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**MHD POWER GENERATION, RESEARCH, DEVELOPMENT,
AND ENGINEERING**

Annual Progress Report for October 1977–September 1978

Work Performed Under Contract No. AC07-78ET10816

The Montana Energy and MHD Research and Development Institute, Inc.
Butte, Montana

U. S. DEPARTMENT OF ENERGY

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MHD
POWER GENERATION

RESEARCH, DEVELOPMENT
AND ENGINEERING

Annual Progress Report
October 1977 to
September 1978
Volume I

THE MONTANA ENERGY AND MHD
RESEARCH AND DEVELOPMENT INSTITUTE, INC.
P.O. Box 3809
Butte, Montana 59701

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Under Contract No. ET-78-C-01-3087

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REPORT INTRODUCTION

The Montana Energy and MHD Research and Development Institute (MERDI) was established in Butte, Montana in 1974 to develop methods for conserving western energy sources and to carry out supporting science and technology tasks for the national magnetohydrodynamics (MHD) program. Under contract to the U.S. Department of Energy (DOE)--formerly the U.S. Energy Research and Development Administration, these tasks were divided among researchers at MERDI, the Montana College of Mineral Science and Technology (MCMST), and Montana State University (MSU).

Work at MCMST has been concentrated on characterizing the properties of coal 1) to evaluate its performance during the combustion process, 2) to evaluate methods for drying western coal efficiently prior to combustion, and 3) to determine the properties of vapors emitted during the drying of coal. Work also is performed to determine the corrosion mechanism and the mechanical deformation (creep) which occur when coal slag reacts with refractory materials being considered for preheater use.

MSU has constructed a large test facility for observing the plugging and flow effects of coal slag moving through a ceramic preheater under standard heat-up and blow-down conditions. Work also includes evaluating coal slag to determine properties such as the thermodynamic characteristics of individual slag components (including the potassium seed), the thermionic emission of coal slag coating MHD electrode materials, and the electrical conductivity and thermal expansion of high-temperature coal slags. Modeling studies are being performed for the MHD combustor, nozzle, channel, and diffuser system and the MHD control system.

MERDI's in-house MHD support is in the areas of thermal transport measurements, ceramic fabrication development, the wettability of coal slags in contact with refractory materials, and the characterization and analysis of trace elements and submicron particles in the effluent stream. Siting studies are being performed in support of DOE's selection of a site for the Engineering Test Facility, an experimental MHD facility scheduled for construction during the second phase of the national MHD program.

This report summarizes the work accomplished from October 1, 1977 to September 30, 1978 by MERDI, MCMST, and MSU.

THE MONTANA COLLEGE OF MINERAL SCIENCE
AND TECHNOLOGY

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Characterization of Coal for Open-Cycle MHD Power Generation System
F. Diebold

ABSTRACT

The research to establish a set of coherent analytical procedures for the rapid, accurate, and precise analysis of coal has involved the investigation of the application of a number of instrumental techniques. The coal properties considered are Btu, proximate and ultimate values, major metal concentrations (Na, K, Ca, Mg, Si, Al, Ti and Fe), minor metal concentrations (Ag, As, B, Ba, Be, Cd, Co, Cr, Cs, Cu, Ga, Hg, La, Li, Mn, Ni, Pb, Rb, Sb, Se, Sn, Sr, U, V, Zn and Zr), and minor non-metal concentrations (P, Cl and F).

The emission spectrographic procedure utilizing the acid-bomb coal solutions with the ARL direct-reading emission spectrograph has indicated it to be relatively rapid and accurate for the elements currently programmed on the recording console, namely, Na, Ca, Mg, Si, Al, Ti, Cu, B, Mn, V, Cr, Ni, Pb, Ba, Sr, and Ga. An intensive evaluation of available inductively coupled plasma-source emission spectrometers has resulted in the selection of the ISA instrument, which will analyze a relatively large number of coals for a comparatively large number of elements in a short time. The atomic absorption spectrometer cold vapor techniques for Mg, As, Se, Sb, and Sn have been established and shown to be adaptable to the acid-bomb coal solutions. The procedure for directly determining the O₂ content in coal has been established using a PE 240 automated C-H-N-O analyzer equipped with an O-kit. The X-ray fluorescence procedure for sulfur in the acid-bomb solutions has been investigated; preliminary results indicate it to be relatively free of interferences compared to the use of solid coal samples. The investigation of the sample preparation procedures has indicated that the combustion and the low-temperature, low-pressure acid digestion of the coal sample is not preferable to the acid-digestion procedure with respect to digestion time and potential loss of volatiles.

The work to establish the variation in coal properties has involved the coal as it exists in the field and as it is fed into a conventional burner system. The O₂ and Mg concentrations of the Dietz No. 2 and Rosebud coal channel samples have been determined; no consistent concentration trends have been observed. Arrangements have been established for receiving Rosebud tippie samples from two power plants and a mine in Eastern Montana. These samples currently are being received, and analytical data is being compiled.

Investigation of useful real-time data and available instrumentation for generating real-time data indicates that neutron activation techniques could ascertain elemental concentrations relatively rapidly. Present efforts are directed toward correlating the elemental concentration data with the required real-time data of Btu, moisture, and ash content in the Rosebud coal samples.

I. OBJECTIVE AND SCOPE OF WORK

The objective of this program is to investigate experimental techniques for their incorporation into a coherent and efficient analytical scheme for the rapid generation of accurate and precise concentration data of the following properties in coal.

- 1) Btu, percent moisture, volatile matter, fixed carbon, ash, S, H, C, O, N, Cl, F and P content.
- 2) Major inorganic metals: Al, Ca, Fe, K, Mg, Na, Si and Ti.
- 3) Minor inorganic metals: Ag, As, B, Ba, Be, Cd, Co, Cr, Cs, Cu, Ga, Hg, La, Li, Mn, Ni, Pb, Rb, Sb, Se, Sn, Sr, U, V, Zn and Zr.

Another objective is to characterize the Western United States standard MHD coal with respect to the above parameters. These data will be of use to the MHD design engineers, who need to consider the time variation in coal properties. In addition, other analytical data will be of use to MHD researchers to study the relationship between the coal properties with the results of coal preparation, preheater material corrosion studies and the behavior of the coal in the burner and channel.

II. SUMMARY OF PROGRESS TO DATE

The following subtasks were undertaken during the period of October 1, 1977 to October 1, 1978:

Analytical Method Development
Laboratory Sample Preparation
Procedures for Ultimate Analysis
Procedures for Metal Analysis
Procedures for Anion Analysis
Real-Time Analysis

Coal Property Determination
Time Variation of Tipple Samples

The direction that the analytical method development has taken is to investigate various analytical procedures for their possible incorporation into an analytical scheme designed to rapidly generate concentration data

that are both accurate and precise. This effort has involved a study of not only analytical procedures but also of appropriate sample preparation and storage techniques.

The storage of the coal samples for future reference with respect to all analytical data generated a search for a suitable storage container. This search has resulted in the selection of an inexpensive multi-layer, sealable, plastic bag of low O₂ and moisture permeability. The sample preparation studies have incorporated the extended use of acid-bomb coal digestion, and the investigation of open-air and microwave acid digestion. An accompanying study has been conducted to identify the organic affinity of elements and thereby their possible loss during sample combustion or digestion.

The method development work on Btu and proximate and ultimate analyses has incorporated the investigation of X-ray fluorescence and ASTM sulfur techniques, the reinvestigation of the C-H-N combustion tube and the ASTM Btu O₂-bomb techniques, and the establishment of a data comparison of proximate techniques. The X-ray fluorescence sulfur procedure for analyzing solid whole coal samples resulted in data exhibiting close similarity to that generated via an ASTM procedure. Due to the potential efficiency using a sample preparation identical to that used for analyzing other elements, an X-ray fluorescence procedure for sulfur in the acid-bomb solutions is being investigated and shows promise of being successful. The ASTM procedures for total pyritic, sulfate, and organic sulfur have been investigated. Some difficulty has been encountered with the pyritic sulfur procedure in that it results in low values.

The automated combustion-tube gas-chromatography technique for C-H-N is being reinvestigated. The current objective is to observe the effect of sample storage in polyethylene bags and the ASTM air-drying step and to compare these data with ASTM procedures. This work is still in progress. The data comparison involved not only C-H-N values but also proximate and Btu values generated in the Montana Tech laboratory via ASTM and other techniques used in various commercial and research laboratories.

The investigation of procedures for metal analysis has incorporated X-ray fluorescence (XRF), atomic absorption (AA), and emission spectrography (both photographic and direct reading) techniques. The XRF of solid whole coal samples for Fe, Cu, Zn, Pb, Mn, Ni, and Ca has indicated interference problems associated with many of these metals in the coal samples. Investigation of the use of acid-bomb aqueous solutions for these metals using the XRF spectrometer is only at a preliminary stage at this time. An AA cold vapor procedure for Mg, As, Sb, and Se has been established and shown to be appropriate for the acid-bomb coal solutions.

The direct reading emission spectrographic (DRES) procedure using coal ash samples has been established for Si, E, Cu, B, Mg, Ma, V, Ca, Cr, Ti, Ni, Pb, Ba, Al, Na, and Sr. The average multi-element experimental precision is ± 10.5 percent of the amount present. Due to the problem of attaining suitable coal standards, the potential of increased accuracy and precision, and the possibility of decreasing the analysis time, the emission spectrographic procedure using acid-bomb solutions was investigated. This involved the completion of the work with the photographic emission spectrograph (PES) initiated during the 1976-1977 re-

porting period and the establishment of the procedures on the DRES. Finally, to analyze a large number of elements in a shorter period of time, an extensive investigation of the capability of inductively coupled emission spectrographis (ICPES) was completed. This work resulted in ordering an ISA ICPES, which is scheduled for delivery in January 1979.

In an attempt to decrease the analysis time, an investigation of a potential technique for the anions F and Cl was reinstated. This has resulted in ordering an anion chromatograph capable of rapid analyses of not only F and Cl but also P and S in the acid-bomb solution. This instrument is scheduled to arrive in October 1978.

A relatively new direction to the analytical method development has been to investigate the necessity of obtaining data on a real-time basis and the availability of instrumentation for generating these data in the necessary time frame. Btu and proximate values appear to be the data of interest on a real-time basis. The instrumental technique that promises to generate real-time data is neutron activation. Finally, the relationship of data generated by neutron activation to Btu data and proximate values will require an investigation of appropriate calculation techniques applicable to the Fort Union Formation coals in Eastern Montana.

An effort has been initiated to obtain coal samples for which the concentration data will represent the time variation in properties expected by the ETF coal-fired MHD power generation system. Specific arrangements have been made for receiving tipple samples obtained at three coal facilities.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Laboratory Sample Preparation

1. Work Accomplished

This work on the laboratory sample preparation has involved a search for appropriate sample storage containers, an extended use of the acid-bomb coal solutions, the investigation of open-air and microwave acid digestion, and the elucidation of the organic affinity of various metals.

A search for a heat-sealable bag that would exhibit low O_2 and moisture permeability generated the information illustrated in Table 1. Due to its availability and substantially lower cost, the Dazey Bag Company's Sambag was selected for testing in the Montana Tech laboratory.

The acid dissolution of the coal samples in the relatively small, 25 ml, Parr teflon-lined bombs has been investigated with respect to sample loss. In those instances in which there is not a noticeable loss of solvent, i.e., concentrated HNO_3 and HF , loss of those elements has not been detected for which analytical procedures have been established. A larger capacity teflon-lined bomb was constructed from

Swagelok fittings and a stainless steel tube. This bomb can be used for the dissolution of approximately one gram of coal, but it has exhibited a higher frequency of solvent loss. A high T&P Parr bomb was used to observe the effect upon dissolution time. The coal sample ($\sim 0.1g$) was dissolved in two hours at $190^{\circ}C$. Additionally, relatively low-temperature (approximately $90^{\circ}C$) and low-pressure (near atmospheric) HNO_3 acid dissolution of coal has been investigated. Teflon erlenmeyer vessels were equipped with a cold finger to retain the solvent and volatile coal constituents. The time required for coal dissolutions was observed to be relatively long compared to the acid bombs, e.g., days compared to the two to ten hours using the Parr bombs.

As a supplement to this effort on coal dissolutions, we have investigated the potential organic affinity of the elements for which XRF and AA techniques currently are being developed in the Montana Tech laboratory. In this investigation, it was necessary to obtain float and sink fractions of 15 Rosebud coal seam samples. Each 100%-minus-150-mesh coal sample was mixed with three different specific gravity mediums, namely, 1.3, 1.4, and 1.6. The float and sink fractions were removed after 24 hours, air-dried, dissolved in HNO_3 in the acid-digestion bombs, and analyzed via AA for Fe, Si, Ca, Cu, Zn, Pb, Mn, and As. The concentration of other metals such as Mg, Se, Sb, and Sn also are scheduled to be determined in these float-sink fractions. The 15 coal samples were taken from three channels distributed along an open face of the Rosebud seam in the Big Sky Mine near Colstrip, Montana. The relationship between the concentration data of the float and sink fractions and the specific gravity of the medium has been interpreted in terms of the organic affinity of the metals. The interpretations are presented in Table 2.

2. Discussion

The information concerning the nylon-surlyn-surlyn film produced by St. Regis Paper Company was obtained in an advertisement provided by Alan Postlewaite.³ We have placed numerous telephone calls to various personnel in several St. Regis offices and have not been able to obtain any additional information concerning their product.

Since our analytical method development has the objective of generating an analysis scheme that not only is rapid but also adopted easily by the many small laboratories charged with the job of analyzing large numbers of coal samples, we have chosen the Dazey Bag Company's Sambag. This bag is relatively inexpensive and can be obtained easily in local stores or in relatively large bulk quantities from the Dazey Bag Company.

The sample preparation technique used in the Montana Tech laboratory, namely acid dissolution of the coal with concentrated HNO_3 and HF in the teflon-lined moderate T&P bomb, has been illustrated to be a valid and time-efficient procedure.^{1,2} The argument against this technique is the relatively high cost of the bombs. Since the direction of our effort is to generate an analytical scheme that can be adopted by the small commercial laboratories that are charged with the task of providing the much needed coal concentration data, the high

cost of the bombs is a major factor to be considered. To increase the number of coal samples that can be prepared per hour, the dissolution time in the Parr high T&P bomb was determined. Even though the cost per sample will be higher with the more expensive, high T&P bomb (i.e., essentially doubled), the laboratory can handle essentially four times as many samples. Still, it should be noted that the dissolution time is unattended time and thus does not represent a significant amount of manhours, except for the loading and cleaning of the bombs. It is the author's opinion that the application of the more expensive high T&P bomb is in the occasional rapid generation of check samples demanded by some known or suspected analytical error.

In a continued effort to decrease the capital cost for sample preparation, the dissolution time of coal in relatively low-temperature teflon erlenmeyer flasks equipped with a teflon cold finger was investigated. Although the results relating mass of coal and volume of concentrated HNO_3 were somewhat erratic, the dissolution time is too long to be of much application. A limited effort will be expended in the near future to observe the effects of microwave heating upon the dissolution time. This has been shown to halve the time for acid dissolution of fish tissue.⁴

An alternative sample preparation technique is to combust the coal sample and dissolve the remaining residue. This dissolution, whether in an open or closed vessel, is accomplished in a relatively shorter time interval than when the organic material also must be dissolved. The possibility of losing elements of interest during this sample preparation procedure should be related to whether the element is incorporated with the organic or inorganic compounds. As noted above, to ascertain this organic or inorganic affinity, a number of float-sink separations using Rosebud coal seam samples were performed. It is argued that those metals exhibiting a significant organic affinity are potential candidates for being lost during sample combustion. Of the elements examined to date, Ca, Zn, Si, and Cu are those to be suspected of having a high probability of being lost. Although fluorine in these float-sink fractions has not yet been analyzed, it has been argued⁵ that it has a high organic affinity in the Rosebud seam. This argument was based upon the loss of fluorine in the sample preparation step during development of the fluorine analytical method.

B. Ultimate, Btu, and Proximate Method Development

1. Sulfur Method Development

a. Work Accomplished

The work in sulfur method development has included investigation of an automated combustion-gas analysis system (utilizing a Perkin Elmer 240 analyzer), the XRF quantometer applied to both liquid and solid samples, and the ASTM procedures.

The combustion-train gas analysis technique, utilizing a PE 240 analyzer, was investigated for its applicability for sulfur analysis in Fort Union Formation coal. The data for the standards thymol blue and phenyl thiourea are presented in Table 3. Analysis of the Rosebud and Dietz No. 2 coal seam samples indicates that the detection limits of this procedure are not appropriate for analyzing these low-sulfur coals, i.e., ± 1 percent sulfur.

A cursory investigation of the application of a scanning electron microscope X-ray fluorescence (SEM-XRF) technique was undertaken. We experienced some success with this technique but did not pursue it, principally because sample preparation takes too much time.

The effort to adapt the Applied Research Laboratory (ARL) XRF quantometer has been continued from the initial work during the last reporting period. The current effort has followed two approaches. One has been to continue to investigate the use of solid coal samples and the other to investigate the use of acid-bomb solutions. The installation of a Cr X-ray source allowed for a much stronger S signal.

To investigate the effects of particle size and chemical form of sulfur in the sample, calibration curves were prepared from the XRF analysis of standards of elemental S, FeS_2 , BaSO_4 , and CaSO_4 . These curves are presented in Figure 1. To pursue the use of solid samples, a calibration curve was generated by the XRF analysis of NBS 1631 A, 1631 B, and 1631 C. Using this calibration curve, 15 Rosebud seam channel samples, 1-E, 5 A-E, and 9 A-E, were analyzed via XRF. An approximately five-gram sample of 100 percent minus-150-mesh coal was pressed into a pellet at a pressure of 25 tons/sq. in. The pellet was dried at 60°C and 20 microns pressure in a vacuum oven for two hours. The sample then was transferred immediately to the XRF spectrometer. The resulting data are presented in Table 4.

We also have investigated the XRF analysis of sulfur in acid-bomb coal solutions using two techniques. In one procedure, we analyzed thin films of BaSO_4 precipitated from the acid-bomb solutions. The other method involved the analysis of an anion exchange resin that had absorbed the sulfate anion from the acid-bomb solutions. The work with XRF analysis of thin films of BaSO_4 has included the elucidation of the parameters essential to the precipitation of BaSO_4 free of interferents. Photographic emission spectrographic analysis was conducted for the relative concentrations of Na, Ca, Mg, Al, Si, Ti, Fe, Ag, and Cu in the BaSO_4 precipitate obtained at various pH's and combinations of KOH and H₂O₂. These data were somewhat erratic, and it is difficult to discuss any trends. A number of thin film samples of varying thickness of BaSO_4 have been prepared. These precipitates of BaSO_4 have been generated from solutions of various known sulfate concentrations.

An additional procedure for obtaining an XRF sample of sulfur from the acid-bomb solutions is currently under study. This involves the removal of metal interferences in a cation exchange resin and collection of sulfate by absorption in an anion exchange resin. To date, the sequential filtering process has been set up, and the appropriate ion exchange resins have been selected.

These samples, both thin films of BaSO_4 and solutions of sulfate ion, require the use of an He mode instead of a vacuum on the XRF spectrometer. These alterations to the spectrometer have been completed, and the analysis of these samples is scheduled for the near future.

We also have initiated an effort to establish the ASTM procedures for total pyritic and sulfate sulfur in the coal samples. Table 4 lists the results of the ASTM Eschka procedure applied to the Rosebud coal samples. These data were used as a comparison for the XRF sulfur data generated on solid coal samples.

Appropriate arrangements have been made with two commercial coal analytical laboratories for the comparison of sulfur, as well as Btu, proximate, C, H, and N data with our analytical results. In addition, similar arrangements will be made with the appropriate analytical personnel at the Grand Forks Research Center.

b. Discussion

The combustion train procedure utilizing the PE 240 C-H-N analyzer with the S-kil yielded sufficiently accurate sulfur data, except in the case of phenyl thiourea diluted with graphite. The assumption is that the presence of the graphite retards the oxidation of sulfur and thereby results in a lowered recovery of sulfur. The explanation for the insufficient detection limits for Rosebud and Dietz No. 2 coals is assumed to be associated with the inefficiency of either the sulfur scrubber (i.e., Ag_2O) or the thermal conductivity detector. Due to the relative long sample loading time, small sample size, and probable successful application of other techniques such as XRF, we did not invest any more time in adapting the PE 240 for analyzing these low-sulfate coals.

The application of SEM-XRF was successful in detecting sulfur in the LRC II coal sample, which is approximately 0.8 percent sulfur. Since only Zr, Nb, Mo, Ru, Rh, Mg, Ti, and Pb have lines within 90 e.u. of the 2327 e.u. S K_2 line, the sulfur signal appears to be relatively free of line interference. A number of problems inherent in this technique make it unsuitable to our needs however:

- 1) The small size of the sample,
- 2) The reported absorption interferences (e.g., Fe and Ca), and
- 3) The lengthy time for sample preparation.

The Cr X-ray source was installed to overcome the inefficiency of sulfur in absorbing the X-ray spectrum generated by our old tungsten X-ray source. The detection limits were improved dramatically, and the time necessary for sulfur excitation has been reduced greatly.

The initial data on XRF of solid samples reported in the 1977 annual report to DOE⁵ indicated the effect of the chemical combination of sulfur. The current data in Figure 1 of this report also illustrates this effect as well as that of the particle size of the sample. Approximately a seven-fold decrease in intensity is observed with an increase in particle size from -38 u.m. to -180 u.m. It has been suggested by Berman and Ergun⁶ that the sample should be ground to -2 u.m. to eliminate the size effect upon XRF signal intensity. The data in Figure 1 also illustrates the effect of the cations Ba and Ca. Yao and Porsche⁷ state that Ba and Ca generally give low results for sulfur. Since we were aware of these potential problems associated with the XRF analysis of sulfur, we performed the experiment to investigate the accuracy of XRF sulfur analysis in Rosebud coal samples. The data in Table 4 indicates close correlation with the total sulfur as determined by the Eschka ASTM procedure.

Even though the CRF of these few coal samples appears to generate surprisingly accurate results, we have elected to pursue the XRF analysis of solutions from which sulfur can be extracted in only one chemical form and relatively free of interferences. As noted above, we attempted to generate BaSO₄ precipitates from the acid-bomb solutions by procedures that would leave the precipitates free of interferences, but analysis of these precipitates produced results that were difficult to interpret in terms of pH and type of base used. Table 5 presents a comparison of the concentrations of metals in the BaSO₄ precipitate generated at pH 3 with the concentration calculated to be present after the evaporation of the acid-bomb solution, i.e., prior to adjustment of pH and the addition of BaCl₂ (aq.). The conclusion is that although the metal concentration data are quite variable, this procedure of precipitating BaSO₄ from the acid-bomb solutions generates an XRF sample in only one chemical form and relatively free of potentially interfering metals.

This procedure of using the acid-bomb solutions for XRF analysis of sulfur was suggested by the personnel in the DOE Grand Forks Energy Research Center. They are analyzing aqueous leach solutions

for sulfur via XRF. Due to the relatively high concentrations of such interferences as Fe in our acid-bomb coal solutions, we have considered their removal via appropriate cation exchange resins. This solution either will be analyzed directly for sulfur and/or an anion exchange resin used for the concentration of sulfur. Campbell, Spano, and Green⁸ have investigated the effects of exchange capacity, pH, salt concentration, competing ion, and distribution of collected ion. On the basis of their results, we plan to use the Whatman papers SA-2 and WB-2 that are loaded with cation and anion exchange resins, respectively, for anion and cation collection under carefully controlled conditions for absorption. It is our opinion that this technique will be relatively simple and rapid compared to the XRF analysis of solid coal samples. The problems associated with metal interferences and chemical form of sulfur will be eliminated, and the acid-bomb coal solutions are to be used in other analytical procedures in the total coal analysis scheme (e.g., metal analysis via emission spectrography and AA).

The initial problems in establishing the ASTM analytical procedures for sulfur in the Fort Union Formation coals involved the effect of excess Br_2 (aq.) and HNO_3 upon the determined concentration of sulfate and pyritic sulfur, respectively. The judicious control of the Br_2 is necessary since an excess requires an inappropriate volume of base to be added to adjust the pH. This dilution effect upon the sulfate causes a significant effect upon the amount of BaSO_4 precipitate. The excess HNO_3 used to dissolve the pyrite also causes a relatively large volume of base to be added to generate the appropriate pH. Some difficulty also has been experienced by incomplete dissolution of the pyrite.

2. Btu and Proximate Development

a. Work Accomplished

No experimental work has been performed on Btu or proximate method development during this reporting period. As was noted in our 1977 annual report, the O_2 bomb calorimeter procedure was set up in our laboratory, and the associated sample preparation technique was investigated. During this current year, personnel have used the O_2 bomb calorimetric procedure for routine analysis of samples generated from their coal drying experiments. Their improved precision, but lengthy analysis time, is worth noting. The analysis time for one sample is approximately $1\frac{1}{2}$ hours with 50 percent of this time spent in reaching constant temperature prior to coal ignition. With sufficient care, the analyst achieved a precision within ± 1 percent, expressed as the relative standard deviation.

b. Discussion

As was noted in the 1977 annual report to ERDA, the O₂ bomb calorimeter procedure is a relatively time-consuming task. Even though the analytical time would be cut approximately in half by using an automated calorimeter, a pressure differential scanning calorimeter (PDSC) promises to be relatively rapid and sufficiently accurate.⁵ Due to the lack of adequate instrumentation in our laboratory, we plan to submit a few samples to commercial vendors of this apparatus and will compare these analytical data with data generated via O₂ bomb calorimetry in our laboratory and several commercial analytical laboratories. An additional effort is planned to establish the validity of several schemes for calculating the Btu value from other ultimate values for the Rosebud coal seam tibble samples. This program will be integrated closely with the effort in "real-time" analytical method development, as described later in this report.

This same program, i.e., establishment of appropriate calculation schemes for the Rosebud coal seam tibble samples, will be extended to the proximate values. In addition, the data provided by the coal companies, via the standard ASTM techniques, on these tibble samples will be compared to that generated by the analytical personnel of the DOE Grand Forks Energy Research Center and by our laboratory via thermal gravimetric analysis.

C. Carbon, Hydrogen, Nitrogen, and Oxygen Method Development

1. Work Accomplished

A method for directly determining the O₂ content of the coal was established. The procedure utilizes a Perkin Elmer Model 240 elemental analyzer equipped with an O₂ analyzer kit. Twelve different NBS acetanilide (No. 1416) samples, 12 benzoic acid primary standard samples, and 12 samples of an Eastern Montana coal (air-dried) were analyzed for their O₂ content to ascertain the experimental precision.

2. Discussion

The procedure for determining the O₂ concentration of the coal involved pyrolysis of the sample at 9750C under helium which has been passed over platinized carbon. The oxygen in the coal is released as carbon monoxide in the helium gas stream and is passed over elemental copper at 900°C and finally through a colorcarb scrubber. The thermal conductivity of the gas stream then is compared before and after scrubbing of the resulting carbon dioxide.

This automated procedure for O₂ via the PE Model 240 elemental analyzer exhibits a sufficient precision and apparent accuracy for discerning differences within and between Fort Union Formation coal seams. The larger precision of the coal sample indicates an approximate ± 2 percent due to sample nonhomogeneity. It should be noted that this same approximate value was observed during our earlier C-H-N method development. Although we were able to reproduce the accepted values for the acetanilide and benzoic acid standards, it is our opinion that the coal sample preparation, i.e., the ASTM air drying step, required further study with respect to its effect not only upon the O₂ but also the C, H, and N data.

Some electronic and mechanical problems occasionally have been experienced with the PE 240 elemental analyzer; this has contributed to not meeting the anticipated speed of C, H, N, and O analysis with this instrumental procedure. The C, H, and N procedure recently has been reinitiated in preparation for the analysis of the tippie samples. The electronic problems, however, have retarded not only these analyses but also the study to ascertain the effect of the ASTM air drying step.

We are planning to submit some of the Rosebud channel and tippie samples to local commercial analytical laboratories for their analysis of C, H, and N via standard ASTM techniques, and the resultant data will be compared with our laboratory data. In addition, these data will be used to elucidate the appropriate schemes for calculating the Btu content for the Rosebud coal seam as noted above.

D. Development of Analytical Procedure for Metals

1. Metal Method Development

a. Work Accomplished

We have continued to investigate the application of three instrumental techniques, namely atomic absorption spectrometry (AAS), emission spectrography--both photographic (PES) and direct reading (DRES)--and X-ray fluorescence spectrometry (XRFS).

The work on establishing the XRFS method for Fe, Cu, Pb, Mn, Zn, and Ca has involved the investigation of the accuracy and precision of a technique involving the use of solid, whole coal samples. Calibration curves have been prepared from the following coal standards: NBS 1632 (two separate batches), NBS 1635, Illinois Geologic Survey coals C18848 and C16543, USGS coals D163187 and D163184, and our laboratory reference coals LRC I and II. The calcium concentration of selected Rosebud seam channel samples was determined and compared to that obtained via PES. These data are presented in Table 7.

The AAS method development has involved the establishment of Hg, As, Se, and Sb cold vapor procedures using the acid-bomb solution. The accuracy and precision of these techniques has been determined; these data are presented in Table 8.

The development of an emission spectrographic analytical procedure for metals has involved establishing a procedure for analyzing solid ashed coal samples with the ARL direct reader (DRES), establishing procedures for analyzing acid-bomb solutions on the photographic emission spectrograph (PES) and the DRES, and intensively evaluating available inductively coupled plasma-emission spectrographs (ICEPS).

The procedure development for analyzing the solid coal ash samples on the ARL DRES for Si, Fe, Cu, B, Mg, Mn, V, Ca, Cr, Ti, Ni, Pb, Ba, Al, Na, Sr, and Ga was near completion at the end of the last reporting period.³ The work during this current period involved the generation of the working curves and the analysis of the Rosebud and Dietz No. 2 coal seam channel samples.¹⁰

During the last reporting period,³ we began to establish the PES method for metals in the acid-bomb aqueous solutions. This work has been directed toward elucidating the effects of various matrix concentrations, choice of balance, and various matrix drying techniques upon the overall analytical precision. The intensities and intensity ratios of the analytical lines and background were tabulated for each ratio of Li_2CO_3 : graphite and each density of packing. Appropriate experiments also were conducted to determine the effects of the Roller-Smith Torsion balance and the Cahn microbalance used to measure the mass of the matrix. To determine the effect of the mode of drying, experiments were conducted in which the matrix was either dried or not dried prior to being loaded into the electrode.

Subsequent to the development of the DRES procedure for the analysis of solid ashed coal samples, efforts have been directed toward adapting the PES solution procedure to the ARL DRES. The initial effort was to analytically describe the responses of the recording console to a specific light intensity. The variables investigated were the lamp current (lamp intensity), the photomultiplier tube voltage, and the integration time. Data generated on each analytical channel were resolved into the following analytical function, the constants for which are noted in Table 9:

$$\log I/T = (aV + b)L + (cV + d)$$

where I = readout number (signal),

T = integration time,

V = voltage setting applied to a PM tube,

a = slope of V v.s. slope of (Log I/T v.s. L),

b = intercept of V v.s. slope of $(\log I/T \text{ v.s. } L)$,
 c = slope of V v.s. intercept of $(\log I/T \text{ v.s. } L)$, and
 d = intercept of V v.s. intercept of $(\log I/T \text{ v.s. } L)$.

For each element number, I readings were taken at different lamp intensities and different settings of applied PM tube voltage. The slopes and intercepts were plotted vs. the V settings to give a , b , c , and d . Voltages were chosen so that a reasonably long or short time would produce a reading within the 0 to 200 mv range of the capacitors and the readout box.

This effort has been extended to incorporate not only the performance of the recording console but also that of the spectrometer. The expanded mathematical model covers all of the basic operations of the spectrometer and the readout console and can be used to characterize the operation of the instrument at any point in the analysis scheme. The model is described by the following equation:

$$R_t = [TVI_r K_c]C + [TV(P_b + P_+ + P_-) + TD]$$

R_t is the readout of the charge built up on the caps, as indicated by the readout box value; T is the integration time for which the caps were charged; V is the conversion and amplification factor of converting light energy to electrical energy by a PM tube which depends on the photoelectric sensitivity of the tube, tube geometry, voltage applied to the tube grids, and the recording console settings for amplification of the AM tube current to the readout box number; I_r is the relative intensity of a given emission line for a given matrix and excitation conditions (expressed as photons per sec emitted per emitting atom or ion); K_c is the ratio of emitting species in the arc to the total number of atoms of that element in the electrode; C is the concentration term expressed as the total number of atoms of an element present in an electrode crater; P_b is the light flux emitted from an arc due to a continuum, molecular band, or spectral interference near or on top of the line, acting as background; P_+ is the amount of light flux gained in the spectrometer at a particular wavelength due to light scatter from dust, optical surfaces, and other surfaces in the spectrometer; P_- is the amount of light flux lost in the spectrometer due to light scatter, imperfect optical parts, and absorption by optical surfaces; and D is the dark current or the rate of flow of electrons from a PM tube when no light reaches the tube and depends on the voltage applied on the tube.

The quantity $(TVI_r K_c)$ is the slope of the working curve using C and R_t as axes, and $[TV(P_b + P_+ + P_-) + TD]$ is the intercept. T , R_t , and D are measureable quantities. I_r can be derived from appropriate tables or determined empirically, and K_c can be determined empirically or as a result of knowing the other parameters.

V is determined from the calibration of the particular PM tube. The relative amounts of P_b can be estimated photographically if one needs to know the amount of light lost or gained by the spectrometer.

The next step was to make the calibration experiment, which had already been performed, compatible with the mathematical mode. Subsequently, the calibration experiment was rewritten, and a computer program was written to allow more efficient use of the calibration equations. The calibration constants were stored on cassette tape for automatic access by the program when needed for computations involving the constants. The use of the program on a Monroe desk computer enables rapid and efficient calculation of correct voltage settings on the PM tubes, the correct photon flux or test lamp setting corresponding to a read-out value, and the correct integration time to be used with the other parameter settings to produce a desired readout value.

Additional work was conducted to establish a more accurate and reliable standardization procedure to ensure that hourly and daily drift was minimal and correctable to comply with the earlier calibration constants and to make comparisons of data that were generated at different times. A standardization procedure was developed that ensures rapid and accurate generation of analytical data.

After the development of the spectrometer analytical model was established and a reliable method for drift control was completed, the excitation conditions were optimized. Some of the work done during development of the solution method on the photographic unit could be applied to the quantometer as well. The sample preparation, matrix choice, electrode types, and gas type are the same as with the photographic procedure. The gas jets, the shield, amperage, CO_2 flow, arc gap, and precision values are different and had to be characterized and reoptimized for use on the quantometer.

The gas jet was determined to be adequate and required no change or modification to improve the procedure. Using maximum detectability, best precision and feasibility of the burn, and rapidity as criteria, the excitation parameters were chosen; amperage is 15 amps d-c, CO_2 flow is optimum when the line pressure is at 0.5 kg/cm, and initial arc gap is 5.5m.

The burn time was determined via a specialized "moving plate" procedure or volatility study for use on the quantometer. The procedure is analogous to that performed in the photographic study. It involved burning a set of "blanks" and samples for five seconds and recording the values, then burning a set for 10 seconds, another for 15 seconds, and so on up to 50 seconds. The readout data are converted to photon flux data, which are plotted and arranged to show instantaneous volatilization trends for each element,

as well as when the majority of a particular element has been registered, to determine the best burn time and to determine if the matrix and sample prep are adequate for this new procedure. From all indications thus far, the matrix and sample prep are adequate.

The burn-time study is related to the consideration of the effect of the ceramic arc shield. A precision study indicated that this shield, although important in the PES technique, offers no advantages to the DRES technique. It was ascertained that the matrix materials' control on the arc's burning is not impaired and that the burn time (50 sec.) is not significantly longer.

The development of suitable working curves has incorporated two efforts to generate a set of reliable standards. Initially, a set of three NBS certified coal standards, an LRC II coal sample, a Rosebud coal sample, and several USGS Fort Union Formation coal samples were acid-digested in the Parr bombs. These coal standards gave plots of signal vs. concentration that exhibited undesirable characteristics. This indicated any one or a combination of the following effects: line interferences, inaccurate concentrations, and contamination. A series of synthetic standards were prepared to discern the existence of any of these three possible problems. A large effort has been expended in the development of these synthetic standards. Samples of these synthetic solutions and certified coal solutions were examined on the DRES, and calibration curves were prepared. Preliminary results exhibit the advantage of using such synthetic standards. Reproduction of certified concentration values for the NBS coals, using the synthetic solution calibration curves, indicates that inaccurately known standard concentrations in the other coals is the root of the problem in achieving satisfactory calibration curves.

An additional effort to decrease the analysis time has involved the investigation of the adaptation of a Model 901 Orion specific ion meter to accept and display the recording console signal. Subsequent to this work, effort has been initiated to generate a computer program for the fit of an analytical function to the data of signal vs. concentration.

In addition to the experimental work performed in our laboratory to establish reliable emission spectrographic techniques, we have made an intensive evaluation of four plasma-source emission spectrometers marketed by Jarrell Ash, Spectrometrics, Instruments, S.A., and the Applied Research Laboratory. Samples were submitted to all four companies, and on-site visits were made to Jarrell Ash, Spectrometrics, and Instruments S. A. Subsequently, an order was placed with ISA, and internal arrangements were made for the January 1979 arrival of the ICPEs system.

b. Discussion

The objective of the work on the XRFS procedure for Fe, Cu, Pb, Mn, Zn, and Ca is the establishment of an independent technique that can be used as a relatively rapid check on the concentrations generated by emission spectrography. This work has been retarded by the XRFS sulfur procedure method development. The recent calibration curves generated by using pellets of whole coal exhibit characteristics which indicate that considerable interferences are present. Only the Ca calibration curve appeared suitable on the basis of its slope and fit to a linear function, but the coal concentration data in Table 7 indicate that the Ca XRFS values are consistently low. A study to ascertain the effect of sample homogeneity and XRFS instrumental precision generated the following results:

	<u>Fe</u>	<u>Zn</u>	<u>Pb</u>	<u>Mn</u>	<u>Cu</u>	<u>Ca</u>
% RSD	<u>+3%</u>	<u>+49%</u>	<u>+79%</u>	<u>+47%</u>	<u>+30%</u>	<u>+2%</u>

It is obvious that a portion of the problem with the calibration curves could be caused by these relative large imprecisions. Primarily for this reason, we plan to investigate the sample preparation procedure involving the use of the acid-bomb coal solutions. An additional reason is that this sample preparation technique currently is being used for the other analytical procedures in our laboratory, namely ES and AA. Therefore, analyzing the acid-bomb solutions should improve sample homogeneity and shorten the total analysis time.

The AAS procedure for Hg involves reaction of the acid-bomb solution with 10 M stannous chloride solution and sweeping the produced gas into an absorption cell. The method for As, Se, and Sb involves diluting the bomb solution for a ratio of 1:25 with distilled water. A 10 percent solution of KI is added to an aliquot of this solution. An aliquot of this solution then is injected into a hydride generating system (containing sodium borohydride solution) and the volatile hydride swept into a hydrogen-air flame within a glass tube placed in the light path of the appropriate hollow cathode lamp.⁴ These procedures are known to generate accurate and sufficiently precise data (see Table 8), and they are relatively rapid.

In analyzing Fort Union Formation coals, further efforts are planned to develop AAS procedures for other metals that are at concentrations below the detection limits of emission spectrography.

The analysis of the ashed Dietz No. 2 and the Rosebud coal seam channel samples with the ARL DRES procedure was done to enable a comparison of this technique with that previously established on the PES. This comparison of the seam averages (i.e., average of all samples) is presented in Table 10.

The experimental data generated by individually varying the arc gap, the arc amperage, CO₂ flow, and shield hole size results in the following interpretation. The variation in arc gap appears to have little effect on the precision of the intensity ratios. For burn symmetry, good Li precision, and lower arc flickering, the 4mm arc gap is preferred. The amperage is observed to significantly affect the precision of the intensity ratios and seems to affect the background intensity more than that of the line intensity. At this arc gap, the best precision in the intensity ratios is obtained at 8.1 amps arc current. It has been observed that the most appropriate CO₂ pressure is a function of the size of the hole in the alumina arc shield. Both of these parameters appear to have a significant effect upon the detection limits and precision. The optimum conditions are a 5mm diameter hole in the shield and a 1.0 kg/cm² CO₂ pressure.

In discussing the work of our existing ARL DRES, it is prudent to emphasize that one of the principal objectives of this task is to develop analytical procedures that will generate accurate and precise analytical data as rapidly and efficiently as possible. Some of our work may appear to be unduly detailed and, therefore, out of harmony with this objective. A case in point is the development of an analytical expression describing the performance of the recording console and spectrometer. It should be noted that this analytical expression will allow us to relate a low- and high-concentration coal solutions sample to the way in which the recording console responds to a specific lamp current; we then can simply calculate the appropriate voltage settings at a specific integration time. It is our firm conviction that the result of this effort will allow much more rapid and accurate establishment of emission procedures and daily or hourly calibration of the spectrometer. In addition, many of these procedures and results are not unique to our spectrometer and are directly applicable to any direct reading spectrometer, which represents a relatively inexpensive addition to a coal analysis laboratory.

The evaluation of the capability of the plasma-source emission spectrometer was essentially completed more than six months ago. In addition, a directive for the acquisition of such an analytical system for the requirements of this task had been received from the last DOE progress review team. This current renewed evaluation has been stimulated primarily by the desire of the MERDI Environmental Division to perform its routine analytical tasks within its own group instead of subcontracting the work. In addition, the recent marketing of an ICPES by ISA required the comparison of this analytical system to that of the other three companies. The MERDI Environmental Division requirements for routine analysis has added a few complications, e.g., the spectrometer must be capable of analyzing samples ranging in matrix from the relatively low dissolved solids content of ground and surface waters to the relatively high dissolved solids content of slag, coal, and soil samples. The following arguments are those supporting the choice of an ICPES system for these varied analytical requirements.

The DRES technique utilizing the solid coal-ash samples will allow one analyst to analyze 120 samples for Si, Fe, As, B, Mg, Mn, V, Ca, Cr, Ti, Ni, Pb, Ba, Al, Na, Sr, and Ga in five days. This analysis time, although relatively rapid compared to that technique on the PES, could be decreased even further by the use of a different sample preparation technique, a computerized data handling system, and a relatively more accurate spectrometer system. Preparing samples by generating acidic aqueous solutions, in which the coal is dissolved, is considered to be relatively fast since the solution is used throughout the laboratory for other analytical procedures. In addition, the time for loading the electrodes also is reduced by the use of a computer and the development of a suitable computer program. Finally, the acquisition of a relatively more accurate spectrometer, e.g., an ICPE, would result in the concentration of more elements being determined simultaneously in a greatly reduced analysis time.

The establishment of the PES procedure utilizing the acid-bomb solutions was initiated during the time the ARL DRES method development for solid coal ash samples was being completed. As noted immediately above, this effort on the PES was directed toward decreasing the overall analytical time by using acid-bomb solutions. These studies with the PES have essentially exhausted the possible experimental conditions that have to be optimized for the analysis of these solutions.

The intensity ratio data generated on the PES by the matrix concentration experiments indicate that improved precision, sensitivity, and lower background intensity are associated with increasing concentration of graphite in the matrix. This effect continues until CN bank intensity becomes excessive. The density of packing the matrix does not appear to significantly affect the precision, sensitivity, and background levels, but the good correlation of element intensities with that of lithium makes the high-density packing of the matrix preferable. In addition, the good correlation of element intensities with matrix in the high-density matrix packing also is desirable. Thus, the best set of matrix conditions are 15 mg of high densely packed 2:1 ratio of graphite to lithium carbonate.

