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MHD POWER GENERATION: RESEARCH, DEVELOPMENT, AND
ENGINEERING

Quarterly Progress Report, January-March 1980

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

Quarterly Progress Report
January to March 1980

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. DE-AC07-78-ET-10816

TABLE OF CONTENTS

REPORT INTRODUCTION.....	1
TASK ABSTRACTS.....	2
<u>Task Title and Principal Investigator</u>	
MONTANA COLLEGE OF MINERAL SCIENCE AND TECHNOLOGY	
Task A--Characterization of Coal for Open-Cycle MHD Power Generation Systems, F. Diebold.....	5
Task B--Compressive Creep and Strength Studies of MHD Preheater Materials, K. Kitto.....	9
Task C--Preparation of Coals for Utilization in Direct Coal- Fired MHD Generation, B. Rhodes.....	21
Task D--Characterization of Volatile Matter in Coal, D. Buerman.....	23
MONTANA ENERGY AND MHD RESEARCH AND DEVELOPMENT INSTITUTE	
Task N--MHD Materials Evaluation, J.J. Rasmussen.....	25
MONTANA STATE UNIVERSITY	
Task E--Operability of the Moderate Temperature Slag Flow Facility, H.W. Townes.....	32
Task F--Slag-Seed Equilibria and Separations Related to the MHD System, R. Howald.....	44
Task H1-MHD Instrumentation, Consolidated/Inversion Simulator, and Data Acquisition, R. Johnson.....	61
Task H3-Combined MHD-Steam Plant Cycle Analysis and Control, D.A. Rudberg.....	71
Task J--Slag Physical Properties: Electrical and Thermal Conductivity, R. Pollina.....	88

REPORT INTRODUCTION

During the fall of 1974, a major portion of Montana's scientific community formed a task force to initiate and aggressively pursue a broad-based program of research, development, and engineering in the field of open-cycle magnetohydrodynamics (MHD). This effort was based on the firm belief that MHD technology, although still early in its development and not fully proven as a practical generator of electric power, is the only non-nuclear, central station electric power generation technology with significant potential for greatly improved fuel efficiency and direct operation with coal. MHD also offers lower environmental impact and a reduced pollution signature. Associated with this high efficiency is the reduced consumption of water--a factor of importance to the semi-arid western regions.

This task force was incorporated into the Montana Energy and MHD Research and Development Institute (MERDI). MERDI is a not-for-profit Montana corporation with performing team members drawn from in-house staff and the research facilities of the Montana College of Mineral Science and Technology (MCMST) in Butte and the Montana State University (MSU) in Bozeman.

With the able and generously provided assistance and advice of the MHD research and development staff of the Avco Everett Research Laboratory in Everett, Massachusetts, MERDI formulated a broad-scope research program to address the key technical problems currently recognized for MHD technology at both fundamental and practical levels. In November 1974, a proposal was submitted to the U.S. Energy Research and Development Administration (ERDA), now the U.S. Department of Energy.

ERDA awarded MERDI a contract in March 1975 for a portion of the MHD supporting science and technology tasks submitted in the original proposal. Work was divided among researchers at the performing elements (MCMST and MSU) on the basis of primary specialization and expertise. MCMST was assigned the tasks relating to coal fuel supply, characterization, preparation, and handling as well as MHD materials engineering. MSU tasks are related to science, heat transfer, mechanical engineering, chemistry, and chemical engineering aspects of MHD technology. MERDI assumed responsibility for overall program management, environmental impact assessment of MHD facilities, and site selection studies of future MHD central station power plants.

This report summarizes the work accomplished under these tasks from January 1980 through March 1980 by MERDI, MCMST, and MSU.

ABSTRACT

MONTANA COLLEGE OF MINERAL SCIENCE AND TECHNOLOGY

Task A--Characterization of Coal for Open-Cycle MHD Power Generation Systems

The work to establish an integrated set of procedures for the rapid analysis of coal samples has been nearly completed. The automated combustion train technique for simultaneous analysis of C, H, and N in the coal samples has been re-established and shown to be comparable in accuracy and precision but superior in efficiency to the ASTM techniques. Elimination of the contamination in the ion chromatographic analysis of F, Cl, S, and P has moved this technique much closer to being established. The addition of appropriate accessories, the availability of new software for the ICPEs, and the near completion of the sample preparation work means that the rapid, accurate, and precise analysis of a large number of metals in coal is a reality. The acquisition of additional Rosebud tippie samples and the continuing preparation and analysis of these samples will result in the completion of this task by the end of this contract period.

Task B--Compressive Creep and Strength Studies of MHD Preheater Materials

During the past quarter, several long-term compressive creep experiments were completed on Norton LS-812 spinel castable material. Tests designed to check the variation of the creep of the material and to check experimental procedures were completed with favorable results. Tests at 1400 K (2060°F) and 6 MPa (870 psi) on LS-812 resulted in secondary creep rates of 0.00052%/hr and 0.00054%/hr or a 3.8% variation. Reproducible results also were obtained for materials from two different cast batches at 1700 K (2600°F) and 1.5 MPa (220 psi). Other compressive creep tests were run between 1400 and 1738 K (2060 and 2670°F) and 0.5 and 15 MPa (70 and 2170 psi).

Compressive strength measurements were made on Monofrax A, Monofrax K-3, and spinel castable materials. The strength of Monofrax A (high alumina) decreased only slightly from approximately 400 MPa (48 kpsi) at room temperature to approximately 387 MPa (56 kpsi) upon heating to 1773 K.

However, Monofrax K-3 (alumina/chrome) showed a rapid decline in strength from 370 MPa at 1373 K to 140 MPa at 1773 K (53.6 psi at 2012°F to 20.3 kpsi at 2732°F). For comparison, Monofrax A and K-3 had considerably more strength at 1773 K (387 MPa and 140 MPa or 56.1 and 20.3 kpsi, respectively) than did Corhart X-317, Corhart RFG, and Monofrax E (100 MPa, 40 MPa, and 35 MPa or 14.5, 4.8, and 5.1 kpsi, respectively).

The compressive strength of Norton LS-812 batches declined to less than 50% of its room temperature value upon heating to 1773 K (2732°F). Taylor 13337 spinel castable lost 50% of its strength, however, at 1437 K (2192°F) and declined to 10% of its room temperature value at 1773 K (2732°F).

Task C--Preparation of Coals for Utilization in Direct Coal-Fired MHD Generation

The major impact on the test runs by Task C during this quarter were the changed drying medium characteristics. The drying gas temperature range was narrowed from that of the indirect-fired air preheater. More nitrogen was introduced into the closed circuit drying system on the one square foot fluid-bed dryer. In cooperation with Task D, gas samples were taken during steady-state continuous operation.

Task D--Characterization of Volatile Matter in Coal

Trouble-shooting of instrument problems was done this quarter. A workshop on instrument repair, trouble-shooting, and modification was attended, and the flame ionization detector (FID) was made operational. The HP capillary column was studied, and published methods of determining the organic content of atmospheres were evaluated.

MONTANA ENERGY AND MHD RESEARCH AND DEVELOPMENT INSTITUTE

Task N--MHD Materials Evaluation

Baseline data on pristine Monofrax A has been obtained to assist in the evaluation of changes which have taken place when this material was exposed to high temperature coal slag in the Montana State University moderate temperature slag flow facility.

Thermal diffusivity measurements have been made as a function of temperature on pristine Monofrax A and Norton LS-812.

Fracture toughness measurements show that the castable refractory compounds have a very low fracture toughness ($\sim 1 \text{ MPa } \sqrt{\text{m}}$) while the fusion-cast refractories containing a high concentration of alumina such as Monofrax A and Monofrax K-3 have significantly higher fracture toughness values ($\sim 3.6 \text{ MPa } \sqrt{\text{m}}$).

The addition of a small amount of platinum to a stabilized ZrO_2 body had no effect on the electrical conductivity mechanism of the ZrO_2 .

Techniques have been developed to cut and polish the samples without structural degradation. Structural data is being obtained using optical microscopy and SEM techniques.

MONTANA STATE UNIVERSITY

Task E--Operability of the Moderate Temperature Slag Flow Facility (MTSFF)

The rebuilding of the moderate temperature slag flow facility (MTSFF) using Monofrax A as the core material was completed. The MTSFF then was operated for 750 hours total (700 hours with slag injection), and five successive cleanouts were made of deposited slag. The Monofrax A at the end of 750 hours of operation was in good condition.

Task F--Slag-Seed Equilibria and Separations Related to the MHD System

Efforts this quarter were directed toward completing the new computer program, finishing a manual describing the program, and applying the program to MHD calculations. The applications of the calculations are described in the paper written for the Seventh International MHD meeting which is included as Appendix A of this quarterly report. Since the paper could not describe details of the operation of the program due to space limitations, some aspects of the calculations are described in more detail in the body of this quarterly report. After completing vapor pressure measurements on the four-component system in December, work in this area was discontinued.

Task H1--MHD Instrumentation, Consolidation/Inversion Simulator, and Data Acquisition

Several different dynamic transients involving up to 10 percent step changes in Faraday load voltage have been simulated using the combustor-nozzle-channel-diffuser program MHDTD. Results are discussed. Notched filtering of three-phase square wave power output to reduce harmonics is nearly operational. Problems with several poor silicon-controlled-rectifiers in one of the phases slightly delayed the completion of the work but has been accomplished.

Task H3--Combined MHD-Steam Plant Cycle Analysis and Control

Combined-cycle MHD-steam power systems are being modeled by digital computer simulations. Methods to provide efficient control of such systems are being investigated by using the simulations to ensure stable modes of response and to obtain coordinated control of many interdependent subsystems. First-principle, dynamic component models have been developed, as has a multi-input, multi-output model of the combustor, nozzle, channel, and diffuser. The component and subsystem models have been assembled into a dynamic, combined-cycle simulator of an ETF-sized plant. The report describes the system modeling, together with policies proposed for plant control.

Task J--Slag Physical Properties: Electrical Conductivity and Thermal Expansion

The experimental measurement of the thermal expansion under load of pristine and slagged Corhart X317 firebrick was completed. The results of those measurements and some preliminary room temperature elastic modulus measurements in Carborundum Monofrax A are presented in the report. Included as an appendix is a copy of a paper on the electrical conductivity of Rosebud coal slag accepted for presentation at the Seventh International Conference on MHD to be held at MIT in June 1980.

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

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:

- A. Btu percent moisture, volatile matter, fixed carbon, ash, and S, H, C, O, N, Cl, F and P content;
- B. Major metals: Al, Ca, Fe, K, Mg, Na, Si, and Ti; and
- C. Minor 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 are to represent the time variation in Rosebud seam properties as the coal is processed through a typical power plant coal feeding system.

II. SUMMARY AND IMPACT

The establishment of the analytical scheme for the rapid, accurate and precise analysis of a large number of coal properties is nearing completion. This quarter's work has resulted in the re-establishment of the analytical procedure for the simultaneous determination of C, H, and N in a coal sample with an accuracy and precision comparable to and an efficiency superior to the ASTM procedures. The work to establish the anion chromatographic procedure for the simultaneous determination of F, Cl, P, and S in the coal has proceeded closer to completion. This procedure for these anions is many orders of magnitude faster than achievable with the procedures previously established in our laboratory or those prescribed by the ASTM. The new accessories installed on the ICPES and the almost completed work on the new sample preparation technique will allow us to rapidly, accurately, and precisely determine the major and minor metal content of the coal samples.

In order to facilitate the experimental testing associated with the burning of coal in the ETF and the CDIF, rapid characterization of the coal and the combustion products must be performed. The application of the analytical scheme will allow for such rapid routine analysis of the coal. With only slight alteration of this analytical scheme, the rapid analysis of the combustion products can be accomplished. An additional application of this analytical procedure is the rapid multi-element analysis of the large number of coal samples required to establish the time variation in the coal properties.

The coal samples acquired from a special Montana Power Company sampling program are being prepared and analyzed. These samples will allow us to chemically characterize the coal feeding system from which we have routinely received tipple samples. These tipple samples also are being prepared and analyzed. It is this data that will allow us to determine the time variation in Rosebud seam coal properties.

III. DETAILED DESCRIPTION

A. Establishment of Analytical Procedures

1) C-H-N

The automated combustion train (PE 240) procedure for C, H, and N has been reinvestigated with the objective of removing the instrumental drift and sample drying effect. The new analytical procedure incorporates the correction for instrumental drift by bracketing each set of unknown samples with standards. The instrumental drift with time, as determined from the standard data, is used to correct the unknown coal data. In addition, each unknown coal sample is run in duplicate and the precisions, expressed as relative standard deviations, for C, H, and N are $\pm 2.06\%$, $\pm 2.73\%$, and $\pm 4.32\%$, respectively. The magnitude of moisture loss for the coal samples in the PE 240 sample compartment was also determined. These coal samples had been previously equilibrated with an atmosphere of 30°C and 15% relative humidity. After 3 hours in the PE 240 sample compartment at the room temperature and in an atmosphere of helium these coal samples lost 8.47% of their initial moisture content, i.e., 3.54% was reduced to 3.24%.

The PE 240 generated nitrogen concentration data in coal was compared to data generated by the ASTM D 3179-73 alternate Kjeldahl method. This comparison is illustrated below for a sample of Rosebud coal.

<u>ASTM</u>	<u>PE 240</u>
0.919 ± 0.03	0.911 ± 0.07
0.909 ± 0.03	0.876 ± 0.02
	0.851 ± 0.03

Each average represents the analysis of at least five coal samples.

Even though the PE 240 procedure involves the analysis of duplicate samples, approximately 23 samples can be analyzed for C, H, and N within one day and with a precision comparable to that recommended by the ASTM. The analysis of this number of samples by the ASTM procedures would take at least 10 times longer.

The sample preparation procedure for C, H, and N has been accelerated by the equilibration of all coal samples to the same moisture content in a controlled atmosphere (30°C and 15% relative humidity). This allows for only a spot check of the moisture content. In addition, the quantification of the small moisture loss of the coal samples in the PE 240 sample chamber prior to analysis means that an insignificant correction must be applied to PE 240 generated N and C values. Since the moisture content of all the coals are brought to the same value prior to analysis, the 30°C and 15% relative humidity equilibrated moisture content can be used for the calculation of all data to a dry basis. These same data will be used to correct for the contribution of the coal moisture to the PE 240 generated H concentration.

The comparison of the data generated by PE 240 and ASTM procedures indicates that comparable accuracy is achieved.

2) F, Cl, P, and S (Ion Chromatography)

The effort to isolate the source of contamination in the ion chromatographic procedure for F, Cl, P, and S has incorporated an extensive set of experiments to determine the effect of various glass and plastic sample storage vessels, the use of dilute acid and commercial cleaning solutions, and different sources of demineralized water. The source of contamination has been determined to be associated with the syringe used for sample injection. Rinsing the outside of the tip and careful insertion into the solution has eliminated the contamination.

The final elimination of the source of contamination will allow us to proceed with the identification of all peaks emanating from the ion chromatographic analysis of solutions prepared by the oxygen bomb combustion of coal samples. This will be proceeded by quantification of matrix affects and the establishment of the calibration curves.

3) Major and Minor Metals (ICPES)

Due to the contamination in commercial atomic absorption single element standards, new sufficiently pure reagents were used to prepare the appropriate multi-element standards for all 24 elements. This has allowed the identification of the inter-element interferences that need to be corrected. The addition of new software for making the background corrections has also allowed the identification of these inter-element interferences.

A peristaltic pump has been installed as the sample aspiration system and has resulted in a significant improvement in the analytical precision. Additionally, the installation of a Pt-Ir needle Zr block concentric nebulizer has allowed the use of solutions of high concentrations of dissolved solids. This nebulizer also exhibits relatively excellent chemical resistance.

Experiments are still continuing in an attempt to reduce the sample preparation time and costs. This has involved the use of various vessels for the relatively low temperature leaching of the coal with aqua regia.

The addition of the various accessories, i.e., the new nebulizer, the peristaltic pump and the new computer software, has resulted in a more sophisticated ICPES for the rapid, accurate, and precise analysis of a large number of metals in the coal. The efficiency of this procedure will be further enhanced by the addition of the coal leaching technique.

B. Time Variation in Rosebud Coal Properties

Routine tipple samples from the Montana Power Company's coal fired electrical generating plant are still being received. In addition, a detailed sampling of coal throughout the plant has recently been completed and these samples have been received.

A portion of these samples are being ground for analysis and the remainder stored under argon. The moisture of these ground samples are being equilibrated with 15% relative humidity at 30°C, and the C, H, and N contents are being determined. The time variation of the chemical content of the coal will be characterized along the entire coal feed system. These data will be compared to analytical data from tipple samples taken daily by the Montana Power Company. The time variation in the properties of the Rosebud coal seam will be based on the comparison of the two sets of data. Major emphasis will be directed at completing analysis of these samples next quarter.

TASK B
Creep Studies on MHD Preheater Materials
K. Kitto

I. OBJECTIVE AND SCOPE OF WORK

The primary objective of this task is to characterize those properties of potential MHD materials that directly aid in engineering design, particularly for the high temperature air heater (HTAH). These property tests include:

- .High temperature compressive creep
- .High temperature compressive strength
- .High temperature creep/strength during and after temperature cycling simulating operating conditions.

The above tests can be performed under the following simulated preheater conditions: a) temperatures to 1973K (3092°F); b) atmospheres, oxidizing or simulating combustion; c) forces indicative of brick positions; d) cycling of temperatures; e) times to 2500 hours (and beyond); and f) materials in their pristine or slagged preheater tested state.

Test samples include such commercial materials as magnesia/magnesia-alumina spinels, magnesia-aluminas, alumina/magnesia-aluminas, chrome-aluminas, aluminas, etc., insulating castables, and innovative laboratory materials. These samples are tested first as pristine materials (for materials ranking), and secondly after being exposed in experimental preheater rigs. Ceramics, before and after testing, are subjected to several microstructural examinations and/or X-ray diffraction analysis.

II. SUMMARY AND IMPACT

A. Test Equipment

The three air atmosphere creep frames and the microprocessor data acquisition system, described in detail in a previous report,¹ were used. Several creep tests on Norton LS-812 spinel castable were completed. In addition to those three frames, two additional creep rigs, one for testing large dense brick samples and one for testing brick size insulating refractories, are nearing completion and should be "on-line" shortly. Simultaneous operation of all five frames will require modification of the microprocessor data acquisition system. This modification will be completed next quarter.

B. Testing

Several long term creep tests (up to 2300 hours) have been completed on a spinel castable² during the past quarter.

High temperature compressive strength tests have been made on fusion cast alumina and alumina-chrome as well as two castable materials with either calcium aluminate or phosphate bonding phase. These data have been supplied to MSU Task E personnel as well as the FluidDyne Engineering Co.

C. Microstructural Examinations

An X-ray analysis program on the calcium aluminate bonded spinel castable was begun during the past quarter. Analysis on pristine and post creep test samples were made to determine if any $\text{CaO}_x(\text{Al}_2\text{O}_3)_y$ binder was lost in the material upon heating to above 1673K (2552°F).

D. Cooperative Programs

Task B personnel continued to interact in cooperative programs with Babcock and Wilcox (HRSR) and Fluidyne Engineering (HTAH).

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Equipment

Table 1 summarizes the planned creep system. In addition to the experimental rigs described in great detail in previous reports,^{1,2} Task B is constructing one more frame. This frame will be used to test refractory brick samples up to 24 cm x 11.4 cm x 10.2 cm in size. Long term/high temperature creep data is seldom available on commercial insulating refractories, yet design work using these insulating materials requires this information. This frame is being added to the system at the specific request of Fluidyne. Currently, design work is beginning at Fluidyne on hot valves, ducts, etc. for which long term/high temperature creep data for these materials are needed. The experimental measuring devices and associated systems will be the same as those previously described.¹

B. Tests and Results

1. Work Accomplished

During the past quarter, creep testing, compressive strength testing, and microstructural examination programs have all continued. Creep testing has concentrated on the spinel castable LS-812,⁺ while compressive strength tests were made on a variety of core, valve and insulating materials: Monofrax A,* LS-812⁺ and 13337°.

* Monofrax A and Monofrax K-3: dense fusion cast refractory, Carborundum Co., Niagara Falls, New York.

+ Norton LS-812: Calcium aluminate bonded spinel grain castable, Norton Co., Worcester, MA.

° Taylor 13337: Phosphate bonded spinel grain castable, Taylor Co., Cincinnati, OH.

2. Discussion

Creep Studies

Isothermal creep testing of LS-812 has continued with two major, primary goals: 1) to determine an approximate activation energy and 2) to determine if any significant variation occurs in the creep rate from batch to batch of the castable prepared by the manufacturer's standard method. Future studies will evaluate the creep properties as a function of casting methods including controlled porosity for improved thermal insulation.

