DOE/MC/10637-94/C0364

COAL ASH BEHAVIOR IN REDUCING ENVIRONMENTS

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Conf-9406131--16

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Contract Number:

DE-FC21-86MC10637

Conference Title:

Coal-Fired Power Systems 94 -- Advances in IGCC and PFBC Review Meeting

Conference Location:

Morgantown, West Virginia

Conference Dates:

June 21-23, 1994

Conference Sponsor:

U.S. Department of Energy, Office of Fossil Energy, Morgantown Energy Technology Center

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Coal Ash Behavior in Reducing Environments

CONTRACT INFORMATION

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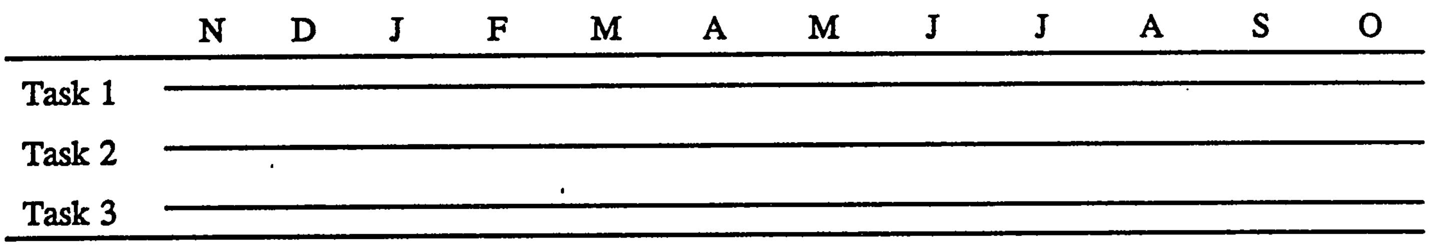
Period of Performance	November 1, 1990, to October 31, 1994

Schedule and Milestones

FY94 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 understanding necessary to operate advanced coal utilization systems efficiently with a minimum of the operational problems associated with ash properties. The program approach is to use carefully controlled, laboratory-scale 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 and materials, and emissions control. Such problems are closely tied to the abundance and association of inorganic components in coal and 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 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, 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 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 four-year program designed to investigate the transformations and properties of coal ash in reducing environment systems. This project is currently midway through its third year. The work to date has emphasized four areas of research: 1) the development of quantitative techniques to analyze reduced species, 2) the production of gasification-type samples under closely controlled conditions, 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 three tasks which provide a strong foundation for the project. 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 scanning electron microscope (SEM) technique most commonly used at the Energy & Environmental Research Center (EERC) to characterize deposits is the scanning electron microscopy point count (SEMPC) technique (Steadman and others, 1990), Figure 1. This technique was developed at the EERC to

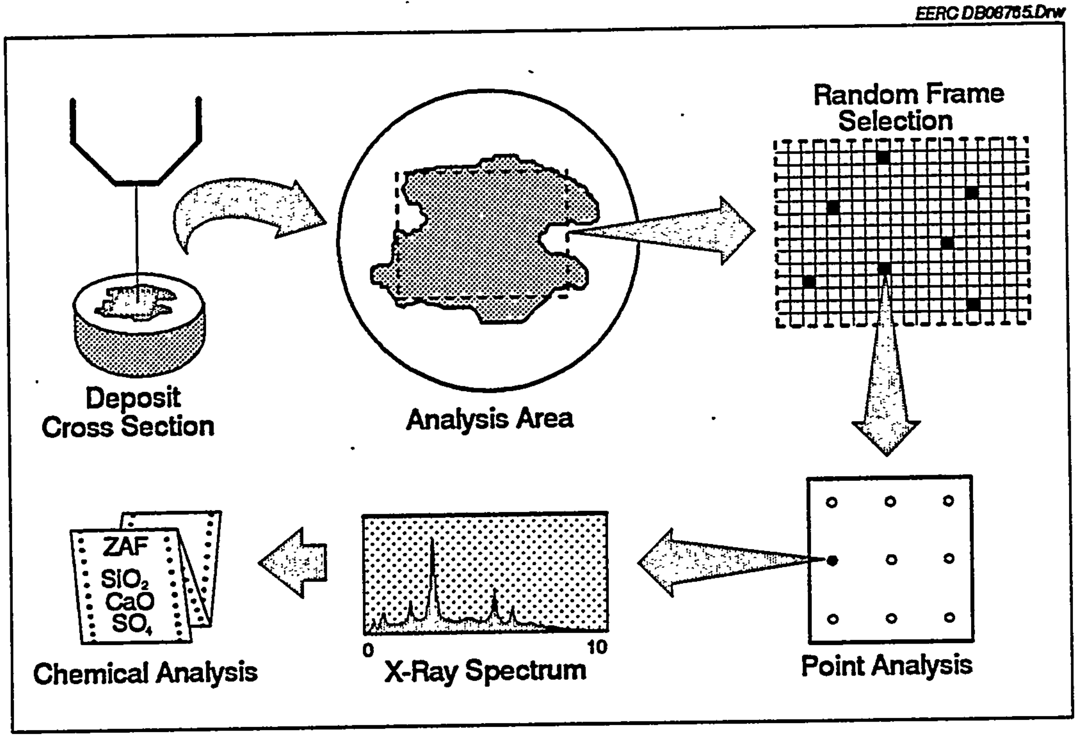


Figure 1. Scanning Electron Microscope Point Count Analysis Routine

quantitatively determine the relative amounts of the 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 was 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 analyses of other elements 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 hinder 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. All samples must be carbon-coated to maintain conductivity under the electron beam. The best result that can be attained under these conditions is a qualitative/semiquantitative determination of carbon and oxygen. The advances made concerning carbon and oxygen determinations have been previously documented (Erickson and Others, 1993)

In conjunction with the SEMPC technique, three data manipulation programs were created to manipulate the data and present them in their best format: MINCLASS© for Microsoft® MS-DOS® (DOS), MINCLASS© for Microsoft® Windows™ (Windows), and VISCALC© for DOS. Each of these codes are discussed below.