The data generated from the balance experiments indicate that the precisions associated with the Roller-Smith and the Cahn balances are not observed to be appreciable in the overall analytical precision of the intensity ratios. Due to the ease of achieving and maintaining calibration, the Cahn microbalance is preferred. Finally, the data generated from the drying experiments indicates that the overall precision can be improved significantly by drying the matrix at 95°C for one hour prior to putting it in the electrodes.

As discussed by Dulka and Risby (Analytical Chemistry, Vol. 48, 1976, pp. 640A-653A), there are various instrumental methods of analysis that are capable of detecting trace and ultratrace concentrations of many of these required trace elements. These instrumental procedures and the respective sensitivities as reported by Dulka and Risby are noted in Table 11. These methods are as follows: neutron activation analysis (NAA); spark source mass spectrometry (SSMS); chemical ionization mass spectrometry (CIMS); inductively coupled plasma sources for atomic emission spectrometry (ICPAES); nonflame atomic absorption spectrometry (NFAAS); X-ray fluorescence spectrometry (XRFS); electron microprobe (EMP); electron spectroscopy for chemical analysis (ASV); differential pulse polarography (DPP); and gas chromatography (GC). EMP, ESCA, and AES are not of direct relation to the analytical task of this project since these procedures are surface techniques. NAA and XRF can analyze samples directly, whereas CIMS, ICPAES, NFAAS, ASV, DPP, and GC require the sample to be in solution, and SSMS requires the oxidation of the organic material. NFAAS, ASV, DPP, and GC have limited application to this task since they are not suitable for multi-element analysis. Since CIMS is limited to metals which form volatile complexes, it also is not applicable to the analytical problems of this task. The purchase cost of the apparatus to perform NAA and SSMS is prohibitive when compared to ICPAES and XRFS. The cost of an ICPAES system is either less than or comparable to that of a modern XRFS system. The capability of XRFS to analyze samples directly is not considered applicable to coal samples. It is anticipated that due to the varying ash content of the coal and the varying mineral composition of the ash, the matrix problems will dictate a sample preparation procedure. This probably would involve ashing the sample and fusing it with lithium tetraborate. To retain the volatile elements, this ashing step would have to be performed in a low-temperature asher (LTA). Two problems now arise; one is the long time (at least eight hours for five samples) for low-temperature ashing of the sample. The other is the uncertainty that some of the more volatile elements would even be retained in an LTA environment. Thus, it would appear that the ICPAES system, which requires the sample to be in the form of a solution, is the preferable technique since our work on sample preparation indicates that the dissolution of coal samples in teflon-lined acid-digestion bombs will retain the volatile elements.

Further support for the use of optical emission spectroscopy is noted by Scott, Loscke, Holboke, and Thompson (Journal of Applied Spectroscopy, Vol. 30, N. 4, July/August 1976, pp. 392-405). "Despite the advantages of optical emission spectrometry for trace analysis of (atmospheric) particulate matter, its use has been relatively limited compared to atomic absorption, neutron activation, and X-ray emission techniques. This is partially due to misconceptions regarding equipment cost and the complexity of the analytical procedures. A direct-reading optical emission spectrometer is certainly less expensive than the equipment nec-

essary for neutron activation analysis, and its cost is less than, or comparable to, the cost of a modern X-ray spectrometer. Furthermore, since emission spectrometry is a multi-element technique, analysis for more than one element is less expensive and more rapid by emission analysis than by atomic absorption analysis." Additional emission support for the emission system comes from the August 16, 1977 consultant report to the Montana Energy and MHD Research and Development Institute by Koirtyohann, Lichte, and Janghorbani. These authors "heartily recommend this purchase (a plasma-source direct reading emission spectrograph) if the equipment is obtained from one of the two U.S. manufacturers that offer it." They also noted in their report that the ICPAES system will not solve all of the analysis problems of this task; but they verbally agreed that if one major equipment purchase was to be made, the ICPAES system would be the preferable choice.

As explained by Govindaraju, Mevelle, and Chouard (Analytical Chemistry, Vol. 48, No. 9, 1976, pp. 1325-1331), there are three general types of plasmas, namely the double-electrode d-c arc plasma jet, the single-electrode capacitatively coupled microwave plasma (CMP), and the electrodeless inductively coupled plasma (ICP). They report that the relatively lower detection limits and generally higher temperature of the ICP make the ICP-OES (inductively coupled plasma-optical emission spectrometer) system relatively free of interelement effects and capable of rapid multi-element analysis at ultratrace levels.

Although there is a limited amount of literature available on the geochemical application of ICPAES system, it has good capability when applied to multi-element analysis of major and trace elements in coal. Personnel at the application laboratories of the various ICPAES suppliers have been contacted with regard to the capability of their respective plasma spectrometers for coal analysis. They have verbally reported excellent results for many of the elements of interest in this task. They are convinced that with further investigation of sample preparation techniques, most of the 34 elements listed in the objectives of this task can be determined by the ICPAES system.

A final point is that with the analytical speed of such a system, hundreds of samples can be analyzed per day. With this rapid, sensitive, multi-element analytical capability, we could schedule our method development and coal characterization work as well as sample analysis work for other MHD tasks.

As noted above, we conducted an intensive technical review of four commercial ICPAES's and narrowed the selection to two systems that appeared to meet our analytical needs. A summary of the critical evaluation of these two systems, namely the Jarrell Ash (JACO) and ISA ICPES, is outlined in the following paragraphs.

- 1) The ISA spectrometer design appears to be relatively free of scattered light sources, and the holographic grating is more capable of handling stray light than in the JACO spectrometer.

On the basis of the guaranteed performance, i.e., detection limits for the elements of interest, the spectrometers appear to be comparable in performance. This would appear to negate the superior spectrometer design and the holographic grating of the ISA system. However, it can be reasoned that if JACO had used the 3X background noise instead of 2X as ISA did, and if ISA had not been so conservative on guaranteed detection limits for our coal samples, the ISA performance would indeed appear better. A rigorous comparison based on detection limits is risky when the differences are small because the reported guaranteed detection limits have some degree of conservatism or liberalism based on the philosophy of the company. The potential of having better detection limits with the ISA unit than with the JACO unit exists because ISA handled the stray light problems better when they arise as outlined in the reports received from Iowa State University (Maas, et al., "Specifications for an Inductively Coupled Plasma Simultaneous Multi-element Spectrometric Analysis System," 15-4353, February, 1978, and Winge, et al., "Evaluation of an Inductively Coupled Plasma Multichannel Spectrometric Analysis System," EPA-600/4-7-032, June 1977). That article recommends the use of holographic gratings and a spectrometer design similar to the ISA unit.

- 2) The ISA spectrometer appears to adapt to the choice of analytical lines easier, based on the apparent crowding of the secondary slits on the Rowland circle in the JACO unit. This could detract from our ability to analyze matrices that are markedly different from a coal solution.

The wider dispersion with the ISA unit would be conducive to better resolution or the ability to isolate one particular line of interest from its neighbors or other spectral interferences. There is more room in which to locate a certain line without resorting to an inferior line for an element because the region is too crowded.

- 3) The computer capacity of the ISA system is relatively greater than that of the JACO system, even considering the expanded capacity of the PDP-8 JACO computer. This limitation of the JACO computer may limit us to the number of elements and matrices that can be handled. In addition, it may limit us with respect to the amount of statistical data treatment.

One of Iowa State's recommendations for a better ICP system is to have the largest computer capacity available. The numerous background and interference corrections demand a high computer capacity to adequately give realistic and accurate data. It also is difficult to assess what sample types and applications will be seen in the future. Therefore, the ability to provide room and adequate interference corrections for expanded use should be given serious consideration.

The MOSS system with the PDP 11-04 computer in the ISA unit is considered an improvement due to its FORTRAN language and the use of non-mechanical relays which are more reliable than the mechanical relays used in core and Bliss systems. The MOSS geometry also allows room for the addition of more peripheral devices, should they be needed in the future.

The computer software developments at ISA over the next 24 months will be made available at no charge. This in itself is of significant value to our laboratory since the exact kind of data treatment is not known at present.

- 4) The question of background correction has received ample attention, and it is our opinion (based on the information received from several sources) that the JACO background correction does not adequately correct for many lines due to the technique involved. It is quite possible that, with our complex matrix, not very many lines will have a clear background to be monitored at only a 0.5 Å distance from the line centers. The background correction system, available from ISA at no extra cost, provides computer-controlled selection of positions away from a spectral line at any position within 14Å on either side of a line at which to monitor the background without interference. This method of selecting the position for background, with a wider range from which to select the background, is considered to be the best way to do a true background correction and is the absolutely best state-of-the-art in background correction.

Some form of background correction is deemed essential by a number of experts in the area for elements at or near the detection limit. Of the two background correction systems, there are clear advantages to using the system provided by ISA.

- 5) The ISA 0.6M scanning monochromator has superior resolution and light-gathering capacity compared to the direct reader. The superior resolution is of considerable use in delineating line interference. The superior light-gathering capacity will be of special advantage in using the scanning monochromator to detect elements of relatively low concentration and, therefore, not programmed on the direct reader. The use

of a 1200 g/mm grating instead of the standard grating normally used in the scanner will not change the statements just made and has other advantages useful for our purposes as outlined in the recommendations correspondence from ISA. The use of the 1200 g/mm holographic grating in the scanner does three things: the advantages listed by ISA are realized, the extra cost is not applicable because the 1200 g/mm grating would not be purchased as a spare, and the replacement of the more expensive standard grating with the less expensive 1200 g/mm will lower the price of the scanning monochromator from the quoted value of the standard system.

The JACO N+1 channel scanning monochromator does not give superior spectral characteristics compared to the direct reader and to the ISA 0.6M scanning monochromator.

Our second and only other choice is the JACO ICPES system with the background corrector and the added computer capacity. Based on the above arguments, we feel the ISA system is technically a better instrument. The arguments are valid and based on many manhours of research and discussion with experts around the country in the field of ICPES and emission spectroscopy in general. Most of the experts were affiliated with the various vendors in some way and probably offered somewhat biased views; but the broad range of people surveyed has generated enough information for an objective analysis.

During the technical review, we were interested to learn that a JACO ICPES was being used in the North Dakota Grand Forks DOE Energy Research Center. Currently, their emission system consists only of the direct reading spectrometer, the Plasma Therm plasma source, and a PDP-8 computer. They do not have any background correction capability and, in the near future, will have the N+1 scanning monochromator installed. Their comments concerning the capacity of the PDP-8 computer was identical to our concern noted above, i.e., it only has the capacity to act as a "slave" computer and cannot handle any major data processing. The lack of the background correction capability, i.e., the vibrating primary diffractor plate, is probably not a great loss for the JACO system. This is based upon the opinion that the JACO background correction system is not applicable for very many elements, especially in a complex matrix of an acid solution of coal. Their addition of the N+1 channel will be of some benefit by allowing the observation of possible background problems but will not allow them to detect any additional elements. Their spectrometer has 40 element lines programmed on its Rowland Circle, but it is interesting to note that they are only able to detect 14 and 17 elements in SRM 1633 and SRM 1632, respectively. We had come to the conclusion that we could only force the ICPES supplier to a guarantee of 25 elements in SRM 1632. It should be pointed out that the sample preparation of their coal sample is identical to that which we are using; thus, we are anticipating slightly better detection limits. As indicated above, our ISA ICPES system will be equipped with a background correction system, which we think is superior to that of JACO, and

with a scanning monochromator, which has superior optical performance over the direct reader. For these reasons, we expect to detect more than just the 14 to 17 elements and possibly more than 25 via the scanning monochromator. Even though the current routine experience at Grand Forks seems to have been using the JACO ICPEs on aqueous leach samples, we think that there will be much to gain by a free exchange of analytical procedures and sample data.

E. Coal Characterization

1. Coal Channel Samples

a. Work Accomplished

The Dietz No. 2 and Rosebud coal channel samples collected early in this research effort have been analyzed for their oxygen concentration via the automated PE 240 combustion-train analyzer. These data are presented in Tables 12 and 13. In addition, the mercury concentrations of 15 selected channel samples of the Rosebud seam coal have been determined and are presented in Table 14.

b. Discussion

The Hg concentrations are plotted (Figure 2) as a function of position in the Rosebud coal seam. Although there are only a few data points, there does not appear to be any observable vertical or horizontal concentration trends.

Table 15 illustrates the horizontal average of the C-H-N-O concentrations for each depth within the Dietz No. 2 and the Rosebud coal seams; it is difficult to discern concentration trends.

2. Tipple Samples

a. Work Accomplished

A program was begun for obtaining tipple samples from the Montana Power Company's power station in Colstrip, Montana and the Westmoreland coal mine in Sarpy Creek, Montana. A similar sampling program is being considered at the Montana Power Company Corette Plant in Billings, Montana.

b. Discussion

The objective of this tipple sampling program is to ascertain the time variation in properties of the coal as it is fed into a conventional coal-fired burner. This time variation will be determined for long and short periods of storage. The former will be represented by the sampling program at the Colstrip plant and at the Sarpy Creek mine. The short time variation in properties will be ascertained with the proposed sampling program at the

Corette Plant in Billings.

A schematic of the Colstrip power station's coal preparation and coal feeding system is presented in Figure 3. It should be pointed out that the variation in the properties of the coal in the field will be altered by the mining practice, the grinding and blending accomplished in the primary, secondary, and tertiary crushers, and the final mills (note the rejection of pyrite here), and the technique of adding and removing the coal from the two open stock piles and the silos.

Figure 4 is a schematic of the coal preparation and storage system at the Sarpy Creek mine. The sample station is at the train loading station, and each sample set represents a trainload of coal, i.e., approximately 100,000 tons. These tibble samples obviously represent the properties of the coal delivered from the 50,000-ton storage bin from which approximately 100,000 tons of coal are shipped per week.

Figure 5 is a schematic of the coal feeding system at the Corette Plant. The coal in the stock pile is Rosebud coal obtained from the Western Energy mine at Colstrip. We intend to sample the coal being fed to the burner from the mill with a frequency at which the samples' concentration data will represent the short time variation in properties.

The obvious argument is that the variation in coal properties being fed into the burners is a function of the portion of the specific coal seam being mined and the specific coal preparation feeding system. Since the CDIF (and possibly the ETF) coal feeding system are not designed similarly to that of any of the three systems being sampled, the time variation in coal properties being fed into the burners at these installations most probably would be different.

F. Real-Time Analysis

1. Work Accomplished

A suggestion was received from Alan Postlethwaite and Leo Sullivan of the DOE MHD Division in Washington, D.C.³ that the objectives of this task include a consideration of real-time analysis. Our primary investigation has involved two relevant questions. One pertains to determining those coal properties for which real-time data would be of some value, and the second pertains to correlating the available instrumentation to the required coal properties.

Various personnel^{11,12,13,14,15} involved in MHD combustor research and development were consulted with respect to their suggestions

concerning those coal properties for which real-time data would be of value. There is general agreement that on-line analysis of calorific value, moisture, and ash content and elemental analysis would be highly beneficial with regard to correlation of the variables with process efficiency and ultimately to use the analytical data to control the feeding system.

Attendance at the 1978 Symposium on Instrumentation and Control for Fossil Demonstration Plants on June 19-21 at Newport Beach, California yielded information concerning not only the properties of coal that should be determined but the current research of analytical techniques that will afford real-time analysis of process streams. This experience has prompted discussions with several research laboratories. Those discussions have generated the following information about instrumental methods presently available for monitoring ash, moisture, and elemental analysis.

a. Determination of Ash Content--Ash Monitors

1) Principle of Operation

The ash monitor measures the backscattering radiation from a sample of coal irradiated by an X-ray source. The radiation absorption coefficient of a chemical element increases with its atomic number. Thus, the elements that constitute the ash reflect fewer X-rays from a radioactive isotope than those which do not produce ash. The ash monitoring apparatus is calibrated with coal of known ash weight percent. Continuous weight percent of ash then can be determined on-line. The method assumes that the composition of the ash is relatively constant throughout the coal seam. This procedure has been used extensively in England to blend coals to specific ash content.

2) Available Instruments

1. Gunson's Sortex, LTD of England^{16,17}
Cost: \$30,000
X-ray Source: plutonium-238 (44 kev; + $\frac{1}{2}$ 89.6 yr)
Penetration into Coal Bed: 40 mm
Accuracy: 0.3-2.2% depending on coal type
Feed Rate: 35 lb/min of smooth--3/16 in coal
Compensation for coal with iron concentrations greater than one percent
Problems: Not effective on coal with greater than eight percent moisture (sampling effects)

2. Humboldt Wedag, West Germany¹⁸
Cost: Unknown at this time
X-ray Source: American-241 (60 kev; + $\frac{1}{2}$ 470 yr.)
Penetration into Coal Bed: 150 mm
Accuracy: 0.3 percent
No compensation for fluxuations in iron concentration
Feed Rate: Five metric tons per hour
No problem with particle size or moisture

b. Determination of moisture content--gamma-ray, microwave technique

Principle of Operation: As the coal flows through a chute located in the process line, microwave and gamma energies are transmitted through the process material. Microwave energy is strongly absorbed by water; therefore, the amount of water present is indicated by a power drop of the microwave signal. Similarly, the absorption of the gamma energy accurately measures the material mass. Percent moisture then is calculated by dividing the water units (from the microwave signal) by the mass units (from the gamma signal).¹⁹

Instruments Available:

Kay-Ray Inc., Kay-Ray Model 1800 Moisture System
Cost: Unknown at this time
Constant percent moisture readout
Accuracy: 0.2 percent for a range of 2 to 30 percent

c. Elemental analysis (ash, moisture, and Btu) by neutron-induced gamma-ray spectroscopy

Principle of Operation: ^{20,21,22,23} Neutrons from a suitable source bomb and the sample, exciting nuclear transitions. Excited nuclear states decay at one with emission of "prompt" gamma rays whose energies are characteristic of the excited neutrons and whose intensities are proportional to source strength, element concentraion, and spectrometer efficiency. The prompt gamma rays appear within milliseconds of neutron interaction. Delayed or activation gamma rays result from the decay of the radioactive products of the initial neutron interaction. Nuclear reactions are the most valuable for their corresponding activation gamma rays. Depending upon the element or elements of interest, the analysis time required and the desired accuracy, one or more of the following techniques may be employed:

1. thermal neutron-prompt gamma analysis,
2. fast neutron-prompt gamma analysis,
3. thermal neutron-activation analysis, or
4. fast neutron-activation analysis.

A neutron-gamma analyzer consists of a neutron source, a gamma ray spectrometer, and a sample presentation system.

Three types of neutron sources can be utilized: radioisotopes, nuclear reactors, or neutron generators. Radioisotope sources have the advantages of small size, solid state construction, and stable output. The only commercial package available, from Columbia Scientific Industries, utilizes radioactive sources for both the fast and slow neutrons. Research being done at Argonne National Laboratories utilizes a radioisotope, Cf^{252} , for the thermal neutron source and a neutron generator for fast neutrons. The neutron generator is cumbersome and as yet, the two techniques have not been integrated into a single analysis system by Argonne.

Instruments Available:

Columbia Scientific Industries, Inc.--Neutron Analysis Systems^{21,22}
 Cost: Basic components, \$100,000--including computer and sample system, \$200,000

Neutron Source: Cf^{252} (slow neutrons)

$\text{Pu}^{238}/\text{Be}$ (fast neutrons)

Present Capabilities: Simultaneous analysis of: $\text{H} \pm 0.01\%$,
 $\text{C} \pm 0.2\%$, $\text{N} \pm 0.1\%$, $\text{Na} \pm 0.01\%$, $\text{Al} \pm .003\%$
 $\text{Si} \pm 0.05\%$, $\text{S} \pm 0.03\%$, $\text{Ca} \pm 0.1\%$, and
 $\text{Fe} \pm 0.1\%$

Analysis Time: 10 minutes

Installation and Testing Time: 12 months

2. Discussion

Since the neutron gamma methods are specific to elements, satisfactory correlation must be verified between the desired component and the elements being measured. Formula exist for defining such quantities as calorific value^{24,25} and total ash²⁷ in terms of elemental constituents. There has been little work in this area, but it is probable that such equations could be used or modified to suit those coals destined for MHD use and that calculated results would be satisfactory. For example, the theoretical calorific value of coal in Btu/lb is given by

$$Q = 145.4 [C] + 620 [H] + 40 [S]$$

where [C], [H], and [S] are the percent by weight of the elements on a dry basis.

Rhodes has reported precisions of 0.2%C, 0.01%H and 0.03%S.²² For a coal containing 70%C, 5.0%H, and 3.0%S, the calorific value would be 13400 Btu/lb and the RMS error would be 30 Btu/lb.

It appears that such an effort to generate real-time data is of some significance to solving potential problems associated with the ETF. In addition, it appears that neutron activation holds the greatest promise of delivering concentration data in a relatively short time interval. Thus, our current effort is being directed toward correlating these elemental concentrations with the required properties.

IV. CONCLUSIONS

Our work on establishing and integrating analytical procedures for the accurate, precise, and rapid analysis of coal for a large number of physical and chemical properties has resulted in relating a number of instrumental techniques to a single sample preparation procedure. Since a relatively large amount of analytical time usually is associated with sample preparation, the use of the acid-bomb coal solutions in as many of the instrumental procedures as possible increases the total analysis efficiency. The successful investigation of the appropriateness of emission spectrography for determining a large number of major and minor metals in coal also has increased the total analysis efficiency dramatically. In addition, the atomic absorption procedures for Hg, Se, Sb, As, and Sn are compatible with the acid-bomb coal solutions and, although not as rapid as emission spectrography, are essential to determine the relatively low concentration metals. The work on establishing the X-ray fluorescence technique for sulfur also is strictly applicable to this objective of rapidly and efficiently analyzing coal samples, especially considering our efforts to adapt the technique to the acid-bomb solutions.

It is anticipated that our current effort in determining the time variation in coal properties to be expected from a specific coal preparation and feeding system will be of benefit to the MHD design engineers responsible for the ETF. Furthermore, these tipple samples will provide a valuable comparison of analytical data and procedures with other laboratories. Finally, the data from these samples will provide input for our intended investigation to establish calculation schemes appropriate for generating real-time data on the Rosebud seam coal.

TABLE 1

Commercially Available Heat-Sealable Bags

<u>Bag</u>	<u>Description</u>	<u>Properties</u>	<u>Producers</u>	<u>Availability</u>
Bolyn-Bag or Sambag	15 gauge polyester coated with 2 mil. medium density polyethylene	6.00g H ₂ O/24 hrs. over 100 inches ² at 100°F 9.00 cm ³ O ₂ /24 hrs. over 100 inches ² at 72°F, 1 atm. & 80% rel. hum.	Dazey Bag Co. Kansas City, Missouri 912-782-7500	Grocery and drug stores
Ceran Bolyn-Bag	Ceran coated version of boiler bag	0.4g H ₂ O/24 hrs. over 100 inches ² at 100°F 1 cm ³ O ₂ /24 hrs. over 100 inches ² at 72°F, 1 atm. & 80% rel. hum.	Modern Pack- aging Mount Holley, New Jersey 609-267-5900	producer
Unknown name	1 mil foil	0.01 cm ³ O ₂ /24 hrs. over 100 inches ² at 72°F, 1 atm. & 80% rel. hum.	Moderan Pack- aging Mount Holley, New Jersey 609-267-5900	producer
Plastic film	3 layers: nylon, surlyn, surlyn	?	St. Regis Paper Company, 150 East 42nd St., New York, New York 212-697-4400	?

TABLE 2
Organic-Inorganic Affinities of Metals in
Rosebud Coal Seam Samples

	Percentage of Total Number of Samples							
	Fe	Ca	Zn	Si	Cu	Pb	Mn	As
Organic		20	20	13	13			
Organic-Inorganic			60					
Intermed.		60						
Inorganic Organic	27			33	13	20		
Inorganic	67			40	46	67	87	73

TABLE 3
Combustion Train (PE 240) Analysis of Sulfur

	<u>Thymol Blue</u>	<u>Phenyl Thiourea + Silica</u>	<u>Phenyl Thiourea + Graphite</u>
Accepted Value	6.87% S	2.11% S	2.11% S
No. of Determinations	11	10	10
Mean	6.74% S	2.11% S	1.53% S
Standard Deviation	<u>+0.41%</u>	<u>+0.41%</u>	<u>+0.16%</u>
Relative Standard Deviation	<u>+6.0%</u>	<u>+19.43%</u>	<u>+10.46%</u>

TABLE 4
XRF Analysis for S in Rosebud Channel Samples

<u>Sample #</u>	<u>XRF</u>	<u>ASTM (Eschka Method)</u>
1A	0.99	0.99
B	0.87	0.96
C	0.86	0.83
D	0.85	0.85
E	0.87	0.92
5A	1.17	1.16
B	0.94	0.97
C	0.91	0.98
D	0.88	0.94
E	3.27	5.73
9A	0.89	
B	0.98	
C	0.84	
D	0.93	
E	1.04	

TABLE 5

BaSO₄ Precipitate vs. Evaporation of Acid Bomb Solution

	Emission Spectrographic Estimated Concentrations $\pm 200\%$ (Wt. %)	Wt. % in Coal (Evaporation of Acid Bomb Solution)
Al	1×10^{-2}	8.5
Si	2×10^{-3}	14.4
Fe	5×10^{-3}	3.9
Cu	8×10^{-5}	6×10^{-3}
Na	0.25	0.15

TABLE 6

Accuracy and Precision of O₂ Procedure

	<u>Acetanitide</u>	<u>Benzoic Acid</u>	<u>Coal Sample</u>
Mean % O ₂	11.84%	26.6%	17.28%
Standard Deviation	$\pm 0.53\%(\pm 4.5\%)$	$\pm 0.62\%(\pm 2.3\%)$	$\pm 1.0\%(\pm 6.0\%)$
Accepted Value	11.84%	26.20%	

TABLE 7

Comparison of XRFS and PES Ca Data

<u>Sample</u>	<u>XRFS</u>	<u>PES</u>
1A	.60	.73
B	.77	1.11
C	.74	1.10
D	4.00	3.98
E	.70	.96
5A	.62	.82
B	1.60	3.24
C	1.39	2.85
D	.73	.99
E	.54	.88
9A	.60	.65
B	.71	.79
C	.66	.40
D	.67	.81
E	.63	.82

TABLE 8

Accuracy and Precision of AAS Data for As, Hg, Se and Sb
(NBS 1632)

	<u>AAS ($\mu\text{g/l}$)</u>	<u>Accepted Value ($\mu\text{g/l}$)</u>
As	5.78 $\pm$.08 ($\pm 1.4\%$)	5.9 $\pm$.6
Se	3.0 $\pm$.07 ($\pm 2.3\%$)	2.9 $\pm$.3
Sb	1.3 $\pm$.10 ($\pm 7.7\%$)	1.4 $\pm$.07
Hg	.11 $\pm$.02 ($\pm 18.2\%$)	.12 $\pm$.02

TABLE 9
Quantometer Calibration Constants

$$\text{Log } I/T = (aV+b)L + (cV+d)$$

El	V Range	a	b	c	d
C	< 6.0	.00351	.01401	.02069	-.96633
C	> 6.0	.01845	-.06343	.10310	-1.53590
Si	< 6.0	-.00281	.16483	.17140	-1.63051
Si	> 6.0	-.00281	.16483	.35850	-2.82601
Fe	< 5.5	-.00160	.15095	.18301	-1.36150
Fe	> 5.5	-.00160	.15095	.31920	-2.06730
Cu	< 4.5	.00089	.13502	.13450	-.71160
Cu	> 4.5	.00089	.13502	.32550	-1.75400
B	< 5.5	-.00070	.14677	.16220	-.83780
B	> 5.5	-.00070	.14677	.33760	-1.80410
Mn	< 6.0	-.02297	.27602	.39409	-4.05661
Mn	> 6.0	-.01516	.28204	.45025	-4.80045
Mg	< 6.2	-.03748	.37660	.53520	-5.29720
Mg	> 6.2	-.01497	.27330	.42261	-4.88760
V	< 5.0	.01087	.05662	.07583	-.69435
V	> 5.0	.00450	.09544	.28161	-1.74604
Ca	< 6.5	-.00054	.14717	.14677	-1.18018
Ca	> 6.5	-.00054	.14717	.37253	-2.67494
Cr	< 5.0	.00082	.13730	.17160	-.80832
Cr	> 5.0	.00082	.13730	.32679	-1.66638
Ti	< 7.0	.00020	.13917	.15194	-.78852
Ti	> 7.0	.00020	.13917	.38158	-2.39725
Ni	< 0-11.0	-.00005	.14400	.25205	-1.13949
Ni	> 0-11.0	-.00005	.14400	.25205	-1.13949
Pb	< 6.0	.00027	.10428	.15343	-1.22558
Pb	> 6.0	.00027	.10428	.31507	-2.18719
Ba	< 5.0	-.00040	.13787	.17311	-1.28941
Ba	> 5.0	-.00040	.13787	.28543	-1.87640

TABLE 9
(CONTINUED)

E1	V Range	a	b	c	d
Al	< 5.0	.01858	.04032	-.00835	-2.37760
Al	> 5.0	.00118	.14620	.31229	-4.09721
Na	< 6.0	-.00699	.19366	.22126	-2.12966
Na	> 6.0	-.00150	.15207	.32843	-2.71483
Sr	< 7.0	-.00842	.18999	.22886	-2.46050
Sr	> 7.0	-.00085	.20349	.49983	4.41228
Ga	< 0-10	-.00654	.16346	.27152	-1.81555
Ga	> 0-10	-.00654	.16346	.27152	-1.81555

Equations:

$$(aV+b)L + (cV+d)$$

$$(-aV-b)L-cV-d$$

$$I = T10$$

$$T = I10$$

$$L = \frac{\log I/T - cV - d}{(aV + b)}$$

$$V = \frac{\log I/T - bL - d}{(aL + c)}$$

I = readout number, T = integration time

V = voltage setting applied to tubes

L = lamp intensity number (also a measure of the amount of light getting to the PM's)

a = slope of V vs. (slope log I/T vs. L)

b = intercept of V vs. (slope log I/T vs. L)

c = slope of V vs. (intercept log I/T vs. L)

d = intercept of V vs. (intercept log I/T vs. L)

TABLE 10

Comparison of DRES and PES Data
Dietz No. 2 Seam
(Trip I)

<u>Element</u>	<u>Direct Reader</u>	<u>Photographic</u>	<u>% Change</u>
Si	0.831%	0.766%	-7.8
Fe	0.234%	0.226%	-3.4
Cu	10.5 ppm	6.5 ppm	-38.1
B	66.5 ppm		
Mg	0.171%	0.159%	-7.0
Mn	8.6 ppm	5.4 ppm	-37.2
V	14.2 ppm	14.5 ppm	2.1
Ca	0.475%	0.457%	-3.8
Cr	8.9 ppm		
Ti	0.0320%	0.0331%	3.4
Ni	8.0 ppm	3.3 ppm	-58.8
Pb	4.1 ppm	3.6 ppm	-12.2
Ba	326 ppm	344 ppm	5.5
Al	0.499%	0.465%	-6.8
Na	1385 ppm	1266 ppm	-8.6
Sr	105.0 ppm		

(Trip II)

Si	1.10 %	1.10 %	0.0
Fe	0.263%	0.252%	-4.2
Cu	11.3 ppm	6.5 ppm	-42.5
B	73.8 ppm		
Mg	0.205%	0.198%	-3.4
Mn	11.0 ppm	6.5 ppm	-40.9
V	15.6 ppm	13.6 ppm	-12.8
Ca	0.775%	0.803%	3.4
Cr	6.5 ppm		
Ti	0.0451%	0.584%	3.6
Ni	5.8 ppm	3.9 ppm	-32.8
Pb	5.0 ppm	3.8 ppm	-24.0
Ba	406 ppm	387 ppm	-4.7
Al	0.814%	0.852%	4.7
Na	18.71 ppm	15.76 ppm	-15.8
Sr	156.2 ppm		

TABLE 10
(CONTINUED)

Rosebud Seam

<u>Element</u>	<u>Direct Reader</u>	<u>Photographic</u>	<u>% Change</u>
Si	2.25 %	2.55 %	13.3
Fe	0.42 %	0.52 %	23.8
Cu	19.3 ppm	7.5 ppm	-61.1
B	90.2 ppm		
Mg	0.213%	0.224%	5.2
Mn	104.1 ppm	104.2 ppm	0.1
V	11.4 ppm	14.3 ppm	25.4
Ca	1.08 %	1.13 %	4.6
Cr	5.5 ppm		
Ti	0.0705%	0.0617%	-12.5
Ni	4.9 ppm	2.1 ppm	-57.1
Pb	6.4 ppm	7.7 ppm	20.3
Ba	339 ppm	304 ppm	-10.3
Al	1.02 %	1.07 %	4.9
Na	303 ppm	230 ppm	-24.1
Sr	96.9 ppm		

TABLE 11
Instrumental Techniques - Trace Analysis

	<u>NAAA</u> (g)	<u>SSMS</u> (ng)	<u>CIMS^b</u> (g)	<u>ICPAES</u> ug/ml	<u>NFAAS</u>	<u>XRFS</u> (ug)	<u>ASV</u>
Ag	10 ⁻¹⁰ -10 ⁻⁹	0.2		0.004	0.001 ng/ml	1.2	0.25 ppb
As	10 ⁻¹⁰ -10 ⁻⁹	0.06				0.11	
B							
Ba	10 ⁻¹⁰ -10 ⁻⁹	0.2		0.001	6x10 ⁻¹² g	0.12	
Be		0.008		0.005	3x10 ⁻¹⁴ g		
Cd	10 ⁻⁹ -10 ⁻⁸	0.3		0.002	0.03 ng/ml	0.40	0.005 ng/ml
Co	10 ⁻¹⁰ -10 ⁻⁹	0.05	1x10 ⁻¹¹	0.003	2x10 ⁻¹² g	0.05	
Cr	10 ⁻⁸ -10 ⁻⁷	0.05	1x10 ⁻¹¹	0.001	1.2x10 ⁻¹² g	0.00006	
Cs	10 ⁻⁹ -10 ⁻⁸	0.1				0.15	
Cu	10 ⁻¹⁰ -10 ⁻⁹	0.08	1x10 ⁻¹¹	0.001	6x10 ⁻¹³ g	0.00002	0.005 ng/ml
Ga	10 ⁻¹⁰ -10 ⁻⁹	0.09		0.014	1x10 ⁻¹² g	0.01	0.4 ng/ml
Hg	10 ⁻¹⁰ -10 ⁻⁹	0.6		0.2	8x10 ⁻¹¹ g	0.24	4.0x10 ⁻⁹ M
La	10 ⁻¹¹ -10 ⁻¹⁰	0.1	5x10 ⁻¹¹	0.003	0.1 ng/ml	0.12	
Li		0.0006					
Mn	10 ⁻¹² -10 ⁻¹¹	0.05	1x10 ⁻¹¹	0.0007	2x10 ⁻¹³ g	0.00015	
Ni	10 ⁻⁸ -10 ⁻⁷		1x10 ⁻¹¹	0.006	4x10 ⁻¹² g	0.06	0.1g/ml
P						0.001	
Pb	10 ⁻⁷ -10 ⁻⁶	0.3		0.008	0.002 ng/ml	0.0003	0.01 ng/ml
Rb						0.0075	
Sb	10 ⁻¹⁰ -10 ⁻¹¹						
Se							
Sn		0.3		0.3	2x10 ⁻¹² g	3.9ppm	2.0 ng/ml
U	10 ⁻¹⁰ -10 ⁻¹¹			0.08		0.00002	
V	10 ⁻¹¹ -10 ⁻¹⁰	0.04	1x10 ⁻¹¹	0.006	5x10 ⁻¹¹ g		
Zn	10 ⁻⁸ -10 ⁻⁷	0.1	1x10 ⁻¹¹	0.002	2x10 ⁻¹⁴ g	0.00004	0.04 ng/ml
Zr	10 ⁻⁸ -10 ⁻⁷	0.1		0.005	5.0 ug/ml	0.00002	

a) Sensitivity based on irradiation period of 0.5 T_{1/2} or 10 h: whichever is less at a flux of 10¹³ neutrons cm⁻² s⁻¹. Activity measured by Na/(Ti) gamma spectrometry.

b) Ation coupled with CIMS

TABLE 12

O₂ Concentration in Dietz No. 2 Coal Seam

(Trip I)

<u>Sample</u>	<u>% Oxygen</u>	<u>Sample</u>	<u>% Oxygen</u>	<u>Sample</u>	<u>% Oxygen</u>
1 A	20.02	1 B	19.88	1 C	21.13
2 A	19.19	2 B	20.16	2 C	19.60
3 A	19.87	3 B	20.10	3 C	19.90
4 A	19.82	4 B	19.81	4 C	20.02
5 A	19.80	5 B	19.61	5 C	17.68
6 A	23.37	6 B	19.54	6 C	19.16
7 A	19.20	7 B	19.64	7 C	18.90
8 A	19.99	8 B	19.64	8 C	19.23
AVG.	20.16	AVG.	19.80	AVG.	19.45
	+1.34		+0.23		+1.00
	+6.64%		+1.18%		+5.12%

<u>Sample</u>	<u>% Oxygen</u>	<u>Sample</u>	<u>% Oxygen</u>	
1 D	19.06	1 E	18.62	
2 D	17.09	2 E	18.86	
3 D	18.41	3 E	18.61	
4 D	19.89	4 E	18.21	
5 D	19.62	5 E	19.73	
6 D	19.05	6 E	19.88	
7 D	19.28	7 E	17.19	
8 D	18.40	8 E	16.76	
AVG.	18.85	AVG.	18.48	Trip I AVERAGE
	+0.88		+1.10	19.40
	+4.68%		+5.95%	+1.06
				+5.44%

(Trip II)

<u>Sample</u>	<u>% Oxygen</u>	<u>Sample</u>	<u>% Oxygen</u>	<u>Sample</u>	<u>% Oxygen</u>
1 A	19.30	1 B	19.82	1 C	19.43
2 A	19.78	2 B	18.92	2 C	20.40
3 A	18.50	3 B	18.92	3 C	19.98
4 A	18.60	4 B	18.38	4 C	21.36
5 A	20.41	5 B	19.47	5 C	19.35
6 A	19.02	6 B	19.23	6 C	20.78
7 A	18.99	7 B	20.81	7 C	20.60
8 A	18.53	8 B	20.70	8 C	19.75
9 A	18.83	9 B	19.47	9 C	20.09
AVG.	19.11	AVG.	19.52	AVG.	20.19
	+0.64		+0.81		+0.66
	+3.33%		+4.15%		+3.26%

TABLE 12
(CONTINUED)

(TRIP II)
(CONTINUED)

<u>Sample</u>	<u>% Oxygen</u>	<u>Sample</u>	<u>% Oxygen</u>	
1 D	20.55	1 E	19.55	
2 D	20.73	2 E	19.20	
3 D	19.63	3 E	19.86	
4 D	19.83	4 E	20.37	
5 D	20.62	5 E	20.49	
6 D	20.52	6 E	19.52	
7 D	19.75	7 E	19.68	
8 D	19.71	8 E	19.75	
9 D	19.73	9 E	20.33	
AVG.	20.12	AVG.	19.86	Trip I & II AVERAGE
	+0.47		+0.44	19.59
	<u>+2.32%</u>		<u>+2.23</u>	<u>+0.91</u>
				<u>+4.62%</u>

TABLE 13

O₂ Concentration in Rosebud Coal Seam

<u>Sample</u>	<u>% Oxygen</u>	<u>Sample</u>	<u>% Oxygen</u>	<u>Sample</u>	<u>% Oxygen</u>
1 A	18.01	1 B	18.46	1 C	18.11
2 A	18.39	2 B	18.24	2 C	17.75
3 A	17.96	3 B	17.60	3 C	17.66
4 A	19.17	4 B	17.95	4 C	17.21
5 A	18.99	5 B	19.54	5 C	18.80
6 A	19.52	6 B	18.09	6 C	18.22
7 A	17.61	7 B	17.84	7 C	17.86
8 A	18.50	8 B	17.80	8 C	19.34
9 A	22.19	9 B	18.00	9 C	17.95
10A	18.23	10B	17.80	10C	16.27
11A	21.41	11B	18.02	11C	17.64
AVG.	19.09	AVG.	18.12	AVG.	17.89
	+1.46		+0.52		+0.79
	<u>+7.66%</u>		<u>+2.90%</u>		<u>+4.44%</u>

<u>Sample</u>	<u>% Oxygen</u>	<u>Sample</u>	<u>% Oxygen</u>		
1 D	18.13	1 E	17.00		
2 D	18.14	2 E	17.42		
3 D	18.16	3 E	17.25		
4 D	17.40	4 E	17.08		
5 D	18.01	5 E	16.69		
6 D	17.54	6 E	18.14		
7 D	17.82	7 E	18.36		
8 D	17.48	8 E	17.47		
9 D	17.84	9 E	17.54		
10D	17.79	10E	16.12		
11D	17.02	11E	16.68		
AVG.	17.76	AVG.	17.25	AVG.	18.02
	+0.36		+0.65		+1.02
	<u>+2.04%</u>		<u>+3.75%</u>		<u>+5.66%</u>

TABLE 14

Hg Concentration in Rosebud Coal Seam

<u>Sample No.</u>	<u>Concentration (ppb)</u>
1-E	.130
-D	.143
-C	.128
-B	.153
-A	.116
6-E	.180
-D	.193
-C	.180
-B	.178
-A	.170
11-E	.158
-D	.173
-C	.113
-B	.148
-A	.133

TABLE 15

C-H-N-O Concentration Averages (at %)

Dietz No. 2 Coal Seam (Trip I)

<u>AVG.</u>	<u>Ash</u>	<u>C</u>	<u>H</u>	<u>O</u>	<u>N</u>	<u>TOTAL</u>
Sample A	8.87	57.53	4.50	20.16	1.65	92.71
Sample B	5.65	56.54	4.02	19.80	1.65	87.66
Sample C	6.88	58.25	3.83	19.45	1.64	90.05
Sample D	6.11	55.89	3.90	18.85	1.52	86.27
Sample E	5.00	57.26	3.99	18.48	1.52	86.05

TOTAL AVG. 88.55

Dietz No. 2 Coal Seam (Trip II)

<u>AVG.</u>	<u>Ash</u>	<u>C</u>	<u>H</u>	<u>O</u>	<u>N</u>	<u>TOTAL</u>
Sample A	10.53	51.29	4.23	19.11	1.39	86.55
Sample B	7.43	51.58	4.22	19.52	1.37	84.12
Sample C	6.76	57.28	4.17	20.19	1.50	89.90
Sample D	6.09	60.73	4.73	20.12	1.38	93.05
Sample E	6.54	52.57	4.48	19.86	1.40	84.85

TOTAL AVG. 87.69

Rosebud Coal Seam

<u>AVG.</u>	<u>Ash</u>	<u>C</u>	<u>H</u>	<u>O</u>	<u>N</u>	<u>TOTAL</u>
Sample A	11.68	54.92	4.14	19.09	.89	90.82
Sample B	9.34	55.37	3.17	18.12	.84	86.84
Sample C	12.59	53.09	3.55	17.26	.83	87.32
Sample D	11.13	58.98	4.12	17.76	.78	92.77
Sample E	12.76	57.79	3.68	17.25	.82	92.30

TOTAL AVG. 89.99

FIGURE 1

XRF Analysis of Standards

FIGURE 3

Western Energy Coal Preparation + Feeding System

FIGURE 2

Hg Concentration in Rosebud Coal Seam

FIGURE 4

Absolutka Coal Mine - Sarpy Creek, Montana

FIGURE 5

The Montana Power Company - Corette Plant, Billings, Montana

There are four separate systems, each consisting of a silo and mill feeding four burners in one boiler.

