INVESTIGATION OF MINERAL TRANSFORMATIONS AND ASH DEPOSITION DURING STAGED COMBUSTION

Quarterly Technical Progress Report
October 1, 1995 to December 31, 1995

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FOREWORD

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

ABSTRACT

Progress during the ninth quarter of a three-year study of ash formation and deposition was made in several areas. One of the key contributions this quarter was the development of an enhanced method for classification of CCSEM data. This classification algorithm permits grouping and comparison of particles previously labeled as "unclassifiable." A second analytical advancement, also made this quarter, provides more detailed information on the distribution of minerals in the coal and the potential for coalescence. This new multiple analysis technique is also applicable to ash and will permit identification of heterogeneous ash particles.

Additional analyses of ash samples were also performed and it was found that the firing of Pittsburgh #8 under staged combustion conditions yields an ash with a significantly larger particle size distribution than that obtained under conventional firing conditions, but without a significant change in composition. The size difference was noted previously, but the new classification algorithm allowed a detailed comparison of all composition groups, including unclassifiable particles, in the ashes. A mechanistic explanation for this behavior has been developed and is provided in the report.

Finally, a paper documenting the new classification algorithm has been prepared and is scheduled for presentation at the March ACS meeting in New Orleans.

OBJECTIVES AND SCOPE

A. Background

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

B. Objectives

This report describes work in the ninth 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 ninth 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. An analytical advancement was made this quarter which provided more detailed information on the distribution of minerals in the coal and the potential for coalescence. CCSEM composition analysis is typically performed at a single point for each of thousands of mineral particles in an automated analysis. In situations where minerals (e.g. pyrite and quartz) are intimately associated, the image analysis routine recognizes the intimately associated particles as a single mineral particle. The composition taken at a single point for that particle may be representative of one or the other of the minerals (e.g. either pyrite or quartz) or a blend of the two which is not necessarily representative of the actual mixture. An alternate method of analysis is to scan the entire mineral particle and obtain an average composition. Scanning has two disadvantages. First, it is impossible with scanning to distinguish between iron in a silica matrix and intimately associated pyrite and quartz. Second, the algorithms used to obtain quantitative weight percents from the spectral data assume analysis at a single point and are not strictly accurate for use with a scanning analysis. In order to overcome the weaknesses of both of the above approaches and provide a method for distinction between intimately associated pyrite/silicates and iron present in the silicates, an alternate analytical procedure was developed. In the new procedure, multiple analysis points are used on a single particle to determine if the composition of the mineral particles is uniform or heterogeneous. The new multiple analysis procedure was used on the Pittsburgh #8 coal to determine if the iron found with the silicates in the coal mineral analysis was present in the silicate matrix or as discrete intimately associated minerals. Results indicated that the iron was found in the silicates. No evidence was found for a significant amount of intimately associated minerals.

Although the above analytical technique was used on the coal, it should prove very useful for ash analysis. The new multiple analysis technique will permit identification of heterogeneous ash particles. Such heterogeneity may result from incomplete coalescence of different mineral grains. We are not aware of any other technique that will allow quantification of heterogeneity in large numbers of individual ash particles. This ability will help distinguish different stages of ash transformations.

Task 2

The purpose of this task was to prepare and test reactor facilities and sampling probes for use in the current experimental program. This testing has been largely completed, although improvements are constantly being made. For example, a modification was recently made to our deposition probe which facilitates control of the probe surface temperature while allowing for easy sample removal and mounting. A high temperature grease was used to greatly enhance thermal contact between the deposition surface and the supporting substrate, permitting much better temperature control. Other improvements are also in progress.

Task 3

During this quarter, ash samples were collected for the Black Thunder coal at a stoichiometric ratio of 0.75 (before downstream air injection). A total of three ash samples were collected at different residence times (heights) in the reactor. A deposit sample was also collected. Analysis of these samples will be formed as part of Task 4 during the upcoming quarter.