MINCLASS©

The phase classification program, MINCLASS© 4.0, has been revised to incorporate advances in hardware and increased knowledge about the analytical demands of the CABRE project. Improvements include modifying the classification algorithms to incorporate quantified oxygen values, which allows any element to be included in the analysis, and tabulating the number of points that make up the various chemical composition summaries. These refinements make it easier to analyze SEMPC data from reducing environment samples where reduced phases are difficult to recognize.

A Windows version of MINCLASS© was also made available to those desiring to operate in that environment. This version of the program requires Windows 3.1 as the operating environment. The input file, classification routine, and output files are the same as the DOS version. Either program will produce the same results. Included in the MINCLASS© for Windows interface is the viscosity calculation program VISCALC©. An example of the output from MINCLASS© 4.0 is given in Table 1.

VISCALC©

A silicate liquid-phase viscosity calculation and viscosity distribution program named VISCALC© 4.0 is available to sponsors for the first time. VISCALC© has been used internally on CABRE samples since the beginning of the project. The program uses the chemistry and mineralogy of silicate and aluminosilicate phases determined by the SEMPC technique. Mineralogy is used to determine which phases to include in the viscosity calculations. Chemistry is used as input to a model developed by Kalmanovitch and Frank (1988) to calculate viscosity. The model is based on a modified version of a metallurgical slag viscosity model developed by Urbain and others (1981). Assumptions in the model include the chemistry expressed as oxides, iron expressed in the ferric state, and calculations performed only on silicate and aluminosilicate phases.

In addition to a file of calculated viscosities, the program includes an interactive graphics feature for comparing viscosities. The present version of VISCALC© allows the user to compare the viscosities of a single sample as three temperatures or up to three different samples at a single temperature. If certain silicate phases are known to be crystalline at the input temperatures, VISCALC© permits them to be excluded from the viscosity calculations. It is up to the user to decide which phases are to be excluded. An example of the output from VISCALC© is given in Table 2.

Task 2 – Inorganic Partitioning and Ash Deposition

The production of gasification-type samples under closely controlled conditions has been the primary goal of Task 2 for the duration 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 large capital investment for equipment.

Table 1. Example Output from MINCLASS© Software

UND-EERC SEMPC Mineral Classification Version 3.1
Run Date: December 17, 1992, Using Definitions File rules. c

Mineral Name	Frequency Percent	Mineral Name	Frequency Percent
Oxide-Rich		Silicon-Rich	
Magnesium Oxide	0.0	Quartz	25.1
Aluminum Oxide	0.0	Albite	0.3
Calcium Oxide	0.0	Anorthite	0.0
Titanium Oxide	0.0	Potassium Feldspar	0.0
Chromium Oxide	0.0	Nepheline	0.0
Iron Oxide	0.3	Hauyne	0.0
Spinel	0.0	Leucite	0.0
Ca–Ti Oxide	0.0	Kaolinite	8.1
Ca–Al Oxide	0.0	Altered Kaolinite	2.7
Mixed Oxide-Rich	1.0	Illite	0.3
Total for Group	1.4	Montmorillonite	2.7
		Pyroxene	0.0
Sulfur-Rich		Wollastonite	0.0
Pyrite	0.0	Calcium Silicate	0.0
Pyrrhotite	0.0	Di Calcium Silicate	0.0
Iron Sulfate	0.0	Na–Ca–SiO_3	0.0
Sodium Sulfate	0.0	Gehlenite	0.0
Calcium Sulfate	0.7	Akermanite	0.0
Na–Ca Sulfate	0.0	Merwinite	0.0
Barite	0.3	Spurrite	0.0
Mixed Sulfur-Rich	0.0	Mullite	0.0
Total for Group	1.0	Mixed Silicon-Rich	0.2
		Total for Group	49.5
Phosphorous-Rich			
Apatite	0.0		
Mixed Phosphorous-Rich	0.0	User-Defined List	
Total for Group	0.0	Ettringite	0.3
		Calcium Aluminate	1.0
Carbon-Rich		Total for Group	1.4
Calcite	7.8		
Altered Calcite	0.0		
Dolomite	0.3		
Sulfated Dolomite	0.0	Other	9.5
Ankerite	0.0		
Sulfated Ankerite	0.0		
Mixed Carbon-Rich	8.8		
Total for Group	36.9		

Table 1 (continued)

Mineral Name	Frequency Percent	Mineral Name	Frequency Percent
Metal-Rich			
Aluminum	0.0		
Titanium	0.0		
Iron	0.0		
Nickel	0.0		
Copper	0.0		
Chromium	0.0		
Mixed Metal-Rich	0.3		
Total for Group	0.3		

Total Number of Points Analyzed = 295
Carbon Threshold for Analysis = 2000
Oxygen Threshold for Analysis = 300