The results of the creep testing program are given in Table 2. As indicated in that table, the results of the initial creep runs on the fusion cast magnesia/magnesia-alumina spinel (Corhart X-317) show that no deformation occurs upon heating to 1923K and upon loading to 1.0 MPa. Even after a 420 hour exposure to high potassium seed in the Fluidyne rig, the material showed no deformation upon heating to 1773K and loading to 2.8 MPa. Secondary creep rates are given for the following conditions: a) 1773K and 4.7 MPa, b) 1773K and 619 MPa and c) 1673K and 15.0 MPa. Thus only a little over 1% creep deformation would occur after 2000 hours at 1773K (2732°F) for a load of 4.7 MPa (680 psi) for this material. These results have been forwarded to the Fluidyne Corporation for evaluation in its design work.

A plot comparing the results of the creep testing program thus far on Norton LS-812 is given in Figure 1. Norton LS-812, the calcium aluminate bonded spinel castable, is being considered for the dome support region in the air heater and as a valve lining material.² In testing, the secondary creep rate increased with increasing stress and increasing temperature. The effect will be more easily understood when the stress exponent and the activation energy for creep can be calculated. Enough data for these calculations will be available by next quarter and the interpretation will be presented then.

As with any castable refractory, the properties of the monolithic brick can be altered by casting methods, firing procedures, or reinforcement technique. Therefore, it was decided to run a check creep test on two samples of the castable taken from two different batches of casting runs made at Fluidyne. The samples were prepared identically, except the second batch had a small amount of residual "stainless steel needles" that had accidentally remained in the mixer from a previous Fluidyne mix. The few residual needles were burned away upon firing and it was felt they would not alter the results of the creep experiment significantly. Apparently, they did not since the results of a creep test at 1400K and 6 MPa on both batches (as shown in Figure 1) differed by only 3.8%. The creep rate was .00052%/hr for batch 1 compared to .00054%/hr for batch 2. Creep results will be sent to the Fluidyne for evaluation in its design effort.

Hot Compressive Strength Tests

During the quarter, high temperature compressive strength tests were completed on Carborundum fusion cast Monofrax A and K-3 and Norton LS-812 and Taylor 1337 fused grain spinels.

Figure 2 is a plot of compressive strength of the fused cast materials versus temperature. One important feature is the remarkable strength of the alumina Monofrax A at high temperatures as compared to all materials except the relatively high alumina-chrome Monofrax K-3. However, as with all fusion cast materials, there is a significant variation in strength and other properties from batch to batch of the cast material. For example, the manufacturer lists the room temperature compressive strength to be ~ 143 MPa (20,000 psi) or approximately one-third our measured value of ~ 425 MPa. These values alone illustrate the need for an effective evaluation program for refractory materials. However, Monofrax A lost little strength upon heating to 1773K while Monofrax K-3 lost much of its strength. However, both materials were stronger than X-317, Monofrax E, or RFG.

It is noted that the material chosen to construct the core of the MTSFF at MSU was Monofrax A. In fact, at this time the material performed successfully for 700 hours (see Task E report).

The results of the high temperature compressive strength tests on the monolithic materials is given in Table 3. The listing compares two batches of LS-812 and Taylor 13337. Table 4 is a listing of the compositions for these same materials. Two compositions are given for Taylor 13337. The analysis by the manufacture lists % P_2O_5 as 1.0, but an analysis made by the Fluidyne Corporation on this particular batch of monolithic 13337 finds that P_2O_5 is not detectable on either a wet chemical analysis or an emission spec. Since phosphate is the bonding phase for this material, the low phosphate composition for this particular batch indicates that possibly an error was made in the manufacture of this material. The decline in hot strength at 1773K to less than 10% of its room temperature value is another indication that problems were encountered in the bonding phase for this particular batch of Taylor 13337.

Also shown in Table 3 is the consistently higher strength of the second batch of LS-812 at similar temperatures than the strength of the first batch. Fluidyne Engineering was contacted concerning the possible differences in casting and firing of the two batches. Fluidyne knew of no differences other than the first batch of LS-812 was older when cast (possibly some hydration of CaO had occurred) and that possibly more or less water might have been used in casting and mixing. Although a chemical analysis has not been made on the batches specifically, the CaO content can vary from batch to batch also. Since the hot strengths of these batches differ significantly and since this could be a potential problem in actual casting situations, the reasons for these differences must be investigated further and fully explained. First, a chemical analysis will be made on the batches, and secondly, a study will be made on the hot strength of the

second batch with different firing schedules. Casting procedures will also be reviewed for both batches as well as future batches. Hopefully a fuller explanation will be ready for inclusion in next quarter's report.

Microstructural Work and Thermal Cycling

The X-ray analysis on pre- and post-creep tested Norton LS-812 samples is not yet completed. The object of the study is to determine if any $\text{CaO}_x(\text{Al}_2\text{O}_3)_y$ binder (a low melting eutectic is in the $\text{CaO-Al}_2\text{O}_3$ system) is lost upon testing above 1673K.

The plans for thermal cycling experiments are continuing on schedule with the FluidDyne Corporation.

C. Work Forecast

During the next quarter, the following subtasks will be continued:

1. Creep testing on Corhart X-317, Norton LS-812, commercial dense refractories, and insulating refractories.
2. High temperature compressive strength tests on pristine, tested, and thermal-cycled refractories of all types.
3. Construction and check out of new equipment.
4. Microstructural examinations.
5. Thermal cycling/stress experiments with FluidDyne Engineering.

TABLE 1

Experimental Creep System at Montana
College of Mineral Science and Technology

	Air Atmosphere (small)	Air Atmosphere (large)	Air Atmosphere (insulating brick)	Air Atmosphere ("Astro")
Number of Frames	3	1	1	1
Maximum Temperature	1973 K	1923 K	1923 K	2023 K
Source	MoSi ₂	MoSi ₂	MoSi ₂	Graphite
Load Cell	50 kg 100 kg 500 kg	1750 kg or greater	1250 kg	50 kg
Sample Size	2.5cm x 2.5cm x 10 cm [1" x 1" x 4"]	13cm cube [5" cube]	23cm x 11cm x 10 cm [9" x 4.5" x 4"]	1.3cm x 5 cm cylinder [0.5" x 2" cylinder]
Temperature Cycle Capability	Yes	Yes	Yes	Yes
Atmosphere Cycle Capability	Major Modification	Major Modification	Major Modification	Yes
Status	All 3 Operating Simultaneously	Under Construction	Under Construction	Under Construction
Controls	Microprocessor	Microprocessor	Microprocessor	Microprocessor
Data Retrieval	Automatic	Automatic	Automatic	Automatic

TABLE 2

Summary of Compressive Creep Results

Material	Temperature (K)	Load (MPa)	psi	Secondary creep rate (%/hr.)
X-317+ (Corhart)	1573	0.34	47.6	no creep (275 hrs.)***
	1623	0.34	47.6	no creep (504 hrs.)***
	1623	0.52	72.8	no creep (300 hrs.)***
	1673	0.52	72.8	no creep (450 hrs.)***
	1773*	0.83	116.2	no creep (528 hrs.)***
	1823*	0.83	116.2	no creep (192 hrs.)***
	1923*	0.83	116.2	no creep (150 hrs.)***
	1773**	2.80	392.0	no creep (950 hrs.)***
	1773	4.70	658.0	0.0006%/hr.
	1773	6.90	966.0	0.0015%/hr.
	1673	15.0	2100.0	0.0047%/hr.
LS-812# (Norton)	1400	5.50	770.0	0.004%/hr.
	1700	1.00	140.0	calculation
	1700	1.00	140.0	calculation (exp. check)
	1400	5.5	770.0	0.0004%/hr.
	1400	4.6	644.0	0.0002%/hr.
	1400	6.0	840.0	0.00052%/hr.
	1400****	6.0	840.0	0.00054%/hr.
	1700	0.5	70.0	0.00272%/hr.
	1700	1.0	140.0	0.0350%/hr.
	1700	1.5	210.0	failed within 2.0 hrs.
	1700****	1.5	210.0	failed within 1.8 hrs.
	1600	1.2	168.0	calculation
	1738	0.5	70.0	in progress
Monofrax A++ (Carborundum)	1773	10.4	1456.0	in progress
K-3000° (B&W)	1500	0.2	28.0	in progress

* One sample

** After 420 hr. exposure to high K-seed in Fluidyne MTF.

*** Thermal Expansion after equilibrium-not exceeding 1.25%

**** Taken from a second casting of LS-812 at Fluidyne.

+ Fusion cast magnesia/magnesia-alumina spinel, Corhart Refractories Co., Louisville, KY.

Calcium aluminate bonded spinel grain castable, Norton Co., Worcester, MA.

++ Fusion cast alumina, Carborundum Co., Niagara Falls, New York

° High alumina insulating firebrick, Babcock and Wilcox, Augusta, GA.

Figure 1. Schematic Results of the Creep Testing Program of LS-812 Spinel Castable

Figure 2

TABLE 3
Castable Spinel Materials
High Temperature Compressive Strengths

TEMPERATURE	STRENGTH MPa		
	BATCH #1 Norton* LS-812	BATCH #2 Norton* LS-812	BATCH #1 Taylor** 13337
Room Temperature	16.8	25.1	24.6
1373 K	16.9	24.8	24.4
1473 K	15.9	25.1	12.2
1573 K	12.2	19.3	5.8
1673 K	10.0	15.5	2.3
1773 K	7.1	11.3	<2.0

* Calcium aluminate bonded

** Phosphate bonded

Note: Standard deviation average-approximately ± 0.2 - ± 0.3 MPa

TABLE 4
Chemical Composition for Norton LS-812 and Taylor 13337

NORTON LS-812*

	Oxide Basis
Al ₂ O ₃	73.9
MgO	22.3
CaO	3.0
SiO ₂	0.4
Fe ₂ O ₃	0.1
Na ₂ O	0.1
Others	0.2

TAYLOR 13337

	Oxide Basis Manufacturer	Oxide Basis Fluidyne
Al ₂ O ₃	70%	65.2
MgO	28%	33.0
P ₂ O ₅	1%	< .01**
CaO		0.9
Fe ₂ O ₃		0.2
SiO ₂		0.5

* Manufacturers' numbers

** Not determined on emission spec or wet chemical analysis.

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

I. OBJECTIVE AND SCOPE OF WORK

Task C is charged with coal preparation studies on Rosebud seam coal for utilization in direct coal-fired MHD power generation plants. Prior studies into the areas of coal preparation have led to the fluidization drying studies to generate engineering data for scale up and applications to the ETF-sized MHD units. These experiments will measure drying rates, the equilibria between the dried coal moisture content and the off-gas humidity, heat and mass transfer coefficients, and entrainment losses for variable drying conditions. They will also include the effect of coal feed rate, inlet drying temperatures, inlet humidity, drying gas mass flow rate, and coal particle size on the preceding parameters. The data will be analyzed to show drying efficiencies while using exit gas energy from the MHD system to show the inter-relationships among the operating and design variables needed to achieve the optimum coal moisture level consistent with minimizing volatile emissions and maintaining highest coal Btu levels for MHD power generation.

II. SUMMARY AND IMPACT

The objective and scope of work has resulted in 1) continuing the coal drying tests, 2) modifying these test parameters to include the dry nitrogen drying medium in combination with an inlet gas temperature range of 500 to 700°F, and 3) studying alternatives to minimize volatile emission while maintaining highest coal Btu levels which include running tests on wet ball mill ground coal in combination with the Niro spray dryer.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

The major impact on the test runs by Task C during this quarter was the changed drying medium characteristics which resulted from the decision to use oxygen as part of the coal combustor firing system. The production of oxygen also produces dry nitrogen in surplus of needs for MHD. Therefore, this nitrogen can be used as a low humidity drying medium for coal preparation for the MHD ETF plant. This decision to supplement the oxygen to the combustor resulted in narrowing the drying gas temperature range from that of the indirect-fired air preheater. The inlet gas drying temperature range for the remainder of this study is from 500 to 650°F which will be carried out by studies at 500, 550, and 650°F.

To achieve the above changes, more nitrogen was introduced into the closed circuit drying system on the one square foot fluid bed dryer. Also, the inlet gas humidity has been decreased to a minimum consistent with a reduction of surface oxydation during drying which should result in a small increase (in the range of 1%) in the dried coal Btu level. Further improvements in air leak reduction into the fans, the wet scrubber, and the dust

collector are under way. We have reached a 10% oxygen drying atmosphere, but this is not good enough. It is more difficult to greatly reduce the inlet humidity because the present system was designed for controlled higher humidity recirculation. However, a silica gel drying step is under study for the continuous system.

Many test runs have been made during this quarter. These runs were made at the 500°F and 550°F inlet gas temperature. The variables studied were the drying rates, the relationship of the dried coal moisture, and the off-gas humidity, the coal feed rate, the inlet drying temperature, the oxygen content of the drying medium, the inlet humidity, the drying medium mass flow rate, and the coal particle size.

Organic emission during drying is inevitable. Therefore, the goal is to reduce the emission to a minimum and to control or capture the emissions that are undesirable. In cooperation with Task D, gas samples were taken during steady state continuous operation at several temperature levels. Task D will report on the testing of these samples.

The very short retention time for drying in a spray dryer will result in fewer organic emissions. Wet grinding of the coal will result in less surface oxidation of the coal particles which will result in higher Btu levels of coal ready for burning in the MHD coal combustor. These advantages will be evaluated against cost to MHD. On the assumption that the heat for drying is waste heat, the added moisture content of a slurry feed can be dried at a lower cost to MHD with heat transfer than with the high nitrogen drying medium of a spray drier.

IV. WORK FORECAST

Fluid bed dryer testing will greatly speed up during the coming quarter as added operator time is available after graduation-- May 11, 1980. Coal crushing is now a scheduled part of the drying process. The series of fluid bed drying tests should be completed by July 31, 1980.

Wet grinding and spray dryer tests will be scheduled to overlap the fluid bed tests, but not interfere with them. The closed circuit drying medium system will be used for these tests by connecting the spray dryer in place of the fluid bed dryer into the system.

TASK D
Characterization of Volatile Matter in Coal
D. Beuerman

I. OBJECTIVE AND SCOPE OF WORK

The objectives of this task are to identify and quantify organic volatile matter evolved during the coal drying process and to assist in determining methods of preventing loss of organics.

II. SUMMARY AND IMPACT

The loss of organics has been noted in previous reports. Results to date indicate that these losses can be minimized by controlling the operating parameters of the coal drying system.

Data gathered this quarter is not sufficiently complete to include in this report.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Work during this quarter consisted of the following:

1. Trouble shooting instrument problems;
2. Attending a workshop in instrument repair, troubleshooting and modification; and
3. Evaluating published methods of determining the organic content of atmospheres.

A. Trouble Shooting Instrument Problems

The gas chromatograph--the thermal conductivity (TC) detector--does not have the sensitivity to detect hydrocarbons in the low ppm range. The detector also sees the water solvent peak which exhibits abnormal tailing and poor resolution from the hydrocarbons. During this quarter, the flame ionization detector (FID) was made operational. This allows the detector to neglect the water peak and prevents the tailing problem. The FID is more sensitive than the TC detector.

It is necessary to obtain better resolution of the organic components in the dryer gas. Considerable time was spent becoming acquainted with the HP capillary column. One concern to date is the fragility of the capillary glass columns. Hewlett Packard has recently developed a type that is more flexible and less brittle. This accessory has been ordered. Capillary columns provide improved resolution on micromilliliter samples. Thus the capillary column does not become overloaded as easily as the conventional packed columns.

B. Attended A Workshop on Instrument Repair, Trouble Shooting, and Modification

Reproducibility of retention times has been a problem in the HPLC studies of the quench water from the fluidized bed dryers. Attendance at a workshop at Salt Lake City revealed that two problems existed: the need for installing guard columns on the instrument and synchronization of the four separate operations necessary to obtain a printout of the CRA-1-A integrator. The instrument has been rewired so these operations are controlled by the microprocessor in a single operation. The instrument must go through a few shake-down tests to prove the reliability of the analysis.

C. Evaluating Published Methods of Determining the Organic Content of Atmospheres

A literature search is continuing in an effort to find existing methods that will analyze these organic components from the dryer off-gas. To date, no information has been uncovered that would improve on the existing methods being used in attacking this problem.

IV. WORK FORECAST

A set of experiments is planned for summer in cooperation with Task C to determine the effectiveness of changes in dryer operations on the organic emissions. The methods development work will continue based on the installation of Golay capillary column into the gas chromatograph. Work on the ability of dried coal to remain dry will be reinstigated. This is a continuation of experiments by Dr. Drew reported in the 1979 Annual Report.

TASK N:
MHD Materials Evaluation

J. J. Rasmussen, R. Parker, T. Morse, M. Johnston

I. OBJECTIVE AND SCOPE OF WORK

The objective of this task is to perform and coordinate MHD materials and evaluation work in support of the national plan for MHD electrical power development formulated by the DOE-FE-MHD Division. The research emphasis is to provide materials support for high temperature air heater (HTAH) development, particularly at MSU (Task E) and Fluidyne Engineering Corporation.

II. SUMMARY AND IMPACT

Work has been progressing to obtain baseline data on pristine Monofrax A⁺ to assist in the evaluation of changes which have taken place when this material was exposed to high temperature coal slag in the Montana State University (MSU) Moderate Temperature Slag Flow Facility (MTSFF).

Thermal diffusivity measurements have been made on the pristine Monofrax A and on Norton castable LS-812^{*}. The thermal conductivity was then calculated from the diffusivity.

Fracture toughness measurements show that the castable refractory compounds have a very low fracture toughness ($\sim 1 \text{ MPa}\sqrt{\text{m}}$) while the fusion cast refractories containing a high concentration of alumina such as Monofrax A and Monofrax K3 have significantly higher fracture toughness values ($\sim 3.6 \text{ MPa}\sqrt{\text{m}}$).

The addition of a small amount of platinum to a stabilized ZrO₂ body had no effect on the electrical conductivity mechanism of the ZrO₂. Techniques have been developed to cut and polish the samples without structural degradation. Structural data is being obtained using optical microscopy and SEM techniques.

Considerable effort was spent obtaining visa approval to bring Dr. David Yerouchalmi to the U.S. to assist in the HTAH work. Approval was received in late March. Dr. Yerouchalmi will arrive in Butte in June.

⁺ Fusion cast α -alumina with a β -alumina grain-boundary phase (99.3% Al₂O₃, 0.4% Na₂O), Carborundum Refractories, Niagara Falls, NY.

^{*} Fused magnesium aluminate spinel castable (75.0% Al₂O₃, 20.8% MgO, 3.4% CeO, 0.4% SiO₂, 0.2% Fe₂O₃), density 2.8 g/cm³, Norton Company, Worcester, MA.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Structural Characterization of MHD Materials

The materials characterization work at MERDI has been directed to obtain baseline data on the pristine materials being used currently in the MSU MTSFF core and hot-liner. Selected samples along the length of the present core are scheduled to be removed from the preheater at the end of 750 hours exposure. Further samples will be selected after 1000 hours or more exposure. These samples will then be divided up and distributed for characterization to MERDI, MSU, and Montana Tech (MT) personnel. Detailed comparison of the structural changes that take place when the material has been exposed for various lengths of time to coal slag and cycling high temperatures in the HTAH tests will be presented in a topical report. The report scheduled for late June or July will cover HTAH operability test results and materials performance on the materials tested for 750 hours.

Samples of as-fabricated Monofrax A have been used to develop cutting and polishing techniques which do not introduce defects such as cracks and voids from pull-outs during the sample preparation. Polished samples of several pristine Monofrax A bricks have been prepared and are under evaluation by optical microscopy, scanning electron microscopy, energy dispersive X-ray analysis, and other techniques.

B. Thermal Transport Properties and Analysis

The new laser flash tube was installed to facilitate thermal transport measurements. It was determined during replacement of the flash tube that the cooling system had not been satisfactorily repaired after the unit was shipped to Butte from California with water in the cooling system. The water had frozen during transit and had caused considerable damage. The necessary cooling system repairs were completed by a refrigeration specialist. The unit has been re-aligned and checked to be sure that the data being obtained currently is consistent with earlier data taken before the flash tube was replaced.

Data taken initially after the tube replacement had high deviations because of a poor signal to noise ratio. Modifications have been made to the temperature measuring equipment to improve the signal to noise ratio.

