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MHD POWER GENERATION, RESEARCH, DEVELOPMENT, AND ENGINEERING

Annual Progress Report for October 1977–September 1978

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

U. S. DEPARTMENT OF ENERGY

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MHD
POWER GENERATION
RESEARCH, DEVELOPMENT
AND ENGINEERING

Annual Progress Report
October 1977 to
September 1978
Volume II

THE MONTANA ENERGY AND MHD
RESEARCH AND DEVELOPMENT INSTITUTE, INC.
P.O. Box 3809
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PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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

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MONTANA STATE UNIVERSITY

Slag Flow and NO_x Kinetics:
Moderate Temperature Slag Flow Facility (MTSFF)
H. W. Townes and T. C. Reihman

ABSTRACT

The moderate temperature slag flow facility (MTSFF) has been operated for over 1150 hours with slag in the combustion air stream. A determination has been made of the effect of particulate size on the rate of pressure drop increase and of the effect of slag on long-term (750 hours) operation of the facility. Plots or tables of temperatures, flow rates, pressure drops, particulate size, and Reynolds numbers for the test conditions during four runs totaling 1150 hours of operation are included.

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 all work to date has 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. Anticipated 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 and MHD seed material on the heat exchanger performance are being determined over a wide range of operational parameters, principally temperature limits of the bed material and flow velocities for the combustion gas and for the air to be heated. The experimental system has been sized so that the above temperatures and velocities can be achieved with a circular flow passage from 0.25 to 1.5 inches in diameter. Initially, 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 the full range that can be expected from the burning of various coals with zero to 95 percent ash removal. The influence of particle size and residence time in the combustor also are being determined.

The overall program consists of analytical as well as experimental work. Analytical studies have been conducted to size the MTSFF, to

determine the geometry of the cored ceramic brick, and to determine the ranges of the variables in the experimental program. Current effort is directed toward studies of the transient response of the entire MTSFF during the start-up and cooldown, toward predictions of the slag deposition rates on the heat exchanger surfaces, and toward development of sets of operational test conditions (flow rates and temperature profiles) representing several maximum stress levels in the ceramic bricks.

II. SUMMARY OF PROGRESS TO DATE

The moderate temperature slag flow facility (MTSFF) has been operated for a total of 1150 hours with slag (no seed) in the combustion gas stream. A determination has been made of the effect of slag particulate size on the rate of pressure drop increase through the MTSFF for three slag particulate sizes over time periods of 100 hours. A 750-hour run with slag has determined an upper time limit for the operation of a heat exchanger without a cleanout mode of operation. During the 750-hour run, a considerable amount of slag was deposited in the flow passages, and the core material was cracked and distorted.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Work Accomplished

A total of six experimental runs have been made in the MTSFF with slag in the combustion gas flow for a total of 1150 hours of operation. The first two runs were made with thermocouples in the gas flow stream. The rates of pressure drop increase were influenced by slag buildup on the thermocouple wires; for this reason, only experimental Runs 3 through 6 are considered valid and are the runs which are discussed in this report.

The objective of Runs 3, 4, and 5 was to determine the effect of particulate size on the rate of pressure drop increase in the MTSFF. Before each of the last four slag flow runs, the flow passages in the MTSFF were cleaned of slag deposits by running a rod through each passage. An examination of the pressure drop across the bed at the beginning of Runs 3 through 6 (as shown in Table 1) indicates that this cleaning process produced reasonable results.

The conditions under which the MTSFF was operated during Runs 3 through 6 are shown in Tables 2 through 4 and in Figures 1 through 10. Table 2 summarizes the temperature and cycle time information for the runs. The top of the core at the end of reheat generally was at a minimum temperature of approximately 1700 K (2600°F). Figures 1 and 2 show typical core temperature profiles taken during Run 6. Figures 3 through 10 show the time history of the temperature at the top and bottom of the core at the end of reheat and blowdown for each of Runs 3 through 6. A data point is shown for each cycle.

The flow rate information for each of the runs is summarized in Table 3. Reynolds numbers and gas velocities for the flow rates given in Table 3 are summarized in Table 4. The Reynolds numbers indicate that flow in the MTSFF always was turbulent.

The rates of pressure drop increase across the MTSFF core are shown in Table 1. Figures 11 through 20 show the actual pressure drop across the core at the end of reheat and blowdown as a function of time for each of the runs. Figures 17 and 18 show the pressure drop over 300 hours for Run 6, while Figures 19 and 20 show the pressure drop over the total 750 hours.

B. Discussion

As can be seen from Table 1, the larger diameter slag particulates caused a lower rate of pressure drop increase in the MTSFF than did the smaller particulates. This result was predicted by the slag deposition model developed by Task E but was contrary to some other theoretical and experimental work. If the Task E model is assumed to apply and to give reasonable results, a decrease in particulate size below ten microns will not give a significant increase in deposition rates. Although the increase in the experimentally measured rate of pressure drop increase is significant (a factor of two going from a particulate diameter of 79 to 19 microns), some other aspects of the MTSFF operation must be considered. Since the material life of the bed is limited and since Run 3 was begun after about 150 hours of operation of the bed with slag, the rate of pressure drop increase during Run 3 may have been reduced by the continued soaking of the upper bricks in the bed with slag. In other words, the initial runs may have had a considerable amount of the deposited slag "sponged up" by the bricks so that this slag did not contribute to a pressure drop increase. The magnitude of this effect is not known but can be determined by beginning an initial run with a new core using smaller particulate sizes. This aspect will be checked with the initial runs on the second core.

Table 1 also shows a different rate of pressure drop increase for reheat and blowdown, which at first does not seem consistent. This is so even if the rates of pressure drop increase are normalized for the temperature and flow rate differences. The rate of pressure drop increase in reheat is still considerably larger than the rate of pressure drop increase in blowdown, although the differences are less than shown in Table 1. The change in the rate of pressure drop increase from reheat to blowdown is significant. Apparently, the deposits in the core have different drag coefficients when the flow is reversed. This change in drag coefficient is common for bodies which are not symmetrical in the direction of flow; and since the slag deposits are very irregular, the result is to be expected rather than to be considered inconsistent.

Run 6 was the last run made on the first core in the MTSFF and lasted a total of 750 hours. As can be seen from Table 1, the rate of pressure drop increase for Run 6 was larger than that for Run 5 although the particulate average diameter was larger. This can be attributed to two effects. The first effect mentioned earlier was that the upper bricks in the bed probably were saturated (or nearly saturated) with slag during the first 450 hours of operation. The second effect may be that during Runs 3, 4, and 5, the particulate size distributions were peaked about the mean given in Table 1, whereas for Run 6 an unsized (as received) distribution with a much flatter or more broad particulate size range distribution was used (although the average particulate diameter was 6.80 microns).

The objective of Run 6 was to determine the effect of slag deposition during long-term operation of the MTSFF. The effects of long-term operation probably are discussed best by referring to the history of pressure drop across the bed during Run 6 (as shown in Figures 17 through 20). Figures 17 and 18 show the pressure drop across the bed during the first 300 hours. As can be seen from these figures, the rate of pressure drop increase was relatively smooth with the exception of a decrease in the pressure drop at 150 hours. As Figures 19 and 20 show, after about 325 hours of operation, the rate of pressure drop increase became erratic, with large increases and decreases in the pressure drop. An examination of the core after disassembly showed that some sections of the core were very badly cracked and that a considerable amount of the flow, as evidenced by the slag accumulation, went between the core and the containment tube in some sections. It is hypothesized that the pressure drop decreases observed during the last 400 hours of operation may be attributable to the cracking of the core. The flow then was able to bypass the restrictions caused by slag deposition.

The apparently wide variation in the core top temperature of Run 6 is not considered to be accurate. Prior to and during Run 6, most of the thermocouples in the upper regions of the core had failed, making it necessary to determine the top core temperature by extrapolation of a curve fit of temperatures lower in the bed. This extrapolation is considered to be the cause of the apparent wide variation of the temperature at the top of the bed.

The condition of the MTSFF core after the completion of Run 6 (a total of 1150 hours with slag in the combustion gas) is shown in Figures 21 through 30. Each of the figures carries a caption giving the location in the bed, the temperature range of operation, and a description of the significant features. The last brick in the bed to show slag runoff was brick number 30 (Figure 30). The maximum temperature at this level was 1400 K (2055°F).

Significant features of the figures include the large amount of slag runoff and the complete plugging of the flow passages in the upper levels of the bed. The severe cracking of the core bricks shown in Figure 27 and the obvious bypassing of the core flow holes support the hypothesis of flow bypass of the core as the cause of the observed pressure drop decreases.

IV. CONCLUSIONS

The particulate size was found to influence the rate of slag deposition significantly. Operation of the MTSFF facility for 100 hours with 0.10 percent slag caused no serious plugging. Operation of the MTSFF for 750 hours, however, caused complete plugging of the core and significant damage to the core material. It is estimated that with 0.10 percent slag concentration in the combustion gas flow, a cleanout cycle of the MTSFF will be necessary at between 200 and 400 hours of operation.

Table 1.--Cross-bed pressure drop for Runs 3 through 6

RUN NUMBER	DURATION HOURS	PARTICLE AVERAGE DIAMETER μ M	SLAG CONCENTRATION PERCENT TOTAL REHEAT FLOW	RATE OF PRESSURE DROP INCREASE 95% CONFIDENCE LEVEL Pa/Hr (PSI/1000-HRS)		PRESSURE DROP END REHEAT INITIAL - FINAL VALUES Pa (PSI)	
				REHEAT	BLOWDOWN	CURVEFIT	DATAPPOINT
3	100	78.7	0.0920	5.44 $\pm$ 0.13 (0.789)	3.84 $\pm$ 0.09 (0.557)	2173 - 2720 - (0.315 - 0.394)	2050 - 2740 (0.297 - 0.397)
4	100	18.5	0.0865	11.5 $\pm$ 0.11 (1.67)	6.61 $\pm$ 0.06 (0.959)	1610 - 2764 (0.234 - 0.401)	1690 - 2710 (0.24 - 0.393)
5	100	4.26	0.0865	12.8 $\pm$ 0.14 (1.86)	9.08 $\pm$ 0.07 (1.32)	2310 - 3590 (0.335 - 0.521)	2120 - 3580 (0.307 - 0.519)
6	750	6.80	0.0879	19.1 $\pm$ 0.11* (2.76)	13.3 $\pm$ 0.14* (1.93)	1630 - 7350* (0.236 - 1.066)	1151 - 7736* (0.167 - 1.122)

*OVER FIRST 300 HOURS

Table 2.--Average reheat and blowdown temperatures
and cycling times for Runs 3 through 6+

RUN NUMBER	AVERAGE TEMPERATURES/S.D.* K (°F)				AVERAGE CYCLE TIMES/S.D.* SECS	
	END OF REHEAT		END OF BLOWDOWN		REHEAT	BLOWDOWN
	TOP	BOTTOM	TOP	BOTTOM		
3	1743/20 (2678)	839/16 (1051)	1687/24 (2577)	725/15 (845)	360	246/11
4	1675/16 (2555)	865/10 (1097)	1632/21 (2478)	767/10 (921)	360	243/13
5	1753/18 (2696)	860/15 (1088)	1685/15 (2573)	741/12 (874)	360	274/15
6 ⁺	1743 (2678)	848 (1067)	1687 (2577)	732 (858)	360	249/27

* S.D. ⇒ STANDARD DEVIATION

+ TEMPERATURE DATA FOR 0-300 HOURS

Table 3.--Average reheat flow, blowdown flow, fuel flow, and air/fuel ratios for Runs 3 through 6

RUN NUMBER	AVERAGE REHEAT TOTAL FLOW/S.D.* Kg/Hr (LBM/SEC)	AVERAGE BLOWDOWN FLOW/S.D.* Kg/Hr (LBM/SEC)	AVERAGE FUEL FLOW/S.D.* Kg/Hr (LBM/SEC)	AVERAGE AIR/FUEL RATIO
3	174/1.5 (0.106)	167/2.3 (0.102)	10.2/0.07 (0.00623)	16.0
4	185/1.8 (0.113)	166/1.4 (0.101)	10.0/0.06 (0.00611)	17.5
5	185/2.6 (0.113)	166/1.9 (0.101)	9.95/0.1 (0.00608)	17.6
6	182/6.5 (0.111)	167/3.1 (0.102)	9.95/0.19 (0.00608)	17.3

*S.D.⇒STANDARD DEVIATION

Table 4.--Reynolds number and gas velocity at end of reheat
and blowdown for Runs 3 through 6

RUN NUMBER	REYNOLDS NUMBER				GAS VELOCITY* M/S (FT/SEC)			
	END OF REHEAT		END OF BLOWDOWN		END OF REHEAT		END OF BLOWDOWN	
	TOP	BOTTOM	TOP	BOTTOM	TOP	BOTTOM	TOP	BOTTOM
3	2960	4550	2900	4780	52.7 (173)	25.6 (84)	49.1 (161)	21.0 (69)
4	3220	4740	2930	4590	53.9 (177)	27.7 (91)	47.2 (155)	22.2 (73)
5	3140	4760	2880	4690	56.3 (185)	27.7 (91)	48.8 (160)	21.3 (70)
6	3100	4720	2900	4750	54.9 (180)	26.7 (88)	48.7 (160)	21.1 (69)

*BASED ON 24.89 IN Hg (122.22 PSIA) PRESSURE AND AIR PROPERTIES

CERAMIC THERMOCOUPLES
360 SEC REHEAT CYCLE

14,46,6 5/13/78
353 SEC INTO CYCLE

Figure 1.--Typical axial temperature profile at the end of
360 second reheat cycle

CERAMIC THERMOCOUPLES
270 SEC BLOWDOWN CYCLE

14:51:8 5/13/78
271 SEC INTO CYCLE

Figure 2.--Typical axial temperature profile at the end of 270 second blowdown cycle

Figure 3.--Temperatures at the end of reheat (slag run number 3)

Figure 4.--Temperatures at the end of blowdown (slag run number 3)

Figure 5.--Temperatures at the end of reheat (slag run number 4)

Figure 6.--Temperatures at the end of blowdown (slag run number 4)

Figure 7.--Temperatures at the end of reheat (slag run number 5)

Figure 8.--Temperatures at the end of blowdown
(slag run number 5)

Figure 9.--Temperatures at the end of reheat
(slag run number 6)

Figure 10.--Temperatures at the end of blowdown
(slag run number 6)

Figure 11.--Pressure drop at the end of reheat
(slag run number 3)

Figure 12.--Pressure drop at the end of blowdown
(slag run number 3)

Figure 13.--Pressure drop at the end of reheat
(slag run number 4)

Figure 14.--Pressure drop at the end of blowdown
(slag run number 4)

Figure 15.--Pressure drop at the end of reheat
(slag run number 5)

Figure 16.--Pressure drop at the end of blowdown
(slag run number 5)

Figure 17.--Pressure drop at the end of reheat
(slag run number 6)

Figure 18.--Pressure drop at the end of blowdown
(slag run number 6)

Figure 19.--Pressure drop at the end of reheat
(slag run number 6)

Figure 20.--Pressure drop at the end of blowdown
(slag run number 6)

Figure 21.--Bricks 1-2 of MTSFF core upon completion of Run 6

Bricks 1-2, the top of the bed

Cycled between 1743K-1687K (2678F-2577F)

The top brick has eroded to approximately 1/3 its original thickness. Both bricks 1 and 2 are badly charred with no slag deposits on either brick. The piece laying on brick 1 was a web in the containment tube which fell onto the top of the bed during the 750 hour run. The containment hot liner tube begins to be slag saturated at the level of the top of the bed. The condition of the insulation brick can be seen.

Figure 22.--Bricks 3-4 of MTSFF core upon completion of Run 6

Bricks 3-5, 6"-15" from top

Cycled between 1719K-1662K (2635F-2531F) at brick 3
and 1695K-1636K (2592F-2485F) at brick 5

Slag has soaked into the outer surface of the bricks. The interior flow holes are clear in brick 3, however. The containment hot liner tube is saturated with slag which has soaked into the inner surface of the insulating firebrick.

Figure 23.--Brick 4 of MTSFF core upon completion of Run 6

Fourth Brick, 9" from top

Cycled between 1707K-1649K (2613F-2508F)

Slag deposits occur in outer region of brick, the center is relatively slag free.

Figure 24.--Bricks 4-7 of MTSFF core upon completion of Run 6

Bricks 4-7, 9"-1'9" from top

Cycled between 1707K-1649K (2613F-2508F) at brick 4
and 1671K-1611K (2549F-2440F) at brick 7

The bricks are heavily soaked with slag. Many of the flow holes are plugged. Some cracking has occurred in the keyways.

Figure 25.--Brick 6 of MTSFF core upon completion of Run 6

Brick 6, 15" from top

Cycled between 1683K-1624K (2570F-2463F)

Heavy slag plugs can be seen in the holes. It appears that little cross flow between holes has occurred, although some flow may have escaped out of the outer row of holes.

Figure 26.--Bricks 6-15 of MTSFF core upon completion of Run 6

Bricks 6-15, 1'3" - 3'9" from top

Cycled between 1683K-1624K (2570F-2463F) at brick 6
and 1576K-1509K (2377F-2256F) at brick 15

The bricks are saturated with slag, although the higher level bricks have a heavier deposit on the outside than those lower. Many of the flow holes are plugged. Some cracking occurred although not as severe as bricks 18-30.

Figure 27.--Bricks 18-25 of MTSFF core upon completion of Run 6

Bricks 18-25, 4'3"-6'3" from top

Cycled between 1540K-1471K (2312F-2188F) at brick 18
and 1457K-1382K (2162F-2027F) at brick 25

The bricks are saturated with slag. Thermal cracking occurred axially along the keyways as well as along the unkeyed face of the bricks. Some transverse cracking of these bricks also occurred. This was the most severe region of thermal cracking in the bed.

Figure 28.--Brick 26 of MTSFF core upon completion of Run 6

Brick 26, 6'6" from top

Cycled between 1445K-1369K (2141F-2004F)

Heavy slag plugs have developed. All the flow holes have plugged with a very hard, glassy deposit.

Figure 29.--Bottom of Brick 28 of MTSFF core upon completion of Run 6

Bottom of Brick 28, 7' from top

Cycled between 1409K-1331K (2076F-1935F)

The brick is severely cracked. The slag deposits at this level have changed from smooth and glassy to a more textured, woody appearance. Slag run-off can be observed in the holes.

Figure 30.--Brick 30 of MTSFF core upon completion of Run 6

Brick 30, 7'6" from top

Cycled between 1397K-1318K (2055F-1913F)

This is the last brick which showed slag run-off occurring.
The brick was badly cracked, as the photo shows.

MILESTONE CHART

STATUS DATE Sept. 1978

TASK E

PROGRESS

MAJOR MILESTONES

1977

O N D J F M A M J J A S

COMPLETE FIRST SERIES OF SLAG FLOW RUNS (1100 HRS TOTAL)

REMOVE FIRST CORE

INSTALL SECOND CORE

COMPLETE DATA ANALYSIS ON FIRST SIX SLAG FLOW RUNS

DO SENSITIVITY ANALYSIS ON SLAG DEPOSITION AND RUNOFF MODELS

START HIGH SLAG CONCENTRATION RUNS

STATUS DATE _____

ABSTRACT

Measurements of potassium vapor pressure over model slag ternary and quaternary systems are continuing, and a substantial effect of calcium oxide content on the potassium vapor pressure has been identified. Composition-temperature-equilibrium-activity correlations have been developed for several binary and ternary slag-related mixed oxide systems; five papers based on these results have been accepted for publication.

I. OBJECTIVE AND SCOPE OF WORK

The objective of this task is the measurement and interpretation of vapor pressures over high-temperature oxide systems and the thermodynamic analysis of these systems. The systems under study are primarily synthetic mixtures, actual slags, and seeded slags. The measurements are performed by using atomic absorption to measure atom concentration produced by diffusion from vapor pressure cells in high-temperature graphite tube furnaces (Woodruff furnaces). The interpretation is designed to provide accurate equations for vapor pressure and activity in multi-component systems for use in engineering design work where slags are encountered in MHD.

II. SUMMARY OF PROGRESS TO DATE

Model slag ternary, quaternary, and five-component samples of the mixed oxides of potassium, calcium, aluminum, silicon, and iron were prepared. Potassium vapor pressure measurements were carried out over K_2O - CaO - SiO_2 and K_2O - CaO - SiO_2 - Al_2O_3 samples. Potassium vapor pressure was found to increase with potassium oxide mole fraction, as expected; it also increases at constant K_2O content when the calcium oxide content increases.

Calcium vapor pressure measurements showed saturation effects probably due to the formation of calcium carbide of long-term stability.