Bulk Chemical Composition, oxide wt%

	A	B	C	D	E	F	G
SiO_2	4.9	1.6	62.2	1.5	48.2	55.5	56.0
Al_2O_3	19.5	26.8	20.1	37.4	15.0	17.4	17.9
Fe_2O_3	14.7	5.9	2.4	5.7	4.6	4.0	4.2
TiO_2	2.2	1.7	0.7	0.9	3.1	1.1	1.3
P_2O_5	0.1	0.0	0.2	0.0	0.1	0.1	0.1
CaO	41.5	30.9	5.1	48.7	17.2	12.7	13.4
MgO	13.2	3.9	2.6	5.0	4.2	3.5	3.6
Na_2O	1.9	0.5	4.2	0.4	5.9	3.2	3.3
K_2O	0.1	0.1	0.5	0.0	0.5	0.3	0.3
SO_3	0.5	3.6	0.4	0.3	0.2	0.8	0.0
Cl_2O_7	0.5	0.4	0.8	0.0	0.2	0.5	0.0
Cr_2O_3	0.1	0.0	0.1	0.0	0.1	0.1	0.0
BaO	0.7	24.6	0.6	0.0	0.7	0.9	0.0
Points	26	3	23	1	1	295	295

A Cumulative bulk composition of other.
B Cumulative bulk composition of mixed oxide-rich.
C Cumulative bulk composition of mixed carbon-rich.
D Cumulative bulk composition of mixed metal-rich.
E Cumulative bulk composition of mixed silicon-rich.
F Cumulative bulk composition of the entire sample.
G SO_3-, Cl_2O_7-, Cr_2O_3-, BaO-free composition of the entire sample.

Table 2. Example Output from VISCALC© Software

12345678 Test Sample
Viscosity Data

Index	1100.0	1300.0	1500.0	Temp. at 3.0 Critical Viscosity
1	4.065	2.868	1.948	1275.1
2	2.963	1.995	1.251	1093.6
3	3.606	2.505	1.658	1203.0
4	7.108	5.281	3.873	1652.1
5	3.810	2.666	1.786	1235.5
6	3.066	2.076	1.316	1111.6
7	3.118	2.117	1.349	1120.8
8	5.728	4.187	3.000	1500.1
9	5.578	4.068	2.905	1481.6
10	5.744	4.199	3.010	1501.8
11	3.670	2.555	1.698	1213.6
12	4.009	2.824	1.912	1266.7
13	4.015	2.828	1.916	1267.6
14	5.707	4.170	2.986	1497.4
15	5.839	4.275	3.070	1513.3
16	5.146	3.725	2.631	1427.1
17	5.530	4.030	2.875	1475.9
18	3.416	2.353	1.537	1171.8
19	3.710	2.587	1.723	1219.7
20	4.842	3.484	2.439	1386.7
21	6.153	4.524	3.269	1549.7
22	6.115	4.493	3.244	1545.3
23	10.084	7.640	5.755	1726.8
24	5.266	3.820	2.707	1442.5

Viscosity frequency distribution data:

0–1	1–2	2–3	3–4	4–5	5–6	6–7	7–8	8–9	9–10	10–11	11–12
1500											

Table 2 (continued)

Viscosity frequency distribution data:

0.0	45.8	25.0	25.0	0.0	4.2	0.0	0.0	0.0	0.0	0.0	0.0
1300											
0.0	4.2	41.7	12.5	33.3	4.2	0.0	4.2	0.0	0.0	0.0	0.0
1100											
0.0	0.0	4.2	29.2	16.7	33.3	8.3	4.2	0.0	0.0	4.2	0.0

T_{cv} cumulative % less than frequency data:

<700	800	900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	>1900
0.0	0.0	0.0	0.0	4.2	16.7	45.8	50.0	70.8	91.7	95.8	100	100	100

The PDTF is a laboratory-scale, vertically oriented, downfired, entrained flow furnace able to perform gasification studies under closely controlled conditions. The PDTF furnace assembly, Figure 2, consists of an upper alumina tube (2.875-in. ID x 55 in. long) and a lower alumina tube (2.875-in. ID x 25 in. long) separated by a flow accelerator. The two vertically oriented tubes are held in position by a slightly larger concentric tube. The tube assembly is heated externally with three high-temperature tube furnaces (four heating zones) equipped with Kanthal Super 33 elements capable of heating the furnace to 1500°C. Each of the heating zones can be controlled separately for temperature profiling. The top two furnaces are used for the gasification zone, while the bottom furnace is used as a deposition and collection zone. The entire reactor, including the heating elements, is housed in a water-jacketed pressure vessel rated at 335 psi.

Fluidized coal, 80% −200 mesh, is introduced into the reactor with a carrier gas (primary gas) through a traversing, water-cooled injector positioned in the center of the tube. The feeding system allows close control of feed rates as low as 0.1 g/min. 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 reactor tube in a laminar flow regime and pass through the accelerator where they are collected by a water-cooled, nitrogen-quenching ash collection probe or water-cooled deposition probe. Particle residence times can be controlled by inserting or retracting the coal injector into the furnace while the collection device remains fixed. Various collection devices can be attached to the outlet of the collection probe to collect the solids. Size segregation of the ash is facilitated by using a multicyclone or impactor in conjunction with a final filter. A bulk filter is used to collect ash for bulk

