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Coal Ash Behavior in Reducing Environments

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Coal Ash Behavior in Reducing Environments

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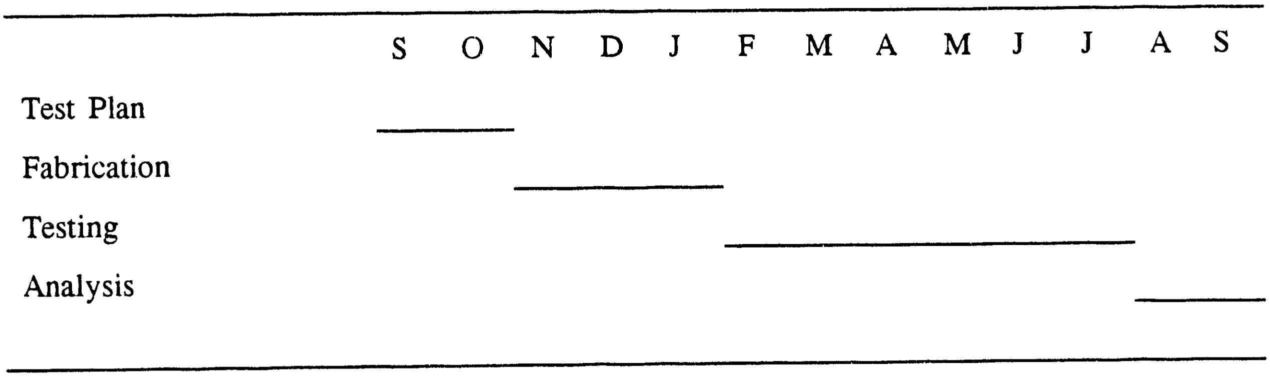
Period of Performance	November 1, 1990, to October 31, 1993

FY'92 Program Schedule



OBJECTIVES

The objective of the Coal Ash Behavior in Reducing Environments (CABRE) program is to advance the knowledge of ash behavior in coal gasification systems; this knowledge will help provide the tools needed to operate advanced coal utilization systems efficiently with a minimum of operational problems associated with ash properties. The program approach is to use carefully controlled, laboratory-scale gasification experiments coupled with detailed analysis of the materials involved to determine the critical fundamental mechanisms of ash behavior in coal gasification systems.

BACKGROUND INFORMATION

A key factor in the successful design and operation of coal gasification systems is the ability to control and mitigate ash-related problems. Some of the major ash-related problems are slag flow control, slag attack on the refractory, ash deposition on heat-transfer surfaces, corrosion and erosion of equipment materials, and emissions control. Such problems are closely tied to the abundance and association of the inorganic components in coal and the gasification conditions.

In general, the inorganic components are associated in the coal as minerals or organic complexes (salts of carboxylic acid groups or organic coordination complexes). The minerals associated in coal vary widely in size, composition, and juxtaposition. Juxtaposition refers to the association of the mineral grains with other mineral grains and coal particles. These associations directly influence the chemical and physical transformations that occur during the gasification process. Depending upon the type of gasification system, the inorganic components are initially partitioned into intermediate species in the form of inorganic gases, liquids, and solids. The state of these species at any given stage or position in the gasifier directly influences their behavior at that stage. The transformations and partitioning of the inorganic species directly influence slag behavior, extent and type of slag attack on the refractory, and corrosion and erosion of materials, as well as growth rate, quantity, and type of ash deposition on heat-transfer surfaces.

PROJECT DESCRIPTION

The CABRE project is a three-year program designed to investigate the transformations and properties of coal ash in reducing environment systems. This project is currently midway through its second year. The first year and a half emphasized four areas of research: 1) the production of quantitative techniques to analyze reduced species, 2) the production of gasification-type samples on a laboratory scale, 3) the systematic gasification of specific coals to produce information about their partitioning during gasification, and 4) the study of the physical properties of ashes and slags under reducing atmospheres.

The CABRE project is organized into a three-task structure which is the backbone of the project's strength. Task 1, Analytical Methods Development, has concentrated on the special needs of analyzing samples produced under a reducing atmosphere as opposed to the more often studied combustion systems. Task 2, Inorganic Partitioning and Ash Deposition, has focused on the production of gasification-type samples under closely controlled conditions for the study of inorganic partitioning that may lead to deposition. Task 3, Ash and Slag Physical Properties, has made large gains in the areas of sintering and strength development of coal ashes under reducing atmospheres for the evaluation of deposition problems.