Results of the thermal diffusivity data and thermal conductivity as calculated taken on a piece of Norton castable LS-812 are shown in Figure 1. A least-squares-fit to the data gives a thermal diffusivity value (α) of $1.212 \times 10^{-2} - 5.944 \times 10^{-6}T$ in the temperature range 200-1200°C, where α has the dimensions ($\text{cm}^2/\text{sec.}$) and T is the temperature in degrees Celsius. As can be seen, the diffusivity of the castable compound is fairly independent of temperature. The thermal conductivity was calculated from the relation $\lambda = \alpha \cdot C_p \cdot \rho$ where

λ =thermal conductivity, C_p =heat capacity = $0.2642 + 3.492 \times 10^{-5}T - 7.358 \times 10^{-8} / (T + 273)^2$, and ρ =density = $2.822 (1 - 300 \times 10^{-6}T)$.

Thermal diffusivity and thermal conductivity calculated from the diffusivity of Monofrax A in the pristine condition are shown in Figure 2.

The Monofrax A curves in Figure 2 actually represent the data taken from two heating and cooling runs between 200 and 1200°C. The data from both runs superimpose precisely on the same curve with the exception of the results on the initial heatup from 200-300°C. Since the source of this thermal diffusivity/conductivity deviation appears to disappear by the time the sample is heated to 350°C, this should have no effect on the engineering properties of Monofrax A when used in MHD high temperature air heaters.

The thermal conductivity of a dense Al_2O_3 polycrystalline sample (Coors A60) is shown for comparison. The Monofrax A conductivity was calculated from the diffusivity values using the relations: $C_p = 0.2595 + 3.682 \times 10^{-5}T - 4.848/(T+273)^2$, and $\rho = 3.76(1 - 2.36 \times 10^{-6}T)$.

Fracture toughness data on a series of pristine commercial refractories samples received from Fluidyne Engineering Co. are summarized in Table 1. All data is reported with a standard deviation of $\pm 1\sigma$. There is limited data available on the castable materials because of their tendency to fracture crosswise rather than along the prescribed crack plane. As expected, the castables have low toughness values ($0.9 - 1.2 \text{ MPa}\sqrt{\text{m}}$) with a limited ability to absorb shock loading without failing.

The fused cast materials had much higher fracture toughness values with the exception of the Corhart RFG. The important thing to note is that the heating of the RFG resulted in a 47% reduction in the value of K_{Ic} . It is interesting to observe that the materials with a high alumina content, Monofrax A and Monofrax K3, are the refractories with the highest toughness values.

The original Monofrax A samples which were broken had visible cracks on the surface. Three extra samples were cut without cracks and toughness data taken on these. As can be observed, there was little change in the value of the measured fracture toughness indicating that K_{Ic} determined by the Fractometer method is not sensitive to out-of-the-crack plane flaws in the samples.

The alumina samples with the highest fracture toughness values were prepared by traditional pressing and sintering techniques.

C. Fabrication of MHD Materials

A small batch of yttria stabilized zirconia was prepared with a dispersion of platinum metal precipitated from an acid solution. The platinum solution had been used to coat ceramic powders for a different

purpose. The concept has a potential to produce a ceramic based electrode with electronic conductivity instead of the usual ionic conductivity.

A sample of the metal-loaded stabilized zirconia has been examined for electrical conductivity using an ac technique. The measurements were made from 300°C to 1100°C and yield an activation energy of 1.29 ev. The data fits an exponential curve (vs. $1/T$) over the entire temperature range and the conductivity becomes negligible below 300°C.

The activation energy of 1.29 ev. is quite close to the value measured in samples of yttria stabilized zirconia without the metallic doping. The activation energies are consistent with literature accepted values for oxygen mobility. This coupled with the oxygen positive pressure dependence of the conductivity (observed but not measured) lead us to conclude that the current carriers in both of these materials are oxygen ions. Further, both metallic doped and undoped samples exhibit substantial electrolysis effects at low temperatures.

Though these samples contained metal, they contained only small amounts (<1%) and tests will have to be repeated using samples with much greater metal concentrations (5-10%) if this concept is to be used to develop a material which can be used as an MHD electrode.

IV. REPORTS

The following two papers were presented at the 82nd Annual American Ceramic Society meeting in Chicago, April 28, 1980.

- (1) J.J. Rasmussen, R. Parker, T. Morse, and R. Guidotti, "Wettability and Corrosion of MHD Preheater Refractories by Coal Slag."
- (2) M.H. Leipold, G.J. Youngblood, and R.S. Parker, "Ceramics for MHD and Photovoltaic Systems."

TABLE 1
Fracture Toughness Values of Commercial Refractories

<u>Sample</u>	<u>Chemical Composition, w/o</u>	<u>Fracture Toughness K_{1c} MPa/m (# samples)</u>
Refractory Castables		
5-487G (Taylor)	spinel	0.908 ± 0.142 (3)
X-13249 (Taylor)	spinel	1.159 ± 0.227 (4)
LS-812 (Norton) (Most samples broke crosswise)	spinel	0.903
Alumina (Coors)	α-Al ₂ O ₃	3.987 ± 0.264 (7)
Monofrax A.	99.3 Al ₂ O ₃ , 0.4 Na ₂ O	3.880 ± 1.387 (3) (w/visible cracks)
	0.1 CaO, 0.1 Fe ₂ O ₃ , 0.1 SiO ₂	3.642 ± 0.942 (6) (all samples)
Monofrax K3 (Carborundum)	60.4 Al ₂ O ₃ , 27.3 Cr ₂ O ₃ ,	3.639 ± 0.827 (3)
	1.8 SiO ₂ , 4.2 Fe ₂ O ₃	
	0.3 Na ₂ O ₃ , 6.0 other	
Monofrax E (Carborundum)	79.7 Cr ₂ O ₃ , 4.7 Al ₂ O ₃	2.580 ± 0.148 (3)
	6.1 Fe ₂ O ₃ , 0.1 Na ₂ O	
	1.3 SiO ₂ , 8.1 other	
RFG (Corhart)	76.0 MgO, 7.2 Cr ₂ O ₃	1.426 ± 0.146 (6) (heated samples)
	8.4 FeO, 4.3 Al ₂ O ₃	2.70 ± 0.23 (2)* (pristine samples)
	1.0 TiO ₂ , 0.5 CaO, 2.6 SiO ₂	

* Oct.-Dec. 1978, Quarterly Report

Figure 1. Thermal Diffusivity and Conductivity of Pristine Norton Castable LS-812

Figure 2. (a) Thermal Diffusivity of Pristine Monofrax A
 (b) Thermal Conductivity of Pristine Monofrax A
 and an Al_2O_3 Standard (A60)

TASK E
Slag Flow and NO_x Kinetics
Moderate Temperature Slag Flow Facility (MTSFF)
H. W. Townes - T. A. Amee

I. OBJECTIVE AND SCOPE OF WORK

The objective of this program is to determine the operational characteristics of a high-temperature packed-bed regenerative heat exchanger for a coal-fired open-cycle MHD system. There is considerable information on the operation of regenerative heat exchangers at temperatures up to 4200°F; but until several years ago, all work had utilized clean fuels such as natural gas. The present work is concentrated on the effects that coal slag and MHD seed material have on the performance of regenerative packed-bed heat exchangers. To date, the experimental work has been concentrated on the effects of slag only in the combustion gas stream. Observed effects include the deposition of coal slag and seed materials along the surfaces, their obstruction of the passages, their chemical interaction with the heat exchanger material, and changes in the friction and heat transfer coefficients of the heat exchanger flow passages.

An experimental facility, the moderate temperature slag flow facility (MTSFF), has been built and is being operated to study the effects that typical open-cycle MHD channel-exit flows have on the high-temperature air preheater. The test core of the MTSFF consists of typical MHD air preheater ceramic bricks. A data acquisition and control system is utilized to record gas flow rates, pressures, and temperatures.

The effects of the coal slag on the heat exchanger performance are being determined initially with these typical operational parameters, a top ceramic temperature of 1750 K (2700°F), and gas velocities of 21-53 m/s (70-170 ft/sec; Reynolds number 3000-4800). The experimental system has been sized so that the above temperatures and velocities are achieved in a 19-hole brick with circular holes 19mm (0.75 inches) in diameter. Natural gas is used as the fuel. Coal ash is being added to simulate the combustion products of coal firing. The amounts of coal ash added to the combustion gas simulate a 10 percent slag carryover (0.1 percent slag by mass in the combustion gas). The carry-over can be varied. The influence of particle size has also been determined.

The experimental runs utilizing the first core of the MTSFF were completed in June 1978. The first core was operated with slag only in the combustion gas for a total of 1150 hours. The six experimental runs made with the first core established the effect of particle size on the rate of pressure drop increase across the core. The objective of the experimental runs with core number two (installation completed December 1978) was a determination of the feasibility of a "melt out" of slag deposits in the MTSFF.

Six experimental runs were made with the second core for a total of 950 hours of operation. Four of the second core runs showed successful "melt-out" of slag deposits while the other two runs were made strictly to test materials suitable for use in the third MTSFF core.

II. SUMMARY AND IMPACT

The moderate temperature slag flow facility (MTSFF) was operated continuously for 750 hours with slag injection. During the 750 hours, five cleanouts of the core were made after the pressure drop across the core had been allowed to increase due to slag deposition. The MTSFF was shut down in the "slagged up" condition after the sixth slagup. The impact of this experimental run is the demonstration of successful multiple cleanouts of a slag deposit.

III. DETAILED DESCRIPTION

The rebuilding of the MTSFF utilizing Carborundum Monofrax A (a high-purity fused cast alumina) as the core material was completed. The 200 hour materials test at the completion of the series of experiments with the Corhart RFG core #2 indicated that the Monofrax A, while not the most slag resistant of the materials tested, would give good performance. The objective of the first experimental run (slag run #13 using the Monofrax A core, the third core used in the MTSFF) was to demonstrate the feasibility of multiple cleanout cycles in the MTSFF. Only slag was injected into the combustion gas stream, and the experimental conditions were held close to those used in previous experiments (see Table 1).

The 750 hour experimental run was started on January 30 and completed on March 1, 1980. The times for the slag-ups and cleanout cycles are shown in Table 2. The times for all of the slag-ups were not the same. The first slag-up from the clean condition required 102 hours of operation. The other successive slag-ups were made for 46, 83, 78, 154, and 59 hours, respectively. The cleanout cycles were run from 8 to 43 hours. In addition to the cleanout (meltout) time, additional time was required to return the heat exchanger to the temperature profile required for cyclic operation. This time is termed "cooldown" time in Table 2.

The pressure drop history across the MTSFF core and the friction factor are shown in Figures 1 and 2, respectively. Since the two figures show essentially the same character (the two are shown in order to give the actual pressure drop information and the dimensionless form), the following discussion will be in terms of the friction factor.

During the first slag-up, the friction factor was allowed to double from a value of 0.06 for the initial clean condition to a value of 0.12 at the end of 102 hours of operation with slag injection. The first cleanout of the core reduced the friction factor to a value of 0.10. The next four cleanout cycles were run with values of the friction factor before and after the cleanout of 0.175 to 0.09, 0.175 to 0.11, 0.24 to 0.06, and 0.325 to 0.13. The value of the friction factor at the end of the sixth slag-up (when the run was stopped) was 0.25.

Although the friction factor did not return to the value of the clean condition at the end of each cleanout cycle, the friction factor was reduced in each cleanout. It is not reasonable to expect an absolutely clean core to be produced by a cleanout cycle. The cleanout done in the fourth cleanout was apparently very good, since the friction factor did return to the clean value of 0.06.

An examination of the core after shutdown and disassembly showed that the bottom brick temperature of 2400°F achieved during the cleanout cycles is marginal for a complete removal of the slag from the bottom core brick. The bottom of the bottom brick is shown in Figure 3. As can be seen from this photograph, there is a considerable amount of slag on the brick which was not removed during the cleanout cycles. The slag trap on the MTSFF is now being modified in order to allow a 2600°F temperature to be achieved on the bottom core brick during the cleanout cycles. This higher temperature should promote the removal of the slag from the bottom brick. The remainder of the core showed no major slag deposits and only one other plug in a flow passage.

In addition to the slag attached to the bottom brick, there were flow holes plugged in the last two bricks (bricks 79 and 80--brick 80 is the bottom core brick). This plugged condition, shown in the photograph of brick 79 in Figure 4, is suspected to be due to the marginal temperature level of 2400°F achieved at the bottom brick during cleanouts.

Slag run #13 on the MTSFF has demonstrated that it is possible to operate a regenerative heat exchanger for a long time period in the slag-up/cleanout mode of operation. The investigators feel confident that the slag deposit on the bottom brick can be removed by a higher temperature during the cleanout cycles.

The general condition of the Monofrax A at the completion of the run was excellent. The top core brick is shown in Figure 5. There was a sluffoff of some of the hot liner castable onto the top core brick as can be seen. However, the condition of the top brick is excellent. During cleanout cycles, the temperature at the top brick was 2800 to 3000°F. The remainder of the core bricks were generally in excellent condition also, although they usually showed some cracking. A complete materials characterization is in progress and will be available as part of a topical report.

IV. REFERENCES

The experimental work described above has been coordinated with personnel at Fluidyne and General Electric. The work has been in direct support of the closed-cycle MHD effort at General Electric. The materials analysis is being coordinated with personnel at Montana State University, MERDI, Battelle Northwest, and Argonne Laboratories.

Table 1.--Slag Run #13 Operating Conditions

CORE BRICK

19 - 3/4 INCH DIAMETER HOLES

20 FEET TOTAL CORE LENGTH

MATERIAL MONOFRAX A (HIGH PURITY ALUMINA)

TEMPERATURES

END OF REHEAT TOP 2700-2800 F

BOTTOM 1000-1200 F

END OF COOLDOWN TOP 2550-2650 F

BOTTOM 800-1000 F

FLOW RATES

REHEAT 185 KG/HR

COOLDOWN 165 KG/HR

SLAG 0.1 % (10 % CARRYOVER)

CYCLE TIMES

REHEAT 6 MIN (FIXED)

COOLDOWN 3-4 MIN (VARIED FOR TEMPERATURE CONTROL)

AIR/FUEL RATIO 21-24:1

Table 2.--Slag Run #13 Operation vs. Time History

750 HOURS TOTAL	700 HOURS WITH SLAG	
	TIME (HRS)	TOTAL RUN TIME (HRS)
1ST SLAG UP	102:00	
		102:00
1ST MELT OUT	14:00	
		116:00
1ST COOLDOWN	4:00	
		120:00
2ND SLAG UP	46:30	
		166:30
2ND MELT OUT	8:46	
		175:16
2ND COOLDOWN	10:02	
		185:18
3RD SLAG UP	83:24	
		268:42
3RD MELT OUT	24:24	
		293:06
3RD COOLDOWN	15:44	
		308:50
4TH SLAG UP	78:40	
		387:30
4TH MELT OUT	22:35	
		410:05
4TH COOLDOWN	9:25	
		419:30
5TH SLAG UP	154:06	
		573:36
5TH MELT OUT	43:40	
		617:16
6TH SLAG UP	59:14	
		684:52
FINAL COOLDOWN	11:06	
		695:58

SLAG RUN # 19
REHEAT DATA
4400 CYCLES

1ST CYCLE AT 16474103 ON 01/30/80
LAST CYCLE AT 4511999 ON 03/01/80

Figure 1

SLAG RUN # 13
REHEAT DATA
4380 CYCLES

1ST CYCLE AT 16474103 ON 01/30/80
LAST CYCLE AT 4511999 ON 03/01/80

Figure 2

Figure 3.

Figure 4.

Figure 5.

TASK F
Slag-Seed Equilibria and Separations Related to the MHD System
R. Howald

I. OBJECTIVE AND SCOPE OF WORK

The objective of Task F is the measurement and interpretation of vapor pressures over high-temperature oxide systems and the thermo-dynamic analysis of these systems. The systems for study are primarily synthetic mixtures, actual slags, and seeded slags. The measurements are performed using atomic absorption to measure atom concentration in high-temperature graphite tube furnaces produced by diffusion from vapor pressure cells. The analysis is aimed at providing accurate equations for vapor pressure and activity in multicomponent systems for use in engineering design work wherever slags and seeded slags are encountered in the MHD system.

II. SUMMARY AND IMPACT

A general computer program for the calculation of chemical equilibria must have two parts--a way to enter thermodynamic data and one or more sub-routines for the minimization of free energy. It also is usually necessary to define the temperature, pressure, and stoichiometry for the particular problem you want solved, and there must be some procedure for reading or estimating an initial set of amounts or concentrations. The necessary details of the input and of the calculation should not be allowed to obscure the fact that the two major aspects are thermodynamic calculations and free energy minimization. Our new program is written so that these two main parts are separable. Both parts are powerful programs in themselves, and it is possible to perform calculations with the separate parts. For example, the thermodynamic data files and thermodynamic calculations can be used to construct tables of the free energy function or tables of equilibrium constants at a series of temperatures. This program was designed for use with non-ideal liquid phases, and activities and activity coefficients can also be calculated at single compositions or over a range of compositions.

For solid-liquid equilibria, it is necessary to have very accurate equilibrium constants or their equivalent. For this reason, equilibria are based upon calculated free energy function values. The program includes provisions for calculating the free energy function as a function of temperature. This requires known expressions for the heat capacities as a function of temperatures and values for the enthalpy and free energy function at one standard temperature. Since much of the development was undertaken for high temperature equilibria, the standard temperature is usually 1000 K, but much of the program will operate with a standard temperature of 298.15 K as well.

Since the program is meant to be very general (applicable to any system), data for particular components and systems are not included in the program. Such data must be provided from a terminal or from a data file before the calculations will proceed.

Data files are normally read under a 6G10.0 format. The card

700 FORMAT (6G 10.0)

appears in almost all subroutines. It allows up to six numbers on a single line to be read. Successive numbers must be entered in fields of ten. It allows for entry of both integers and decimal fractions. Decimal fractions can be entered in either decimal or exponential notation: 0.00435 or .435E-2. The decimal point must be included in all numbers except when integers are read, and the integral exponents in E format must be located at the end of a field of ten spaces. This is not as convenient to use as widthless G format, but it is more easily transferred from one computer to another.

III. DETAILS OF TECHNICAL PROGRESS

A. Composition Dependence of Thermodynamic Properties

The dependence of activities in condensed phases upon the mole fractions is one of our major concerns. The temperature dependence as expressed in heat capacities and the free energy function are involved in almost all equilibrium problems. But there is a large class of important equilibrium problems in which one also needs activities and activity coefficients as functions of composition.

The most general composition variable available is the mole fraction, and we can expect to represent the thermodynamic properties of liquid and solid solutions as power series in the mole fractions.

Power series expansions of thermodynamic properties in terms of mole fraction have long been used.

The earliest proposed set of power series representations is that of Margules, shown here for a two-component system:

$$\bar{Y}_1 - Y_1^0 = (1-x_1)^2 (A_1 + B_1 x_1 + C_1 x_1^2 \dots)$$

$$\bar{Y}_2 - Y_2^0 = x_1^2 (A_2 + B_2 x_1 + C_2 x_1^2 \dots)$$

$$Y^e = x_1 x_2 (A_e + B_e x_1 + C_e x_1^2 \dots).$$

Y is used to represent an arbitrary thermodynamic quantity such as enthalpy, free energy, logarithm of activity coefficient, and so forth. $\bar{Y}_i$ stands for the partial molal quantity defined as $\partial Y / \partial n_i$, Y_i^0 is the value of the thermodynamic property for the pure material, and Y^e is the excess quantity of mixing. As required, at the composition of either of the pure materials, the excess quantity of mixing goes to zero and the partial molal quantities go to the molar values of the pure materials, i.e., $\bar{Y}_1 = Y_1^0$ at $x_1 = 1$.

Although the Margules equations have these essential qualities, there are some disadvantages to using this simple power series. First, a different set of coefficients appears in each of the equations above. Second, the mole fraction terms within a given equation are not orthogonal. If the terms were orthogonal, the first three terms of a four term series would be identical to those of a three term series. The decision of how many terms to use in a power series fit of a set of thermodynamic data points is facilitated by knowing the approximate magnitude of the individual term contributions. This is possible when the terms are somewhat orthogonal.

A reasonable compromise between orthogonality and convenience is provided by the Redlich-Kister equations:

$$\bar{Y}_1 - Y_1^o = x_2^2 \left[A + B(4x_1 - 1) + C(6x_1 - 1)(2x_1 - 1) + D(8x_1 - 1)(2x_1 - 1)^2 \dots \right]$$

$$\bar{Y}_2 - Y_2^o = x_1^2 \left[A + B(4x_1 - 3) + C(6x_1 - 5)(2x_1 - 1) + D(8x_1 - 7)(2x_1 - 1)^2 \dots \right]$$

$$Y^e = x_1 x_2 \left[A + B(2x_1 - 1) + C(2x_1 - 1)^2 + D(2x_1 - 1)^3 \dots \right]$$

The coefficients are the same in each equation and although the terms in a particular equation are not exactly orthogonal with respect to each other, approximate orthogonality does exist.