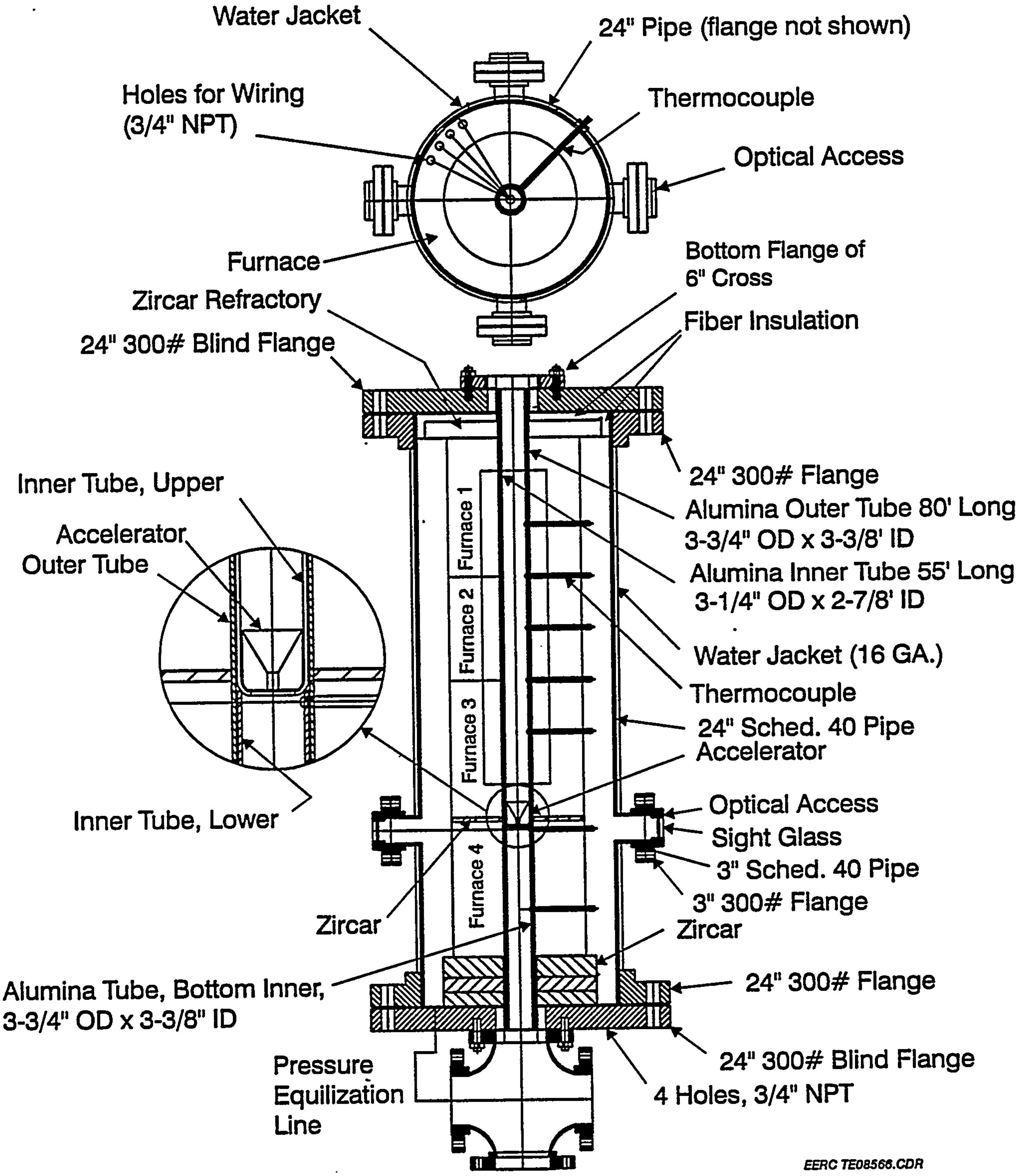


Figure 2. PDTF Assembly

chemistry. The process gases exiting the collection device are monitored on-line by O_2, CO, or CO_2 gas analyzers or off-line by a gas chromatograph (GC).

Deposition tests were conducted over the last twelve months on five coals: Sufco/Hiawatha, Illinois No. 6, Pittsburgh No. 8, Drayton, and Rochelle. These tests were conducted at a gasification temperature of 1500°C and deposition zone temperatures of 1000° and 800°C. The results from these tests are currently being investigated, and replicate runs are being performed for verification.

To enhance the work done in the PDTF, thermochemical equilibrium modeling was done to predict slag flow behavior. Thermochemical equilibrium modeling is an effective method to predict behavior in well-mixed equilibrium systems. Though slag in a gasifier is not an equilibrium mixture, it does approach equilibrium because of its high molten state. PHOEBE©, a thermochemical equilibrium code developed at the EERC, has been used extensively in the past to model high-temperature slags and deposits in combustion systems. With the latest enhancements to its database, it is now capable of modeling gasification systems as well. Three of the coals from the CABRE project have been run through the code at temperatures ranging from 1500° to 3000°F (815° to 1650°C). Both the viscosity and percent of ash as liquid phase were recorded for each temperature and coal.

The chemical compositions used in these predictions come from the original coal analysis (ultimate and x-ray flouresence). It should be noted that the composition of a slag in a real gasifier may be different because of the partitioning of specific species caused by the aerodynamic properties of the reactor. Figures 3–5 show the results of the modeling predictions. Each of the three graphs shows a temperature range at which there is no appreciable amount of liquid phase present, followed by an increase in the liquid phase amount and a decrease in its viscosity. The phases and their corresponding viscosities change as a function of temperature.