Thermodynamic analyses of the above model slag systems as well as systems containing, in addition to the above, sodium oxide have resulted in elucidation of the phase diagrams, equilibria, vapor pressure-temperature-composition relations, and other thermodynamic parameters of these model slag systems. The results are being published in five papers.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Vapor Pressure Measurements

1. Synthetic Slag Sample Preparation

Ternary samples ($KO_{0.5}$ - CaO - SiO_2), quaternary samples ($KO_{0.5}$ - SiO_2 - $AlO_{1.5}$ - CaO), and five component samples ($KO_{0.5}$ - SiO_2 - $AlO_{1.5}$ - CaO - $FeO_{1.5}$)

were prepared during this period. The materials and procedures for making these synthetic slags, with the exception of iron-containing ones, were described in the April to June quarterly report of this task. The iron-containing samples were made from the same materials with the addition of ferric oxide (Fe_2O_3), a Baker Reagent Grade chemical.

A new procedure for grinding samples in a ball mill was developed. This type of grinding would eliminate any uncertainty in the homogeneity of hand-ground samples. Duplicate samples (KSAC #6, 9, and 13) were prepared by machine-grinding to enable comparison of vapor pressure measurements for the same samples with different grinding procedures.

The mole fraction compositions of the various samples prepared are shown in Table 1.* As is apparent from the table, the compositions cover several sets of variations in one of the components while keeping other components or ratios constant.

2. Potassium Vapor Pressures Over Ternary and Quarternary Synthetic Slag Model Systems

As can be seen from Table 1, our initial approach to the model slag three- and four-component systems covers a wide range of compositions. Thus, the results reported for this quarter serve as a preliminary survey intended to point out identified trends. The measurements on both systems are still in progress and are still being checked.

The data obtained thus far on eight ternary model slag samples and ten quarternary samples are summarized in Tables 2 and 3. Figures 1 through 5 show the dependence of potassium vapor pressure on temperature and sample composition. Figures 6, 7, and 8 show the variation of potassium pressure as a function of the mole fraction of CaO at 1700 K for several ternary and quarternary samples. These results have been obtained in platinum cups using experimental procedures described in previous reports.

Table 2 and Figure 1 summarize the results to date on eight samples in the $\text{CaO-SiO}_2\text{-K}_{0.5}$ system. Figure 2 shows the increase of potassium vapor pressure with increasing potassium oxide mole fraction at constant $(x_{\text{CaO}}+x_{\text{SiO}_2})$ ratio. Figures 3 and 6 show that the potassium vapor pressure also increases at constant K_2O content when the CaO content increases.

*The compositions for KSAC #1-5 (see April to June quarterly report of this task) have been recalculated and the corrected values are given in this report.

A similar trend in the quaternary system is indicated by the results shown in Table 3 and Figures 4, 5, 7, and 8. Figure 4 shows the potassium vapor pressures for a series of samples in which the ratio of x_{K_2O} to $(x_{Al_2O_3} + x_{SiO_2})$ is kept constant, while the CaO content increases. Figure 5 shows potassium vapor pressures over a set of samples in which $x_{Al_2O_3}$, x_{SiO_2} , and $(x_{CaO} + x_{K_2O})$ are constant, while potassium oxide is replaced by CaO. Figures 7 and 8 show the effect of CaO on potassium vapor pressure at a constant temperature (1700 K).

While no attempt to obtain quantitative relations from these data has been made as yet, the influence of the CaO content and its ratio to other components on the potassium activity in these systems is apparent.

The measurements of both the ternary and quaternary systems, using existing as well as new samples, are to be continued for some time. Measurements of potassium vapor pressures over five-component, iron-containing samples are being started. The possibility of measuring iron vapor pressures, either alone or simultaneously with potassium, is being explored.

3. Calcium Vapor Pressure Measurements

Attempts at measuring calcium vapor pressure have shown that calcium saturation effects exist in the graphite furnace. Calcium carbide is apparently stable enough to remain stored in the graphite tubes and insulation for long periods of time. Enough calcium vapor is released into the optical path at high temperatures to absorb most of the calcium light from the hollow cathode tube. Additional studies therefore are necessary before calcium vapor pressures can be measured.

B. Thermodynamic Analysis

The thermodynamic analysis of MHD-related mixed oxide systems during this period has resulted in five papers which have been accepted for publication. They deal with model slag systems containing potassium oxide, silicon oxide, aluminum oxide, calcium oxide, and sodium oxide. These papers provide binary and ternary phase diagrams, equilibrium constants, free energy, enthalpy and heat capacity correlations, and activity data as a function of composition and temperature. Further details are contained in Appendices A through E.

IV. CONCLUSIONS

The experimental results on three-component and four-component model slag systems containing calcium oxide clearly indicate that the vapor pressure of potassium is substantially affected by the presence of calcium oxide as detailed in the previous section. Since the calcium oxide content is one of the main differences between Western and Eastern coals, the choice of either of these coals for MHD power generation should take into account

the results which have been obtained in this study.

The theoretical thermodynamic analysis now is providing correlations between composition, temperature, and vapor pressures for slag model systems of three- and four-components which should approach the behavior of real slags and, therefore, should be useful in the design of slag-seed separation components of the MHD system and other MHD components where slag interactions are substantial.

Table 1.--Composition data for three- four- and five-component synthetic slag samples used for vapor pressure measurements

Ternary samples ($\text{K}_0.5\text{-CaO-SiO}_2$)

<u>Sample Designation</u>		<u>Sample Composition</u>			
KSC#	$x_{\text{K}_0.5}$	x_{CaO}	x_{SiO_2}	$x_{\text{CaO}}/(x_{\text{CaO}}+x_{\text{SiO}_2})$	
1	.05	.32	.63	.34	
2	.10	.30	.60	.33	
3	.15	.38	.57	.50	
4	.20	.27	.53	.34	
5	.10	.18	.72	.20	
6	.20	.16	.64	.20	
7	.10	.36	.54	.40	
8	.20	.32	.48	.40	

Quarternary samples ($\text{K}_0.5\text{-SiO}_2\text{-AlO}_{1.5}\text{-CaO}$)

KSAC#	$x_{\text{K}_0.5}$	x_{SiO_2}	$x_{\text{AlO}_{1.5}}$	x_{CaO}	$x_{\text{SiO}_2}/x_{\text{AlO}_{1.5}}$	$x_{\text{CaO}}/(x_{\text{CaO}}+x_{\text{SiO}_2}+x_{\text{AlO}_{1.5}})$
1	.01	.396	.396	.198	1.0	.2
2	.022	.390	.392	.196	1.0	.2
3	.048	.038	.381	.191	1.0	.2
4	.079	.368	.369	.184	1.0	.2
5	.117	.353	.353	.177	1.0	.2
19	.200	.320	.320	.160	1.0	.2
20	.300	.280	.280	.140	1.0	.2

Table 1.--Continued

Quarternary Samples, (Continued)

KSAC#	$x_{K0.5}$	x_{SiO_2}	$x_{AlO_{1.5}}$	x_{CaO}	$x_{K0.5} / (x_{AlO_{1.5}} + x_{SiO_2})$	$x_{SiO_2} / x_{AlO_{1.5}}$
6	.23	.36	.36	.05	.319	1.0
7	.22	.34	.34	.10	.323	1.0
19	.20	.32	.32	.16	.312	1.0
8	.16	.27	.27	.30	.296	1.0
9	.14	.23	.23	.40	.302	1.0
					$(x_{K0.5} + x_{CaO})$	$x_{SiO_2} / x_{AlO_{1.5}}$
10	.31	.32	.32	.05	.36	1.0
11	.26	.32	.32	.10	.36	1.0
19	.20	.32	.32	.10	.36	1.0
12	.10	.32	.32	.26	.36	1.0
13	.05	.32	.32	.31	.36	1.0
					$x_{SiO_2} / x_{AlO_{1.5}}$	$x_{CaO} / (x_{CaO} + x_{SiO_2} + x_{AlO_{1.5}})$
14	.05	.51	.25	.19	2.0	.2
15	.10	.48	.24	.18	2.0	.2
16	.20	.42	.21	.16	2.0	.2
17	.30	.37	.19	.14	2.0	.2
18	.40	.32	.16	.20	2.0	.2

Five Component Samples ($K0.5-SiO_2-AlO_{1.5}-CaO-FeO_{1.5}$)

KSACF#	$x_{K0.5}$	x_{SiO_2}	$x_{AlO_{1.5}}$	x_{CaO}	$x_{FeO_{1.5}}$
1	.079	.33	.33	.17	.086
2	.119	.32	.32	.16	.087
3	.202	.28	.28	.14	.089
4	.304	.24	.24	.12	.089

Table 2.--Potassium vapor pressure over potassium oxide-
calcium oxide-silicon oxide samples

Sample	$X_{K_2O} : X_{CaO} : X_{SiO_2}$	Temperature K	$(1/T) \times 10^4$ K^{-1}	Pressure $\times 10^6$ atm.
KCS 4	0.20 : 0.27 : 0.53	1416	7.063	0.147
		1538	6.503	1.781
		1649	6.063	11.59
		1701	5.878	31.65
		1595	6.270	3.755
		1416	7.063	0.171
		1538	6.503	1.781
KCS 6	0.20 : 0.16 : 0.64	1538	6.502	0.679
		1649	6.063	4.675
		1751	5.712	25.94
		1701	5.878	11.47
		1595	6.270	1.947
		1649	6.063	4.392
		1538	6.503	0.754
KCS 8	0.20 : 0.32 : 0.48	1538	6.503	4.563
		1416	7.063	0.446
		1478	6.765	1.578
		1595	6.270	10.33
		1538	6.503	4.135
		1416	7.063	0.431
KCS 1	0.05 : 0.32 : 0.63	1416	7.063	0.049
		1538	6.503	0.224
		1649	6.063	0.772
		1751	5.712	3.268
		1701	5.878	1.724
		1538	6.503	0.196
KCS 2	0.10 : 0.30 : 0.60	1416	7.063	0.087
		1538	6.503	0.481
		1649	6.063	2.362
		1751	5.712	10.94
		1701	5.878	5.243
		1595	6.270	1.049
		1538	6.503	0.462
KCS 3	0.15 : 0.38 : 0.57	1416	7.063	0.107
		1538	6.503	0.660
		1649	6.063	4.490
		1701	5.878	10.66
		1595	6.269	1.516
		1538	6.503	0.651
		1416	7.063	0.067
		1649	6.063	4.298

Table 2.--Continued

Sample	$X_{K_2O} : X_{CaO} : X_{SiO_2}$	Temperature K	$(1/T) \times 10^4$ K^{-1}	Pressure $\times 10^6$ atm.
KCS 5	0.10 : 0.18 : 0.72	1416	7.063	0.093
		1538	6.502	0.6219
		1649	6.062	2.703
		1751	5.712	16.44
		1538	6.502	0.7304
		1701	5.877	7.434
		1751	5.712	14.79
		1649	6.062	2.963
KCS 7	0.10 : 0.36 : 0.48	1416	7.063	0.0156
		1538	6.502	0.3988
		1649	6.062	5.377
		1751	5.712	25.86
		1701	5.877	11.39
		1595	6.270	1.583
		1538	6.502	0.6855
		1751	5.712	22.88

Table 3.--Potassium vapor pressure over potassium oxide-calcium
oxide-aluminum oxide-silicon oxide samples

Sample	$X_{K_2O} : X_{CaO} : X_{Al_2O_3} : X_{SiO_2}$	Temp. K	$(1/T) \times 10^4$ K^{-1}	Pressure $\times 10^6$ atm.
KCAS 5	0.12 : 0.18 : 0.353 : 0.353	1751	5.712	11.53
		1701	5.878	4.94
		1538	6.502	.361
		1650	6.062	1.969
		1751	5.712	10.97
		1538	6.502	.187
		1751	5.712	12.58
		1701	5.878	5.21
		1649	6.062	1.733
		1797	5.564	27.14
		1701	5.878	5.378
KCAS 6	0.23 : 0.05 : 0.36 : 0.36	1797	5.564	22.49
		1650	6.062	2.485
		1751	5.712	9.864
		1701	5.878	3.713
		1649	6.062	1.729
		1797	5.564	20.94
KCAS 7	0.22 : 0.10 : 0.34 : 0.34	1751	5.712	17.00
		1797	5.564	35.66
		1649	6.062	2.859
		1701	5.878	6.984
		1797	5.564	34.68
		1750	5.712	14.20
		1649	6.062	3.071
KCAS 8	0.16 : 0.30 : 0.27 : 0.27	1416	7.062	.355
		1650	6.062	42.5
		1538	6.502	4.875
		1595	6.269	13.31
		1478	6.765	1.289
		1538	6.502	4.517
		1649	6.062	35.23
		1595	6.269	11.46
		1478	6.765	1.167
KCAS 9	0.14 : 0.40 : 0.23 : 0.23	1416	7.062	.251
		1649	6.062	57.98
		1538	6.502	7.21
		1478	6.765	2.045
		1595	6.269	21.10
		1650	6.062	53.67
		1538	6.502	6.656
		1478	6.765	1.763

Table 3.--Continued

Sample	$X_{K_2O} : X_{CaO} : X_{Al_2O_3} : X_{SiO_2}$	Temp. K	$(1/T) 10^4$ K ⁻¹	Pressure x 10 ⁶ atm.
KCAS 19	0.20 : 0.16 : 0.32 : 0.32	1751	5.712	41.35
		1797	5.564	100.81
		1701	5.878	19.71
		1650	6.062	7.60
KCAS 10	0.31 : 0.05 : 0.32 : 0.32	1416	7.062	0.503
		1650	6.062	29.2
		1538	6.502	4.537
		1701	5.878	66.62
		1650	6.062	25.3
		1595	6.269	10.0
		1416	7.062	0.714
KCAS 11	0.26 : 0.10 : 0.32 : 0.32	1538	6.502	1.59
		1751	5.712	101.0
		1650	6.062	17.94
		1701	5.877	46.41
		1595	6.269	5.095
		1751	5.712	87.228
		1538	6.502	1.623
KCAS 12	0.10 : 0.26 : 0.32 : 0.32	1751	5.712	20.46
		1797	5.564	43.99
		1650	6.062	3.38
		1701	5.877	5.49
		1797	5.564	43.02
		1701	5.877	7.45
KCAS 13	0.05 : 0.31 : 0.32 : 0.32	1650	6.062	15.38
		1751	5.712	90.30
		1701	5.877	43.43
		1797	5.564	184.9
		1595	6.269	6.60
		1701	5.878	37.52
		1751	5.712	76.84
		1797	5.564	154.70

Figure 1.--Vapor Pressure of Potassium Over Ternary Synthetic Slag
Model System K_2O - CaO - SiO_2

Figure 2.--Vapor Pressure of Potassium at Constant $X_{\text{K}_{0.5}}$ Over Ternary System $\text{K}_{0.5}\text{-CaO-SiO}_2$

Figure 3.--Vapor Pressure of Potassium at Constant $x_{CaO}/(x_{CaO}+x_{SiO_2})$
Over Ternary System K_{0.5}-CaO-SiO₂

Figure 4.--Vapor Pressure of Potassium at constant $x_{K0.5} / (x_{SiO_2} + x_{AlO_{1.5}})$ Over Quaternary Synthetic Slag Model System $K0.5-CaO-AlO_{1.5}-SiO_2$

Figure 5.--Vapor Pressure of Potassium at Constant x_{SiO_2} and $x_{AlO_{1.5}}$ Over Quaternary

System $K_{0.5}$ - CaO - $AlO_{1.5}$ - SiO_2

Figure 6.--Potassium Vapor Pressure as a Function of Calcium Oxide Mole Fraction for System $\text{K}_{0.5}\text{-CaO-SiO}_2$ at 1700 K and Constant $X_{\text{K}_{0.5}}$

Figure 7.--Potassium Vapor Pressure Dependence on Mole Fraction of Calcium Oxide for System $\text{K}_{0.5}\text{-CaO-Al}_{0.5}\text{-SiO}_2$ at 1700 K and Constant $(X_{\text{K}_{0.5}} + X_{\text{CaO}})$

Figure 8.--Potassium Vapor Pressure as a Function of Mole Fraction of Calcium Oxide for System $K_{0.5}-CaO-Al_{0.5}-SiO_2$ at 1700° K and Constant

$$x_{K_{0.5}} / (x_{Al_{0.5}} + x_{SiO_2})$$

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APPENDIX A

THE ENTHALPY OF SODIUM SILICATE GLASSES AND LIQUIDS

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ABSTRACT

The enthalpy data of Hummel and Schwiете (1) for sodium silicate glasses at 298.15 K have been fitted by power series in the mole fraction. It is shown that four coefficients provide an excellent fit of the data ($X_1 = .1818$ to $.6667$) but five are required for a reasonable extrapolation to pure $\text{NaO}_{.5}(\text{X}_1=1)$. If estimates for the partial molal enthalpy of SiO_2 are included in the least squares, the equation also extrapolates well to pure SiO_2 . Combining these values with the expressions for the excess heat capacity of mixing (2) and known solubility data (3,4) for the binary system, one obtains a consistent set of coefficients for the calculation of enthalpies and activities at any temperature and composition. The $\text{NaO}_{.5}\text{-SiO}_2$ phase diagram calculated from these values is shown.

Introduction

It is well known that any of a number of equivalent power series (Margules (5), Redlich-Kister (6,7) and Bale-Pelton (8)) can represent the properties of nearly ideal binary systems over the full range of compositions with one to three terms. At the other extreme one finds systems where the chemical interactions are so substantial for some particular stoichiometry that it is reasonable to reclassify the compound as a component. The requirement for this approach is that the activity of each species approach a value very close to zero as its mole fraction approaches zero. Thus one may treat liquid sodium oxides as the $\text{NaO}_{.5}\text{-O}$ system instead of Na-O since the equilibrium O_2 pressure for stoichiometric $\text{NaO}_{.5}$ is very small compared to the observed pressure with even one mole percent of sodium peroxide in the liquid. For the large number of binary and pseudobinary systems lying between these extremes one can represent the data accurately with either separate two term expressions (subregular) for different concentration ranges, or by increasing the number of terms used in the power series. Our initial expectation was that it might take as many as seven or eight terms for silicate liquids and glasses. There are very substantial acid-base interactions in the $\text{NaO}_{.5}\text{-SiO}_2$ system, but we have found nevertheless that the enthalpy and activity data for this system are quite accurately represented by five term Redlich-Kister equations. We have previously shown (2) that the excess heat capacity of mixing in this system can be represented by a single temperature dependent coefficient

$$A(C_p) = 6.8 - .0194 (T - 1000) + 13.8 \times 10^{-6} (T - 1000)^2$$

This paper is concerned with the more substantial deviations from ideality shown in the enthalpy and activity data for this system.

Enthalpy

Solid sodium silicates are known with three well characterized stoichiometries, Na_4SiO_4 , Na_2SiO_3 , and $\text{Na}_2\text{Si}_2\text{O}_5$. The formation of each of these solids from the separate solid oxides is a highly exothermic reaction. For example $\Delta H = -238.03 \text{ kJ mol}^{-1}$ for the reaction

This large exothermicity is due to the strong acid base interaction present and persists in the liquid and glass states.

The preparation of sodium silicate glasses is not difficult, and a substantial quantity of enthalpy data is available from the heats of solution of the glasses. Many of the glasses are soluble in water or dilute HF (9,10), however the hydrolysis of Si-O-Si linkages is slow in

Figure 1. Excess enthalpy of mixing at 298 K in $\text{NaO}_5 - \text{SiO}_2$ glasses. The solid line is from the final calculation with five Redlich-Kister coefficients. A preliminary three term calculation is shown as a dotted line. The experimental or tabulated values are: dark circles-Hummel and Schwiete (1); open circles-Kracek and JANAF (22, 23); diamonds-Takahashi and Yoshio (10); squares-Matveev and Zhuravlev (24). The triangles show the corresponding values for crystalline solids which give a lower limit for values for the glasses.

dilute HF, and the solution obtained may not be in equilibrium unless a temperature well above 298K or an HF concentration of at least 15% is used. Thus, the recent work of Takahashi and Yoshio (10) is of limited validity, and the best data over a substantial range of compositions is that of Hummel and Schwiete (1). This is illustrated by the relative amounts of scatter shown by the different points plotted in figure 1. Values for the excess enthalpy of mixing at 298.15 K are available from Hummel and Schwiete for 9 glasses with mole fractions of NaO_5 from .1818 to .6667. These can be fitted accurately with either three or four Redlich-Kister coefficients. The three term least squares gave the values $A(H) = -265743$, $B(H) = -274109$ and $C(H) = -180944 \text{ J mol}^{-1}$. This set of coefficients shows a large amount of curvature for H_2 below the first experiment point, X_1 from 0 to .1818, and it is necessary to add an additional constraint to avoid values for the partial molal enthalpies which are too negative for NaO_5 and too positive for SiO_2 .