RESULTS

Task 1 - Analytical Methods Development

The SEM technique most commonly used at the Energy and Environmental Research Center (EERC) to characterize deposits is the scanning electron microscopy point count (SEMPC) technique (Steadman et al., 1990). This technique was developed at the EERC to quantitatively determine the relative amount of phases present in entrained ashes and deposits. The method involves microprobe analysis (for chemical compositions) of a large number of random points on a polished cross section of a sample. A data manipulation program then classifies each chemical composition into a phase category based on various weight and molar ratios. The criteria for the classification procedure have been developed from the stoichiometry of the various phases.

The most important addition to this technique from the CABRE project is the qualitative examination of carbon and oxygen during analysis. Carbon and oxygen are two of the more important chemical components in reducing environments. A rapid and accurate analysis of these elements, concurrent with the other elements analyzed in an energy dispersive x-ray spectrometer system, is very advantageous. However, due to the complexity of the samples analyzed in this project, problems arise which deter the quantification of carbon and oxygen. The samples vary widely in composition and, therefore, do not present a consistent background matrix to the correction routines, and all samples must be carbon-coated to maintain conductivity under the electron beam. The best results that can be attained under these conditions are qualitative determinations of carbon and oxygen.

During the routine SEMPC analysis, the number of x-ray counts included in the carbon and oxygen x-ray peaks can be measured, but not subsequently compared to a reference standard. The standard array of elements are quantified and placed into a data file along with the raw x-ray counts that were recorded for carbon and oxygen. The carbon and oxygen counts can then be compared to each other and to the elemental composition of the analysis to determine the presence of oxides, carbonates, sulfides/sulfates, and various other phases. The following tests were preformed to demonstrate the usefulness of the SEMPC technique.

Carbonates. A test was performed on a calcite ($CaCO_3$) standard and reagent-grade calcium oxide (CaO). Figure 1 shows the x-ray spectra for the two compounds. Although carbon and oxygen peak heights appear to be similar in both cases, the calcium peak is about twice as high in the calcium oxide sample. The Ca/O ratio of the CaO sample was 35, while that for the $CaCO_3$ was 20. This ratio shows a large enough difference to distinguish consistently between calcium oxide and calcium carbonate.

Iron Sulfides. Testing was performed on samples of pyrite (FeS_2), pyrrhotite ($Fe_{1-x}S$), and troilite (FeS). The weight percent Fe/S ratios of the analyzed minerals were pyrite, 0.88; pyrrhotite, 1.53; and troilite, 1.74. These numbers match the theoretical ratios for stoichiometric pyrite and troilite minerals. Thus it is possible to differentiate among the sulfide minerals with this technique. However, in a combustion or gasification system, there is no guarantee that the minerals present in a deposit or ash will be stoichiometric.

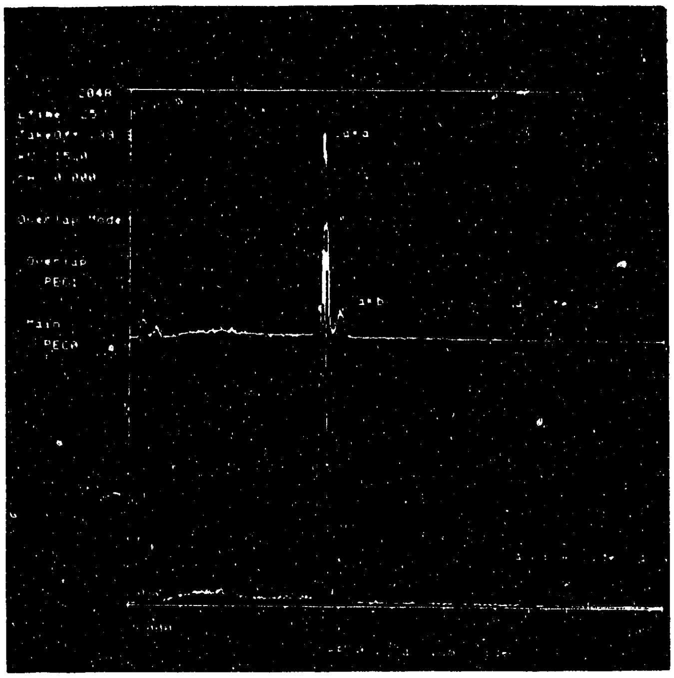


Figure 1. Comparison of X-Ray Spectra for Calcite and Calcium Oxide

Iron Oxide and Metal. Testing was performed on hematite (Fe_2O_3) and metallic iron (Fe). Figure 2 shows the x-ray spectra of the two phases. The hematite spectra shows a very noticeable oxygen peak where the metallic shows none; thus it is relatively easy to distinguish these two species.