Task 4

The principal contributions made during the quarter were performed as part of this task. These contributions included an important analytical advance which is described in the paragraphs which follow. The new analytical technique, as well as others, was applied to samples from the Pittsburgh #8 coal collected at various residence times in the combustor to order to further understand ash transformation mechanisms during staged combustion.

CCSEM Particle Classification Algorithm

One of the key contributions this quarter was the development of an enhanced method for classification of CCSEM data. Composition data from CCSEM analyses are typically reported in terms of the amounts of mineralogical species or phases, such as quartz, illite, pyrite, and calcite. Mineral transformations are tracked by noting changes in the phase distribution as well as changes in the distribution of elements between phases. For example, pyrite transformations are observed by tracking changes in the amount of pyrite, pyrrhotite, and iron oxide, as well as the amount of iron accounted for by these phase and the clay species. A drawback of this approach is that ash particles frequently do not fit into the predefined classifications and are group as "unclassified." For example, 24% of the particles in one of the Pittsburgh #8 ash samples discussed last quarter were unclassifiable, including nearly half of the particles containing five mole percent or more iron. Since it is important to know what sort of particles contain iron in order to determine to

what extent mixing and coalescence are occurring, a new classification algorithm was developed and applied to the unclassified particles. Using linear algebra and nonlinear optimization techniques, the previously unclassified particles were grouped according to which of the known phases they came closest to fitting. In this case, the iron-containing particles fell into nine major groupings, the mean compositions of which are listed in Table 1. The column labeled "%" indicates the percentage of the total particles in the phase.

Recalling that pyrite coalesced with aluminosilicate clays, the large number of particles with high iron contents listed as "near" the various aluminosilicates is expected. In most cases, particles did not fit into their nearest phases because they contained too much of a minor constituent. Cutoffs are typically five mole percent. In the "near Fe-Al-Silicate" phase, 44% of the particles contained too much calcium, 32% contained too much potassium, and 18% contained too much sodium. Many particles violated more than one constraint; i.e. they contained too much of two or more elements.

The presence of these sorts of particles suggests that coalescence of mineral grains during combustion is a major effect. In sampling, the molten particles are quenched before the more common crystalline phases can form. The high iron concentrations indicate that pyrite particles must be mixing with the aluminosilicates, since there is no other high-iron source in the coal. This agrees with the conclusion drawn earlier based on the iron distribution.

Table 1. Nearest Phase Classification of Iron Particles in Pittsburgh #8 Ash

Nearest Phase	%	Na	Mg	Al	Si	K	Ca	Fe
Gehlenite-Na melilite	0.6	0.8	1.8	23.9	27.4	0.4	24.8	13.4
Akermanite-Na melilite	1.4	1.5	5.4	15.0	26.4	0.1	25.3	17.8
Anorthite	0.6	0.5	2.1	32.5	34.7	0.7	15.0	10.3
Plagioclase	1.2	3.4	2.4	29.0	36.9	2.1	8.9	10.6
Kaolinite	2.7	0.7	0.9	21.3	68.1	1.6	1.2	2.1
Ca-Al-Silicate	3.7	1.2	4.3	28.4	35.0	1.1	19.0	5.8
K-Al-Silicate	2.0	3.9	1.4	31.1	39.8	7.7	1.3	4.4
Fe-Al-Silicate	9.0	2.7	2.8	30.0	37.4	3.2	4.2	15.5
Iron Silicate	1.7	1.9	1.6	10.7	23.9	0.6	4.9	49.3

Transformation Mechanisms for Ash Formation from the Pittsburgh #8 Coal

The long residence time Pittsburgh #8 fly ash samples obtained and discussed last quarter have been further examined this quarter. As mentioned in the last report, the effect of staged combustion on the final ash was to increase the particle size without changing the composition.

Our recent efforts have yielded more evidence for this conclusion, as well as a possible explanation for it.

In our last quarterly report, we presented the distributions of two key elements, iron and potassium, in the ash from combustion experiments performed under conventional firing conditions (SR = 1.04 initially) and staged combustion (SR = 0.75 initially). Although some differences were observed in samples taken at short residence times, the final ashes were essentially identical with respect to the distribution of these two elements.