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Corrosion Studies of MHD Preheater Materials
K. Kitto

ABSTRACT

Slag and slag-seed corrosion tests have been conducted at elevated temperatures on a number of ceramic refractory materials which have potential use in MHD preheater units. Laboratory tests were conducted as a function of elapsed time at temperatures between 1500°C and 1600°C in a synthetic four-component slag and a slag-seed containing 15 weight percent K₂SO₄; ambient atmospheres were both air and a simulated combustion atmosphere. A dynamic dipping test was used wherein there was forced fluid flow past the refractory surface. Of the materials tested, chrome-containing commercial refractories were the most corrosion resistant, followed by alumina, magnesia-alumina spinel, and finally, magnesia. Photomicrographic and microprobe analyses of corroded materials provided insight into the processes of corrosion. There appears to be no correlation between the degree of corrosion and slag penetration for several of the materials. Penetration of slag appears to occur along grain boundaries and into pore regions for some of the materials. For single crystals and fully dense polycrystalline materials, there was no slag penetration, and the rate of diffusion of slag species was very low.

The creep apparatus has been redesigned partially, and system assembly has continued as various components have been received. Development of a new pre-corrosion technique has begun. Work on the control of the creep system by a microprocessor has continued. Assembly of interface boards has continued, and work on the software control programs has begun. Actual experimental running conditions of the creep apparatus will be set to simulate the anticipated preheater conditions.

I. OBJECTIVE AND SCOPE OF WORK

The primary objective of this task is to characterize the behavior of potential MHD preheater materials under the following conditions: a) in gaseous atmospheres simulating the MHD preheater environment, b) at elevated temperatures to 3100°F (1700°C), c) for exposure periods up to 500 hours, and d) while being exposed to a slag that may or may not contain potassium.

A. Corrosion of Preheater Materials

Experimental systems were constructed to permit dynamic or static corrosion tests at temperatures up to 3100°F and for periods of time up to 500 hours. The design included the capability of passing the desired gas mixture into the furnace chamber containing the slag-immersed sample. Gaseous environments included air and a simulated combustion atmosphere whose composition was in accordance with NBS computations for air combustion of seeded coal.

Synthetic slags and slag-seeds were prepared. Initial tests began with a simple four-component slag to provide very basic engineering data. Further tests employed a more complex system to include the addition of potassium seed. These compositions were representative of slags resulting from the combustion of typical coals found in the United States with later tests concentrating on slags representative of combusted Montana Rosebud coal. Since the slag compositions appearing in the preheater region may be quite different than the starting coal slag, synthetic slags were prepared to duplicated compositions of condensed products resulting from the combustion of coal at the University of Tennessee Space Institute's MHD combustion facility.

During corrosion tests, the slag was sampled periodically to determine compositional changes (especially in potassium content) and changes caused by the dissolution of refractory constituents.

After the high-temperature exposure to the slag during corrosion testing, the refractory samples were recovered, and dimensional changes were recorded. Metallographic and microprobe investigations were made so that corrosion mechanisms might be ascertained.

Except for work on the pre-corrosion of samples for creep testing, all work on the corrosion of potential MHD preheater materials ceased on May 15, 1978.

B. Creep of Preheater Materials

Experimental systems will be constructed to creep test pristine and pre-corroded potential preheater materials at temperatures up to 3100°F and for periods of time up to 500 hours. Loading will be controlled by a microprocessor via a stepping motor to maintain a constant compressive stress level during test runs. Dimensional changes of the sample will be measured by linear variable differential transformers (LVDT's) and will be recorded continuously on the microprocessor along with other important experimental conditions.

Slag penetration tests will be conducted on the potential creep test materials to ascertain the amount of slag penetration with time after various slag exposure times. Based on these results, a new pre-corrosion technique will be developed that will serve the creep testing apparatus better.

Synthetic slags will be prepared in the same manner as previously described for corrosion testing. Post-creep microstructural examination also will be made utilizing techniques developed for post-corrosion specimens.

The candidate materials to be tested will be high purity, single crystal or dense polycrystalline materials to include Al_2O_3 and MgO . Also, materials will be prepared to determine microstructural effects on creep rates. Pristine sample materials will be characterized with respect to chemical composition, microstructure, density and open porosity. The microstructure of pre-corroded creep specimens also will be examined.

After creep testing, samples will be recovered, and metallographic and microprobe investigations will be made.

During the past year, our efforts have involved several projects. High-temperature corrosion tests were continued and finished on several test materials, and a reliable method of making chemical analyses on pre- and post-corrosion was found. Microstructural examination of both pristine and corroded materials was conducted. Before and after corrosion tests, slags were analyzed chemically to determine if tests altered the slag compositions. We also looked into the possibility of examining fluid-mechanical parameters in the slag and their influence on corrosion. Several materials were analyzed which had been corroded with an electron microprobe to correlate the degree of corrosion with penetration and diffusion of slag constituents. Room temperature tests were preformed with various rods and solutions to help ascertain corrosion mechanisms. A creep apparatus design was finalized, and components and equipment for that design were ordered. Effort also was dedicated to work on creep apparatus system control with a microprocessor, and creep equipment was interfaced with the microprocessor. A new pre-corrosion technique for the creep apparatus was developed. Slag penetration tests were preformed to determine slag penetration with time after slag exposure, and an apparatus was constructed for use in conducting high-temperature creep tests on specimens which have been pre-corroded in slag or slag-seeds.

II. SUMMARY OF PROGRESS TO DATE

Corrosion tests have been conducted on a number of materials at elevated temperatures in both slag and slag-seed mixtures. Several different alumina materials have been tested under identical corrosion conditions to determine which material characteristics determine corrosion resistance. The commercial magnesia-chrome which has been installed in prototype MHD preheaters has been corrosion-tested to fill in data gaps. A polycrystalline magnesia which experienced very rapid corrosion has been examined using both static and dipping tests in order to investigate differences in microstructure at the slag-specimen interface.

Microprobe analyses have been conducted on several alumina materials which have been corroded at elevated temperatures in order to 1) examine the degree of diffusion and penetration of the slag constituents into the various materials, 2) determine if this diffusion and penetration is dependent upon position along the length of a specimen which was corroded in a dipping test, 3) determine if the ambient atmosphere (air or simulated combustion) influences the rate of diffusion of any of the slag species into the alumina material, and 4) examine the adherent slag layer for concentration of slag species in this adherent layer to that of the bulk slag.

Room-temperature tests have been performed on rods of sodium chloride in a variety of solutions to identify corrosion mechanisms in environments which may be controlled and varied in a convenient manner. Solution parameters of interest were solution viscosity, density, and surface tension. These parameters not only influenced corrosion, but also the resultant shape of the corroded specimen.

Chemical analyses have been performed on a single slag-seed by several analytical laboratories to ascertain the accuracy of analysis by a local laboratory. Several slags subsequently were analyzed before and after testing.

The creep apparatus has been redesigned partially; final design plan have been completed. Most components have arrived, and creep apparatus assembly has been continuing as those components are received.

Due to the nature of the creep apparatus design, a new pre-corrosion technique development program has begun. Slag penetration tests have continued to ascertain the amount of slag constituent penetration with time after slag exposure of various time lengths. Tests for measuring the flow of the adherent layer of slag on the specimen also have been conducted.

Work on the control of the creep system by a microprocessor and assembly of interface boards for the microprocessor have continued. Some computer programming has been done, and the microprocessor is running test programs to determine the quality of interface connections.

Experimental factors have been considered, and creep test running conditions will be set to simulate anticipated preheater conditions. Factors important to creep include 1) stress level, 2) temperature, 3) thermal cycling, 4) creep test method, 5) specimen microstructure, and 6) slag penetration.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Work Accomplished

The chemical analysis of a single slag-seed by several analytical laboratories revealed moderate variations in the concentrations of the constituents. By comparison, the results of tests performed by a local laboratory appeared satisfactory, and further analyses were made on several slags and slag-seeds both before and after corrosion. It appears that there is some slight alteration of composition due to corrosion products.

A number of high-temperature corrosion tests were performed on ceramic refractory materials under a variety of experimental conditions (atmosphere, temperature, time, and slag-seed composition). These tests were directed toward 1) filling in some of the data gaps which existed from previous tests and 2) correlating our corrosion results and those obtained by Fluidyne Corporation in their prototype preheater.

Material characterization with respect to density, grain size, and impurity content has been performed on several alumina materials which have been corrosion-tested.

Several magnesia-alumina materials have been ordered which, upon receipt, will be pre-corroded and creep-tested at elevated temperatures. One composition is the stoichiometric material; three others contain excess

magnesia. Both spinal and periclase phases are present in varying relative amounts; and three other compositions contain excess alumina and, therefore, are composed of both spinel and corundum phases.

In addition, the MERDI Applied Research Division has been contacted and has agreed to produce some polycrystalline alumina materials. In one series of materials, grain size is to be held constant while the porosity is varied. Materials in the other series have a constant porosity with a variation in grain size. These materials will be tested to ascertain the influence of grain size and porosity on the creep of materials. These new materials will be characterized fully in 1) pristine condition, 2) post- and pre-corrosion conditions, and 3) post-creep condition.

During the past year, design changes were made to the creep apparatus which included 1) load application by a hydraulic system controlled by a microprocessor via a stepping motor to maintain a constant stress level, 2) local measurement by a load cell, and 3) strain, temperature, and load measured and monitored continuously by a microprocessor.

Most components for the creep apparatus arrived, and construction is continuing as ordered components arrive. Since the microprocessor arrived, most interface boards to the control system have been built and connected. Programs for the control system have been developed to a limited extent. However, the microprocessor is running test programs to determine the quality and operation of completed interface boards. Work will continue on this microprocessor control system.

Due to the nature of the creep apparatus, a new pre-corrosion technique must be developed; work has begun on the new technique. First, slag penetration tests will be conducted on potential sample materials to determine the amount of penetration by slag constituents with time after exposure to slag for various time periods.

A literature survey of all recent (post-1966) creep work has been completed. A summary of all the work consulted in our creep design and experimntal condition considerations is presented at the end of this report (see Appendix A).

Stress levels and temperatures for creep testing will be chosen to simulate probable actual preheater conditions. Creep tests will begin by setting a constant stress level and then measuring the resulting strain. Pending the outcome of testing procedure modifications, future tests will set an allowable creep rate and then determine maximum stress level permitted for that creep level.

B. Discussion

1. Corrosion Tests

The furnaces used for slag preparation and corrosion tests in air employed MoSi₂ heating elements and were designed and built in-house. Their maximum temperature capability in air is approximately 1650°C. For tests in the simulated combustion atmosphere, two Astro 1000-A graphite heating element furnaces with 3-1/2 inch

diameter muffle tubes were employed. The temperatures of the MoSi₂ furnaces were measured with Pt-6 percent Rh/Pt-30 percent Rh (type B) thermocouples, whereas graphite/boron-graphite thermocouples were used for the Astros. Corrosion tests have been made between 1450°C and 1600°C.

The simulated combustion atmosphere has a composition of 0.78 mole fraction N₂, 0.16 CO₂, and 0.06 H₂O, which is in accordance with predictions made by the National Bureau of Standards (NBS) for the combustion of CH_{0.7} with a stoichiometric quantity of air.¹ One system for each of the Astro furnaces now supplies this atmosphere at a flow rate of 0.6 liter/min. The N₂ is bubbled through a water bath which is held at the appropriate temperature to give the desired water vapor pressure; this then is mixed with CO₂ to give the appropriate ratio of the three gaseous components.

During a corrosion test, the slag or slag-seed is contained in a Pt-30 percent Rh crucible. The crucible is cylindrical with an inside diameter of 1-3/4 inches, a height of 2 inches, and a wall thickness of 0.030 inch. The slag has a composition of 45 weight percent SiO₂, 25 percent Al₂O₃, 25 percent CaO, and 5 percent Fe₂O₃, which is typical of that resulting from the combustion of Montana Rosebud coal. All of the Al₂O₃ and part of the SiO₂ are added as a clay; the alumina goes into solution more rapidly in this form than when it is added as powdered Al₂O₃. The slag is prepared first by mixing the powdered constituents in the right proportions. The mixture then is melted in one of the Pt-Rh crucibles by inserting it into a furnace at about 1500°C. More powdered material is added until the slag level is 1/2 to 3/4 of an inch from the crucible top. It then is homogenized by soaking at between 1550°C and 1600°C for eight to ten hours. The corrosion test then is carried out in this same furnace. At the conclusion of the test, the slag is remelted in another furnace and poured from the crucible; a portion of the slag is retained for post-corrosion analysis.

Seeded slags have been prepared by adding K₂SO₄ to the powdered slag mixture. Only one composition has been prepared, having 15 weight percent K₂SO₄. At compositions greater than about 25 percent K₂SO₄, an immiscible layer forms on the slag when it is molten. The sulfate probably decomposes to give K₂O and SO₃ during the homogenization heat treatment. Analyses of seeded slags before and after corrosion reveal a virtual absence of sulfur.

For the dipping corrosion tests, about one inch of the specimen is immersed in the slag at the bottom of the cycle, and approximately 3/4 inch of this lower extremity of the specimen translates into and out of the bath. Between 3/4 inch and one inch of the sample was immersed during the rotating rod tests.

Different corrosion shapes were obtained from the rotating rod and dipping tests; these are shown in Figures 1a and 1b, respectively. For virtually all rotating rod tests, excessive corrosion

occurred at the position of the slag-atmosphere interface. As a consequence, many samples completely necked-off at the slag line and fell into the bath before appreciable bulk corrosion had occurred; thus, it was difficult to measure large amounts of corrosion. Steps were taken to reduce or eliminate this slag-line corrosion;² however, none were successful. This enhanced slag-line corrosion is a common phenomenon at the liquid-air interface when a molten slag or glass bath is in contact with a refractory. It is not well understood but may be a result of enhanced fluid flow at the surface due to convection because of thermal and/or density gradients.

The appearance of a specimen which has experienced corrosion from the dipping test is somewhat different (Figure 1b). The greatest amount of corrosion is at the position of the upper slag-atmosphere interface, and the specimen's diameter increases approximately linearly with length to that portion of the sample which remains in the slag. The degree of corrosion is measured as volume percent of sample removed from the point of maximum corrosion (the upper slag-air interface) to a point 1/2 inch below. All corrosion data presented in this report are from the dipping test with volume percent corrosion computed in this manner.

A number of materials have been examined as to their resistance to corrosion by the slag and slag-seed at temperatures between 1500°C and 1600°C. The slag and slag-seed become so viscous at 1450°C that dynamic corrosion tests are impossible to make. This accounts for the lower temperature limit; the upper limit is dictated by the corrosion behavior of the refractories, most of which corrode very rapidly at 1600°C. Those materials tested include alumina, magnesia-alumina spinel, magnesia, and various commercially available ceramic refractories. The influence of time, seed, atmosphere, and temperature have been investigated.

The majority of tests have been conducted on several alumina materials which are reputed to be at least 99 percent pure and have a variety of densities and grain sizes. The alumina materials tested were sapphire or single crystal alumina purchased from Union Carbide Corporation; Lucalox (which is a fully dense and polycrystalline alumina material) manufactured by General Electric Vistal, which is similar to Lucalox except that it has a smaller grain size and is produced by Coors Porcelain Company; AP-35, a moderately dense and polycrystalline alumina which is manufactured by McDanel Refractories Company; a very fine-grained and almost fully dense alumina which was fabricated by the MERDI Applied Research Division; and finally, a commercial alumina refractory which is produced by Norton Company and designated as AH-199B. The densities and average grain sizes of these six materials are tabulated in Table I. The Norton AH-199B alumina has a duplex grain structure consisting of both very large grains ($\sim 250\mu$) and very small grains ($< 10\mu$); a photomicrograph of this material is shown in Figure 2. Figures 3 and 4 show photomicrographs for AP-35 and the MERDI alumina, respectively. Semiquantitative emission spectrographic analyses were performed on these materials at Montana Tech, and the results are shown in Table II. Analyses are provided by the manufacturers for

the AP-35 and the Norton materials; these are included in the tabulation also. There is reasonable agreement between the two sets of analyses for both materials. It is suspected that the SiO_2 concentration is high for some of these materials. The results of electron microprobe analyses on corroded materials (to be described below) indicate that SiO_2 concentrations are probably no greater than 0.04 percent for the sapphire, Lucalox, and Vistal.

Figure 5 presents corrosion data for these six materials as volume percent corrosion as a function of time; test conditions were 1550°C, an unseeded slag, and an air atmosphere; corrosion times ranged between two and ten hours. Straight line segments have been drawn through the sets of data points. Norton AH-199B specimens experienced failure at both two and four hours, making this the alumina material most susceptible to corrosion. For sapphire, the corrosion rate (slope of the line segment) initially is moderately high, then appears to decrease dramatically, being virtually independent of time between eight and ten hours. A single data point is included for the Lucalox; its corrosion behavior probably is about the same as the sapphire and Vistal. The corrosion rate of the Vistal appears to be constant and about the same as the initial rate of the sapphire. The magnitudes of corrosion were similar between four and eight hours for both the sapphire and the Vistal. For AP-35, the corrosion rate decreased as time increased, and the volume percent corrosion for times between four and ten hours was less than for sapphire and Vistal. Finally, the corrosion rate of the MERDI alumina appears to increase with time. Initially, it is the most corrosion resistant of these materials; however, its total amount of corrosion surpasses that for AP-35 at eight hours and approaches the values measured for sapphire and Vistal. It is a little surprising that the polycrystalline materials, which are not completely dense, are generally more resistant to corrosion than the sapphire and fully dense polycrystalline materials (Lucalox and Vistal) for these corrosion times.

Investigations have been made as to the processes which occur during corrosion so that the results may be explained and the mechanisms elucidated. These studies have utilized photomicrographic, SEM, and electron microprobe techniques. The results of the investigations on the alumina materials are given below.

Figure 6 shows a photomicrograph at the edge of a corroded Norton AH-199B specimen which did not experience failure: the bakelite mount is at the right of the micrograph. This specimen was exposed to a seeded slag for four hours at 1500°C. Microprobe analyses have shown that the dark gray areas are regions of slag, while the lighter areas are uncorroded alumina. A residual slag layer may be observed at the right of the micrograph. It also is evident that the slag has penetrated into the regions around the alumina grains. Comparison of Figure 6 with Figure 2 (which is a photomicrograph of the pristine material at a lower magnification) indicates that the slag has penetrated into the pore regions between the large grains and has dissolved a large fraction of the smaller grains. Undoubtedly, some dissolution of the larger grains has occurred; and many of them at the slag-specimen interface

probably become completely engulfed by slag eventually as the interface advances inward. Photomicrographs also were taken at the center of this same specimen, which revealed virtually the same microstructure (i.e., complete penetration of slag into pore areas and some dissolution of the smaller grains). Evidently this penetration process is a very rapid one, and the high susceptibility to corrosion of this material probably is a result of its relatively high porosity, which permits the slag penetration. Thus, there is an extremely large contact area between the slag and the alumina grains (especially the small ones) such that the dissolution process may proceed at a very rapid rate.

Table IIIa presents a tabulation for this corroded AH-199B of the slag concentration as measured by the electron microprobe at three different positions--the adherent outer layer, just inside this layer between the undissolved grains, and near the center of the specimen. Five measurements were made at each position, and averages were taken. It appears that the Al_2O_3 concentration was approximately 10 percent greater at regions within the sample than in the outer slag. This is to be expected since most corrosion undoubtedly takes place around the alumina particles by this slag, which is entrained within the pore regions. There subsequently is an enhancement of the alumina content in the slag and diffusion via this entrained slag out into the slag bath. It is interesting that the alumina concentration in the slag is approximately the same at intergranular regions at the center of the specimen and just inside of the outer slag layer.

Table IIIb lists the average concentration of slag species in the undissolved alumina grains near the outer edge adjacent to the adherent slag layer and also near the center of the specimen. For CaO , Fe_2O_3 , and K_2O , there is not a significant difference in concentration between the two positions. However, the grains near the outer surface appear to have a much higher concentration of SiO_2 than those at the center. Apparently, SiO_2 diffuses more rapidly into this alumina than do the other slag constituents and, since the outer grains have been exposed to the slag for a longer time than those at the center, would have a higher SiO_2 concentration. The smaller grains appear to have a slightly greater concentration of the slag species than do the larger grains since the smaller grains have shorter diffusion path lengths.

It was decided to measure the degree of slag penetration and diffusion using the electron microprobe for the other five alumina materials which were corrosion-tested. All of the materials were subjected to a standard corrosion test: eight hours at $1550^{\circ}C$ in air with unseeded slag. A transverse section cut from each specimen at the same longitudinal position subsequently was polished and examined visually. The sapphire and Lucalox materials were perfectly clear, as in the pristine state; the Vistal was clear in the center, but the outer 2mm rim was slightly clouded; and the AP-35 appeared unaltered in its appearance. The MERDI alumina was discolored severely throughout most of the uncorroded material.

The concentrations of SiO_2 , CaO , and Fe_2O_3 were measured from the slag-specimen interface (which was distinguished easily) using the electron microprobe. The diameters of the specimens were approximately 8mm. To reduce scatter in the data, traverses were made at radial positions which were either 100 or 200 microns apart; these traverses were about 70 microns long and perpendicular to the radius. A 20 micron diameter electron beam was used. In this report, all concentration profiles which utilized the microprobe were measured in this manner. Normal procedures were employed for standardization and measuring background counts.

Concentration profiles for the diffusion of CaO into the MERDI alumina, AP-35, and Vistal are shown in Figure 7. There was considerable scatter of the data; data points are not included in the plots, and "best lines" through the data points have been drawn. Two concentration scales are used, one for the MERDI alumina, and the other for the AP-35 and the Vistal. It should be noted that diffusion of CaO into the MERDI alumina was extensive, ranging on the order of 14 percent at the interface down to about eight percent near the center. For the AP-35, the diffusion of CaO was considerably less; the concentration at the surface was about 1.8 percent, which tailed off rapidly to a constant value of about 0.1 percent. For Vistal (in this same figure), there appears to have been very little diffusion of the CaO ; most measured concentrations were only slightly above background readings.

Similar concentration profiles were obtained for the diffusion of SiO_2 and Fe_2O_3 in these three materials, which are contained in a previous report.³ The SiO_2 profile is shifted to higher concentrations for both the MERDI alumina and AP-35, inasmuch as the SiO_2 content in the slag is greater than the CaO content. For Fe_2O_3 , the profile drops to lower concentrations since its content in the slag was below that of the CaO .

Diffusion of the slag species into sapphire, Vistal, and Lucalox (the fully dense materials) was minimal with respect to the MERDI alumina and the AP-35. It was decided to make a comparison of the diffusion of the impurity slag species into these three fully dense materials. The average concentrations of SiO_2 , CaO , and Fe_2O_3 were computer from all of the measurements which were taken into the specimen up to 2.5mm from the slag-specimen interface. These data are presented in Table IV. Because most of the measured values were very close to the background counting level, they might lead to uncertainties in these results. At any rate, the concentrations of all of these constituents are 0.05 weight percent or less, and it appears that there is not a significant difference in the concentration of any one constituent among the three aluminas. Calcium oxide may exist in a higher concentration in the Vistal than in either sapphire or Lucalox.

The measured SiO_2 impurity content for the pristine materials in Table II is suspect in light of the microprobe data for the corroded materials (Table IV). For the sapphire, Lucalox, and

of slag species decreases since the volume fraction of slag decreases. The presence of this entrained slag accounts for the discoloration of the transverse section as described above.

From Figure 8, it appears that (for some reason) the grain boundaries of the MERDI alumina are extremely susceptible to slag attack since the outer grains are surrounded completely by slag. Also, these grains are much larger than those in the pristine material (compare Figure 8 to Figure 4). Apparently, there is a dissolution-exsolution process in operation in which small grains go into solution in the slag and the larger particles grow by the exsolution of alumina because of the localized excess of this constituent in the slag in the vicinity of the grains. It is difficult to explain why this material experiences less corrosion than the dense materials. This proposed dissolution-exsolution process is operative; it might retard the movement of the slag-specimen interface.

Since this corroded material is highly penetrated with slag, its mechanical stability would be expected to be very poor. Whether or not this is the case will be revealed by the high-temperature corrosion-creep tests which are scheduled to be carried out in the near future. If its mechanical properties are found to be lacking, this MERDI refractory will be an unsuitable preheater material.

A photomicrograph of the edge of an AP-35 specimen which also was corroded for eight hours in unseeded slag at 1550°C in air is shown in Figure 9 (microhardness indentations which are shown in the micrograph served as markers for the microprobe analyses). The outer slag layer (at the right of the micrograph) again appears darker than the undissolved material. For this AP-35, there is very limited observable penetration of slag into the regions around the grains at the slag-specimen interface. This may be contrasted to the MERDI alumina (Figure 9) for which there was extensive penetration and dissolution of the grains near the interface. The MERDI alumina has a higher density than the AP-35 but a smaller grain size (Table I). For some reason, the grain boundaries of the AP-35 seem to be more resistant to attack by the slag. From Figure 9, it appears that the texture of the specimen near the interface is different than the interior regions. This probably is due to some penetration of slag around the grains and diffusion of the slag into them. The actual corrosion or dissolution process appears to be confined to the region at or very near to the slag-specimen interface.

The corrosion interfaces of several of the dense and polycrystalline alumina materials (Vistal and Lucalox) have been examined for possible indications as to corrosion processes. There is a very sharp and distinct boundary between the slag and the uncorroded specimen, indicating that there is virtually no penetration of the grain boundaries. Figure 10 shows a micrograph of the edge of a Lucalox specimen which was corroded using the rotating rod technique. The specimen has been polished and thermally etched.

Vistal, the emission spectrographic concentrations for SiO_2 are from four to eight times greater than the impurity levels in the corroded materials. It is highly unlikely that there would be out-diffusion of SiO_2 in this slag environment.

When the corrosion and diffusion data are compared for the five alumina materials which did not fail (Table IV and Figures 5 and 7), it is evident that there really is no consistency between corrosion and diffusion. For example, the MERDI and AP-35 aluminas experienced less corrosion than did the other materials (Figure 5) and yet had far greater penetration and diffusion of the slag constituents (Figure 7). Those materials with the larger grain sizes and the least porosity suffered the greatest corrosion (Figure 5 and Table I). On the basis of the corrosion results on the AH-199B, one would expect the opposite behavior (i.e., more penetration and corrosion of smaller grained and more porous materials).

The microstructure of a corroded MERDI specimen was examined to gain some insight regarding the mechanisms by which corrosion occurred. Figure 8 is a photomicrograph of the edge of a specimen which was corroded in unseeded slag for eight hours in air; a portion of the bakelite mount is shown at the extreme right. Two different phases are evident in this micrograph a dark gray one that has been identified by microprobe analyses as slag and a lighter phase which is undissolved alumina. There also is an adherent slag layer which is much thinner on this specimen than on the other alumina materials which were corroded under identical conditions. The compositions of the slag constituents for this outer layer, as well as slag which entrained between the alumina grains in this micrograph, are tabulated in Table V. These averages were taken from five measurements each, and there appears to be very little variation in the composition of the two. There is an increase in the alumina content of the slag (which was originally 25 weight percent) which is a result of the dissolution of the specimen. The concentrations of SiO_2 , CaO , and Fe_2O_3 in several of the alumina grains in this micrograph also are presented in Table V. Comparison of these values with values measured by emission spectrographic analyses on the pristine material (Table II) indicates that there has been substantial diffusion of the slag species into the grains. It appears that corrosion occurs in this material by penetration of the slag along grain boundaries and pores and then by dissolution of the individual grains.

In Figure 8, it may be observed that the undissolved grains are smaller at the interface and the size of the grains increases in moving away from the interface. This probably is because these surface grains have been exposed to the slag and have experienced dissolution for a longer time than those which are removed from the interface. Also, the relative fraction of entrained slag decreases in moving to the interior of the specimen. This explains the concentration profile in Figure 7; the outer surface essentially is pure slag; and in moving away from the interface, the concentration

The sample was corroded at 1550°C in air for 92 hours and in a slag of different composition which was seeded with 20 percent K_2SO_4 . It should be noted that there is no evidence of slag penetration along the grain boundaries at the interface and that corrosion appears to occur uniformly across the exposed grain faces. Examinations have not been made on specimens which were corroded using the dipping technique; however, similar results would be expected.

The influence of K_2SO_4 seed, atmosphere, and temperature on corrosion have been examined for several of the alumina materials. Figure 11 shows corrosion data for sapphire at 1550°C in air, in both seeded and unseeded slag, and in the unseeded slag in the combustion atmosphere. The corrosion rate (the slope of each line segment in the figure) appears to decrease because of the presence of the seed in the slag for the tests made in air, even though the amount of corrosion is enhanced in the seed for short corrosion times. On the basis of the single data point for the test made in the simulated combustion atmosphere in the unseeded slag, it appears that this material might be slightly more susceptible to corrosion in air at short corrosion times.

Figure 12 presents data for the Vistal at 1550°C for seeded and unseeded slags in both air and the simulated combustion atmosphere. From these data, it appears that the corrosion rate is enhanced in both atmospheres when 15 percent K_2SO_4 is added. Also, in seeded and unseeded slags, the corrosion rate is approximately the same in both atmospheres, but the overall total corrosion is lower in the simulated combustion atmosphere. For the sapphire material (Figure 11), the presence of the same concentration of K_2SO_4 decreased the rate of corrosion in air, which is just opposite to the behavior for the Vistal. The main differences between these two materials is the presence of grain boundaries and a higher concentration of MgO in the Vistal. It is not possible at this time to make a correlation between this disparity in corrosion behavior and the differences in character of Vistal and sapphire. Also, for both of these materials, the volume percent corrosion appears to be slightly lower in the combustion atmosphere.

The influence of seed on the corrosion behavior of AP-35 alumina is shown in Figure 13. It appears that the corrosion rate is virtually unaffected by the addition of K_2SO_4 --the slopes of the line segments between six and eight hours are about the same for both seeded and unseeded slags. However, the total volume percent corrosion is greater when the K_2SO_4 is added. For Vistal, the total corrosion also was increased by the addition of the seed.

Figure 14 shows how the corrosion behavior of Vistal and AP-35 depend upon temperature for an unseeded slag in an air atmosphere. Data for Vistal is at 1500°C and 1550°C; while for the AP-35, it is at 1550°C and 1600°C. For both materials, it should be noted how the corrosion rate (or line segment slope) increases with increasing temperature. Also, as expected, at some specific time, the volume percent corrosion is greater at the higher temperature.

Other results from the microprobe investigations have shed light on the corrosion processes. The influence of time on the concentration profiles of the slag species also was examined. Figure 15 shows data points for the concentration of CaO as a function of distance from the slag-specimen interface for AP-35 specimens which were corroded in the unseeded slag at 1550°C in air for time periods of both four and eight hours. There is considerable scatter in the data (especially for the four-hour test); however, the two sets of data points coincide fairly well with one another, and a best line has been drawn through both. Similar results were obtained for the diffusion of SiO₂ and Fe₂O₃ for the two tests. This indicates that the diffusion concentration profile in front of the moving slag-specimen interface for AP-35 is independent of time, at least for small and moderate amounts of corrosion.

Microprobe analyses were made to ascertain whether or not the ambient atmosphere influences the rate of diffusion of any slag species into the aluminas. Two Vistal samples were corroded in an unseeded slag for eight hours at 1550°C; one in air and the other in the simulated combustion atmosphere. After the analyses, it appeared that there was no difference in diffusion for the CaO and Fe₂O₃. However, the SiO₂ seemed to diffuse more rapidly in the combustion atmosphere, as shown in the concentration profile in Figure 16.

It was decided to examine a specimen which had been corroded by dipping to see if the diffusion rate of slag species in a radial direction was dependent on longitudinal position. A Vistal sample was corroded at 1550°C in slag plus 15 percent K₂SO₄ and in air for six hours. Transverse sections then were cut from three different positions: near the upper-most corroded region; at the center of the sample section which was alternately dipped into and out of the slag-seed; and from that region which always was immersed fully. The results of the microprobe analyses are shown in Table VI for the SiO₂, CaO, Fe₂O₃, and K₂O. Compositions are average values taken up to 2.5mm into the specimen. Diffusion of the four constituents does not appear dependent on the longitudinal position in this material. Again, the concentrations are very low and barely above the background level.

A slag-seed layer remained intact on the surface of this same Vistal specimen after removal from the molten bath and upon cooling down after the conclusion of the corrosion test. Its thickness ranged between about 100 and 150 microns. Concentration profiles of this layer were measured using the electron microprobe for specimens taken from the same three longitudinal positions as described above. No concentration gradients were observed across the layers. Average values were computed for upper, center, and lower regions, which are tabulated in Table VII; measurements were taken at ten micron intervals. These results at the three different longitudinal positions are very close to one another and near to the expected bulk slag composition after some corrosion has occurred.

Adherent slag layers were present on the sapphire, Lucalox, Vistal, MERDI, and AP-35 materials which were corroded in the unseeded slag at 1550°C in air for eight hours. These layers varied in thickness from about 50 to 150 microns. Concentration profiles were measured across these slag layers for all but the MERDI alumina; no gradients were observed. Average values of compositions of the slag species were computed; Table VIII lists the computed compositions, along with the intended composition of the slag prior to corrosion. As expected, the alumina content was greater in all cases than the intended compositions since it is the corrosion product. There were attendant decreases in concentrations of SiO_2 , CaO , and Fe_2O_3 , which values were remarkably close to one another for the four materials corroded. The Fe_2O_3 concentration is considerably lower in the slag layer on the sapphire than on the other three aluminas.

It was felt that chemical analyses were necessary of both the pre- and post-corroded slags and slag-seeds to determine if the compositions were close to what was intended and also to measure the alteration of the compositions by corrosion products. These tests are difficult to make with a high degree of accuracy; therefore, one slag-seed specimen was sent to four different laboratories for analysis. The results were included in a previous report⁴ and will not be presented here. There were moderate variations in the analyses made by the different laboratories and also some deviations from the intended composition. A number of chemical analyses have been made for both pre- and post-corrosion slags by one of these laboratories.

A chemical analysis was made on an unseeded slag in which a Vistal sample was corroded for eight hours at 1550°C in air; this specimen experienced about 52 volume percent corrosion. In addition, a microprobe analysis was made on the residual slag layer, and the alteration of the composition of the slag bath was computed from the volume of alumina corroded, as measured from an enlarged photograph of the corroded specimen. These results are presented in Table IX for the three different techniques. There are some variations of the concentrations of the slag components. The intended concentration of alumina was 25 percent; it is unlikely that its concentration would be increased by only 0.8 percent, as measured by the chemical analysis. On the basis of this and other chemical analyses, some doubt is cast as to the validity of the compositions which are measured by this technique. Although no concentration gradients were measured across the slag layer which adhered to this specimen, it is possible that this layer might be different in composition than the bulk slag. The concentration as measured from the photograph of the corroded specimen is either intermediate between the other two analyses or close to values as measured at the interface by the microprobe. It is felt that either of these two latter techniques is more reliable than the chemical analyses.

The influence on corrosion of the alteration of slag composition by corrosion products has been investigated on the Vistal. The tests were performed by immersing a pristine sample in a slag for six hours, removing the sample, and then corroding another pristine sample of the same material in this slag which had been altered in composition by corrosion products from the first specimen. This procedure was repeated three more times using the same slag and a new pristine sample each time; then, the volume percent corrosion of each specimen was compared. The data is tabulated in Table X for this alumina; it should be noted that the volume percent corrosion decreased as the concentration of the alumina in the slag increased. For the fresh slag, a specimen experienced 32.2 volume percent corrosion during a six hour exposure to 1550°C. This corrosion dropped to 19.9 percent after the slag had corroded the alumina materials for 18 hours.

Corrosion runs were attempted on single crystal MgO specimens, but none were successful. After corrosion and upon removal from the furnace, the specimens experienced extensive fracture probably as a result of thermal stresses which were set up due to severe temperature gradients. The fractures appeared to be cleavage ones. Also, the specimen may have experienced preferential corrosion across certain crystallographic planes as evidenced by the corrosion shape.

A few corrosion tests were performed on a polycrystalline MgO material which had a density approximately 97 percent of theoretical and a small grain size* (density and grain size measurements have not been made). For the dipping tests, the material was highly susceptible to corrosion in the slag. One specimen which was corroded at 1500°C for four hours in the unseeded slag and air experienced 60.4 volume percent corrosion; this is a high degree of corrosion for four hours at this temperature. Figure 17 is a photomicrograph which shows the outer slag-specimen interface for this corroded specimen. There appears to be only a very thin rim which probably is some type of reaction layer (at the lower right of the micrograph), since it appears different than the specimen material and is penetrated with the slag which has a dark gray color. This outer reaction slag layer easily flaked off of the surface at some regions of the specimen. X-ray diffraction analyses revealed that this material (probably the reaction layer) is magnesia-alumina spinel.

Investigators at Westinghouse have found polycrystalline MgO to be very corrosion resistant in static tests; in fact, they use this material for their electrochemical corrosion test cells.⁵ They observe a magnesia-alumina spinel layer which was formed at the slag-specimen interface as a result of a reaction between the

*Fabricated by Trans-Tech, Incorporated, Gaithersburg, Maryland.

magnesia sample and the alumina in the slag. Apparently, this layer acts to protect the magnesia and slow down the corrosion reaction. For our dipping tests, this layer is relatively thin (Figure 17) and not very adherent to the surface.

A static corrosion test was performed with the same experimental conditions as the dipping one (at 1500°C for four hours in unseeded slag in air). Corrosion at the slag-air interface was excessive, and the diameter of the remainder of the submerged specimen was uniform. There was very little corrosion in this region; a volume percent corrosion of about 17 percent was computed on the basis of the original and corroded diameters, which is substantially less than for the dynamically tested material (60.4 volume percent).

A photomicrograph at the slag-specimen interface is shown in Figure 18. The dark gray region on the right is a residual slag layer which was very adherent to the specimen surface. A reaction layer also is present just inside the slag layer which appears to be penetrated by the slag; its thickness is on the order of 300 microns; and there is a very sharp and distinct interface between it and the light-colored magnesia specimen. Microprobe analyses confirmed that the dark gray region (to the right of the reaction layer) and light regions (to the left of the reaction layer) were slag and magnesia, respectively. Similar analyses were made for Fe_2O_3 , SiO_2 , CaO , Al_2O_3 , and MgO on both light and dark areas in the reaction layer. Because there was considerable scatter in the data, only the qualitative results will be presented. The dark regions undoubtedly are areas of slag; the concentration of MgO is high (averaging about 20 percent) since it is a corrosion product. Concentrations of other species are on the order of what would be expected in a corrosion slag. For the light regions, the concentrations of SiO_2 and CaO are much lower than for the slag (both ranging between one and ten percent); whereas, the Fe_2O_3 and Al_2O_3 contents are high. The average Fe_2O_3 concentration is about 12 percent; for Al_2O_3 , it is almost 50 percent. On the basis of these and the X-ray analyses of the outer corrosion layer for the dynamically tested specimen, it is felt that this reaction layer contains magnesia-alumina spinel grains which form as a result of a reaction between the magnesia sample material and the Al_2O_3 and Fe_2O_3 in the slag; these grains have been penetrated by the slag in this reaction layer.

Concentration profiles were measured with the microprobe for the slag species in both the statically and dynamically tested specimens beginning just inside the reaction layer and working toward the center of the sample, a distance of about 3mm. Distinct diffusion profiles were not discernable, so average concentrations of slag species were measured; these are presented in Table XI. It appears that the average compositions of both SiO_2 and Al_2O_3 are moderately higher in the specimen which was corroded using the dipping test.

Therefore, for magnesia, the amount of corrosion, the nature of the interface at the slag-specimen boundary, and the rate of diffusion of slag species into the material depend on the nature of the motion of the slag at the interface. For minimal fluid flow, a magnesia-alumina spinel layer forms which probably aids in reducing the corrosion rate and also the diffusion of SiO_2 and Al_2O_3 .

A concentration profile was measured for the residual slag layer for the specimen which was corroded statically, and there was a variation of MgO with position. This is illustrated in Figure 19 which is a plot of concentration of MgO as a function of distance away from the interface into the slag. The concentration near the interface was about four percent; at a position between 200 and 250 microns into the slag, the concentration increased abruptly to about 11 percent. This indicates that for some reason the MgO corrosion product in the slag concentrated away from the interface between the slag and the specimen.

Magnesia-alumina spinel is another type of material which has been tested. Three different spinel materials have been examined: single crystals and two polycrystalline and high density spinels, one stoichiometric in composition and the other containing an excess of magnesia (65 and 35 mole percents of magnesia and alumina, respectively). Since the latter material contains an excess of magnesia, it is composed of two phases, periclase and spinel. These materials were prepared by the MERDI Applied Research Division and are reported to be approximately 98 percent of theoretical density.⁶ The average grain size of the stoichiometric material is about 25 microns; for the 65 to 35 spinel, the average grain size of both phases is on the order of ten microns.

Figure 20 shows the corrosion behavior of these three materials as volume percent corrosion versus corrosion time between two and eight hours; the other experimental conditions were 1550°C in air using an unseeded slag. From these data, it appears that the single crystal material has the highest corrosion rate, yet the least amount of total corrosion. The polycrystalline and magnesia-rich materials are next in resistance to corrosion, followed by the other stoichiometric spinel. These materials as a group are not as resistant to corrosion as the aluminas under the same experimental conditions (compare Figures 20 and 5).

Samples of both polycrystalline materials which were corroded for four hours were sectioned in a radial direction and subsequently polished in preparation for microstructural and microprobe analyses. The diameters were approximately 1 cm each, and the outer 1 mm rim on the 65 to 35 specimen was discolored, indicating penetration of slag into the material. Electron microprobe analyses then were conducted, and concentration profiles for Fe_2O_3 are shown for both in Figure 21. A normal diffusion profile results for the 65 to 35 spinel, which is indicated by the solid curve that has been drawn through the data points. At the surface, the Fe_2O_3 concentration is approximately four percent (very near

to that in the slag) which decreases rapidly down to a constant value of about 0.05 percent at a distance of 2mm into the specimen. Similar profiles were obtained for both SiO_2 and CaO in this material. Thus, the discoloration of this specimen around the outer edge is most probably a result of the relatively high concentrations of slag constituents in this region.

For the stoichiometric material, there is relatively little diffusion of Fe_2O_3 (as well as SiO_2 and CaO), as is also shown in Figure 21. The concentration of Fe_2O_3 is virtually independent of position within the specimen, averaging about 0.04 percent for the outer 3mm. Average concentrations for SiO_2 and CaO were approximately 0.8 percent and 0.5 percent, respectively. Therefore, even though the 65 to 35 spinel experiences less net corrosion than the stoichiometric material, diffusion and penetration of slag species is much greater, especially for the outer 2mm of the specimen. This same phenomenon was observed for the MERDI and AP-35 aluminas, as discussed above.

The microstructures of these same two corroded specimens then were examined. A photomicrograph of the outer edge of the corroded 65 to 35 spinel is shown in Figure 22. It is evident that there is no slag layer present and that the microstructure consists of both light and dark regions. In moving from this outer edge in a radial direction into the center of the specimen, this microstructure exists for approximately the outer 2mm, and then there is an abrupt change to just the lighter areas and pores.