Another addition to the SEMPC program from the CABRE project is the ability to record the sample images during analyses for later manipulation. Since the SEMPC technique utilizes the selection of frames over the area to be analyzed, either randomly chosen by the program or user-specified, these images can be digitally stored for later recall. After the analysis is completed, it is possible to visually inspect any analysis point since the location and frame number of each point has been stored in a data file. A program has been created to recall the proper image and to circle the analysis point when given the frame number and point number. Visual inspection of the image can be enhanced by the use of the powerful image-processing capabilities available. The ability to recall a previously analyzed point produces the very valuable ability to verify the presence of a specific phase on a sample by visual inspection after the analysis has located its presence.

In addition to the chemical analysis of an ash deposit, the physical characteristics of a deposit can be recorded also. The porosity of any solid can generally be determined by SEM using backscatter electron (BSE) imaging and image analysis of a polished cross section of the material. After the deposit sample has been prepared for SEMPC, the same sample mount can be used for image analysis. Since the BSE imaging technique is sensitive to the average atomic number of all of the elements

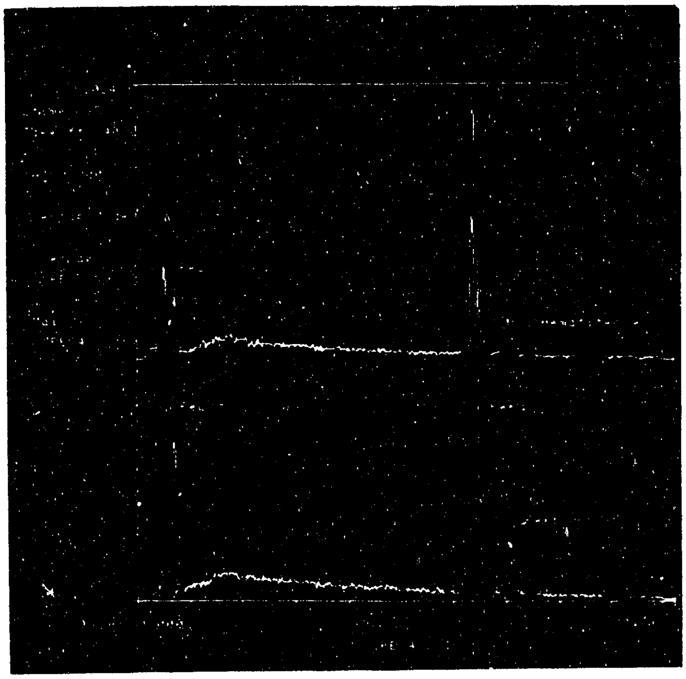


Figure 2. Comparison of X-Ray Spectra for Hematite and Iron

of any point under the beam, brightness contrast between the mounting medium and the deposit material results. The mounting medium, usually epoxy, has a low average atomic number and shows darker on the image than the higher average atomic number deposit. This effect can be used to generate a binary image of just the epoxy areas on the BSE image. By using an image histogram to carefully choose the brightness levels that coincide with the area of interest, a binary image is created, Figure 3. The area covered by the binary image, representing epoxv areas, can be compared to the area of the BSE image, and a percent porosity can be determined. The ability to determine the porosity of a deposit is very important when investigating the development of strength in deposits.

To accept enhancements and additions made to the SEMPC program, a new data manipulation program has been written that allows minerals or other phases to be defined and has the ability to insert or withdraw them from the list of phases considered by the matching routine, with virtual ease. In addition, the phases are grouped according to their dominant chemical component. The current groups which are initially examined for are elemental metals, sulfates/sulfides, oxides, phosphates, and silicates. User-defined phases can likewise be inserted into the potential phase list. A particular list of phases can be assembled to fit a particular sample type and fine-tuned, which will be of great importance and use in the study of gasification-produced ash and deposits.