Task 3 – Ash and Slag Physical Properties

The third task of the CABRE project has concentrated on the various physical processes that take place in the formation of slags and deposits on various heat-exchange surfaces. The primary emphasis has been on the process of strength development under reducing conditions. The results of this project, along with literature on similar subjects, have pointed to the presence of three different strength development regimes (Figure 6) as defined by the dominant liquid phases: sulfides, sulfided silicates, and silicates. Figure 7 shows the thermal stability of various sulfides as determined under an atmosphere of $H_2S/CO_2/CO$.

Much of the work over the past year has focused on the effects of water vapor on the sintering potential of coal ashes. Three different sulfides were tested in a thermogravimetric analyzer (TGA) with and without the presence of water vapor. The results for $Fe_{1-x}S$, CaS, and Na_2S-1.7FeS are shown in Figures 8, 9, and 10, respectively. The iron sulfide appears to be relatively unaffected by the presence of the water vapor. The stability of the calcium sulfide is shifted to lower temperatures by the presence of water vapor. The Na_2S-1.7FeS system appears to undergo a more complex interaction with the water vapor which involves the addition of weight to the system. It is possible that some of the sodium sulfide is being replaced with NaOH, which would involve a slight increase in weight.

FUTURE WORK

Over the final half year, the CABRE project will continue to study the transformations of inorganic species into ashes and deposits under reducing atmospheres. The following areas of research will be emphasized over the remainder of the project:

- The study of deposition and strength development mechanisms using the PDTF
- The continued evaluation of the physical properties affecting ashes and deposits which result in high-strength deposits

ACKNOWLEDGMENTS

The Energy & Environmental Research Center would like to thank the sponsors of this project for their desire to continue developing the future of the Fossil Energy Program. The six sponsors are Shell Oil Company, Texaco, DOW Chemical Company, Netherlands Energy Research Foundation the Electric Power Research Institute, and the U.S. Department of Energy.

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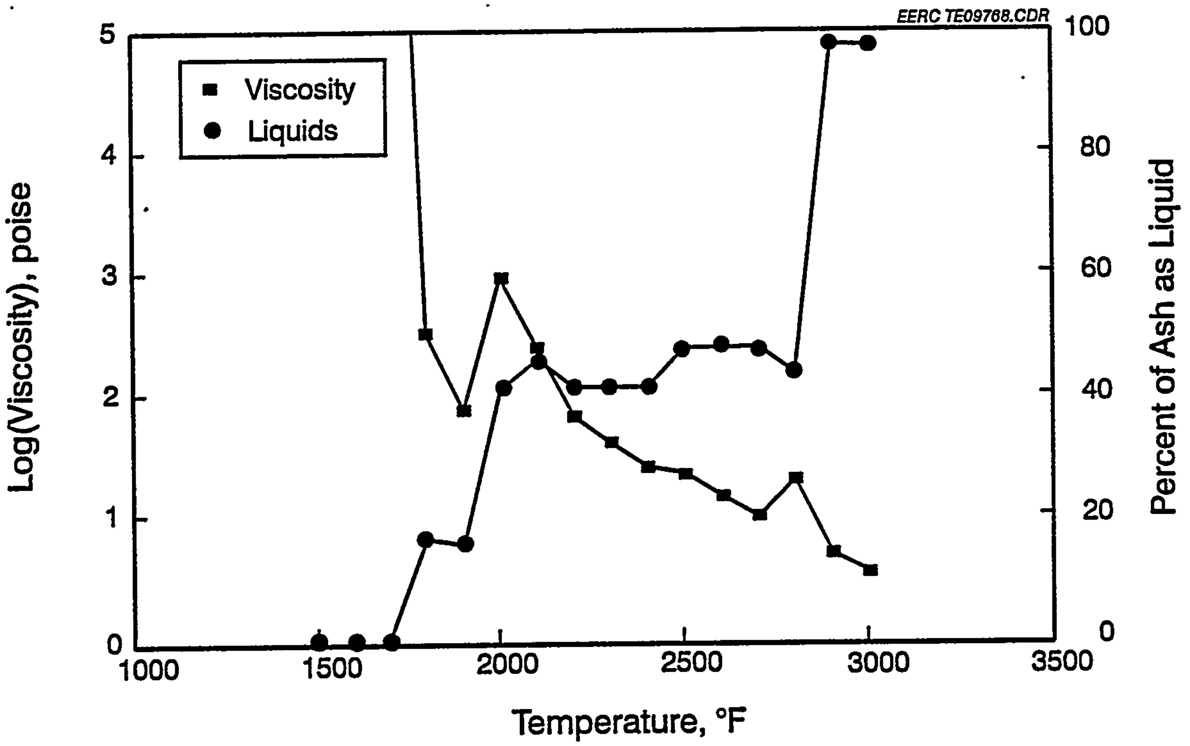

Figure 3. Thermochemical Equilibrium Modeling of a Slag Formed from the Gasification of Coal A