Point microprobe analyses were made of both the light and dark areas with some significant scatter in the measured concentrations. There were, however, substantial compositional differences for these different regions, as is shown in Table XII. The dark areas apparently are a slag phase which contains MgO and probably some alumina as corrosion products. Since the light regions primarily are composed of alumina and magnesia, they probably are spinel grains. The composition given in the table is very close to that for the stoichiometric spinel; some of the Fe_2O_3 from the slag probably got into the solid solution in the spinel, which would account for the relatively high content of this constituent. Since this material originally contained two phases (periclase and spinel) and after corrosion there is no evidence of the periclase at regions where there had been slag penetration, it is likely that there had been selective corrosion of this phase. This seems reasonable since (as is shown above) MgO is highly susceptible to corrosion. The slag had penetrated into regions where this phase existed, and there undoubtedly had been some exsolution of the spinel by a high degree of saturation of both Al_2O_3 and MgO in the slag. This was reported as the mechanism of corrosion for a commercial magnesia-chrome material which contained both periclase and complex spinel phases.³

The microstructure of the corroded stoichiometric but polycrystalline spinel also was examined. A slag layer about 60 microns thick was present, and yet the slag-specimen boundary was very

distinct. There was no observable penetration of the slag into any of the sample. A micrograph is not included, but the microstructure is very similar to that for the corroded AP-35 alumina which is shown in Figure 9.

These results concerning corrosion behavior, corrosion microstructures, and diffusion and penetration of slag species are analogous to those for the MERDI and AP-35 aluminas. Even though a material might not experience substantial corrosion, there can be extensive penetration of the slag into the interior through pores by grain boundary attack and/or selective corrosion of one phase if two are present. This high degree of penetration is reflected by a discoloration of the outer rim of the specimen. These materials probably will experience corrosion failure prior to those which do not suffer penetration even though the measured corrosion amounts for short times are similar. The high-temperature creep properties of these penetrated materials would be expected to be inferior to those which do not suffer penetration.

When concentrations were measured across the outer slag layer for the MERDI stoichiometric spinel, a gradient was found to exist for MgO (but none of the slag species). This is shown in Figure 23, where it should be noted that the MgO decreases from a concentration of about 4.7 percent at the interface down to about 3.7 percent at the outside of the layer. Apparently, the MgO which is dissolved in the slag prefers to locate itself near the slag-specimen interface. Just the opposite behavior was observed for the corrosion of magnesia (Figure 19).

The influence of both seed and atmosphere were examined for some of the spinel materials. Figure 24 shows the influence of the addition of 15 percent K_2SO_4 on the corrosion behavior of both single crystal and MERDI stoichiometric spinels at 1550°C in air. For the single crystal material and on the basis of a single data point, the presence of seed appears to enhance the corrosion. Just the opposite affect is observed for the MERDI material, i.e., a decrease in corrosion with the addition of the seed.

A single data point is included for a commercial spinel (stoichiometric) which is manufactured by Norton Company. It failed after a four-hour test and probably experienced at least 80 percent corrosion. The microstructure is similar to that for the AH-199B alumina, i.e., very large particles which are surrounded by pores and a matrix of smaller particles. The small particles in this spinel probably are on an order of magnitude larger than those in the AH-199B.

Figure 25 presents data for single crystal and MERDI spinels and shows the influence on corrosion of combustion atmosphere at 1550°C in the unseeded slag. For the single crystal material, corrosion appears to be greater in the simulated combustion atmosphere than in air. The combustion atmosphere evidently decreases corrosion for the MERDI material. It is not known why both the

presence of seed and the simulated combustion atmosphere enhances the corrosion of the single crystals and decreases the corrosion of the polycrystalline material.

Corrosion tests have been conducted on a number of commercially available refractory materials, some of which exhibit much better resistance to corrosion than the materials previously discussed. Table XIII lists the phases present, fabrication method, and apparent porosity for four of these materials, all of which are designated by their trade names. All contain Cr_2O_3 (ranging between ten and 78 percent) and in addition have two phases present.

In Figure 26, volume percent corrosion is plotted versus time for these four materials; tests were conducted in unseeded slag at 1550°C in air. It is important to note that the time scale runs up to 100 hours, whereas for materials discussed above, the maximum corrosion time in tests at 1550°C was ten hours. Comparison of Figures 26 and 5 shows that all of these commercial materials are superior to the aluminas with respect to their ability to resist corrosion. For example, the Monofrax E sustained less than 20 volume percent corrosion after a 72-hour exposure to the slag. The aluminas in Figure 5 corroded approximately this same amount after three to six hours of exposure to this same slag at the same temperature.

The Ruby and RFG appear to be comparable in their corrosion susceptibility, followed by the Monofrax K-3 and, finally, Monofrax E. It might be inferred from the corrosion behavior (Figure 26) and the material's characteristics (Table XIII) that the corrosion behavior depends on the apparent porosity and the chromia content. Monofrax E has a very high concentration of Cr_2O_3 (78 percent), a moderately low apparent porosity (five percent), and is the most corrosion resistant. The Ruby and RFG have much lower Cr_2O_3 concentrations and higher porosities and are more susceptible to corrosion.

Extensive microstructural studies have been conducted only on the RFG material, the results of which were reported previously.³ Very briefly, the results of the investigation led to the conclusion that slag-seed penetration into the pore regions is very rapid and that the periclase is much more susceptible to corrosion than the spinel phase.

Microstructural changes and slag penetration occur even in these commercial materials which are very resistant to corrosion. Figure 27 shows a micrograph of the pristine Monofrax E; the two different phases have not been distinguished yet (one is spinel, the other is corundum). Figure 28 shows a micrograph taken at the center of a section of the same material which was corroded for 72 hours. The white and light gray phases are still present: in addition, there also is a darker gray phase which undoubtedly is slag which has penetrated into the center of the specimen. It also appears to be attacking some of the lighter grains along their boundaries.

The presence of the potassium seed appears to increase both the corrosion rate and the total amounts of corrosion for Monofrax E and K-3 and the RFG. This is demonstrated in Figure 29, and it is evident that this influence is appreciable for both Monofraxes. It is not known why this is the case

The combustion atmosphere and the combination of the presence of seed and the combustion atmosphere affect the corrosion behavior of Monofrax E and K-3. Tables XIV and XV contain data (some of which is extrapolated) which indicates the direction of influence of these two experimental parameters for Monofrax E and K-3, respectively; data is for a single time. As described above, the presence of seed in air serves to enhance corrosion of both materials. The combustion atmosphere in the unseeded slag causes a very dramatic decrease in corrosion. For Monofrax E, the combined combustion atmosphere and seed serve to decrease corrosion even further (only six volume percent corrosion is experienced after 72 hours at 1550°C). This trend appears to be reversed for the Monofrax K-3; corrosion increases dramatically from either unseeded slag in air or seeded slag in the combustion atmosphere.

On the basis of this rather scant data, it is difficult to explain the above results. If the corrosion resistance of these commercial materials is indeed a result of the presence of Cr_2O_3 , then a possible explanation for the reduction in corrosion in going from air to the combustion atmosphere may be offered. Chromium can be very volatile in certain oxidation states, as discussed in Reference 7. The oxidation state, in turn, depends upon the ambient oxygen partial pressure. Thus, it is possible to have some loss of Cr in a chrome-containing refractory due to the volatilization which is dependent on the oxygen partial pressure. Reference 7 points out that, as the oxygen pressure is lowered, the vapor pressure of Cr decreases.

Significant Cr losses have been observed in some refractory materials after lengthy exposures at elevated temperatures.⁸ It is possible that Cr losses experienced by these Monofrax chrome spinels would be less in the simulated combustion atmosphere with a relatively low oxygen partial pressure than in air. If corrosion resistance is dependent upon the amount of Cr present in the refractory, this would explain the dependence of corrosion on atmosphere. We have observed evidence of the volatilization of Cr in our high-temperature corrosion furnaces; the alumina interior furnace parts take on a pinkish tinge after a test on a chrome-containing refractory.

Slag-seed corrosion tests have been conducted on a variety of ceramic materials in a prototype preheater by Fluidyne Corporation. Details of the test rig are described in Reference 9. Tests were made using both gas and air cycles. The gas cycle was at a temperature of about 1700°C with a cycle time of 30 minutes; for the air cycle, temperature and time were 1450°C for 15 minutes, respectively. Total test times ranged between five and 200 hours.

The slag-seed used was a mixture of about 95 percent K_2SO_4 and five percent ash from the combustion of a Rosebud coal; thus, their slag-seed is much richer in K_2SO_4 than is ours (which contains only 15 percent). The conditions of exposure to the molten slag-seeds between the two tests probably were different. For their tests, the slag was brought into contact with the refractory either as fine liquid droplets entrained in a fast-moving gas or by fluid flow over the refractory surface. Our specimens were completely immersed in the slag bath for a portion of the cycle, and a slag layer was caused to flow over the surface for the remainder of the cycle.

Although quantitative measurements of corrosion were not made by the FluidDyne investigators, they observed a lower degree of corrosion than we did for the same material at comparable corrosion times and temperatures.⁸

It was decided to take some of the same materials which have been corrosion tested in both of these investigations, rank them as to their relative resistances to corrosion, and then make a comparison of the two. This is presented in Table XVI from the most to the least corrosion resistant of the several materials for the two investigations. Included in FluidDyne's ranking list is X-317, a commercial refractory which contains both magnesia-alumina spinel and periclase phases and is fabricated by fusion casting. X-317 and Lucalox are the most resistant of the materials that FluidDyne examined.

There are some differences between these two ranking lists. From FluidDyne's tests, the spinels are near the top (including the dense alumina, Lucalox), followed by chrome-containing Monofrax materials, RFG and Ruby; and finally, at the bottom of the list, the AH-199B alumina. We have found the chrome-containing materials to exhibit the best corrosion resistance, followed by the aluminas, then the spinels, magnesia, and finally, AH-199B. This is most probably a consequence of differences in the testing techniques, slag-seed composition, and/or the exposure conditions including the influence of atmosphere.

2. Creep Tests

a. Design of apparatus

Basically, the design of the creep apparatus is centered around a system that applies a constant compressive load to a vertically held specimen. All constant stress levels, furnace temperatures, and data acquisitions will be controlled by a microprocessor control system that has been interfaced to various components.

A general diagram of the specimen loading system is shown in Figure 30. As shown in the schematic, the specimen will be held vertically between sapphire platens that have been placed upon 998 alumina disk. Since platinum is relatively soft at

these high temperatures, a thin sheet of it will be placed between the specimen and the platens to act as a lubricant for the expansion of the sample faces and to help maintain a uni-axial stress. Strains will be measured with linear variable differential transformers (LVDT's) that are connected to the sample expansion region by sapphire push rods. Sapphire was chosen for the rods and platens because the material 1) withstands corrosion of residual slag left on the sample by pre-corrosion, 2) provides necessary lubrication to the specimen faces as they expand under a compressive load, 3) possesses an extremely low creep rate at test temperatures, and 4) may be purchased with reasonable cost and availability.

Rams made from castable alumina will transmit the load to the specimen. Caps of 998 alumina then will be fired to the hot ends of the rams to provide protection to the ram itself and to the data acquisition system. Steel ram holders will be water-cooled to protect the electronics of the system (the LVDT's and the load cell) from excessive furnace heat that could disrupt data collection.

The position of the furnace that surrounds the specimen also is shown in Figure 30. Furnace heating will be provided by Kanthal Super 33 MoSi_2 elements. To facilitate experimental operation of the system, the furnace is designed to open into two separate pieces; each half containing two heating elements. The two portions will open and close by means of a mechanical device that draws the parts together or pulls them apart.

As seen in Figure 31, the compressive load to the apparatus will be supplied from a microprocessor-controlled hydraulic system. The load cell that is attached to the ram holder will measure (BCD output) the load applied from the hydraulic system to the specimen. Loading must be applied to maintain a constant stress level. This will be accomplished via a stepping motor/weight/hydraulic cylinder section which again is interfaced to the microprocessor.

Much of the construction work during this past year in the creep equipment has been devoted to the microprocessor control system. The microprocessor that was purchased is a Cromenco Z2-D with a Z-80 central processing unit (CPU), a 48K RAM (random access memory), and S-100 bus, and a dual 5 inch (81K) disk drive system. A schematic of the electronics of the Z2-D is shown in Figure 32. The figure also shows the arrangement of the graphic boards, serial and parallel ports, teletype and TV display, power supply, and interface network connections.

Figure 33 shows the interface network and mechanical arrangement of the system. The exact nature of the control network is shown. The following components are in the microprocessor control: 1) thermocouples; 2) LVDT's; 3) stepping

motors; 4) temperature controllers; 5) power supplies; 6) real-time clocks; and 7) load cells. Therefore, constant stress levels and temperature cycles are controlled automatically with software programs. A graphics component recently was added to the system that is capable of holding 16 different displays in memory simultaneously. Thus, all real-time experimental data will be displayed on a TV monitor and stored as the experiment continues. Real-time updated graphic displays also will be used.

Individual interface and designs are shown in Figures 34 through 40. All interface design and construction will be done by the task.

Software directories for the following systems are listed in Table XVII: 1) system setup, operation, disk control, and BASIC; 2) assembly language program writing; and 3) graphic display in BASIC, FORTRAN, and assembly language.

b. Experimental considerations

1) precorrosion

Since the initiation of our creep work, a large amount of time has been devoted to studying the feasibility of testing ceramic preheater materials in compressive creep and considering how creep will be influenced by 1) degree of slag penetration; 2) thermal cycling (in simulation of actual preheater heat-up and blow-down cycles); 3) stress magnitude; 4) temperature; and 5) atmosphere. Subsequent to this study, our task has design a compressive creep rig and has received permission to commence testing. Much time has been spent during this reporting period on setting experimental conditions that are vitally important to the actual procedure used in creep testing.

One of the most difficult experimental conditions to achieve will be the pre-corrosion of ceramic specimens in a manner suitable for creep testing. In a previous report,¹⁵ four alternatives were presented as possible solutions: 1) immerse the specimen in a slag bath while performing the creep test; 2) drip fresh slag onto the specimen while it is being creep-tested in a horizontal position; 3) drill a cylindrical hole along a portion of the length of the longitudinal axis of the cylindrical specimen (after filling the hole with powdered slag, the creep rate could be measured as the slag corrodes from the inside out); and 4) pre-corrode the specimen and then creep test it without any subsequent contact with the slag (samples could be pre-corroded to various degrees prior to creep tests). For reasons stated in that report, the last alternative was thought to be the best.

Since that time, many corrosion tests have been conducted on quite a few materials. Results obtained from microprobe studies on materials that had been corroded by dipping the specimen in and out of slag show that for most materials, the degree of slag penetration into the interior of the sample is not significant. From this viewpoint, it then is felt that pre-corroding a sample in slag would alter its mechanical properties very little. However, it should be noted that our corrosion tests have been dynamic in nature as directed by our work statements, and it could very well be that the dissolution of ceramic is more rapid than slag penetration; thus, we would expect to see only a small amount of slag penetration in front of rapid dissolution. We will conduct a series of tests during the assembly of the creep rig to determine the actual amount of slag penetration with time after static slag exposure.

Since the actual preheater will see conditions of slag exposure followed by periods of air flow, slag penetration tests will be conducted to simulate those conditions. Materials which are potential creep specimens will be placed into molten slag and held there for various times. After the exposure to slag, the specimen will be held at temperature (1550°C) for several more hours. The specimen then will be exposed to slag again followed by a period at temperature. Cycling will continue until a total time of 200 to 1,000 hours is reached. Slag and temperature air exposure times will be varied from run to run to determine fully the amount of slag penetration under given conditions. Some materials will not be exposed to slag after the initial treatment to study the effect of slag replenishment on the surface.

After the specimen undergoes testing, it will be examined for actual slag penetrations under these static conditions. Pending the outcome of these tests, a pre-corrosion procedure will be developed for samples to be creep-tested.

These tests also will provide another valuable piece of information. Since the specimens will be corroded with slag, there is a thin layer of slag that adheres to the specimen surface. If this layer flows from the specimen while being held at temperature, it also will do so while undergoing creep-testing. If this is the case, then this slag may cause a problem in the creep rig with regard to friction and corrosion of the sapphire platens and alumina disks used to hold the specimen in place. If this slag does cause a problem, the sample will have to be held horizontally in the creep furnace, and the creep apparatus will have to be modified. Problems also may be encountered by attempting to apply a compressive load horizontally.

2) materials

During the last quarter of this reporting period, an extensive amount of thought was given to the character of the materials to be tested under corrosion-creep conditions. According to Vasilos and Passmore,¹¹ the relationship between creep rate and test variables is given by

$$\dot{\epsilon} = \sum_0^N F_1(\sigma, T, S)$$

where σ is stress, T is temperature, and S describes the ceramic structure. They then remark that although S could include such parameters as porosity and substructure, it usually denotes only grain size. However, it is recognized that other structure factors, such as alloying affects, stoichiometric deviations, crystallographic structure, and porosity, alter creep rates depending on the mechanisms involved in that creep.

Since it is our task to evaluate potential MHD pre-heater materials with respect to corrosion-creep, it would be worthwhile to test the potential materials while investigating the effect of the above parameters. For example, the effect of grain size on creep rate is widely recognized and is vital in determining creep mechanisms; yet the work relating to its effect on creep really has been insufficient for most ceramic materials. Likewise, the effect of porosity on creep has been studied insufficiently for most ceramic materials.

Thus, we have contacted the MERDI Applied Research Division to product some polycrystalline alumina materials in which grain size is held constant and porosity is varied and in which porosity is held constant while grain size is varied. While we do recognize the limitations of testing these materials (since it is impossible to control exact grain boundary impurity concentrations and other such conditions), we also feel that these tests may give insight into grain size alterations on creep rates. Although these materials originally were to be used for the study of these effects on corrosion resistance, we feel that they may be very important to the creep study of MHD materials work itself. Similar studies are to be conducted on other materials.

Regarding stoichiometric deviations and alloying effects on creep rate, we hope to determine their effect by first testing a series of spinel materials which have been ordered from Trans-Tech. The compositions vary from stoichiometric magnesia-alumina spinel to compositions which have both excess alumina and excess magnesia.

The materials just described represent only a small portion of those materials that actually will be tested.

For example, we have on hand ceramics varying in porosity, grain size, and fabrication method for alumina materials. The percent theoretical density and average grain sizes for several pristine alumina materials has been listed in Table I. Impurity content measurements for those same materials is given in Table II.

We now are considering materials that would be potentially excellent preheater materials. One such material which was considered is a magnesia-chrome spinel. A study would be made with excess magnesia, stoichiometric spinel, and excess chromia in a manner similar to the magnesia-alumina spinel tests. A similar ternary material with the addition of Al or Fe also is being considered. However, before these materials will be ordered, the compositions will be selected on the basis of thermodynamic aspects (depending on the amount of thermodynamic data available for these ceramic binary and ternary systems).

Also on hand are several commercial refractory materials that have been obtained for corrosion studies. We have previously characterized these materials, and a creep study could be conducted on them as well.

Since the creep studies of materials should be as complete as possible, creep tests also will be made on pristine samples.

3) other

In a previous report,¹⁶ cyclic temperature ranges and anticipated stress levels (neglecting thermal stresses) for a regenerative preheater employing a brick checkwork were presented. Data were taken from Reference 10 assuming a linear variation of temperature with preheater height. Also given in that report was a tabulation of extrapolated stress values to produce a creep rate of $3 \times 10^{-10} \text{sec}^{-1}$ for fully dense and polycrystalline alumina of two different grain sizes. Although these stress levels and temperatures could be used for rough estimates of preheater conditions, it should be noted that they were based on experimental work that is now quite old (pre-1964).

Since Fluidyne Corporation now is engaged in preheater research and since they are running tests with a prototype preheater, better estimates of stress levels and anticipated temperatures for new preheater design could be obtained from them. Fluidyne has been contacted, and they have agreed to confer with our task on temperature and stress levels as well as cycle times. This conference will take place soon, and experimental creep stress levels and temperatures with corresponding stress levels for potential test materials then will be recalculated and presented in a later report.

Consideration as to the method of creep testing also has been given thought. After assembly of the creep apparatus, tests first will be conducted at a set constant stress level, and subsequent measurements of strain will be made. However, after that initial work is complete, tests will be conducted to ascertain the maximum allowable stress level for a given fixed creep rate.

C. Work Forecast

Except for studies pertaining to pre-corroding of samples for creep testing, no corrosion work on sample materials is planned. New work statements contained no mention of corrosion testing for periods after May 15, 1978.

Microstructural examinations of the new magnesia-alumina materials from Trans-Tech and the new polycrystalline alumina materials from the MERDI Applied Research Division will begin. Some Trans-Tech materials have arrived, and the other materials are expected shortly. All materials will be characterized with respect to grain size, open porosity, density, and phase identification using Optical, SEM-EDAX, and X-RAY techniques.

A new pre-corrosion technique will be developed to better serve the new creep equipment. Slag penetration tests will continue for potential test materials. Following these tests, microstructural examinations will be made.

Construction will continue on the creep apparatus. Some design modification might be necessary pending the outcome of slag flow and slag penetration tests on potential test materials. Unless unforeseen delays arise, equipment checkout should be completed within the next reporting period.

The interface boards for the microprocessor control system will be completed. Test programs checking these interface connections will be run and completed. Writing of the actual programs for system control and data storage will begin.

Stress levels for actual system operation will be computer for sample materials based on predictions of actual preheater conditions. Operational experimental conditions will be set and tested.

IV. CONCLUSIONS

The degree of corrosion experienced by ceramic refractory materials using the laboratory reciprocating dipping test probably is much less than would be experienced in an actual air preheater under similar conditions of temperature and atmosphere. Commercial refractories which contain chrome were found to be the most corrosion resistant of the various materials tested. Of other tested materials which were of high density and at least 99 percent pure, alumina materials were most corrosion resistant followed by magnesia-alumina spinels, and magnesia.

The shape of the surface of a corroded cylindrical specimen which has been corroded in a dynamic laboratory test depends on the manner in which the fluid flow is induced. Corrosion results from a dipping test are more reproducible than those from the rotating rod test.

From tests conducted on several alumina materials, the following may be concluded. A commercial alumina, which is about 80 percent dense and has a duplex grain structure of very large and small grains, experiences the greatest degree of corrosion. From microstructural analysis, it appears that the slag penetrates into the pore regions and dissolves the fine-grained matrix.

For the other aluminas, it appeared that the sapphire and fully dense, polycrystalline materials were slightly more susceptible to corrosion than the polycrystalline materials that were not fully dense (up to about 50 to 60 percent corrosion). The corrosion of sapphire appears to become relatively independent of time between eight and ten hours. For the MERDI alumina which is fine-grained and approximately 99 percent dense, there was extensive penetration of slag into the specimen as discerned by concentration profiles of slag species which were measured with the electron microprobe. Also, the slag appeared to penetrate along grain boundaries and completely entrain grains near the slag-specimen interface. A dissolution-exsolution phenomenon might have been operative since undissolved grains were larger than the original grains in the pristine material.

Another polycrystalline alumina (AP-35), which was approximately 93 percent dense with slightly larger grains than the MERDI material, exhibited considerably less diffusion and penetration of slag constituents as determined from microprobe and photomicrograph examinations.

There was very little diffusion of slag species into the sapphire and dense polycrystalline aluminas (Lucalox and Vistal), and there was no correlation between corrosion and diffusion of slag constituents into the refractory specimens. For sapphire, at relatively short corrosion times, the addition of K_2SO_4 seed appears to decrease the rate of corrosion slightly. The corrosion rate for a fully dense, polycrystalline alumina (Vistal) is slightly greater when 15 percent K_2SO_4 is added to the slag. This holds true in both air and simulated combustion atmospheres. For one of the polycrystalline materials that was not fully dense (AP-35), the K_2SO_4 seed enhanced the overall corrosion, but had virtually no influence on corrosion rate.

For polycrystalline materials, both total corrosion and corrosion rate increased with increasing temperature. Concentration profiles for slag species in the AP-35 polycrystalline alumina appear to be independent of time for moderate amounts of corrosion.

The diffusion rate of SiO_2 into the Vistal appears to be greater in the simulated combustion atmosphere than in air. There appeared to be an absence of concentration gradients across residual slag layers which adhered to corroded specimens. Alteration of the slag composition with corrosion products decreased the corrosiveness of the slag.

The following may be concluded from tests conducted on a fine-grained and almost fully dense magnesia material. The rate of corrosion is much greater when fluid flow is induced (using the dipping test) than when the test is a static one (natural convection only). For the dipping test, a very thin magnesia-alumina spinel layer that formed at the slag-specimen interface did not adhere well to the surface. A relatively thick reaction layer forms during the static test. It probably is a slag-penetrated magnesia-alumina spinel which adheres to the specimen and retards the corrosion process. The MgO in the residual slag layer of the statically corroded material segregated away from the slag-specimen interface.

For tests made on several different magnesia-alumina spinels (single crystal, polycrystalline and stoichiometric, and polycrystalline with excess magnesia), the following may be concluded. The corrosion rate is slightly greater for the single crystal material although overall corrosion is less than for the other two. The presence of K_2SO_4 seed served to enhance the corrosion rate of all three materials. In unseeded slag, the corrosion was lower in the combustion atmosphere than in air. The combined influence of combustion atmosphere and seed appeared to lower corrosion in one material and appreciably enhance the corrosion of another.

A ranking was made of the materials tested as to their resistance to corrosion; this was compared to results from prototype preheater tests performed by Fluidyne Corporation on the same materials. Some noted discrepancies may be explained by differences in experimental conditions.

There are no conclusions at this time concerning the corrosion-creep behavior of potential MHD preheater materials.

TABLE I.

A tabulation of percent of theoretical density and average grain size for several pristine alumina materials

Material	Percent Theoretical Density	Ave. Grain Size (Microns)
Sapphire	100	Single Crystal
Lucalox	100	22
Vista1	100	12
AP-35	92.8	5
MERDI	99.25	~1
AH-199B	79	250, <10

TABLE II.

A tabulation of the impurity levels in several pristine alumina materials (emission spectrographic analyses were performed at the Montana College of Mineral Science and Technology)

Material	Analysis Type*	IMPURITY CONTENT, WT. %					
		SiO ₂	MgO	Fe ₂ O ₃	CaO	Na ₂ O	Other
Sapphire	ES	0.22	0.002	0.017	0.001	0.006	0.01
Lucalox	ES	0.21	0.16	<0.001	<0.001	0.006	0.03
Vista1	ES	0.32	0.085	0.001	0.002	0.008	0.11
AP-35	ES	0.72	0.05	0.011	0.008	0.024	0.028
	Manuf.	0.7	0.07	0.07	0.03	0.05	0.08
MERDI	ES	0.58	0.017	0.006	0.003	0.003	0.013
AH-199B	ES	0.42	0.077	0.052	<0.001	0.007	0.06
	Manuf.	0.07	-	0.09	-	0.25	0.04

*ES = emission spectrographic

Manuf. = as given by the manufacturer

TABLE IIIa.

A tabulation of slag concentrations for a
AH-199B alumina specimen which was corroded for four hours at
1500°C in seeded slag and in air

Position*	AVE. COMPOSITION, WT. %					
	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	Total
Outer slag layer	35.6	34.3	20.6	4.2	8.5	103.2
Just inside of outer layer	27.2	43.8	21.5	3.6	6.9	103.0
Interior	30.3	32.2	17.3	2.6	6.5	100.0

*Positions of the slag which adhered to
or which was entrained within the sample

TABLE IIIb.

A tabulation of the slag impurity content in AH-199B
alumina grains corroded for four hours at 1500°C in a seed
slag and in air.

Position	AVE. COMPOSITION, WT. %			
	SiO ₂	CaO	Fe ₂ O ₃	K ₂ O
Near outer edge	0.019	0.049	0.032	0.032
Interior	<0.001	0.050	0.051	0.022

TABLE IV

A tabulation of average impurity content of slag impurities in three alumina materials corroded in an unseeded slag for eight hours at 1550°C and in air.

Material	AVE. COMPOSITION, WT. %*		
	SiO ₂	CaO	Fe ₂ O ₃
Sapphire	0.038	0.005	0.012
Lucalox	0.052	0.002	0.010
Vistal	0.046	0.034	0.019

*Averages were taken from values measured from the surface into the specimens a distance of 2.5mm using an electron microprobe

TABLE V

A tabulation of slag composition at two positions and of alumina grains in a MERDI alumina which was corroded at 1550°C for eight hours in an unseeded slag and in air.

Position	AVE. COMPOSITION, WT. %				
	SiO ₂	CaO	Fe ₂ O ₃	Al ₂ O ₃	Total
Outer slag layer	35.1	23.6	4.8	37.8	101.3
Entrained slag	34.8	24.6	5.1	37.9	102.4
Alumina gains	0.8	0.7	1.2	-	-

TABLE VI

A tabulation of the average impurity content at three different positions for Vistal which was corroded in seeded slag for six hours at 1550°C in air and using the dipping test

Position*	AVE. COMPOSITION, WT. %			
	SiO ₂	CaO	Fe ₂ O ₃	K ₂ O
Upper	0.066	0.023	0.011	0.009
Center	0.080	0.018	0.013	0.009
Lower	0.113	0.024	0.015	0.007

*The upper position corresponds to the upper slag-air interface; the center position is near the center of the region which cycled into and out of the bath; the lower specimen position always remained in the slag.

TABLE VII

A tabulation of the average composition at three different positions of the slag-seed layer which remained on the surface of the corroded specimen (corrosion conditions were 1550°C for six hours in air atmosphere and slag plus 15% K_2SO_4)

Position	AVE. COMPOSITION, WT. %			
	SiO ₂	CaO	Fe ₂ O ₃	K ₂ O
Upper	36.5	22.2	3.9	6.0
Center	38.1	20.6	4.1	6.8
Lower	34.4	21.6	4.0	6.1

TABLE VIII

A tabulation of the intended initial slag composition, and the compositions of slag layers remaining on several alumina materials corroded in unseeded slag for eight hours at 1550°C and in air

Alumina Sample Corroded	AVE. COMPOSITION, WT. %			
	SiO ₂	CaO	Fe ₂ O ₃	Al ₂ O ₃ *
Intended	45	25	5	25
Sapphire	39.3	20.8	2.0	37.9
Lucalox	39.6**	22.5	4.6**	33.3
Vista1	39.6	23.7	4.8	31.9
AP-35	37.7	22.5	4.6	35.2

*Obtained by subtracting sum of those other constituents tabulated from 100%

**Based on one data point only

TABLE IX

A tabulation of compositions of slag on
Vistal alumina after corrosion in an unseeded slag using
three different techniques (corrosion was for eight hours at
1550°C and in air)

Slag Component	AVE. COMPOSITION, WT. %		
	Chemical (Bulk)	Microprobe (Interface)	Corrosion Photo
SiO ₂	48.2	39.6	43.5
Al ₂ O ₃	25.8	31.8	27.5
CaO	19.4	23.7	24.2
Fe ₂ O ₃	7.0	4.8	4.8

TABLE X

A tabulation of data for the corrosion of Vistal showing how corrosion can be altered due to the accumulation of corrosion products (the corrosion test was performed at 1550°C in unseeded slag and in air)

Slag Corrosion Time Prior to Test (Hrs.)	0	6	12	18
Volume Percent Corrosion	32.2	25.4	22.5	19.9

TABLE XI

A tabulation of the slag impurity content in polycrystalline magnesia which was tested both statically and dynamically (dipping). (Both tests were made at 1500°C in an unseeded slag and in air):

Test Type	AVE. COMPOSITION, WT. %*			
	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃
Static	0.51	0.035	0.042	0.039
Dynamic	1.2	0.094	0.050	0.026

*Average composition measured a distance of 3mm from the slag-sample or sample-spinel interface

TABLE XII

A tabulation of the average compositions of the light and dark regions in the photomicrograph shown in Figure 22 for corroded MERDI 65-35 spinel

Sample Region	AVE. COMPOSITION, WT. %				
	SiO ₂	CaO	Fe ₂ O ₃	Al ₂ O ₃	MgO
Light Areas	1.1	0.84	2.1	66.8	29.2
Dark Areas	38.1	24.3	2.2	21.0	10.7

TABLE XIII

A tabulation of the characteristics for
four commercial refractory materials which have been
corrosion tested

Material	Composition* (Wt. %)	Phases Present	Fabrication Method	Porosity*
Monofrax E	Cr ₂ O ₃ - 78 Al ₂ O ₃ - 4 MgO - 9 Fe ₂ O ₃ - 8 Other - 1	Spinel, Corundum	Fused Cast	5
Monofrax K-3	Cr ₂ O ₃ - 27 Al ₂ O ₃ - 60 MgO - 6 Fe ₂ O ₃ - 4 Other - 3	Spinel, Corundum	Fused Cast	4
RFG	MgO - 56 Cr ₂ O ₃ - 20 Al ₂ O ₃ - 8 FeO - 11 Other - 5	Spinel, Periclase	Fused Grain, Cold Pressed, Sintered	14
Ruby	Al ₂ O ₃ - 90 Cr ₂ O ₃ - 10	Corundum, Chromia- Alumina Solid Soln.	Fused Grain, Cold Pressed, Sintered	16.5 to 19.5

*From Manufacturer

TABLE XIV

A tabulation of corrosion data showing the influence of seed, combustion atmosphere, and both seed and combustion atmosphere on the corrosion behavior of Monofrax E. (Corrosion was at 1550°C for 72 hours)

% K_2SO_4	Atmosphere	Vol. % Corrosion
0	Air	18.5
15	Air	32.0*
0	Combust.	9.5*
15	Combust.	6.0

*Interpolated values

TABLE XV

A tabulation of corrosion data showing the influence of seed, combustion atmosphere, and both seed and combustion atmosphere on the corrosion behavior of Monofrax K-3. (Corrosion was at 1550°C for 24 hours)

% K_2SO_4	Atmosphere	Vol. % Corrosion
0	Air	31.3
15	Air	34.7
0	Combust.	9.6 + 4.6
15	Combust.	59.0**

**Estimated from a data point taken at 72 hours

TABLE XVI

Rankings for the relative corrosion resistance
of several ceramic refractory materials which have
resulted from FluidDyne's and our corrosion tests

Relative Corrosion Resistance	FluidDyne Ranking (8)	Montana Tech Ranking
<p>Most Resistant</p> <p>↓</p> <p>Least Resistant</p>	<p>X-317</p> <p>Lucalox</p> <p>Magnesia-Alumina Spinel</p> <p>Monofrax K-3</p> <p>Monofrax E</p> <p>RFG</p> <p>Ruby</p> <p>AH-199B Alumina</p>	<p>Monofrax E</p> <p>Monofrax K-3</p> <p>RFG } Ruby }</p> <p>Aluminas</p> <p>Magnesia-Alumina Spinel</p> <p>Magnesia } AH-199B Alumina }</p>

TABLE XVII

Listing of the software directories for: 1) system
setup; 2) assembly language program writing; and 3)
graphic display

System Set Up - Total Kbytes: 58		
DUMP	COM	2/1
EDIT	COM	6/1
INIT	COM	1/1
STAT	COM	1/1
WRTSYS	COM	1/1
XFER	COM	2/1
DOSMIN 48	SYS	7/1
BASIC	COM	19/1
Assembly Language Writing - Total Kbytes: 73		
ASMB	COM	12/1
ASMLTR	REL	2/1
LINK	COM	7/1
DEBUG	COM	8/1
EXAMPLE	Z80	2/1
EXAMPLE	CMD	1/1
TRANSLAT	COM	3/1
16KZTEST	COM	2/1
Graphic Display - Total Kbytes: 62		
GRAPHZ80	REL	2/1
GDEMO	COM	3/1
BARPLOT	COM	15/1
GRAPHX	COM	3/1
ROTATE	LIS	3/1
CROMEMCO	DAT	1/1
DAZZPLOT	COM	3/1

Figure 1a
Corroded specimen from a rotating-
rod test

Figure 1b
Corroded specimen from a dipping test

Figure 2 Photomicrograph of pristine AH-199B alumina
Magnification - 50x

Figure 3 Photomicrograph of pristine AP-35 alumina
Magnification - 240x

Figure 4 Photomicrograph of pristine MERDI alumina
Magnification - 240x

Figure 5 Volume percent corrosion as a function of corrosion time for several alumina materials at 1550°C, in unseeded slag and air

Figure 6 Photomicrograph of AH-199B which was corroded at 1500°C, for four hours, in seeded slag and in air. Photo was taken at the corrosion interface and at a magnification of 130x

Figure 7 Concentration profiles for CaO in MERDI, AP-35, and Vistal aluminas which were corroded in unseeded slag, for 8 hours, at 1550°C, and in air

Figure 8 Photomicrograph of corroded MERDI alumina at the slag-specimen interface (corroded in unseeded slag, for eight hours, at 1550°C, and in air) Magnification - 240x

Figure 9 Photomicrograph of corroded AP-35 alumina at the slag-specimen interface (corroded in unseeded slag, for eight hours, at 1550°C, and in air) Magnification - 130x

Figure 10 Photomicrograph of corroded Lucalox alumina at the slag-specimen interface which has been thermally etched (corroded in a seeded slag, for 92 hours, at 1550°C, in air, and using the rotating rod test) Magnification - 240x

Figure 11 Volume percent corrosion versus corrosion time for single crystal alumina (sapphire) at 1550°C

Figure 12 Volume percent corrosion versus corrosion time for Vistal (at 1550°C for seeded and unseeded slags in both air and simulated combustion atmospheres)

Figure 13 Volume percent corrosion versus corrosion time for AP-35 alumina (at 1550°C, in air, and both seeded and unseeded slags)

Figure 14 Volume percent corrosion as a function of corrosion time for Vistal and AP-35 aluminas showing the influence of temperature (corroded in air and unseeded slag)

Figure 15 Concentration profile for CaO in corroded AP-35 at both four hours and eight hours (corroded at 1550°C in unseeded slag).

Figure 16 Concentration profiles for SiO_2 in Vistal alumina specimens which were corroded in an unseeded slag, for 8 hours, at 1550°C , and in both air and simulated combustion atmospheres

Figure 17 Photomicrograph at the slag-specimen interface of a polycrystalline magnesia which was corroded using the dipping technique (corroded for four hours, at 1500°C, in unseeded slag and in air) Magnification - 130x

Figure 18 Photomicrograph at the slag-specimen interface of a polycrystalline magnesia which was statically corroded (corroded for four hours, at 1500°C, in unseeded slag and in air) Magnification - 130x

Figure 19. Concentration profile in the outer slag layer for a statically corroded polycrystalline magnesia

Figure 20 Volume percent corrosion versus corrosion time for three different magnesia-alumina spinels (corroded at 1550°C, in unseeded slag and in air)

Figure 21 Concentration profiles for Fe_2O_3 in corroded MERDI 65-35 and stoichiometric spinels (corroded at 1550°C , for four hours, in unseeded slag and in air)

Figure 22 Photomicrograph at the specimen interface of corroded 65-35 spinel (corroded at 1550°C, for four hours, in unseeded slag, and in air)

Figure 23 Concentration profile for MgO in the outer slag layer for a corroded MERDI stoichiometric spinel (corroded at 1550°C, for four hours, in unseeded slag, and in air)

Figure 24 Volume percent corrosion versus corrosion time for three different spinels which were corroded in a seeded slag (corroded at 1550°C and in air)

Figure 25 Volume percent corrosion versus corrosion time for single crystal and MERDI spinels which were corroded in the simulated combustion atmosphere (corroded at 1550°C in an unseeded slag)

Figure 26 Volume percent corrosion versus corrosion time for four different commercial refractory materials (corroded at 1550°C, in unseeded slag and in air)

Figure 27 Photomicrograph of pristine Monofrax E
Magnification - 240x

Figure 28 Photomicrograph of corroded Monofrax E
taken at the center of the specimen (cor-
roded at 1550°C, for 72 hours, in unseeded
slag, and in air) Magnification - 240x

Figure 29 Volume percent corrosion as a function of time for three commercial refractory materials which were corroded in a seeded slag (corroded at 1550°C and in air)

Figure 30 General diagram of the specimen loading system

Figure 31 Schematic of the microprocessor controlled system

MICROPROCESSOR

Figure 32 General diagram of the electronics of the "Z-2D" microprocessor.

INTERFACE NETWORK

MECHANICAL

DATA FROM:

2 THERMOCOUPLES
 2 LVDT'S
 LOAD CELL
 15 V POWER SUPPLY
 24 V POWER SUPPLY
 5 V POWER SUPPLY
 2 TEMPERATURE PROBES

Figure 33 Interface network and mechanical arrangement of the system

Figure 34 Electronics of the "in" control card

Figure 35 Electronics of the "out" control card

Figure 36 Electronics of the display unit

TOP OF 7404 AND CONNECTIONS:

Figure 37 Electronics of the debouncing card

Figure 30 Electronics of miscellaneous card one

Figure 39 Electronics of miscellaneous card two

12 & 13 ONE SWITCH
M & N ONE SWITCH

Figure 40 Electronics of the display panel

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Appendix

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Preparation of Coals for Utilization in Direct Coal-Fired MHD Generation
B. Rhodes

ABSTRACT

This contract period saw the completion of the work that characterized the fluidization behavior of Rosebud coal in a six-inch column operated at ambient temperature. The organic volatile study was transferred to the Characterization of Volatile Matter in Cial task on May 16, 1978. However, work continues through close coordination between the two tasks on the organic volatile loss area. This study also includes the effect that drying has on Btu values. Work continues on continuous and batch studies of coal drying in the six-inch stainless steel fluid bed dryer. These studies will be supplemented by the completion of a one square foot fluid bed unit (a scale-up of five times the bed area of the six-inch column) during the next three months and the operation of this unit to complete the study of fluid bed drying of Rosebud coal.

The completed work demonstrated the following points: 1) drying Rosebud coal in laboratory bench four-hour tests results in slight loss of organic volatiles, but this loss probably is less than 0.1 percent; 2) the decrease of But value while drying is reduced greatly by drying in an inert atmosphere; 3) a better method of measuring the total water present in subbituminous coal is needed because of the special negative effect of moisture on conductivity in the MHD channel; 4) the very volatile liquid caught in a liquid nitrogen trap during laboratory drying tests needs further identification; 5) the ambient batch fluidization studies showed that fluidization curves were sensitive to changes in the bed load and changes in particle diameter; 6) particle breakdown during fluidization was caused by particle collision and particle decrepitation due to moisture loss; 7) air velocity profile investigations in the ambient batch fluid bed concluded that the dished-designed plate was superior in producing more intense turbulence within the fluidized bed; 8) in all coal fractions investigated, the bed pressure gradient gradually diminished over each batch test; and 9) the pilot plant equipment for continuous drying can prepare samples of coal for burning in test coal combustors which will demonstrate the varying effects on the temperature and conductivity in MHD usage.

I. OBJECTIVE AND SCOPE OF WORK

Rosebud seam coal (Colstrip, Montana) has been designated as a potential MHD reference coal to fuel prototype MHD combustors. Associated with the utilization of this coal in an MHD power generation

facility are potential problem areas in coal preparation. These include the phenomena of coal dust pyrophoricity and explosivity, the reactivity of hot processed coal upon exposure to "inertized" atmospheres containing variable amounts of oxygen and water vapor, and the efficacy of beneficiating the candidate coal for possible removal of slag-forming minerals ahead of combustion. In addition, fluidization drying of Rosebud coal is a potential processing method about which very little information is available. The collection of information in the aforementioned areas is the objective of this continuation research task. The scope of this work is outlined below.