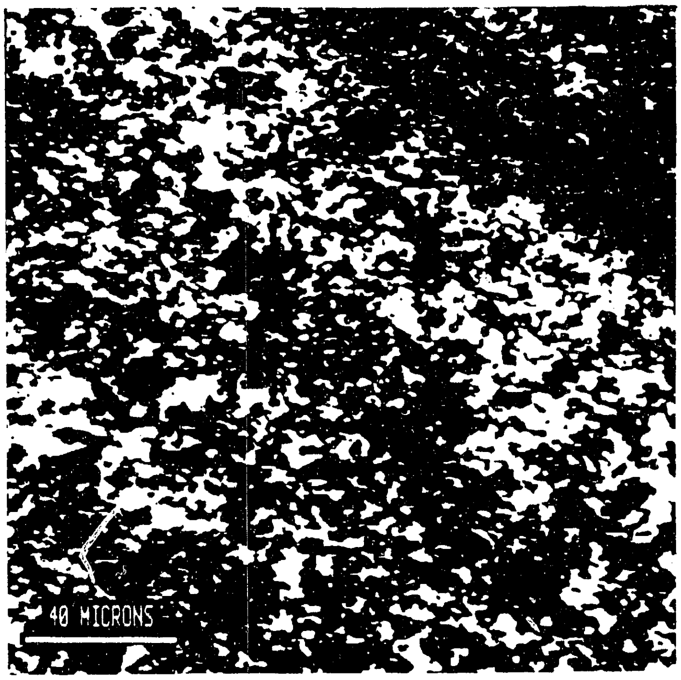


Figure 3. Binary Image of Deposit, White Areas Show Porosity

During the operation of the above-mentioned manipulation program, unclassified phases remain after the classification scheme and are assumed to be amorphous. The chemistry of the collective amorphous phases is calculated and can be related to viscosity of the melt at a given temperature. The new data manipulation program allows for multiple viscosity calculations at various temperatures. The program calculates a viscosity distribution at each temperature and displays a three-dimensional graph of the results. The results are output to a file in tabular ASCII format that is importable to Lotus® 123® for further processing and hard copy output.

Task 2 - Inorganic Partitioning and Ash Deposition

The production of gasification-type samples under closely controlled conditions was the primary goal of Task 2 during the first year of this project. A Pressurized Drop-Tube Furnace (PDTF) is used to produce the gasification samples. The PDTF can closely control the temperature profile, pressure, atmosphere, and residence time. The use of a small-scale gasifier such as this allows for the fundamental research of coal gasification without a huge investment for equipment.

The PDTF, Figure 4, is a laboratory-scale, entrained flow, tube furnace with the capability to perform experiments under closely controlled conditions. Significant design features of the PDTF include a heat