Comparison of the major mineralogical phases determined in these ashes (Fig. 1) gives broader support to the conclusion that their compositions are the same. The observed differences in the relative amounts of the major phases are less than the experimental errors associated with CCSEM; thus the classifiable portions of the ashes have the same composition.

It is still possible to have differences in the composition of the unclassifiable particles which constitute a significant fraction of the total ash particles for both the conventional and staged combustion cases. Both of the ashes have similar amounts of unclassifiable particles. The compositions of these particles were studied using the algebraic classification scheme described above. Using this algorithm, particles are grouped with the phase that they most nearly fit. Results are presented in Table 2, and are reported in terms of the nearest phases (designated by number). Phase names have been omitted to simplify the table.

Table 2. Mean Compositions of Unclassifiable Particle Groupings in Pittsburgh #8 Ash

Phase Number	Firing Condition	Pct of Total Particles	Na	Mg	Al	Si	K	Ca	Fe
45	Conv.	1.3	1.5	5.3	15.0	26.4	0.1	25.4	17.6
	Staged	0.7	1.0	4.6	15.7	30.3	0.3	27.0	13.3
48	Conv.	1.2	3.4	2.4	29.0	36.9	2.1	8.9	10.6
	Staged	0.8	2.9	2.1	30.2	38.1	2.2	9.5	9.5
49	Conv.	2.7	0.7	0.9	21.3	68.1	1.6	1.2	2.1
	Staged	2.0	0.5	0.4	24.4	65.1	1.2	1.4	2.0
50	Conv.	3.7	1.2	4.3	28.4	35.0	1.1	19.0	5.8
	Staged	3.5	0.8	4.2	28.2	34.3	1.0	19.3	6.3
52	Conv.	2.0	3.9	1.4	31.1	39.8	7.7	1.3	4.4
	Staged	1.6	2.4	1.0	34.7	43.3	4.2	1.6	5.1
53	Conv.	9.0	2.7	2.8	30.1	37.5	3.2	4.1	15.5
	Staged	7.3	2.5	2.2	31.5	38.3	3.3	3.9	15.0
55	Conv.	1.7	1.9	1.6	10.7	23.9	0.6	4.9	49.3
	Staged	1.0	1.9	2.0	12.1	25.4	0.9	6.3	48.3

Several observations can be made from Table 2. First, a relatively small number of groups was needed to account for most of the unclassifiable particles in both ashes. Second, the same groups sufficed in both cases, although the groups accounted for slightly more of the ash from the conventional firing conditions than they did of the staged ash. This difference is evident in all of the phases and may indicate a difference in the formation mechanism. However, from a practical point of view (i.e. effect on ash behavior), the observed differences are not significant. Finally, the mean composition of the key elements was approximately the same in a given group. Since both the classifiable compositions (Fig. 1) and the unclassifiable compositions (Table 2) were similar for both the staged and conventional ashes, we concluded that staged combustion did not significantly affect the *composition* of the long residence time ash for the Pittsburgh #8 coal.

The number-averaged particle size distributions of the ash samples are plotted in Fig. 2. As reported previously, staged combustion yielded a larger ash. The major difference lies in the 10-15 µm size category, where a much larger number of particles was found under staged combustion. This difference is clearly evident in Fig. 3 which shows an increased fraction of particles in the 10-15 µm range for all of the major species classifications. Since large ash particles are formed by agglomeration or coalescence of smaller mineral grains, the results in Figs. 2 and 3 are consistent with increased coalescence under staged combustion conditions.