A. Stability of Processed Rosebud Coal and Derived Coal Dusts

Processed Rosebud coal has been observed in vendor drying tests to abstract oxygen and moisture from the atmosphere after drying, to ignite when hot upon contact with ambient air, to exhibit potential for explosion or autoignition, and to self-heat in storage after discharge from a dryer. To characterize certain of these effects, work has been initiated to 1) measure the explosion severity, ignition sensitivity, and index of explosibility for Rosebud coal dust and 2) measure the uptake of oxygen and water vapor from a synthesized gas by sized fractions of coal relative to oxygen concentration, humidity, and coal temperature. A collateral study will measure and identify non-aqueous volatiles associated with demineralizing Rosebud coal in the temperature range up to 400°F.

B. Coal Beneficiation

The rejection of slag-forming minerals from Rosebud coal before combustion would decrease sensible heat losses from the combustion train. To examine this processing alternative, a program has been initiated to identify the type and amount of the major mineral components in a selected sample of Rosebud coal and to determine the relationship between size reduction and mineral liberation. Washability curves for sink-float separation in heavy liquids will be constructed, and the applicability of froth flotation and electrostatic methods for separating coal will be evaluated.

C. Fluidized Drying

Fluidization was found to be a viable processing alternative for drying Rosebud coal to low moisture levels. While vendor fluid bed drying tests demonstrated the feasibility of the drying method, the tests did not shed much light on the behavior of Rosebud coal in a fluidized state, on the influence of processing variables, or on the heat and mass transfer phenomena associated with drying. To obtain engineering data of this nature, a program has been initiated to construct a two-foot diameter fluid bed dryer and associated equipment. The work during this contract period will concern the design, construction, and assembly of the fluid bed drying facility and initial shake-down testing.

II. SUMMARY OF PROGRESS TO DATE

Work continues in the areas of 1) collection and identification of organic volatiles lost during drying of Rosebud coal; 2) fluid-bed coal drying in a six-inch unit; and 3) fabrication and installation of a one square foot fluid bed (a scale-up of five over the bed area of the six-inch unit) coal dryer. Work was completed on characterizing the fluidization behavior of Rosebud coal in a six-inch column operated at ambient temperature.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Organic Volatile Losses

1. Work Accomplished

Continued collection and identification of organic volatiles released during the drying of Rosebud coal has shed additional light on this study area. Tests at various coal-drying temperatures were carried out to capture and subsequently identify the vapors released. Method development resulted in improved data collection. The various conditions of drying in inert atmospheres were tested for their effects on the Btu value of coal after drying. Coal samples dried in a nitrogen or helium atmosphere retained most of their Btu value when compared on a dry basis with coal before drying, whereas a greater decrease in Btu value was found for air-dried coal samples.

The inert atmosphere drying tests indicated that Rosebud coal dried at 1050C is not dry. Actually, water continues to be released above this temperature. Tests at drying temperatures as high as 1900C resulted in the collection of significant additional quantities of water. The question must be asked--Does a tighter, more representative test need to be adopted for all MHD work on subbituminous coal? If it is the total actual moisture left in dried coal that affects plasma conductivity as an exponential function in the MHD channel, a truly accurate test that will determine the total moisture in the coal needs to be adopted.

It also was determined that a liquid was collected in a liquid nitrogen trap on the gas stream following a water condenser and an ice bath collection system. This was thought to be oxygen and was to be completely identified in Task D work following the changeover. This liquid was observed to be collected when the coal bed temperature was between 1350C and 1700C. Approximately 2cc were collected from a sample of 300g of 21 percent moisture coal. Further testing under Task D also was planned to determine if the coal contains any low boiling organic volatiles.

A third piece of information obtained from the drying tests was that very little organic volatiles were collected under an inert gas atmosphere, even when the coal bed temperature was raised

as high as 190°C. The quantity of condensables retained in the water-cooled gas condenser was difficult to determine, but it was less than 0.1 percent and maybe as little as 0.01 percent of the starting coal weight. On this basis, further work needs to be done to determine more accurately how much organic volatiles are released during drying. It also was determined that the Btu value of the coal dried under a nitrogen or helium atmosphere does not show as large a loss. Continued work needs to be done in this area since the accuracy of the Btu test method has certain variances which can be from one to five percent.

2. Discussion

Because questions had been raised concerning Btu losses of coal on drying, a method for drying coal under an inert atmosphere was developed. Four possible causes for Btu loss after drying are listed below:

- a. Organic volatiles could be given off during drying in enough quantity to cause Btu reduction of the dried coal;
- b. Surface oxidation of the coal during drying could cause the reduction in Btu value;
- c. Testing variation of the Btu test method and individual reproducibility could explain the variance; and
- d. A combination of any or all of the above.

To determine the influence of each of the above, further tests were run and the statistical reproducibility of the Btu test and the operator were studied.

The method of drying under an inert atmosphere blanket and purge gas stream was developed. Further condensing and trapping of any condensate and volatiles was added, including a liquid nitrogen trap. Both literature checks on the possible error in Btu testing and a statistical study of the operator on other tests were made.

The bench drying tests used the following equipment: a fluidized sand bath as the heat source, a 500ml three-necked flask, a water condenser, and an ice bath-cooled flask containing distilled water through which the gases were bubbled. Tests were run on drying in air and under nitrogen. Then, when a liquid nitrogen trap was added, a helium atmosphere was used. A series of drying tests were run to check on various drying coal bed temperatures and the volatiles that could be captured. Also, special attention was given to taking samples of coal for Btu determination and to having the test run by a person experienced in running these tests.

The major conclusions reached were that water continued to be released from the coal at all temperatures above 105°C and up to 190°C which was as high as these tests were run (only because the thermometers for checking the sand bath were 200°C thermometers). Therefore, a new understanding and agreement on how much water is in coal is required to truly predict the plasma conductivity in the MHD channel when "dried" coal is burned. This understanding must relate to coal drying and specifications for the coal to be burned in coal combustors. The quantity of volatiles collected in the tap water-cooled condenser was small with none being collected in the ice water-cooled flask. The small amount of organics was collected by washing the condenser with an organic solvent which later was allowed to evaporate. Enough was collected to run GC tests which confirmed the organics already identified. However, the quantity of such organics was less than 0.1 percent and could be much less.

The last bench test was run under a helium atmosphere with a slow helium gas purge. The liquid nitrogen trap was added to see if any volatiles with very low boiling points were escaping notice following the ice bath. Some liquid started to appear in the nitrogen trap at about 135°C bed temperature and kept coming off through the 170°C range, at which point the nitrogen trap thimble was changed. No further liquid was collected up to 190°C bed temperature. About 2cc of liquid were recovered which volatilized very rapidly during weighing. At the time, a true identification of this highly volatile liquid was not made. It was felt that it probably was oxygen. Dr. Beuerman planned to make sure of this when the new heating elements came for the sand bath (the first set burned out at this time). The source of this oxygen is unknown at this time.

The Btu testing studies showed that the operator doing the testing before May 16, 1978 had a record of very high reproducibility of less than ± 1 percent deviation in replicated tests. Each new operator's accuracy must be analyzed statistically. The Btu tests on the coal samples referred to above resulted in the least loss of Btu's after drying under an inert atmosphere of nitrogen or helium. The sample dried in air showed the greater loss of Btu values by about four percent. Therefore, it is recommended that coal drying for MHD be carried out in as inert an atmosphere as can be justified economically. Also, further testing based on pilot plant dried samples should be analyzed since the drying time is less than seven to ten minutes compared to three to four hours by bench methods. Certainly, air oxidation during drying must be taken into account in evaluating how the loss of organic volatiles affects the Btu value of coal during drying.

B. Batch Fluidization Studies at Ambient Temperature

1. Work Accomplished

During this report period, a six-inch plastic fluidization column was operated to develop data to characterize the fluidization of Rosebud coal at ambient temperature. The final report has been completed and is on file at the Montana College of Mineral Science and Technology as written by J. LeFever for his master's thesis

entitled Fluidization Studies on Rosebud Coal. An eight-page excerpt, including his conclusions, follows in the discussion portion of this report. Results from the LeFever report will guide the operation of the fluid bed pilot plant tests of Rosebud coal.

2. Discussion

The batch fluidization curves investigated were run on 6 x 8 mesh, 8 x 10 mesh, 10 x 14 mesh, 14 x 20 mesh, and 20 x 28 mesh fractions of Rosebud coal.

A series of fluidization curves were collected to depict the relationship between the variation of pressure gradient across the bed of particles to the superficial velocity flowing through the bed. These curves show that the superficial velocity (the velocity of gas through the fluid bed area without any impediments) increases with increasing particle size and bed weight, resulting in a higher pressure drop at incipient fluidization. The inclined static bed portion of each curve was established as having a slope of 1.53, which agrees quite well with reported values in the literature for other materials.

Fluidization takes place when the bed pressure gradient equals the weight of the bed per unit area or when

$$\Delta P_B \approx \frac{W_{\text{coal}}}{A_{\text{bed}}} \frac{g}{g_c}, \text{ lb}_f/\text{ft}^2 \quad (1)$$

where

ΔP_B = Bed pressure differential,

g = Acceleration of gravity at sea level

g_c = Acceleration of gravity corrector for altitude,

W_{coal} = Weight of coal, and

A_{bed} = Area of bed.

It was found that the measured pressure drop across the bed was approximately 83 percent of the calculated value, suggesting that the ratio of the static bed height to the column diameter has an effect on the equivalence of the two pressure drops. The wall effect and the effects of electrostatic charge buildup during fluidization have been reported and discussed by Lewis, Gilliland, and Bauer. Electrostatic effects were readily apparent during fluidization testing in the plexiglass experimental unit. Coincidence of the calculated and actual pressure drops occurs when the static bed height exceeds 1.5 times the column diameter.

It was determined from the fluidization tests that the minimum fluidization velocity is proportional to the geometric particle diameter average (D_p) raised to the 0.45 power, i.e.,

$$V_s \text{ min } \propto D_p^{0.45} \quad (2)$$

This correlation was obtained from Figure 1 where the incipient superficial velocity is plotted against the Reynolds Numbers on log-log coordinates. The slope of the line equals 0.45. Linear regression of N_{Re} on V_s gave

$$V_s = 0.41 N_{Re}^{0.45} \quad (3)$$

with a coefficient of determination equal to 0.945.

As fluidization velocity is increased beyond the point of incipient fluidization, the bed pressure gradient gradually diminishes. This behavior, confirmed by visual observation, is characteristic of aggregative or spouting fluidization. The spouting effects at higher Reynolds Numbers caused some difficulty in measuring the expanded bed height accurately.

To examine the effects of increased fluid flow and bed expansion, plots were developed as shown in Figure 2, in which the bed expansion ratio (l_e) is plotted against the Reynolds Number (N_{Re}). Assuming that the expansion ratio is a linear function of the Reynolds Number over the entire fluidization range, regression analysis showed that a straight line and general equation could be generated for each size group investigated. Due to data scatter, some difficulty was encountered in correlating the 8 x 10 mesh size group.

Figure 3 is the composite correlation of bed porosity (ϵ_B) to the ratio of particle to fluid bed friction factors ($\frac{C_D}{f_F}$). The correlation is a composite of all data points collected in this study.

Regression analysis gave a slope of 0.144. The horizontal portion of the line, shown from 0.001 at approximately 0.015 $\frac{C_D}{f_F}$, represents static bed conditions.

At approximately 0.015 $\frac{C_D}{f_F}$, the bed begins to expand and continues to do so until the bed porosity and the ratio of particle drag coefficient to fluidization friction factor equal 1.0 by extrapolation, i.e., until the particles move unhindered at their terminal velocities.

Figure 3 shows the bed porosity (ϵ_B) to be proportional to the ratio of particle drag coefficient to fluidization friction factor ($\frac{C_D}{f_F}$) raised to the 0.144 power, viz.,

$$\epsilon_B \propto \left(\frac{C_D}{f_F}\right)^{0.144} \quad (4)$$

or

$$\epsilon_B^{\frac{1}{0.144}} \propto \left(\frac{C_D}{f_F}\right) \quad (5)$$

or

$$C_D = f_F \epsilon_B^{6.944} \quad (6)$$

Lewis, Gilliland, and Gauer found that they were able to correlate their results for different systems under hindered settling by plotting the relation (as found in Equation 6) as a function of the Reynolds Number (N_{Re}). This was done for all data points and is shown in Figure 4. Most data points fall along a straight line of negative slope equal to 0.896. Regression analysis gave

$$y = 40.556 x^{-0.896} \quad (7)$$

or

$$f_F \epsilon_B^{6.944} = 40.556 N_{Re}^{-0.896} \quad (8)$$

or

$$f_F = \frac{40.556}{\epsilon_B^{6.944} N_{Re}^{0.896}} \quad (9)$$

with a coefficient of determination equal to 0.971. Equation 9 has the form of a particle friction factor for Reynolds Numbers corresponding to viscous flow. That is, the support of the coal particles in the fluid bed is due largely to viscous drag. Since

$$f_F = \frac{4g D_p (\rho_s - \rho_f)}{3 V_s^2 \rho_f} \quad (10)$$

and

$$N_{Re} = \frac{\rho_f V_s D_p}{\mu} \quad (11)$$

Equation 9 can be rearranged by substitution to the form

$$V_s = \left[\frac{0.05 g^{0.91} D_p^{1.72} (\rho_s - \rho_f)^{0.91} \epsilon_B^{6.32}}{\mu^{0.81} \rho_f^{0.009}} \right] \quad (12)$$

The composite correlations shown in Figures 3 and 4 enable the prediction of bed porosity for a given set of conditions in batch fluidization. For example, given that

$D_p = 0.0033$ ft., geometric particle diameter,

$V_s = 2.5$ FPS, fluidization velocity,

$\rho_c = 78.52$ lb/ft.³, coal specific weight,

$\mu = 1.208 \times 10^{-5}$ lb/ft.-sec., fluid viscosity (air), and

$\rho_f = 0.0604$ lb/ft.³, fluid specific weight (air),

the calculated particle Reynolds Number is 41.2. From Equation 10, the friction factor, $f_F = 29.4$, and from Figure 4, $f_F B^{6.944}$ equals 1.45. Hence, the bed voidage is

$$\epsilon_B = \left[\frac{1.45}{29.4} \right]^{\frac{1}{6.944}} = 0.648$$

a value which corresponds quite closely with those found experimentally.

C. Continuous Fluidization Drying Studies

1. Work Accomplished

During the past twelve months, a continuous six-inch diameter fluid bed drying system has been engineered, purchased, erected, and placed in operation. Pictures of this system are shown in Figures 5, 6, 9, 10, 11, 12, and 13. The six-inch stainless column, shown in Figure 5, is designed for flows up to a 50cfm flow rate. The shake-down period indicated that several changes were required. The mass flow meter for gas velocity determination was unsatisfactory, and a pitot tube system was used as a fall-back method. A better flow rate system is needed and under study. The continuous humidity sensor did not operate satisfactorily. However, wet bulb-dry bulb temperature readings were found to give acceptable humidity measurements on the inlet and off gases.

The electric air heater, as shown in Figure 6, works quite well for the six-inch bed, but a 9 KW capacity puts an upper limit of slightly over 500°F on inlet gas temperatures. A VAR electric power measuring system was installed to measure air heater power input.

Both batch and continuous drying tests have been run on the six-inch stainless steel fluid-bed unit. A reproduction of a batch drying curve from this unit is shown in Figure 7.

Figure 8 is a plot of the batch moisture content of the coal samples and bed temperatures plotted against time. This plot illustrates the constant rate and the falling rate portions of the batch

drying cycle. Moisture samples were taken every 2-1/2 minutes. These data corroborate earlier findings that the drying cycle consists of three regions: a constant rate period, a falling rate period (diffusion controlled), and a later falling rate period (capillary controlled). These different drying portions will be studied separately, as well as together, in the coming year.

Over 30 continuous coal-drying tests have been run. The feed rate control, based on the fluid bed temperature, is working satisfactorily. Several changes have been made in the coal feed inlet to the dryer and its downcomer. In general, the feed downcomer has been enlarged to decrease feed pipe plugging. The feed inlet point has been raised to lengthen the downcomer which will help control the amount of air or inert gas drawn down the feed pipe with the coal.

2. Discussion

The six-inch (continuous) fluid bed dryer and its auxiliaries were assembled and started in operation during the past year. It took longer than planned to assemble, but it is operating quite satisfactorily at present. The distribution plate through which the hot inlet air is forced is made from stainless steel into which 68 1/4 inch stainless steel pipe plugs were threaded. Each plug has a larger center hole drilled up from the bottom almost to the top. These are connected with four small holes per plug or one on each side with a 30 percent downward slope toward the upper side of the plate. In this way, very little coal can get through the plate even when the bed is collapsed. This totals 244 holes with a size such that we have a five percent open area plate. A photograph of this plate is attached (Figure 9).

The operation of the fluid bed is controlled from a control panel which is pictured in Figure 10. The 24-point recorder is keeping records of the hot-gas inlet temperature; the temperatures at 1-1/2, 2-1/2, 6, and 36 inches above the bed as well as at the top of the disengaging column; the inlet and outlet temperatures of the dust collector; the inlet and outlet temperatures of the Ducon scrubber; the inlet temperature to the variable speed fan; and the inlet temperature of the water recirculating pump. Pressure measurements include the drop across the plate; the drop across the bed; the drop across the plate and bed together; the drop across the baghouse; the pressure at the inlet of the dust collector; the pressure at the outlet of the dust collection fan; the pressure at the inlet of the Ducon scrubber; and the pressure at the outlet of the Ducon scrubber. We also continuously monitor the oxygen in the system gases, control the temperature of the exit gas from the electric heater, continuously record the VAR's of power used by the electric heater, and take millivolt readings of two flux meters attached to the outer wall of the bed to measure the rate of heat loss through our insulation cover on the fluid bed column. The water for the Ducon scrubber (humidity controller) is recirculated and stored in a tank that holds over 100 gallons. Should any organics condense in the scrubber, they would appear as a layer on the water in this tank. To date, only trace amounts have been found.

The gas stream is a totally enclosed recycle system in which the scrubber condenses water and cools the air stream to a saturated condition at the exit emperature of the Ducon scrubber. This is fed to the variable speed fan which pushes the air through the electric heater and through the distributor plate into the fluid bed. The gas stream passes through the coal bed, into a disengaging column, and into the flexible duct leading into the dust collector baghouse, as shown in Figure 11. The gas is drawn through the bags by the dust collector fan which pushes it through the flexible duct into the bottom of the Ducon scrubber, as illustrated in Figure 12. The gas then flows up through the water-cooled, packed-bed scrubber through the water spray, and out of the scrubber through a demister section.

There are no gas outlets open, but bubbles of gas go through the liquid vapor trap seal at the bottom of the scrubber with the water and appear in the 100-gallon open-topped tank. Nitrogen is fed at a slow continuous rate into the dust collector system and is used as the gas that blows and shakes the bags in the baghouse. A tight seal on the shaft of the fans is not a part of the equipment, so some air is sucked into the fan chamber along the shaft. Also, some air has been drawn into the feed pipe with the coal. The downcomer system has reduced this air greatly, and the latest change should bring this leakage to a halt.

The bed depth of the coal in the fluid bed is measured by stopping the coal feed and air flow; a three-inch plug at the top of the disengaging column is opened, and a large rubber stopped at the end of a measuring stick is dropped onto the collapsed bed. From this the in-process coal is calcualted. The mass flow meter and pitot tube measuring points are in a section of 2-1/2 inch pipe more than 20 pipe diameters in length, between the variable speed inlet fan and the electric heater, as shown in Figure 6. Actual wet-bulb and dry-bulb temperature measurements are made at this same velocity measuring point and at the three-inch plug opening at the top of the column. Samples of coal are obtained from a T-section on the pipe leading from the six-inch coal discharge point above the plate into a sealed five-gallon weighing bucket (or a 55-gallon sealed steel drum) by means of a pipe union connection. The amount of dust removed from the bed is caught in a ten-gallon sealed can that can be separated from the bottom of the dust collector for weighing at the end of each run. The wet coal is weighed at the start of the run, and the time length of the run is measured through the vibrating feeder as seen in Figure 13. This results in an accurate average feed rate. Apparent density of the collapsed coal in the bed is measured by weighing a known volumn of dried coal at the end of the run.

The continuous tests are being run based on pre-setting the variables at set points, except for one variable which is studied at a separate setting for each test. The unit is brought to equilibrium before the start of the measured feed by introducing previoulsy dried, non-dusty coal and a little water until balanced conditions are reached. At the start of the run, the only changes are the switching from a 55-gallon drum union connection to the five-gallon can union

connection on the dried product holder and the introduction of the pre-weighed amount of feed into the vibrating feeder. It takes several minutes to steady everything from the changeover at the desired set points, but no major temperature, pressure, humidity, velocity, bed depth, or other changes are necessary. In this way, continuous steady-state runs are made, with ten-gram samples of dried coal product being moisture tested on the Braebender moisture tester during the duration of the run. The test program will perform drying runs in the constant rate portion of the drying curve. Other tests will be in the falling rate, diffusion-controlled portion of the curve (by feeding previously surface-dried coal), and still other tests will be run in the capillary portion of the drying cycle.

Two continuous tests were run at bed temperatures of 190°C to see what organic volatiles were collected by the scrubber. Very little could be seen after three hours of running. Gas samples were taken as well as coal samples. Some tar-like odor was noted. Table I lists the data from which Figure 8 was plotted.

D. Work Forecast

1. Organic Volatile Losses

This area of work was changed into Task D to be carried out under separate reporting. Further work needs to be done on determining the exact quantity of organic volatile loss during drying. Also, further work needs to be done on the exact identification and determination of the portion of volatiles caught in the liquid nitrogen trap. Work also needs to be carried out at the pilot plant drying level on the effect of inertization of the atmosphere on Btu level after drying as compared to Btu level before drying. All findings then should be incorporated in the absolute specifications of the coal to be used in coal combustors, especially in relation to the additional water present in dried coal and in relation to the adsorbed oxygen which could be lost during some stringent drying conditions.

2. Continuous Fluidization Drying Studies

Continuous testing on the six-inch fluid bed dryer will be carried on for the next three months. During that time, the one square foot bed dryer will be installed. By changing the outlet duct and the inlet air pipe, the same auxiliary equipment will be ready to run the larger unit at a scale-up factor of five on bed area. Also, during the coming twelve months, an improvement on the method of measuring mass flow will be adopted. A higher capacity variable speed fan will be necessary for good control of the one square foot bed.

Further tests will be run to try to collect more organic volatiles from the drying phase. Combined efforts of Task D and Task C are being directed toward a way to test the tail gases continuously from the drier for specific portions of the organics volatile fraction.

In addition, the one square foot fluid bed dryer could be used to help prepare pre-specified coal samples for combustor testing at various dryness and particle size ranges.

IV. CONCLUSIONS

The following conclusions summarize the work accomplished and outline the work still to be done on this task.

Drying Rosebud coal at temperatures above 1500F results in slight loss of organic volatiles; but even at temperatures as high as 3740F, this loss is probably less than 0.1 percent. The decrease in Btu value noted in previous reports probably is due in part to coal oxidation that occurs when drying in an air atmosphere. Samples dried in either a nitrogen or a helium atmosphere retained much more of their Btu value during drying. Thus, it is recommended that coal drying be conducted in as inert an atmosphere as economically feasible.

Present standard methods of moisture testing are not accurate enough for determining the total moisture in Rosebud subbituminous coal for MHD purposes. Significant water continues to be given off in drying temperatures as high as 190°C. Since moisture has a detrimental exponential effect on plasma conductivity in the MHD channel, it is imperative to learn the actual total moisture in the coal and establish strict specifications based on this knowledge.

During bench-scale drying tests, a significant amount of a liquid at liquid nitrogen temperature was caught at a coal bed temperature over 1350C. Complete identification of this emission, which is thought to be oxygen and/or very low boiling organics, needs to be accomplished. Some determination of the value of this probable sorbed oxygen needs to be made in relation to its help in achieving the best coal combustor operation. If it helps enough, coal drying temperature needs to be kept low enough to leave most of this in the coal during drying.

Ambient batch fluidization studies were completed. Data were correlated by dimensionless equations which are useful in predicting performance of other fluid bed coal dryers. Fluidization curves were found to be sensitive to changes in bed load and particle diameter. The inclined static-bed portion of these curves was established at a slope of 1.54. It was found that particle breakdown during fluidization was caused by two mechanisms: particle collision and particle decrepitation due to moisture loss. Size distribution plots indicated that the breakage mechanism is constant for all sizes of feed product investigated; however, it is controlled by the initial size of the feed product entering the unit.

On an average, Rosebud coal contained 22.0 percent moisture by weight; that is, 15.0 percent by weight as superficial moisture and 7.0 percent by weight as inherent interstitial moisture. It was found that all the superficial moisture could be removed by fluidizing, using ambient temperature air. Air velocity profile investigations in the ambient batch fluid bed concluded that the dished-designed plate was superior because

it produced more intense turbulences within the fluidized bed. It also appeared that the three or five percent open area plate produced less slugging and resulted in a more uniform fluid mass. Also in the ambient batch fluid bed tests in all coal fractions investigated, it was found that the bed pressure gradient would gradually diminish. This finding would indicate an aggregative or spouting type of fluidization. This also was confirmed by visual observation.

Both batch and continuous drying tests with controlled variables, including inert atmosphere, will be conducted in a six-inch stainless steel pilot plant fluid bed. The completion of the one square foot fluid bed dryer will be expedited to achieve a scale-up by a factor of five and confirm the engineering data being gathered on the six-inch unit. Coordination of aocl dried under carefully controlled conditions and its effect on coal combustor performance needs to be carried out. Specific samples should be prepared to demonstrate their effect and to confirm the computer programmed projected results for these variables

TABLE I

<u>Time, min.</u>	<u>Bed Temperature °F</u>	<u>Moisture</u>
0	98	19.0%
2½	105	17.5%
5	110	16.6%
7½	112	15.4%
10	119	13.8%
12½	126	11.8%
15	133	9.9%
17½	142	8.1%
20	154	6.0%
22½	165	4.9%
25	173	3.7%
27½	185	3.0%
30	196	2.5%
32½	200	2.1%
35	203	2.0%
37½	205	1.7%
40	208	1.5%
42½	210	1.4%
45	212	1.2%

Figure 1. Composite, superficial velocities at incipient fluidization for Rosebud coal (composite of all tests correlated)

Figure 2. Composite, correlation of bed expansion ratio, l_e , with the particle Reynolds number (composite of all tests correlated)

Figure 3. Composite correlation of bed porosity, ϵ_B , with ratio of particle to fluid-bed friction factors for Rosebud coal (composite of all tests)

Figure 4. Composite correlation of fluidization friction factor and particle Reynolds Number for Rosebud coal in air at ambient temperature (composite of all tests correlated)

Figure 5. Fluid-bed hot zone, pressure taps, and thermocouples

Figure 6. Fan, heater, and flow measurement system

Figure 7. Typical temperature recorder log sheet for batch drying test

Figure 8. Batch drying curves (moisture vs. time and temperature vs. time)

Figure 9. Fluid-bed distribution plate

Figure 10. Instrument control panel

Figure 11. View of auxillary equipment, dust collector, etc.

Figure 12. Ducon scrubber

Figure 13. Coal feeder

Characterization of Volatile Matter in Coal
D. Beuerman

ABSTRACT

The loss of Btu value during the drying process has been shown to be due to the loss of organic matter during the heating cycle. Tests have shown that this heat loss is not due to surface oxidation of the coal.

Techniques for the separation and identification of organic compounds lost from the coal during heating have been improved. New compound identifications are reported.

In an effort to close the material balance on the amount of volatile organics lost, bench tests were made in which highly volatile material was collected in a liquid nitrogen trap. A considerable amount of highly volatile matter apparently is lost from the coal during drying. This loss could include oxygen (absorbed) and low-chain alkanes (methane, ethane, etc.). This material as yet has not been characterized.

I. OBJECTIVE AND SCOPE OF WORK

Task D has been in existence since May 15, 1978. The objective and scope of the task is based on work reported previously as a subtask of Task C. This previous work, annual report October 1977, has shown that organic material is lost by volatilization during the drying of Rosebud coal prior to use in the MHD generator. These organics represent a loss in Btu value and a disposal problem of environmental interest. The loss of organics was substantiated by mass spectra and gas chromatograms, comparison of four analytical methods for moisture, and the loss of Btu measured before and after the drying process.

II. SUMMARY OF PROGRESS TO DATE

A. Btu Loss During Drying

A loss of Btu/lb. of dried coal has been observed during the drying of Rosebud coal and reported previously. These results were obtained with a limited number of samples that had been stored in sealed Mason jars for two or more years. To verify this loss of Btu values, the work will be continued during this contract period using fresh samples in bench-scale drying experiments and analyzing the feed stock and product from a fluidized bed dryer which is operated under an inert atmosphere by Task C.

B. Identify Volatile Organic Compounds of the Dryer Gas

The components of a small amount of volatile matter were separated previously in a chromatographic column. The parameters affecting the separation on the chromatogram will be refined during this contract period to improve the resolution, thus reducing the amount of mixtures eluted from the column and improving the purity of the emerging compounds. New mass spectra will be obtained for interpretation. Determining a material balance during the drying process will continue in an attempt to trap and identify the very low volatile compounds in the dryer gas. A study to identify the organics in the quench water from the fluidized bed dryer pilot plant will begin during this period.

C. Quantization of Organic Volatiles

Quantization of the volatile components will be made using the improved separation procedures developed above, and the response factors will be determined for known or suspected components in the effluent gas from the coal dryer.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Btu Loss on Drying

1. Work Accomplished

It was reported previously that when coal is dried at elevated temperatures, it loses 3 to 7 percent of its Btu value. This Btu loss is believed to be associated with a loss of low volatile organics during the heating cycle. However, the opinion that this Btu loss is due to surface oxidation of the coal when heated in an atmosphere of air has been expressed to this investigator. During this contract period, different samples of coal were dried in an atmosphere of nitrogen, helium, or vacuum to minimize this surface oxidation of the coal and possible Btu loss from this source. The samples were blanketed with the inert gas before heating commenced and the head-space was swept with the inert gas during the heating cycle. The typical heating rate curve for these experiments (except experiments Nns. 12 and 13) is shown in Figure 1. Although the maximum temperature reached during each experiment varied within 10°C, the shape of the curve is similar for each experiment.

Btu values were determined for each sample before and after drying, and the results for the samples before drying were corrected for the loss in weight experienced during the heating cycle. These results are shown in Table 1.

2. Discussion

The opinion has been expressed to this investigator that the reported loss in Btu values during the drying process may be due to the surface oxidation of the coal and not by the loss of organic matter during the heating cycle. Therefore, additional experiments

were made in atmospheres of nitrogen and helium and in vacuum to determine if there was merit to the above opinion.

The data in Table 1 shows that, without exception, the Btu value per pound of dried coal was decreased during heating to the temperatures found in the dryer. Also, it should be noted from this table that the average Btu value loss from coal which was stored for two to three months is 3.8 percent greater than from coal which was stored over two years. Nevertheless, some volatile material evidently was released from the coal matrix during prolonged storage, and this loss produced a loss in Btu/lb. of dried coal.

A 1.3 percent loss in Btu value is shown in Experiment 18. This coal sample was previously dried by the spray drying technique. However, during the experiment, this supposedly dry coal lost an additional 7 percent of its initial weight. The reported fact that dry coal tends to absorb moisture from the atmosphere would account for the further loss in weight by the stored, dried coal during the present experiment. However, the subsequent loss of the absorbed water could hardly account for the 1.3 percent loss in Btu value. It may be that coal contains volatile organics in the matrix which slowly diffuse out of the matrix and are lost to the atmosphere. The rate of diffusion would undoubtedly be increased by the increased temperature during the drying process. Also, the fact that the loss of Btu values from coal dried in a vacuum at room temperature is of the same range as coal dried at elevated temperatures gives added impetus to this diffusion suggestion.

3. Future Work

No future work is planned at this time. However, some work may be coordinated with samples from the fluidized bed dryer operated by Task C, since the residence time in this dryer is much shorter than in the bench experiments completed to date. The effect of dryer residence time and mesh size of the samples on the loss of Btu values have not been studied thoroughly to date.

B. Identification of Volatile Compounds in Dryer Gas

1. Work Accomplished

a. Interpretation of previous work

It was reported that coal heated to 95° lost at least 16 compounds; these were tentatively identified in a previous report. This list has since been found to contain errors due to unknown contamination present in the gas chromatograph and/or mass spectrometer instrumentation. Gas chromatograms (Figure 2) and new mass spectra were obtained. The new identifications are listed in Table 2. A schematic set-up for all bench scale drying experiments is shown in Figure 3.

b. Improvement of the resolution during the chromatographic separation process

The separation of the components is done to the mass spectral analysis by passing the material through a gas chromatographic column. The parameters which affect this separation of the components in the instrument were studied in an attempt to obtain better resolution (separation) on the chromatograms. These parameters include temperature programming, type and loading of the organic stationary phase on the chromatographic support, column size, flow rate of the helium, etc. Columns of alkylated silicones such as OV-1, OV-101, DC710, Carbowax 20 and Kel-F, a poly-fluorinated compound, were constructed and evaluated. The following conditions were chosen for the experimental gas chromatographic separations from the results of these evaluations:

Column	5% OV-1 coated on silinized, acid-washed Chromosorb W
Column size	6 ft. x 1/8 inch
Initial temperature	35°C (held constant for 5 minutes)
Temperature progress rate	50/minute
Final temperature	140°C
He flow rate	10 ml/20 seconds

c. Organics in quench water for the fluidized bed dryer operated by Task C

The drying gases from the fluidized bed dryer are cooled in a packed tower by a spray of water. This water is collected in a holding tank prior to being recycled back through the packed cooling tower. While this water was recycled, a thin film formed on the surface of the water, and gas bubbles escaped up through the water from the inlet tube to the tank. The surface of the reservoir was skimmed into a sample bottle. Various organic solvents were used to extract this aqueous layer in an attempt to remove any organics from the solution. Mass spectra were obtained for these extracts; typical spectra are shown in Figures 4 through 7. However, poor chromatographic separations were obtained due to a breakdown of the temperature programmer on the chromatograph in the analytical sequence. Therefore, Figures 5 through 7 are a series of spectra obtained at different periods of elution from the chromatograph.

When the quench water was allowed to set in the holding tank for 24 hours or more, this thin film coagulated into pools of iridescent material which was collected for further experimental

work. The packing material from the cooling tower was removed and washed with organic solvents, such as carbon tetrachloride, ether, alcohol, etc., to remove any organics which built up on the packing. These washings have not been tested to date.

2. Discussion

Table 2 shows that the major components in the volatile material collected while heating coal to 950°C are straight and branched chain alkanes and alkanes of the C₅ to C₇ range. This is to be expected since the boiling point of these compounds is as low as 49°C. A small amount of benzene, thiophene, and toluene were detected in this experiment. However, the samples collected from quench water of the fluidized bed dryer, where the residence time is estimated at ten minutes instead of four hours, showed no detectable benzene. Although Figures 4 through 7 are mass spectra of mixtures, there are no parent peaks that correspond to a M/e ratio of 78, the molecular weight of benzene. The peak at a M/e ratio of 91 in Figure 3 is very small. This could be due to alkylated benzenes such as toluene or it could be due to a fragmentation of aliphatic hydrocarbons. Mass fragments greater than 120 were very weak and rare in these runs, and they were attributed to instrument background.

Low-temperature volatilization of coal, as mentioned in the bulk of the literature, refers to low-temperature pyrolysis at temperatures which are 2500°C or more above the temperature of the coal bed in the dryer. It has been reported that over 60 components have been found in the gases from the heating of coal to 1500°C. These experiments were conducted in a vacuum system, thus lowering the vapor pressure of the "volatile" compounds reported, causing the volatilization of more compounds having high molecular weights and high boiling points than would be expected from a coal dryer. Therefore, the conditions of these experiments are not the same as those found in a coal dryer. To date, our investigations show that benzene and its alkylated analogs have been detected only when the residence time of the coal in a drying atmosphere is prolonged (four hours).

3. Future Work

This work will be continued using actual samples from the fluidized bed dryer. A high-pressure liquid chromatograph with an ultraviolet detector will be used to determine the presence or absence of polynucleated aromatics in the samples. This instrument is quite specific for these compounds in very low concentrations. However, some methods development work must precede any experimentation.

It would be helpful to know what the maximum temperature, minimum moisture level, and the residence time will be in the proposed coal dryer planned for use in the treatment plant for MHD coal. This would give some guidelines to follow in the future work of this task.

D. Quantization of Volatile Matter

1. Work Accomplished

a. Volatiles evolved from coal which is heated to 95°C

Quantization of the volatiles given off at 95°C (four hours residence time) was made from the gas chromatograms and response factors determined previously. These values are listed in Table 2 as a percentage of the recovered organics, not as a percentage of the total volatiles lost during the heating cycle. As can be seen from Table 3, the total amount of volatiles has not been recovered, and therefore, quantization cannot be based on the total amount of material lost while heating in a drying process.

b. Material balance

The apparatus shown in Figure 3 was used to obtain a material balance as well as to trap the volatiles for further identification. The coal was weighed before and after heating, and the volume of the condensate caught in the cold trap (No. 5) was measured. This condensate was not weighed due to low volatility of some of the components as shown by the drifting of the analytical balance when weighing was attempted. The density of the condensate was assumed to be one gram/milliliter, since the bulk of the condensate was water. These material balances show a loss of unrecovered volatile material as listed in Table 3.

2. Discussion

The data in Table 3 show that 1.3 to 3.9 percent of the loss in weight of coal samples when heated was not recovered by condensation of the effluent gases. Some of this material could be entrained from the system by the flow of helium through the apparatus. However, the flow of helium through the apparatus was less than 3 ml/minute, just enough to maintain a positive flow and hardly enough to entrain 2 to 4 percent of the weight of the sample from the system.

This unrecovered material could also be a loss of low volatile alkanes, alkenes and/or alkynes (C_1 to C_4) which do not condense at the temperatures of the first cold trap (No. 5 in Figure 3).

In two experiments, about 2 ml of liquid were condensed in the liquid nitrogen scavenger trap (No. 6 in Figure 3). Inclusion of this material would close the material balance considerably. However, this liquid was so volatile that it evaporated in less than 30 seconds after being removed from the liquid nitrogen. It is unlikely that this liquid is air from the headspace of the apparatus since helium was purged through the system for one hour before the heating cycle was started and the traps were cooled.

The viewpoint was expressed to this investigator that perhaps this material was oxygen which was adsorbed on the surface of the coal during storage and released during the heating cycle. However, two milliliters of liquid oxygen would correspond to 2.8 liters of the gas adsorbed on 300 grams of the coal sample. This theory may account for part of the liquid in the trap, but it is unlikely that it would explain the complete phenomenon.

Perhaps it is carbon dioxide from surface reaction of oxygen with the coal during storage and still adsorbed on the surface. Carbon dioxide is a solid at the temperature of liquid nitrogen which precludes this explanation unless the liquid is a solution containing carbon dioxide.

Another explanation could be that the liquid is a mixture of low molecular weight hydrocarbons (C_1 and C_4) as mentioned above. These alkanes, alkenes and/or alkynes are liquids at the temperature of liquid nitrogen.

The presence of methane, ethane, propane, etc. in coal fields is well-known. The evolution of these hydrocarbons during the drying process could be a real phenomenon and might explain the loss in Btu values of 3 to 8 percent during the drying process.

3. Future Work

During the coming contract period, this material balance study will be continued, and the identification of this material from the liquid nitrogen trap will be attempted. Some work with a vacuum system will be attempted to aid in this investigation.

E. Toxicology Studies

1. Work Accomplished

Arrangements for toxicology studies have not been made since the information regarding the composition of the full range of volatiles has not been completed.

IV. CONCLUSIONS

From the aforementioned work, it is concluded that

1. Coal loses Btu value during the drying process.
2. Coal may lose Btu value during prolonged storage.
3. The bulk of the organics collected during the drying of Rosebud coal are aliphatic hydrocarbons.
4. Benzene and other aromatics have been detected in the volatiles when the drying time is prolonged.

5. No benzene and other aromatics have been detected to date in the quench water from the fluidized bed dryer, utilizing a short residence time for the coal feed stock.
6. Some volatiles have not been collected and identified, as evidenced by a poor material balance.

Table 1
Blu Loss on Drying

Experiment Number	Drying Atmosphere	Time in Storage	Btu/lb Dry Coal		% Loss
			As Received	Dried	
1	air	over 2 years	11053	10629	3.8
2	nitrogen	over 2 years	10933	10531	3.7
3	nitrogen	over 2 years	10896	10523	3.4
4	nitrogen	2-3 months	12369	11325	8.4
5	nitrogen	2-3 months	12379	11435	7.6
6	nitrogen	2-3 months	12262	11398	7.1
7	nitrogen	2-3 months	12404	11464	7.6
8	helium	2-3 months	12021	11395	5.2
9	helium	2-3 months	12387	11377	8.1
10	helium	freshly mined	12307	11375	7.6
11	helium	freshly mined	12375	11391	7.9
12	vacuum	freshly mined	11815	11010	6.8
13	vacuum	freshly mined	10971	10170	7.3
14	nitrogen	unknown	10596	10184	3.9
15	nitrogen	unknown	11455	11053	3.5
16	helium	unknown	11556	11197	3.1
17	helium	unknown	11961	11179	6.5
18*	helium	unknown	11327	11175	1.3

*This sample was previously dried by the spray drying technique and stored.

Table 2

Identification and Quantization of Peaks from Figure 2

<u>Peak Number</u>	<u>Identification</u>	<u>Percent of Total Recovered Organics</u>
1	2, 2 dimethyl butane	{ 27.40*
2	1, hexene	
3	2, or 3 hexene	
4	methyl pentane mixture	21.78
5	n-hexane	10.19
6	benzene	0.13
7	unknown	0.13
8	cyclohexane	7.87
9	thiophene	0.13
10	cyclohexene	6.31
11	2, heptene	{ 7.32*
12	3, heptene	
13	n-heptane	
14	2, 2, 4, (?) trimethyl pentane**	3.98
15	methyl cyclohexane	1.30
16	methyl cyclohexene	2.31
17	toluene	0.13
18	methyl heptane	<u>2.14</u>
		99.98

*Peaks numbers 1-2, and 11-12 were quantized collectively due to insufficient resolution of the peaks.

**The branching for compound Number 14 is not certain.

Table 3
Material Balance of Coal During Heating Process

<u>Experiment Number</u>	<u>Purge Gas</u>	<u>% Loss in Weight</u>	<u>% Recovered</u>	<u>% Unrecovered</u>
25	Helium	13.3	11.6	1.7
26	Helium	13.3	9.4	3.9
27	Helium	19.8	17.8	2.0
28	Helium	20.5	17.0	3.5
29	Helium	22.8	20.0	2.8
30*	Helium	22.2	20.1	2.1
31**	Helium	7.1	5.3	1.8

*Two milliliters were estimated to be in the liquid nitrogen trap but are not included in the above calculations since it could not be weighed.