Good values for the partial molal enthalpy of SiO_2 can be estimated from the temperature dependence of the activity coefficient of SiO_2 from points on the cristobalite liquidus above 1744K down to temperatures around 1120K where immiscibility is observed in metastable sodium silicate glasses (11-13). Our initial estimate was $H_2 - H_2^0 = 1700 \text{ J mol}^{-1}$ for SiO_2 at a mole fraction of 0.2 and 1350K. Using our values (2) for the excess heat capacity in this system, based on a substantial body of heat capacity data (9, 14-17) this can be corrected to a partial molal enthalpy of $H - H^0 = 954 \text{ J mol}^{-1}$ for SiO_2 at 298.15K and a mole fraction of 0.2 for NaO_5 . Adding this value heavily weighted to the least squares fit of Hummel and Schwiete's excess enthalpy values (1) gave the three Redlich-Kister coefficients listed in the second line of Table 1, with the only substantial change being a less negative value for $C(H)$. These enthalpy values corrected to higher temperatures were used to correct all the $\log \gamma$ values from solubility measurements (3,4) to a standard temperature of 1000K. These $\log \gamma_{1000}$ values were then fitted with a four term Redlich-Kister expansion, which combined with the

enthalpy and heat capacity values gave a fairly good calculated phase diagram. A successive approximation procedure was used to improve the fit. The $A(\log \gamma)$ at 1120 K was adjusted to give a critical point at this temperature, and these values were used to obtain $\log \gamma_{\text{Na}}$ values for five compositions from $X = .04736$ to $.2423$ where high temperature values were available from Kracek's phase diagram work (3,4). Enthalpy values at 298K were then calculated for SiO_2 at these five compositions, and put into the least squares calculation for the enthalpy, with the results shown in the third line of Table 1. This iteration procedure can give good enthalpy values and good $\log \gamma$ values at the liquidus temperature. However it does not converge to values showing immiscibility at 1120K, and the parameters obtained do not extrapolate well to the region of mole fractions above $X_1 = 0.8$.

For example, calculating the liquidus for Na_4SiO_4 from $X_1 = .72$ to $.80$ requires and gives a good value of enthalpy of the solid orthosilicate. Comparing this value with the calculated enthalpy for a liquid with $X_1 = .90$, indicates that a mixture of solid NaO and solid Na_4SiO_4 would have a negative heat of fusion. This problem arises from doing a four term least squares for the enthalpy with no experimental values above $X = .667$. It is easily solved by adding a value for the excess enthalpy of mixing in the liquid at $X_1 = .90$ chosen to agree with an estimate for the enthalpy for solid Na_4SiO_4 . This was done together with new values for H_2 in the SiO_2 rich region in the second refinement cycle, giving the set of five Redlich-Kister coefficients in the fourth line of Table 1.

The main function of the fourth and fifth terms in the power series is to give improved H_2 values because the calculated phase diagram is extremely sensitive to changes in H_2 values which can be as

Figure 2. Excess enthalpy and partial molal enthalpies at 1000K for $\text{Na}_{0.5} - \text{SiO}_2$ liquids.

Table 1. Redlich-Kister coefficients for enthalpy (J mol^{-1}) for $\text{Na}_{0.5} - \text{SiO}_2$ liquids and glasses. All the values are for 298.15K, except for the last line.

	A(H)	B(H)	C(H)	D(H)	E(H)
Reference 1 alone	-265743	-274109	-180944		
Ref. 1 with $H_2=794$	-256262	-267102	-129763		
First iteration	-265135	-265031	-200279	-68601	
Second Cycle	-267914	-279783	-143977	121961	136828
Final Calculation	-268420	-253068	-105023	81902	71543
Same at 1000 K	-256232	-253068	-105023	81902	71543

small as 100 J. Thus, the calculation is extremely sensitive to the values used for $\log \gamma_2$ at 1120 K, and the successive approximation procedure outlined above does not give uniformly good convergence. Instead, equations in the Redlich-Kister coefficients were developed

$$.509735 = .296A - .625152B + .584214C - .407632D + .210406E$$

$$.598281 = 2A - 2.448B - 1.053824C + 4.271867D - 5.970533E$$

to insure zero slope and zero second derivative at a mole fraction of $X_1 = .148$ in a plot of a_2 vs. X_1 . With these two equations, activity curves with immiscibility just occurring at $X_2 = .148$ can be obtained over a wide range of γ_1 values, and $\log \gamma_2$ may vary between about 0.04 and 0.08. From the experimental data (3,4) on the cristobalite liquidus we know $\log \gamma_2 = .051728$ at 1827K and $X_1 = .15329$. It appears that the only solution to the high temperature immiscibility problem is to insist that $\log \gamma_2$ at 1120K and $X_1 = .15329$ be larger, $\log \gamma_2 = .056$ for instance. Using the two equations above and the additional requirements that $\log \gamma_2 = .056$ and $\log \gamma_1 = -5.2$ at $X = .15329$ gave a good set of $\log \gamma_2$ values for 1120K. H_2 values were calculated from these, and included in the least squares calculation, giving the Redlich-Kister coefficient for enthalpy shown in the fifth and sixth lines of Table 1.

The calculated enthalpy values for these coefficients are plotted in Figures 1 and 2, which demonstrate how well a five term power series can fit the expected behavior for H_2 of two approximately linear regions meeting in a minimum with substantial curvature near the orthosilicate composition. The three term expression from line 2 of Table 1 also shows this general behavior quite well as shown by the dotted line in Figure 1.

Logarithm of Activity Coefficients

In the final least squares calculation of the enthalpy coefficients, the calculated H_2 values were weighted very heavily compared to the H_2 values from reference 11 and the estimated value for $X = .90$. With these enthalpy values, all the activity coefficient data from the liquidus curves could be corrected to a common temperature of 1000K. The corrected values were then included in a common least squares calculation constrained to give zero slope and zero second derivative in $\log a_2$ vs X at $X = .148$ and 1120K. In order to come close to fitting $\log \gamma_2$ values (of the order of 0.1) along with large negative $\log \gamma_1 \gamma_2$ values (between -11 and -12), high relative weights, 100 to 1000, were assigned to the $\log \gamma_2$ values. The final least squares calculation also reduced the weight given to the point at $X = .0473$. Also zero weight was assigned to all the $\log \gamma_1 \gamma_2$ points from the $\text{Na}_2\text{Si}_2\text{O}_5$ liquidus, because the entropy value for this solid appeared to be in error by approximately $5 \text{ J mol}^{-1}\text{K}^{-1}$. In addition the value from the melting point of Na_2SiO_3 , $X = .66667$, was weighted 20 times as heavily as the other points on this liquidus. Table 2 shows the full set of Redlich-Kister coefficients obtained for the $\text{NaO}_{.5}\text{-SiO}_2$ system in this weighted, constrained least squares procedure. The justification for the relative weights assigned to the different kinds of data

Table 2. Redlich-Kister coefficients for three phases in the $\text{NaO}_{.5} - \text{SiO}_2$ system. All values are for 1000 K in SI units (J, mol, and K).

		A	B	C	D	E
Liquid	$\log \gamma$	-12.285423	-11.389696	-5.971358	-.944872	.697897
	enthalpy	-256232	-253068	-105023	81902	71543
	C_p	28.45				
	dC_p/dT	.08117				
	d^2C_p/dT^2	.00011548				
Tridymite	$\log \gamma$	-4.2841				
	enthalpy	-88297				
Na_4SiO_4	$\log \gamma$	-9.06884	-19.34282			
	enthalpy	-222588	-254905

Figure 3. Calculated phase diagram for the $\text{NaO}_5 - \text{SiO}_2$ system, compared with the experimental points of Kracek (3, 4). The region of metastable immiscibility in $\text{NaO}_5 - \text{SiO}_2$ glasses is shown with a dotted line.

is the accuracy with which the entire set of phase diagram data can be fitted. This agreement is shown in Figure 3. The solid lines are calculated curves using the Redlich-Kister coefficients from Table 2 for the liquid phase, and for two solid phases of variable composition, tridymite and Na_4SiO_4 . The degree of agreement with the experimental values of Kracek (3,4) shown as circles in Figure 3 is clear. The calculated region of immiscibility in metastable glasses is shown with a dotted line in Figure 3. This has the correct general shape found experimentally (11-13) with a maximum at $X = .148$ and 1120K as required by the constraints in the least squares calculation. The thermodynamic values used for the SiO_2 phases (liquid, cristobalite, tridymite, and quartz) are those chosen in connection with our treatment of the $\text{KO}_5 - \text{SiO}_2$ system (18). The Redlich-Kister coefficients for NaO_5 in tridymite are those necessary to give the quartz-tridymite and tridymite-cristobalite equilibria at 1143 and 1743K respectively, as reported by Kracek (3).

Kracek's interpretation of the Na_4SiO_4 data as incongruent melting at 1396K is suspected, since there is no reasonable solid phase which could be formed at this temperature. The alternative explanation of the observations used for Figure 3 is that excess SiO_2 can be accommodated in the Na_4SiO_4 crystals so that there is a very broad maximum around a congruent melting point at 1396K. Two Redlich-Kister coefficients can be evaluated from the activities of solid NaO_5 and SiO_2 at a single temperature, and this was done at 1295K and 1396K to obtain the values shown for this phase in Table 2. The reference states used are solid NaO_5 and cristobalite. The properties of Na_4SiO_4 can be calculated over a range of temperature and compositions from the values in Table 2, and the calculation for $X = .8$ is the basis for the values tabulated in Table 3 for the pure stoichiometric orthosilicate.

Table 3. Thermodynamic properties for the pure materials in SI units. The equation used for C_p ($J mol^{-1} K^{-1}$) is $C_p = a + b(T-1000) + c(T-1000)^2 + d(T-1000)^3$.

Material	$H^\circ_{298.15}$	H°_{1000}	Φ°_{1000}	a	10^3b	10^6c	10^9d
NaO _{1.5} (s)	-208991	-178983	57.6764	47.360	7.387	-2.158	
(l)	-185539	-155415	74.3020	47.907	7.531		
SiO ₂ (quartz)	-910857	-865502	70.7054	68.952	10.042		
(cristobalite)	-905489	-863578	75.7756	69.964	8.593	-6.911	2.704
(tridymite)	-907928	-863714	73.3284	69.964	8.593	-6.911	2.704
(l)	-902656	-859389	76.0509	69.496	13.501	5.181	
Na ₂ Si ₂ O ₅ (s, A)	-2471614	-2318258	268.3676	228.446			
(s, B)	-2477723	-2324367	262.1334	228.446			
Na ₂ SiO ₃ (s)	-1561427	-1457798	182.1755	169.127	43.100	-8.929	
Na ₄ SiO ₄ (s)	-2041877	-1879935	343.5010	259.102	38.140	-15.542	2.704

We do not expect the Redlich-Kister coefficients for NaO_{1.5}-SiO₂ liquids to extrapolate well for X_1 values over 0.8, just as the enthalpy least squares were too negative in this region until the estimate for $X = .9$ was included in the calculations. Thus, Figure 3 does not extend above $X = 0.87$.

It has been customary (19-20) to represent activity data in this system in a plot of a_{SiO_2} vs. composition. The equations used here can be applied at any temperature and composition so that graphical interpolation is no longer necessary. Nevertheless this graph in Figure 4 is shown to allow a comparison of our results with earlier work. The calculations of Callow (20) are substantially in error at low silica, because the rate of vaporization data of Preston and Turner (21) on which this calculation was based are not highly reliable. In this region our calculation is in excellent agreement with that of Charles (11), because both are using the JANAF (22) data for Na₂SiO₃. At high silica, our values agree better with those of Callow (20), primarily because Charles (11) has used a molecular weight of 61.979 for dissolved sodium oxide, and therefore an initial slope which is half of that for the other two calculations.

Thermodynamic Values for Solid Phases

One of the byproducts of a computer calculation of a phase diagram is the confirmation or improvement in the values for the various solid phases involved. As noted above the values for tridymite are those used in our treatment of the KO_{1.5}-SiO₂ system (18). The very narrow tridymite region in Figure 3 is the correct behavior with these parameters; however, our published KO_{1.5}-SiO₂ diagram (18) used earlier, less accurate values for the free energy function of tridymite.

The points on the Na₂Si₂O₅ liquidus were omitted from the least squares treatment for $\log \gamma$ because of uncertainty in the entropy of this solid. The values adopted to give the fit in Figure 3 correspond to $S^\circ = 169.314 J mol^{-1} K^{-1}$ at 298K, only slightly outside the JANAF (22) reported range of 164.055 ± 4.2 .

We initially selected the enthalpy data of Hummel and Schwiete (1) for solid Na₂SiO₃, but we found early in the calculations that the value of Kracek (23) selected in JANAF (22) gave a better fit of the shape of the Na₂SiO₃ liquidus. Figure 1 also shows that Kracek's (23) enthalpies for the glass, shown as open circles, are in slightly better agreement with our calculated line than are the points of Hummel and Schwiete (1) which were used in the least squares procedure. By weighting the Na₂SiO₃ melting point in the least squares calculation rather heavily, we obtained a good fit for this liquidus with no change in the thermodynamic properties for solid Na₂SiO₃ from those in the JANAF tables (22). Table 3 summarizes the thermodynamic data used for the pure solids and liquids in the binary system. The enthalpy of the glass at 298K should be more positive than that of crystals at each composition. The enthalpies of the solids at 298K relative to the pure liquids are plotted as triangles in Figure 1 to facilitate this comparison. All the heats of fusion at 298K are in the range of 7 to 24 kJ mol⁻¹.

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Figure 4. Calculated curves for the activity of liquid SiO_2 at 1673 K as a function of the percentage of SiO_2 by weight. The solid line calculated in this work is compared with earlier calculations of Callow (20) -the dashed line- and Charles (11) -shown with long and short dashes.

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APPENDIX B

THE THERMODYNAMIC PROPERTIES OF MULLITE

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ABSTRACT

Mullite can be considered as a solution of cristobalite in corundum, and with these reference states the activities of SiO_2 and $\text{AlO}_{1.5}$ can be expressed as functions of temperature and mole fraction using equations of the Redlich-Kister form.

The Redlich-Kister coefficients are evaluated from experimental data on sillimanite and mullite. They can be used to calculate the mole fractions and SiO_2 activities for mullite saturated with corundum ($X_1=.7702$, $a_1=1.000$, $a_2=.4221$ at 2123 K). These calculations suggest that mullite is not saturated with corundum at its incongruent melting point, $X_1=.7508$, 2123 K. It is proposed that mullite melts incongruently to liquid and a high-temperature form of alumina in which SiO_2 is appreciably soluble. This suggestion is shown to reconcile apparently contradictory data on the $\text{AlO}_{1.5}$ - SiO_2 system, and a new phase diagram is calculated using Redlich-Kister coefficients for mullite, liquid, and gamma alumina phases.

INTRODUCTION

Mullite is the major compound formed in the $\text{AlO}_{1.5}\text{-SiO}_2$ system at atmospheric pressure and temperatures of 1500-2000 K. Thus, it is of great importance in a variety of ceramic systems, and it is important to know its thermodynamic properties accurately. While the nominal formula $\text{Al}_6\text{Si}_2\text{O}_{13}$, corresponding to $X_{\text{AlO}_{1.5}} = .75$, falls within the range of easily prepared mullite crystals, forms with both more and less $\text{AlO}_{1.5}$ are well known.

Crystals with X_1 approximately .80 can be grown from $\text{AlO}_{1.5}\text{-SiO}_2$ melts and sillimanite, Al_2SiO_5 , $X_1 = .66667$, has essentially the same crystal structure as mullite and can be considered as an aluminum deficient mullite. Thus, it is essential to know the thermodynamic properties over at least the range of $X_1 = .74$ to .77 found in the equilibrium phase diagram,¹ and it is desirable to have accurate values which cover a range of metastable compositions down to $X_1 = .66667$ and up to $X_1 = .80$. We wish to show in this paper that the enthalpy and free energy of mullite can be represented quite accurately over this range of compositions by a three term Redlich-Kister^{2,3} expansion. We have used these values in a quantitative consideration of the phase equilibria in the $\text{AlO}_{1.5}\text{-SiO}_2$ system, and show how it is possible to reconcile the phase diagrams proposed by Bowen and Grieg,⁴ Aramaki and Roy,⁵ and Aksay and Pask¹ by the inclusion of an unstable high-temperature form of alumina in which SiO_2 is appreciably soluble.

The Redlich-Kister coefficients, A, B, C, etc., appear when the excess enthalpy of mixing, H^e , or a similar quantity is written as a power series in $X_1 - X_2$

$$H^e = H/(n_1+n_2) - X_1H_1^0 - X_2H_2^0 = X_1X_2[A + B(X_1-X_2) + C(X_1-X_2)^2 + \dots].$$

Simple equations are known for the partial molal quantities using these

same coefficients

$$\bar{H}_1 - H_1^0 = X_2^2 [A + B(-1+4X_1) + C(-1+6X_1)(-1+2X_1) + \dots];$$

$$\bar{H}_2 - H_2^0 = X_1^2 [A + B(-3+4X_1) + C(-5+6X_1)(-1+2X_1) + \dots].$$

THE ENTHALPY OF MULLITE

Mullite and sillimanite are both well studied compounds which have been included in the JANAF⁶ tables with the selection of heat capacity data of Pankratz^{7,8} and the enthalpy data of Holm and Kleppa⁹ from oxide melt calorimetry at 968 K. The heat of formation of $Al_6Si_2O_{13}$ from corundum and quartz is reported^{6,9} as $+5.44 \pm .35$ kcal mole⁻¹ at this temperature. Its formation is clearly endothermic, and mullite is only stable at high temperatures because of a favorable entropy, due primarily to the mixing of Si and Al atoms in the tetrahedral positions of the crystal lattice. The ideal mullite crystal structure has one octahedral site and two different tetrahedral sites all equally occupied with metal atoms, so the idealized formula for a mullite of $X=.75$ (called 3:2 mullite from the ratio $3Al_2O_3$ to $2SiO_2$) would be $Al_{(1/3)}Al_{(1/3)}(Al_{(1/12)}Si_{(1/4)})O_{(13/8)}V_{(1/24)}$ which would correspond to an ideal entropy of mixing of $+.3725$ or $.7597$ eu depending upon whether the necessary oxygen vacancies (indicated by V) are randomly distributed or not. This compares very favorably with the zero point entropy of $.5875$ eu (per mole of metal atoms) selected by JANAF⁶ from the SiO_2 activity in equilibrium with corundum and mullite in the $CaO-AlO_{1.5}-SiO_2$ system^{10,11} at 1823 K. This value does not really refer to $X=.75$ mullite and needs some modification as shown in the following section of this paper, but it is sufficiently accurate to indicate that the entropy should overbalance the endothermicity at least above $(5440/8)/.5875=1157$ K.

The heat capacity values for mullite selected for JANAF⁶ in the range from 1000 to 2200 K can be fitted by the power series

$$C_p = 122.6575 + .0169466(T-1000) - .94688 \times 10^{-5}(T-1000)^2 + .31801 \times 10^{-8}(T-1000)^3. \quad (1)$$

One would expect that the equilibrium disorder in a mullite crystal would increase with increasing temperature and that this would give an increased heat capacity. However, there is no clear evidence for this in the above heat capacity equation which at most temperatures gives values less than $6C_p(\text{AlO}_{1.5}, \text{corundum}) + 2C_p(\text{cristobalite})$. The heat capacity expression for mullite is apparently based upon measurements in which disorder equilibrium was not reached or even approached as the temperature was changed.

At the stoichiometry of $X=.66667$ one may have a perfectly ordered crystal with the mullite structure, $\text{Al}_{(1/3)}\text{Al}_{(1/3)}\text{Si}_{(1/3)}\text{O}_{(5/3)}$. Such a material would be classified as sillimanite, although natural sillimanites which are apparently crystallized at about 1100 K contain some Al-Si disorder, as in $\text{Al}_{(1/3)}(\text{Al}_{(1/3-Y)}\text{Si}_Y)(\text{Al}_Y\text{Si}_{(1/3-Y)})\text{O}_{(5/3)}$. Both enthalpy¹² and equilibrium¹³ measurements indicate an enthalpy increase of 15 to 16 kcal mole⁻¹ for Al-Si interchange in sillimanite, and an increase in the disorder to about $Y=.091$ as the temperature increases to 1750 K. As in the mullite case, this disorder contribution to the heat capacity is not evident in the JANAF heat capacity values.⁶ It is evident in heat of solution values for sillimanite samples which are held under pressure over 1700 K for a period of hours.¹²

Once we have enthalpy values for mullite-sillimanite structures (at $X=.75$ and $.66667$) it is possible to calculate the excess enthalpy of mixing at these compositions and to fit them with Redlich-Kister coefficients. The first step is to choose enthalpy values for the pure SiO_2 and $\text{AlO}_{1.5}$ components. It is interesting to speculate on the energy pure SiO_2 or pure $\text{AlO}_{1.5}$ would have if it assumed the mullite crystal structure, but these energies are unrealistically high and purely speculative in any case. We

can avoid grossly unrealistic extrapolations of partial molal enthalpy if we pick well known crystal structures for the pure components, and we have chosen to represent sillimanite and mullite as solid solutions of corundum in cristobalite. If we choose to use primarily the enthalpies and heat capacities selected in JANAF,⁶ the excess enthalpies of mixing at 1000 K are -529.7 calories mol⁻¹ at X=.66667 and +674.5 calories mol⁻¹ at X=.75. The same calculation at 1823 K gives -230.7 and +629.1 calories mol⁻¹. All four of these values are fitted by the Redlich-Kister coefficients

	A	B	
for enthalpy	-14345	35885.	(2)
for heat capacity	6.7	-11.6	

corresponding to the equation

$$H^e = X(1-X)[(-14385+6.7(T-1000))+(35885-11.6(T-1000))(-1+2X)] \quad (3)$$

for the excess enthalpy of formation of mullites as a function of T and X. The calculations described in this paper have been carried to completion with these Redlich-Kister coefficients.