Based on the above discussion we are left with two conclusions: 1) there is no significant difference in the composition of the ashes from the staged and conventional combustion experiments, and 2) the size of the ash formed during staged combustion is larger than that formed during firing under conventional conditions. At first glance these conclusions may appear to be inconsistent. In other words, one might expect that a size increase due to increased coalescence would result in significant changes in composition due to mixing of particles. This situation is shown schematically in Fig. 4a where the mineral in the coal is in the form of relatively large grains of different composition. Fig. 4 b-d show alternate possibilities for the form of the mineral matter and the resulting ash. In each of these situations, the composition of the ash from conventional and staged firing is similar, even though the size is different. Ash formed through any or all of these scenarios would be consistent with our data for the Pittsburgh #8 coal. None of these situations involves the coalescence of large mineral grains. In fact, coalescence of large mineral grains would not be expected from this coal which forms cenospheres that would tend to separate the large grains.

Finally, we are left to postulate a mechanism to explain increased coalescence under staged combustion. It is our current opinion that the coalescence is due to the fact that the char remains intact longer under staged conditions than under conventional firing conditions. This provides increased opportunity for coalescence. Consequently, the behavior observed here for the

Pittsburgh coal will be different for coals of different mineral content and char morphology.

D. Plans for the Next Quarter

1. Analyze Black Thunder ash samples and determine the effect of staged combustion on ash formation. Analyses will be similar to those used for the Pittsburgh #8 coal.
2. Collect and analyze deposit samples from both the Black Thunder and Pittsburgh #8 coals and quantify the effects of staged combustion on deposit formation.