**The sample was previously dried by spray drying techniques and stored.

Figure 1

Typical Heating Rate Curve for Experiments in Table I

Figure 3

Schematic of Laboratory Bench Scale Drying Experiments

Key:

Dryer

1. Helium source
2. Reaction vessel
3. Fluidized sand heating bath
4. Water cooled condenser
5. Cold trap
6. Liquid nitrogen scavenger trap

Separation

7. Extraction step
8. Gas chromatograph

Identification

9. Mass Spectrometer
10. Recorder

Figure 4

Mass Spectrum (Methanol Extract of Quench Water)

Figure 5

Mass Spectrum. (Ether Extract of Quench Water--First in Sequence)

Figure 6

Mass Spectrum (Ether Extract of Quench Water--Second in Sequence)

Figure 7

Mass Spectrum (Ether Extract of Quench Water--Third in Sequence)

THE MONTANA ENERGY AND MHD
RESEARCH AND DEVELOPMENT INSTITUTE

ABSTRACT

Development of powder preparation and sintering procedures for fabricating magnesia/magnesia-alumina spinel hardware and test pieces formed by isostatic pressing, slip-casting, and extrusion are reported.

Several commercially available binders and other ceramic fabrication aids were evaluated. A special topical report covering these studies is in preparation.

Characterization of degradation in commercial refractories and technical ceramics exposed to simulated coal-fired MHD preheater operating conditions is reported. Measurements of changes in the thermal diffusivity are related to microstructural and mechanical properties degradation.

Pristine RFG, a rebonded fused-grain magnesite chrome refractory used as the core material in the Montana State University (MSU) preheater test facility, degraded substantially when thermally cycled between 1040 to 1180°C and 1300 to 1400°C ranges for up to 7000 cycles in air. No significant degradation was observed for RFG cycled in a lower temperature range (127 to 777°C). A small amount of degradation occurred when RFG was held in air at a constant temperature of 1400°C for similar periods of time. Maximum degradation consisted of a 30% decrease in thermal diffusivity and 17% increase in open porosity (measured at MERDI) and a 90% decrease in compressive strength (measured at MSU).

Pristine X317, a commercial fused-cast magnesia/magnesia-alumina spinel, was cycled through four consecutive heating-cooling cycles from room temperature to 1100°C. The thermal diffusivity displayed large reproducible "hysteresis loops" which are attributed to the shrinking and separation of primary periclase

within the spinel matrix--a type of microcracking. Analysis of optical and scanning electron micrographs confirm this conclusion. The microcracked structure is thought to be largely responsible for the enhanced thermal shock resistance exhibited by this material.

The thermal conductivity/diffusivity of high-purity, dense, polycrystalline, magnesia-rich magnesia-alumina spinels is shown to depend primarily on the excess amount of high-conductivity magnesia phase. At room temperature, the thermal conductivity of magnesia is about a factor of four higher than that of magnesia-alumina spinel.

The thermal conductivity was calculated to range from 1.3 to 2.0 watts/m²K for amorphous and partially crystallized Montana Rosebud coal slag, respectively.

The thermal diffusivity equipment was upgraded by the addition of a low-temperature thermocouple and a high-temperature photodiode transient temperature detector.

The wetting behavior of molten Rosebud coal slag with a series of dense, high-purity, MgO/MgAl₂O₄ composites with compositions varying in excess MgO from 0 to 86 m/o, was studied. Stoichiometric MgAl₂O₄ substrates were more non-wetting and less reactive with Rosebud (unseeded) coal slag than either MgO or Al₂O₃ substrates or MgO/MgAl₂O₄ composite substrates. For this reason, an extensive development program for MgAl₂O₄ hardware development and fabrication has been initiated at MERDI.

I. OBJECTIVE AND SCOPE OF WORK

The objective of this task is to provide technical and administrative management of research being conducted by the units of the Montana University System, and to perform and coordinate the materials research and evaluation work conducted in Montana in support of the national plan for MHD electrical power development formulated by the DOE-FE-MHD Division. The research emphasis is placed on elements of open-cycle MHD utilizing coal as the primary fuel.

The objectives will be met by including the following subtasks at MERDI:

- . Maintain a survey of MHD materials development to keep aware of advances in problems in this area;
- . Select, evaluate, and characterize materials, including testing to simulate performance under actual MHD conditions;
- . Perform pre- and post-test analysis of materials and materials from components tested under simulated or actual MHD conditions; and
- . Provide materials and specimen fabrication facilities and services required to assist other experimental investigators in obtaining data needed to supply well-characterized materials for MHD test applications.

Specific activities designed to meet these objectives which are described in this report are:

- A. Development, fabrication, and characterization of controlled structure and MHD materials;
- B. Studies of the thermal conductivity and diffusivity of MHD materials; and
- C. Studies of wettability of MHD materials by slag-seed mixtures.

II. SUMMARY OF PROGRESS TO DATE

A. MHD Materials Development, Fabrication, and Characterization

Development of powder preparation and sintering procedures for various magnesia/magnesia-alumina spinel composites continues. Alumina and spinel hardware and test pieces are being fabricated by isostatic pressing, slip-casting, and extrusion. Evaluation of binders and other aids for use in ceramics fabrication has been initiated. A scanning electron microscope/energy dispersive x-ray analysis facility is being added to the optical microscopy laboratory for materials characterization purposes.

B. Thermal Conductivity and Diffusivity of MHD Materials

In cooperation with researchers at Montana State University and Fluidyne Engineering Corporation, the MERDI program to characterize the thermal

transport properties of several candidate MHD-preheater refractories is continuing. Detailed thermal cycling effects on the thermal diffusivity of RFG (a rebonded fused-grain magnesite chrome refractory) and X317 (a fused-cast magnesia/magnesia-alumina spinel refractory) are described in this report.

The primary effect of thermal cycling RFG in air (up to 7000 cycles between 1310 and 1670K) is enhancement of the open-porosity fraction and attendant swelling. As a result, the thermal conductivity/diffusivity and compressive strength decreased up to 30% and 90%, respectively. The fact that hysteresis in the thermal diffusivity of X317 is reproducible after four consecutive heating-cooling cycles, indicates that crack propagation may be restricted by microcracking between the periclase nodules and spinel matrix, which leads to enhanced thermal shock and fatigue resistance in this material.

Thermal diffusivity/conductivity values were determined for a series of dense, high-purity magnesia/magnesia-alumina spinel composites and were related to the amount of excess high-conductivity MgO in the material. Analytic expressions were derived for the thermal diffusivity, thermal conductivity, and heat capacity for each composition.

Positive or negative changes in the thermal diffusivity/conductivity and density of initially dense and amorphous Montana Rosebud slag are related to simultaneously occurring phase changes--crystallization and pore formation.

A low-temperature furnace and a thermocouple transient-temperature detector were added to the thermal diffusivity rig to enable data acquisition down to 25°C. A photodiode detector also was added to expand the high-temperature range to ~ 2000°C.

C. Wettability and Reaction of MHD Materials with Slag-Seed Mixtures

Wettability and interface reaction data for molten Montana Rosebud slag with substrates of several technical and commercial refractories are reported. The sessile drop method for determining the coal slag surface tension and wetting contact angle is described. Post-test analysis of the slag-substrate interface is carried out with the aid of optical microscopy.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. MHD Materials Development, Fabrication, and Characterization (Ted Morse, C. Wood, Larry Bentsen, and G. E. Youngblood)

1. Introduction

Refractories that are generally chemically and mechanically stable during thermal cycling at high operating temperatures and somewhat reducing atmospheres encountered in the steel-making industry are primarily mixtures of magnesia-alumina spinel (MgAl_2O_4) with excess periclase (MgO) or alumina (Al_2O_3) or periclase.¹⁻³ For economic as well as technical reasons, many of these materials also are candidates for use in direct coal-fired MHD-preheater cores, hot-liners, and valves.⁴ The corrosive/abrasive action of the slags coupled with high-temperature thermal cycling cause refractory degradation in steel-making operations similar to those expected in a MHD-preheater, with the exception that high seed (mostly K_2O or K_2SO_4) contents are contained in MHD slags. Moreover, the similarity extends to the indirect coal-fired MHD-preheater where the slag would not contain the high concentrations of alkali, but would nevertheless be highly corrosive.

Well-developed direct bonding between spinel and periclase grains is reported as one of the sources of the good ceramic properties and service behavior of these refractories.⁵ It is well-known that spinel has many complex forms with easy substitution of Fe^{++} , Ni^{++} , Zn^{++} , and Mn^{++} for Mg^{++} or Fe^{+++} , Cr^{+++} , and Mn^{+++} , for Al^{+++} .⁶ For this reason, spinel should be resistant to the action of iron oxide-containing slags, and should be more resistant than alumina to the action of basic slags. According to Binns,⁷ it reacts with FeO , for example, to form a spinel phase containing iron oxide:

Any excess FeO will then go into solid solution with MgO . A considerable increase in FeO would be needed before any liquid phase appeared, so that spinel should have a similar capability to MgO in "mopping up" FeO , apparently a troublesome constituent of most coal slags as well. Resulting complex spinels, or solid solutions thereof, should have high solidus temperatures in the range of 1800 to 2500°C.⁸ Absorption of too much iron oxide can lead to swelling, followed by cracking

and spalling, however.⁹ It also is reported that MgCr_2O_4 spinel exhibits better slag resistance than magnesite in contact with slags possessing a CaO/SiO_2 ratio less than $\sim 2:1$ (which is characteristic of coal slags). Conversely, high-purity magnesite bricks are more compatible with highly basic slags.¹⁰

Both MgO and MgAl_2O_4 were selected as interelectrode insulators for the U-02 test modules.¹¹ It was determined in these tests that MgO is a better electrical insulator, but that MgAl_2O_4 was less subject to thermal stress fracturing and has less serious reactions with liquid seed.¹² Plasma sprayed layers of "pure" spinel, in particular, are better than dense MgO on the sides of ceramic electrodes where close attention must be paid to diffusion of Fe and thermal expansion matching.¹³

Previous MHD-preheater test work on commercially available refractories has demonstrated that magnesite-chrome and spinel-bonded magnesite bricks have superior corrosion resistance.¹⁴ However, commercially available magnesite-chrome materials will not withstand the alternating oxidizing-reducing atmosphere or thermal fluctuations that will occur in an actual MHD air heater system. In addition, simulated corrosion tests suggest that magnesite-alumina spinel is better suited for MHD air heater use than is magnesite.¹⁴

For these reasons, development and testing of materials at MERDI for application in MHD components (particularly components that require large volumes of material) have emphasized characterization of the reaction of spinel, as well as alumina, periclase, and their mixtures, with molten coal slag with and without K_2O (or K_2SO_4) seed. Much of this work has been performed in cooperation with researchers at Fluidyne Engineering Corporation and Montana State University, where MHD-preheater engineering and development programs presently are underway.

2. Fabrication of Magnesite-Alumina Spinel

To better understand the fundamental processes of slag corrosion and interaction, test samples of MgO , Al_2O_3 , MgAl_2O_4 , and two-phase mixtures of these components are being fabricated starting with high-purity oxide powders. The compositions of the high-purity and high-density materials that will be fabricated and tested at MERDI are indicated on the $\text{MgO-Al}_2\text{O}_3$ phase diagram of Figure 1. Compositions range from 100% MgO ,

through two-phase mixtures of MgO and MgAl_2O_4 , stoichiometric MgAl_2O_4 , two-phase mixtures of MgAl_2O_4 and Al_2O_3 , and to 100% Al_2O_3 . To date, compositions of $\text{MgO}/\text{Al}_2\text{O}_3$ with mole percent ratios 100/0, 65/35, 50/50, 35/65, and 0/100 have been prepared. The compositions of high-purity, dense specimens, obtained from outside vendors to supplement compositions fabricated in-house, also are shown in Figure 1.

Powder preparation procedures and binder/lubricant systems were developed, depending on the powder mixture and fabrication method. Generally, conventional calcining and sintering schedules were adopted. Dense ($\geq 98\%$ theoretical), uniformly small-grained ($\leq 50 \mu\text{m}$), and polycrystalline disc-shaped wafers were fabricated for MERDI thermal conductivity/diffusivity and wettability studies (see Sections B and C). Rods (1/2" diameter by 6" long) were fabricated for use in slag-corrosion testing by Montana Tech (Task B) researchers. Boats and crucibles of various compositions for slag-corrosion testing and containment of molten slag were fabricated, primarily for use by Montana State University (Task J) researchers. Detailed fabrication procedures for preparing these test specimens were described completely in previous quarterly reports¹⁵⁻¹⁷ and will not be repeated here.

At this time, a master batch of thrice-ground and thrice-calcined, stoichiometric, magnesia-alumina powder has been prepared. High-purity starting oxide powders were used as raw material.* Small batches of magnesia-or alumina-rich spinels will be prepared from this master batch by adding the appropriate amount of oxide powder or nitrate salt, calcining, and regrinding. All grinding will be performed using high-purity alumina media in a newly purchased alumina jar mill. It is important for composition control to adjust for ball wear and loss on ignition, also. Although this procedure involves many steps, it yields a high quality end-product. The two different starting powders (MgO and Al_2O_3) must be uniformly distributed for final sintered pieces to be homogeneous, and to have a high-density, a controllable grain-size, and (presumably) a uniform elemental distribution. Elimination of the second and third calcine and intermediate milling steps resulted in sintered pieces which were visibly non-uniform. Low interdiffusion compositions require that fine

* α -alumina (RC-HP-DBM + 0.023 % MgO), Reynolds Aluminum Co., Bauxite, Arkansas, 99.98% MgO ($0.3 \mu\text{m}$), Adolf Meller Co., Providence, Rhode Island.

Figure 1.--Phase diagram for the MgO:Al₂O₃ system showing the composition of various test samples fabricated at MERDI (dashed arrow) or obtained from outside vendors (solid arrow)

powders be uniformly mixed initially. This can be achieved by co-precipitation, gel processing, or slurry mixing followed by spray drying in some cases. However, with equipment limitations considered, the 10-step procedure outlined previously was adopted to achieve uniformity.¹⁶

By starting with a base of MgAl_2O_4 and adding the desired amounts of MgO (or Al_2O_3) powders, no large volume differential changes between different phases of magnesia-rich spinel, and only small differential changes during sintering of alumina-rich spinels, are expected to take place during sintering. A high success rate is therefore expected for fabricating dense ceramic samples and hardware of any desired magnesia-alumina composition from this starting powder mixture.

The primary constituents of commercial refractories tested (at MERDI) are similar to the constituents contained in the disc, rod, and crucible test specimens made from the high-purity starting materials. Hence, characterization data for the compositions of these specimens serve as a baseline for comparison to the thermal transport and slag-wettability/interaction data obtained for several commercial refractories (described in Sections B and C).

3. Evaluation of Binders and Other Aids for Use in Ceramics Fabrication

To meet materials requirements for MHD components or test procedures, it is necessary to fabricate ceramics into specific shapes with controlled dimensional tolerances as well as optimum physical and chemical properties. Fabrication methods such as isostatic pressing, slip-casting, and extrusion generally require organic additives as aids in processing ceramic powders. These additives directly affect the green and final fired densities, the grain-size, -orientation, and -size distribution, and the micro- and macroporosities (which in turn determine the range of physical and chemical properties for any specific material). The selection of binders, lubricants, dispersants, and antifoams (individually or in combination) which are compatible with a given ceramic body formulation and processing procedure can present very complex problems. Therefore, a systematic survey of commercially available additives and their effects in ceramic processing (especially isostatic pressing, slip-casting, and extrusion) was initiated. All of the processes are used at MERDI to

fabricate parts for MHD materials testing in-house or in support of Montana Tech or Montana State University MHD research programs.

A preliminary topical report, "Evaluation of Binders, Lubricants, Dispersants, and Antifoams for Use in Ceramic Body Formulation," by Ted Morse and J. J. Rasmussen was issued in January and is available from MERDI on request.* This report describes the expected results in ceramic formulation when using various commercially available binders, lubricants, dispersants, and antifoams. In Tables I-III, listed herein, the additive names (described in the topical report), and principal effects are summarized. Studies presently in progress will emphasize evaluation of the additives based on evaluation of various ceramic end-products. A second topical report will be released when these studies have been completed.

TABLE I.--Additives Used in Ceramic Processing--Binders

Product	Source	Specific Effect
B-72	Rohm & Haas Company Independence Mall West Philadelphia, Pennsylvania 19105	Hard parts, high strength, brittle. Brittle unless plasticizer (Triton X-100) is used.
B-82	"	Extremely hard parts, good green strength, brittle. Should be used with plasticizer (Triton X-100).
B-60 A	"	Good green density, non-brittle parts may be green machined, can be used in either water or alcohol. Should be plasticized if used in water.
PVA Polyvinyl Alcohol 71-30	DuPont Company, Plastic Dept. Polymer Products Division Wilmington, Delaware 19808	High green strength, but produces brittle green ware. A good general overall binder. Needs lubricant.
PVB Polyvinyl Butyral B-76	Monsanto Industrial Chem. Co. 800 Lindburgh Blvd. St. Louis, Missouri 63166	Dual purpose - dry press or extrusion. Medium green density - fair green strength.

* Requests should be addressed to Ted Morse, The Montana Energy MHD Research and Development Institute, Inc., P. O. Box 3809, Butte, Montana 59701.

TABLE I.--Additives Used in Ceramic Processing--Binders

<u>Product</u>	<u>Source</u>	<u>Specific Binders</u>
Mobilcer JM	Mobil Oil Co. P. O. Box 900 Dallas, Texas 75222	High green density, high purity, self-lubricating. May be used in dry ball milling.
Polyox WSR-301	Union Carbide Co. Chemicals & Plastics New York, New York 10017	Good green density when used with oleic acid in dry ball mill. (Characterization in progress on this product.)
Methocel A-4C	Dow Chemical Co. Midland, Michigan 48640	Good binder but no lubricating qualities. Excellent extrusion binder. Water provides lubrication.
Carbowax 20M	Union Carbide Co. Chemicals & Plastics New York, New York 10017	Good binder. Self-lubricating at low pressure (3 to 10 kpsi).
Paraffin Wax	Frank B. Ross Co., Inc. Jersey City, New Jersey 07304	Gives high green densities, low green strength. Requires special hot emulsifying process to use in H ₂ O base batches.
Japan Wax	"	Laboratory tests have shown good potential but tests are incomplete at this time.
Carnauba Wax	"	Laboratory evaluation tests in progress.

TABLE II.--Additives Used in Ceramic Processing--Lubricants

Products	Source	Specific Effect
Oleic Acid	Armac Chem. Co. P. O. Box 1805 Chicago, Illinois 60607	One of the better lubricants. Rapid burn-off over a narrow temperature range.
NeO-Fat	"	Similar to above - good lubricating qualities.
Aqua Dag (Colloidal Graphite)	Rohm & Haas Co. Independence Mall West Philadelphia, Pennsylvania 19105	Promotes good green densities in parts to be air-fired. Wide burn-out temperature range.
Butyl Stearate		Good lubrication qualities. Moderate burn-off temperature range with slow burn-off rate. Also serves as a good mold release.
Powdered Aluminum	Minnesota Mining & Mfg. Co. St. Paul, Minnesota	Excellent lubricating qualities for Al_2O_3 bodies. (Converts to Al_2O_3 in air-firing of parts)

TABLE III.--Additives Used in Ceramic Processing--Dispersants and Antifoams

Product	Source	Specific Effect
<u>Dispersants</u>		
Darvan #7	R. T. Vanderbilt Co., Inc. 30 Winfield St. Norwalk, Connecticut 06855	Polyelectrolyte salt of ammonia. An excellent dispersant. Contains some sodium.
Darvan "C"	"	Same as above except does not contain sodium.
Tamol 731	Rohm & Haas Co. Independence Mall West Philadelphia, Pennsylvania 19105	Powerful dispersant and surfactant. Promotes a tough foam which is difficult to break.
Triton X-100	"	Acts as dispersant, surfactant and plasticizer. Versatile.
Aerosol OT-75%	American Cyanamid Co.	General purpose wetting agent.
<u>Antifoams</u>		
Tributyl Phosphate	J. T. Baker Chemical Co.	Very effective in aqueous base slips. Also acts as a light lubricant.
Nopco Foamaster "P"	Diamond Shamrock P. O. Box 2386 R Morristown, New Jersey 07960	Very effective. Used sparingly.
DB-31, DB-110	Dow Corning Corp. Midland, Michigan 48640	Very effective. Contains trace amounts of silica.

4. Ceramic Hardware Fabrication

Table IV lists the types of ceramic test pieces and hardware fabricated in the MERDI laboratories and their nominal compositions, densities, porosities, and intended use. Figure 2 illustrates the shapes and relative sizes of various ceramic pieces; shown in this figure are slip-cast spinel boats and crucibles for containing molten coal slag, isostatically pressed rods for slag-corrosion studies, isostatically pressed wafers for slag-wettability and interaction studies, and a section of an extruded spinel thermocouple rod. High-density spinel (MgAl_2O_4) boats, crucibles, and thermocouple protection rods, more resistant to slag/seed corrosion than the normally-used alumina hardware, are generally not commercially available.

5. Materials Characterization

Procedures for characterizing materials both before and after testing presently consist of:

- 1) density and porosity determinations by liquid immersion,
- 2) optical microscopy of mounted, polished, and etched ceramic specimens, and
- 3) low magnification photography.

In addition, x-ray diffraction analysis of powders and reaction surfaces of solids exposed to high temperatures and molten coal slag/seed mixtures are performed at Montana Tech or Montana State University facilities.

A scanning electron microscope (SEM) and an energy dispersive x-ray (EDX) system* has been purchased and will be put into operation during the next quarter. The SEM unit will be equipped with a large specimen chamber which will allow analysis of a three inch diameter sample or a number of smaller samples arranged on a rotatable turret without breaking vacuum. Arrangements have been made with researchers at the University of Utah to perform quantitative elemental distribution analysis with an electron microprobe on selected samples once they have been screened in-house using a semi-quantitative mode.

* An ISI-40 SEM with a Robinson back-scatter electron detector and a PGT 1000 XCEL semi-quantitative EDX.

TABLE IV.--Types and Characteristics of Ceramic Test Pieces and Hardware Fabricated at MERDI

Type	Fabrication Process	Nominal Composition MgO/Al ₂ O ₄ (in m/o ratio)	Density (gm/cc)	Porosity %	Grain Size (μ m)
Discs ^a (1" dia. x 1/4" tk.)	uniaxial die press and sinter*	100/0	3.52	1.7	< 10
		85/15 ⁺	-	-	-
		65/35	3.51	2.0	< 10
		55/45 ⁺	-	-	-
		50/50 ⁺	3.53	1.4	20-60
		40/60 ⁺	-	-	-
		35/65 ⁺	3.50	-	-
		22/78 ⁺	-	-	-
		0/100	3.89	2.5	< 10
Boats ^b (1/2" w x 1/2" h x 2" l)	slip cast and sinter*	50/50	3.52	1.7	20
Crucibles ⁺ (2" dia. x 2 1/2" h)	slip cast and sinter*	50/50	3.52	1.7	20
		100/0	3.36	6	-
Rods ^c (1/2" dia. x 5" l)	isostatic press and sinter*	65/35	3.53	1.4	< 10
		50/50	3.52	1.7	20-40
		0/100	3.95	1.0	< 10
Thermocouple Rods ⁺ (1/4" dia., 2-.030" holes)	extrude and sinter*	50/50	3.38	6	-

a Used for MERDI in-house fabrication procedure development, slag-wettability and -interaction tests, and thermal transport properties tests.

b Used for slag/seed containment during slag electrical conductivity tests by MSU researchers.

c Used for slag/seed corrosion tests by Montana Tech researchers.

* MgO/MgAl₂O₄ compounds sintered at 1600°C (160 minutes); Al₂O₃ compounds sintered at 1520°C (4 hours).

+ In process of development.

Figure 2.--Ceramic hardware and test pieces fabricated in MERU laboratories by isostatic pressing, slip-casting, and extrusion

B. Thermal Conductivity/Diffusivity of MHD Materials
(Larry Bentsen and G. E. Youngblood)

1. Introduction

Efforts during this past year were directed primarily toward the rapid evaluation of thermal transport properties of MHD materials--particularly the changes in the thermal diffusivity/conductivity of commercial refractories that have received various degrees of exposure to simulated coal-fired MHD-preheater operating conditions. The changes then are related to the observed structural changes (both macro and micro) in the exposed refractories.

The choice of which refractory type to use in a particular engineering facility must be guided by studies of refractory performance in simulated in-service environments on a small scale. Refractory material costs generally represent a large proportion of the capital costs of a high-temperature facility. Furthermore, replacement costs and downtime due to gross refractory degradation and premature failure cannot be tolerated in a large facility. Hence, it is important to understand the expected degradation mechanisms in order to select the proper refractories for optimum service from the beginning. In addition, since the refractory structure (macro and micro) can be modified through processing control, fabrication techniques can be utilized to provide the best refractory for expected in-service conditions. Also, the data will provide input for engineering calculations of the magnitudes of thermal stresses and of overall heat energy balance and efficiency for various heat exchanger designs using ceramic heat storage.

This portion of the work was carried out in cooperation with researchers at Montana State University and FluidDyne Engineering Corporation. To provide a data base, thermal transport data were collected on other potential MHD materials or technical ceramics. These materials were provided by the following cooperating MHD contractors or subcontractors:

- . Montana Rosebud coal slag (seeded and natural)--
Montana State University
- . Synthetic coal slags--Montana Tech

- $\text{La}_x\text{Sr}_{1-x}\text{CrO}_3$ and $\text{La}_x\text{Sr}_{1-x}\text{FeO}_3$ --A.T. Research
- $\text{MgO}/\text{MgAl}_2\text{O}_4$ composites--TransTech, Inc.
- $\text{Al}_2\text{O}_3/\text{SiC}$ composites--University of Utah
- $\text{MgO}/\text{MgAl}_2\text{O}_4$ composites--MERDI (in-house)
- MgO and MgAl_2O_4 hot-pressed substrates--Ceradyne, Inc.

In turn, the collected thermal transport data and analysis is provided directly to the contractors.

2. Theory

The laser-flash diffusivity technique was selected as the primary method for determining the thermal diffusivity (α), mainly because of its simplicity and high-temperature adaptability. The thermal conductivity (λ) can be calculated from α , the density (ρ), and the specific heat capacity (C_p) by the equation

$$\lambda(T) = \alpha(T) \cdot \rho(T) \cdot C_p(T) \quad (1)$$

where all of the terms are functions of temperature (T). When possible, values of $\lambda(T)$ and $\alpha(T)$ are expressed in analytic form for ready application in engineering design or systems thermal analysis. These data are particularly necessary since many other physical properties (such as electrical conductivity, viscosity, diffusion, reaction rates, creep rates, strength, etc.) are so sensitive to temperature or temperature distribution, which in turn is dependent on the heat flux and values of thermal conductivity.

The technique, equipment check-out, and numerous experiments designed to provide a data base necessary to characterize MHD materials are described in detail in the Task N section of last year's Annual Report (Reference 22).

3. Experimental Technique and Equipment Upgrading

The transient temperature detection system used in the laser-flash diffusivity system has been expanded to extend the temperature range for thermal diffusivity measurements. The infrared detector is capable of measurements in the 200-1200°C temperature range. A thermocouple detector to cover the 20-400°C range, and a photodiode detector to

cover the 1000°C-2000°C range, were designed and built. The thermocouple is a spring-loaded intrinsic type which not only has a fast response time, but also facilitates rapid sample placement and removal. With the low-temperature rig, the thermal transport properties can be quickly surveyed over a limited temperature range, or even at one temperature for a large number of samples in one day. For measurements at very high temperatures, a silicon-diffused pin photodiode with associated electronics was mounted in a holder which swings into alignment using the same alignment pins as are used for the infrared detector. The present arrangement of the laser-flash diffusivity apparatus is shown in Figure 3.

The thermal diffusivity of a hot-pressed, high-purity, Al_2O_3 reference sample, as determined from measurements by each of the three overlapping detection techniques, is shown in Figure 4. The close agreement with reference values¹⁸ and in the overlap temperature range indicates that the thermal diffusivity can now be measured routinely from room temperature to 1800°C. The thermal diffusivity values for Armco iron, Corning C9606, (a glass-ceramic), and high-purity MgO, reported in previous quarterly reports, also were determined over the temperature range 25 to ~ 1200°C; they compared favorably ($< \pm 3\%$) with reference values. Future upgrading will concentrate on installing computer data acquisition and control capability.

4. Preheater Refractories

Work this past year emphasized determination of the thermal transport properties of several commercial refractories before and after exposure to simulated coal-fired MHD-preheater operating conditions. The changes in the thermal diffusivity/conductivity were related to macro- and micro-structural changes that occurred in the refractory test samples exposed to the cycling slag/seed/gas atmosphere in a temperature range of 1700 to 2000 K for times up to 500 hours in the Fluidyne Engineering Corporation preheater tests. A complete copy of a report^{*} describing these results appears as the appendix in reference 16. Only the major highlights of this report will be summarized here.

Table V lists the thermal conductivity values calculated from Eq. (1) for the tested refractories as well as their measured bulk densities and open porosities. Similar values for dense polycrystalline

* Report also is available from MERDI by request

Figure 3.--Experimental facilities for measuring the thermal diffusivity by the laser-flash technique

Figure 4.-- Thermal diffusivity of reference α -alumina as determined by three methods of temperature transient measurement. The open (closed) symbols indicate measurements made on heating (cooling).

TABLE V.--Calculated Thermal Conductivity Values for Several Commercial Refractories Before and After Exposure to Simulated MHD-Preheater Operating Conditions

Material	Exposure	Density (gm/cm ³)	Open Porosity (v/o)	Thermal Conductivity			Hysteresis Observed?
				200°C	1000°C	1500°C	
(watts/m ² K)							
RFG	pristine	3.30	13	5.0	3.2	2.0	yes
	100 hrs	3.59	3	4.7	3.4	2.6	yes
	200 hrs	3.39	7	3.8	2.8	2.1	no
E	pristine	4.44	7	3.4	2.9	2.9	no
	500 hrs	4.28	3	3.6	3.4	3.0	no
K3	pristine	3.95	4	6.1	3.9	3.1	no
	500 hrs	3.83	3	5.0	3.6	3.0	no
X317	pristine	3.38	2	11.1	5.5	4.3	yes
	500 hrs	3.53	0.2	5.7	3.9	3.8	no
SX487A	pristine	2.90	13	5.3	2.6	2.4	no
	200 hrs	2.80	12	(no suitable sample obtainable)			
<u>For Reference</u>							
BeO*		2.95	1	157	29	17	-
MgO		3.58	< .5	29.0	7.3	6.5 [†]	no
Al ₂ O ₃		3.98	< .5	21.0	6.2	5.5 [†]	no
65MgO/35Al ₂ O ₃ (m/o)		3.54	< .5	10.1	5.3	4.5	no
50MgO/50Al ₂ O ₃ "		3.57	< .5	9.7	5.0	4.4	no
70Al ₂ O ₃ /30Cr ₂ O ₃ "		4.28	~ 0	6.5	4.5	-	no
ZrO ₂ -cubic form*		5.7		2.1	2.3	2.5	-
Rosebud Coal Slag (amorphous)		2.81	~ 0	1.3	1.4 [†]	-	yes

* Data were taken from Reference 20.

magnesia, alumina, a magnesia/magnesia-alumina spinel composite, magnesia-alumina spinel, alumina-chromia solid solution, cubic phase zirconia, and a solid amorphous slag are listed for reference. Refractories exposed to slagging conditions in the preheater tests are listed according to their time-lengths of exposure. Refractories tested included RFG, a rebonded, fused-grain magnesite-chrome; E, a fused-cast chrome spinel; K3, a fused-cast chrome-alumina; X317, a fused-cast magnesia/magnesia-alumina spinel; and SX487A, a direct-bonded, fused-grain, stoichiometric magnesia-alumina spinel.⁺

Only thermal conductivity values calculated from thermal diffusivities measured during heat-up are listed in Table V. The last column indicates whether or not there was hysteresis in the measured thermal diffusivity on heating and cooling, i.e., yes (no) means $\alpha(T)$ was (not) reproducible during increasing and decreasing temperature cycles.

Of the refractories tested, pristine X317 had the highest thermal conductivity/diffusivity; after 500 hours exposure at 1700 to 2000 K in a cycling slag/seed air stream it appeared to perform better than the other refractories tested. Refractory K3 performed well; RFG performed moderately well. Swelling and/or slag corrosion were particularly severe in refractories E and SX487A.

As seen by comparing the values of thermal conductivity for a "reasonably good" ceramic conductor (MgO) and a "poor" ceramic conductor (amorphous Rosebud Ash) at 200 and 1000°C, the ratios are about 24 and 5, respectively. The larger ratio and much wider variation observed at 200°C are due to the fact that phonon conduction is sensitive to extrinsic scattering or blocking mechanisms (i.e., due to impurities, solid solution atoms, porosity, microcracks, etc.) in the lowest temperature range. Hence, low-temperature thermal conductivity is a good monitor for chemical and structural changes taking place as a result of degradation in a ceramic material. At higher temperatures ($\sim 1000^\circ\text{C}$ or above), thermal conductivity decreases due to phonon-phonon scattering are, for the most part, independent of structural details. For instance, the mean free path for phonon scattering in alumina is $\sim 4 \text{ \AA}$ at 1000°C , and would not be expected to go much lower. Little difference in the thermal conductivities of "good"

⁺ RFG composition is given on page 20; see Table XII for compositions of the other refractories.

or "poor" conductors is observed above 1500°C; thermal conductivities lie within a narrow range of from 2 to 6 watts/m⁰K for engineering ceramics in general.

Details of further tests used to analyze the thermal transport behavior of specific materials follow.

RFG⁺ - Since RFG is being used extensively in present test preheaters, analytic expressions derived from the measured or calculated data to show the temperature dependence of specific heat capacity, thermal diffusivity, and thermal conductivity are given in Table VI for use in engineering modeling or design. The analytic expressions cover the temperature range 673 to 1773 K. Although the coefficients are given to three significant figures, the results for Cp are probably reliable to ±5%, and for α and λ to ±25%. The primary uncertainty in α and λ is sample nonhomogeneity, particularly due to porosity texture and distribution in RFG.

The decrease in strength (MOR) of RFG that had been thermally cycled in air or molten slag was shown to be related to a decrease in the room temperature thermal diffusivity.¹⁹ Lowering of both strength and thermal diffusivity, presumably, is caused by the extension of cracks which are effective thermal transport barriers at low temperatures (T < 1500 K). Even though crack propagation during thermal cycling probably enhances the rate of penetration and thermo-chemical disruption in this material, the combination of many interlocking phases would act as crack stoppers and would prevent catastrophic failure due to thermal stress cracking. A micrograph of a polished surface and a SEM fractograph for pristine RFG are shown in Figures 5 and 6, respectively. These figures illustrate the complex structure. For instance, note in Figure 6 the small (~ 1 μm) white grains exsolved MgO/(Fe,Cr)₂O₃ spinel within the periclase matrix of pristine RFG.

Room temperature values of thermal diffusivity were obtained for a series of RFG cylindrical cores (3" long by 5/8" diameter) which had been thermally cycled in air (no slag exposures) between two furnaces, each

⁺ Corhart Refractories Company, Louisville, Kentucky - chemical composition in w/o : 56MgO-20Cr₂O₃-8Al₂O₃-11FeO-2.5SiO₂-0.5CaO-1.5TiO₂.

TABLE VI.--Linear Least Squares Representation of the Thermal Transport Properties of RFG Before and After Slag/Seed Exposure*

Quantity	Before (pristine)	After (200 hours exposure)
$C_p(\text{cal/gm}^\circ\text{K})$	$0.233 + 3.23 \times 10^{-5}(\text{°K})$	$0.229 + 3.63 \times 10^{-5}(\text{°K})$
$\alpha(\text{cm}^2/\text{sec})$	$0.0181 - 7.36 \times 10^{-6}(\text{°K})$	$0.0126 - 4.18 \times 10^{-6}(\text{°K})$
$\lambda(\text{watts/m}^\circ\text{K})$	$6.06 + 2.27 \times 10^{-3}(\text{°K})$	$4.39 - 1.27 \times 10^{-3}(\text{°K})$

* Exposed to 1/2 hour cycles of heating and cooling within a 1700 to 2000 K temperature envelope - see Reference 16 for more details. The expressions cover the temperature range 673 to 1773 K.

Fig. 5--Pristine RFG microstructure by reflected light. The large white phase is $\text{MgO}:\text{Cr}_2\text{O}_3$, the light gray phase is MgO , the small white phase within light phase is exsolved $\text{MgO}:(\text{Fe},\text{Cr})_2\text{O}_3$, the dark gray phase is silicate, and the darkest gray phase is porosity. The 1 cm. bar = 20 μm .

Fig. 6.--Scanning electron micrograph (SEM) of pristine RFG fracture surface. showing exsolved complex spinel within MgO phase. The 2.9 cm bar = 20 μm .

maintained at a different temperature.* The temperature ranges and cycle times were picked to establish similar levels of thermal stress at the sample surface. Twenty-four samples were divided into four groups of eight samples each. One group was cycled between 400 and 1050 K (Low range = L), another between 1310 and 1450 K (Medium range = M), and another between 1570 and 1670 K (High range = H). A final group made up of pristine samples served as a reference (R group). Cycle times varied from two to five minutes for a total of from 300 to 7000 cycles. At the completion of the thermal cycles, discs were cut from the center of each cylinder for diffusivity, density, and open porosity measurements. The two end pieces were tested for strength degradation in axial compression.²¹

Average results are listed in Table VII. The limits represent standard deviations calculated from the variation of measured data for the eight samples in each group.

No significant decreases in thermal diffusivity or increases in porosity were observed in RFG samples cycled up to 7000 times between 400 and 1050 K. Substantial decreases in thermal diffusivity/conductivity and a simultaneous increase in porosity were observed for RFG samples cycled over 600 times between the M and H temperature ranges. Thus, the degradation in thermal transport is observed to be directly correlated to an increase in open porosity with higher temperature cycling.

Previous work^{22,23} on porous materials indicated that a semi-empirical equation

$$\lambda/\lambda_0 = \frac{1-P}{1+\beta P} \quad (2)$$

can be used for analysis. In this equation λ and λ_0 are the thermal conductivities of porous and nonporous materials, respectively; P is the fractional porosity; and β is a parameter which depends upon pore shape, P , and T . For a given density, connected open pores or flattened pores found in direct or rebonded refractories were more effective in lowering thermal conductivity than were isolated spherical pores found in normally sintered ceramic or in fused-cast refractories. Values of β from 2-5 are characteristic of rebonded or direct-bonded refractories near 200°C,¹⁵ whereas $\beta = 0.5$ for theoretical, isolated, vacuum-filled, spherical pores with no radiation conduction.²⁴ At higher temperatures,

* This work was carried out as part of a thesis project at MSU (see Reference 21).

TABLE VII.--Room Temperature Thermal Diffusivity/Conductivity Values and Open Porosity of Thermally-Cycled RFG

Group	Thermal Diffusivity (cm ² /sec)	Thermal Conductivity (watt/m°K)	Open Porosity (%)
R	0.019 ± .002	6.6 ± 0.6	12.6 ± 0.7
L	0.019 ± .002	6.6 ± 0.4	12.8 ± 0.8
M	0.016 ± .002	5.1 ± 0.7	13.5 ± 1.0
H	0.014 ± .002	4.6 ± 0.9	14.7 ± 1.5

however, where radiation effects are strong ($T > 1500$ K), β approaches -1.²⁴ That is, the porosity effect generally becomes insignificant in a refractory at a temperature within the temperature operating range of a preheater. Also, microcracks or macrocracks, which do not contribute to P to any extent, are not effective as thermal barriers in a refractory at high operating temperatures.

At room temperature, however, β is very sensitive to pore shape. The extension of pores or cracks in the bonding phase region between fused-grains in RFG would result in an increase in β without a significant increase in P itself.

Using Eq. (1) and the relation $\rho = \rho_0(1-P)$, Eq. (2) can be cast in terms of thermal diffusivity and porosity by

$$\alpha_0/\alpha = 1 + \beta P \quad (3)$$

where $\alpha_0 = \lambda_0/\rho_0 C_p$, the thermal diffusivity of nonporous material.

If reasonable values are picked for α_0 ,^{*} β can be calculated from the thermal diffusivity and porosity data. Although there is a large amount of scatter in this data, it is apparent that β approximately doubles when going from pristine RFG to samples which experienced the most severe high-temperature cycling.

When the compressive strengths of the thermally-cycled samples are compared to the mean strength of the control group, the data indicated that multiple thermal shock damage to RFG increased with the temperature level and number of cycles. However, thermal cycling in the low range (group L) produced no observable change in strength corresponding to an absence of change in porosity and thermal diffusivity. It is noteworthy that the compressive strength of samples held for ten days at a constant high temperature of 1673 K decreased about 40%, while the strength of a sample cycled 3000 times for a total exposure time of four days in the H range decreased almost 90%. It also was observed that the largest changes in porosity, thermal diffusivity, and compressive strengths occurred during the initial thermal cycles; succeeding cycles had a diminished effect.

* By reference to Figure 12, α_0 is expected to have a value between 0.03 and 0.04 cm²/sec at 25°C.

Insufficient data exist at this time to make predictions about the useful lifetime of the RFG refractory in a MHD-preheater environment; however, the following conclusion, based on physical processes as well as experimental evidence, can be made concerning the degradation of RFG. The main effect of temperature cycling in the medium temperature range or above ($T \geq 1310$ K) is an increase in porosity, most likely by extension of existing pores in the bonding phase. The stress required to propagate the cracks, in turn, is probably due to thermal expansion mismatch between the MgO bonding phase and the fused-grain spinel phase. Although these stresses are expected to be larger for the lower temperature range (larger ΔT), the bonding strength must fall off rapidly with increasing temperature and the thermal stress exceeds the bonding strength only during the medium- and high-temperature cycles. In addition, the increase in the parameter β with increasing severity of thermal shock cycling indicates extreme crack propagation. Thus, thermal transport and mechanical properties degradation are then related to the enhanced porosity effect. Increased penetration and, thus, corrosion by slag/seed would be expected in RFG exposed simultaneously to high-temperature cycling and a slag/seed environment, also.

X317^{*} - It has been reported that the commercial refractory X317, a fused-cast magnesia/magnesia-alumina spinel ($\text{MgO}/\text{MgAl}_2\text{O}_4$), performed well in the cycling high-temperature, slagging atmosphere, preheater tests at Fluidyne Engineering. Of several commercial refractories tested by MERDI, X317 exhibited the highest thermal conductivity/diffusivity.¹⁹ However, X317 had poor thermal cycling stability, as indicated by the non-reproducibility of the thermal diffusivity when measured during heating and cooling cycles.¹⁶

To check the thermal cycling stability further, thermal diffusivity measurements were made on pristine X317 during a series of four consecutive heating-cooling cycles to $\sim 1100^\circ\text{C}$. The results are shown in Figure 7. For clarity, Cycles 3 and 4 are offset from Cycles 1 and 2. Basically, the hysteresis loops themselves are reproducible in this material.

*Corhart Refractories Co., Louisville, Kentucky - chemical composition in w/o $67\text{MgO}-31\text{Al}_2\text{O}_3-0.8\text{Fe}_2\text{O}_3-0.5\text{CaO}-0.5\text{SiO}_2$.

Figure 7.-- Thermal diffusivity of fused-cast magnesia/magnesia-alumina spinel (X317) during four consecutive heating-cooling cycles showing reproducibility of "hysteresis loops."