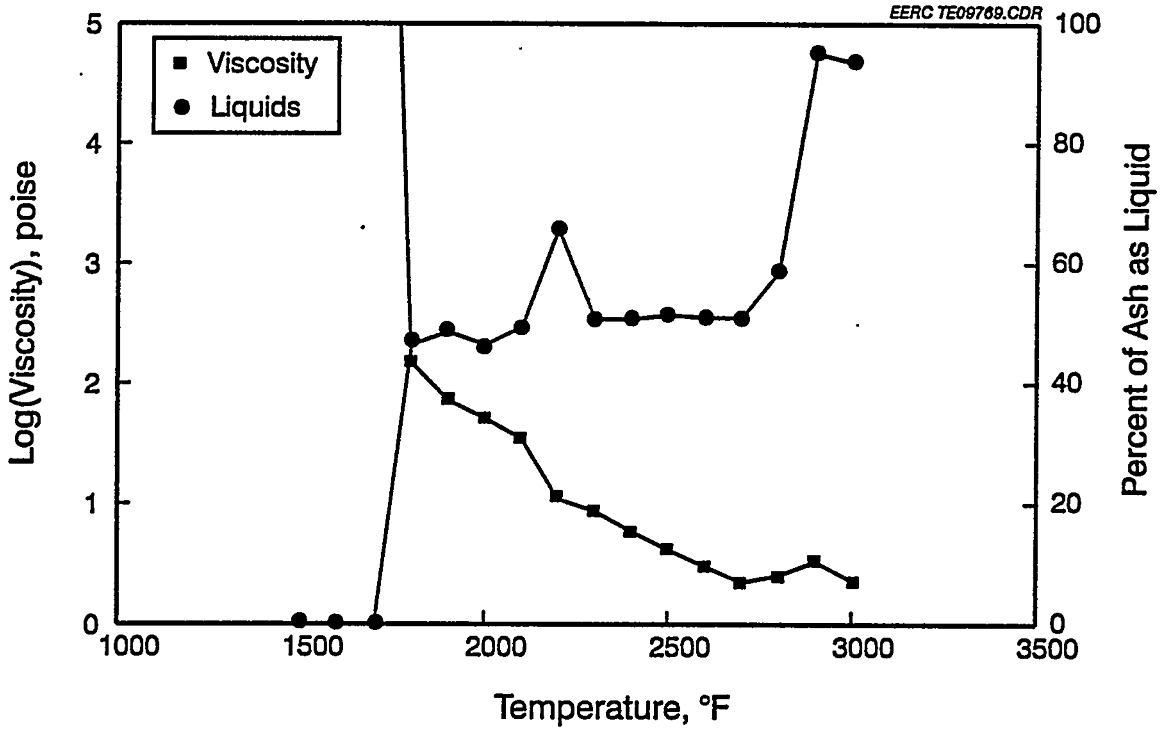

Figure 4. Thermochemical Equilibrium Modeling of a Slag Formed from the Gasification of Coal B

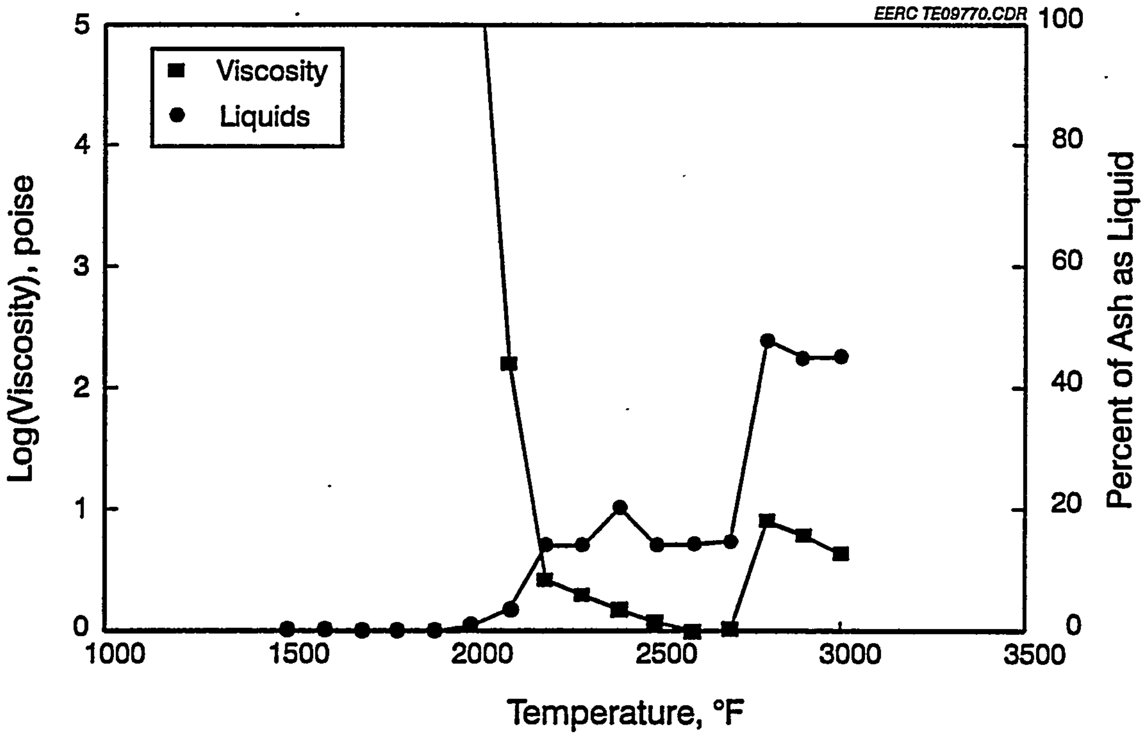

Figure 5. **Thermochemical Equilibrium Modeling of a Slag Formed from the Gasification of Coal C**