However, the Holm and Kleppa paper⁹ on which these enthalpies are based has been superceded by more detailed studies of the enthalpy of sillimanites.^{12,14} Thus, the enthalpy of sillimanite at 974 K should be increased^{14,15} by about 1.36 kcal mol⁻¹ of Al₂SiO₅ as a result of improved calorimetry.^{14,15} Also, the heat capacity of sillimanite should be increased by $C_p = 1.175 + .0012784(T-1000)$ to allow for the calculated¹² increasing disorder with increasing temperature. Table 1 shows the revised input data for thermodynamic calculations for sillimanite in a standard form¹⁶ along with the values used for cristobalite and corundum. The other common crystalline forms of Al₂SiO₅ are included in Table 1 to facilitate the use

of Kleppa's careful enthalpy measurements^{14,15} on these species. The cristobalite and liquid SiO₂ entries are discussed in a paper on the K_{0.5}-SiO₂ system.¹⁷ The AlO_{1.5} and mullite entries will be considered later in this paper.

With the revised sillimanite and cristobalite values, the excess enthalpies for X=.66667 become -157.25 and 608.4 calories mol⁻¹ at 1000 K and 1823 K respectively.

The values for H^e at X=.75 are changed only slightly, to 607.0 and 561.6 kcal mol⁻¹ for 1000 K and 1823 K. These values give the Redlich-Kister coefficients for enthalpy and heat capacity shown in Table 2.

ACTIVITY COEFFICIENTS IN THE MULLITE PHASE

The free energy function for sillimanite at 1000 K for Table 1 is obtained by correcting the JANAF value⁶ for the calculated disorder entropy (+.35) and enthalpy (-.28 cal mol⁻¹ K⁻¹). With this value the andalusite-sillimanite equilibrium lies at 1085 K, at 1 atm pressure. This is less than 40 K above the reported¹⁸ equilibrium temperature for this transformation (1048 K), compared to an error of 580 K using the uncorrected JANAF values for sillimanite. From Table 1, we can calculate the equilibrium constant for the reaction

which is $K_{1823} = .96423 = a_1^{2/3} a_2^{1/3}$. Dividing this by $(2/3)^{2/3} (1/3)^{1/3} = .52913$ we obtain

$$\log \gamma^e = (2/3)\log \gamma_1 + (1/3)\log \gamma_2 = .26026 \quad (5)$$

at X=.66667 and 1823 K. One could do a similar computation for X=.75 using the JANAF free energy function for mullite. However, the JANAF value is

based upon a measured¹¹ cristobalite activity of .460 for a mullite saturated with corundum at 1823 K. This measurement gives us activity coefficients for both $\text{AlO}_{1.5}$ and SiO_2 for this particular composition, which is not $X=.75$. Aksay and Pask's¹ measurements of mullite apparently saturated with corundum correspond to $X=.77035$. If we assume that this value applies at 1823 K, we can readily calculate $\log \gamma_1 = .113312$ and $\log \gamma_2 = .301691$ at this temperature and composition. The three equations ($\log \gamma^e$ at $X=.66667$ and $\log \gamma_1$ and $\log \gamma_2$ at $X=.77035$) are sufficient to calculate the Redlich-Kister coefficients $A(\log \gamma_1 \text{ 1823})=3.554180$, $B(\log \gamma_1 \text{ 1823}) = -10.692984$, and $C(\log \gamma_1 \text{ 1823})=10.646443$ from which the values for 1000 K in Table 2 are calculated.

With the values in Table 2 we can calculate the activities of solid SiO_2 and $\text{AlO}_{1.5}$ in equilibrium with mullite over a range of temperatures and compositions. A very good check on the calculation is provided by calculating the composition of mullite which is saturated with pure cristobalite ($a_2=1.00$) at 1820 K. For this activity, one finds $X_1=.7422$ in excellent agreement with a variety of data including that of Aksay and Pask¹ for the compositions of silica-rich mullite. We are thus in a position to examine a variety of equilibrium reactions of mullite, including the stable and metastable melting behavior. However, before we can do this quantitatively, it is necessary to examine the thermodynamic properties of liquid $\text{AlO}_{1.5}$.

THE MELTING BEHAVIOR OF ALUMINA

There are serious difficulties in experimental work above 2200 K, so it is not surprising that there are some uncertainties in the melting point and heat of fusion of corundum. Nevertheless, these are important quantities, and a great deal of effort has been recently concentrated on the

accurate measurement of the melting point of quite pure alumina samples.¹⁹⁻²¹ On the basis of some of this work, the 1974 JANAF tables²² revised the melting point of corundum from 2318 K to 2327 K. The thermodynamic values for $\text{AlO}_{1.5}(\text{c, corundum})$ given in Table 1 are taken from this work.²² The JANAF text²² suggests further that some of the forthcoming Russian work might resolve some of the discrepancies on the heat capacity of the liquid. Averaging values which differ by $13 \text{ cal mole}^{-1} \text{ K}^{-1}$ does not instill a high degree of confidence, and it is fortunate that the suggested²² further clarification is now available.^{23,24} Shpil'rain's²⁴ work explains the problem by means of a high heat capacity for liquid $\text{AlO}_{1.5}$ in the vicinity of the melting point, so that the actual equilibrium heat of fusion is relatively small, but the enthalpy difference between the solid and a liquid 50 to 150 K hotter is quite substantial. We have accepted the heat of fusion of $12.85 \text{ kcal mol}^{-1}$ found by Shpil'rain et al.²⁴ and have used their heat capacity expression

$$C_p = 27.66 - .00296(T-1000) \text{ cal mol}^{-1} \text{ K}^{-1} \quad (6)$$

for all temperatures above 2000 K. One cannot expect this heat capacity equation to extrapolate to low temperatures, and we have arbitrarily picked 2000 K for an abrupt change in C_p , using the old JANAF value⁶ (17.312) below 2000 K. With these choices and Shpil'rain's²⁴ selection of 2323 K as the equilibrium melting point, one obtains the values summarized in Table 1, from which an equilibrium constant for the melting of $\text{AlO}_{1.5}$ can be calculated at any temperature. For example, $K_{1820} = .51683$ at the SiO_2 -mullite eutectic temperature. The original Bowen and Grieg⁴ eutectic corrected to the international temperature scale corresponds to $X = .064192$ and 1820 K. This temperature was revised upward by about 50 K by Shairer

and Bowen²⁵ on the basis of measurements in ternary systems with alkali oxide added. However, the interpretation of this data is complicated by the extensive solubility²⁶ of KAlO_2 in cristobalite and tridymite, and the original temperature is the better value. It is possible that the liquid observed by Aksay and Pask¹ at 1823 K was supercooled by over 40 K, but it is more likely that this temperature is at or above the eutectic.

THE MELTING BEHAVIOR OF MULLITE

Mullite can be crystallized directly from melts and can be melted congruently²⁷⁻³⁰ at a temperature of 2170 ± 20 K.²⁷⁻³¹ However, nearly every study where the sample was held for hours at high temperatures^{1,4,31-34} has been interpreted as incongruent melting of mullite at a lower temperature, 2123 ± 10 K. It is impossible to cite all the pertinent references and all the phase diagrams which have been proposed, but there are two major discrepancies in the data. The first concerns the position of the corundum liquidus, which either comes down not too far from the ideal solution curve to give an eutectic on the $\text{AlO}_{1.5}$ rich side of mullite^{5,27,28} or lies shifted strongly toward the SiO_2 side of the phase diagram where the experimental points of Bowen and Grieg⁴ and Aksay and Pask¹ lie. Here one is tempted to accept the diffusion couple data of Aksay and Pask¹ and ignore the alternative suggestions.

The second major discrepancy is in the work of Aramaki and Roy.⁵ They have taken the lower temperature, 2123 ± 10 K, and drawn a phase diagram in which mullite melts congruently at this temperature. This phase diagram agrees reasonably with Toropov and Galakhov^{27,28} on the position of the corundum liquidus, but the temperature discrepancy for the melting point of mullite is beyond the experimental error. Even more obviously, it conflicts strongly with all the phase diagrams which show incongruent melting for

to show that at this temperature mullite in equilibrium with pure corundum has a mole fraction $X_1 = .7702$ and a cristobalite activity of .4221. The equilibrium constant for melting of cristobalite at this temperature (calculated from data in Table 1) is 1.03755. Thus

$$a_{2,l} = 1.03755(.4221) = .4378 \quad (7)$$

$$\gamma_2 = .4378/(1-.57) = 1.0183$$

and one has an activity coefficient for SiO_2 in the liquid phase which looks reasonable, but which is inconsistent with the substantial positive deviations from ideality shown by $\text{AlO}_{1.5}\text{-SiO}_2$ liquids at the eutectic,⁴ along the mullite liquidus,^{1,32,36} and which cause liquid-liquid immiscibility at lower temperatures in metastable glasses.³⁵⁻³⁷ The discrepancy is not large, and it can be eliminated by suitable enthalpy terms for the liquid. However, this requires unrealistic partial molal enthalpies, over 30 kcal mol^{-1} , for the $\text{AlO}_{1.5}\text{-SiO}_2$ liquid system. This discrepancy can also be resolved by a substantial solubility of SiO_2 in corundum at these temperatures. However, this requires $X_2 = .10$ or greater, and this is definitely not indicated in the Aksay and Pask data,³⁸ and clearly disproved in the X-ray data reported by Aramaki and Roy.⁵ Corundum is definitely present in Aksay and Pask's diffusion couples,¹ but the possibility that it is coated with a thin layer of another solid in which SiO_2 is appreciably soluble does exist. A similar situation occurs in the Davis and Pask diffusion couples³² at 1823 and 1853 K where the corundum is coated with a layer of mullite too thin to be clearly identified in the electron microprobe analysis. Only when we finally clearly recognized this possibility was it possible to calculate a reasonable $\text{AlO}_{1.5}\text{-SiO}_2$ phase diagram keeping Rein and Chipman's cristobalite activity. Then we recognized that this

mullite. Nevertheless, the work of Aramaki and Roy is so carefully done and so convincing that all the figures in "Phase Diagrams for Ceramists"³⁵ have been revised to show this behavior.

The answer to these two difficulties, although surprisingly hard to see, is quite simple. Mullite melts incongruently at 2123 ± 10 K, but not to corundum. This is consistent with the experiments of Aramaki and Roy. Mullite samples heated below this temperature and quenched showed well crystallized mullite grains along with some quench mullite, fine mullite crystals formed during the cooling process. Samples heated above this temperature were mainly quench mullite with no well crystallized mullite and no corundum. Some glass was present in most of these samples with more glass present if they were heated longer or to a higher temperature. The absence of substantial amounts of corundum proves that corundum is not a product of the incongruent melting of mullite, but the quantity and distribution of glass suggests incongruent melting to a small amount of liquid and a large amount of a silica-rich solid. The crystals formed when mullite melts incongruently must decompose to "quench mullite" on cooling, and are probably a solution of SiO_2 in an unstable crystalline form of alumina, possibly gamma alumina. We will show that the thermodynamic properties of gamma alumina are consistent with this interpretation of the data.

We were led to the conclusion that the liquidus curve of Aksay and Pask¹ above 2126 K must be that for a solid other than corundum by a quantitative discrepancy between the measured liquidus curves and Rein and Chipman's¹¹ measured SiO_2 activity for a mullite. At about 2123 K, mullite melts incongruently to give a liquid with $X_l=0.57$ according to the Aksay and Pask liquidus curve. Using the thermodynamic quantities for mullite solid solutions obtained in the previous sections of this paper, it is easy

completely new kind of phase diagram was the key to reconciling the apparently divergent experimental data on this system. Table 3 shows the Redlich-Kister values we have assigned to the liquid and gamma alumina phases to calculate the equilibrium phase diagram in Figure 1. If the new alumina phase does not form, one gets the metastable phase diagram of Figure 2 which is in surprisingly good agreement with that shown by Toropov and Galakhov.^{27,28} None of their experimental data was used in the calculation. The enthalpy value used for the $\text{AlO}_{1.5}\text{-SiO}_2$ liquid is based on an estimate for the heat of fusion of mullite obtained from the relative DTA halts for mullite and corundum shown in the published cooling curves of Horibe and Kuwabara.³⁴ The Redlich-Kister values for the liquid are obtained by a least squares fitting of the eutectic,⁴ the mullite liquidus points of Davis and Pask³² omitting the 1823 and 1853 points, and an interpolated point at $X=.57$ and 2123 K. Thus, this section of the phase diagram is fitted well. However, the agreement with the gamma alumina liquidus in Figure 1 is almost as good. The Redlich-Kister coefficients for the liquid phase are also in agreement with liquid-liquid immiscibility below 1647 K, as plotted in Figure 3. This is in good qualitative agreement with the known behavior of glasses at these temperatures.^{36,37}

THERMODYNAMIC PROPERTIES OF GAMMA ALUMINA

The structure of gamma alumina is that of a spinel with aluminum vacancies to compensate for the fact that there are no +2 ions. It is formed quite readily on dehydrating aluminum hydroxides. As formed at low temperatures, it is poorly crystallized. If it is heated to 1300 K or above it is converted to corundum, the stable form. Corundum contains only octahedral aluminum, and the fact that SiO_2 is not very soluble in corundum⁵

is not surprising. One would predict a higher SiO_2 solubility in an $\text{AlO}_{1.5}$ crystal with some tetrahedral Al, and in fact it is possible to prepare gamma alumina catalysts with 5 to 6 percent of silica.^{39,40} The heat of solution of gamma alumina has been measured in a variety of solvents,⁴¹⁻⁴³ including the molten oxides used by Kleppa^{9,43} in which corundum dissolves. Thus, there is a good value⁴² for the heat of the gamma alumina-corundum transformation which is used in the JANAF compilation.²² We can expect that equilibrium compositions for SiO_2 in gamma alumina may become available, but at present the enthalpy is the only firm piece of data available. This determines the slope of the line of gamma alumina compositions saturated with corundum. To keep the gamma alumina region as close to pure alumina as possible without getting an $\alpha \rightarrow \gamma$ transition before the melting point of pure alumina, we have placed the intercept of this curve just above the melting point, at 2342 K. This fixes the activities of gamma alumina and cristobalite at the mullite incongruent melting point at $a_1 = .80040$ and $a_2 = .70967$ respectively. The silica shows very large positive deviations from ideality, so we expect that X_1 is smaller than a_1 , but we expect it to be larger than the mole fraction of alumina in the mullite phase at this temperature, .7508. Any value between .751 and .800 would be possible, and $X_1 = .79$ was arbitrarily chosen to obtain the Redlich-Kister values shown for gamma alumina in Table 3. The Redlich-Kister coefficients are expected to decrease with increasing temperature according to equations of the form

$$N(\log \gamma)_T = N(\log \gamma)_\infty + N(H)/4.575628T \quad (8)$$

where N stands for any one of the Redlich-Kister coefficients, A, B, etc.

Since there are no experimental data on heats of mixing in this phase, we have obtained the enthalpy coefficients, $N(H)$, by arbitrarily setting $N(\log \gamma)_{\infty}=0$. This is a common approximate method related to Hildebrand's concept of regular solutions.⁴⁴ With these values, gamma alumina can be stabilized sufficiently by the addition of SiO_2 to appear in the equilibrium phase diagram between 1950 and 2315 K. This is illustrated in Figure 1.

TABLE 1.--Thermodynamic Properties Used for the Pure Materials

Substance	$H_{298.15}^{\circ}$ kcal mol ⁻¹ ^a	H_{1000}° kcal mol ⁻¹ ^a	ϕ_{1000}° cal mol ⁻¹ K ⁻¹ ^b	C_p equation ^c A	C_p equation ^c Bx10 ³	Cx10 ⁶	Dx10 ⁹
Al ₂ SiO ₅ (c)							
sillimanite	-617.7025	-588.7375	41.8993	47.4262	9.7017	-1.8672	0.60931
andalusite	-613.350	-589.436	41.311	46.3090	7.96224	-2.0156	0.68443
kyanite	-619.3173	-590.2253	39.061	46.9219	8.52864	-2.9766	1.1602
SiO ₂							
crystalite	-215.417	-206.400	18.1108	16.72175	2.05366	-1.6518	0.6463
liquid	-215.740	-205.399	18.1766	16.61	3.2268	1.2384	
AlO _{1.5}							
corundum	-200.250	-190.933	12.2175	14.908	2.3471	-1.2717	0.34615
c, gamma	-197.600	-188.283	13.34896	14.908	2.3471	-1.272	0.3462
liquid > 2000K	-190.358	-191.020	19.1587	27.66	-2.96		
liquid < 2000K	-190.358	-182.152	16.5551	17.312			

a) H_T° is defined as $\Delta H_f^{\circ}(298.15) + \int_{298.15}^T C_p dT$.

b) ϕ_T° is the free energy function defined as $S_T^{\circ} - (H_T^{\circ} - H_{298.15}^{\circ})/T$

c) Heat capacities are given by power series of the form $C_p = A + B(T-1000) + C(T-1000)^2 + D(T-1000)^3$

TABLE 2.--Redlich-Kister Coefficients for Mullite and Sillimanite, Referred to $\text{AlO}_{1.5}$ (c,corundum) and SiO_2 (c,cristobalite).

	A	B	C
$\log \gamma_{1000}$	3.134095	-9.233145	10.646443
enthalpy ^a	-8598.	23670.	
heat capacity	13.15	-26.88	

a) The Redlich-Kister coefficients for the enthalpy are given for a temperature of 1000 K in units of calories mol^{-1} .

$$H_{1000}^e = x_1 x_2 [-8598 + 23670(x_1 - x_2)]$$

TABLE 3.--Redlich-Kister Coefficients for the Liquid and Gamma Alumina Phases

phase	component 1	component 2	quantity	A	B	C
liquid	$\text{AlO}_{1.5}$ (l)	SiO_2 (l)	$\log \gamma_{1000}$	1.330516	-.212719	.096297
			enthalpy	6400. cal. mol ⁻¹ K ⁻¹		
gamma	$\text{AlO}_{1.5}$ (c,gamma)	SiO_2 (c.cristobalite)	$\log \gamma_{1000}$	1.920984	-.762753	
			enthalpy	8790.	-3490. cal. mol ⁻¹ K ⁻¹	

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Figure 1 - Phase diagram for the $\text{AlO}_{1.5}$ - SiO_2 system, calculated using Redlich-Kister coefficients for the mullite, liquid, and gamma-alumina phases.

Figure 2 - Calculated metastable phase diagram for the $\text{AlO}_{1.5}$ - SiO_2 system assuming that gamma-alumina is not formed.

Figure 3 - Liquid-liquid immiscibility in $\text{AlO}_{1.5}\text{-SiO}_2$ metastable glass, calculated from the Redlich-Kister coefficients for the liquid.

APPENDIX C

VAPOR PRESSURE MEASUREMENTS, THERMODYNAMIC
PARAMETERS AND PHASE DIAGRAM FOR THE SYSTEM
POTASSIUM OXIDE-SILICON OXIDE AT HIGH TEMPERATURES*

by

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ABSTRACT

Potassium oxide vaporizes from solutions in SiO_2 primarily according to the equation:

We have studied this equilibrium using atomic absorption in a constant temperature graphite furnace to measure the absorbance of the steady-state distribution of potassium atoms. The potassium atoms were introduced at the center of the furnace by diffusion through an orifice in sample cells which we developed for vapor pressure measurement. We have shown both experimentally and theoretically that at a particular temperature, the absorbance we measure is proportional to the rate of diffusion of potassium atoms from the vapor pressure sample cells. For a particular cell with a particular orifice, there is a temperature-dependent conversion factor between absorbance and pressure which we evaluated from measurements with potassium-aluminate standards in the cells.