The microstructure of pristine X317, depicted in Figure 8, consists of a continuous phase of MgAl_2O_4 which contains isolated, rounded grains of primary periclase (MgO) of about 20 to 50 μm size. The porosity ($\sim 5\%$) occurs primarily as isolated "shrinkage" voids of from 20 to 100 μm size. A few isolated macrovoids of up to ~ 1 cm diameter can also occur. There is little microporosity or connected porosity in this material. Such structures obtained by fused-casting are reported to have higher hot-strength, increased mechanical and abrasion resistance, and better resistance than chemically bonded or sintered refractories to corrosive attack from molten slags.²⁵

Figures 9A and 9B are scanning electron micrographs of a freshly fractured surface of X317. The region shown in 9A lies within one mm of the cast surface (skin), while the region in 9B is located about one inch from the skin. In a few places the rounded periclase grains appear to have been pulled out leaving a pit (P), while in other places the periclase grains appear as nodules (N). The fracture surface itself appears lacy in the region near the skin (as in 9A), while in the interior region (as in 9B), the surface is smooth. The fracture mode evidently changes from intergranular to transgranular as the crack propagates from the skin into the interior. This is probably due to a grain-size effect.

Figure 10A shows a higher magnification SEM view of one of the scattered white particles observed in Figure 9A. The lacy surface is now seen to be due to the intergranular mode of fracture where the grain size is small ($\sim 2 \mu\text{m}$). Figure 10B is an energy dispersive x-ray (EDX) dot map which identifies calcium as one of the main constituents in the isolated white particle pictured in Figure 10A. Another dot map of the same region (but not pictured here) showed only a slight increase of silicon concentration above background in the white particle.

Figure 11 shows a SEM micrograph of a ground and polished surface of X317 with detailed EDX spectra indicated for selected microstructural features. Two of the spectra (#1 and #4) identify the primary phase periclase grains, while two others (#2 and #3) identify the MgAl_2O_4 continuous phase. EDX spectrum #5 indicates fairly high concentrations

Figure 8.-- Microstructure of pristine X317. The rounded grains are primary periclase, the continuous phase is magnesia-alumina spinel, and the dark spots are isolated pores. The 1 cm bar = 100 μm .

Figure 9 (A-B).--Scanning electron micrographs of a fracture surface of X317. Figure 9A shows a region ~ 1 mm from the cast surface where P = a pit where a periclase grain has been removed while N = a periclase nodule exposed by the fracture. Figure 9B shows a stereo pair of a similar region located ~ 1 " from the cast surface

Figure 10A.--Scanning electron micrograph at high magnification showing intergranular fracture in region near the cast surface (same as in Figure 9A)

Figure 10B.--Energy dispersive X-ray (EDX) dot map showing calcium distribution in corresponding region depicted in Figure 10A

Figure 11.-- Scanning electron micrograph of polished surface of X317 showing EDX spectra for indicated regions. From left to right the peaks represent Mg, Al, Si, and Ca relative concentrations.

of both Si and Ca (as well as Mg and Al), while spectrum #3 shows moderate and about equal Si and Ca concentrations. Si and Ca peaks are barely observable above background in spectra #1, #2, and #4. No Fe peaks were observed in expanded spectra even though Fe has a higher nominal concentration in X317 than either Si or Ca. For convenience, the spectra shown here were reduced along the horizontal energy scale, even though actual examination extended to 15 KeV.

It was proposed in the March quarterly report¹⁶ that the rounded periclase grains shrink away from the surrounding spinel matrix upon cooling from fusion temperatures due to the higher thermal expansion of the MgO relative to the spinel matrix. The bond between these two phases is subject to separation during relatively slow rates of temperature cycling, thus resulting in the observed "reproducible hysteresis" in the thermal diffusivity. The well delineated MgO-MgAl₂O₄ boundary surrounding a primary periclase particle (depicted in the SEM view of Figure 11) is about a micron wide, which is about that expected for a shrinkage crack (or microcrack) between materials differing in thermal expansion by approximately $5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ (see Figure 13). It also is proposed that the presence of these microcracks, rather than porosity, is responsible for the enhanced thermal shock resistance for some fusion-cast MgO-MgAl₂O₄ refractories. At the same time, the strength should be controlled mainly by the continuous spinel matrix. However, it may be degraded by the extensive network of weak or cracked boundary layers.

The Ca and Si compounds appear to be isolated in clumps or around pores rather than distributed throughout a grain boundary phase as is normally found in conventional sintered refractories. Thin intergranular or bonding phases would act as effective thermal barriers as well as being responsible for reduced strength or creep resistance.¹ For instance, the thermal conductivity of X317, where the Ca and Si compounds appear to be isolated in clumps, is at least a factor of two higher than that of RFG. In addition, the isolation of the Ca-Si phase in clumps results in good high-temperature strength for X317.²⁶ Finally, the isolation of the pores, as well as the Ca-Si phase, within the stable and dense spinel matrix is responsible, in part, for lower slag penetration and rates of corrosion observed for X317 in the Fluidyne preheater tests.²⁷

Apparently, the Fe (which has a nominal concentration of 0.8 w/o in X317) goes into solid solution in both the MgO and MgAl_2O_4 as discussed in the introduction, and does not appear in large enough concentration at any location to show up in the EDX spectra. Therefore, the Fe should not contribute to degradation of the thermal or mechanical properties to any extent. Since Fe is one of the main constituents in most coal slags, the ability of MgO or MgAl_2O_4 to contain various amounts of Fe in solid solution or within a complex spinel structure without any degradation would be an advantage for using such compounds in coal-fired facilities.

Further work will examine the influence of various thermal shock treatments on the structure, thermal diffusivity, and fracture toughness of X317.

Spinel-A study to examine the effects on thermal transport properties of a high-conductivity oxide phase, MgO, in a two-phase mixture of MgO and MgAl_2O_4 was initiated during the last two quarters. The range of values determined for these high-purity, dense ceramics will serve as a reference for many commercial refractories with similar composition.

Isostatically pressed and sintered bars and hot-pressed plates of various compositions were provided by Trans-Tech, Inc. and Ceradyne, Inc., respectively. Baseline data for the "as-received" samples are given in Table VIII.

All of these high-purity materials were sintered or hot-pressed to a density exceeding 3.52 gm/cc (>98% TD) except S78. The anomalously lower density measured here (3.41 gm/cc) indicates that this particular sample contained a higher porosity, which also accounts for the lower than expected values of thermal diffusivity observed. By Eq. (3), less than a two percent correction in α or λ is expected for isolated porosity of one percent or less. The large grain-size for the two phase mixtures was smaller (< 25 μm) than for the single phase materials (40 μm or greater).

Bar samples ($\sim 1" \times 1" \times 7"$) will be exposed to cycling high-temperature slag/seed/gas atmospheres in the FluidDyne preheater materials degradation testing, after which thermal diffusivity and microstructural analysis will be conducted. Substrates will be tested in the MERDI

TABLE VIII.--Baseline Data (Composition, Density, Grain-Size, Thermal Expansion, and Room Temperature Thermal Diffusivity) for As-Received High-Purity, Polycrystalline, Magnesia-Rich Magnesia-Alumina Spinel

Sample ¹	Composition ¹		Density ² (gm/cc)	Large Grain-Size ² μm	Thermal Expansion ¹ 25 - 300°C ($\times 10^{-6} \text{ } ^\circ\text{C}^{-1}$)	Thermal Diffusivity ² at 25°C ($\times 10^{-2} \text{ cm}^2/\text{sec}$)
	MgO(m/o)	Al ₂ O ₃ (m/o)				
MgAl ₂ O ₄ HP*	50.0	50.0	3.55	20 - 40	7.7	4.25
S71 ⁺	51.0	49.0	3.51	20 - 25	7.1	4.48
S78 ⁺	56.3	43.2	3.41	10 - 15	7.8	4.22
S98 ⁺	89.5	15.5	3.52	5 - 10	9.3	6.88
S110 ⁺	93.0	7.0	3.52	5 - 10	11.0	8.52
MgO HP*	100.0	0.0	3.57 ₃	100	11.9	14.9

* Ceradyne, Inc., Santa Ana, California.

+ Trans-Tech., Inc., Gaithersburg, Maryland.

¹ Information provided by sample suppliers.

² Measured at MERDI for specific samples received.

wettability and slag interaction tests as well. In this section, only the dependence of thermal transport properties on composition of pristine materials will be discussed.

Since all of the spinel composites consist of a mixture of MgO and MgAl_2O_4 (confirmed by x-ray analysis), it is easier to think of these two compounds as the end members of a pseudo-binary phase diagram. It also is noted that the theoretical density of both MgO and MgAl_2O_4 is 3.58 to 3.59 gm/cc; therefore, weight percent and volume percent are essentially equivalent. The approximate volume percent (v/o) for a MgO- MgAl_2O_4 diagram is estimated assuming that the two phases are pure MgO and stoichiometric MgAl_2O_4 . The approximate v/o scale is indicated below the normal MgO- Al_2O_3 weight percent (w/o) scale in Figure 1. The four Trans-Tech and two Ceradyne samples, plus the MERDI fabricated 65/35 and 50/50 magnesia-alumina samples,* are indicated on the phase diagram according to their composition in weight percent alumina as well as in volume percent (equivalent to weight percent) MgAl_2O_4 .

Figure 12 shows the temperature dependence of the thermal diffusivity measured on heating (open symbols) and cooling (closed symbols) from room temperature to 1400°C for three two-phase mixtures of MgO and MgAl_2O_4 of 3.51 - 3.52 gm/cc density compared to that of single-phase, hot pressed MgO and MgAl_2O_4 of 3.55 gm/cc density or greater. Approximate values of calculated thermal conductivity also are included in Figure 12. For this approximation, an average calculated heat capacity accurate to $\pm 5\%$ was used for all the samples regardless of composition or temperature. It is apparent that, in these materials, the highly conductive magnesia phase contributes significantly to the overall thermal diffusivity/conductivity of the two-phase mixtures.

Analytic expressions for the heat capacity and thermal conductivity for each composition were then derived with the use of the Kopp-Neuman mixtures law⁶ and Eq. (1). The measured room temperature densities were corrected for thermal expansion at higher temperatures. These expressions, as well as that for thermal diffusivity, are given in Table IX.

More analytic treatments are available for describing the resulting conductivity of ceramic materials composed of mixtures of one or more solid phases together with a pore phase.²⁸ Most

*The sample designation indicates the composition in mole percent magnesia/alumina ratio. Fabrication procedures and characterization for these materials are discussed in Section A of this report.

Figure 12.--Thermal diffusivity as a function of temperature of two-phase mixtures of MgO and MgAl_2O_4 compared to that of single-phase MgO and MgAl_2O_4 . The approximate thermal conductivity values are indicated also.

TABLE IX.--Linear Least Squares Representation of the Thermal Transport Properties of Magnesia, Magnesia-Rich Magnesia-Alumina Spinel, and Magnesia-Alumina Spinel for the Temperature Range $298 \leq ^\circ\text{K} \leq 1673^+$

	Density
<u>MgO HP (100.0MgO / 0.0MgAl₂O₄)</u>	3.57 ₃ gm/cc
$\alpha^{-1} = 0.0321(^{\circ}\text{K}) - 0.0103$	
$C_p = 0.283 + 2.405 \times 10^{-5}(^{\circ}\text{K}) - 6.10 \times 10^3(^{\circ}\text{K})^{-2}$	
$\lambda^{-1} = 6.80 \times 10^{-5}(^{\circ}\text{K}) + 0.00548$	
<u>S110 (78MgO / 22MgAl₂O₄)</u>	3.52 gm/cc
$\alpha^{-1} = 0.0152(^{\circ}\text{K}) - 0.1931$	
$C_p = 0.275 + 3.08 \times 10^{-5}(^{\circ}\text{K}) - 5.41 \times 10^3(^{\circ}\text{K})^{-2}$	
$\lambda^{-1} = 9.38 \times 10^{-5}(^{\circ}\text{K}) + 0.0111$	
<u>S98 (62MgO / 38MgAl₂O₄)</u>	3.52 gm/cc
$\alpha^{-1} = 0.0549(^{\circ}\text{K}) + 0.195$	
$C_p = 0.265 + 3.82 \times 10^{-5}(^{\circ}\text{K}) - 4.58 \times 10^3(^{\circ}\text{K})^{-2}$	
$\lambda^{-1} = 1.110 \times 10^{-4}(^{\circ}\text{K}) + 0.0166$	
<u>S71 (1.0MgO / 99MgAl₂O₄)</u>	3.51 gm/cc
$\alpha^{-1} = 0.0621(^{\circ}\text{K}) + 11.09$	
$C_p = 0.243 + 5.55 \times 10^{-5}(^{\circ}\text{K}) - 279 \times 10^3(^{\circ}\text{K})^{-2}$	
$\lambda^{-1} = 1.144 \times 10^{-4}(^{\circ}\text{K}) + 0.0534$	
<u>MgAl₂O₄ HP (0.0MgO / 100.0MgAl₂O₄)</u>	3.55 gm/cc
$\alpha^{-1} = 0.0590(^{\circ}\text{K}) + 13.95$	
$C_p = 0.243 + 5.55 \times 10^{-5}(^{\circ}\text{K}) - 2.79 \times 10^3(^{\circ}\text{K})^{-2}$	
$\lambda^{-1} = 1.091 \times 10^{-4}(^{\circ}\text{K}) + 0.0585$	

+ The compositions are given in MgO/MgAl₂O₄ w/o or v/o ratio, α^{-1} in units of sec/cm², C_p in units of cal/gm^oK, and λ^{-1} in units of m^oK/watts.

treatments yield values of thermal conductivity that fall somewhere between the values derived from the cases for conduction parallel or perpendicular to a set of parallel slabs of two different solid phases.⁶ In Figure 13, the calculated room temperature thermal conductivity⁺ is observed to generally follow the curve for conduction perpendicular to a set of parallel slabs of MgO and MgAl₂O₄ (series case) when these components exist as a small-grained, random mixture of the two phases. The series case formula for the overall thermal conductivity (λ_m) of a mixture of two phases is given by the equation

$$\lambda_m = \frac{\lambda_1 \lambda_2}{V_1 \lambda_2 + V_2 \lambda_1} \quad (4)$$

where λ 's and V's are individual component thermal conductivities and volume fractions, respectively.

Also shown in Figure 13 are the calculated thermal conductivities of MERDI-fabricated 65/35 and 50/50 magnesia/alumina spinels with similar densities. The room temperature thermal conductivities are observed to be about 30 percent lower than the series case curve. This is probably due to the fact that these materials contained about one percent impurities, mostly CaO and SiO₂. Such compounds are known to form intergranular phases that can act as very effective thermal barriers.²²

Finally, the lower half of Figure 13 shows that the overall thermal expansion coefficients for these materials also are linearly dependent on the excess MgO concentration. Thermal expansion of a set of parallel MgO and MgAl₂O₄ slabs results in such a linear dependence, thus following a series model analogous to that followed by the thermal conductivity.

5. Montana Rosebud Slag--Crystallization Effects

The most extensive survey of thermal transport properties of both molten and solid coal slags has been reported by Bates, et al,^{29,30} where he showed that the thermal diffusivity of solid slags exhibited wide variations dependent upon the previous heat treatment, temperature, slag composition, and degree of crystallinity. The thermal diffusivity values for a wide variety of solid and synthetic slags (both seeded with K₂O and unseeded) fell within a band between 0.003 and 0.012 cm²/sec--the higher values being attained by those slags with a higher degree of

⁺ For the purposes of this plot, the calculated thermal conductivity of S78 was corrected to an equivalent density of 3.52 gm/cc by the use of Eq. (3).

Figure 13.--Thermal conductivity at 25°C and linear thermal expansion coefficient values for several two-phase mixtures of MgO and MgAl_2O_4 compared to theoretical parallel and series model for mixtures of two solid phases

crystallinity. At high enough temperatures, where the slags were mostly liquid, the difference in magnitudes of the diffusivities were smaller. However, the thermal diffusivities had positive temperature dependences, indicating a strong radiative heat transfer component.

Radiation heat transfer in a partially transparent material at higher temperatures ($T \geq 1000^\circ\text{C}$) depends on the material's absorption and the reemission properties.³¹ It also depends on scattering at boundaries and sometimes on sample thickness.³² Radiation heat transfer through a semi-transparent material, such as a solid or molten slag, can be significantly larger than phonon heat transfer, and therefore is an important consideration in MHD thermal engineering. However, due to the complexity of the interpretation of the radiation mode of heat transfer, experimental measurements reported here will be confined to temperatures $\leq 1000^\circ\text{C}$.

In order to examine some of the effects of thermal history on thermal transport properties in a natural slag, a well-homogenized amorphous slag was prepared for starting material.* Some of the results to date are summarized in Table X. The temperature dependence of the thermal diffusivity for several natural Rosebud slag samples is shown in Figure 14.

Upon heat-up, the thermal diffusivity values for all three as-received amorphous Rosebud slags were the same to 900°C . The thermal diffusivity increases 32% during the one-half hour heat-up time between 900 and 1000°C for Rosebud #1, #2, and #3, however. No additional changes were observed during subsequent cooling of Rosebud #2 to 750°C . After a fast reheat to 1000°C , the thermal diffusivity increased another 13% during a two-hour soak at 1000°C . Finally, the thermal diffusivity of Rosebud #3 increased 33% during an eight-hour soak at 1000°C . In this case, data were taken at 15-minute intervals--all the change occurred during the first interval. On cooling from 1000°C , the thermal diffusivity exhibited no temperature dependence down to 200°C . All of these heat treatments took place in situ during the diffusivity measurements; hence the atmosphere was flowing N_2 . When densities were checked at

* Obtained from R. Pollina, Montana State University. See Reference 16, pp.166-67 for a description of the slag preparation. Nominal composition of the Montana Rosebud slag was $42\text{SiO}_2\text{-}27\text{Al}_2\text{O}_3\text{-}20\text{CaO-}6\text{MgO-}4\text{Fe}_2\text{O}_3\text{-}1.0\text{K}_2\text{O}$ and Na_2O (in w/o).

TABLE X.--Heat Treatment Effects on Density, Thermal Diffusivity, and Degree of Crystallinity of a Natural Rosebud Slag

Sample	Heat Treatment	Density (gm/cc)	Thermal Diffusivity* (cm ² /sec)	Crystallinity
BM synthetic ⁺	as-received	2.54	0.0048	amorphous
Rosebud #1	as-received	2.80	0.0044	amorphous
	1000°C - 1/2 hr in N ₂	-	0.0058	some
Rosebud #2	as-received	2.81	0.0045	amorphous
	1000°C - 3 hr in N ₂	2.97	0.0064	some
Rosebud #3	as-received	2.79	0.0045	amorphous
	1000°C - 8 hr in N ₂	2.94	0.0060	some
Rosebud #4	1050°C - 40 hr in air	2.00	0.0054 [†]	some

+ Prepared by W. Seymour, Montana Tech. The nominal composition was 60SiO₂-15Al₂O₃-25MgO (in w/o).

* Measured at 800°C..

† Measured at 25°C.

Figure 14.--Thermal diffusivity of Rosebud natural ash during heating, cooling, and recycling

completion of runs #2 and #3, they showed increases of 5 to 6%.

A crystallization phenomena apparently is taking place in Rosebud slag in the 900 to 1000°C range, and is responsible for the enhanced thermal diffusivity and density. A DTA scan was performed on a powdered slag sample; it verified that a large first-order endothermic peak occurs at 985°C.

Anomalous regions in the electrical conductivity behavior of Rosebud ash have been observed by Pollina and Larsen²² at 1378 and 1150°C when measurements were made during cooling from the melt. These researchers confirmed crystallization of anorthite from liquid Rosebud slag as responsible for the anomaly at 1378°C; however, the anomaly at 1150°C is unexplained at this time. Bates and Mellinger³⁰ also reported discontinuities in the α -versus-T curves between 900 and 1000°C for some of the slags they tested. In contrast, the diffusivity decreased 10 to 20% in this temperature range in most instances.

An attempt was made to induce a maximum amount of crystallinity in an originally amorphous sample (Rosebud #4), and thus establish the highest possible values of thermal diffusivity/conductivity for the Rosebud slag composition. It was hoped that this could be accomplished by heating the slag sample slowly in air to 1050°C, soaking it at that temperature for 40 hours, and then slowly cooling it to room temperature. However, following this heat treatment, the density increased only 3% and the room temperature diffusivity increased only slightly.

Following the various heat treatments, micrographs were taken of polished slag surfaces for comparison to that of an as-received amorphous sample. Figures 15(A-C) depict the completely amorphous starting slag, Rosebud #3 (after soaking at 1000°C for three hours in N₂), and Rosebud #4 (after soaking at 1050°C for 40 hours in air), respectively.

Only a small number of randomly scattered, isolated pores are observed in the amorphous (apparently single-phase) starting slag (Figure 15A). However, during the reheat and soak for three hours at 1000°C in N₂ there appears to be a separation into two phases, as indicated by the alternating light and dark gray fringes depicted in Figure 15B. There is an obvious crystalline phase emerging as well during the 40-hour 1050°C soak in air (Figure 15C). In addition,

Figure 15.--Micrographs showing cross-section of Rosebud slag diffusivity samples after several heat treatments. (A) As-received amorphous slag, (B) Rosebud #3 after soaking at 1000°C for 3 hours, (C) Rosebud #4 after soaking at 1050°C for 40 hours, and (D) another view of Rosebud #4 showing porosity forming along mid-plane of disc samples.

porosity appears to form and grow along the mid-plane of the disc-shaped samples that are annealed either in N_2 or air above $1000^\circ C$. Figure 15D shows another location along the mid-plane of Rosebud #4 where a large ($\sim 300 \mu m$) pore has formed.

There are apparently three simultaneous phase changes that take place in this critical 900 to $1000^\circ C$ temperature range in an amorphous Rosebud slag. The separation into what appears to be alternating crystalline-amorphous layers proceeds rapidly, while the scattered white crystalline particles require more time to crystallize out. Each of these phase changes tends to increase the thermal diffusivity and density. At the same time, a pore phase forms which tends to decrease both the thermal diffusivity and density. Therefore, assuming that similar phase changes can occur in coal slags of other compositions, the thermal diffusivity temperature dependence and density can show positive or negative discontinuities depending upon whichever process, crystallization or pore formation, dominates.

Using estimated values of heat capacity, the thermal conductivity was calculated to range from 1.3 to 2.0 watts/ $m^\circ K$ for amorphous and partially crystallized Rosebud slag, respectively. This compares favorable to a value of 1.5 ± 0.2 watts/ $m^\circ K$ (temperature independent to $600^\circ C$) determined by direct thermal conductivity measurements of a sample of a slightly porous and crystallized natural Rosebud ash made at MSU.³³

Future cooperative work with MSU researchers will attempt to describe in detail the conditions necessary for crystallization to take place in Rosebud ash as a function of thermal history and seed content, and the physical property changes which occur as a result. In particular, the thermal diffusivity/conductivity, density, thermal expansion, and electrical conductivity will be correlated with the degree and type of crystallization in the ash. Obviously, x-ray analysis will be needed to supplement the present methods of characterization.

Since water-cooled electrodes will be covered with a layer of solid slag as well as liquid slag, and physical property data are generally lacking for solid Rosebud slag, it is extremely important to obtain the thermal and electrical conductivity data under various conditions for optimum MHD-channel operations and design. In addition,

the design and operation of a preheater system as well as a seed recovery system, will depend on the physical state of the condensed slag melt or solid.

6. Other Materials

Thermal diffusivity measurements for a perovskite ($\text{La}_{.84}\text{Sr}_{.16}\text{CrO}_3$), a potential electrode material, and for SiAlON (fabricated from clay and coal by a proprietary process) were reported in earlier quarterly reports,^{15,16} and will not be repeated here.

C. Wettability and Reaction of MHD Materials with Slag and Slag-Seed Mixtures (Larry Bentsen, Jon Carlson, and G. E. Youngblood)

1. Introduction

Wettability and reaction studies are being carried out as part of the program to evaluate refractory materials behavior in direct contact with molten coal slag. The basic experiment consists of photographing sessile drops of molten slags on several solid ceramic substrates at temperatures above the slag deformation point. Photographs of the slag profile are used to determine the wetting contact angle and the slag surface tension as a function of temperature and atmosphere. Post-test analyses characterize the amount and mode of slag-substrate reaction at the interface as well as slag penetration into a slightly porous substrate.

Molten coal slag is very corrosive. Dissolution of materials in contact with molten slag results in geometry changes of refractories as well as impurity contamination--particularly in the electrodes and insulators of the MHD channel. Furthermore, the slag composition and physical characteristics also will change as a result of the dissolution.

With reference to present "cold" or "medium" temperature channel design, an equilibrium layer of molten coal slag is required to protect the solid surfaces (either metal or ceramic) from direct contact with the high-temperature plasma.¹¹ This appears to require the existence of generally opposing characteristics of good wettability and low reactivity. In contrast, the "high" temperature channel designs would require minimum wetting by condensed slag so that the electrodes and insulators remain clean.¹¹

In the design of a combination refractory metal-ceramic (a cermet) electrode or electrode lead-out, the metal must thoroughly wet the ceramic to maintain both the mechanical and electrical integrity of the module. Again, factors that will affect bonding and fabrication are the nature and degree of interaction between components, wettability, and surface energy at the interfacial boundary. Although no attempts have been made at this time to examine the nature of molten metal-ceramic interaction, the techniques developed during the high-temperature coal slag-ceramic studies reported herein are immediately applicable to the metal-ceramic case.

A major emphasis of the materials research effort at MERDI has been the characterization of the interaction between refractory materials with molten coal slag and seed. Dense, high-purity ceramics, with compositions similar to commercial refractories, have been fabricated for coal slag wettability-reaction baseline studies. Parallel with this effort, commercial refractories are obtained from MHD contractors involved in preheater design and operation--principally Fluidyne Engineering Company and Montana State University.

For these studies, a large supply of one slag composition, a natural Montana Rosebud, will be used in tests with both the technical and commercial refractories. The effects of temperature and atmosphere will be examined. Later, the effects of composition changes will be examined--particularly that of adding seed either in the K_2SO_4 or K_2CO_3 form. The added influence of porosity will be assessed in the case of commercial refractories. It is noted that even though the starting slag composition is well-known, dissolution of the refractory substrate can cause significant changes to take place in the slag composition and therefore the wettability and surface tension values, also.

2. Theory

The wetting of a solid refractory can be quantified in terms of a wetting or contact angle θ , which is the angle formed by the tangent to the liquid surface at a point of contact with the solid (see Figure 16). Complete wetting occurs when $\theta = 0$, partial wetting when $0 < \theta \leq 90^\circ$, and

Figure 16.--Schematic of contact angle of liquid drop on solid surface

nonwetting when $\theta > 90^\circ$. The contact angle of a drop of liquid resting on a flat surface is determined primarily by the equilibrium between the surface energy of the solid-vapor interface γ_{sv} , the surface energy or tension of the liquid-vapor interface γ_{lv} , and the solid-liquid interfacial energy γ_{sl} through the classic Young-Dupre equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (5)$$

In general, the solid, liquid, and vapor interface energies are different in the mutually saturated condition than for initially pure phases. Composition changes as a function of time alter Young's relationship such that cases of "delayed" wetting or "dewetting" are known to occur. Also, reaction at the interface between the liquid-slag and refractory results in lowering γ_{sl} by a contribution of the free energy of the reaction which could result in enhanced wetting or spreading of the slag on the refractory substrate.

For reference, water has a surface tension of 72 mN/m; ^{*} fused halides range from 100 to 200 mN/m; high-temperature liquid oxides range from 300 to 700 mN/m; and liquid metals up to 1935 mN/m.³⁵ Measurements of γ_{sl} reported in the literature are highly divergent. Materials with high surface energies, particularly, are subject to the effects of minor contaminants, i.e. fluxing. Attempts have been made to express

* A millinewton/meter is equivalent to a dyne/cm. or an erg/cm².

the surface tension of silicates near common glass compositions (about 70% SiO_2) as the sum of factors given x weight or mole percent of the oxide in the glass. An abbreviated list from Kingery³⁵ is presented in Table XI.

The surface tension in most materials decreases approximately linearly from the "liquidus" temperature to a few degrees below the critical temperature to where it approaches zero. The change of surface tension can be represented by various relations, among which

$$\gamma = \gamma_0 (1 - T/T_c)^n \quad (6)$$

is the most general. This relation indicates that $d\gamma/dT$ should be negative; however, positive temperature coefficients sometimes observed for liquid oxides (SiO_2) are believed to be due to dissociation in the liquid at high temperatures.³⁵

It is important to note that the potential causing flow of liquid slag across a flat surface or within a capillary (connected porosity) will be proportional to the product of the surface tension γ_{lv} and $\cos \theta$. Likewise, the work of adhesion (W_{ad}) depends on the product $\gamma_{lv} \cos \theta$ through the expression:

$$W_{ad} = \gamma_{lv} (1 + \cos \theta) \quad (7)$$

The rate at which a slag flows will be proportional to the potential and inversely proportional to the slag viscosity. Hence, the attainment of an equilibrium configuration of a sessile drop not only depends on the kinetics of reactions which affect the various surface energies, but also the slag viscosity for any given atmosphere and temperature.

The sessile drop method for examining liquid surface tension and wetting contact angle has several advantages. The most important feature is that the contact angle and surface tension can be measured coincidentally. It also is feasible to photographically record time changes in the case of non-equilibrium. Unfortunately, the attainment of equilibrium may not be possible within the time frame of a reasonable experiment.

TABLE XI.--Additive Factors for Calculating Surface Tension of Silicate Glasses at 1200°C

Oxide	x Mole %	x Weight %
Al_2O_3	3.4	6.0
SiO_2	3.4	3.2 ₅
CaO	4.7	4.9
MgO	5.8	5.8
K_2O	0.7	0.0

Previous experimental attempts to determine γ_{lv} for molten coal slags³⁵ were hindered by the high degree of wetting with most substrates. This made it difficult to determine precisely the degree of curvature of the sessile drop from which γ_{lv} is eventually calculated. In addition, distortions in the shape of the drop can occur due to nonhomogeneities in the slag composition or the slag-substrate reaction products (all of which can change with time).

The calculation of the surface tension, requiring a theoretical curve fitting routine and computer solution of a non-linear second order differential equation, has been well-documented.³⁷ The same computer program developed by Rasmussen at BNW is being used at this time.

3. Experimental Technique

Tests were performed in air in a high-temperature sintering furnace^{*} equipped with a muffle tube. Figure 17 shows a typical arrangement of equipment for the sessile drop technique. The furnace chamber was initially leveled with the aid of a He-Ne laser, and then braced and weighted to minimize vibrations. A pellet of slag (0.6 cm diameter by $\sim$ 0.6 cm long) was placed on each of two different ceramic substrates (typically 1 - 1 1/4 inches diameter or square by 1/4 inches thick) which were positioned side-by-side at the center of the furnace hot-zone. The He-Ne laser was used again to insure that the substrates themselves were level. Thus, qualitative comparison of the performance of two substrates (or slags) always were obtained.

The slag pellets were core-drilled from a larger, dense slug of well-annealed Montana Rosebud[†] which was part of the same slag prepared by R. Pollina and used in previously discussed thermal and electrical property measurements.³³ The substrate surfaces were ground flat with a 70 μ m diamond wheel, then polished further with 15 μ m grit. Both the slag and substrates were ultrasonically cleaned in alcohol.

* Centorr Associates, Inc., Model 10-4x8-G-G-EK0, Suncook, New Hampshire, 03275.

† For specific composition see page 45 .

Figure 17.--Sessile drop experimental apparatus arrangement

Key

- (1) Back lighting lens and collimation tube
- (2) High-temperature furnace
- (3) Digital temperature indicator
- (4) Camera with zoom lens
- (5) Furnace power supply and temperature controller
- (6) Optical port
- (7) Atmosphere control
- (8) Muffle and dee sample support

The samples were backlighted with parallel light with the aid of a light source positioned at the focal point of a convex lens. The lens was attached to a collimating tube and aligned to produce even illumination of the furnace chamber. This technique produced substantially better definition of the sessile drop profile than the use of emitted light.

Sample rate of heating was controlled by a rotating drum power controller attached to the furnace power supply. By varying the speed of drum rotation any heating/cooling rate needed to attain thermal equilibrium may be selected. Heating and cooling rates at temperatures below the slag softening point were generally held to less than 5°C per minute.

The sessile drops were photographed through a 200 mm telephoto lens and bellows attached to a 35 mm single lens reflex camera^{*} with motor wind. Exposures were taken at specific time intervals on Kodak Panatomic-X film, which was selected for having very fine grain. Enlargements up to 8" x 10" were then made, having a final magnification of up to x5.

The wetting contact angles were determined directly from the enlarged photographic prints, and were taken as the angle formed by the tangent to the liquid surface at the point of contact with the solid. In all cases the measured contact angle was less than ninety degrees (wetting).

In order to determine surface tension values, the shape of the slag drop profile is analyzed with the aid of a chart scanner.⁺ The position of up to 50 points along the drop profile is recorded to the nearest 0.001 inch. These position points then are used in the curve fitting routine and computer determination of surface tension.

After removal from the furnace, the slag-substrates were sectioned with a diamond saw, mounted in Bakelite holders, and polished to 0.05 μm finish. The relative amount and mode of slag-substrate interaction was examined using SEM, EDX, electron microprobe, and optical light microscopy when appropriate.

* Olympus OM-2.

+ Geophysical Research Corporation, Model IS-2, Tulsa, Oklahoma.

The characteristics of the various refractory substrates examined are listed in Table XII, from which it is evident a wide spectrum of properties exist. Most of the aluminas, spinels, and MgO-rich spinels (with the exception of the single crystals) are very pure, dense ceramics fabricated by either isopressing or hot-pressing. These materials generally have very low porosity with a uniform grain-size. A few materials (such as X317, E, and K3) are fused-cast refractories. These products have more porosity and are thus less dense. They also have a wider variability of grain-size and contain more impurities.

4. Test Results

In previous reports,^{15-17,22} qualitative wettability and surface tension results for two synthetic slags on alumina and spinel substrates were presented. Improvements in photographic and measuring technique dictated that the experimental parameters be reevaluated. It also was decided to characterize wettability/interaction effects of Rosebud coal slag only for the time being. Initially, an isothermal run with an $\alpha\text{-Al}_2\text{O}_3$ substrate polished to a 70 μm finish was performed. The temperature was held constant about 10°C above the slag slumping point (1415°C). The measured contact angles as a function of time are shown in Figure 18. The contact angle decreases continuously throughout the time of measurement at a rate of about one degree every six minutes and never reaches an equilibrium value. A micrograph of the slag-substrate interaction region (Figure 19) shows that, although there is little apparent penetration of slag into the $\alpha\text{-Al}_2\text{O}_3$, there is a continuous crystallized slag layer $\sim 10 \mu\text{m}$ thick at the interface. This indicates a significant dissolution of $\alpha\text{-Al}_2\text{O}_3$ in Rosebud slag at a temperature barely above liquidus and precipitation as a higher concentration alumina-silicate.

Rate tests then were conducted to select an optimum heating rate at temperatures above the slag-slumping temperature. Contact angles for Rosebud slag on 70 μm finished Al_2O_3 with 5°C/min and 2.5°C/min heating rates are compared in Figure 20 which indicates the contact angles for the slower rate are only slightly lower near the slag slumping temperature. The data also show that equilibrium is reached near 1520°C or after about 45 minutes exposure above 1415°C.

TABLE XII.--Substrate Characteristics for Slag-Wettability/Interaction Tests

Substrate	Nominal Composition (in m/o)	Source [†]	Density (gm/cc)	Porosity (%)	Grain-Size (μ m)
α -Al ₂ O ₃ (sapphire)	99.9 Al ₂ O ₃	1	3.99	0	single crystal
α -Al ₂ O ₃ (isopressed)	99.3 Al ₂ O ₃	2	3.80	4.8	< 10
spinel(single crystal)	50.0/50.0 MgO/Al ₂ O ₃	1	3.59	0	single crystal
spinel(hot pressed)	50.0/50.0 MgO/Al ₂ O ₃	3	3.51	2.2	< 10
spinel(isopressed)	50/50 MgO/Al ₂ O ₃	2	3.53	1.7	20-60
S71	51/49 MgO/Al ₂ O ₃	4	3.51	2.2	20-25
S78	56.8/43.2 MgO/Al ₂ O ₃	4	3.41	5.0	10-15
65/35	65/35 MgO/Al ₂ O ₃	2	3.53	1.7	10-12
S98	84.5/15.5 MgO/Al ₂ O ₃	4	3.52	1.9	5-10
S110	93.0/7.0 MgO/Al ₂ O ₃	4	3.52	1.9	5-10
X317	67/31 MgO/Al ₂ O ₃	5	3.4	6	--
DD8	62.3/37.7 MgO/Al ₂ O ₃	6	3.4	6	--
E	~8/80/5/6 MgO/Cr ₂ O ₃ /Al ₂ O ₃ /Fe ₂ O ₃ (in w/o)	7	4.4	5	--
K3	~6/27/60/4 MgO/Cr ₂ O ₃ /Fe ₂ O ₃ (in w/o)	7	4.0	4	--

- [†]1. Union Carbide Crystal Products, San Diego, California
 2. MERDI - fabricated, Butte, Montana
 3. Ceradyne, Inc., Santa Ana, California
 4. Trans-Tech, Inc., Gaithersburg, Maryland
 5. Corhart Refractories Co., Louisville, Kentucky (also contains 0.8% Fe₂O₃, 0.5% CaO, and 0.5% SiO₂)
 6. A. P. Green Refractories Co., Mexico, Missouri (also contains 0.10% Fe₂O₃, 0.15% CaO, and 0.14% SiO₂)
 7. Carborundum Co., Niagara Falls, New York

Figure 18.--Contact angle as a function of time for Rosebud coal slag on $\alpha\text{-Al}_2\text{O}_3$ substrate at 1428°C

Figure 19.--Micrograph showing interfacial region between
Rosebud coal slag and α - Al_2O_3 substrate

Figure 20.--Effect of two different heating rates on the contact angle for Rosebud coal slag and α -Al₂O₃

Figures 21 (A and B) show significant slag penetration into the dense $\alpha\text{-Al}_2\text{O}_3$ for the higher temperature exposure. Again, crystallization in the slag near the interface is readily apparent.

The effect of surface roughness on contact angle was demonstrated in a side-by-side comparison of $\alpha\text{-Al}_2\text{O}_3$ polished to 70 μm and 15 μm ; resulting contact angles are given in Figure 22 for a heating rate of 2.5°C/minute. The 70 μm finish yields significantly lower values, possibly indicating a faster reaction rate due to the greater amount of surface area present. Post-test microstructural analyses, shown in Figures 23 (A-B), however, are similar to each other as well as to previous runs. A $\sim 500\text{ }\mu\text{m}$ -wide penetration and porosity band is quite noticeable below the slag-crystallization region near the interface.

As a result of these tests, all future runs were made at a heating rate of 2.5-3°C/min to insure that the slag drop profile had reached equilibrium. Likewise, to minimize the reaction rate and also enable comparisons to be made with the work of other researchers doing similar work, almost all substrates were polished to 15 μm before testing.

The wettability/interaction of Rosebud slag with two single crystals, MgAl_2O_4 and $\alpha\text{-Al}_2\text{O}_3$, were then compared. Each substrate already had an optical finish, so no further surface preparation was necessary. The measured contact angles for a 2.5°C/min heating rate are depicted in Figure 24 for the two single crystal substrates.

Surprisingly, the contact angle with sapphire decreased more rapidly with increasing temperature than the contact angles with polycrystalline $\alpha\text{-Al}_2\text{O}_3$. However, the contact angle leveled off at $\sim 10^\circ$ for both substrates, although at a higher temperature for Al_2O_3 polished to 70 μm (see Figure 20). The contact angle with single crystal MgAl_2O_4 decreased slowly and continuously throughout the course of the experiment, but remained relatively high.

The micrographs in Figures 25 (A-B) display a marked difference in reaction at the interfacial region for these two samples. The slag-spinel crystal boundary is very smooth with little evidence of interaction. In contrast, the slag-sapphire boundary region contains

Figure 21 (A-B).--Micrographs showing interfacial region between Rosebud coal slag and $\alpha\text{-Al}_2\text{O}_3$ for two different heating rates to 1540°C .

Figure 22.--Effect of substrate surface roughness on contact angle

Figure 23 (A-B).--Micrographs showing interfacial region between Rosebud coal slag and $\alpha\text{-Al}_2\text{O}_3$ with two types of surface roughness

Figure 24.--Contact angle as a function of temperature for Rosebud coal slag on Al_2O_3 and MgAl_2O_4 single crystal substrates

Figure 25 (A-B).--Micrographs showing interfacial region between Rosebud coal slag and MgAl_2O_4 and $\alpha\text{-Al}_2\text{O}_3$ (sapphire) single crystals

a $\sim 15 \mu\text{m}$ -wide interaction layer, most likely mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). Strong bonding evidently occurs since the sapphire crystal was severely cracked after testing. Researchers conducting wetting tests of molten silicon on sapphire in air have observed similar results.³⁷

The wetting behavior of Rosebud coal slag on a series of dense refractories with compositions ranging from stoichiometric MgAl_2O_4 to 86 m/o excess MgO /spinel was examined. Contact angle results are summarized in Figure 26 with the materials listed in terms of the magnesia-to-spinel comparison ratio. For comparison purposes, contact angles for single crystal spinel are reproduced from Figure 24 and are seen to be the highest (least wetting).

The next highest contact angles were obtained for polycrystalline stoichiometric spinel fabricated at MERDI (so-called 50/50; see Figure 1). The contact angle decreases rapidly over a short temperature range and then levels out and decreases very slowly for the remainder of the test. The interfacial region depicted in Figure 27 shows slight enhancement of porosity near the spinel-slag interface, but there is little evidence of slag-substrate reaction.

Spinel containing two m/o excess of MgO exhibited wetting angles only slightly less than that of the stoichiometric spinel. The micrograph in Figure 28, however, shows more evidence of crystallization in the slag and reaction at the boundary for this case.

The three materials containing 20 m/o excess MgO or more exhibited extreme wetting with Rosebud slag. The contact angle decreased quite rapidly after the slag slumped, becoming too small to accurately measure within a temperature range of less than 10°C . The slag then actually covered the entire surface, ran down the sides, and began wetting the underside of the substrate. Figures 29 and 30 are photomicrographs of the two substrates highest in MgO content. Both indicate extreme reaction at the interface with a slag penetration band ($\sim 60 \mu\text{m}$ wide) clearly visible. The reaction between the slag and the substrate becomes increasingly more severe with increased free MgO content.

Further analysis by SEM/EDX techniques of the reaction interface between the mixed $\text{MgO}/\text{MgAl}_2\text{O}_4$ compositions and Rosebud slag are in progress. However, it is apparent from these preliminary results

Figure 26.--Contact angle as a function of temperature for Rosebud coal slag on dense, high-purity $\text{MgO}/\text{MgAl}_2\text{O}_4$ composite substrates with different amounts of excess MgO

Figure 27.--Micrograph showing interfacial region between
Rosebud coal slag and dense, stoichiometric
 MgAl_2O_4 , polycrystalline substrate

Figure 28.--Micrograph showing interfacial region between
Rosebud coal slag and 51/49 $\text{MgO}/\text{Al}_2\text{O}_3$ (S71)
composite substrate

Figure 29.--Micrograph showing interfacial region between
Rosebud coal slag and 86/14 MgO/Al₂O₃ (S110)
composite substrate

Figure 30.--Micrograph showing interfacial region between
Rosebud coal slag and 69/31 MgO/Al₂O₃ composite
substrate

that MgAl_2O_4 is much more inert to reaction with Rosebud slag in air than either MgO or Al_2O_3 . For this reason, an extensive program has been initiated to develop and fabricate MgAl_2O_4 hardware--crucibles, boats, thermocouple rods, etc.--for use in slag-preparation and-characterization tests and MHD-facility instrumentation (see Section A).