The reason that the coefficients can be the same in each equation is that the partial molal equations are derived from their relationship to the excess quantity equation. From the definition of the partial molal quantity

$$\bar{Y}_1 = \left. \frac{\partial Y}{\partial n_1} \right|_{n_2, T, P}$$

and the expression for the thermodynamic quantity

$$Y = n_1 Y_1^o + n_2 Y_2^o + (n_1 + n_2) Y^e$$

the following relationship can be derived:

$$\bar{Y}_1 = Y_1^o + Y^e + (n_1 + n_2) \frac{\partial Y^e}{\partial n_1}$$

Since $\frac{\partial Y^e}{\partial n_1} = \left(\frac{\partial Y^e}{\partial x_1} \right) \left(\frac{\partial x_1}{\partial n_1} \right)$ and $\frac{\partial x_1}{\partial n_1} = \frac{x_2}{n_1 + n_2}$ one can write

$$\bar{Y}_1 - Y_1^o = Y^e + x_2 \frac{\partial Y^e}{\partial x_1}.$$

The equation for Y^e can be rewritten as

$$Y^e = A(-x_1^2 + x_1) + B(-2x_1^3 + 3x_1^2 - x_1) + C(-4x_1^4 + 8x_1^3 - 5x_1^2 + x_1)$$

and

$$x_2 \frac{\partial Y^e}{\partial x_1} = A(-2x_1x_2 + x_2) + B(-6x_1^2x_2 + 6x_1x_2 - x_2) + C(-16x_1^3x_2 + 24x_1^2x_2 - 10x_1x_2 + x_2)$$

$$\begin{aligned} Y^e + x_2 \frac{\partial Y^e}{\partial x_1} = & A(-x_1^2 + x_1 - 2x_1x_2 + x_2) \\ & + B(-2x_1^3 + 3x_1^2 - x_1 - 6x_1^2x_2 + 6x_1x_2 - x_2) \\ & + C(-4x_1^4 + 8x_1^3 - 5x_1^2 + x_1 - 16x_1^3x_2 + 24x_1^2x_2 - 10x_1x_2 + x_2). \end{aligned}$$

Using $x_1 + x_2 = 1$, this equation can be rearranged to

$$Y^e + x_2 \frac{\partial Y^e}{\partial x_1} = x_2^2 \left[A + B(4x_1 - 1) + C(6x_1 - 1)(2x_1 - 1) \dots \right] = \bar{Y}_1 - Y_1^o.$$

B. Extended Redlich-Kister Notation

One of the major advantages of power series representations in the study of phase equilibria is that, in principle, all of the thermodynamic information of multicomponent systems can be represented by a relatively small number of power series coefficients. The previous discussion has been oriented toward two component systems. However, a notation for extending Redlich-Kister power series representations to multicomponent systems has been developed and will be described here.

Ideally, the description of a multicomponent system will include contributions from each of the binary, ternary, quaternary, etc. subsystems plus contributions from the properties of the components when all are present at once. The coefficients through E terms for a three component system with the newest notation are shown in Table 1. The first three columns correspond to the Redlich-Kister coefficients for the three binary subsystems. The remainder of the terms must be determined from thermodynamic property measurement in the three component system.

Table 1.--Three-Component Extended Redlich-Kister Coefficients.

A_{12}	A_{13}	A_{23}				
B_{12}	B_{13}	B_{23}	B_{123}^a			
C_{12}	C_{13}	C_{23}	C_{123}^a	C_{123}^b		
D_{12}	D_{13}	D_{23}	D_{123}^a	D_{123}^b	D_{123}^c	
E_{12}	E_{13}	E_{23}	E_{123}^a	E_{123}^b	E_{123}^c	E_{123}^d

For the excess quantity, the mole fraction terms which are multiplied by these coefficients are coded for by the subscripts and superscripts.

As for the binary power series, the coefficients times mole fraction products in the first three columns are $A_{12}x_1x_2$, $E_{13}x_1x_3(x_1-x_3)^4$, $C_{23}x_2x_3(x_2-x_3)^2$, etc.

The number of superscripts is always two less than the number of subscripts. The number of subscripts starts at two for each capital letter and can increase to a maximum of one more than the position of the letter in the alphabet or to the number of components considered, whichever is smaller. For example, the maximum number of subscripts for E is six if six or more components are being considered but is limited to three for a three component system.

The A term is second power in mole fraction, the B term is third power and so on. The small case letters also code for powers; the following scheme is helpful:

	A	B	C	D	E	F	G	H . . .
a	b	c	d	e	f	g	h	i j . . .
0	1	2	3	4	5	6	7	8 9 . . .

The contribution to the excess thermodynamic property of E_{123}^b is sixth power in mole fraction, and the first three mole fractions are $x_1x_2x_3$ the subscripts 1 through 3. The next mole fraction term is $(V-x_1)^m$ where m is the number of the capital letter, which is 6 for E, minus the number of subscripts and minus the total of the numbers for the superscripts. In this case, m is $6-3-1 = 2$. In $V-x_1$, i is the first subscript and V is a sum over all subscripts, $V = \sum_j x_j$. For E_{123}^b , i is 1; so far this gives $E_{123}^b x_3x_2x_1(V-x_1)^2$. The superscripts are correlated with the subscripts starting from the right. Therefore, for a coefficient such as E_{1234}^{ca} , a

correlates with 4 and c correlates with 3. For each superscript, there is a Z^n term where n is corresponding power of the superscript. Z is defined as $(x_j - x_k)$ where j is the second subscript from the left and K is the subscript correlated with this Z term's superscript. For E_{123}^b , the only Z term corresponds to the superscript b which is correlated with the subscript 3. This gives j equal 2, k equal 3, and $n=b=1$. The complete contribution is $E_{123}^b x_1 x_2 x_3 T^{3-1} Z^1 = E_{123}^b x_1 x_2 x_3 (V-x_1)^2 (x_2-x_3)$.

This can be extended to terms that can appear in systems with more than three components such as G_{12345}^{aca} where i equals 1, m equals $8-5-2 = 1$, and j equals 2. For the first, a k is 3 and n is 0, giving $(x_2-x_3)^0 = 1$. For c, superscript k is 4 and n is 2 giving $(x_2-x_4)^2$. The second a superscript gives k equal 5 but the power is zero again and x_2-x_5 does not appear in the final expression. The total contribution of G_{12345}^{aca} to the excess quantity is

$$G_{12345}^{aca} x_1 x_2 x_3 x_4 x_5 (V-x_1) (x_2-x_4)^2.$$

Some more examples are shown below:

$$D_{3254}^{ba} x_3 x_2 x_5 x_4 (x_2-x_5)$$

$$F_{23564}^{aac} x_2 x_3 x_5 x_6 x_4 (x_3-x_4)^2$$

$$C_{614}^b x_6 x_1 x_4 (x_1-x_4)$$

$$E_{1234}^{bb} x_1 x_2 x_3 x_4 (x_2-x_3) (x_2-x_4)$$

$$G_{345}^c x_3 x_4 x_5 (V-x_3)^3 (x_4-x_5)^2.$$

The use of the extended Redlich-Kister equations in phase equilibria work is very involved and will not be fully explained here. However, the sample problems included in the program manual illustrate the use of Redlich-Kister equations and the entry of extended Redlich-Kister coefficients into the SOGEQ program.

C. Minimization of the Free Energy

The program as it stands uses a thermodynamic data file for the properties of pure materials and for the coefficients of a set of balanced chemical equations for the reactions to be considered in approaching equilibrium. Thus, the problem is set up to be solved by varying the extent of each of these reactions until chemical equilibrium is reached. Thus, we are seeking to minimize the free energy, using the extent of reaction in a designated set of balanced equations as the independent variables. This approach is fairly common in chemical equilibrium programs, but it is not the only one possible. One feature of this program is separating the various aspects of the equilibrium calculation so that different approaches can be tried by replacing one or two subroutines. The minimization method used in the version covered by this manual is that of Murtagh and Sargent¹ with some small modifications to handle situations which arise giving calculated negative numbers of moles for some species.

Since various methods of approaching equilibrium can be used, it is important to include in the manual a reasonably complex sample problem so that comparisons can be made. We have chosen a completely gas phase problem for this comparison because good data for complex condensed phases are not yet available and because some of the programs which we want to compare with are not set up to handle mixtures of condensed materials. The most successful gas phase equilibrium programs including the NASA Lewis chemical equilibrium code² and the program SOLGAS³ use variations of White's method⁴ of free energy minimization.

As an example, we have selected a portion of one of the NASA program sample problems, a combustion of C_2H_4 in a limited supply of air at 2000 K and 0.10 atm for the comparison. This particular problem involves appreciable concentration of 11 species, CO_2 , H_2O , N_2 , Ar, O, CO, O_2 , H_2 , H, OH, and NO, composed of five kinds of atoms. Thus, there are $11-5 = 6$ independent balanced chemical reactions which can be selected, and we have chosen the following particular set:

and

White's method⁴ uses the chemical potential of the atoms as the independent variables, varying these until the stoichiometric conditions are met. This approach works exceptionally well for gas phase problems so the comparison with our program which is written primarily to handle non-ideal condensed phases is somewhat unfair. We seriously considered incorporating White's method into our program when we recognized the superior convergence it gives in gas phase problems. However, White's method requires calculating the amounts of the individual species present for equilibrium from the designated values of $\bar{G}$. This calculation is trivial for ideal gases, pure solids and liquids, and even for ideal solutions. But it is difficult, requiring some sort of iteration procedure, for non-ideal solutions. It is likely that including highly interacting species as in high temperature oxide systems will create convergence problems in White's method of free energy minimization. We believe that an intermediate approach incorporating some features of this program and some from White's method can be written and that it will give much improved convergence on gas phase problems and still handle mixed oxide liquid phases. However, the current situation is that, for this sample calculation, the NASA program² converges in 11 iterations. The SOGEQ program described here requires over 40 iterations for a similar degree of convergence and improves further for 57 iterations. While this convergence is distinctly inferior to that of the NASA program,² it is nevertheless approximately equivalent to a variety of other common equilibrium programs in widespread use. It is distinctly superior to the simplex method⁵ of free energy minimization incorporated in the NPL program,⁶ which is the best other current program containing a general procedure for activity coefficients in three-component liquid phases. Thus, although we are continuing to search for better procedures for convergence to equilibrium, it is worthwhile to describe this part of the current program in some detail. This is also necessary in order to provide values with which to check the operation of the program on different computer systems. These details on the current program are included in the full computer manual.

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ACTIVITY COEFFICIENTS IN SEEDED COAL SLAG AND THEIR EFFECTS ON VAPORIZATION AND CRYSTALLIZATION EQUILIBRIA

H. J. Byker,¹ R. E. R. Craig, I. Eliezer,² N. Eliezer,²
R. A. Howald, P. Viswanadham,³ and R. Woodruff

Chemistry Department
Montana State University
Bozeman, Montana

Potassium vapor pressures over four component synthetic seeded slag samples have been measured by a diffusion technique⁴ in Woodruff furnaces.⁵ These data have been used along with thermodynamic and equilibrium values from the literature to construct a mathematical model for activity coefficients in the four component system $KO_{0.5}-CaO-AlO_{1.5}-SiO_2$. The mathematical model used the extended Redlich-Kister^{6,7} notation of Howald and Eliezer.^{8,9} A new computer program has been written, incorporating this model. This permits calculations of vaporization and crystallization equilibria within the model for the behavior of actual seeded slags. Calculated potassium vapor pressures are compared to measurements on synthetic four component samples and to measurements on actual seeded slags of known composition. The drastic effect of calcium oxide content on $KO_{0.5}$ solubility in slag is documented.

Calculations on the equilibrium vaporization of slag in a slag rejecting combustor are shown for several typical compositions and compared with similar calculations from Aerodyne¹⁰ and Argonne National Laboratory.¹¹ The adequacy of approximations based upon ideality of mixing in silicates is evaluated. It is shown that calcium vaporization is not well described by ideal models including CaO as a component.

Calculations are presented on the crystallization of anorthite from seeded slag layers under channel conditions, and the effect of this crystallization on observed electrical conductivities¹² is discussed.

The four component model and computer program have been applied to calculations on the amount of potassium which would be lost to slags of various compositions as a function of the temperature of the gas at the point in the system where slag is removed.

INTRODUCTION

The efficient generation of electricity or other useful work from coal is one of the major technological challenges of the present age. In general, high efficiency requires high temperatures, and high temperatures lead to increased problems with corrosion, with finding materials which can hold up satisfactorily for an extended period of time. Magnetohydrodynamics is a very promising technology because the only moving part at high temperatures is a stable gas, but one still faces corrosion problems with the electrodes and insulators on the walls. Magnetohydrodynamics is particularly promising since it has been shown that a thin replenishable layer of coal slag over the electrodes and insulators can serve as a conductor without major shorting between electrodes. To MHD, coal slag is not just

an unavoidable complication found in using coal, it serves as an integral part of the system. Good data on the properties of coal slags and seeded coal slags as a function of composition are important if not essential in the design of all the MHD components in contact with seed or slag.

Two of the critical variables in the channel itself are the electrical conductivities of the slag and of the gas. Both of these are strongly influenced by composition and temperature, and it is important to know where the vaporization equilibria of the various slag and seed components are over the wide ranges of composition encountered, since this will affect the compositions found, and hence the properties observed.

We have developed a reasonably rapid and accurate method for measuring potassium vapor pressures over slags and synthetic slags using the steady state atomic absorbance produced in a Woodruff furnace after introducing a sample in a small molybdenum cell with a small hole through which gases can diffuse. The apparatus and technique are described elsewhere.⁴ The emphases in this paper are on the data obtained, and on the interpolation and extrapolation procedures developed to treat the complex mixtures encountered.

Vapor Pressure Measurements

For a particular slag sample it is desirable to have equilibrium potassium pressures as a function of the seed content. Figure 1 shows $\log P$ vs $1/T$ for a slag from Rosebud fly ash with a known composition,¹³ and two additional solid lines for samples with 7 percent and 14 percent $KO_{0.5}$ obtained by adding 10 percent and 20 percent K_2CO_3 .¹³ The published analysis¹³ of the Rosebud ash is repeated in Table 1, together with the calculated mole fractions. Similar data for a series of synthetic samples with varying amounts of CaO present are plotted in Figure 2. These experimental curves are plots of $\log P_K$ vs $1/T$ for particular compositions. For comparisons of different samples, it is convenient to tabulate the equilibrium potassium pressures at a particular temperature like 1700 K. Table 2 shows interpolated or extrapolated pressures at 1700 K for a number of different compositions in the four component system $KO_{0.5}-CaO-AlO_{1.5}-SiO_2$. The pressures are strongly dependent on the mole fractions of $KO_{0.5}$ and CaO as illustrated in Figures 1 and 2, and considerably less dependent upon the third independent variable which can be the mole fraction of either $AlO_{1.5}$ or SiO_2 .

Thermodynamic Analysis

It is possible to develop separate power series for the dependence of the potassium oxide activities on the mole fractions of $KO_{0.5}$ and CaO in the samples. However, for the $KO_{0.5}-SiO_2$ binary, we have used terms through the

seventh power in mole fractions (six Redlich-Kister^{6,7} coefficients) to represent the data, and we do not have enough measured potassium pressures for any single ratio of $\text{CaO-Al}_2\text{O}_3$ and SiO_2 concentrations to evaluate this many coefficients. Also, there is a substantial body of phase equilibria data¹⁴ and measurements of SiO_2 activities¹⁵⁻¹⁷ which should be included in the data analysis.

The general procedure which we have adopted for ternary systems is to first select Redlich-Kister coefficients for the three binary subsystems, and calculate initial values for the extended Redlich-Kister^{8,9,18} coefficients by a modification of the TOOP¹⁹ interpolation procedure. The next step is successive adjustments of the values until they give calculated activities and enthalpies in reasonable agreement with all known values over a substantial concentration range.

The CaO-SiO_2 binary system has been studied in detail^{14,20-23} and shows a sharp break in partial molal quantities at the calcium orthosilicate composition. Thus, one cannot use a single power series of 5 or 6 terms over the entire composition range. It is possible to use separate sets of coefficients for acidic and basic slags. The latest selection of values for acidic slags in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ ternary are listed in Table 3. With these values, we can calculate the compositions of liquid in equilibrium with solids such as calcium orthosilicate and gehlenite at various temperatures. Figure 3 shows calculated solubilities at 1723 K along with contour lines for activity of CaO in the acidic liquids at this temperature.

Computer Program

To calculate and use activity values, it is necessary to be able to calculate the thermodynamic properties of pure liquids and solids and to have a standardized notation and set of equations for the calculation of activity coefficients. It is also desirable to have a program which will vary the compositions to find the equilibrium concentrations. It is possible to combine these three kinds of calculations in a single computer program. With suitable overlay techniques, even a large program suitable for use with nine component liquid phases can be put together and run on medium or large computers. We now have a useful computer program of this form available with a large manual with sixteen sample problems. The sample problems range from calculation of free energy function values for a single material to convergence to equilibrium in three component liquid or complex gaseous problems. We are continuing to improve the convergence properties of the equilibrium part of the program and extending the calculations to phases with more components.

We have chosen to write and dimension the programs to cover systems of nine components and power of mole fractions through the seventh. Higher powers are desirable for some applications, but would lead to unreasonably large dimensions for nine component systems. At present, no full set of parameters is available for systems of more than five components, but this situation is rapidly changing as theory is developing to handle the complex systems encountered in engineering practice, and it would be a mistake to limit the program to seven components. There is an appreciable advantage to using a prime number of components, but 11 is too large a number to fit with our computer, and nine is a good compromise.

Even for nine components, there are 6552 separate terms for a single phase. We have arranged these terms for four phases as a $4 \times 732 \times 9$ three-dimensional matrix RKA (4,732,9). The arrangement of terms has been selected, and the method of entering values has been worked out and programmed.

The calculation of activities of individual solute species is most conveniently done using pseudobinary Redlich-Kister coefficients. The calculation of the pseudobinary coefficients for a multicomponent system is complex simply because of the large number of terms. However, we have general equations for the various terms, and the programming is now complete for three and four component systems.

The calculation of activities from the Redlich-Kister coefficients is simple and has been programmed a number of times. Incorporating this calculation into our large program does not present any new problems. The systematic stepping through nine components in this calculation is operational.

The activities and activity coefficients are functions of all the mole fractions in a phase. They are calculated from extended Redlich-Kister coefficients contained in a separate input file like Table 2.

The input is arranged in separate sections for subsystems with 2, 3 and 4 components, each introduced by a line of integers starting with the number of components. For binary subsystems, this is followed by eight lines listing Redlich-Kister coefficients for $\log \gamma_{1000}$, enthalpy, heat capacity, dC_p/dT , d^2C_p/dT^2 , volume, dV/dT , and dV/dP respectively. The same order is used for three component terms, however since ten or fifteen extended Redlich-Kister coefficients are required for a three component system, two or three lines of six numbers are required for each kind of data. The extended Redlich-Kister coefficients are entered in the standard order

B_{123}^a	C_{123}^a	C_{123}^b	D_{123}^a	D_{123}^b	D_{123}^c
E_{123}^a	E_{123}^b	E_{123}^c	E_{123}^d	F_{123}^a	F_{123}^b
F_{123}^c	F_{123}^d	F_{123}^e			

This notation is described in more detail elsewhere^{8,9,18}. It provides plenty of flexibility for accurate evaluation of this many constants is still a slow, tedious process.

The calculation of the free energy function for pure materials also requires a standardized input file of values for H_{298} , ϕ_{1000} , H_{1000}° , H_{298}° and some equation for the heat capacity as a function of temperature. This part of the program is complete, including a variety of options. The standard version uses SI units, Joules, moles and K, but it can be switched to use calories instead. The calculation of equilibrium constants is not required for the minimization of free energy, but it is included in the options programmed to make comparisons with other calculations easier.

A large number of computer programs for finding equilibrium concentrations in chemical systems are available. Many programs are directed toward particular kinds of problems such as aqueous solutions, gas equilibria, or phase diagram calculations, but in principle the same kinds of programs can be used for all kinds of systems. In practice most of the programs used for aqueous solutions are equilibrium constant procedures of various kinds.²⁴⁻²⁷ Adaptations of White's method^{28,29} of free energy minimization predominate in gas and rocket calculations.^{30,31} The best program available for phase diagram calculations on ternary systems has been that of the National Physical Laboratory,³² which is a free energy minimization program using the simplex method of Nelder and Mead.³³ This method is not recommended for convergence in complex problems³⁴ so that the clear lead for rapid convergence to equilibrium among existing programs belongs to the programs^{30,31} based upon White's methods.²⁸ The principal limitation of this approach is that it requires calculations of moles and mole fractions from the free energy, and this part of the calculation is difficult if the activity coefficients are strongly dependent upon concentrations as in silicates.