The pressure of potassium atoms was measured over a sufficient range of temperature to obtain the heat of vaporization. The Redlich-Kister coefficients for the enthalpy of mixing of liquid K_2O and SiO_2 : $A = -86$, $B = -53 \text{ kcal mol}^{-1}$, were obtained from this data and estimates for the thermodynamic properties of $\text{K}_2\text{O}(\text{liquid})$, literature data on the enthalpy of glasses, the temperature dependence of rate of vaporization, and the variation of the activity of SiO_2 with temperature.

Redlich-Kister coefficients for $\log \gamma_{\text{K}_2\text{O}}$ were obtained from the concentration dependence of the vapor pressure of potassium over the K_2O - SiO_2 samples: $A = -10.9923$, $B = -6.7801$, and $C = -1.0101$ at 1500 K.

From these values, together with the enthalpy coefficients above, activities of both K_2O and SiO_2 can be calculated over a wide range of temperatures and compositions. The K_2O - SiO_2 phase diagram was calculated from these values. Thermodynamic quantities are given for tridymite and for two potassium silicates, $\text{K}_2\text{Si}_4\text{O}_9$ and $\text{K}_2\text{Si}_2\text{O}_5$.

INTRODUCTION

The high sensitivity of atomic absorption for atoms in the gas phase suggests its use for vapor pressure measurements. A number of studies of this type are available in the literature for samples which can be confined in quartz cells (1-2). However, there is a substantial need for vapor pressure measurements for samples and for temperatures which are incompatible with window materials. Effusion measurements in vacuum are commonly used for vapor pressure measurements at high temperatures with a variety of detectors for the material vaporized from a Knudsen cell. A similar experiment can be performed with atomic absorption detection of the vapors provided an inert atmosphere is present to slow the transfer of vapor away from the cell. In this case, material leaves the sample cell by diffusion as opposed to effusion. We have developed this new method for vapor pressure measurements and applied it to the measurement of potassium pressures in equilibrium with liquids in the K_2O - SiO_2 system. The data obtained are used together with published values for a thermodynamic analysis of this binary system, including a calculated phase diagram.

The samples are placed in molybdenum or platinum cells with a small drilled hole through which vapors can diffuse at high temperatures. These cells are inserted into the center of an electrically heated graphite tube furnace in an atmosphere of argon (Woodruff furnace, (3)), and the relative

amount of potassium atoms in the graphite tube is measured by atomic absorption. The measured absorbance normally increases within 5-15 minutes to a steady-state value, where the rate of diffusion out of the cell equals the rate at which potassium atoms leave through the ends and walls of the graphite tube. For a particular sample cell, the steady-state absorbance is proportional to the pressure of potassium atoms inside the cell. There is, however, a substantial exponential temperature dependence for the proportionality constant:

$$P = c_{\text{cell}} e^{-39/RT} (\text{absorbance})$$

The value of 39 kcal mol^{-1} is the average obtained with two separate graphite tubes with cells filled with a mixture of corundum and potassium β -alumina. The equilibrium vapor pressures for this system are known from the work of Plante, et al. (4), and these values serve to calibrate the various cells used in this work.

Equation 1 also fits the temperature dependence observed in a second graphite tube furnace. The agreement between the data in the different furnaces is a clear indication that the value 39 kcal mol^{-1} , depends more on the nature of the potassium-graphite interaction (diffusion coefficients and the equilibrium constant for compound formation) than on the geometry of a particular Woodruff furnace. The mechanisms for transport of potassium out of a graphite tube furnace are considered elsewhere (5).

EXPERIMENTAL

1. Preparation and Analysis of Samples

Samples in the system $\text{K}_{0.5}\text{AlO}_{1.5}$ were prepared by grinding together and then heating weighed amounts of Al_2O_3 and KHCO_3 in covered platinum

crucibles in a gas furnace. The temperature was gradually increased to around 1000°C during 1-4 hours, then to 1000-1100°C where it was kept for 8-12 hours, and finally to 1250°C for another 8-12 hours. About 600 mg for each sample were prepared.

$KO_{.5}-SiO_{.2}$ samples were prepared by grinding mixtures of potassium silicate and either potassium bicarbonate or silica, heating to 630-650°C for about 5 hours, grinding again, and storing in a desiccator. The potassium content of samples was determined by dissolving them and measuring potassium concentration in the solutions using the Varian Atomic Absorption Spectrophotometer, model 1100. Some samples dissolved in 49 percent HF, but other samples had to be treated with mixtures of HF and HNO_3 , H_2SO_4 or HCl, and evaporated to dryness before a suitable analytical solution was obtained.

2. Potassium Vapor Pressure Measurements

These measurements were carried out by atomic absorption using a graphite furnace. The essential features of the furnace are described in (3), and its modifications for vapor pressure measurements are reported in (5). The temperature of the area where the sample is introduced was measured by optical pyrometer. The sample cells were made of platinum or molybdenum. Molybdenum has sufficient strength at high temperatures to allow the use of cells with a screw closure. Molybdenum has a tendency to stick, and to prevent sealing the cell into the furnace, the pedestal on which the molybdenum cells sit was rotated during the time the cell was in the furnace. With the molybdenum cells, different tops with different hole sizes could be screwed onto the base holding any particular sample. However, for loading platinum cups, the bottom was sawed off, the sample was introduced, and the bottom was welded back on.

Calibration was carried out for each cup, before and several times between measurements. A $\text{K}_2\text{O}\text{-Al}_2\text{O}_3$ sample was put in the furnace and plateau transmittance values were recorded. The same procedure was followed for measurements of $\text{K}_2\text{O}\text{-SiO}_2$ samples.

Two different procedures were used in collecting data. With one furnace, each sample was measured at a series of temperatures once it was inserted into the furnace. In the other furnace, the usual procedure was to adjust the furnace temperature and then take readings on a series of samples. Both procedures gave accurate vapor pressures and no distinction is made between them in the analysis of the data.

RESULTS AND DISCUSSION

1. Enthalpy Data

In analyzing a two component system like $\text{K}_2\text{O}\text{-SiO}_2$, it is desirable to have enthalpy data available as well as activity data. However, there are only a few measurements of the high temperature enthalpies or heat capacities of liquid potassium silicates, and even the heats of fusion of potassium silicates are not well-established. The enthalpies at 25°C for two potassium silicate glasses have been measured (6) and reported (7) although the details promised (8) were apparently never published. These values can be combined with our selected values for liquid K_2O and SiO_2 at 25°C to obtain Redlich-Kister coefficients (9,10) ($A(H) = -82$, $B(H) = -61 \text{ kcal mol}^{-1}$) for the enthalpy at 298 K. The values at high temperatures should be similar; in fact, this is confirmed by measurements on the temperature dependence of activity coefficients.

Recent measurements of the heat capacity of a potassium silicate glass (11) indicate that there is a substantial positive excess heat capacity of

mixing around 1000 K in the $\text{K}_{0.5}\text{-SiO}_2$ system. This data is fitted by a Redlich-Kister coefficient of about $A(C_p) = 8.0 \text{ cal mol}^{-1} \text{ K}^{-1}$ above the glass transition temperature. Thus, we can expect the coefficient $A(H)$ to increase with increasing temperature, and the values for 1500 K should be about $A(H) = -75.4$ and $B(H) = -61 \text{ kcal mol}^{-1}$. The uncertainty in these values is around $\pm 20 \text{ kcal mol}^{-1}$, and we have attempted to improve the accuracy by considering additional data from the temperature dependence of vaporization and solubility.

It is hard to obtain accurate vapor pressure measurements on $\text{K}_{0.5}\text{-SiO}_2$ liquid of a particular composition over a wide temperature range, because at low temperatures the liquids are quite viscous. They may be present as homogeneous glass, but it is also possible to have a liquid saturated with a solid such as tridymite or even an intermediate non-equilibrium state. This is illustrated by the calculated lines in Figure 1 for a sample with the overall composition $X_{\text{K}_{0.5}} = .144$. The lower solid line shows the pressure for liquid of .1444 mole fraction $\text{K}_{0.5}$, and the higher line at lower temperatures corresponds to liquids in equilibrium with solid tridymite at the various temperatures. If the lower temperature values are included in a least-squares analysis, the apparent heat of vaporization is low, and if they are omitted, one is left with a temperature range of only 111°. We have omitted points at temperatures where a solid would be present at equilibrium from the initial treatment of the data. This leaves five samples for which the measurements span a temperature range of at least 200°. One of these ($X = .4719$) is in error for reasons considered below and must be dropped from consideration. Table 1 shows the values for $\bar{H}_1$ calculated from our data. These values correspond to Redlich-Kister values of $A(H) = -132$ and $B(H) = -9 \text{ kcal mol}^{-1}$.

The only additional information necessary to fix the thermodynamic quantities shown in Table 3 for $KO_{.5}$ are the estimates of Ehlert (23) for the melting point and heat of fusion of $KO_{.5}$ (1370 K and 5.0 kcal mol⁻¹). The values shown in Table 3 for cristobalite, quartz, and SiO_2 (liquid) are values chosen to fit the JANAF tables (16) except that the free energy functions of cristobalite and liquid have been adjusted by .0262 cal mol⁻¹ K⁻¹ to bring the quartz-cristobalite equilibrium temperature to 1175 K, the minimum temperature observed by Holmquist (24) for the formation of cristobalite from quartz. This temperature must lie above the quartz-tridymite equilibrium temperature of 1150 K.

3. Redlich-Kister Equations for log γ

Every measured potassium pressure can be converted to an activity of $KO_{.5}$ by assuming that $P_{O_2} = 1/4 P_K$ and dividing $P_K P_{O_2}^{1/4} = .707 P_K^{5/4}$ by the equilibrium constant for the reaction

which can be calculated from the values in Table 3.

The calculated activities can be divided by the mole fractions to get activity coefficients at the experimental temperature, and these values can be corrected to a standard temperature of 1500 K using the equation

$$d \log \gamma_1 / d(1/T) = -\bar{H}_1 / 4.575428 \quad (5)$$

and values of $\bar{H}_1$ from the Redlich-Kister equation

$$\bar{H}_1 = (1-x)^2 [-8600 - 5300(-1 + 4x)] \quad (6)$$

Our computer program permits us to easily include the temperature dependence of $\bar{H}_1$ corresponding to

One can supplement our enthalpy values with others from the literature, but there are problems in all these cases. The latest NBS measurements (12) are not given in detail. The earlier values (4) have been analyzed without any allowance for a composition dependence of the heat of vaporization. Preston and Turner (13) have accurately measured the rate of evaporation of potassium oxide from $\text{K}_{0.5}\text{-SiO}_2$ glasses over a wide temperature range, but the heats of vaporization which they found are too low to correspond to the process

The most reasonable interpretation of their data is that they were measuring evaporation by the process

Using values selected for the thermodynamic properties of $\text{KOH}(\text{g})$ (14) gives $\bar{H}_f$ values consistent with ours and with the one average value in (4).

These values correspond to Redlich-Kister coefficients of $A(\text{H}) = -97$ and $B(\text{H}) = -24$. A combined least-squares treatment of our values and those in (13) gives $A(\text{H}) = -118$, $B(\text{H}) = -5 \text{ kcal mol}^{-1}$.

It is clear from these determinations, summarized in Table 2, that A is around $-100 \text{ kcal mol}^{-1}$, but the value for B is not fixed very closely. A good value for B can be obtained, however, from the temperature dependence of $\log \gamma_2$. $\log \gamma_2$ is known at several temperatures and compositions from the phase diagram measurements (15). We have selected $T = 1784 \text{ K}$, $X = .102$, $K = .94293$, $\log \gamma_2 = .0212$, because we have a substantial amount of vapor pressure data at this temperature. The other point selected is $T = 1150 \text{ K}$, $X = .297$, $K = .78139$, $\log \gamma_2 = .0459$. Using our values for $\log \gamma_1$

as a function of composition at 1784 K, one can get $\log \gamma_2 = -0.012$ at $X = .293$, $T = 1784$ K by a Gibbs-Duhem integration. This corresponds to a value of $\bar{H}_2 = 860 \pm 700 \text{ cal mol}^{-1}$ for $X = .297$. This establishes the equation: $A - 1.812B = 9.7 \pm 8 \text{ kcal mol}^{-1}$.

The vector $A + .5519B$ is orthogonal to $A - 1.812B$ and, therefore, we have evaluated $A + .5519B = -115$ from the values in Table 2 and combined this with the value for $A - 1.812B$, obtaining $A(H) = -86$, $B(H) = -53.5 \text{ kcal mol}^{-1}$.

The new measurements on the heat capacity of a $KO_{.5}\text{-SiO}_2$ glass with $X_{KO_{.5}} = .390$ provide additional enthalpy data. Kracek's measurements on room temperature glasses can be interpolated to give an excess enthalpy of mixing for the liquids of $H_e = -16.3 \text{ kcal mol}^{-1}$ for this particular composition. Using $H_{1000} - H_{298}$ from Table 3 for the liquids and a graphical integration of the heat capacity (11) for the mixture converts this to $H_e = -16.0 \text{ kcal mol}^{-1}$ at 1000 K. Assuming that C_p for the mixture remains constant to 1500 K, this value will change to $H_e = -15.0$ at 1500 K. The Redlich-Kister parameters we have selected correspond to $H_e = -17.7$ for $X = .390$ so the discrepancy is less than 3 kcal mol^{-1} . Figure 2 shows the comparison of $\bar{H}_j$ values calculated from the selected enthalpy coefficients with the individual values from the temperature dependence of the vapor pressure or rate of vaporization.

2. Thermodynamic Data for $KO_{.5}$

Pure liquid $KO_{.5}$ is extremely difficult to prepare and handle, and its thermodynamic properties have not yet been successfully measured. It is however, possible to make reasonable estimates as shown in Table 3, and these estimates were used as the basis for the calculations in this paper. The standard (16-17) heat of formation of solid $KO_{.5}$ at 298.15 of -43.2

kcal mol^{-1} is based upon heat of solution measurements reported in 1907 (18). We have estimated the entropy of K_2O at 1000 K as $S_{\text{Na}_2\text{O}} + S_{\text{KF}} - S_{\text{NaF}} = 20.958 + 31.50 - 27.370 = 25.09$ using JANAF (16) values for the other solids. The heat capacity for potassium oxide estimated in the JANAF tables is much too large, and we have made alternative estimates for the high temperature heat capacities of solid and liquid K_2O as $9.097 + .00096 (T - 1000)$ and $11.45 + .00180 (T - 1000)$ respectively assuming heat capacity additivity in the values of White (19) for KAlSi_3O_8 crystal and glass. The data of White (19) is apparently the basis for the enthalpy values listed in current compilations (20,21). We have not attempted to find heat capacity equations valid down to 298 K, but instead have estimated $H_{1000} - H_{298}$ values for K_2O from the measurements on KAlSi_3O_8 .

Since these equations were developed, the heat capacity of a K_2O - SiO_2 glass has been published (11) with the value $16.7 \text{ cal mol}^{-1} \text{ deg}^{-1}$ for $X_{\text{K}_2\text{O}} = .390$ at about 1000 K. This corresponds to $C_p(\text{K}_2\text{O}(\ell)) = 26 \text{ cal mol}^{-1} \text{ deg}^{-1}$ if additivity of heat capacities were correct. The heat capacity of this particular glass must be influenced substantially by interactions between the oxides. There is evidently a substantial positive excess heat capacity of mixing at this composition. It is reasonable to assign a Redlich-Kister parameter of $A = 8.0$ for the excess heat capacity of mixing in the K_2O - SiO_2 system. Sodium oxide shows a similar near additivity of heat capacities in solid silicates (16), titanates (22), alumino-silicates (20) and $\text{NaAlSi}_3\text{O}_8$ glass (20) but a substantial positive excess heat capacity of mixing in the Na_2O - SiO_2 liquid system (11,16). This behavior is also expected on theoretical grounds, since the addition of alkali oxide will break Si-O-Si bonds, allowing more anharmonic vibrations above the glass transition temperature.

$$\overline{C_{p1}} = (1 - x)^2 [8.0] \quad (7)$$

The values of $\log \gamma_1$ corrected to 1500 K are plotted in Figure 3. Compositions which would have solid present at equilibrium appear twice in Figure 3, as diamonds assuming a non-equilibrium glass of the stoichiometric composition and as squares for the equilibrium liquid composition from the phase diagram of Kracek, et al. (15). Most of these points are closer to the line when the equilibrium liquid assumption is used, but for some, the stoichiometric glass is clearly a better approximation. A choice has been made for each point, and the corresponding square or diamond is shown in solid black. An increased experimental scatter for points at mole fractions above 0.4 is clearly evident in Figure 3. This is probably related to the problems of maintaining a uniform known composition when the vapor pressure of $KO_{.5}$ is relatively high. The effect is most pronounced at lower temperatures and higher $KO_{.5}$ concentrations and is sufficient to prevent an accurate determination of the heat of vaporization of $KO_{.5}$ from the sample at $X = .4719$ with our apparatus.

The points in Figure 3 are fitted by the Redlich-Kister coefficients, $A (\log \gamma) = -11.2116$, $B (\log \gamma) = -7.4673$, $C (\log \gamma) = -1.6695$. Figure 3 indicates a consistent tendency toward low values for $\log \gamma$ at $X = .06664$, which is particularly pronounced at lower temperatures. Thus, it is best to drop all the points at this composition from the least-squares treatment. Just as with the enthalpy data, the data for potassium oxide alone do not determine the intercept at $X = 0$ accurately, and a better set of coefficients is obtained by including a value for $\log \gamma_2$ from the phase diagram (15) in the treatment. With these two adjustments, we obtained the final Redlich-Kister coefficients, $A (\log \gamma) = -10.9923$, $B (\log \gamma) = -6.7801$, $C (\log \gamma) = -1.0101$, which give the calculated solid line in Figure 3.

This is a smooth curve with no sign of the pronounced break at high silica concentrations which Callow (25) found necessary in his treatment of this binary system. We believe that it is primarily the inclusion of the temperature dependence of $\log \gamma_2$ in determining the enthalpy, and not just the additional experimental data, which is responsible for this qualitative difference in the final curves. The other published analysis of this binary system (26) is based upon the assumption that $\log \gamma_2$ is given by the equation

$$\log \gamma_2 = C/T \quad (7)$$

and no experimental enthalpy data. This assumption is qualitatively correct insofar as the large Redlich-Kister coefficients do get closer to zero with increasing temperature. For example B ($\log \gamma$) is given by the equation

$$B(\log \gamma) = +.942 - 11583/T \quad (8)$$

and has only a small part independent of T. This treatment (26) is, however, based upon the mole fraction of K_2O instead of $KO_{.5}$, and does not give the correct Henry's law behavior at low potassium oxide concentration.

The Redlich-Kister parameters for $KO_{.5}$ - SiO_2 liquid mixtures are summarized in Table 4 which gives the corresponding Bale-Pelton (27) coefficients as well. With these values one can calculate the activities of $KO_{.5}$ and SiO_2 at any temperature and composition. The experimental data used do not extend beyond $X_{KO_{.5}} = 0.55$, and any use of these coefficients for solutions richer in potassium oxide than this should be recognized as an extrapolation. The calculated activities can be combined with vapor pressures for pure $KO_{.5}(l)$ calculated from Table 3 to give equilibrium pressures of potassium as a function of temperature and composition. The solid lines in Figure 1 were calculated in this way.

4. The Thermodynamic Properties of Tridymite

There is still a lively controversy in the literature over whether or not tridymite is a stable form of pure silica (24,28-29). Tridymite only forms from quartz or cristobalite in the presence of impurities such as alkali oxides, and it is possible that it is thermodynamically stable only with a small percentage of dissolved material. For the reasons outlined below, we believe that pure tridymite is not thermodynamically stable. The calculations thus far have not made any use of data for tridymite--the solubilities used at 1784 and 1150 K in determining $\bar{H}_2$ and $\log \gamma_2$ are based upon cristobalite and quartz.

The enthalpy (30) and heat capacity (31) of tridymite are known, and the only remaining uncertainty is the equilibrium constant for the reaction

at 1175 K where quartz and cristobalite are in equilibrium. If cristobalite and pure tridymite are in equilibrium at 1743 K, where the tridymite-cristobalite transition is observed in the presence of potassium oxide, K_{1175} is equal to 1.00455. On the other hand, the constants chosen for tridymite in Table 3 give $K_{1175} = .99658$. Thus, the total range in question is less than 1 percent and tridymite is either stable or unstable at 1175 K with a margin of less than 0.5 percent. A satisfactory phase diagram can be drawn for either of these situations; however, there are two pieces of experimental data which favor tridymite stabilized by dissolved alkali oxide.