The wetting of several multiphase fused-cast commercial refractories by Rosebud slag also was examined. Measured contact angles for these materials, as well as for some other spinels, are shown in Figure 31. Contact angles for the MERDI-fabricated 50/50 polycrystalline spinel are shown dashed for reference.

Monofrax K3 and Monofrax E, two alumina/chromia refractories, were wet the least among the refractories in this group. In the micrographs (Figures 32 and 33, respectively) the variety of grain-sizes and large amount of porosity is apparent. Very little penetration of the slag into Monofrax E is observed and there appears to be no slag crystallization at the interface. No slag layer is visible on Monofrax K3 since the slag had separated completely from the substrate on cooling.

The contact angle results for the stoichiometric hot-pressed spinel are surprisingly low in light of the values obtained for both the single crystal and polycrystalline isopressed spinels. Unfortunately, no post-test microstructural analysis could be performed since the sample was badly deteriorated after a furnace malfunction.

The A.P. Green spinel, having a composition close to that of MERDI 65/35, yielded similar contact angle values. The micrograph (Figure 34) shows little interfacial reaction and no recrystallization in the slag. In this case, the sample was quenched after its temperature had dropped below the slag slumping point, however. The X317 spinel, also having much the same composition, gave similar results. Once melted, the slag penetrated the substrate very rapidly and completely; no reaction or slag is visible in the micrograph (Figure 35). The effect of open and connected porosity, however, remains to be assessed for the commercial refractories at this time.

The wetting of dense $\alpha\text{-Al}_2\text{O}_3$ and MgAl_2O_4 by Rosebud slag containing 17 w/o $\text{K}_2(\text{Na}_2)\text{O}$ also was examined. Bubbles began forming on the

Figure 31.--Contact angle as a function of temperature for Rosebud coal slag on several commercial refractory substrates

Figure 32. Micrograph showing interfacial region between Rosebud coal slag and Monofrax K3 refractory substrate

Figure 33. Micrograph showing interfacial region between Rosebud coal slag and Monofrax E refractory substrate

Figure 34. Micrograph showing interfacial region between Rosebud coal slag and A.P. Green DD8 refractory substrate

Figure 35. Micrograph showing interfacial region between Rosebud coal slag and Corhart X317 refractory substrate

slag pellets at 1230°C. At 1455°C, the slag slumped; however, a good meniscus shape was never attained and hence no contact angle measurement could be made. Further measurements will be attempted with a seeded Rosebud slag containing about one-half of this seed concentration.

IV. CONCLUSIONS

- . Magnesia-alumina spinel generally is more resistant to corrosion by Montana Rosebud coal slag than alumina or magnesia. Therefore a program to develop techniques to fabricate spinel hardware and test pieces of various shapes has been initiated by MERDI.
- . Thermal diffusivity data, when related to micro- or macrostructural changes, are a sensitive monitor of materials degradation behavior in expected MHD environments. In addition, the thermal transport properties data of the MHD materials tested is being used directly for engineering component design and operations modeling by other MHD contractors.
- . The sessile drop method of photographically monitoring the wettability of a liquid drop with a solid substrate has demonstrated several advantages. When characterizing the behavior of molten coal slag with dense ceramics or refractory substrates, the wetting and slag surface tension are obtained simultaneously as a function of temperature, time, and/or atmosphere. Post-test analyses by optical microscopy, SEM/EDX microscopy and/or electron microprobe have been shown to be a valuable way to relate the wetting behavior with slag-substrate interactions.

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MHD Siting and Environmental Screening
Jeff Chaffee

ABSTRACT

Utilizing the experience gained in previous MHD siting studies and the current literature, an MHD siting methodology has been formulated to aid in locating facilities such as the Engineering Test Facility (ETF). In support of this document, a socioeconomic impact assessment methodology and a computer siting capability are being developed. The combination of these three documents should result in a comprehensive siting package that is highly versatile and readily applicable to both MHD and conventional facilities.

I. OBJECTIVE AND SCOPE OF WORK

The objective of the Montana Energy Research and Development Institute's (MERDI) MHD siting and environmental screening task is to facilitate the Department of Energy's (DOE) initial site activities. To meet this objective, MERDI will provide DOE with a methodology for evaluating sites for the construction of MHD power plants and major test facilities.

II. SUMMARY OF PROGRESS TO DATE

In prior studies, application of Phase I and II of an MHD ETF siting procedure resulted in the identification of five 20-mile radius candidate site areas in Montana. Environmental baseline studies of these five sites were conducted in Phase III of the process to develop a background data base for screening potential ETF sites. However, the need for documentation of a siting methodology was emphasized before actual site screening proceeded. Therefore, MERDI compiled the knowledge gained through previous siting studies and combined it with a literature review of documented siting techniques in formulating a methodology for siting MHD power plants. Although oriented toward the siting of MHD facilities (i.e., the ETF), the methodology (through modification) can be used in site screening for conventional power plants. A basic siting procedure, which commonly is used to reduce the size of a study area, is described along with methodology characteristics and alternative screening techniques (e.g., map overlay, computer composite mapping, etc.). Following a description of siting constraints which can be utilized in a siting methodology, the screening techniques are organized into an orderly plan for siting MHD facilities.

In addition to the methodology development, a significant effort was expended in identifying local, state, and federal laws which will effect the siting of an MHD ETF in Montana. The results of this research are presented in a report entitled Survey of Federal, State, and Local Laws and Regulations Affecting the Siting, Construction, and Operation of the MHD ETF in Montana. Although the ETF was the main focus of the effort, the document applies generally to thermal power plants.

Task efforts during the last quarter of FY 78 focused on revision of the MHD siting methodology, on development of an accompanying socioeconomic impact assessment methodology, and on installation of computer siting programs on MERDI's computer system.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

New input from a power plant siting conference and additional information confirmed the need for a revision of the draft siting methodology. To emphasize the importance of the siting methodology and to identify the revisions, a brief outline of the siting document is presented in the following paragraphs.

A. Alternative Siting Techniques

1. Basic Procedure

There seems to be no single methodology suitable for universal application in siting power plants. The specific techniques vary with the region of the country being investigated and the type of facility being planned. However, there is a basic procedure which commonly is employed to decrease the size of a study area and thus to concentrate the search for suitable sites. Figure 1 illustrates this procedure as a narrowing process in which the size of the study area is reduced systematically. In the final stage, the investigation becomes centered around a number of small candidate sites until one or more preferred sites are identified.

Time and financial considerations are the primary motives for dividing the methodology into stages. Early in the process, large land masses may be eliminated using very general data from existing literature sources. In the final stages, data collection becomes more detailed (e.g., field monitoring, housing surveys, etc.) because the study area usually has decreased sufficiently to make this degree of effort feasible.

2. Characteristics of Siting Methodologies

Within this basic procedure, specific methodologies vary considerably. However, certain characteristics and tools commonly are employed in any systematic screening process. Those characteristics most frequently used are described in the following list.

Figure 1.--Basic Procedure for Siting Power Plants

- a. A checklist of siting constraints and impact considerations generally is developed to ensure that every relevant factor has been addressed.
- b. Relevant, current, and compatible data is collected as a basic requirement for intelligent decision-making.
- c. Attribute weighting is a commonly used method of assigning relative values to the siting constraints.
- d. Alternative location ranking is applied to objectively or subjectively rate the quality of areas based on the siting criteria.
- e. Preferred sites generally are indicated by combining the ranking and weighting results into a final score for each alternative site.

Many of the siting techniques can be applied either manually or through the use of a computer. Computer siting techniques have the advantage of being able to handle large quantities of data in a rapid manner.

B. Major Siting Constraints for an MHD Facility

An index of major siting constraints was developed for consideration in the MHD siting methodology. The following attributes were divided into three principle categories--engineering, environmental, and economic--based upon their specific characteristics or expected impacts. In addition, siting laws and regulations are discussed because of their impact on site selection. Refinement of this index may be necessary to coordinate the siting constraints with the particular characteristics of the facility being studied.

- 1. Engineering Constraints
 - a. Water availability and control
 - b. Transportation facilities
 - c. Geology/Seismicity
 - d. Land characteristics
 - e. Transmission system
 - f. Waste heat utilization
- 2. Environmental Constraints
 - a. Air quality/meteorology
 - b. Water quality

- c. Solid waste
 - d. Land use
 - e. Aesthetics
 - f. Ecology
 - g. Noise and magnetic fields
 - h. Socioeconomics
3. Economic Constraints
- a. Fuel costs
 - b. Water costs
 - c. Transmission costs
 - d. Property acquisition/access costs
 - e. Construction and materials costs
 - f. Taxes
4. Siting Laws and Regulations
- a. National Environmental Policy Act
 - b. Clean Air Act and amendments
 - c. Federal Water Pollution Control Act
 - d. Resource Conservation and Recovery Act

Because of the general nature of the MHD siting methodology, only major federal environmental laws are discussed; state and local legislation must be addressed on a case-by-case basis.

C. MHD Siting Methodology

A methodology for siting MHD power plants was derived from previous ETF siting studies and from research into documented siting techniques and procedures. This site selection process, as outlined in Figure 2, may be utilized for siting other facilities also. The four-phase process is described in more detail below.

1. Phase I

Primary screening involves eliminating large portions of land which are unsuitable for siting an MHD plant. A composite overlay mapping technique may be employed for this purpose. The remaining regions then become candidate areas for Phase II screening.

Figure 2.--MHD SITING AND ENVIRONMENTAL SCREENING GENERALIZED
SITE SELECTION AND EVALUATION PROCESS

2. Phase II

Candidate site areas may be identified within the candidate areas by applying a base population figure and/or a computer composite mapping system (CMS) and constraint trade-off analysis.

3. Phase III

The number of candidate site areas may be reduced by applying a multi-attributed decision model. Only those areas with the highest final scores should be retained for further investigation. Together with refinement of the siting attributes, the remaining candidate site areas may be screened by using computer constraint trade-off analyses and computer CMS. Sensitivity analysis may be included to assure that the resulting candidate sites are the most acceptable alternatives.

4. Phase IV

Preferred sites may be selected based on the results of another multi-attributable decision model. Detailed field studies are required to develop an adequate data base for this fine level of screening. A computer may be utilized to compile the data and to compute the final scores.

The results from this siting study may be used as groundwork for preparing an environmental impact assessment (EIA) and, if necessary, an environmental impact statement (EIS).

D. Socioeconomic Impact Assessment Methodology

A methodology for assessing the socioeconomic effects of siting an MHD (or conventional) power plant is being developed to accompany the siting methodology. This document will summarize available literature and will tie together present techniques in a workable plan for conducting socioeconomic impact assessments. Similar to the siting methodology, the socioeconomic assessment methodology will be oriented toward the siting of MHD facilities; however, minor modifications will make it adaptable for most siting situations.

E. Computer Siting Programs

Two siting programs are being developed and entered in the MERDI computer system--composite mapping system (CMS) and constraint trade-off analysis. These programs will be useful in many phases of the siting process and will aid researchers by incorporating the speed and vast data handling capabilities of a computer into a comprehensive siting plan.

1. Constraint Trade-off Analysis

The constraint trade-off program will be designed to weigh the importance of siting attributes before they are entered into a composite mapping program. Constraints will be compared with each other--two at a time--by decision-makers, and then all attributes will be compared

simultaneously by the computer. The computer will print out a numerical analysis, in percent, of comparison consistency and a list of relative constraint weights.

2. Composite Mapping

A composite mapping program is used to indicate the physical location of various levels of impact associated with individual siting attributes. The program combines the attribute importance weightings with the ratings assigned to the various levels of impact and prints out (in map form) the suitability of various areas for siting a power plant.

F. Work Forecast

The socioeconomic methodology and computer siting programs will be completed and attached to the revised siting methodology (either as appendices or supplemental documents). Upon finalization of these subtasks, the completed package will be submitted to DOE for its approval and use.

IV. CONCLUSIONS

A review of existing literature has demonstrated a need for a systematic procedure for siting MHD power plants. Few siting methodologies are comprehensive enough to address the site selection process from regional evaluation to the development of an environmental impact statement on preferred sites. Those methodologies available tend either to be too general in nature or too specifically oriented toward a particular case.

The MHD siting methodology developed by the ETF siting group addresses these problem areas by presenting a step-by-step process for site screening MHD facilities. Furthermore, it can be adapted easily to most siting problems--MHD or conventional. When combined with the socioeconomic impact assessment methodology and the computer siting programs, a Methodology for Siting an MHD Power Plant presents a comprehensive siting package which is easily applicable and very versatile.

Environmental Analysis of Trace Elements and Submicron
Particles from MHD Test Facilities

N. Egan, B. Moody, K. Runnion, G. Huddleston, and S. Lundberg

ABSTRACT

The sampling, analysis, and computer modeling of trace elements and submicron particle emissions will allow these emissions to be characterized and possible control methods to be identified. Samples have been taken from the University of Tennessee Space Institute (UTSI) and TRW, Incorporated; analysis shows element partitioning in both facilities, and element enrichment was evident in three samples taken previously from the Pittsburgh Energy Research Center (PERC). A computer model has been written for a quench system, and the chemical equilibrium model was run successfully with data from three sources.

During the past quarter, several MHD prototype facilities were evaluated and three were sampled: TRW, UTSI, and AVCO Everett Research Laboratories. A subcontract was let to Spectron Development Laboratories to define laser measurement systems for in situ use at MHD facilities; a report has been received recommending a phased approach. An RFP was issued for the design, fabrication, and calibration of a high-temperature extractive sampler. Two proposals were received and are being evaluated.

Bulk analysis has been subcontracted to the Environmental Trace Substances Research Center (ETSRC). Inductively coupled plasma (ICP) emission and instrumental neutron activation analysis (INAA) were employed. Surface analysis was subcontracted to Montana State University (MSU). MSU utilized a scanning electron microscope with an X-ray fluorescence attachment to analyze samples. Two methods of analysis were employed: single element mapping and complete elemental analysis of a spot or region.

Work has continued on computer modeling to assess possible NO_x emissions from the Component Development and Integration Facility (CDIF). The MHDV program was modified to enable gas flow simulation of an Engineering Test Facility (ETF) design provided by AVCO Everett Research Laboratories, and results from the chemical equilibrium program were compared to other similar programs. The comparison was satisfactory.

I. OBJECTIVE AND SCOPE OF WORK

Both the toxicity and essentiality to life of certain trace elements are well documented. Exhaustive studies have been performed to determine the fate of coal trace elements released during the combustion in conventional power plants. More recent studies have involved analyses from coal-fired magnetohydrodynamic (MHD) facilities.

The higher temperatures generated in coal-fired MHD facilities result in 1) vaporization of more chemical species than in conventional facilities and 2) production of higher concentrations of fine particulates which are collected inefficiently by present pollution control systems. These variations will change the emission profile, thereby affecting the distribution of both toxic and essential trace elements.

The objective of this task is to characterize trace elements and sub-micron particles from MHD facilities. This task has been divided into three subtasks.

Subtask A involves selecting and sampling MHD facilities that will furnish representative samples for trace element and particulate characterization. A significant portion of the sampling is to identify and implement appropriate sampling techniques.

Subtask B covers the bulk and surface trace and major elements analyses of MHD emissions. Most of the analytical work of characterization has been subcontracted to the Environmental Trace Substances Research Center (ETSRC) at the University of Missouri at Rolla and to Montana State University (MSU).

Subtask C obtains and develops computer programs and data files (where applicable) to analyze MHD process emissions. Process effects on the composition and concentration of emissions are being identified, particularly trace elements and submicron particles. Data obtained from Subtasks A and B will be used to validate and modify computer models. Emphasis is being placed on obtaining the best computer models already in use to evaluate MHD environmental effects. The programs obtained are being modified to evaluate potential emissions, including the effects of a water quench applied to the exhaust gases as presently is done at several facilities and will be done at the Component Development and Integration Facility.

II. SUMMARY OF PROGRESS TO DATE

Since the beginning of FY 78, significant progress has been made in the sampling, analysis, and modeling of trace elements and particulate emissions from magnetohydrodynamic (MHD) facilities.

A. Subtask A--Sampling

The University of Tennessee Space Institute (UTSI) and TRW, Incorporated were chosen as sampling sites because both facilities use coal as their primary fuel and approach MHD operating temperatures in their combustors. Samples of the coal, slag, and total particulates were taken during a seeded run at UTSI. Water from the slag tank and quench water samples were taken during unseeded runs at TRW. Other facilities were contacted, but they have been unavailable for sampling.

A preliminary sampling plan was developed for the CDIF Test Train 1A which includes stack monitoring, sampling before the quench and clean-up devices, and in-stream sampling. The in situ sampling would be accomplished by an emission diagnostic section (EDS), a water-jacketed duct located before the quench.

High temperatures in MHD exhaust streams necessitate new and innovative sampling and measurement techniques to provide better samples. A request for proposal was issued for work on the design, fabrication, and calibration of ceramic cyclones for high-temperature particulate extractive sampling. Spectron Development Laboratories (SDL) was subcontracted to assess laser-based measurement and instrumentation capabilities applicable to MHD environmental analysis. SDL has completed Phase I of its work and initiated Phase II.

B. Subtask B--Analysis

The Environmental Trace Substances Research Center (ETSRC) and Montana State University (MSU) were subcontracted to perform bulk and surface analyses of the samples obtained in Subtask A. In addition, analyses were performed on samples obtained from the Pittsburgh Energy Research Center (PERC) during the previous fiscal year.

ETSRC used two methods for bulk analysis: inductively coupled plasma emission (ICP) and instrumental neutron activation analyses (INAA). The results from 16 elements analyzed by these processes were used to evaluate trace element distributions in the samples. Trace and major element partitioning is apparent to a certain extent in all facilities samples. Trace and major element enrichment was evident in samples gathered at three different sites in the PERC facility.

Surface analysis determines if certain elements concentrate on the surface of small particles. MSU has used a scanning electron microscope (SEM) with an X-ray fluorescence attachment to determine particle size, particle number density, and surface particle composition and concentration by size. Initial particle sizing measurements showed a predominance of particulates in the one-micron or less range. A quadrupole mass spectrometer was supplied to MSU for use with a secondary ion mass spectrometer to complete desired surface analyses.

C. Subtask C--Computer Modeling

General MHD modeling programs that have been tested include chemical equilibrium, combustor, and steady-state MHD channel flow. The chemical equilibrium program consists of the Naval Ordnance Test Station (NOTS) propellant evaluation program as modified by the University of New Hampshire. The first step in the program, thermodynamic data handling and manipulation, was converted and tested successfully on the MERDI computer. A full data file was established on the computer, and the program was debugged. Comparison of the chemical equilibrium program with two other chemical equilibrium programs showed very close agreement in evaluating major chemical species from coal combustion. The combustor and channel programs developed at MSU have been entered into MERDI's computer, and program assessment has been initiated for models of particle nucleation.

A quench model was developed to determine the cooling rate of hot gases when they are sprayed with water in a quench similar to that planned for the CDIF. This model has been run on the computer and is especially valuable in determining potential nitrogen oxides emissions. Initial results show little reduction in NO_x with single-stage water injection, but NO_x reductions can be achieved by lower quenching rates (primarily through multiple injection staging).

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Subtask A--Sampling

1. Facilities

Literature was updated and expanded on MHD prototype facilities that may be used for sampling. The facilities examined were Argonne National Laboratory (ANL), AVCO Everett Research Laboratories, the Component Development and Integration Facility (CDIF), the Coal-Fired Flow Facility (CFFF), Mississippi State University, Pittsburgh Energy Research Center (PERC), Rocketdyne, Stanford University, University of Tennessee Space Institute (UTSI), and TRW, Incorporated. The facilities were evaluated in terms of equipment design, operating conditions, and test programs and objectives. The facilities must be monitored continually to determine test schedules, equipment modifications, and results of research programs. Facilities were sampled based on the above evaluation, the type of coal used, availability, and contribution to the trace element task. Samples were collected from three MHD facilities: TRW, AVCO, and UTSI. Run data corresponding with the samples collected were obtained to study and compare the affects of operating parameters on the samples.

In setting up sampling of MHD facilities, the trace element task was referred to Mr. Dwight Shelor, Department of Energy (DOE), Washington, D.C. Mr. Shelor is DOE Project Officer for the MHD combustor contractors, AVCO, TRW, and Rocketdyne. After explaining the project to Mr. Shelor, he fully approved sampling at the MHD combustor facilities and offered his assistance in interfacing with these facilities.

The TRW facility (see Figure 1) consists of a two-stage combustor, water quench, cyclone, and scrubber. Approximately 1700 pounds per hour of pulverized coal and 2900°F vitiated air are burned in the first stage of the combustor, while the second stage is oxygen-fired. Partial slag removal is achieved in the first stage. The scrubber is used only with high sulfur coals. Potassium carbonate (K_2CO_3) seed in an oil slurry is injected into the second stage of the combustor during seeded runs. Samples of the Montana Rosebud coal, pre-slag tank water, post slag tank water, slag, pre-quench water, post quench water, and cyclone slag were collected from three unseeded and one seeded run. The objective of TRW's runs was to optimize run conditions and coal feed configuration to achieve an even slag coating on the walls of the combustor and maximize slag rejection in the first stage.

AVCO's coal combustion test rig is shown in Figure 2. The high-temperature regenerative air preheater facility burns natural gas to supply 2500°F preheated air to the pulverized coal combustor. "Dry" Montana Rosebud coal is fed through a star rotary feeder and fluidized with nitrogen carrier gas. Coal is injected into the combustor from the top through a water-cooled injector at a nominal feed rate of 400 pounds per hour. The combustion chamber consists of a water-cooled copper coil with alumina refractory between the spacings and the water-cooled jacket. Gas sample ports are spaced axially along the combustion chamber. An adjustable orifice is used to regulate the combustion pressure. The exit gases are water-quenched and exhausted to the atmosphere.

The objective of the test at AVCO was to study the combustion of Montana Rosebud coal. The air-to-fuel ratio was varied from 0.55 to 1.90; the gases were analyzed axially; and quench water plus slag samples were collected. Four quench water plus slag samples were collected for the trace element task along with coal and pre- and post-quench water samples.

The UTSI Cell III MHD facility (see Figure 3) consists of a combustor, nozzle, simulated channel, diffuser, and water-jacketed hot gas cyclone. UTSI has redesigned the downstream equipment in Cell III since samples were collected during previous quarters. A water-jacketed cooling section, a two-stage secondary combustor, and a water-cooled tube heat exchanger have replaced the old exhaust system. Provisions also were made for injecting nitrogen (N_2) into both the primary and secondary combustor for NO_x studies. Between the two tests that were sampled, further modifications to the facility included the addition of a larger heat exchanger to lower the stack temperature, changes to air injection into the secondary combustor to increase mixing, and the addition of a gaseous sampling port before the secondary combustor.

The objectives of the sampled test at UTSI were to burn the remaining combustibles in the combustion gas with minimum NO_x formation, study the reactions of the sulfur species, and measure particulate size.

Figure 1 .--TRW MHD COMBUSTOR FACILITY
(Top View)

Figure 2.--AVCO COAL COMBUSTION TEST RIG

Figure 3 .--UTSI MHD CELL III FLOW TRAIN

A mixture of Illinois No. 6 coal and K_2CO_3 seed were fed at a rate of 2000 pounds per hour into the primary combustor, which is designed for 100 percent slag carryover and burned with 85 percent stoichiometric oxygen (O_2). The first stage of the secondary combustor then was fired with sufficient O_2 and N_2 to provide complete combustion. In Test 37-03, the N_2 flow to the primary and secondary combustors was varied throughout the run. Test 37-07 was run at steady conditions for one hour with no N_2 flow into the primary combustor and constant flow of O_2 and N_2 into the secondary combustor. Process and stack gases were monitored for NO_x , SO_2 , H_2S , CO_2 , CO , and O_2 . Samples were collected of the coal, slag from the diffuser bucket, slag from the cyclone, and slag from the heat exchanger. Fly ash samples were collected from the stack using a water-cooled probe with an alundum thimble filter.

2. Laser Measurement Systems

A subcontract was let to Spectron Development Laboratories (SDL) to search for and define laser measurement systems which would be suitable for in situ use at MHD facilities. SDL currently is developing state-of-the-art laser anemometers and particle sizing instruments. They have experience in high temperature and dirty systems--e.g., fluidized bed combustors.

The expected characteristics and ranges of parameters in MHD systems were given to SDL to use in its analysis. SDL's report gives the approximate cost, range of usefulness, and accuracy for each of the types of instruments considered. Dr. Smart of SDL felt that laser anemometry and particle sizing would be possible but that other types of measurements (temperature, species concentrations) might not be feasible with currently available instruments.

The report recommended a phased approach to making in situ measurements. Some candidate systems would be selected and used in quick-look experiments where operating parameters were varied to determine the range of suitability and applicability of the instruments. These experiments would be performed with borrowed or rented equipment to minimize the expense involved in the initial phase. This equipment probably would not be optimized for this application but should perform well enough to prove the applicability of the technique. (Window problems, slag coating, opacity of the optical path, and particle loading also would be defined better.) The data from these experiments would be combined with information on the basic accuracy and reliability of the instruments tested to decide which systems should be funded for hardware implementation and utilization. The closer systems then would be checked out carefully in laboratory tests and used for MHD diagnostics.

Discussions also were held with UTSI, AEDC, TAI, and Stanford on the status and capabilities of their respective measurement systems. AEDC, in particular, was enthusiastic about its ability to make measurements in MHD systems. (This was based on AEDC's experience with making

similar measurements in rocket engines.) Dr. Self at Stanford was contacted regarding his work on laser diagnostics in MHD systems. His work is aimed mainly at electrical generator diagnostics (electron concentration, enthalpy, boundary layers) rather than environmental aspects--however, he is developing a far infrared (IR) technique that shows good promise for measuring temperature. Dr. Self is using the far IR laser technique to measure electron concentration and mobility. However, electron concentration is strongly dependent upon temperature and, therefore, knowing the electron concentration allows one to calculate the temperature.

The far IR radiation is less affected by the presence of small particles (< 5 microns) than is visible radiation. Thus, this technique also may be applicable to measuring species concentration in the presence of a particulate loading that would rule out measurements at visible frequencies.

3. High-Temperature Extractive Sampler

Exhaust gas cooling and clean-up equipment on MHD test facilities is atypical of what an MHD plant will look like. Samples must be collected before downstream equipment in order to characterize the emission. Because of high temperatures in MHD exhaust streams, new and innovative sampling techniques are needed to provide better particulate samples. A request for proposal (RFP) was issued for the design, fabrication, and calibration of a high-temperature extractive sampler. The scope of work from the RFP is shown in the attached appendix. Two proposals were received in response to the RFP. Acurex Corporation of Mountain View, California submitted a proposal for using two- to four-inch ceramic cyclones for sizing and collecting one gram quantities of particulates. M.J. Pilat, Incorporated of Seattle, Washington (affiliated with the University of Washington) submitted a proposal to provide a four-inch cascade impactor for sizing and collecting MHD particulate emissions in microgram quantities. Technical evaluation of the two proposals is being conducted to determine the sampler design that will provide representative particulate samples for analysis.

4. Travel

A visit was made to the Environmental Protection Agency (EPA), Research Triangle Park, North Carolina to discuss particulate sampling.

EPA has a lot of experience in sampling stacks at low temperature. High-temperature sampling is a problem they presently are addressing. Acurex has a contract with EPA to build a high-temperature (1500°F), high-pressure (nine atm) sampling train to be used on a fluidized bed combustor at Exxon. The sampling train is being tested at Exxon now. Cyclones, designed by Southern Research Institute, are being used for particle collection in the Acurex high-temperature, high-pressure sampling train. Problems have been encountered with leakage around seals at the high temperature.

EPA suggested we take two approaches to sampling particulates in the high-temperature exhaust gases of MHD. Ceramic cyclones can be used at high temperatures to collect samples at temperatures equal to those in the process stream. Results from this can be compared to samples collected using a water-cooled probe connected to a cascade impactor.

Sampling and coordination trips were made to TRW, AVCO, and UTSI to collect slag and particulate samples and to interface with facility personnel.

B. Subtask B--Analysis

The Environmental Trace Substances Research Center (ETSRC) presently is completing bulk trace and major element analyses on UTSI coal, slag, and fly ash samples. Montana State University has finished the surface analyses of the UTSI fly ash samples and the PERC total particulate and cascade impactor samples.

1. Bulk Analysis--ETSRC¹

The intent of this period was 1) perform a literature review of various analytical procedures applicable to coal, slag, fly ash, and water sample preparation and analysis; 2) develop and validate acceptable analytical methods for analysis of certain specified elements; and 3) analyze samples collected at the University of Tennessee Space Institute (UTSI) MHD facility to determine trace and major element partitioning and enrichment.²

The literature review of over one hundred references has been completed. Information gathered during the review on various sample preparation and analysis techniques was evaluated with the most promising methods being employed by ETSRC to develop and validate methods for specific element analyses. Inductively coupled plasma emission (ICP) digestion procedures presently being tested include a) open acid digestion after dry ashing; b) refluxing acid digestion after dry ashing; c) acid bomb digestion after dry ashing; d) base fusion/HCl digestion after dry ashing; and e) base fusion/HNO₃ digestion after dry ashing. Instrumental neutron activation analysis (INAA)

¹Clevenger, Tom E., Method Development and Analysis for Trace Elements in Samples from Small MHD Plants, Interim Report, Subcontract No. 8-11015F, Environmental Trace Substances Research Center, University of Missouri, Columbia, Missouri, September 1978.

²During coal combustion, certain elements tend to become concentrated in various ashes. The tendency to concentrate according to location in the facility is called element partitioning, and the tendency to concentrate in particles of a certain size is called particle enrichment.

efforts were directed at minimizing standard vaporization during evaporation, providing a matrix for standards which would allow for post-irradiation transfer which eliminates irradiation container background and blank problems, optimizing standards with respect to the quantity of each element necessary in the ETSRC experimental configuration, and preparing compatible multi-element standards to expedite standard preparation.

Difficulties encountered during the long irradiation (INAA) of several samples have required that the samples be irradiated a second time. In order to allow ETSRC to supply complete data from these samples, a time extension has been granted until November 15, 1978.

2. Surface Analysis--Montana State University^{3,4}

The scanning electron microscope (SEM) with X-ray fluorescence attachment was utilized during this period to analyze one PERC total particulate sample, four PERC cascade impactor samples, and one UTSI total particulate sample. An NBS fly ash (No. 1633) was used for standardization purposes. Two methods of analysis were employed: 1) single element mapping and 2) complete elemental analysis of a spot or region.

a. Single Element Mapping

In single element mapping, the pulse height analyzer (PHA) in the X-ray fluorescence attachment is tuned to accept only pulses in the characteristic X-ray range of an element of interest. The output pulses from the PHA result in a lighted dot appearing on the SEM oscilloscope screen. Concentration variations of the elements are then identified by the dot density on the screen--a high dot density indicating a high element concentration. This technique was applied to the PERC cascade impactor samples and the PERC total particulate sample. These samples appeared quite homogeneous, with only the 2.1 μm impactor stage showing any element segregation. On this stage, areas of enhanced silicon (Si) and calcium (Ca) levels were observed.

³Gobby, P.L., Surface Analytical Studies of Micron and Submicron Fly Ash from Coal-Fired MHD, Subcontract No. 77-027, Montana State University, Bozeman, Montana, July 1978.

⁴Gobby, P.L., Surface Analytical Studies of Micron and Submicron Fly Ash from Coal-Fired MHD, Subcontract No. 8-71016E, Montana State University, Bozeman, Montana, September 1978.

b. Complete Elemental Analysis

In the complete elemental analysis, the pulse height analyzer (pha) in the X-ray fluorescence attachment is tuned to accept pulses from elements emitting X-rays in the 0 to 25 KEV energy range. Concentration levels are determined by element peak heights as displayed on the oscilloscope. This method was used to attempt quantitative analysis of the PERC cascade impactor samples as well as the UTSI and PERC total particulate material. The results are presented in Tables 1 and 2 as relative concentrations and were determined as follows:

- 1) The X-ray spectrum of the National Bureau of Standards #1633 fly ash standard was acquired. The individual peak heights above background were measured and using known NBS concentrations^{5,6} and the calculated peak counts (peak height) per unit concentration for each element were determined.
- 2) The X-ray spectras of the PERC and UTSI samples then were acquired under the same experimental conditions as above. The individual peak heights above background were measured, and these values were divided by the corresponding counts per above unit concentration numbers determined in 1. Since counting rates vary slightly between spectra (because of machine instabilities), the calculated number is only proportional to the concentrations in the PERC and UTSI samples.
- 3) The silicon (Si) concentration then was set arbitrarily at 100, with the other element numbers being adjusted accordingly.

Although insufficient data presently has been collected to verify the observed results definitely, certain observations about element trends can be made. The elements magnesium (Mg), aluminum (Al), potassium (K), and manganese (Mn) in the PERC cascade impactor stages (2.1 μm to 0.43 μm) appear to be showing definite surface enrichment tendencies. Also, the levels of Mg and K in the PERC total particulate samples are higher than in the impactor

⁵Ondov, J.M. et al, "Elemental Concentrations in the National Bureau of Standards' Environmental Coal and Fly Ash Standard Reference Materials," Analytical Chemistry, Volume 47, pp. 1102, June 1975.

⁶It must be noted that the known values of the NBS standard were determined by bulk analysis and that element concentrations may vary with particle depth.

Table 1.--PERC Samples

Relative Elemental Concentrations

([Si] = 100)

<u>Element</u>	<u>2.1μm</u>	<u>1.1μm</u>	<u>.65μm</u>	<u>.43μm</u>	<u>Total Particulate</u>	<u>NBS Standard</u>
Na	N.D.	N.D.	N.D.	N.D.	8.23	1.52
Mg	22.8	28.4	7.16	49.9	96.3	8.57
Al	28.0	28.4	19.85	40.3	57.6	60.5
Si	100	100	100	100	100	100
K	2.07	5.09	4.85	7.70	21.6	7.67
Ca	70.0	82.6	75.5	77.6	67.8	22.4
Ti	2.97	3.29	2.48	2.68	2.85	3.52
Mn	.41	1.03	.42	1.2	1.74	.236
Fe	17.5	23.7	16.4	15.7	18.5	29.5
Zn	.11	.47	.076	.37	.73	.103
Sr	2.22	1.00	1.31	1.96	2.63	.810

Table 2.--UTSI Total Particulate

[Si] = 100

<u>Element</u>	<u>UTSI</u>	<u>NBS Standard</u>
Al	2.2	60.5
Si	100	100
S	213	1.43
K	729	7.67
Ti	1.2	3.52
Mn	.14	.236
Fe	76	29.5
Cu	.26	.063
Zn	.59	.103

samples, possibly indicating a concentration of these elements in the finer particles collected only on the total particulate filters.

Several differences also are apparent in the total particulate samples (PERC and UTSI) and the NBS standard values. PERC total particulate levels of sodium (Na), magnesium (Mg), potassium (K), calcium (Ca), manganese (Mn), strontium (Sr), and zinc (Zn) and UTSI levels of sulfur (S), potassium (K), copper (Cu), and zinc (Zn) are considerably higher than those found in the NBS standard.⁷ This indicates possible MHD problem areas and shows differences in prototype MHD and conventionally produced fly ashes.

C. Subtask C--Computer Modeling

The computer modeling subtask includes program development for both general MHD and specific Component Development and Integration Facility (CDIF) emissions. Computer modeling assists in the accurate and reliable prediction of MHD emissions, which is necessary for the review, analysis, and approval of facilities required for technology development.

1. CDIF NO_x Emissions

An assessment of possible NO_x emissions from the CDIF was continued. A refined temperature profile was developed and subsequently used in the NO_x kinetics/quench model developed by the Energy Environmental Research Company (EER) and MERDI. The study showed that with staged injection of the cooling water, NO_x concentration could be lowered one-third to one-half depending on the gas stoichiometry. It also was apparent that the location of the shock (supersonic to subsonic) will have a significant effect on the final NO_x concentration. Complete results from the CDIF NO_x prediction are being issued as a separate report.

7.

"This material is a blend of coal fly ashes supplies by five electrical plants: Tennessee Valley Authority, Stevenson, Alabama; Commonwealth Edison, Chicago, Illinois; Baltimore Gas and Electric Co., Baltimore, Maryland; Carolina Light and Power Co., Roxboro, North Carolina; and Potomac Electric Power Co., Washington D. C. These plants were specially selected to provide fly ashes that covered a broad spectrum of the fly ashes from the coal mining industry. Five of the fly ashes were collected by electrostatic precipitators and one by a mechanical collector. The fly ashes were sieved and the portion passing through a 170 mesh sieve was taken (88 micrometers diameter or less). After sieving, the fly ashes were blended in a double-coned blender. After 1 hour the material was immediately removed and bottled." National Bureau of Standards #1633 Data Sheet.

2. MHD AV

Modifications were made to an existing MERDI computer program (MHD AV) to enable gas flow simulation of an ETF conceptual design. The simulation will provide a temperature profile on which to base subsequent analyses of the emission potential of the gas stream. AVCO's ETF was chosen as the base case because the size was adequate and sufficient design information exists.

3. University of New Hampshire Equilibrium Program

The general equilibrium program received from the University of New Hampshire (UNH) has been compared to other similar programs for a few elements (carbon, oxygen, nitrogen, sulfur, potassium, and hydrogen) and was found to agree satisfactorily. The UNH program has the capability of examining several trace elements; computer capacity is the limiting factor. Current evaluations will determine the maximum permissible elements that may be considered in the program on MERDI's computer and on the Argonne East system. The UNH program will be used to predict the equilibrium (solid, liquid, and vapor) of the coal constituents throughout the MHD system; ETF will be the example.

D. Work Forecast

1. Sampling

MHD prototype facilities are used as sampling sites to collect coal, slag, fly ash, and water quench samples. Facilities must be continually evaluated to determine test schedules, equipment design, operating conditions, and applicability to sampling. MHD facilities that will be monitored during FY 79 are UTSI, CFFF, TRW, PERC, Rocketdyne, Stanford University, AVCO, Mississippi State University, ANL, and the CDIF. Representative samples collected by the facilities for their own test purposes will be utilized when possible. Facilities will be sampled based on the previous evaluation as to their contribution to the trace element task.

A subcontract will be negotiated to design, fabricate, and calibrate a particulate sampler, suitable for sampling an MHD combustor exhaust stream of 2000° to 2500°F, which will classify the collected particulate into three size ranges. Check-out of the sampler will be conducted on MHD test facilities and any modifications or additions necessary to collect further samples will be determined.

Review of in situ laser measurement techniques to look at particulates will continue. Far IR technique development for temperature measurement will be closely followed. Feasibility studies will determine exhaust stream opacity and access port requirements. Recommendations as to the direction and/or feasibility for an environmental laser measurement program will be determined.

2. Analysis

Bulk Analysis--MHD prototype facility samples from UTSI, TRW, PERC, and CFFF will be analyzed by the ETSRC. Bulk trace and major element analyses will be performed by instrumental neutron activation analysis, inductively coupled plasma emission spectroscopy, and atomic absorption spectroscopy.

Surface Analysis--Dr. D.F.S. Natusch (Colorado State University), an expert in the field of surface analytical methodology for combustion product analysis, will provide the consulting for the Trace Element Project. Dr. Natusch will critique present surface analysis efforts and recommend other areas of surface analysis which could be performed.

MERDI will perform particle sizing studies and surface mapping on fly ash using the scanning electron microscope with X-ray attachment.

Colorado State University (CSU) will perform surface analysis studies including surface and depth profiling. Surface profiling will chemically characterize the surface of slag and fly ash samples. Methods of analysis include electron spectroscopy for chemical analysis (ESCA), Auger electron spectrometry (AES), and secondary ion mass spectrometry (SIMS). The depth profiling (i.e., the measurement of chemical concentration by depth in a particle) is also performed by AES and SIMS.

3. Computer Modeling

Partitioning of trace elements will be evaluated by analytical models simulating chemical equilibrium that determine state (gas, liquid, solid) and which evaluate the sensitivity of the chemical state with various operating parameters.

Nucleation effects on trace element partitioning and enrichment will be evaluated through computer models available at ANL and by a subcontract with a researcher performing nucleation work, possibly STD or Aerodyne.

IV. CONCLUSIONS

Characterization of trace element profiles from small MHD plants and development of computer models enable the anticipation of future difficulties at an early enough stage to prevent costly and time-consuming changes in major MHD facilities. Therefore, it is important to the overall environmental engineering program to provide predictive initial information through the use of available small-scale MHD facilities presently in operation. The analyses of samples to be collected at these facilities will 1) allow development of new analytical techniques, 2) allow assessment of emission profiles, and 3) offer material with which to evaluate presently developed computer models. While our quarterly work is still in the review process, the following conclusions can be made: trace and major element partitioning, common in conventional coal-fired facilities, appears to occur in MHD prototype facilities; and element enrichment is apparent in the Pittsburgh Energy Research Center cascade impactor samples.

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APPENDIX

DESIGN AND FABRICATION OF A HIGH TEMPERATURE SAMPLER

SCOPE OF WORK

General

The overall objective of this program is to design, fabricate, and calibrate a particulate sampler suitable for sampling an MHD combustor exhaust stream at 2000° to 2500°F and classifying the collected particulate into three size ranges. The program will be divided into two phases, as detailed under the program schedule. The initiation of Phase II will depend on the acceptable completion of Phase I.

The proposed device will be capable of sampling isokinetically and will be fabricated from suitable materials to withstand the environment of MHD combustor exhaust streams at between 2000° to 2500°F. After particulate collection is accomplished, the sampled gas stream will be regulated as necessary for measurement and analysis. In the design phase of the project, specific recommendations for particulate collection and sizing equipment, gas analysis, and other functions necessary for characterizing the exhaust stream (e.g., flow regulation, cooling, gas analysis) will be made.

Components

Major components to be designed, fabricated, and calibrated include the following:

Isokinetic probe--to obtain isokinetic sampling conditions, several probe tips will be supplied to cover a range of duct velocities.

Particle sizing device--cut sizes desired are 3 micron, 1 micron, and <1 micron absolute collection at exhaust temperature. Numerous researchers have shown performance calculations for particulate sizing devices may not be accurate (especially at higher temperatures); therefore, actual performance testing of the devices will be conducted to determine fractional efficiencies at various conditions. Calibration conditions should be representative of actual conditions expected during sampling. The effect on the collectors' behavior due to changes in gas flow rate and particle density as well as temperature will be determined.

Selection of the structural materials for the sampling device will be part of the design process. Selection of suitable materials will take into account MERDI's analytical requirements. The highest purity materials will be selected to minimize contamination when trace element analysis of collected particulate is performed.

Major concerns in the system design will be the ease of operation, efficient recovery of collected material, and expected life of the sampling system under operational conditions. MERDI will be consulted at decision points in the design process.

Program Schedule

The proposed work will be performed in two major phases: Phase I will be design effort, while Phase II will be devoted to fabrication, testing, calibration, and delivery.

Phase I

During the design effort, fabrication and assembly drawings will be prepared for the sampler system. A major objective of the design will be to provide efficient sample recovery. Preliminary drawings and a system description will be provided to MFRDI two weeks prior to a design review meeting with the subcontractor. Four weeks after the review meeting a decision will be made by MERDI whether to proceed with Phase II. A report summarizing the Phase I program will be written.

Phase II

Following release of the drawings all required components will be fabricated. Following assembly, calibration tests will be performed with additional time allowed for particle size analysis needed to obtain fractional efficiency curves. At the conclusion of Phase II, a final report will be written containing calibration test data, fractional efficiency curves, operating procedures, and pertinent comments summarizing the entire program. In addition, a separate operating manual and fabrication drawings will be required.