All these computer programs use some sort of successive approximation procedure to find the equilibrium concentrations. For calculations at a fixed temperature and pressure, the search locates a minimum in G , whether or not the search procedure is explicitly written in this form or not. The available programs vary greatly in the efficiency of the search procedure. When one includes highly non-ideal condensed phases in the calculations, the problem of convergence is greater, and the time required for each calculation also increases. For both of these reasons, further improvements in the search procedures are desirable.

The Vaporization of Slag

The vaporization processes for pure CaO , Al_2O_3 and SiO_2 liquids are fairly well understood. For example, SiO_2 vaporizes principally as $\text{SiO}(\text{g})$ with a smaller amount of $\text{SiO}_2(\text{g})$ and traces of $\text{Si}(\text{g})$. The equilibrium constant for the reaction

is .002837 at 2700 K. Thus the equilibrium SiO pressure will be given by

$$P_{\text{SiO}} = .002837 a_{\text{SiO}_2}/P_{\text{O}_2}^{1/2}$$

For fuel rich MHD coal combustion products at 2700 K and 3.50 atm, the equilibrium pressure of O_2 is about 0.00846 atm. The pressure of $\text{SiO}(\text{g})$ over pure liquid SiO_2 would be $.002837/(.00846)^{1/2} = .03085$ atm, comparable to the pressure of silicon species which one would have if all the silicon in a coal sample were vaporized. The amount of silicon actually vaporized in a slag rejecting combustor will depend upon the kinetics and on the details of the combustor design. However, we may assume as a first approximation that with 90 percent ash rejection the pressure of SiO at the combustor outlet will be about 0.003 atm. If the slag droplets carried over are to be in equilibrium with this gas, they will have an activity of about 0.10 in SiO_2 .

A slag with the mole fractions 0.226, 0.323, and 0.1451 as given in the last column of Table 1 (both MgO and $\text{FeO}_{1.5}$ omitted) will have activities at 2700 K of .000849, .337, and .387 for CaO , Al_2O_3 , and SiO_2 respectively. Note that the calculation at 2700 K gives a CaO activity substantially less than the mole fraction. This effect is even more pronounced at lower temperatures as shown by the CaO activity lines in Figure 3. The values at 1773 K are readily checked against the known phase equilibria at this temperature. The extrapolation to 2700 K is based upon the known heats of reaction of CaO with SiO_2 and Al_2O_3 and should not be seriously in error.

If SiO_2 vaporizes as $\text{SiO}(\text{g})$ from this three component slag until the activity of $\text{SiO}_2(\text{l})$ is 0.100, one will obtain the mole fractions .305, .435, 0.26 and activities .00307, .432, and .100 for CaO , Al_2O_3 , and SiO_2 respectively. Vaporizing part of the SiO_2 increases the activity of CaO , but the activity coefficient is still only 0.010, so any calculation using the mole fraction for the activity of CaO will be substantially in error.

The vaporization products of CaO at 2700 K in the presence of 0.270 atm H_2O and 0.00846 atm O_2 include $\text{Ca}(\text{g})$, $\text{CaOH}(\text{g})$, $\text{CaO}(\text{g})$, and $\text{Ca}(\text{OH})_2(\text{g})$, giving a total pressure of calcium containing species of 3.33×10^{-4} atm. With $a_{\text{CaO}} = .00307$ this corresponds to a pressure of 1.02×10^{-6} atm, corresponding to vaporization of considerably less than one percent of the calcium in the 10 percent of the ash not removed in the combustor. Earlier calculations^{10,11,35} show considerably more calcium vaporization in the range of 2 to 20 percent of the carry-over slag, presumably because they did not have accurate data available on the calcium oxide activity. On the other hand, the present calculations show that for Al_2O_3 the slags can be treated as ideal solutions. The major uncertainty in aluminum vaporization in MHD combustors concerns the thermodynamic properties of $\text{Al}_2\text{O}_3(\text{g})$.

The vaporization of slag components in an MHD combustor is significant primarily in determining the effects of condensation on the electrical properties particularly at the downstream end of the channel.¹⁰ Magnesium and iron are considerably more volatile than calcium and aluminum, and it is important to extend the thermodynamic model for liquid silicates at 2700 K to include these species.

Calculations in Process

Figure 3 shows a set of liquid compositions in equilibrium with solid anorthite at 1773 K. The crystallization of anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$, from MHD slags is a phenomenon of considerable importance, since it leaves a liquid phase higher in potassium and iron, elements which contribute substantially to the electrical conductivity of the slag. In some cases, Fe^{++} and Fe^{+++} can be concentrated in the remaining liquid enough to provide significant electronic conductivity.

We have already provided a treatment of the K_2O - Al_2O_3 - SiO_2 ternary system³⁶ using terms through the fourth powers in mole fractions. With the current program, it will be possible to add fifth through seventh

powers to provide a considerably more accurate representation of this important ternary system. It is important to get coefficients for the four component system KO_2 - CaO - $AlO_{1.5}$ - SiO_2 as accurate as possible so that comparisons with potassium pressures over actual slags can provide a good test of the adequacy of a four component slag model in representing actual seeded slags. At the same time, work is proceeding toward extending the computer model to more components. For calculations for the heat recovery-seed recovery sections of MHD systems the most important additional component is SO_3 so that equilibria with two liquid phases, sulfate and silicate rich, can be treated.

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Table 1. Composition of Rosebud Ash Samples

Component	Wt%	Mole Fraction	Simplified Models		
SiO ₂	40.34	.3966	.411	.411	.451
AlO _{1.5}	24.60	.2350	.295	.295	.323
CaO	18.90	.1991	.206	.294	.226
MgO	5.80	.0850	.088		
FeO _{1.5}	4.40	.0326			
KO _{.5}	.53	.0066			
NaO _{.5}	.46	.0088			
SO ₃	.28	.0021			

Table 2. Potassium Pressures Interpolated or Extrapolated to 1667 K for Selected Samples

Sample	$P_K \times 10^6$ atm	Composition		(Mole Fraction)	
		KO _{1.5}	CaO	AlO _{1.5}	SiO ₂
43	3.3	.10	.18	.432	.288
52	7	.10	.18	.48	.24
58	1.7	.10	.225	.225	.450
55	46	.10	.36	.36	.18
44	5	.20	.16	.384	.256
53	12	.20	.16	.43	.22
69	20	.20	.32	.240	.240
56	27	.20	.32	.32	.16
66	12	.30	.049	.326	.326
45	60	.30	.14	.333	.206
71	120	.30	.28	.21	.21
74	80	.30	.389	.156	.156

Table 3. Input Parameters for Activity and Enthalpy Calculations in the Ternary System 2-3-4: CaO-Al₂O₃-SiO₂

[illegible]

Figure 1. Measured Potassium Pressures on Rosebud Slag Samples With 0.5, 7, and 14 Percent K_2O by Weight.

Figure 2. Measured Potassium Pressures for Four Samples From Table 2, Sample Numbers 43, 52, 58, and 55.

Figure 3. Calculated Solubilities and CaO Activities in the Three-Component System $\text{CaO}-\text{AlO}_{1.5}-\text{SiO}_2$ at 1773 K.

TASK H1
MHD Instrumentation and Data Acquisition
R. Johnson

I. OBJECTIVE AND SCOPE OF WORK

The work to be performed is in the general area of MHD systems, instrumentation, and control. The two categories of work are defined below.

A. Combustor-Nozzle-Channel-Diffuser Model

A time-dependent nozzle-channel-diffuser (NCD) model has been completed in sufficient detail to study some configurations of supersonic MHD/steam power plants. Several CDIF and ETF case studies have been started and will continue to be analyzed. In order to properly simulate the strong coupling between the combustor and the channel present in subsonic MHD flow, the theory of a time-dependent (dynamic) one-dimensional, two-stage combustor model is to be developed suitable for coupling to the present NCD model to form a dynamic CNCD model when programming is completed. The plug-flow combustor model from the MHD Steam Plant Modeling task will be used to provide the initial state conditions for the model.

B. Consolidation/Inversion Simulator

The design of a table-sized generalized consolidation/inversion simulator is to be undertaken to provide the basis for study and evaluation of several proposed dc to ac power conversion schemes. The system should be modular to permit the maximum flexibility possible in the interchangeability of components; studies of hybrid schemes involving the best features of competing designs then will be possible.

Component selection will emphasize existing devices and technology to minimize subsequent development efforts for commercial-scale systems.

C. Hybrid Modeling

A study is to be performed to evaluate the potential of a hybrid computer system for detailed analysis of complete MHD/steam power plant systems designs and control.

II. SUMMARY AND IMPACT

A. Time Dependent Combustor-Nozzle-Channel-Diffuser Model Program (MHTD)

Several rather severe transients induced by step changes in the Faraday load voltage of an MHD ETF-sized topping cycle have been simulated during the quarter. In particular, a 10 percent change (reduction) in Faraday load voltage was induced on a generator operating subsonically at a load factor of .819 with an electrical power output of 80MWE. An instantaneous power output increase of 30 percent resulted, followed by a very rapid decay in power output to a new steady-state power output value of

77.8MWE in approximately 5 milliseconds. In actual practice, the transient would be somewhat less severe and of longer duration because of the effect of power grid system line inductance. The assumed load in the simulation was a pure resistance.

B. Consolidation/Inversion Simulator

A four-electrode pair inverter system under computer control in either a line or force commutated configuration has been completed. The inverter system utilizes programmable power supplies to simulate the MHD generator under control of a DEC LSI 11/03 microcomputer.

The triple Z80 microcomputer control based McMurray SCR bridge inverter system underwent testing during the quarter of its three-phase notch-filtering, line synchronization, and voltage regulation capabilities. Software tests confirm the code validity for line synchronization and notch filtering. The synchronization tests were conducted with reference to a 60 Hz crystal reference. Notch filtering of the generator voltage output waveform is as shown in Figure A-1. The voltage control software is currently still under test; some necessary minor code modifications have been identified and are being made.

Initial contacts with Stanford University have identified the transformers that will be necessary to invert the Stanford high field channel output (four electrode pairs worth.) These transformers have been priced; an order will be placed immediately if suitable transformers cannot be obtained on loan from the Montana Power Company for the Stanford tests.

C. Hybrid Computer Formulation

The DEC VAX 11/780-ADI AD10 computer system on which a real-time simulation of an MHD/steam power plant can be carried out has now been ordered. It appears that the system will not have any particular difficulty processing the Cycle Analysis and Control group's System Model IV MHD/steam power plant simulation in real time.

By connecting the MHD Instrumentation and Data Acquisition group's consolidation/inverter system to the high speed analog/digital converter processor of the AD10, it will be possible to study the effects of power grid-inverter-MHD generator system interaction and control.

III. DETAILED DESCRIPTION

A. Combustor-Nozzle-Channel-Diffuser Model Program MHTD

Some preliminary results of a transient run on an ETF-sized MHD topping cycle have been obtained by running the MHTD program. These results which are for rather coarse axial discretization of the power channel are described in the enclosed paper "Dynamic Simulation of MHD Topping Cycles," which will be delivered at the IEEE-AIAA Summer Simulation Conference in Seattle, August 25-28, 1980. This approximation was made to minimize program run-time during program checkout.

Since this paper was written, the number of axial state variables in the combustor-nozzle-channel-diffuser power train simulation has been doubled with a consequent increase in solution precision (and integration time). A 5 ms. problem time transient solution requires approximately one-half hour of SEL 32/55 computer time. Although finer detail in the model can be obtained by further descertainment, no further work is presently in progress on the program since the program is under reformulation for the VAX-AD10 computer. Preliminary calculations indicate that MHDTD can be converted (to the same precision) to run on the VAX-AD10 computer in approximately 18 seconds/run.

B. MHD Inverter System

The present consolidation/inverter system is presently under the control of a LSI 11/03 microcomputer and three slave Z80 microcomputers.

The necessity of taking experimental data in real time on the system for post experiment analysis requires that the system be updated with a rapid access disk for storage and increased computer bus backplane capacity to permit additional analog/digital conversion boards. Orders for this equipment were placed at the end of last year and the equipment (Disk, A/D board, card reader, backplane, and software) is scheduled for delivery this next quarter. The layout of the new system is now complete and construction of the computer chassis is proceeding. A diagram of the planned system is shown in Figure A-2.

The programmable load (Figure A-2) has been designed to operate at 1KVA and is under construction. Load variations of 1.0, 0.9, 0.8, and 0.7 power factor leading and lagging and resistive loads of 25 percent, 50 percent, and 75 percent of full load are provided.

Components of all three poles of the McMurray bridges have been experimentally optimized for the higher speed notch filtering (Figure A-1). This has necessitated some SCR and capacitor value changes.

FIGURE A-1

MHD CONSOLIDATION/INVERTER SIMULATOR SYSTEM

FIGURE A-2

DYNAMIC SIMULATION OF MHD TOPPING CYCLES

R. Johnson and D. Bartle

Department of Electrical Engineering

Montana State University

Bozeman, Montana 59717

ABSTRACT

Combined Cycle MHD (magnetohydrodynamics)/steam power plants show promise of achieving high efficiency in coal energy conversion to electricity. The plants are composed of an MHD topping cycle operating in the combustion gas temperature range of 3000 - 2000 K and a bottoming cycle consisting of a modified steam power plant in the steam temperature range of 810 - 300 K.

This paper describes the model and some results of simulating the dynamic performance of a combustor-nozzle-channel-diffuser (CNCD) MHD topping cycle on a general purpose digital computer.

INTRODUCTION

Magnetohydrodynamic power generation occurs when a combustion gas, artificially seeded to form a conducting plasma, is expanded through a high magnetic field [1]. Although any fuel oxidant mixture may be used, current interest centers around the use of finely ground coal combustion using preheated air or oxygen as the oxidizer [2].

The interest on coal stems not only from the fact that coal is relatively abundant in the United States, but that it can be burned directly to form electricity without the necessity of initial conversion to other refined forms of synthetic fuel.

The seed material, which is an easily ionizable compound (at a particular temperature) is usually assumed to be Potassium Carbonate, K_2CO_3 producing K^+ ions which form the conducting material in the gas. Coal combustion takes place in a pressurized combustor; in order to obtain the necessary temperature range of 2500 - 3000 K it is necessary to preheat the combustion air to 1900 K using regenerative air preheaters [3]. The very high temperature range of the process is the reason for the predicted high cycle efficiency; it is also a necessary temperature range in order that the electrical conductivity of the resulting combustion plasma be high enough to produce electricity at an attainable magnetic field level.

MHD Modeling - Steady State and Dynamics

Early modeling of MHD systems concentrated on steady-state system behavior [4]; this was because of the inherent difficulty of the MHD equations to be integrated and the lack of experimental knowledge of MHD processes in general [5]. The understanding of the physics of MHD combustion plasmas (equilibrium) is now quite well understood and work in these past few years has shifted into the direction of engineering design and analysis of commercial sized power plants [6]. For a more detailed derivation of the equations which follow, see Rosa [7], or Roache [8].

Steady-State Equations

This paper is concerned with the dynamic simulation of an MHD topping cycle combustor-nozzle-channel-diffuser system (CNCD); it is, however, necessary to establish a set of steady-state initial boundary conditions for the gaseous flow duct before such a dynamic simulation can occur. To establish these initial conditions, an MHD channel is usually designed using a steady-state design program; the designed system is then analyzed with a steady-state analysis program to ascertain a steady-state set of operating conditions. With a few exceptions, most MHD codes are one-dimensional approximations in which the independent variables are axial position x and time t . The dependent variables are gaseous momentum density, mass density, and stagnation energy. The one-dimensional equations are:

*Reasonable magnetic fields are in the 4-6 Tesla range which is attainable at low power dissipation levels using superconducting magnets.

$$\dot{m} = \rho v A \quad (\text{Continuity}) \quad (1)$$

$$\rho v \frac{dh}{dx} + \frac{dP}{dx} = (\underline{J} \times \underline{B})_x - F_x \quad (\text{Momentum}) \quad (2)$$

$$\rho v \frac{dh}{dx} + \rho v^2 \frac{dv}{dx} = (\underline{J} \cdot \underline{E}) - G \quad (\text{Energy}) \quad (3)$$

where

- ρ = gas mass density
- P = gaseous pressure
- v = axial velocity in the x direction
- h = gaseous specific enthalpy
- F = friction factor
- G = heat transfer term
- $(\underline{J} \times \underline{B})_x$ = axial Lorentz force term
- E = electric field strength
- A = duct cross-sectional area
- $\underline{J}$ = Faraday current density
- $\dot{m}$ = gaseous mass flow rate

All quantities are in MKS units. To these equations must be added the equation of state

$$\rho = \frac{12026}{T} \times 10^{-3} \text{ PM}$$

Here M is the equivalent molecular weight of the conduction gas mixture and T is the absolute temperature. The electrical properties of the combustion gas are defined for the particular loading; in this paper the connection is Faraday with the defining equations

- $J_x = 0$ Axial current density
- $J_y = \sigma v B(1-K)$ Transverse Faraday current density
- $E_x = \sigma v B(1-K)$ Axial electric field
- $E_y = K v B$ Transverse electric field
- $\underline{J} \cdot \underline{E} = -K(1-K) \sigma v^2 B^2$ Electrical power density
- $(\underline{J} \times \underline{B})_x = -\sigma v B^2(1-K)$ Lorentz force
- $K =$ Load factor

Time Dependent or Dynamic Equations

After obtaining a steady-state solution to the above system to provide initial conditions, the time-dependent or dynamic fluid equations must be solved. They are, after making again one-dimensional approximations,

$$\frac{\partial}{\partial t} \begin{bmatrix} \rho \\ \omega \\ E_s \end{bmatrix} = - \frac{\partial}{\partial x} \begin{bmatrix} \omega \\ \omega 2/\rho + P \\ \omega(E_s + P)/\rho \end{bmatrix} + \begin{bmatrix} - \frac{\omega}{A} \frac{dA}{dx} \\ (\underline{J} \times \underline{B})_x - F - \frac{\omega^2}{\rho A} \frac{dA}{dx} \\ (\underline{J} \cdot \underline{E}) - Q - \frac{\omega}{A} (E_s + P) \frac{dA}{dx} \end{bmatrix} \quad (4)$$

where

$$\begin{aligned} w &= \rho v && \text{momentum density} \\ E_s &= \rho \left(h + \frac{v^2}{2} \right) && \text{stagnation energy density} \\ Q &= && \text{heat transfer} \end{aligned}$$

These equations were integrated with respect to time by use of the Lax-Wendroff two-step integration scheme [9]. The equations (4) are in so-called conservation form [10]. When coupled with a numerical integration algorithm which is also conservative in form (such as Lax-Wendroff) the fluid flow equations may be integrated correctly through shock regions since the Rankine-Hugoniot relations are satisfied.

Dynamic Combustor Model

Since commercial scale MHD power plants will probably be operated subsonically, the coupling between the MHD channel and the pressurized coal combustor can be quite strong; this implies that a dynamic model of the coal combustor is necessary. The desire of the present work is to concentrate on the effects of load variations on channel performance; to study a large number of load variation transients so as to ascertain whether there are regions of unstable topping cycle operation or regions of operation deleterious to long component life. A detailed pyrokinetic model of the combustor, if known, could be used but almost certainly would be very slow in execution. Instead, the combustor is modeled as a quasi-static pressurized "hot bottle" with constant mass flow input of fuel, preheated oxidant and seed during the transient duration but variable output massflow as the combustor responds to changing downstream pressure gradients caused by load variations. The steady-state performance of the combustor at various operational pressures, firing rates, etc., has been obtained by many runs of a plug flow combustor model [11]. New steady-state conditions are imposed on the combustor every 2 to 3 ms. of transient; this period is very short compared to the overage transit for particles in the combustor (50-70 ms).

Dynamic Response to a 10% Voltage Variation

To illustrate the behavior of the transient model, a 10% step change in Faraday connected electrode voltage level was imposed upon a 250 MW (thermal) input MHD topping cycle.

A plot of the cross-sectional area variation $A(x)$ with duct length x is shown in Figure 1. Since very rapid changes in duct velocity occur within the flow acceleration nozzle portion of the duct, a small spacial step size is used in the nozzle and careful attention to contour smoothness (note the sensitivity to rapid changes in spacial variations in x exhibited in the dynamic Equation (4) is assured by use of cubic spline functions [12] representation in this region.

Figure 2 shows the time response of several system variables at various duct positions as the result of the externally induced 10% step electrode voltage transient at time $t = .5$ ms. (variable 2). Note the total power output (the sum of the power output from all Faraday connected electrode pair loads) at first rises sharply (variable 1) but then rapidly decreases to a steady-state value within a period of approximately 4 ms. Slow settling time in momentum is confined to the MHD electrode interaction region (variable 4).