Holmquist (24) heated a mixture which was .00484 mole fraction $\text{NaO}_{.5}$ with quartz to 1623 K for a period of weeks. He found both cristobalite and tridymite to be present at equilibrium in this sample. This is a clear indication that the solubility of $\text{NaO}_{.5}$ in cristobalite is less than a mole

fraction of .00484 while the solubility in tridymite is greater than this value at 1623 K. Thus, the equilibrium constant for cristobalite to tridymite at 1623 K is apparently less than .99526. The value $K_{1175} = .99658$ was chosen to make K_{1623} equal to .993, a reasonable amount smaller than .995.

The compositions of liquid in equilibrium with tridymite are known over the temperature range from 1040 to 1743 K (15). With the Redlich-Kister coefficients we have obtained for the liquid, we can calculate the activities of solid $KO_{.5}$ in tridymite saturated with the equilibrium liquid. With either set of equilibrium constants for tridymite, this data gives a partial molal enthalpy of $KO_{.5}$ in tridymite of about $-36 \text{ kcal mol}^{-1}$. If the entropy of solution of $KO_{.5}$ is approximately ideal and $\bar{H}_1 = -36$, the solubility of $KO_{.5}$ in tridymite at 1743 K (activity of $KO_{.5}(s) = .7157 \times 10^{-6}$) will be a mole fraction of about .0234. This suggests that the cristobalite to tridymite equilibrium constant may be as small as 0.98, and the choice $K_{1175} = .99658$ is preferable to an equilibrium constant larger than 1.00.

With K_{1175} chosen as .99658 the activities of both solid SiO_2 and $KO_{.5}$ are known for tridymite in equilibrium with liquid at 1743 and 1150 K. This fixes a single Redlich-Kister coefficient at each temperature (-4.0764 and -6.3938 respectively), corresponding to $A(\log \gamma)_{1000} = -7.41556$ and $A(H) = -35842 \text{ cal mol}^{-1}$.

These values together with those of Table 4 are sufficient to calculate the concentration vs. temperature lines in the phase diagram for equilibria involving solid SiO_2 . The calculated phase diagram is shown in Figure 4 together with the experimental liquidus points. Tridymite is shown to be stable with mole fractions of $KO_{.5}$ from .0033 to .0091. The

calculated phase diagram does not show the large $KO_{.5}$ solubility at low temperature suggested by Holmquist (24), primarily because we have fixed the quartz-cristobalite equilibrium much lower than the value of 1323 K which he used.

5: Thermodynamic Values for Solid Potassium Silicates

The measured liquidus curves for $K_2Si_4O_9$ and $K_2Si_2O_5$, together with calculated activities for $KO_{.5}$ and SiO_2 along these curves, are sufficient to fix the enthalpy and free energy function for these solids. The selected values are shown in Table 3, and Figure 4 shows the liquidus curves calculated from these values. ΔH° for the reaction

is $117 \text{ kcal mol}^{-1}$ at its melting point, 1034 K. However, allowing for the partial molal enthalpies of the liquids at $X_l = .3333$, the calculated heat of fusion is 21 kcal mol^{-1} . Similarly, the heat of fusion of $K_2Si_2O_5$ at 1325 K is 17 kcal mol^{-1} .

There is surprisingly little data available on the thermodynamic properties of potassium silicates for comparison. The heats of fusion are substantially different from heats of fusion at 298 K (4.62 and $4.47 \text{ kcal mol}^{-1}$ respectively) from the data of Kracek et al. (6). $K_2Si_4O_9$ appears in the phase diagram only over a narrow temperature range, and the enthalpy value for it reported in Table 3 could be substantially in error. However, the standard enthalpy of formation of $K_2Si_2O_5$ at 298.15 K in Table 3 differs by only $11.4 \text{ kcal mol}^{-1}$ from the value ($-598.3 \text{ kcal mol}^{-1}$) calculated from the heat of solution in HF (6). The uncertainty in the heat capacity of the solid could easily account for the discrepancy.

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Figure 1.--Potassium vapor pressures over a K_2O-SiO_2 sample with $X_{K_{0.5}} = .1444$.

Figure 2.--Comparison of $\bar{H}_1$ values from enthalpy coefficients and from vapor pressure temperature dependence. The solid line is calculated. The data of Preston and Turner¹³ is represented by diamonds, that of Plante, et al. by squares, and our values by circles.

Figure 3.-- $-\log \gamma_1$ vs. mole fraction. The triangles represent experimental values for points where the sample is fully liquid at equilibrium. Points where a solid forms at equilibrium are plotted twice, as squares for liquid in equilibrium with the solid and as diamonds for the metastable glass. The point of each pair closest to the calculated curve is shown in black.

Figure 4.--Phase diagram of the $\text{K}_2\text{O}-\text{SiO}_2$ system.

TABLE 1.--Partial Molal Enthalpy of K_2O from $\ln P$ vs. $1/T$

<u>X</u>	<u>$\bar{H}_1$</u>
.21537	-82.7
.28548	-63.2
.33497	-59.4
.34025	-63.0

TABLE 2 .--Redlich-Kister Coefficients for Enthalpy
in the $\text{K}0.5\text{-SiO}_2$ System at 1500 K

	<u>A(H)</u>	<u>B(H)</u>	<u>A+.5519B</u>
data this work	-132	- 9	-137
Plante data (12)	-116	-103	-173
rate of vaporization (13)	- 97	- 24	-110
joint, ref 13 and this work	-118	- 5	-121
enthalpy of glasses, 25°C (6-8)	- 75	- 61	-109
corrected to 1500 K (6,11)	- 71	- 43	- 95
selected, including $\log \gamma_2$ data	- 86	- 53	-115

TABLE 3.--Thermodynamic Properties for the Pure Materials

Material	C_p equation ²				$b \times 10^3$	$c \times 10^6$	$d \times 10^9$
	$H_{298.15}^\circ$ cal mol ⁻¹	H_{1000}° cal mol ⁻¹	Φ_{1000}° cal mol ⁻¹ K ⁻¹	a			
KO _{1.5} (c)	-43200.	-36200.	18.090	9.097	.96		
KO _{1.5} (l)	-40628.	-32128.	19.4256	11.45	1.80		
SiO ₂ (quartz)	-217700.	-206860.	16.899	16.48	2.4		
SiO ₂ (cristobalite)	-216417.	-206640.	18.1108	16.72175	2.05366	-1.65179	.6463
421 SiO ₂ (tridymite)	-217000.	-206432.6	17.5259	16.72175	2.05366	-1.65179	.6463
SiO ₂ (l)	-215740.	-205399.	18.1766	16.61	3.2268	1.2384	
K ₂ Si ₄ O ₉ (s)	-1059818.	-1003060.	89.8337	85.081	9.0876	-3.1173	
K ₂ Si ₂ O ₅ (s)	-609691.4	-557657.4	67.1074	51.638	5.504	-1.55864	

1) H_{1000}° is defined as $\Delta H_{f,298.15}^\circ + (H_{1000}^\circ - H_{298.15}^\circ)$

2) The power series for C_p (generally valid for 1000-2200 K) is $C_p = a + b(T-1000) + c(T-1000)^2 + d(T-1000)^3$

TABLE 4.--Summary of Power Series Coefficients
at 1500 K for $KO_{.5}$ in SiO_2

	<u>Redlich-Kister</u>			<u>Bale-Pelton</u>		
	A	B	C	q_0	q_1	q_2
<u>Liquid</u>						
Log γ	-10.9923	-6.7801	-1.0101	-11.3290	-6.7801	-.6734
H	-86000.	-53000.		-86000.	-53000.	
C_p	8.			8.		
<u>Tridymite</u>						
Log γ	-4.8045			-4.8045		
H	-35842.			-35842.		

APPENDIX D

THE HEAT CAPACITIES OF ALKALI SILICATE LIQUIDS

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Abstract

It has been customary to assume that heat capacities are additive in silicate glasses and liquids. However, with the accumulation of data on the heat capacities over a wider range of liquid and glass compositions it has become clear that this is not true, particularly for liquid silicates near 1000 K. Estimates of the heat capacities of $\text{KO}_{.5}$, $\text{NaO}_{.5}$ and CaO liquids are presented. The excess heat capacity of mixing for alkali silicates at 1000 K can be represented by the equation

$$C_p^e = 8.0X_{\text{KO}_{.5}}X_{\text{SiO}_2} + 6.8X_{\text{NaO}_{.5}}X_{\text{SiO}_2}$$

in units of $\text{cal mol}^{-1} \text{K}^{-1}$. Equations are given for $\text{KO}_{.5}$ - $\text{NaO}_{.5}$ - SiO_2 and $\text{NaO}_{.5}$ - CaO - SiO_2 liquids for temperatures from 900 to 1800 K.

Introduction

The structural changes in silicates as Si-O-Si linkages react with oxide ions are well known.

The resulting cleavage of silica chains has profound effects upon the viscosity¹ and thermodynamic properties² of silicate liquids. It may be expected to allow for increased anharmonicity of the vibrations in a liquid, and thus contribute to a positive excess heat capacity of mixing. A substantial amount of heat capacity data on silicate glasses and liquids has been recently summarized³. However, the composition range covered in individual studies has generally been quite small. This, together with uncertainties in appropriate values for the heat capacities of metal oxides as glasses and liquids accommodates models with additivity of heat capacity³ for glasses in the range 300 - 700 K. Above the glass to liquid transition temperatures the failure of additivity is considerably more pronounced. We have examined the published data on liquid silicates of sodium^{4, -7}, potassium⁵⁻⁷, and calcium⁸ and show how the excess heat capacities of mixing found in these systems can be represented mathematically.

The NaO_{.5} - SiO₂ System --

Of the binary silicate systems under consideration here, the NaO_{.5} - SiO₂ system has been studied most widely and over the largest range of compositions. Figure 1 shows the values of Naylor⁴, Schweite and Ziegler⁵,

which on differentiation gives the equation

$$C_p = 15.8488 - .8738 \times 10^{-3} (T-1000) \quad (9)$$

The heat capacity actually decreases slightly with increasing temperature.

At 1500 K the excess heat capacity of mixing for this composition

($X_{\text{KO}_{.5}} = .4444$) is $-.373 \text{ cal mol}^{-1} \text{ K}^{-1}$, even more of a decrease than that shown by the sodium silicate glass of Naylor⁴. Thus a minimum of zero for C_p^e at 1500 or 1600 K is reasonable for the $\text{KO}_{.5}\text{-SiO}_2$ system. We have used 1600 K so that the equation can be used to higher temperatures, and obtained the equation

$$C_p^e = [8.0 - 26.7 \times 10^{-3} (T-1000) + 22.2 \times 10^{-6} (T-1000)^2] X_{\text{KO}_{.5}} X_{\text{SiO}_2}$$

for potassium silicate glasses and liquids. The decrease in C_p^e with increasing temperature agrees with the approximately constant C_p^e for the glass with $X_{\text{KO}_{.5}} = .39$ shown in the work of Moynihan et al.⁷, but over a smaller temperature range.

The $\text{CaO} - \text{SiO}_2$ system.

The JANAF tables¹⁰ use $C_p = 15.0 \text{ cal mol}^{-1} \text{ K}^{-1}$ for liquid CaO at high temperatures (over 2100 K), but assume that in the range 1000 - 1500 K, the heat capacity is the same as that of the solid. The heat capacity⁸ of liquid CaSiO_3 at 1000 K is $32.8 \text{ cal mol}^{-1} \text{ K}^{-1}$, corresponding to a positive C_p^e of mixing of 0.6 or $1.7 \text{ cal mol}^{-1} \text{ K}^{-1}$ for these two different estimates of the heat capacity of CaO (15.0 and $12.845 \text{ cal mol}^{-1} \text{ K}^{-1}$, respectively).

Takahashi and Yoshio⁶, and Moynihan et al.⁷ plotted as C_p per mole of $\text{NaO}_{.5}$ plus SiO_2 vs. mole fractions at a temperature of 1000 K.

The data of Takahashi and Yoshio have been plotted as estimates from their figures. Points calculated from the equations cited by Matveev and Zhuravlev⁹ are included as open circles in the figure, although some are estimated values without a clear experimental basis.

The curvature in figure 1 is obvious, and the only remaining uncertainty is in the value to use for the heat capacity of pure liquid $\text{NaO}_{.5}$ at 1000 K. The estimate in the JANAF tables,¹⁰ i.e. $12.5 \text{ cal mol}^{-1} \text{ K}^{-1}$ independent of temperature, is based primarily on the sodium silicate heat capacities of Naylor⁴, and thus is probably somewhat high. A least squares treatment leaving $C_p^0(\text{NaO}_{.5})$ to be determined gave $C_p^0(\text{NaO}_{.5}) = 9.5 \text{ cal mol}^{-1} \text{ K}^{-1}$ at 1000 K. This value is too close to the Dulong and Pettit value of $9.0 \text{ cal mol}^{-1} \text{ K}^{-1}$ for a liquid which should show considerable vibrational anharmonicity at this temperature, and we have adopted a value of $C_p = 11.45 \pm 1 \text{ cal mol}^{-1} \text{ K}^{-1}$ at 1000 K for $\text{NaO}_{.5}$. This value then leads to the calculated least squares line in figure 1 of

$$C_p = 11.45 X_1 + 16.61 X_2 + 6.8 X_1 X_2 \quad (1)$$

Naylor's measurements extend to 1744 K, with an approximately constant heat capacity. Since the heat capacity of liquid SiO_2 increases substantially with temperature and a similar increase is expected for liquid $\text{NaO}_{.5}$, the excess heat capacity of mixing must decrease with increasing temperature.

At 1500 K the heat capacity of liquid $\text{Na}_2\text{Si}_2\text{O}_5$ corresponds to

$$C_p = 15.59 = 11.45 X_1 + 18.53 X_2 + 2.28 X_1 X_2 \quad (2)$$

$$C_p = 15.59 = 12.64 X_1 + 18.53 X_2 + 0.00 X_1 X_2 \quad (3)$$

or some intermediate combination. The heat capacity for SiO_2 (4) is given by the equation

$$C_p^0(\text{SiO}_2) = 16.61 = 3.2268 \times 10^{-3} (T-1000) + 1.2384 \times 10^{-6} (T-1000)^2 \quad (4)$$

which was obtained^{11,12} as a least squares fit of JANAF¹⁰ values. It is reasonable to expect that the $X_1 X_2$ term approaches a minimum value of 0.00 at some temperature between 1500 and 2000 K. We have chosen to place this minimum at 1700 K, so that

$$C_p^e = [6.8 - 19.4 \times 10^{-3} (T-1000) + 13.8 \times 10^{-6} (T-1000)^2] X_1 X_2 \quad (5)$$

This choice gives

$$C_p^0(\text{NaO}_{.5}) = 11.45 + 1.80 \times 10^{-3} (T-1000) \quad (6)$$

for the heat capacity of pure liquid $\text{NaO}_{.5}$, which is exactly the same as the equation we have been using for liquid $\text{KO}_{.5}$ ^{11,12}. The agreement is forced to the extent that we have not been willing to accept heat capacity estimates for liquid $\text{NaO}_{.5}$ higher than the values we are using for liquid $\text{KO}_{.5}$.

The System $\text{KO}_{.5} - \text{SiO}_2$

The heat capacity equation for pure liquid $\text{KO}_{.5}$

$$C_p^0(\text{KO}_{.5}) = 11.45 + 1.80 \times 10^{-3} (T-1000) \text{ cal mol}^{-1} \text{ K}^{-1} \quad (7)$$

was picked^{11,12} in connection with previous work on potassium oxide. The JANAF estimates¹⁰ for heat capacities of $\text{KO}_{.5}$ are too high for both solid and liquid, and a more reasonable estimate was required to calculate the equilibrium vapor pressure of liquid $\text{KO}_{.5}$ in connection with the calculation of activity coefficients for the $\text{KO}_{.5} - \text{SiO}_2$ system^{11,12}. Thus it was possible to evaluate the excess heat capacity of mixing in $\text{KO}_{.5} - \text{SiO}_2$ as $8 X_{\text{KO}_{.5}} X_{\text{SiO}_2}$ from the heat capacity at the single composition studied by Moynihan et al.⁷

Figure 2 shows that the addition of further points from a more exhaustive literature search does not lead to any change in this equation. Moynihan et al. studied a number of mixed sodium - potassium silicates with $X_{\text{SiO}_2} = .61$, with the conclusion that there is no excess heat capacity on mixing the liquid having $X_{\text{KO}_{.5}} = .39$ with the liquid having $X_{\text{NaO}_{.5}} = .39$. Thus there is no need for a term in $X_{\text{KO}_{.5}} X_{\text{NaO}_{.5}}$. Heat capacities at 1000 K in ternary $\text{KO}_{.5} - \text{NaO}_{.5} - \text{SiO}_2$ liquids are given by the equation

$$C_p^e = 8 X_{\text{KO}_{.5}} X_{\text{SiO}_2} + 6.8 X_{\text{NaO}_{.5}} X_{\text{SiO}_2} \quad (8)$$

With this expression, the heat capacity and hence the specific heat can be calculated for any mixture of $\text{KO}_{.5}$, $\text{NaO}_{.5}$, and SiO_2 liquids.

Figure 3 shows calculated contour lines for the specific heat ($\text{cal g}^{-1} \text{K}^{-1}$) plotted against weight percentages in the ternary system at 1000 K.

The potassium silicate glass studied over the widest temperature range is that with $X_{\text{KO}_{.5}} = .4444$ in the work of Schwiete and Ziegler⁵. The enthalpy data given in their Table 1 can be fitted to a power series in $T-1000$

We have chosen to estimate C_p for liquid CaO in this range as 5% greater than C_p for the solid since this changes smoothly into a value close to 15.0 above 2100 K. This gives the equation

(11)

$$C_p = 13.487 + 1.4217 \times 10^{-3} (T-1000) - .3563 \times 10^{-6} (T-1000)^2 + .1199 \times 10^{-9} (T-1000)^3$$

for CaO(l), and this choice leads to $C_p^e = 1.4 \text{ cal mol}^{-1} \text{ K}^{-1}$ and the equation

$$C_p^e = 5.6 X_{\text{CaO}} X_{\text{SiO}_2} \quad (12)$$

One sodium calcium silicate glass was included in the study of Schwiete and Ziegler⁵. The equation

$$C_p^e = 6.8 X_{\text{NaO}.5} X_{\text{SiO}_2} + 5.6 X_{\text{CaO}} X_{\text{SiO}_2} \quad (13)$$

gives a calculated C_p of $16.5 \text{ cal mol}^{-1} \text{ K}^{-1}$ at 1000 K for this glass, the composition of which is $X_{\text{NaO}.5} = .2222$, $X_{\text{CaO}} = .1111$, $X_{\text{SiO}_2} = .6667$. This C_p value is in good agreement with the experimental value, $17.2 \text{ cal mol}^{-1} \text{ K}^{-1}$ ⁵. The agreement can be made exact by the addition of the term

$$38 X_{\text{NaO}.5} X_{\text{CaO}} X_{\text{SiO}_2}$$

A slightly different ternary composition was studied by Tydlit et al.¹³,

$X_{\text{NaO}.5} = .3301$, $X_{\text{CaO}} = .0858$, $X_{\text{SiO}_2} = .5841$ to 1578 K. The value of C_p^e at

1000 K is $2.32 \text{ cal mol}^{-1} \text{ K}^{-1}$, in excellent agreement with the equation

(14)

$$C_p^e = 6.8 X_{\text{NaO}.5} X_{\text{SiO}_2} + 5.6 X_{\text{CaO}} X_{\text{SiO}_2} + 38. X_{\text{NaO}.T} X_{\text{CaO}} X_{\text{SiO}_2} = 2.22 \quad (14)$$

The value for C_p^e at 1500 K is smaller, $17.27 - 16.11 + 1.16 \text{ cal mol}^{-1} \text{ K}^{-1}$,

but it does not appear that the terms in X_{CaO} decrease to zero at 1700 K. For

the data currently available the approximation that the 5.6 and 38. values are

independent of temperature appears to be satisfactory. Thus the current

equation for C_p^e for $\text{NaO}_{.5} - \text{CaO} - \text{SiO}_2$ liquids is

$$C_p^e = [6.8 - 19.4 \times 10^{-3}(T-1000) + 13.8 \times 10^{-6}(T-1000)^2] X_{\text{NaO}_{.5}} X_{\text{SiO}_2} \\ + 5.6 X_{\text{CaO}} X_{\text{SiO}_2} + 38. X_{\text{NaO}_{.5}} X_{\text{CaO}} X_{\text{SiO}_2} \quad (15)$$

This gives $C_p^e = 1.05$ at 1500 K (experimental value¹³ of 1.16). The solid

line for $H_T - H_{1000}$ calculated using this equation is shown in figure 4 along

with the experimental values¹³ for this particular composition.