3. Determine the differences, if any, between the transformations of included and excluded mineral particles during staged combustion.
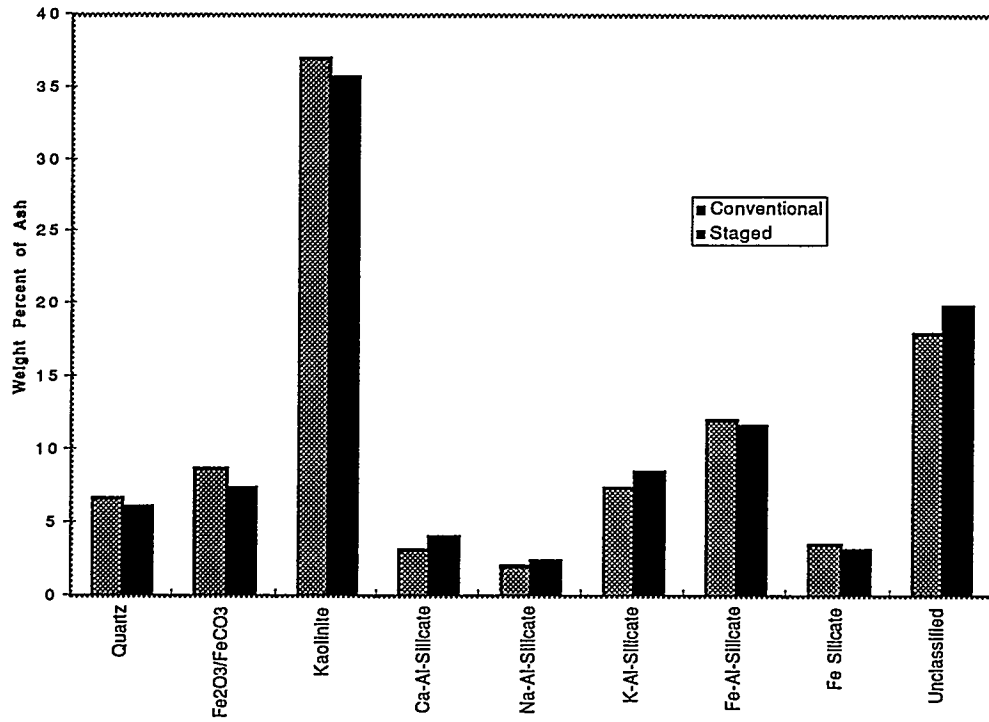
Figure 1. Mineral Distribution in Pittsburgh #8 Ash
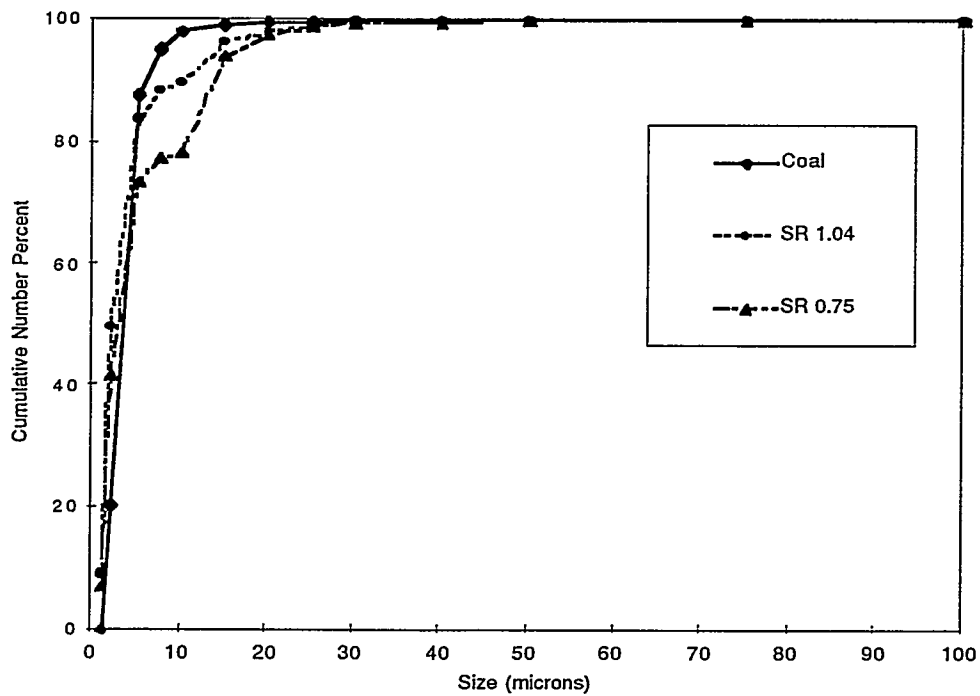
Figure 2. Particle Size Distribution of Pittsburgh #8 Ash
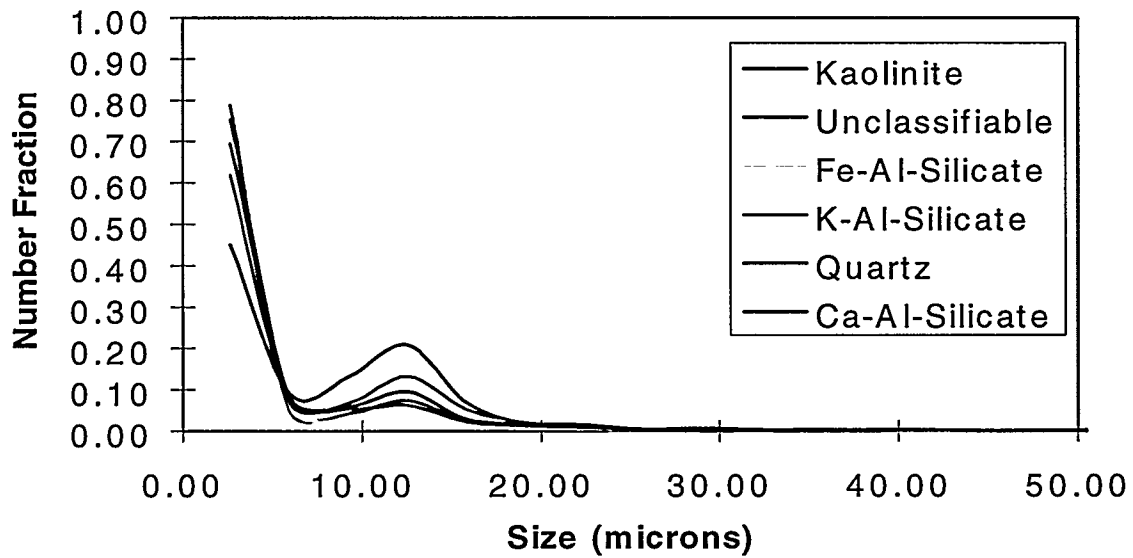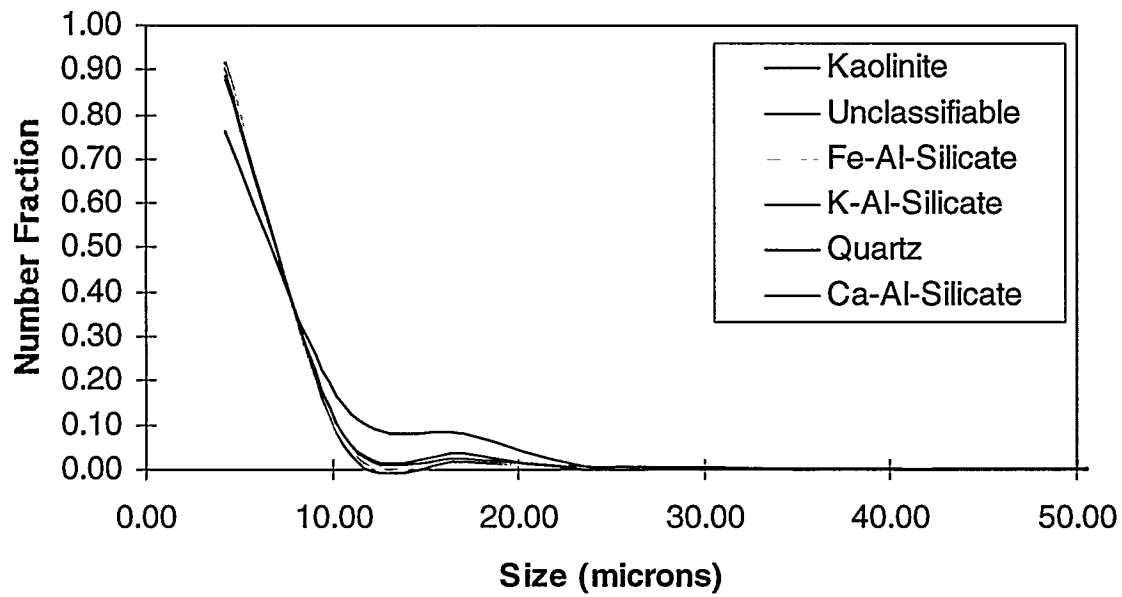
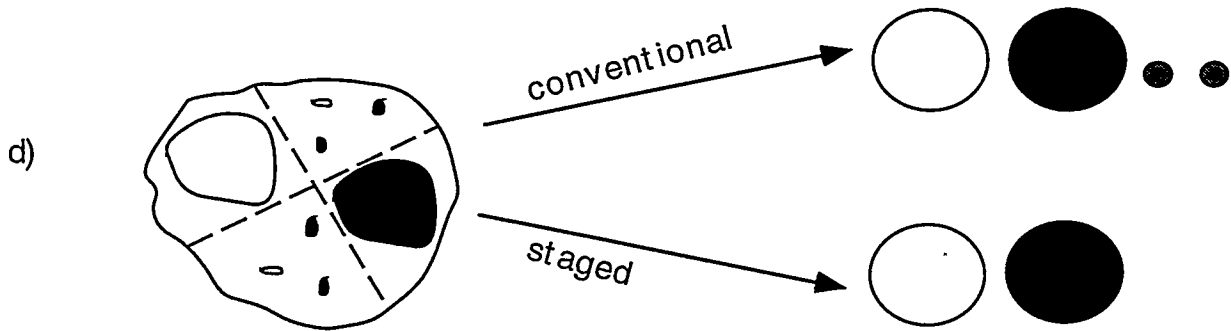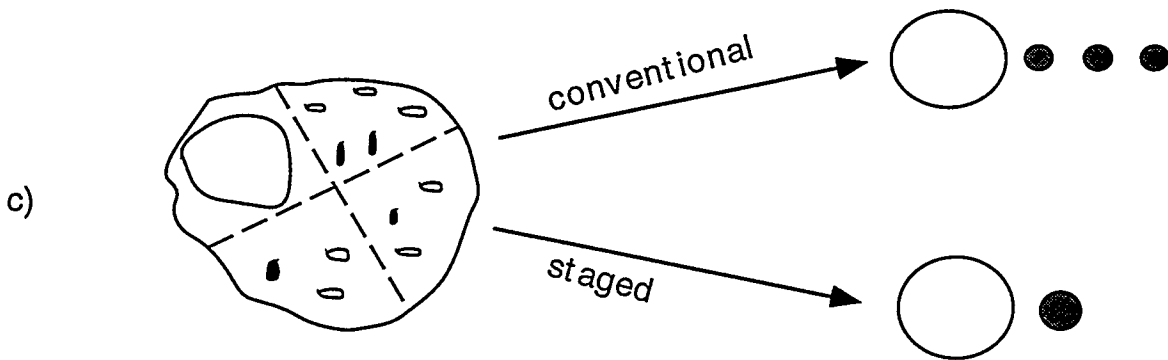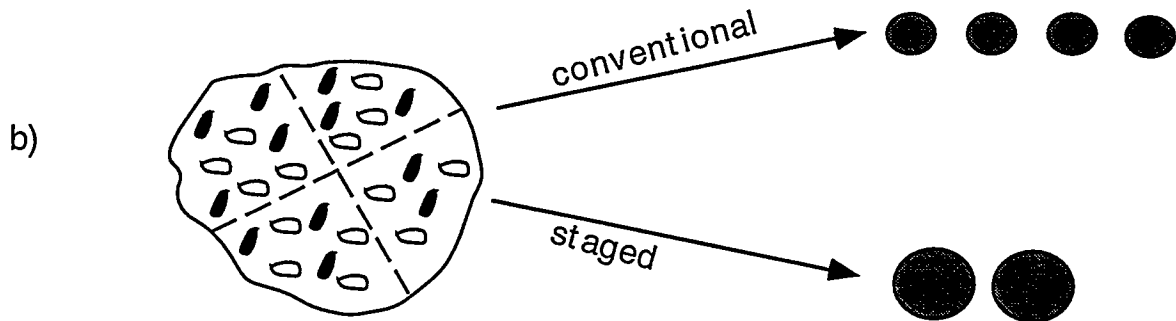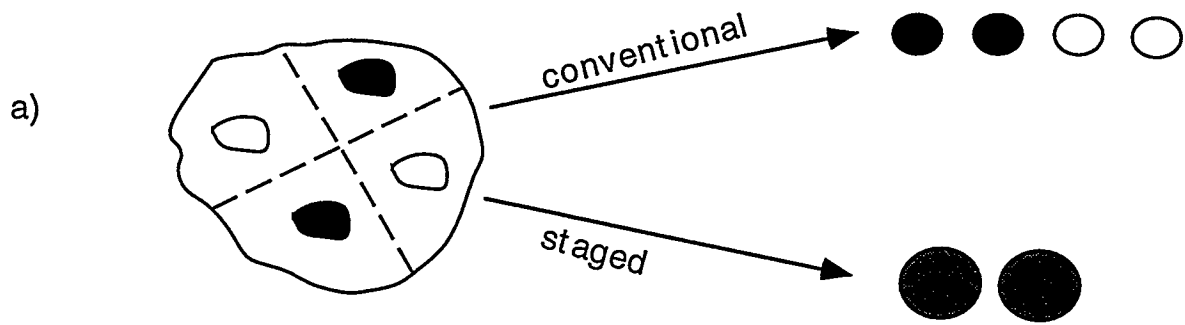Figure 3. Particle Size Distribution of Major Species in Pittsburgh #8 Ash

Figure 4.   Possible coalescence mechanisms