Figure 3 shows the duct spacial variation of electrode voltage, electrode current, combustion gas momentum, pressure and temperature at $t = 0$ ms. (before the step change in electrode voltage is imposed).

The electrode current and voltage waveforms (4), (5) are both zero except in the channel region (only region with magnetic field present.) The current is the upper, more jagged waveform.

The jaggedness of the current distribution relative to the voltage results from two factors: first, the voltage distribution is set in the steady-state design program while the current distribution is an output result and, second, the integration scheme for the time dependent model is different (Lax-Wendroff vs. Runge Kutta) than for the steady-state model so that the current distribution is not really initially at "steady-state" for the dynamic model. In practice this problem is overcome by running the initial conditions to steady-state in the dynamic

model before a new disturbance is imposed on the system; it was decided to leave the current distribution "jagged" in this paper for purposes of illustrating the problem. The power output per electrode pair is greater in the entrance region of the channel (81,600 watts/electrode) than the exit region (64,000 watts/electrode); this is because of the higher temperature and resultant conductivity in the upstream end of the channel. The higher voltage at the exit is because of the expansion in channel width as the channel area is increased (Figure 2) and because the design load factor ($K = E/(vB)$) has been maintained fixed.

In Figure 4 the same variables are shown at time $t = 1$ ms. after initiation of the voltage step disturbance. Note the current scale is larger and that the current has increased by approximately 27 percent and the distribution is somewhat smoother. The voltage, of course, is depressed.

In Figure 5 (at 2 ms) the peak electrode current has already dropped by 9 percent but the exit end of the generator has only dropped by 3 percent; the current distribution in the first half of the generator is depressed relative to the last half distribution. The current depression appears to be flowing like a "wave" through the generator.

In Figure 6, (at $t = 5$ ms.) the current distribution (as well as the other variables) have essentially reached steady-state values. The only other variable which undergoes noticeable variations in the plots is the momentum; the momentum decreases during the transient while the pressure distribution remains nearly constant. This implies that the gas density (temperature is also essentially constant) remains nearly constant so that the gas velocity is depressed relative to the initial channel distribution.

SUMMARY

A dynamic, one-dimensional, model of an MHD Faraday connected, electric power generator has been programmed and initial results described. The model is formulated in conservation form and is therefore applicable to general transonic transients. Although the model describes only the gross behavior of the CNCD system it is detailed enough to permit the study of general generator transients for purposes of system control design.

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Figure 1

Figure 2.

Figure 3. Duct Variables vs. Distance at $t = 0$ ms.

Figure 4. Duct Variables vs. Distance at $t = 1$ ms.

Figure 5. Duct Variables vs. Distance at $t = 2$ ms.

Figure 6. Duct Variables vs. Distance at $t = 5$ ms.

TASK H3

Cycle Analysis and Control

D. A. Rudberg, D. A. Pierre, and Dan Goldsworthy

I. OBJECTIVE AND SCOPE OF WORK

We are developing system component models which are suitable for control system simulation studies. The purpose of these studies is to determine control structure and controller parameter values which result in safe, stable, fast, and smooth transitions in operating points. The results of the studies are to be generally applicable to the ETF and commercial MHD-steam power plants. By performing these studies now, it may be possible to influence the design of MHD-steam plants to make them more reliable, efficient, and easier to control.

The time-dependent combustor model is important from the view points of combustion stability and channel response. Combustion stability is an extremely important topic because it affects plant integrity and safety and smoothly controllable response. A time-dependent model incorporating compressible fluid flow, chemical equilibrium and enthalpy, char particle heating and burnout kinetics, devolatilization (its rate and general endothermic nature), and heat loss from radiation and convection will be an effective tool in studying combustion stability and associated topics of acoustic wave propagation and standing waves within the combustor.

The time-dependent combustor model will also constitute an essential part of the overall time-dependent model that will permit analysis of channel electrical and fluid dynamic response to perturbations originating in the combustor. It will be one of the parent model sets used in generating input-output models, which are described below. The model will be a combination of fluid dynamic equations and solution techniques from time-dependent channel work done by other researchers at MSU and of chemical equilibrium, char burnout kinetics, heat loss, etc., from a steady-state, plug-flow, two-stage combustor model developed by our previous efforts.

From the detailed time-dependent models, input-output models will be produced for specific ETF and base-load MHD components. Input-output models contain no internal detail, consisting only of a set of curve fits of desired outputs to input values. Parameters of the system are implicit in the curve fit coefficients. In this manner, models of large systems can be run in orders of magnitude less time and greatly reduced computer requirements than if detailed parent models were used. A change of system parameters requires only that another set of input-output models be made from the detailed parent models, thus embodying those new parameters.

Several input-output modeling runs already have been made using existing parent models of the plug-flow, steady-state combustor for combustor input-output models and detailed chemical-equilibrium, electrical conductivity, and enthalpy programs for channel gas modeling. An automatic parameter sweeping routine is used, and the results are stored in a file for reduction to input-output models by an existent multi-variable curve fitting routine.

The computer-controlled combined-cycle plant model is an important step in the progression from conceptual system studies to a functional piece of hardware. There is a tendency to confuse control system information flow and selection of information processing algorithms with the completion of the control problem. But the selection of system topology, information flow, and control algorithms are only initial steps (albeit essential ones) in the process of ultimately exerting effective control. The mechanization of specified information flow, of algorithmic computation, and of assertion of control variables at proper points in the controlled plant are the finale in real time control.

It has been the investigators' experience in providing real time computer control for an aluminum processing plant and other smaller projects that actual coding of algorithms and supervisory programs immensely sharpens the understanding of preceding conceptual studies. It crystallizes the notion that a physical plant (in this case the MHD/steam plant) having a set of measurable variables, a set of controllable variables, and a system of dynamics by which it operates is being dealt with.

The investigators will use their set of system models to act as the plant. The computer controller will be a set of algorithms and a simple supervisory routine to properly sequence data inputs, algorithm computation, and control signal assertion at proper points. The value of beginning this essential step as early as possible lies in its intrinsic feedback to the conceptual process as well as its being a necessary bridge between conceptual studies and hardware.

II. SUMMARY AND IMPACT

A first-principle dynamic control system model has been developed for combined-cycle MHD-steam power plants. The model, called System Model IV, is used both to test alternative dynamic control strategies and to obtain controller coefficients.

System Model IV is composed of two parts: (1) a nondynamic model of the MHD topping plant, consisting of combustor, nozzle, channel, and diffuser (the CNCD model) and (2) a fully dynamic model of the steam bottoming plant, containing the feedwater system, radiant steam generator, drum, superheaters and reheaters, air heaters, air compressors, coal feed system, steam lines, turbine, and generator-exciter combination. The CNCD model is nondynamic because its time constants are so much shorter than those of the remainder of the system that for all purposes it exhibits instantaneous response.

Generation of System Model IV is supported by a number of other routines, principally a pulverized-coal-fired combustor model, a chemical equilibrium routine for gas property predictions, a channel-diffuser design program, a steady-state energy balance routine for steam plants, and dynamic models of steam plant components.

The dynamic models composing the steam plant are based on physical laws and are, therefore, so-called first-principle models. Physical parameters and variables that appear in the actual plant (e.g., temperatures of steam, metal, and combustion gases, pressures of steam and combustion air, mass flow rates, control valve areas, etc.) also appear in the dynamic model. This distinguishes the model from earlier MHD-steam combined-plant models that are based primarily on power-flow transfer function representations.^{1,2} Also, the first-principle models used are lumped parameter models in contrast to mathematically more intractable distributed models. This lumped nature requires that care be taken in developing the model structure to avoid non-physical behavior, an example of which will be discussed briefly in the section on waterwalls. Because first-principle models have been produced for conventional steam plants,³⁻⁶ the details that are presented are those that differ significantly from conventional plants.

A paper based on System Model IV was presented to the Fourth Symposium on Power Plant Dynamics, Control and Testing.¹⁰

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. System Model IV

1. Plant Structure

The plant under discussion is of the general size and configuration initially proposed for the national Engineering Test Facility (ETF).⁷⁻⁹ The plant, shown in Figure 1 in simplified conceptual elevation view, is based primarily on the AVCO ETF conceptual design.⁷ Total thermal input is about 355 MW_t; electrical output is 59 MW_e from the MHD portion and 68 MW_e from the turbine generator. A nonreheat turbine operating at 8.96 MPa and 783 K (1300 psi, 950°F) and a turbine driving a compressor for the combustion air system are specified. Also drawing steam is a small turbine for the boiler feedpump which, although somewhat unrealistic for this size plant, was included for control studies as a likely entity in a larger plant. Steam generation from the forced-circulation drum boiler is 89.8 Kg/sec (712,700 lb/hr). Figures 2, 3, and 4 are schematic diagrams of the gas, water/steam, and air paths, including major and minor control points for the plant model. The complete set of nominal operating conditions is given in Table 1.

An important aspect of this model is the inclusion of an indirectly fired high-temperature air heater delivering air at 1922 K (3000°F) to the two-stage combustor. Recently, a trend has developed toward an

ETF plant design using oxygen-enriched low-temperature air, thus eliminating the high-temperature air heater. This change will be incorporated in future plant models. The plant concept is shown in Figure 1. It employs steam generation in the diffuser walls and in the seed condenser, along with a conventional gas attemperator (combustion gas recycling) near the top of the seed condenser.

2. Combined Plant Model Structure

The combined plant model, called System Model IV, is coded in six sections: (1) air path, (2) gas path, (3) feedwater system, (4) boiler and drum, (5) superheaters and turbine-generator, and (6) control. Figures 2 and 3 show the air path and gas path; Figure 4 shows the combined flow of water and steam. Pertinent control points exist in each section as shown. The overall system model consists of a subroutine for each section plus a control routine and several supervisory and housekeeping routines.

The following is a list of significant model features:

- (1) Code is block structured, having been created in a top-down manner. This greatly facilitates maintenance and modification.
- (2) All equations are first-order differential or algebraic. No iterative solutions are required.
- (3) No argument lists are passed. All communication is through labeled common.
- (4) SI units are used throughout.
- (5) Coding is in standard FORTRAN IV.

Generation of the overall dynamic model is supported by a number of programs, principally a pulverized-coal-fired combustor model, a two-phase chemical equilibrium routine for gas-liquid thermochemical predictions, a combined design and simulation program for the nozzle-channel-diffuser group, and a steady-state energy balance routine for combined-cycle plants. Results from these models have been integrated with first-principle dynamic models of steam plant components to form what is called System Model IV. System Model IV currently consists of (1) a set of eleven quadratic curve fit equations, typically in four variables, to represent the combustor-nozzle-channel-diffuser, (2) fifty-three differential equations with some one hundred supporting and constraint equations for the steam plant, and (3) twenty-seven differential equations with forty-two supporting equations for plant control. The number of equations makes it impractical to completely present System Model IV in this report. However, most of the equations can be inferred from descriptions of operation and from similar equations published in the literature. In those instances where variations from conventional first-principle models have been made, the distinctive features are described.

Also, it is recognized that a major problem of combined MHD-steam plant modeling is lack of an existent plant for model verification. This has been considered from the outset. By adhering to first-principle descriptions to the greatest reasonable extent and by eschewing plant-specific relations, extrapolation of the model to simulate conventional plants should be facilitated. Only the bottoming portion can be evaluated in this way. Topping plant modeling will be evaluated vis-a-vis the Component Development and Integration Facility (CDIF) test runs of a 50 MW_t channel, scheduled to begin in mid-1980. And finally, because of several prior expositions of first-principle steam plant models by various authors,⁴⁻⁶ only the distinguishing sections of the combined plant model are presented below. They are the gas path and the control section.

3. The Gas Path

The gas path is the path of combustion gases, beginning at the inputs to the pressurized combustor and terminating at the stack. It contains several non-dynamically modeled components, viz., the MHD topping plant, consisting of the combustor, nozzle, channel and diffuser (CNCD) and the coal dryer. The CNCD has been made non-dynamic because its time constants are so much shorter than those of the remainder of the system. From the perspective of the bottoming plant, the CNCD exhibits instantaneous response. Typical times are 60 to 120 msec combustor residence time and 20 msec total channel-diffuser passage time. All other gas-path components are either first-principle models or are represented by time lag expressions to emulate inherently complex behavior (e.g., characteristic mixing times for merging of turbulent gas flows).

4. CNCD Modeling

The CNCD model is a set of algebraic relations having six inputs and six outputs. The six inputs are air flow rate, coal flow rate, seed flow rate, preheated air temperature, initial level of channel current, and current slope down the channel. The six outputs are electrical power output, diffuser outlet gas temperature, heat transfer to cooling water in each unit, combustor pressure required for the specified flows, peak Hall electric field, and peak current density. Such input-output models contain no internal detail, consisting only of a set of curves fitted to results of detailed parent models. The programs from which the CNCD equations are derived include the pulverized-coal-fired combustor, the quasi-one-dimensional nozzle-channel-diffuser model based on continuity, momentum, and energy equations of compressible fluid flow, and the chemical equilibrium routine. Parameters of the CNCD system are implicit in the curve coefficients. In this manner, models of large systems can be run in

orders of magnitude less time than with the detailed parent models and with greatly reduced computer storage requirements. A change of system parameters requires that another set of coefficients be determined from the parent models, thus embodying those new parameters.

The CNCD model is computed in three stages as shown in Figure 5. Stage 1 calculates a set of curve fits of gas thermochemical properties as functions of gas composition, temperature, and pressure. Stage 2 creates curve fits of combustor outputs as functions of flow-rates, preheated air temperature, and combustor pressure. Stage 3 combines the results of the first two stages to produce actual CNCD output curve fits. In the first part of Stage 3, outputs from the nozzle-channel-diffuser model are generated using 28 distinct sets of input conditions. For each input set, the quasi-one-dimensional model is used to solve a two-point boundary-value problem: if the assumed combustor pressure results in a diffuser outlet pressure greater (less) than 1.2 atmospheres, a new lower (higher) combustor pressure is calculated by interpolation or extrapolation, and the quasi-one-dimensional model is rerun. The process repeats until the proper outlet pressure is obtained. In the second part of Stage 3, after the boundary-value problem has been solved 28 times (one for each of 28 sets of input conditions), standard procedures are used to find the coefficients of quadratic functions which map the input data into the output data.

5. Waterwalls

The plant shown in Figure 1 contains three large chambers with waterwalls for steam generation: the radiant boiler, the seed condenser, and the secondary furnace. (Diffuser steam generation is calculated in the boiler-drum model.) Equations describing lags of flow rate change from input to output of each chamber are

$$\frac{dW_{g_{out}}}{dt} = (W_{g_{in}} - W_{g_{out}})/\tau_1 \quad (1)$$

where $W_{g_{in}}$ and $W_{g_{out}}$ are mass flows into and out of each chamber, and τ_1 is a time constant linked to the chamber volume. This equation accounts for the slight compressibility of gas in each chamber.

Heat transfer to the waterwalls is given by the radiation-dominant expression

$$Q_g = K_1 (\bar{T}_g^4 - T_m^4) \quad (2)$$

where Q_g is megawatts transfer, from gas to metal, $\bar{T}_g$ and T_m are average gas temperature and metal temperature. K_1 is a coefficient combining emissivity and chamber geometry, having values of $.353 \times 10^{-11}$ for the radiant boiler, $.257 \times 10^{-11}$ for the seed condenser, and $.544 \times 10^{-11}$ for the secondary furnace. Originally, $T_{g_{in}}$ was used

in equations of this form, but it was found that a step increase of gas temperature into a chamber (as might occur with complete or partial failure of enthalpy extraction in the MHD topping plant) resulted in a decline in outlet gas temperature because excessive heat transfer from gas to metal was calculated. This emphasizes that care must be taken in making lumped approximations of distributed systems.

A first-order lag describes $\bar{T}_g$ variation

$$\frac{d\bar{T}_g}{dt} = \left(\left(\frac{T_{g_{in}} + T_{g_{out}}}{2} \right) - \bar{T}_g \right) W_{g_{in}} / \tau^* \quad (3)$$

where $\tau^*/W_{g_{in}}$ is a modified time constant to account for variation of residence time with flow rate. It has typical values of .66 seconds.

Specific enthalpy change is calculated by

$$\frac{dh_{g_{out}}}{dt} = (h_{g_{in}} - h_{g_{out}} - Q_g/W_{g_{out}}) W_{g_{in}} / \tau^* \quad (4)$$

in which $h_{g_{in}}$ and $h_{g_{out}}$ are specific enthalpies of gas in MJ/Kg.

6. Secondary Air Injection

Combustion gas specific enthalpy after secondary air injection is denoted by $h_{gs_{out}}$ and is described by the following:

$$\frac{dh_{gs_{out}}}{dt} = (((h_{g_{in}} + .1689) W_{g_{in}} + h_{a_{in}} W_{a_{in}}) / W_{g_{in}} - h_{gs_{out}}) / \tau_5 \quad (5)$$

where $h_{g_{in}}$ is specific enthalpy of incoming gas, $h_{a_{in}}$ and $W_{a_{in}}$ are specific enthalpy and mass flow of secondary air. A value of .17 seconds is suitable for τ_5 . Energy release by completing combustion is .1689 MJ/Kg of incoming gas, for an equivalence ratio of 0.95 of incoming gas and an equivalence ratio greater than or equal to 1.00 of outgoing gas. The value of .1689 MJ/Kg is particular to Montana Rosebud coal at .95 stoichiometry, with air as oxidant. It will vary only slightly among coals but is quite sensitive to initial equivalence ratio.

7. Convective-Radiative Transfer

Heat transfer in convective-radiative units such as economizer, air heaters, and superheaters is given by

$$Q_g = K_2 W_g^{0.6} (\bar{T}_g - T_m) + K_3 (\bar{T}_g^4 - T_m^4) \quad (6)$$

which is fairly standard. Q_g is the gas-to-metal heat transfer rate in MW, while K_2 and K_3 depend on geometry and emissivity.

8. Control

a. Plant Control Points

Figures 2, 3, and 4 show sixteen control points within the system. In initial simulation runs, dynamic control is asserted at nine of them as follows: main turbine control valve, air compressor turbine valve, boiler feed-pump turbine valve, condensate feed-pump valve, spray attemperator valve, turbine bleed point valve, combustion gas recycle valve, and two parameters dictating electrical current distribution from the channel. Other control points remain fixed during initial tests, except for seed and coal valves which are slaved to air flow to maintain both seed and fraction and stoichiometry constant. Later simulations will involve dynamics for the coal, seed feed, and secondary air valves. Also, the valves controlling flow through each waterwall section will be allowed to operate to prohibit excessive metal temperatures.

b. Coordinated Control

Under normal operating conditions, it is expected that a plant of this size will produce approximately half its electrical power from the MHD topping cycle and the other half from the steam plant cycle. Under rapid changes in power demand, the fast responding MHD section would be expected to initially accommodate a disproportionately large share of the load change, reducing to a proportionate share as the more slowly responding steam plant reacts to the new load demand. Such a control philosophy coordinates the MHD topping plant with the boiler and turbine-generator and is especially desirable if the plant is to operate under a wide-area economic-load-dispatch system.

The main controlled quantities in this coordinated control of electrical generation are 1) the combustor firing rate, 2) the steam flow into the high-pressure turbine, and 3) the MHD inverter characteristics. Although other methods of generation control will be investigated, initial implementation of control for these quantities is discussed in the three paragraphs that follow.

First, the combustor firing rate is dominated by the response time of the air compressor in Figure 4 and its associated steam-turbine drive. In the present simulation, the control for this turbine-compressor combination is based both on throttle pressure error and on megawatt demand. Throttle pressure error is input to a PID controller, and megawatt demand is input to a feedforward rate-action controller. The outputs from these two controllers are summed to form the input to the valve actuator. Appropriate dynamics and rate and magnitude limits are imposed on valve action.

Second, steam flow into the high-pressure turbine is controlled by the main turbine valve. The actuator for this valve is driven by the sum of two controller outputs (one a PID controller whose input is megawatt error and the other a feedforward derivative controller whose input is megawatt demand). It would be straightforward to include throttle pressure error as an additional influencing factor on the control of the main turbine valve.

And third, the electrical power from the MHD channel is regulated by dc to ac inverters connected to channel electrodes. Both electrical firing angles and firing points in the inverter circuits can be controlled. Changes in these firing times result in changes in electrical currents extracted from the channel. The present simulation has two parameters that can be controlled to influence power extraction from the channel. No attempt has been made, however, to include inverter models in the simulation. The controlled parameters characterize electrical current distribution down the channel. Under normal operating conditions, the primary adjustment of these parameters is made according to a set schedule depending on fuel, air, and seed flow rates. To take advantage of rapid load change capabilities of the channel, as mentioned previously, a secondary adjustment to the channel parameters is made by use of a feedforward rate-action controller operating on power demand. An obvious limitation on this mode of control would be the long-term power handling capabilities of the channel.