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Figure 1 - Heat capacity per mole at 1000 K for $NaO_{.5}-SiO_2$ liquids, C_p in units of $cal\ mol^{-1}\ K^{-1}$ is plotted against the mole fraction of $NaO_{.5}$. The dark symbols represent data of Naylor⁴ (circles), Schwiete and Ziegler⁵ (diamond), and Moynihan et al.⁷ (square). The open diamonds are experimental values from the figures of Takahashi and Yoshio⁶, and values calculated from the formulas cited by Matveev and Zhuravlev⁹ are shown as open circles. The solid line is calculated from equation 1.

Figure 2 - Heat capacity per mole at 1000 K for $\text{KO}_{.5}\text{-SiO}_2$ liquids. C_p in units of $\text{cal mol}^{-1} \text{K}^{-1}$ is plotted against the mole fraction of $\text{KO}_{.5}$. The dark symbols represent data of Schwiete and Ziegler⁵ (diamond) and Moynihan et al.⁷ (square). The open diamonds are experimental values from the figures of Takahashi and Yoshio⁶, and values calculated from the formulas cited by Matveev and Zhuravlev⁹ are shown as open circles. The solid line is calculated from the equation¹² $C_p^e = 8.0 X_{\text{KO}.5} X_{\text{SiO}_2}$.

Figure 3 - Contour lines for specific heat as a function of weight per cent in the ternary system $\text{KO}_{.5}\text{-NaO}_{.5}\text{-SiO}_2$ at 1000 K. The values are calculated from equation 8.

Figure 4 - Comparison of calculated and experimental¹³ values of

$H_T - H_{1000}$ for a glass of the composition $X_{\text{NaO}_{.5}} = .3301$, $X_{\text{CaO}} = .0858$
and $X_{\text{SiO}_2} = .5841$.

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APPENDIX E

Calculation of Activities in the System $\text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$

Isaac Eliezer, Naomi Eliezer, Reed A. Howald
and Mary C. Verwolf.

ABSTRACT

The vapor pressure of potassium has been measured as a function of temperature in the Al_2O_3 - and SiO_2 - rich regions of the $\text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system. Combining this data with the known solubility relations in the system and mathematical analyses of activities in the binary subsystems leads to calculated activities for all three species as a function of temperature and composition for liquids in the system $\text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$. These calculations provide refinements in the phase diagram and in the thermodynamic properties of $\text{K}_2\text{Si}_4\text{O}_9$, KAlO_2 , sanidine, leucite, and KAlSiO_4 .

Introduction

A ternary system can be analyzed thermodynamically if the activity of one component can be measured over the full range of compositions. We have measured potassium pressures over SiO_2 rich liquids in the $\text{KO}_{.5}$ - $\text{AlO}_{1.5}$ - SiO_2 system using atomic absorption measurements of the vapor diffusing from a sample cell. The technique and apparatus are described in an earlier paper on the $\text{KO}_{.5}$ - SiO_2 binary system¹. However no single technique can provide accurate vapor pressure measurements over the range of pressures covered in this ternary system at a single temperature, or over the whole range of temperatures required by the high melting points of leucite, KAlSiO_4 , KAlO_2 , corundum, and mullite. Our vapor pressure measurements over systems of three coexisting solids in the high $\text{AlO}_{1.5}$ region of the phase diagram have confirmed the stability² of the leucite - corundum - orthorhombic KAlSiO_4 set of three solids, which shows an activity of $10^{-5.92}$ for liquid $\text{KO}_{.5}$ at 1700 K. Shairer and Bowen² have found that this set of three solids is in equilibrium with the liquid ternary of composition $X_{\text{KO}_{.5}} = .2514$, $X_{\text{AlO}_{1.5}} = .3303$ at 1826 K, at which point the three liquid activities are calculated to be $a_{\text{KO}_{.5}} = 10^{-5.46}$, $a_{\text{AlO}_{1.5}} = .522$ and $a_{\text{SiO}_2} = .360$. It is thus possible to obtain all three activities at temperatures and compositions for the liquid where it is in equilibrium with three solids, and the thermodynamic analysis of the liquid should include this data.

We have analyzed the liquids in the binary subsystems $\text{KO}_{.5}$ - SiO_2 ¹, $\text{KO}_{.5}$ - $\text{AlO}_{1.5}$ ³ and $\text{AlO}_{1.5}$ - SiO_2 ⁴ using Redlich - Kister power series with terms through the fourth power of mole fractions.

If the full ternary can also be treated with reasonable accuracy with only terms through the fourth power, this is a particularly favorable situation, since there are only three additional independent terms for a ternary system through the fourth power beyond the terms known for the binary subsystems. We have chosen⁵ to label these B_{321}^a , C_{321}^a , and C_{321}^b and to write the contributions to the excess free energy of mixing as $B_{321}^a X_1 X_2 X_3$, $C_{321}^a X_1 X_2 X_3 (1 - X_3)$ and $C_{321}^b X_1 X_2 X_3 (X_1 - X_2)$. The three unknowns B_{321}^a , C_{321}^a , and C_{321}^b can be evaluated from the three known activities for a liquid in equilibrium with three known solids as in the above example.

As expected, the experimental errors in the equilibrium temperatures and compositions together with uncertainties in the thermodynamic properties and compositions of the solids lead to substantially different values for B_{321}^a , C_{321}^a , and C_{321}^b from different liquids even at similar temperatures. The major discrepancies in the first calculation were in the reported² eutectic composition for sanidine - tridymite - mullite and in the relative SiO_2 activities for two liquids, one in equilibrium with sanidine - leucite - $\text{K}_2\text{Si}_2\text{O}_5$ and the other with sanidine - K_2SiO_5 - $\text{K}_2\text{Si}_4\text{O}_9$.

Liquid compositions near the sanidine - tridymite - mullite eutectic are so viscous² that substantial experimental errors in the solubility data are not unexpected, and the uncertainties in SiO_2 activities can be resolved by reasonable adjustments in the thermodynamic values for $\text{K}_2\text{Si}_4\text{O}_9$, sanidine, and leucite, as described in this paper.

Literature values for the thermodynamic properties of the solids. -

The three major potassium aluminum silicates at high temperatures are sanidine, $(\text{KAlSi}_3\text{O}_8)$, leucite $(\text{KAlSi}_2\text{O}_6)$, and orthorhombic KAlSiO_4 . Heat of formation values for all three compounds are listed in the standard compilation of Robie and Waldbaum⁶. These values must be recalculated on the basis of revised enthalpies of formation of the secondary standards used for aluminum compounds. We have recalculated the enthalpies of these three compounds from the original data⁷⁻⁹ using improved heats of formation for gibbsite¹⁰, gamma alumina¹¹, and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ¹². Our value of $\Delta H_{f,298}^\circ = -726.21 \text{ kcal mol}^{-1}$ for leucite is based upon comparison to gibbsite, instead of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ as in the original calculations of Barani and Adami¹² and the recalculation of Thompson¹³. For KAlSiO_4 and sanidine our recalculated values are in agreement with previously published values recalculated by Thompson¹³ and Chatterjee and Johannes¹⁴ respectively. The values we have used in our calculation are given in Table 1.

The KAlSiO_4 and leucite values in Table 1 are within 100 calories of the value tabulated by Hemingway and Robie¹⁵, and the discrepancy between this compilation¹⁵ and our choice⁴ for sanidine is now only 660 cal mol^{-1} .

There are third law entropies available now for these three compositions: KAlSi_3O_8 (as adularia)¹⁶, KAlSi_2O_6 (c, leucite)¹⁶ and KAlSiO_4 ¹⁶ (as a synthetic material called kaliophilite). Natural kaliophilite cannot be synthesized, and the temperature of synthesis and reported X-ray data indicate that this entropy value actually applies to the orthorhombic form of KAlSiO_4 . We attempted to use

these third law entropies (uncorrected) for sanidine, leucite, and orthorhombic KAlSiO_4 . However these values would allow sanidine to disproportionate into cristobalite and leucite at 1200 K, and are therefore not satisfactory. Even the small excess entropy (0.79eu) used by Chatterjee and Johannes¹⁴ is not sufficient stabilization for sanidine. Using $\Phi_{1000} = 85.38$ for sanidine is sufficient to prevent disproportionation of sanidine before its incongruent melting point, but it leaves leucite as the third solid in equilibrium with $\text{K}_2\text{Si}_4\text{O}_9$ and $\text{K}_2\text{Si}_2\text{O}_5$ at 900 K in contradiction to phase diagram data of Shairer and Bowen². If the free energy function of sanidine is increased by 2 or 3 cal mol⁻¹ K⁻¹, leucite disproportionates unless its entropy is increased relative to that of kaliophilite as well. We concluded that both leucite and sanidine may have substantial entropies of mixing due to Al - Si disorder, and we have relied on equilibrium measurements to evaluate the entropies.

There is more entropy of mixing in sanidine than in leucite or KAlSiO_4 . We have considered Φ_{1000} values for sanidine from 85.38 to 90 cal mol⁻¹ K⁻¹. The calculated excess entropy of mixing (4.4 cal mol⁻¹ K⁻¹) used by Robie and Waldbaum⁶ for sanidine corresponds to a value $\Phi_{1000} = 87.76$ cal mol⁻¹ K⁻¹ which is in the middle of this range. The final value for sanidine in Table 1 is $\Phi_{1000} = 85.78$ cal mol⁻¹ K⁻¹. This value was obtained by using six of the best activity coefficient data which were independent of the absolute entropies of the potassium aluminum silicates to get a first set of estimates for B_{321}^a , C_{321}^a and C_{321}^b , and calculating Q_{SiO_2} (= .360) for the liquid present at the 1826 K eutectic for orthorhombic KAlSiO_4 , leucite, and corundum.

The thermodynamic properties of the solid potassium silicates¹

and of mullite⁴ have been discussed in connection with the corresponding binary systems. There is not much data available for potassium aluminate, KAlO_2 , but its properties are fixed fairly closely by the vapor pressure measurements of Plante et al.¹⁷ Thus at 1400 K KAlO_2 in equilibrium with beta aluminate has a potassium pressure of 5.608×10^{-6} atm, corresponding to an activity of $\text{KO}_{.5}$ (s) of 4.598×10^{-5} . The corundum - beta alumina system at this temperature has a much lower $\text{KO}_{.5}$ activity: 2.700×10^{-8} . The activity of alumina also varies with the composition of the beta alumina to satisfy the Gibbs - Duhem relationship. The ratio of mole fractions is somewhere between $.1/.9 = .111$ and $.167/.833 = .200$. For a beta alumina in equilibrium with KAlO_2 at this temperature, $a_1 = 4.598 \times 10^{-2}$ and $a_2 = .319 \pm .118$. When the calculation is repeated at another temperature, we have both enthalpy and entropy of KAlO_2 fixed at least approximately to the values shown in Table 1. The melting point of KAlO_2 is approximately 2373 K⁽¹⁸⁾. From the compositions of the solid and liquid in equilibrium at 2096 K¹⁹ we have estimated the equilibrium constant for the reaction of KAlO_2 (s) $\rightarrow \text{KAlO}_2$ (l) as .834, and the heat of fusion as $12.92 \text{ kcal mol}^{-1}$. This fixes the Redlich - Kister A values for enthalpy and $\log \gamma$ for the $\text{KO}_{.5} - \text{AlO}_{1.5}$ binary liquid system. The B values also shown in Table 2 are arbitrarily picked as $1/3$ A, so that $\bar{H}_1$ and $\log \gamma$ reach maxima at $X_1 = 0$, because this is closer to the behavior found for the $\text{KO}_{.5} - \text{SiO}_2$ systems than setting the B values equal to zero.

Adjustment of the thermodynamic values for $\text{K}_2\text{Si}_4\text{O}_9$, sanidine, leucite, and KAlSiO_4 .

We have measured vapor pressures of potassium over systems of

three coexisting solid phases in the alumina rich region of the ternary phase diagram. Three reproducible pressure vs. temperature curves were observed in addition to that for the beta alumina - corundum system known from the binary system. These four lines of $\log P$ vs $1/T$ are shown in figure 1, labelled as L, B, M and H in order of increasing activity of K_2O . They correspond to activities for liquid K_2O at 1700 K of $10^{-5.921}$, $10^{-5.705}$, $10^{-5.095}$ and $10^{-4.544}$ respectively. One of these values should correspond to equilibrium with leucite and orthorhombic KAlSiO_4 . The third law entropy values for these solids gave $(I_{\text{K}_2\text{O}} = 10^{-5.646}$ for the leucite - orthorhombic KAlSiO_4 - corundum system at 1700 K, which is between the values for the L and M curves. We have tried adjustments of the entropy values to bring the K_2O liquid activity to $10^{-5.921}$ for KAlSiO_4 - leucite - corundum or to $10^{-5.095}$ for KAlSiO_4 - leucite - β alumina. The first of these assignments is not only consistent with the solubility data of Shairer and Bowen², but provides an overall better (smaller positive deviations from ideality for SiO_2) set of activities and activity coefficients over the full range of compositions for the ternary system.

Solid $\text{K}_2\text{Si}_4\text{O}_9$ melts at 1043 K and appears in the phase diagram in equilibrium with liquid down to the eutectic with $\text{K}_2\text{Si}_2\text{O}_5$ at 1015 K. At 1015 K the activity of liquid SiO_2 in equilibrium with these two solid potassium silicates is about .323. Although this value should decrease with decreasing temperature, if the enthalpies from reference 1 are used, the activity of liquid SiO_2 in equilibrium with the two solids at 968 K is too low - only .250. It appears that the narrow temperature range between 1043 and 1015 K is not sufficient to give the enthalpy accurately enough to extrapolate down to 968 K. The phase diagram

of Shairer and Bowen² shows the $K_2Si_2O_5$ - $K_2Si_4O_9$ - liquid curve at higher SiO_2 mole fractions and activities than the leucite - sanidine - liquid line. While most of the adjustment to bring about agreement has been in the entropies of leucite and sanidine, we have also adjusted the enthalpy of $K_2Si_4O_9$ to reduce ΔH for the reaction

down to $1.3 \text{ kcal mol}^{-1}$ (instead of $7.3 \text{ kcal mol}^{-1}$). With this adjustment, the activities of SiO_2 and $KO_{.5}$ in the equilibrium eutectic liquid at 968 K are $a_{SiO_2} = .313$ and $a_{KO_{.5}} = .269 \times 10^{-9}$. Thus, two of the activity coefficients in this liquid are known even if the entropy of sanidine is uncertain.

In the course of a long series of trials on this ternary system we came to the conclusion that the most reliable equilibrium data of Shairer and Bowen for liquid in the presence of three solids was at 1826 K, with the values at 968, 1083, and 1588 K the next most reliable data. The 1083 K equilibrium with sanidine, leucite and $K_2Si_2O_5$ is extremely dependent upon the values selected for sanidine and leucite, but the other 3 points each supply two clearly established activities and activity coefficients. In principle, six values are enough to calculate the values and temperature dependence of B_{321}^a , C_{321}^a and C_{321}^b . However in practice, the least squares treatment had to be limited to fewer unknowns to avoid magnification of random errors. We have arbitrarily assumed that each of these values has a temperature dependence such that a linear plot of B_{321}^a , C_{321}^a , and C_{321}^b vs. $1/T$ passes through the origin. For example $B_{321}^a(T) = B_{321}^a(1000) \left[(1000)/T \right]$. These assumptions applied to our six selected data points gave $B_{321}^a = 0.75$, $C_{321}^a = -1.30$, and $C_{321}^b = -5.58$ at 1000 K. With these values, we calculated $a_{SiO_2} = .360$ for the eutectic liquid at 1826 K, of

composition $X_{\text{SiO}_2} = .417$, $X_{\text{AlO}_{1.5}} = .330$, and $X_{\text{K}_2\text{O}_{.5}} = .252$. This fixes the free energy function values for orthorhombic KAlSiO_4 and leucite at the values shown in Table 1. The value for sanidine is then determined by the sanidine - leucite - $\text{K}_2\text{Si}_2\text{O}_5$ - liquid equilibrium at 1083 K. Once these values are fixed, the four major points give a total of 12 activity coefficient values.

A new least squares treatment of these 12 values gave the final values $B_{321}^a = 1.4667$, $C_{321}^a = -2.4659$ and $C_{321}^b = -4.8201$ at 1000 K.

Sanidine occupies a position in a great variety of equilibria of geological and technical importance. Thus there have been and will continue to be heated arguments in the literature on the best interpretation of the available thermodynamic and equilibrium data. We are making the point in this paper that solubilities and vapor pressures in the $\text{K}_2\text{O}_{.5}$ - $\text{AlO}_{1.5}$ - SiO_2 system provide data on these values, but we do not wish to discount the information from hydrothermal equilibria or even calculations of the temperature dependent disorder present in the crystals. The important point to be established now is that information from a great variety of sources is becoming available, and the remaining uncertainties are getting smaller. Thus we feel that Table 3 comparing our values with other recent papers^{14, 15} will be of more value than arguing the relative merits of the differing values.

Extended Redlich - Kister Coefficients for the Ternary System. -

As mentioned in the introduction, since the binary subsystems are represented with reasonable accuracy with two or three Redlich - Kister coefficients, we can expect that we can do a similarly adequate job for the entire ternary using only terms through the fourth power in mole

fractions. This is convenient because it leaves only the three terms B_{321}^a , C_{321}^a and C_{321}^b to be evaluated at a particular temperature, and this can be accomplished from three activity coefficients for a single liquid. Thus, those liquid compositions found by Shairer and Bowen² to be in equilibrium with three solids of differing stoichiometry take on special significance. Shairer and Bowen² have identified eight such liquids, and it is possible to calculate values for B_{321}^a , C_{321}^a , and C_{321}^b for each one. Unfortunately the calculated values are very sensitive to the entropy values used for the solid potassium aluminum silicates, and it was necessary to get estimates for the three terms from the few activity coefficients independent of these entropy values. The values were then refined by least squares to give the final values in Table 4. The enthalpy coefficients are fixed by the form of the temperature dependence which was assumed ($B_{123}^a(T) = B_{123}^a(1000) [1000/T]$, etc.) The single heat capacity value, $B_{321}^a(C_p) = -32 \text{ cal mol}^{-1} \text{ K}^{-1}$ was selected to cancel most of the contribution from $B_{13} = +8$ along the $\text{SiO}_2 - \text{K}_{.5} \text{Al}_{.5}\text{O}$ join.

With these values we can calculate the activities of all three components for any selected temperature and composition for the liquid phase. Table 5 shows a comparison of the activities for the liquids found by Shairer and Bowen in equilibrium with three solids of different compositions. The agreement for the 1826 K point is very good, while the values for the other 3 points included in the least squares procedure are within $\pm 35\%$. The fit at the 968 K eutectic is the least satisfactory. It can however be improved considerably by a small adjustment in the temperature and composition (from 968 K, $X_1 = .356$, $X_2 = .0346$, $X_3 = .6409$ to 973 K, $X_1 = .372$, $X_2 = .045$, $X_3 = .583$).

For the points not included in the least squares in Table 5, (generally at higher mole fractions of SiO_2), the agreement is not as good. Shifting the compositions to less SiO_2 generally improves the fit, but it is also clear that using this set of Redlich - Kister coefficients exaggerates the positive deviations from ideality shown by SiO_2 . The calculation does come quite close to the measured cristobalite solubilities at higher temperatures, but apparently this set of parameters gives too large a temperature dependence for $\log \gamma_{\text{SiO}_2}$;

the values of $\bar{H}_{\text{SiO}_2}$ are too large. Since the major contribution to $\bar{H}_{\text{SiO}_2}$ in this region is from B_{13} , it is clear that an improved fit of these points will require more accurate enthalpy data for the $\text{KO}_{.5} - \text{SiO}_2$ binary system. (This may be obtainable from data on heat capacities and heats of solution of glasses in the $\text{KO}_{.5} - \text{NaO}_{.5} - \text{SiO}_2$ ternary system). Nevertheless, this set allows calculations of reasonable accuracy ($\pm 50\%$) over much of the composition range.

Figure 2 shows a comparison of the calculated and experimental potassium pressures for two selected compositions in the high SiO_2 region.

The thermodynamic properties of the tetragonal phase. -

The data of Cook et. al.¹⁹ on the $\text{SiO}_2 - \text{KAlO}_2$ join in this ternary system show that there is a tetragonal phase with a composition approximately $\text{K}_{.57}\text{Al}_{.57}\text{Si}_{.43}\text{O}_2$ in equilibrium with orthorhombic KAlSiO_4 at 1700 K. Thus one expects to find vapor pressure readings for the set of three solids $\text{KAlSiO}_4 - \text{K}_{.57}\text{Al}_{.57}\text{Si}_{.43}\text{O}_2 - \beta$ alumina, and we have assigned the free energy of $\text{K}_{.57}\text{Al}_{.57}\text{Si}_{.43}\text{O}_2$

at 1700 K to fit the observed K_2O activity on the H curve, $10^{-4.544}$, for this equilibrium set of solids. The X-ray data¹⁹ clearly indicate that the tetragonal phase is a high temperature material, so the reaction

is expected to be endothermic. If it is endothermic by as much as 2 kcal mol^{-1} the calculated melting point for $\text{K}_{.57} \text{Al}_{.57} \text{Si}_{.43} \text{O}_2$ is too high, (over 2300 K). The enthalpy and entropy values in Table 1 for $\text{K}_{.57} \text{Al}_{.57} \text{Si}_{.43} \text{O}_2$ are assigned assuming $\Delta H = 1 \pm 1 \text{ kcal mol}^{-1}$ for this reaction.

