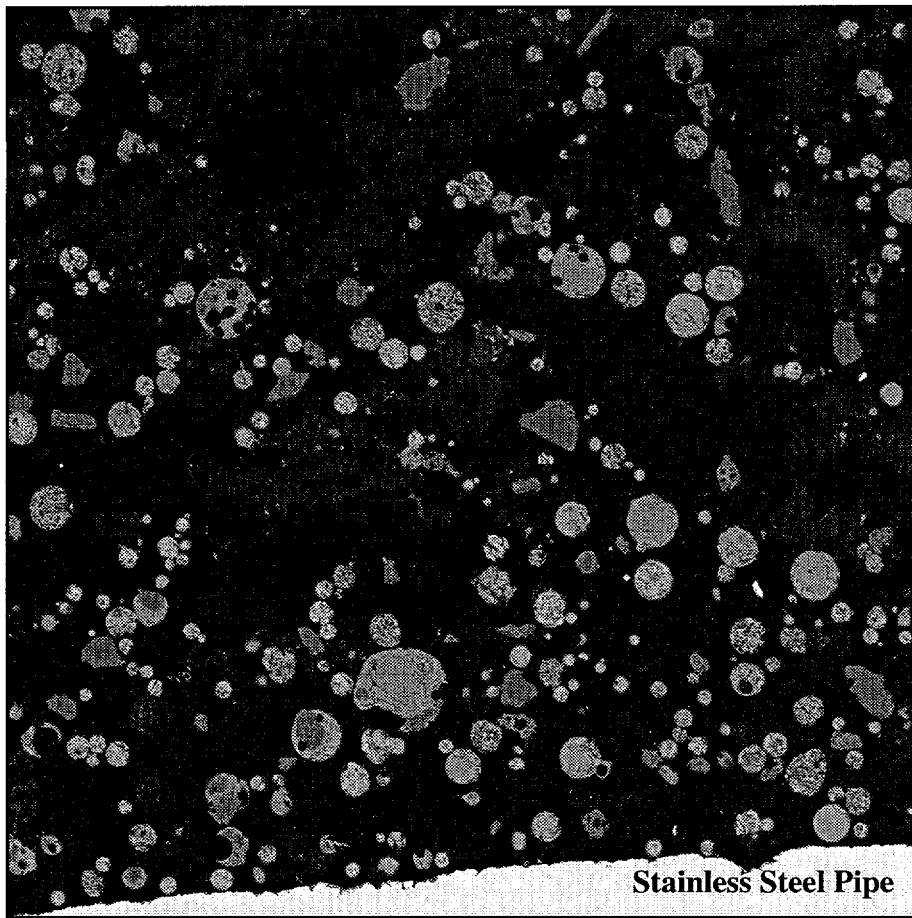


**Figure 4 Pyrite oxidation data for included and excluded particles**





**Figure 5 1000X image of lacy ash skeleton**



Stainless Steel Pipe

100  $\mu$ m

**Figure 6 100X image of a deposit grown at long residence time in oxidizing conditions**