It is likely that the initial control philosophy for first-generation MHD-steam plants will be somewhat different from that described above. MHD channel protection will have a high priority: changes in thermal gradients in the channel may need to be restricted severely, and Hall fields high enough to cause electrical arcing between electrodes will have to be avoided. Thus, initial channel operation probably will be restricted to a narrow range of operating conditions.

9. Balance of Plant Control

a. Condensate Feed Pump

The condensate feed pump outflow is controlled to maintain the water level in the deaerator storage tank (DST). The difference between DST set-point level and actual level is input to a PI controller, the output of which controls a feedwater flow valve with rate and magnitude limits.

b. Boiler Feed Pump

The boiler feed pump is controlled on the basis of four inputs: drum level, water flow into the drum, steam flow leaving the drum, and steam throttle pressure. The final control signal is the sum of outputs from the following: 1) a proportional controller with dead band operating on the error in drum level; 2) a PI controller operating on the difference between steam mass flow leaving the drum and water mass flow into the drum; and 3) a feedforward derivative controller acting on steam throttle pressure. Valve, turbine, and pump dynamics are included as are rate and magnitude limits on valve area.

c. Spray Attenuator

The spray attenuator is controlled on the basis of two inputs. A PI controller operates on the difference between output steam temperature and a temperature reference to form the primary control signal. Added to this is a secondary control signal obtained through a feedforward derivative controller operating on input steam temperature. Valve dynamics are included, and magnitude limits are imposed on the spray.

d. Recycled Gas Control

A fraction of the exhaust combustion gas is recycled into the top of the seed condenser chamber to maintain a condensation temperature range. Control is influenced by two temperatures: gas temperature at the outlet of the seed condenser and gas temperature at the inlet. The difference between seed condenser outlet gas temperature and a set point temperature is input to a PI controller, the output of which is added to a secondary control signal to drive a damper in the recycled gas line.

The secondary control signal is formed by a feedforward derivative controller acting on the temperature of the gas entering the seed condenser.

e. Steam Bleed Control

The bleed valve on the turbine in Figure 3 controls the amount of bleed steam which passes directly from the turbine to the deaerating feedwater heater. A PI controller acts on the difference between the reference temperature for the water in the DST and the actual water temperature. The output of the controller drives a valve actuator; valve dynamics with rate and magnitude limits are included.

Table 1. Nominal Operating Conditions of Combined-Cycle Plant at Steady-State

CAS CYCLE	HEAT LOSS (MW)	OUTLET TEMP (DEG K)	ENTHALPY (MJ/KG)	FLOW RATE (KG/S)	EFFICIENCY
COMBUSTOR - NOZZLE	23.000				0.980
CHANNEL	8.500				0.960
DIFFUSER WW	19.200	2261.000	2.656	88.740	0.980
RADIANT BOILER WW	63.425	1866.000	1.942	88.740	0.960
AFTER SECONDARY AIR	20.414	1895.171	1.988	96.950	
AFTER RECYCLED GAS	-2.286	1705.277	1.696	114.950	
SECONDARY SUPERHEATER	21.449	1460.391	1.357	114.950	0.990
UPPER SEED CONDENSER WW	17.549	1460.391	1.357	114.950	1.000
LOWER SEED CONDENSER WW	9.750	1350.000	1.282	113.550	1.000
SECONDARY FURNACE WW	14.763	1253.532	1.152	113.550	0.985
LOW TEMP AIR HEATER	27.094	1072.238	0.913	113.550	0.980
PRIMARY SUPERHEATER	41.171	781.815	0.551	113.550	0.990
ECONOMIZER	40.008	480.008	0.198	113.550	0.990
COAL DRYING	8.113	416.638	0.127	113.550	0.970
GAS RECYCLING	2.286	416.638	0.127	95.550	

OTHER HEATS

RECYCLED GAS	2.286	416.638	0.127	18.000	
SECONDARY AIR	3.414	780.000	0.416	8.210	
SECONDARY COMBUSTION	17.000				
EXTRACTED SEED	0.780			1.400	
STACK LOSS	12.134	416.638	0.127	95.550	

FRACTION OF SC HEAT IN UPPER WW AND SH: 0.800

FRACTION OF ABOVE HEAT IN SH: 0.550

PERCENT OF HEAT IN SECONDARY FURNACE TO WW: 0.120

STEAM CYCLE	HEAT TO STEAM (MW)	OUTLET TEMP (DEG K)	OUTLET PRESSURE (PSI)	ENTHALPY (MJ/KG)	FLOW RATE (KG/S)
CONDENSER	-164.117	319.600	1.500	0.195	77.326
CONDENSATE FEED PUMP	0.144	319.700	230.000	0.196	77.326
CHANNEL	8.160	345.003	150.000	0.302	77.326
DEAERATOR STORAGE TANK	27.533	407.839	45.000	0.566	89.807
BOILER FEED PUMP	1.044	408.800	1700.000	0.578	89.807
ECONOMIZER	89.600	508.737	1640.000	1.019	89.807
FEED WATER HEATER	8.834	528.971	1610.000	1.117	89.807
COMBUSTOR - NOZZLE	22.810	577.600	1500.000	1.368	89.807
DIFFUSER WW	18.816	586.590	1500.000	2.722	96.574
RADIANT BOILER WW	60.888	586.590	1500.000	2.722	812.510
LOWER SEED CONDENSER WW	9.750	586.590	1500.000	2.722	105.084
UPPER SEED CONDENSER WW	17.549	506.590	1500.000	2.722	105.084
SECONDARY FURNACE WW	14.542	586.590	1500.000	2.722	55.978
PRIMARY SUPERHEATER	49.759	678.098	1070.000	0.176	89.807
SECONDARY SUPERHEATER	21.233	783.100	1300.000	3.412	89.807
ALL WATERWALLS SUPERHEATERS	121.848 61.994				
BLEED POINT 1 (TO FWH)	8.924	680.891	650.686	3.232	4.074
EXHAUST FROM FWH	4.245	513.722	625.686	1.042	4.074
BLEED POINT 2 (TO DST)	23.288	440.379	60.000	2.770	8.406
TURBINE OUTLET		319.600	1.500	2.317	58.166

AIR CYCLE

AIR COMPRESSOR	15.802	499.000	95.000	0.203	77.960
LOW TEMP AIR HEATER	26.052	816.198	90.000	0.543	77.960
HIGH TEMP AIR HEATER	102.394	1922.000	87.000	1.857	77.960
STACK LOSS	5.796	422.000	14.700	0.133	43.444
HIGH TEMP AIR HEATER FUEL	117.371			41.500	2.828

OTHER POWERS

	(MW)	(KG/S)	HEAT SUMMARY	(MW)
STEAM TO BFP (EFF = 72%)	1.228	1.121	BOT PLANT AVAIL HEAT	285.448
STEAM TO AIR COMP (EFF = 68%)	19.753	18.039	TOTAL AVAILABLE HEAT	306.148
REMAINING AUXILIARIES	4.000			
NET TURB-CEN OUTPUT (EFF = 83%)	67.723	70.646	BOT PLANT HEAT TO STEAM	204.322
NET MD POWER	59.000		TOTAL HEAT TO STEAM	253.838
GROSS PLANT OUTPUT	147.704		TOTAL HEAT TRAN IN BOT PLANT	238.744
NET PLANT OUTPUT	122.723		TOTAL HEAT TRANSFER	288.260
TOTAL PLANT INPUT	335.371		HEAT LOST IN BOT PLANT	16.704
COMBUSTION AIR INPUT	144.748	77.960	TOTAL HEAT LOST TO AMBIENT	17.688
COMBUSTION COAL INPUT	230.000	10.657		
TOTAL COMBUSTOR INPUT	382.749			
GROSS PLANT EFFICIENCY (%)	41.563			
NET PLANT EFFICIENCY (%)	34.534

Figure 1A.

Figure 1B.

Figures 1A & 1B. Simplified Elevation of Conceptual MHD-Steam Plant

Figure 2. Air Path Subsystem

Figure 3. Gas Path Subsystem

Figure 4. Water-Steam Subsystem

Figure 5. Stages of CNCD Modeling

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TASK J
Slag Physical Properties:
Electrical and Thermal Conductivity
R. Pollina

I. OBJECTIVE AND SCOPE OF WORK

The objectives of this task are to study the physical properties (thermal, electrical, and mechanical) of slags and refractory materials. Two- and four-lead dc and two-lead ac electrical conductivity measurements are done to 2000 K in an oxygen-containing environment and to 2600 K in vacuum or inert atmospheres. Thermal expansion measurements are made with and without applied mechanical loading to 1925 K. An on-line microprocessor controlled data acquisition system is used and offers the capability of studying long-duration time-dependent effects in these experiments. The effect of slag corrosion on these properties is also studied. This and other materials capabilities are part of an overall materials effort to study high-temperature air heaters and other downstream components.

II. SUMMARY AND IMPACT

A. Electrical Conductivity

This past quarter, we have terminated the electrical conductivity measurements in Rosebud coal ash and have begun preparing a final topical report summarizing our results and findings over the past five years of effort. The anticipated completion of this topical report is for the quarterly report for the third quarter of this fiscal year.

B. Characterization of Refractory Materials

Work during this past quarter on this subtask centered around the study of the thermal expansion under load of pristine and slagged Corhart X-317 firebrick (Figures 1 and 2). The slagged samples were obtained from a 400 hour test run in the FluidDyne test facility. The results of these measurements indicate the following: (1) The effect of a slagging exposure on thermal expansion of Corhart X-317 firebrick under no load is small. The slagged firebrick exhibits an approximately eight percent increase in linear thermal expansion over the pristine firebrick. (2) The onset of creep in X-317 is as low as 1600 K (2420°F) at about a 10 megapascal (1500 psi) load. (3) Previous creep in the X-317 material tends to strengthen the brick by raising the yield point approximately 50 K. This primary creep appears to eliminate some of the primary slip mechanisms and causes a slightly less prominent deviation of the brick expansion from the behavior of an unloaded sample. (4) A 400 hour exposure to seeded slag weakened the material producing, at 10 megapascal or 1500 psi, a yield point slightly lower than 1550 K or 2325°F for the onset of creep. At 6.9 megapascal or 1000 psi, yield point was approximately 1700 K or about 2600°F. Creep rates appear

to be substantially larger. (5) X-317 has a substantially smaller thermal expansion than seeded Rosebud slag at 21.2 weight percent K_2O seed level.

This raises the possibility of differential thermal stresses between the matrix and the slag on cooldown. The values of the parameters are such that the stress on the X-317 matrix will be tensional--the weakest mode for a ceramic. More work must be done on the mechanical properties of slag before one can determine whether or not this is a real problem for an air preheater facility.

Finally, we have done some room temperature measurements of the elastic modulus of Monofrax A. In the region 20.7 to 26.6 megapascal or 3000 to 4000 psi, we find variations from sample to sample in the elastic modulus from $13.2 \times 10^{+6}$ psi to $36.5 \times 10^{+6}$ psi, 49.1×10^{-4} to 2.5×10^{-5} megapascals. The data is shown in Figure 3. The spread in this data points out the need for further study to determine whether or not this variation is characteristic of a single production run of firebrick or whether it is characteristic of the location in the firebrick from which the sample was taken. These facts have an obvious bearing on the calculations of stress levels in the material for an air preheater.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Thermal Expansion and TEUL

We have completed measurements of thermal expansion under several levels of compressive stress for a $MgO \cdot MgAl_2O_4$ firebrick, Corhart X-317.

This material has been used successfully in air preheater tests at Fluidyne Corporation. Figure 1 shows the thermal expansion of three samples of X-317 over a temperature range from 293 to ≈ 1900 K. The curves are plots of regression fits to the data from several runs for each sample. The equations of fits are given in Table 1. Plots of thermal expansion for two Rosebud slag samples are included in Figure 1 for comparison.

The curve labeled "Pristine X-317" is for a sample taken from the dense outer region of a brick from the first batch of X-317 produced by the manufacturer. The same sample was later held for 35 hours at 1900 K under 10.34 MPa (1500 psi) compressive stress resulting in secondary creep in the sample. Subsequent thermal expansion measurements are shown in the long-dashed curve in Figure 1. The short-dashed curve shows the thermal expansion of a sample taken from a cored matrix brick which had been exposed for 400 hours to a K_2SO_4 /slag environment in Fluidyne air preheater tests.

As the figure shows, exposure of X-317 to the severe conditions represented by these samples has relatively little effect on its thermal expansion under no-load conditions. Expansion coefficients for the three samples are tabulated in Table 2.

We have also plotted the thermal expansion of seeded and unseeded Rosebud coal ash to illustrate the differences between the two slags and the X-317 material. The presence of seeded coal slag in X-317 will lead to additional tensile stresses in the material on cooling in seeded MHD environment. We hope at some time in the future to be able to address this problem to determine whether or not this effect will be of importance in an MHD air heater.

Table 1.--Coefficients for equations describing the thermal expansion of Corhart X-317.

The equations are in the form:

$$\Delta l/l_{293} = C_0 + C_1 T + C_2 T^2 + C_3 T^3 + C_4 T^4,$$

where T is temperature in Kelvin.

	T	C ₀	C ₁	C ₂	C ₃	C ₄
Pristine (cut from	293-1293 K	- 0.295	+0.001269	-1.2496 x 10 ⁻⁶	+1.3384 x 10 ⁻⁹	-4.1717 x 10 ⁻¹³
"as received" brick)	1293-1860 K	-18.705	+0.047902	-4.48386 x 10 ⁻⁵	+1.90525 x 10 ⁻⁸	-3.03106 x 10 ⁻¹²
after 35 hrs. in	293-1293 K	- 0.187	+0.000547	+3.883 x 10 ⁻⁷	-2.73 x 10 ⁻¹⁰	+1.267 x 10 ⁻¹³
creep at 1900 K and	1293-1880 K	+18.301	-0.050248	+5.1741 x 10 ⁻⁵	-2.28265 x 10 ⁻⁸	-3.7368 x 10 ⁻¹²
10.34 MPa						
after 400 hrs in	293-1293 K	-0.274	+0.001042	-5.675 x 10 ⁻⁷	+5.991 x 10 ⁻¹⁰	-1.43 x 10 ⁻¹³
Fluidyne test	1293-1900 K	-2.204	+0.004318	-1.9051 x 10 ⁻⁶	+3.845 x 10 ⁻¹⁰	-----

Table 2.--Coefficients of linear thermal expansion, α (in K^{-1}), for Corhart X-317.

Temperature (K)	α for pristine sample	α for sample after 35 hrs. in creep at 1900 K and 10.35 MPa	α for sample from 400 hr. Fluidyne test
400	8.1×10^{-6}	7.6×10^{-6}	8.4×10^{-6}
600	8.6 "	8.3 "	8.8 "
800	9.9 "	9.0 "	9.9 "
1000	11.2 "	10.1 "	11.3 "
1200	11.7 "	11.8 "	12.8 "
1400	11.1 "	14.2 "	12.4 "
1600	10.8 "	12.4 "	11.7 "
1800	9.7 "	13.2 "	12.0 "

Figure 2 (a,b, & c) shows thermal expansion under load (TEUL) for the same three X-317 samples. As in Figure 1, the curves are plots of equations of fit. Comparing plot b to plot a indicates little change in the response of X-317 to compressive stress at elevated temperatures after 35 hours in creep. The higher apparent yield temperature in plot b for 10.34 MPa (1500 psi) compressive stress probably reflects the effects of secondary or steady-state creep on the thermal expansion, whereas primary creep is responsible for apparent yield in plot a. This indicates that the primary creep rate is substantially greater than the secondary creep rate for X-317.

Creep frame tests on pristine X-317, done by Task B at Montana Tech, have shown yield at 6.9 MPa compressive stress at 1773 K.¹ Because the creep rates are low under these conditions (.0036%/hr primary creep and .00144%/hr secondary creep), the yield temperature is not evident in our thermal expansion curve for pristine X-317 at 6.9 MPa. A heating rate substantially lower than the standard 56 K/hr would be needed to observe the effect of yield at 6.9MPa in thermal expansion measurements for pristine X-317 to 1860 K.

The thermal expansion curves in plot c of Figure 2 show some changes in the effects of compressive stress on X-317 that has been exposed to a slag/seed environment in air preheater tests at Fluidyne. Apparent yield temperatures are lower for the slagged material, and creep rates appear to

be substantially higher. Thermal expansion data up to 1900 K show no evidence of yield under compressive stress less than 3.45 MPa (500 psi). The same material showed no yield at 2.8 MPa and 1773 during a 950 hr test performed by Task B.² If compressive stresses from thermal cycling in an air preheater do not exceed ≈ 3 MPa in the hottest portion of the core, X-317 should perform well under liquid K_2SO_4 /slag conditions.

Figure 1.

Figure 2

Figure 3

REFERENCES

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ELECTRICAL CONDUCTION STUDIES IN SLAG

Richard Pollina, Walter F. Anderson, and Ray Larsen
Physics Department - Montana State University
Bozeman, Montana

ABSTRACT

We present some final results of a project to study the electrical characteristics of a Rosebud coal slag as it relates to the operation of an MHD generator. These include the electrical conductivity of Rosebud coal slag seeded with potassium carbonate from 700 to 1450°C, and from 0.5 to thirty weight-percent equivalent K_2O seed concentration in the slag; channel calculations, including the conductivity in the Faraday direction, the slag layer leakage resistance, and the voltage drops and electric field gradients in the layer; estimates of slag polarization effects; and thermionic emission experiments.

I. INTRODUCTION

The presence of slag on the channel walls of an MHD generator will influence the electrical performance of the generator in ways that are only partly understood at this time. The physical and chemical properties of coal slag under channel operating conditions pose substantial problems for channel and electrode design. Finding workable solutions will require more complete knowledge of slag properties and successful incorporation of this new knowledge into engineering design.

We have completed an experimental program to measure the electrical conductivity of Rosebud coal slag seeded with potassium carbonate. In presenting our results, we will pay particular attention to slag layer characteristics which affect the electrical performance of an MHD channel, including: slag layer resistance (axial and transverse); potential gradient through a slag layer; slag layer polarization due to ion migration; electrochemical compatibility of electrode materials with slags (particularly Rosebud coal slag); electrochemical reactions involving slag; slag layer critical current density; and thermionic emission properties of slag. Of the operating parameters that influence these characteristics, we will consider the effects of slag composition and seed content, electrode composition and conduction mechanisms, and electrode wall temperature.

Although the arc mode of MHD channel operation appears at present to be a viable approach in designs using electrodes of very high thermal conductivity, for other design concepts employing metal or ceramic electrodes, it is necessary to run in the diffuse mode because of the destructive effects of arcing. In the diffuse mode the channel current ($\approx 1 \text{ amp/cm}^2$) is supplied uniformly over the cathode surface by thermionic emission. For slag-covered cathodes, the thermionic emission properties of the slag are the relevant factors in determining whether sufficient thermionic current can be supplied to prevent arcing.

Although some of our results apply to slags in general, many slag properties are quite sensitive to composition. Therefore, our work should be interpreted as pertaining specifically to Montana Rosebud ash or ash from compositionally similar western coal seams, unless otherwise noted.

II. ELECTRICAL CONDUCTIVITY

We have measured the electrical conductivity of seeded Rosebud ash at potassium concentrations from 0.5 weight percent (natural ash) to 30 weight percent as K_2O over a temperature range from 973 K to 1723 K by methods previously described.¹ The data presented graphically in this report are dc conductivities measured isothermally by the 4-lead technique and curves were obtained by a computer fit to the data. Figure 1 is a three-dimensional plot which graphically illustrates the electrical conductivity of Rosebud coal slag in a parametric space of temperature, conductivity, and seed level.

Figure 1. Electrical Conductivity of Rosebud Slag

At the lower temperatures, the data is characterized by a family of similar isothermal curves up to approximately 1300 K at the low K_2O concentrations and 1500 K at the high concentrations. Above this family of curves, there is a region of anomalous behavior in the conductivity data that extends the full range of seed levels. This represents the temperature region in which a glass network forms within the slag layer. The uppermost isotherms in the figure show relatively little variation in conductivity as a function of seed content. At these temperatures, the slags are liquids or liquid/crystalline mixtures (depending on seed concentration). We have included as a dashed line the region of phase transition marking the crystallization of anorthite in the coal slag as the slag is cooled. The broad, solid line represents the glass network formation temperature. At temperatures below this broad line, Rosebud coal slag is a mixture of glass and crystalline phases.