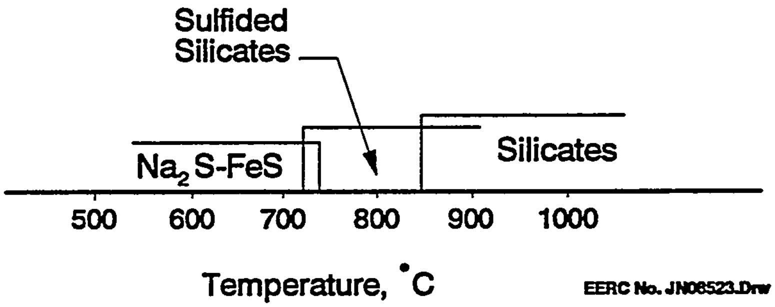

Figure 6. **Diagram Showing a Sintering Model of Coal Ashes in Three Different Ranges of Temperatures and in the Presence of Three Possible Liquid Phases**

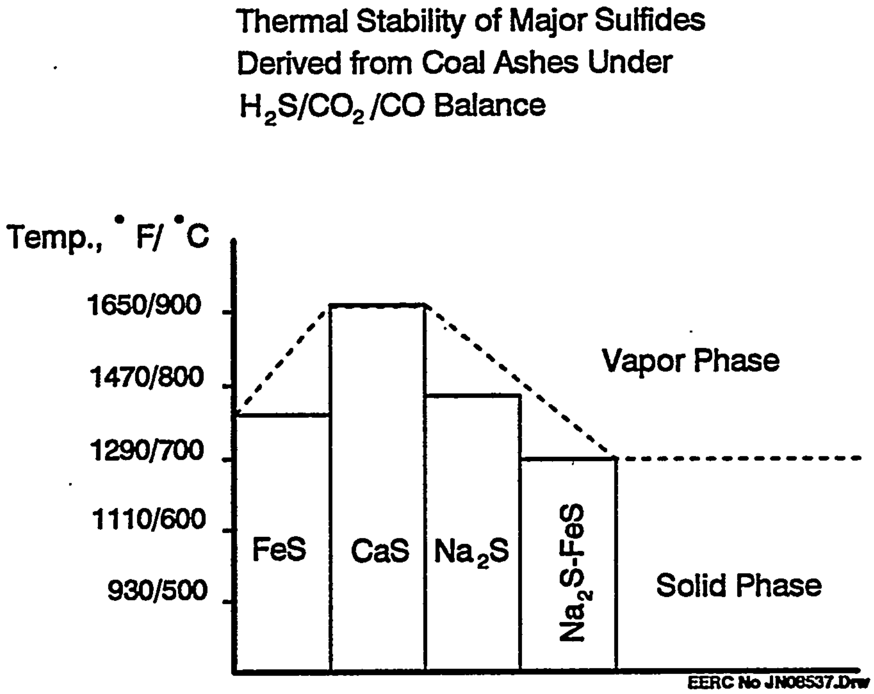

Figure 7. Thermal Stability of Major Sulfides Derived from Coal Ashes under Gasification Conditions

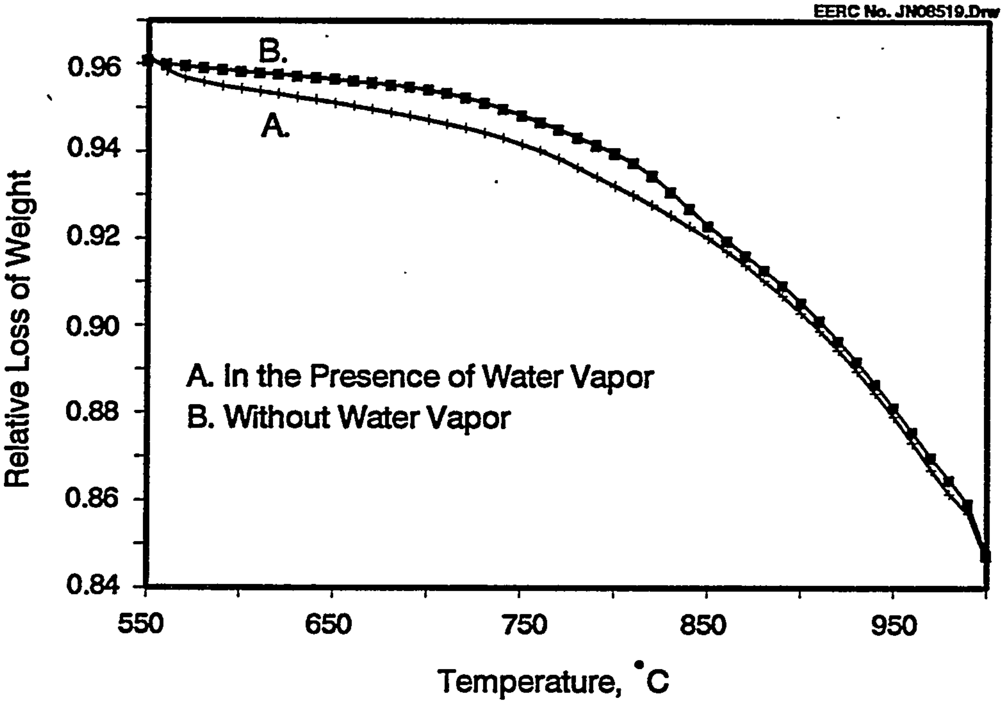

Figure 8. The Relative Loss of Weight of $Fe_{1-x}S$ in the Presence and Absence of Water Gas under Reducing Conditions