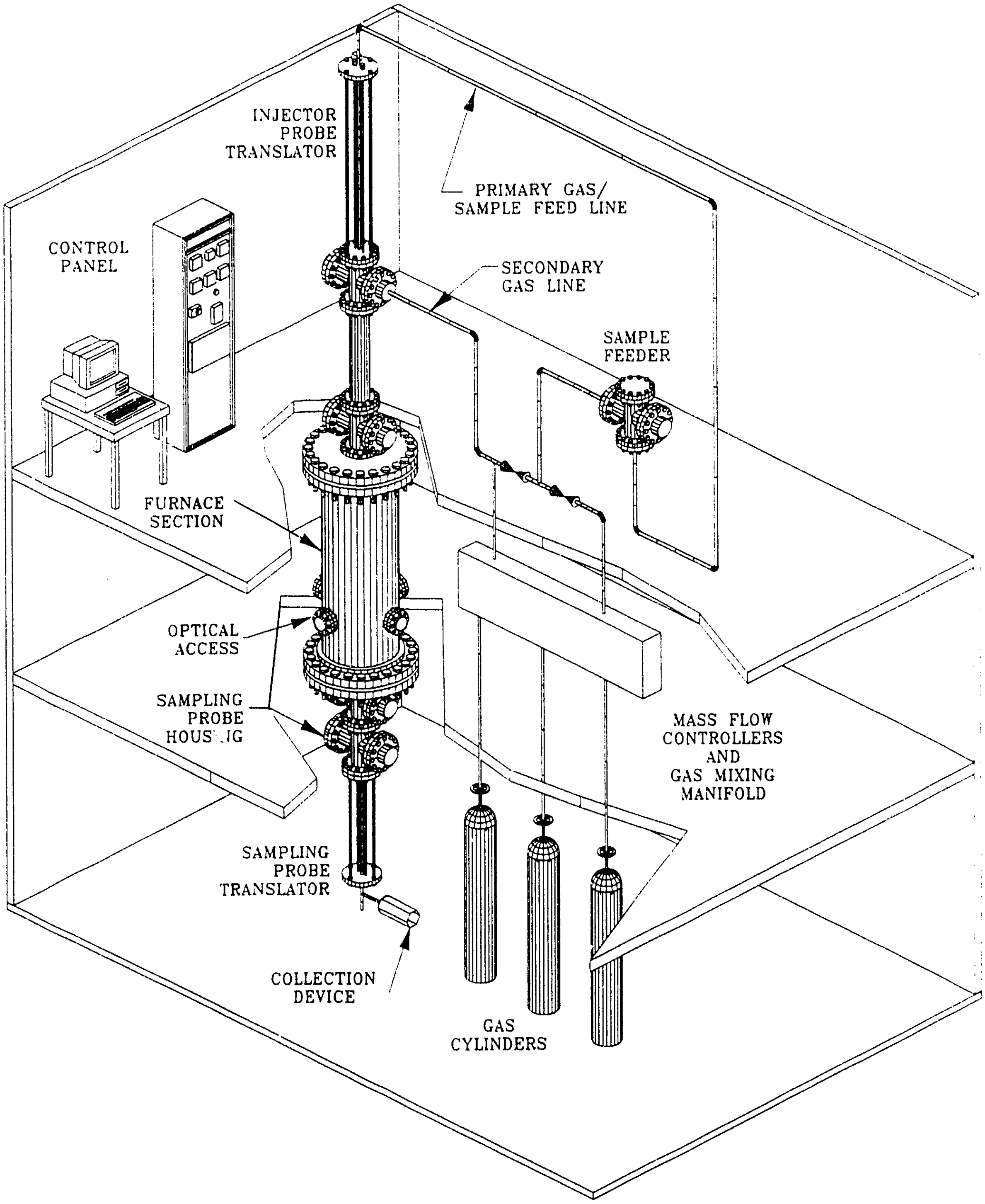


Figure 4. Overview of the Pressurized Drop-Tube Furnace

source which is independent of pressure with a maximum operating temperature of 1500°C over an operating pressure range of 0-300 psi. The PDTF furnace assembly consists of a 3-inch-ID alumina tube reaction chamber, heated externally by high-temperature tube furnaces equipped with Kanthal Super 33 elements. The entire reactor and the heating elements are housed in a water-jacketed pressure vessel. Coal is introduced into the reactor with a carrier gas through a traversing, water-cooled injector located in the center of the tube. Optional, secondary, gas enters the reactor at the top of the tube and flows down through the tube around the injector assembly. The coal residue and process gases travel down the tube in a laminar flow regime and pass through an accelerator at the base of the reaction area where they are collected in a water-cooled, nitrogen-quenching collection probe. Size segregation of the ash is obtained using a multicyclone or impactor in conjunction with a final filter. The process gases are monitored by on-line O_2, CO, and CO_2 gas analyzers and by off-line gas chromatography.

The PDTF furnace has successfully produced gasification-type samples that have initially compared very favorably to the samples produced in a full-scale facility. Carbon burnouts ranging from 86% to 91% and CO/CO_2 ratios greater than 15 have been obtained during initial testing at 1500°C and 125 psi. Testing has been carried out under a wide set of conditions with positive results. The PDTF is currently being modified to improve the ability to operate at high pressures and at high pressures under gasification conditions. Under the new configuration, it is expected that burnouts of up to 95% can be obtained. Samples produced from the PDTF are currently being analyzed using the techniques created in Task 1.

Task 3 - Ash and Slag Physical Properties

Studies have been carried out to interpret the physical properties of ashes and slags under gasification conditions. Studies have been carried out on the following subjects:

- Eutectic formation from the interaction of sodium, calcium, and iron sulfides and, therein, the role of strength formation in gasification-type deposits.
- Silicate and aluminosilicate glasses under reducing conditions.
- Exchange of sulfur and oxygen in glasses under gasification conditions.
- Sulfide- and silicate-sintering mechanisms.

Studies involved the use of thermal gravinometric analysis (TGA), differential thermal analysis (DTA), thermal conductivity analysis, surface tension analysis, and slag viscosity analysis using a rotating bob viscometer.

FUTURE WORK

The following areas are currently being emphasized for future work in the CABRE project:

- Modification of the SEMPC data manipulation program will continue. This will include the addition of a user-friendly interface to be added to the code. Testing will continue on the program to ensure its accuracy in defining ash related phases.

- The PDTF will be used to produce gasification type ash samples from the following range of conditions:
  - 1000 to 1500°C
  - 0 to 250 psi
  - C/O ratios of 1.0 to 2.0
  - Residence times of 5.0 to 15.0 seconds

- Samples produced from the above-mentioned testing will be analyzed using the analytical techniques developed in this project for reduced samples.

- Physical properties testing will continue in the areas previously mentioned. The major emphasis being on the gas atmosphere during gasification.

ACKNOWLEDGMENTS

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