At K₂O concentrations greater than 12 weight percent a second crystalline phase has been seen in powder diffraction patterns. We have tentatively identified the phase as a high-temperature form of KAISiO₄. Since no samples in the six to twelve weight percent K₂O range have been studied by X-ray diffraction, we do not know at what seed level this phase first occurs.

Plante and Cook² reported a KAISiO₄ phase in a synthetic melt with a composition that simulated a "typical" seeded channel slag for western sub-bituminous coal. They reported a high liquidus temperature (>1873 K) for the synthetic mixture. Our experience with seeded Rosebud ash melts also indicates a high liquidus temperature (>1773 K) for samples with a high crystalline KAISiO₄ content. The effects of this phase on electrical conductivity in seeded Rosebud ash have not been determined, but the inclusion of potassium in a crystalline phase may partially account for the lack of sensitivity to K₂O content seen in Figure 1 for the K₂O range from 8 to 15 weight percent K₂O.

Slag Layer Calculations

Until recently, it was not possible to predict the effects of slag layer behavior on MHD channel performance. Slag conductivity had been measured at various temperatures for a few slag samples of widely varying compositions, but systematic studies of conductivity variation with both composition and temperature had not been attempted for oxide mixtures as complex as coal slags. During the past five years, some attempts have been made to correlate conductivity measurements with slag compositions.^{1,4} Now, using a data base of more than two hundred independent measurements on seeded Rosebud ash, we have developed a set of equations to accurately estimate the electrical conductivity of Rosebud slag within our range of study.

If we consider the simple model of a layer of seeded Rosebud slag of uniform composition and thickness, we can calculate a transverse voltage drop across the layer for diffuse current by numerically evaluating:

$$V = J \int_0^s dy/\sigma(T)$$

where J is current density, s is slag layer thickness and σ is calculated as a function of temperature for a given K₂O concentration. A similar calculation can be used to estimate axial resistance in such a slag layer. Table 1 shows calculated values for three selected wall temperatures at three selected seed levels. We have assumed a Faraday current density of 1 amp/cm² to calculate transverse voltage drops and electrode dimensions of 15 cm x 1 cm with 0.2 cm interelectrode spacing to calculate axial resistance. An assumed slag/plasma surface temperature of 1720 K, independent of wall temperature, and a linear relationship between slag thickness and wall temperature were based on measurements for seeded Rosebud slag on duct walls at the Stanford test facility.⁵ A linear temperature gradient through the slag layer was also assumed in the calculations.

*The high liquidus temperature for the KAISiO₄ phase might explain the sharp increase in the rate of electrochemical corrosion of 3MgAl₂O₄·1Fe₃O₄ electrodes in seeded Rosebud slag observed by Cadoff, et. al.³ at temperatures above 1750 K.

Table 1. Slag Layer Voltage Drop and Leakage Resistance

Assume: 15cm x 1cm electrodes
2mm electrode spacing
Slag-Plasma Temperature - 1720 K

Wall Temp.	%K ₂ O	Voltage Drop	Leakage Resistance
1000 K	0.5	22,500 V	19.7 Ω
	23	308	6.0
	30	16.7	1.1
1300 K	0.5	950	19.9
	23	54	6.1
	30	2.9	1.2
1600 K	0.5	4.7	21.9
	23	0.9	8.2
	30	0.2	1.9

The calculations show an enormous dependence of the transverse voltage drop on both the wall temperature and the seed content of the slag. The calculated axial resistances show very little dependence on wall temperature. Transverse slag layer resistance is controlled by the region of the slag layer near the electrode which is very sensitive to wall temperature, while axial resistance is controlled by the resistivity of slag at or near the plasma surface temperature which is insensitive to wall temperature. However, interelectrode resistances would show sensitivity to wall temperature because the current path passes through the region of the slag layer near the electrodes.

Using the simple uniform composition model, Figures 2 and 3 show the voltage drop in the slag layer and the potential gradient (or electric field) in a slag layer for several selected percentages of K₂O. These are

calculated values based on the same assumptions as were described for Table 1. The data is presented as a function both of distance from the wall in millimeters and of slag temperature in degrees Kelvin. Figure 2 is a plot of the voltage at any point on the slag layer referenced to the wall and so the curves are plotted as volts above wall potential. We have plotted five selected weight percents of K₂O from 15 to 30 percent.

These are 15, 20, 22, 24 and 30 weight percent. The breaks in the dashed lines at approximately 1460 K result from a glass network transition which affects the electrical conductivity. This is the same phase boundary that was plotted on Figure 1 as a broad, solid line. Note that if we elevate the wall temperature from 973 K to 1173 K, we reduce the potential drop in the slag layer to one-third of its value at a 973 K wall temperature. The same calculations are presented in Figure 3 as a plot of the potential gradient or the electric field assuming a one amp per square centimeter diffuse mode conduction in the slag layer. Potential gradients are plotted in kilovolts per meter. Note that in the region between 20 and 24 weight percent K₂O, the data falls in a relatively narrow band. This corresponds to the percent seed level expected for slag on an electrode wall.² This is fortuitous for generator operation, since it indicates that variations in "bulk" seed concentration within this range would not significantly affect conductivity related characteristics of a slag layer from Rosebud coal. This lack of sensitivity to K₂O content reflects the conductivity behavior seen

in Figure 1 as a region of relative flatness in the isothermal curves between 20 and 24 weight percent K₂O. Sensitivity to wall temperature is also evident in Figure 3. If we raise the wall temperature by

Figure 2. Slag Layer Voltage Distribution

200 K, we have a reduction in these electric field gradients; for example, at 15 weight percent K_2O , we have a reduction of almost a factor of 6 in the potential gradient near the slag/electrode interface.

Calculations based on the uniform composition model described above should be viewed with caution in predicting the behavior of a real channel slag layer. Modeling slag layer behavior on the basis of conductivity data involves certain assumptions regarding charge transfer mechanisms. In the model just described, it is implicitly assumed that charge transfer at the slag/electrode and slag/plasma boundaries is completely efficient and that the current is carried by the same charged species with the same transference numbers in all three components. In other words, the model assumes that electrochemical reactions and/or polarization of the slag layer do not occur and that ohmic resistance is the sole determining factor influencing the electrical characteristics of the slag layer. This, of course, is not the case in an operating channel.

Nevertheless, the calculations are useful when their limitations are taken into account. Axial resistance calculations should be applicable to the anodic slag layer of an operating channel. Polarization of the slag layer should not significantly affect the composition of the region near the slag/plasma boundary which would still be the low resistance path for axial current. At the cathode, accumulation of potassium and iron in the colder region of the slag layer would substantially decrease axial resistance resulting in leakage currents that are significantly greater than the uniform composition model would indicate.⁶ Calculations based on conductivity data for a seeded New Hampshire slag⁷ are in good agreement with interelectrode resistance measurements for the AVCO channel with no magnetic field.⁸ Koester and Nelson calculated axial resistances for slag layers in the Stanford test Channel and found good agreement for anode slag ac resistance measurements during arc mode operation.⁹

Figure 3. Slag Layer Electrical Field

Transverse resistance and voltage drop calculations are subject to similar restrictions in their applications to channel behavior. They do not apply to arc mode current and do not take into account polarization effects. At the cathode of an operating channel, transverse slag layer resistance may be lower than calculated values due to accumulation of potassium and iron within the layer and at the electrode surface. Polarization of the anodic slag layer can lead to a highly resistive layer near the electrode where these elements are depleted. Calculations made by Koester and Perkins for seeded Illinois #6 slag agreed fairly well with channel measurements of slag layer resistance over a mild steel anode.¹⁰ The electrode provided iron cations to the slag layer, minimizing polarization effects. Slag layer measurements with a nickel anode indicated slag layer resistance was an order of magnitude greater than the calculated values, demonstrating the effects of slag layer polarization.

Another example of a simple calculation based on a uniform composition model can be found in correlating empirically determined voltages for slag layer electrochemical reactions to wall temperatures or seed concentrations needed to avoid such reactions. Electrochemical cell tests with eastern and western slags and several electronically conducting candidate ceramic electrode materials indicated that voltages greater than 1.7V resulted in oxygen bubble formation at the anode and formation of metallic iron at the cathode.³ We can calculate a minimum electrode surface temperature to prevent such reactions from occurring in a seeded Rosebud slag layer at any specified K_2O content up to 30 weight percent. At a K_2O concentration of 22.7 weight percent, as suggested by Plante and Cook for modeling channel slags from western coals,² the electrode surface temperature would have to be about 1550 K or greater.

To include polarization effects, we can use a method for estimating the critical current density for electrothermal instability of the slag layer, outlined by Koester and Perkins.¹⁰ The calculations use a correlation function for critical current density:

$$J_c = \sqrt{k \sigma_w T_w / s^2 n}$$

where k is the slag thermal conductivity, T_w is the temperature of the electrode/slag interface, σ_w is the slag electrical conductivity at T_w , and s is the thickness of the slag layer. The term n is an estimate of $d \ln \sigma / d \ln T$, and $1/\sqrt{n}$ is suggested by Koester and Perkins as an approximation for a more complicated function.

Table 2 illustrates the effect of slag layer polarization on critical current density calculated for seeded Rosebud slag at several anode wall temperatures. The calculations assume a "bulk" seed content of 22.7 weight percent as K_2O in the slag layer. Slag thickness was calculated on the basis of measurements at various wall temperatures for seeded Rosebud slag with a plasma temperature of 1720 K.⁵ A value for thermal conductivity of 1.4 watts/m-K was calculated from slag thickness and heat flux measurements⁵ by the equation: $s = k(T_s - T_w)/q$. This value agrees with a measured s value of $1.5 \pm .2$ watts/m-K for Rosebud slag below 900 K.¹¹ The values for n and σ_w are calculated from our model for seeded Rosebud ash electrical conductivity.

Table 2. Estimated Critical Current Densities for Polarized and Non-polarized Anodic Rosebud Slag Layers

Wall T (K)	Critical Current Densities (amp/cm ²)	
	Polarized Slag Layer	Non-polarized Slag Layer
1000	0.0063	0.099
1100	0.0143	0.160
1200	0.030	0.25
1300	0.060	0.40
1400	0.28	0.65
1500	0.49	1.52
1600	1.73	5.09

The two cases in Table 2 are for extreme polarization such as might occur at a noble metal anode, and for no polarization, i.e., uniform slag layer composition. Only the effects of potassium depletion at the anode are included in the calculations for the polarized case, and a slag K_2O content of 0.1 weight percent at the anode surface was used in making these estimates. Although the calculated values for critical current density may not prove too accurate, due to the many approximations incorporated into the calculations, the magnitude of the difference between the polarized and non-polarized cases should correspond well to real channel slag layers.

III. THERMIONIC EMISSION OF COAL SLAG

The experimental equipment and procedures we used have been described elsewhere.¹² Briefly, the slag sample under study was in the form of a thin layer resting on an ohmically heated tantalum or iridium foil. The

thermionic current was collected in a vacuum of 10^{-6} to 10^{-5} Torr using a standard anode-guard ring structure, as described previously.¹² The measured current density j was used to calculate a thermionic work function ϕ according to the Richardson equation:

$$j = 120T^2 \exp \left\{ -\frac{e\phi}{kT} \right\} \quad (1)$$

where T is the absolute temperature, e is the charge on the electron, k is Boltzmann's constant. In this context, ϕ must be regarded as a convenient parameter for characterizing the thermionic emission, rather than an accurate representation of a rigorously defined true work function.

The temperature was measured with an optical pyrometer making estimates of the spectral emissivity (0.7) by comparison with the platinum substrate and ignoring possible effects due to transparency of the slag. Particular attention was paid to the presence of potassium in the slag and on its surface because of the well-known property of alkali metals in lowering the work function of most surfaces. Accordingly, we used Auger electron spectroscopy (AES) to monitor the relative amount of potassium on or near the slag surface and to follow changes in potassium coverage. The slag samples were mostly 5 or 6 component synthetic slags obtained from the National Bureau of Standards and also included some natural slags obtained from Stanford University.⁹ Table 3 shows the composition of some of the slags studied.

Table 3

Slag #	K492	K510	K539	K488	Ill. #6
SiO ₂	38	32	28	40	45
Al ₂ O ₃	14.25	12	10.5	15	20
Fe ₃ O ₄	14.25	12	10.5	15	9
CaO	19	16	14	20	-
MgO	9.5	8	7	10	-
K ₂ O	5	20	30	-	25
ϕ (1500 K)	4.1eV	3.7	3.7	4.5	3.9

Experimental Results

The general behavior of the thermionic work function for a synthetic slag for the temperature range over which systematic data were taken is shown in Figure 4. The high temperatures were limited by slag behavior. A low melting point slag is harder to handle at higher temperatures and X-ray fluorescence measurements indicated that potassium was lost by evaporation at an appreciable rate above 1600 K. As Figure 4 shows, for K488, ϕ is temperature dependent, increasing from about 4.3 eV at 1400 K to 5.1 eV at 1750 K. For K510, ϕ is also temperature dependent, with perhaps a smaller slope, but the major result is that the presence of K_2O in the slag lowers ϕ by a significant amount -- about 0.75 eV at 1500 K. (See Table 3). This effect is apparent despite scatter in the data which is due to the difficulty of heating the slag sample uniformly. The result for K510 is representative of all the potassium-containing slags except for the low potassium sample K492 (5% K_2O) where the slope was greater and ϕ attained a value of 4.1 eV at 1500 K.

Figure 4. Thermionic Work Function of Synthetic Slag K488 as a Function of Temperature

In the course of the measurements, it was found that upon heating to a temperature below about 1400 K, the emission current decreased with time over a few minutes and reached a lower steady state value. Auger measurements showed this to be due to a loss of potassium from the surface resulting in an increased work function. Figure 5 shows a representative decay curve under these conditions. During the time intervals A, B, C, and D, the anode was moved away from the slag to permit Auger measurements. In the insert, the right-hand column shows the work function variation, the left-hand column shows the ratio of the potassium to oxygen lines in the Auger spectrum, and the middle column shows the potassium coverage -- the relative number of potassium to oxygen (assumed unchanged) atoms seen by the Auger measurements. The K/O ratio is probably accurate but the coverage determination is on a less firm footing because Auger analysis has not yet reached full development into a quantitative tool. No decay in current or potassium coverage was observed for temperatures at or somewhat above 1400 K.

Figure 6 shows, for a natural slag sample, the steady state K/O ratio as a function of temperature. The sharp transition in K shown here lies between 1400 K and 1500 K and the curve is reversible as the temperature is alternately raised and lowered.

Figure 5. Decrease of Thermionic Emission Current with Time due to Potassium Leaving the Surface. The Insert shows the Ratio of the Potassium to Oxygen Auger Lines (K/O), Inferred Potassium Coverage, and Work Function, at Those Portions of the Curve Marked A, B, C, and D.

It is reasonable to suppose that if surface potassium does lower the work function, there should be some influence on the thermionic emission by such a transition. This is in fact born out in Figure 7 which shows a set of runs on the same natural slag with an inflection or dip occurring at the transition temperature. Improved instrumentation at the time these data were taken permitted us to run to higher temperatures and reduced the scatter observed earlier thus allowing this effect to be seen. We believe that there is little doubt that the effect we observed is due to the temperature variation of potassium coverage observed in the Auger measurements but we have not been able to follow up these experiments so as to characterize the effect in a more systematic way. We might note here that the calcium coverage behavior was quite parallel to that observed for potassium.

Discussion

The principal results to come out of the thermionic emission study are the thermionic work functions of some representative slags as measured in vacuum, the variation of ϕ with temperature, and the effect of potassium seed. The picture that emerges seems to be the following: The work function depends on the amount

- Figure 6. Relative Potassium Coverage on Illinois #6 Slag as a Function of Temperature

- Figure 7. Variation of the Thermionic Emission of Slag With Temperature, Showing the Inflection or Dip at Around the Transition Temperature.

of potassium on or near the surface of the slag. Beginning with an initial potassium coverage determined in some way by slag history, the coverage at a given temperature is time-dependent until some steady-state coverage is attained which is determined by a balance between evaporation from the surface and diffusion from the interior. Evaporation dominates at temperatures below about 1400 K but between 1400 K and 1500 K, the supply to the surface increases sufficiently to offset evaporation. The fact that the apparent increased diffusion rate occurs over such a small temperature range suggests that the chemistry of the slag is involved in the process. The mechanism may be related to the incorporation of potassium in a phase that separates out at the transition temperature. Electrical conductivity measurements have shown a break in the conductivity curve at 1433 K in a reducing atmosphere which is correlated with the appearance of a KAISiO_4 phase.¹³ Alternatively, the formation of the glass network at this temperature may impede diffusion of potassium. Above the transition temperature, the potassium coverage does not continue to increase and above 1500 K - 1600 K drops off again probably due to very rapid evaporation which above 1600 K can, in fact, significantly deplete the total potassium in the sample, at least to the depth (1 micrometer) probed by the X-ray fluorescence technique.

IV. CONCLUSIONS

The results we have reported are derived from laboratory scale experiments. When they are combined with observations from engineering channel tests, many of the electrical and electrochemical characteristics of slag layers in MHD channels can be understood more clearly. Models for calculating the effects of operating parameters on slag layer behavior require a systematic data base which can be used to characterize important physical and chemical properties of slag. Careful utilization of laboratory data offers the most efficient means for obtaining that data base and for selecting and applying successful models.

The simple calculations we have presented are not adequate for a complete description of slag layer behavior. However, because so many important slag layer characteristics are strongly influenced by electrical conductivity, and because slag conductivity is very sensitive to temperature and composition, simple models which describe the effects of temperature and composition on conductivity can be quite useful when applied to problems in channel design and materials selection.

The predominant charge carrier in seeded Rosebud slag is the K^+ cation. But the choice of electrode materials can alter the composition of the slag layer and lead to other charge-carrying mechanisms. Anodes capped with a noble metal result in polarization of the slag layer with depletion of potassium near the electrode. Since Rosebud slag is a poor electronic conductor, arcing is the only mode of current transport available with noble metals. Depletion of iron and calcium near electronically conducting anode materials have been shown in laboratory studies of slags.¹⁰ Although they do not appear to contribute significantly to conductivity in Rosebud ash at its natural composition, addition of Fe_2O_3 to Rosebud ash enhances conduction to an extent comparable to adding K_2CO_3 . If mild steel is used as an anode material, iron is oxidized at the anode/slag interface and is incorporated into the slag replacing the depleted potassium as the predominant charge carrier. So long as iron can be supplied at a sufficient

rate from the "sacrificial" anode, polarization effects are minimized, as has been observed.¹⁰ Other laboratory studies indicate that zirconia anodes can reduce polarization problems.¹⁴ Potassium depletion would still occur near a zirconia anode, but since zirconia is an ionic conductor, an ionic conduction mechanism involving oxygen anions from the anode could provide for diffuse current through the slag layer if wall temperatures are sufficiently high.

In the cathodic slag layer, axial leakage current problems due to the formation of metallic iron may be less severe with Rosebud slag than with slag from eastern coals. Nevertheless, accumulation of potassium near any cathode material which is blocking to K^+ ions will lower the axial resistance of the slag layer. Electrochemical degradation of cathode materials will also be aggravated by slag layer polarization.³

Thermionic emission results in vacuum indicate that it is difficult to remove electrons from a slag layer. Current densities as large as one amp per square centimeter would promote substantial arcing under these conditions. But these experiments also show that positive ions such as K^+ can be removed from the anode slag layer surface quite easily even near the one amp per square centimeter rate if, as the experiments indicate, the potassium desorbs from the surface as ions. Increased potassium vapor pressure over the cathode slag layer enhances the slag's ability to emit electrons but, until further work is done, we can only surmise on the basis of channel experiments that the enhancement may not be sufficient to prevent arcing. There is also an observed difference in behavior between cathode and anode wall arcing. This could be explained by our preliminary thermionic emission experiments which indicate that the cathode wall should arc unless generator conditions significantly lower the work function.

Further laboratory studies relevant to the electrical behavior of slag layers are indicated by what has already been done. Measurements of thermionic emission from slags in the presence of potassium vapor to determine the effects of potassium pressure on the work function are strongly indicated. Though some measurements of electrical conductivity have been made at several oxygen partial pressures for Rosebud ash with Fe_2O_3 added there is not yet enough data to do systematic modeling with these composition variables. Systematic conductivity data for seeded eastern slags is also lacking. Finally, application of electrical conductivity results to a model for slag layer polarization calculations such as that proposed recently,¹⁴ could lead to a much more complete understanding slag layer electrical behavior. However, the complex nature of slag electrochemistry would require that polarization calculations be mated with a good model for thermodynamic calculations. The thermodynamic calculations are feasible using a power series notation system already developed for this purpose.¹⁵ Hopefully, the work of several independent investigations can eventually be combined to give a sound understanding of slag layer behavior which can be applied to practical solutions for a number of important problems in MHD channel design.

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