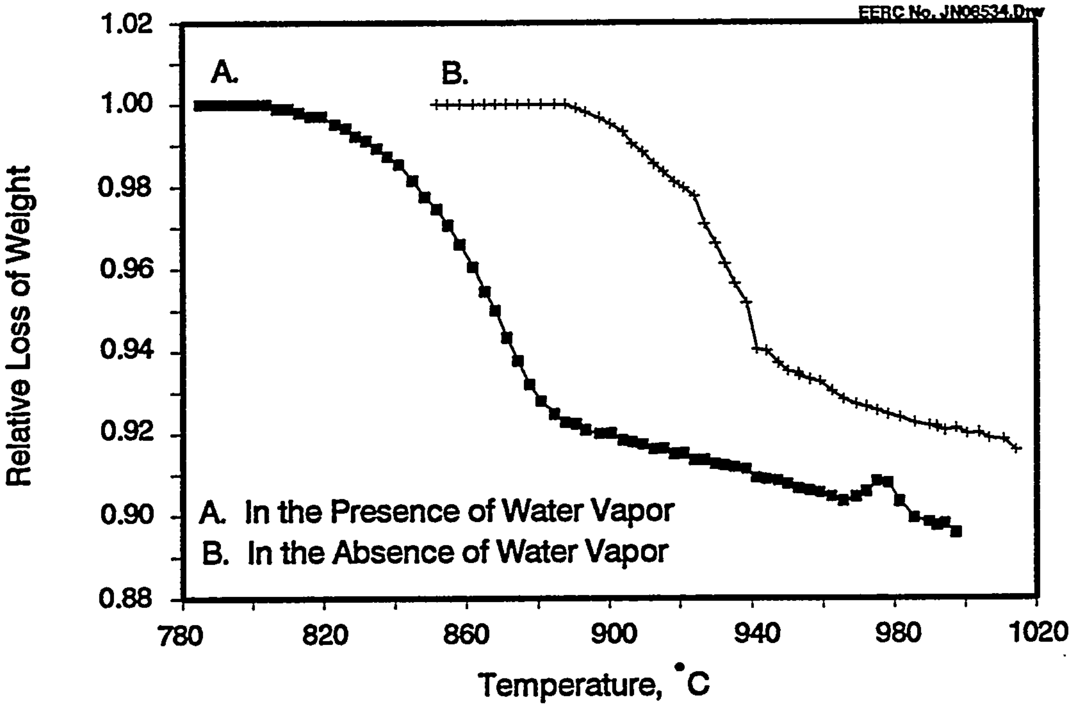

Figure 9. The Relative Loss of Weight of CaS in the Presence and Absence of Water Gas under Reducing Conditions

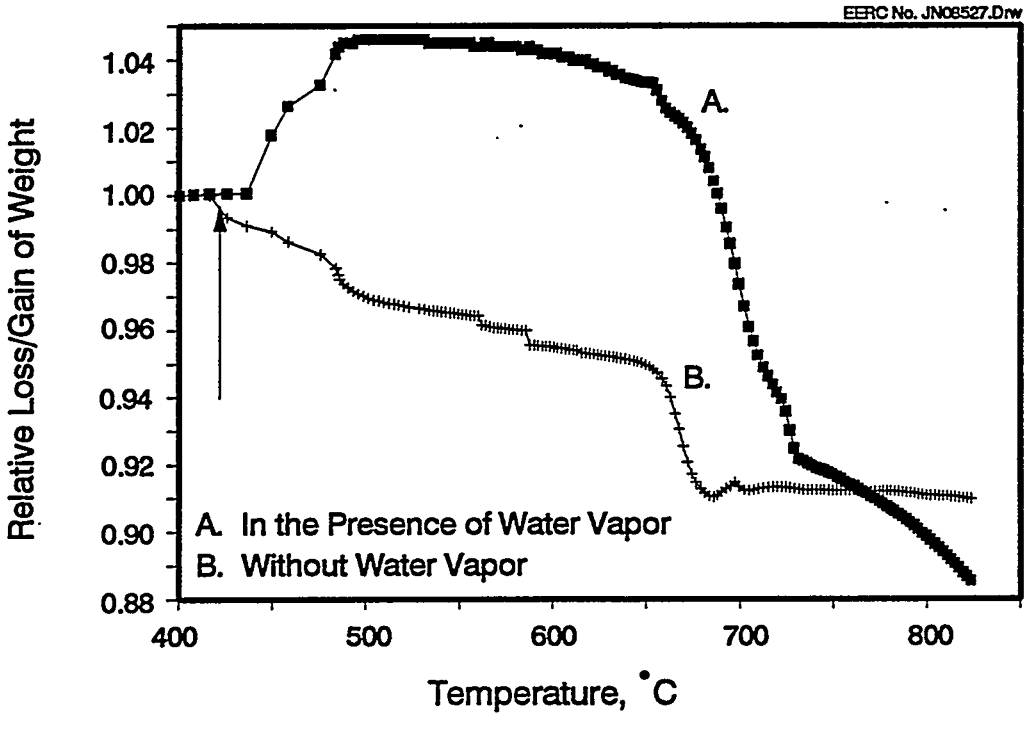

Figure 10. The Relative Loss of Weight of Na_2S-1.7 FeS in the Presence and Absence of Water Gas under Reducing Conditions