Calculations of Phase Equilibria on the SiO_2 - $\text{K}_{.5} \text{Al}_{.5} \text{O}$ Join. -

The extended Redlich - Kister coefficients in Table 4 allow one to calculate Redlich - Kister coefficients for various pseudobinary mixtures within the ternary phase diagram.⁵ The SiO_2 - $\text{K}_{.5} \text{Al}_{.5} \text{O}$ pseudobinary is one of the most important of these because of the number of potassium aluminum silicates found along it. The Redlich - Kister coefficients calculated for this pseudobinary are listed in Table 6, and figure 3 shows a calculated phase diagram for the low SiO_2 region along this join where the melting points are so high that they are not well established. The excessive positive deviations from ideality calculated from these values at lower temperatures and high SiO_2 mole fraction introduce substantial distortions of the phase diagram for $X_{\text{SiO}_2} > 0.6$, so this region is not shown in the figure. Leucite, KAlSiO_4 , and $\text{K}_{.57} \text{Al}_{.57} \text{Si}_{.43} \text{O}_2$ have been treated as stoichiometric compounds

for this calculation, although they all have been shown to have somewhat variable composition⁽¹⁹⁾. The solubility of SiO_2 in $\text{K}_{.5}\text{Al}_{.5}\text{O}$ is so substantial that it has been necessary to assign Redlich - Kister parameters for the $\text{K}_{.5}\text{Al}_{.5}\text{O}$ cubic phase: $A_{12} = 1.499$ and $B_{12} = 5.934$. These values were selected to give a eutectic between $\text{K}_{.5}\text{Al}_{.5}\text{O}$ and the tetragonal phase at 2100 K, and they give calculated equilibrium compositions for $\text{K}_{.5}\text{Al}_{.5}\text{O}$ at lower temperatures in substantial agreement with the X-ray data⁽¹⁹⁾.

The liquidus curve for $\text{K}_{.5}\text{Al}_{.5}\text{O}$ saturated with SiO_2 is very sensitive to the melting point of pure $\text{K}_{.5}\text{Al}_{.5}\text{O}$ and the assumption made concerning its heat of fusion. Therefore the lines are likely to be substantially in error and are shown as dotted lines in Figure 3. They are excessively steep because the assumption we have used requires SiO_2 to stabilize solid $\text{K}_{.5}\text{Al}_{.5}\text{O}$ more than the liquid, and thus suggests that SiO_2 addition may raise rather than depress the melting point of potassium aluminate. This possibility is worth considering in interpreting the scanty data available on the melting point of potassium aluminate (18,20).

Potassium Vapor Pressures in the High $\text{AlO}_{1.5}$ Region. -

In the course of these calculations we have assigned three of the four observed potassium pressure vs temperature curves in Figure 1 to equilibrium sets of three solid materials as follows

L curve	leucite - KAlSiO_4 - corundum
B curve	KAlSiO_4 - corundum - β alumina
and H curve	KAlSiO_4 - tetragonal phase - β alumina

These assignments serve to fix the thermodynamic properties of these solids, so the agreement between calculated and observed potassium pressures must be good. One can however check the assignments using any other equilibrium measurement on the solids. Seki and Kennedy⁽²¹⁾ have studied the disproportionation of leucite

as a function of temperature and pressure. Knowing the volume change for this reaction and the equilibrium pressures, one can estimate that the equilibrium constant is about 0.28 at 1000 K and 1 atm pressure. The thermodynamic data in Table 1 show $K_{1000} = .58$ for the reaction

which is certainly of the correct order of magnitude, even allowing for a small difference in free energy between kalsilite and the orthorhombic crystals:

The other curve, M in figure 1, must represent vapor pressure equilibrium for some metastable system. One of the most likely non-equilibrium sets of solids is leucite - tetragonal crystals - β alumina for which the calculated liquid $\text{KO}_{.5}$ activity at 1700 K is $10^{-5.374}$, within a factor of 2 of the value for the M curve, $10^{-5.095}$.

It is clear that the values proposed here for the thermodynamic quantities for the solid and liquid phases reproduce the major features of the ternary system $\text{KO}_{.5}$ - $\text{AlO}_{1.5}$ - SiO_2 . There are however enough discrepancies within a factor of 2 to indicate that better fits can be obtained in the future. However we have had to consider entropy values over a range of $\pm 4 \text{ cal mol}^{-1} \text{ K}^{-1}$, and factors of 2 present a substantial improvement over uncertainties of a factor of 8;

In fact no thermochemical data at all has been available for the trigonal phase. Even such approximate values for the activities in the equilibrium liquids improve the thermodynamic characterization of the solids in complex ternary systems like this, and we can look forward to even better values as better enthalpy data and better computer programs for activity coefficients in multicomponent system become available.

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Table 1

Thermodynamic values selected for solids and pure liquids

	H_{298}° ^a kcal mol ⁻¹	H_{1000}° ^a kcal mol ⁻¹	Φ_{1000}° ^b cal mol ⁻¹ K ⁻¹	C_p ^c A	B	C	D
KO _{1.5} (c)	-43.2	-36.2	18.09	9.097	.96		
KO _{1.5} (l)	-40.628	-32.128	19.4526	11.45	1.8		
SiO ₂ (c, cristobalite)	-216.417	-206.4	18.1108	16.72175	2.05366	-1.6518	.6463
SiO ₂ (c, quartz)	-217.7	-206.86	16.859	16.48	.0024		
SiO ₂ (l)	-215.74	-205.40	18.1766	16.61	3.2268	1.2384	
AlO _{1.5} (c)	-200.25	-190.933	12.2175	14.908	2.3471	-1.2727	.34615
AlO _{1.5} (l)	-190.358	-182.152	16.555	17.312	d		
K ₂ Si ₄ O ₉ (c)	-1047.818	-991.050	101.339	85.081	9.0876	-3.1173	
KSio _{2.5} (c)	-304.8457	-288.8287	33.5537	25.819	25.819	2.752	-.77932
KAlO ₂ (c)	-272.9628	-256.6458	31.3415	24.005			
KAlSi ₃ O ₈ (c, sanidine)	-945.636	-898.786	85.78	75.5	10.0		
KAlSi ₂ O ₆ (c, leucite)	-726.210	-688.280	68.585	56.5	3.14		
KAlSiO ₄ (c, orthorhombic)	-506.870	-479.770	50.161	42.5			
KAlSiO ₄ (c, kalsilite)	-508.0846	-480.9846	50.474	42.5			
K _{.57} Al _{.57} Si _{.43} O ₂ (c)	-255.1689	-241.2315	26.478	21.6357	.4629	-.17804	.04846

a) H_T° is defined as $\Delta H_{f,298.15}^{\circ} + \int_{298.15}^T C_p dT$

b) Φ_T° is the free energy function defined as $S_T^{\circ} - (H_T^{\circ} - H_{298}^{\circ})/T$

c) Heat capacities are expressed by the power series $C_p = A + B \times 10^{-3}(T - 1000) + C \times 10^{-6}(T - 1000)^2 + D \times 10^{-9}(T - 1000)^3$

d) At temperatures over 2000 K the values are changed to $A = 27.66$ and $B = -2.96$.

Table 2

Redlich - Kister Coefficients for the Binary Subsystems.

system	quantity	A	B	C
KO _{.5} - SiO ₂	log γ ₁₀₀₀	-17.42266	-10.64114	-1.010074
	enthalpy	-90000.	-53000.	
	C _p	8.		
SiO ₂ - AlO _{1.5}	log γ ₁₀₀₀	1.330516	-.212799	.096297
	enthalpy	6400.		
KO _{.5} - AlO _{1.5}	log γ ₁₀₀₀	-13.3805	-4.4601	
	enthalpy	-75792.	-25264.	

Table 3

Comparison of thermodynamic values at 298.15 K for high sanidine
from recent work

	H_{298}° kcal mol ⁻¹	S_{298}° cal mol ⁻¹ K ⁻¹
this work	-945.686	54.96
Chatterjee and Johannes ¹⁴		
Z = .0984	-945.521	53.38
Z = .1607	-945.686	53.26
Hemingway and Robie ¹⁵	-946.350	55.664

Table 4

Extended Redlich-Kister coefficients for the ternary liquid system

 $\text{KO}_{.5} - \text{AlO}_{1.5} - \text{SiO}_2$

term	$\log \gamma_{1000}$	H_{1000} kcal mol ⁻¹	C_p cal mol ⁻¹ K ⁻¹
A_{12}	-13.3805	-75.792	0
B_{12}	-4.4601	-25.264	0
A_{13}	-17.42266	-90.000	8.
B_{13}	-10.64114	-53.000	0
C_{13}	-1.010074	0	0
A_{23}	1.330516	6.4	0
B_{23}	-0.212799	0	0
C_{23}	0.096297	0	0
B_{321}^a	1.4667	6.711	-32.
C_{321}^a	-2.4659	-11.283	0
C_{321}^b	-4.8201	-22.055	0

Table 5

Comparison of calculated activities for liquids in equilibrium with three solids of three different compositions.

symbol	C	S	R	A	P	U	N	M
temperature K	1826	968	1083	1588	983	1178	1413	1258
solids	leucite	sanidine	sanidine	leucite	sanidine	leucite	sanidine	sanidine
present	KAlSiO ₄	K ₂ Si ₄ O ₉	leucite	mullite	quartz	kalsilite	leucite	tridymite
	corundum	K ₂ Si ₂ O ₅	corundum	corundum	K ₂ Si ₄ O ₉	K ₂ Si ₂ O ₅	mullite	mullite
composition	X ₁ .2524	.3559	.3730	.1655	.2720	.4467	.1471	.1159
of	X ₂ .3303	.03462	.05689	.2035	.04078	.08192	.1526	.1229
liquid	X ₃ .4173	.6094	.5702	.6310	.6873	.4713	.7003	.7612
activities								
calculated	$a_1 \times 10^9$ 3468.	.2688	4.730	68.01	.0817	27.15	17.87	.3727
from properties	a_2 .5216	.00076	.00021	.3450	.00036	.000274	.2340	.1351
of solids	a_3 .3604	.3134	.3033	.7672	.7004	.3655	.4912	.7757
calculated	$a_1 \times 10^9$							
from	a_1 3824.	.1613	3.354	95.92	.0312	185.9	11.46	1.157
Redlich - Kister	a_2 .5290	.00060	.00021	.3085	.00033	.00259	.2214	.2119
coefficients	a_3 .3721	.4060	.3047	.9310	1.004	.05243	1.065	1.123

Table 6

Redlich-Kister coefficients for the $\text{SiO}_2 - \text{K}_{.5}\text{Al}_{.5}\text{O}$ pseudobinary subsystem.

term	$\log \gamma_{1000}$	H_{1000} kcal mol ⁻¹	C_p cal mol ⁻¹ K ⁻¹
A'	-3.343539	-16.0933	0
B'	4.023792	20.4465	4.
C'	-0.411118	-0.7052	0

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Figure 1. - Four lines of potassium pressure vs. $1/T$ observed for high alumina samples in the system.

Figure 2

Comparison of measured and calculated (solid lines) pressures of potassium atoms. The diamonds and upper line are for a composition of $X_{\text{KO}_{.5}} = .36$, $X_{\text{AlO}_{1.5}} = .04$, $X_{\text{SiO}_2} = .60$. The circles and the lower line are for a sample with $X_{\text{KO}_{.5}} = .13$, $X_{\text{AlO}_{1.5}} = .07$, $X_{\text{SiO}_2} = .80$.

Figure 3. - A Calculated Portion of the Phase Diagram from Leucite to KAlO_2 .

Physical Properties of Coal Slag and Electrode Materials:
Thermionic Emission and Effects of Electrical Conduction

G. Lapeyre and J. Anderson

ABSTRACT

Thermionic emission measurements were made on five six-component synthetic slags containing from zero to 30 percent K_2O . The effective work function, ϕ_e , was found to be dependent on temperature and on the presence or absence of potassium. For the slag without potassium, ϕ_e varied from 4.3 eV to about 5.1 eV over the temperature range 1400 K to 1700 K. For the slags with added potassium, ϕ_e generally varied from 3.2 eV at 1100 K to about 4.0 eV at 1600 K. The slags with the higher potassium content appeared to have a somewhat lower ϕ_e at the higher temperatures than those with smaller amounts of potassium. X-ray fluorescence measurements showed that the slag samples lost appreciable amounts of potassium at the higher measuring temperatures. Slag measurements at higher background pressures, up to one torr, of argon and oxygen showed that the argon reduced the emission current only slightly. The emission current recovered when the argon was removed. Oxygen apparently produced a permanent effect on the surface chemistry of the slag because the emission was reduced by more than two orders of magnitude and did not recover when the oxygen was removed. The thermionic emission of strontium-doped lanthanum chromite was measured over the temperature range 1300 K to 1800 K and found to be 3.28 ± 0.08 eV. Preliminary electrolysis experiments were carried out on samples of synthetic coal slag. X-ray fluorescence measurements showed a motion of cations toward the negative electrode when current was passed through the slag at a temperature of 1000°C.

I. OBJECTIVE AND SCOPE OF WORK

The objective of this project is to determine the thermionic emission properties (e.g., thermionic work function) of coal slag, including slag-seed mixtures. Evaluation of the need for thermionic emission data on electrode materials will be made in the context of clean electrodes in hot-wall, coal-fired channels, and exploratory measurements will be made.

Initial measurements will be performed on synthetic slags of various compositions at temperatures both below and above the temperature at which the slag is liquid.

Since the actual surface composition is of paramount importance in determining the work function and the thermionic emission, in situ surface analysis will be carried out by Auger electron spectroscopy. Materials desorbing and evaporating from the surface will be determined by mass spectrometry.

II. SUMMARY OF PROGRESS TO DATE

The experimental work for this period consisted mainly of two parts: 1) measurements of the thermionic emission of the series of low-silica (≈ 40 percent by weight) synthetic slags and 2) initial study of the electrolytic effects that occur in coal slag as a consequence of the conduction of electrical current. In addition, the thermionic emission of strontium-doped lanthanum chromite ($\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3$) was measured in the temperature range 1300 K to 1800 K. In preparation for future experiments, some preliminary experiments were performed on the thermionic emission of synthetic coal slag at higher pressures (up to one torr) of argon and oxygen.

A brief overview of the experimental results follows

A. Synthetic Slag

A series of six-component slags, obtained from the National Bureau of Standards, contained from zero to 30 percent K_2O by weight. Of the other five components, SiO_2 comprised 40 percent by weight with lesser amounts of Al_2O_3 , Fe_3O_4 , CaO , and MgO (see Table I). The effective work functions, ϕ_e , were measured over the temperature range 1100 K to about 1600 K. Qualitatively, for all the samples measured, ϕ_e was found to increase with temperature, and there was a marked distinction between the slag samples with and without K_2O . Samples without potassium were found to have ϕ_e varying from 4.2 eV to 5.0 eV over the temperature range measured, while for those with potassium, ϕ_e varied from about 3.2 eV to 4.2 eV. Clearly, potassium on the slag surface lowers the work function. However, it appears that the amount of potassium on the surface depends on the temperature and thermal history of the slag. X-ray fluorescence measurements after heating have shown a loss of bulk potassium from the slag, which is significant for temperatures above 1600 K. Since the potassium is actively evaporating from the slag surface at elevated temperatures, its surface concentration also may be a function of temperature. This may explain the observed increase in ϕ_e with temperature and the fact that the high-silica slags, which were run at somewhat higher temperatures than the low-silica slags, exhibited quite high work functions, ≈ 4.5 eV, regardless of the potassium content.

B. Ceramics

For the strontium-doped lanthanum chromite sample, the effective work function was found to be 3.28 ± 0.08 eV, which is close to but slightly larger than the value of 3.13 ± 0.04 eV found previously for the magnesium- and aluminum-doped lanthanum chromite.

C. Electrolysis Studies

The electrolysis, or mass transport, experiments were carried out on two slag samples, one with 30 percent K_2O and the other without K_2O . An electric current was passed through the samples while they were heated to a temperature of 1000°C in a furnace. When cool, they were sectioned and examined visually and with the X-ray fluorescence attachment on the

scanning electron microscope. For the slag sample containing potassium, it was found that potassium had indeed migrated toward the negative electrode. For the slag sample without potassium, both iron and calcium were found to have accumulated at the interface region near the negative electrode. At the positive electrode, a light brown layer had been formed during the experiment, but the measurements showed no particular accumulation of any element. The scanning auger microprobe, recently acquired by the University, may provide improved tracing of the motion of the ionic components of the slag, particularly since it is sensitive to the light elements including oxygen.

D. Thermionic Emission at Higher Pressures

Some preliminary experiments were carried out to measure the effect of a higher pressure of background gases on the thermionic emission of slag. Both argon and oxygen were tried at pressures up to one torr. The argon caused a small decrease in the emission which was recovered when the argon was pumped out and which probably can be attributed to a small cooling effect. On the other hand, oxygen, at the higher pressures, caused a decrease in the emission by at least two orders of magnitude, and the emission did not recover upon removal of the oxygen. The cause of this behavior is not yet known.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Work Accomplished

1. Thermionic Emission from Coal Slag

A large number of thermionic emission measurements were made on a series of five low-silica synthetic slags containing from zero percent to 30 percent K_2O by weight. In this series of six-component slags, the weight percent ratios of the five components, excluding K_2O , were constant at 40 : 15 : 15 : 20 : 10 for SiO_2 , Al_2O_3 , Fe_3O_4 , CaO , and MgO , respectively. The number designations and compositions of the slags that were measured are listed in Table I.

The slag samples were prepared for measurement by cutting or grinding a small disc (about 6mm in diameter by 1mm thick) and placing it on a small, thin piece of iridium foil which, in turn, was spot-welded to a thin tantalum strip which, in the vacuum system, served to heat the iridium and slag when a large electric current was passed through it. Alternatively, the slag was prepared in powder form and spread in a thin layer on the iridium. The slag then was heated and melted in a vacuum to form a thin layer over the iridium. The thermionic emission current at various temperatures was measured using the diode-guard ring arrangement described in earlier reports. The anode consisted of a massive copper block. This form was chosen to keep the anode relatively cool and prevent thermal re-emission of positive ions which was found earlier to interfere with the measurement of the thermionic emission of electrons from the slag.

The results of the measurements of ϕ_e at various temperatures for the five slag samples mentioned previously are shown in Figures 1 through 5. These figures are ordered according to increasing K_2O content from zero percent (Figure 1) to 30 percent (Figure 5). The various symbols in a single figure correspond to different samples of the same slag. In some of the figures, an open symbol is connected by a vertical line to a solid symbol. The meaning of this is explained below; but the solid symbols denote ϕ_e at the indicated temperature for a particular slag. The line drawn through the experimental points represents a least squares fit. For the slag sample without K_2O , the range of measurement temperatures is somewhat higher than for the other slags. This is because at the lower temperatures, the emission current was too low to measure accurately due to the relatively high work function.

The data show that the slags with the added K_2O have a lower ϕ_e than the one without K_2O (K488). The effective work functions of the potassium-containing slags is as low as 3.2 eV at the lower temperatures; this is the first clear evidence that the potassium has the effect of lowering the work function of the slag surface to a significant degree. This contrasts to the case of the high-silica slags where little effect was found. The reason probably lies in the higher temperatures at which the latter slags were measured, as is discussed below. It is also to be noted that ϕ_e increased with increasing temperature. A possible explanation for the temperature dependence is the varying degree of potassium surface coverage over the temperature range. Of course, this cannot explain why K488 also exhibits a similar temperature dependence.

In the course of performing the measurements, it was observed that the thermionic emission from the potassium-containing slags showed a dependence on time and thermal history. Specifically, when the slag temperature was raised, the emission current would instantaneously attain a relatively high level, decay within a few minutes to a lower value, and then remain stable. The corresponding increase of ϕ_e is represented by the vertical line connecting the two data points, as mentioned above. Figure 6 illustrates this behavior. It is believed that this behavior represents the decrease in the surface concentration of potassium as the slag temperature is increased. If the temperature is subsequently lowered, the lower work function is mostly recovered; however, there is some evidence that an irreversible change to a slightly higher work function occurs. This irreversible change may be related to a net loss of potassium by evaporation from the slag.

To check on the possibility of potassium loss through evaporation, X-ray fluorescence measurements were made on a sample of K510 slag before heating and after heating to successively higher temperatures. Figure 7 shows a typical X-ray spectrum taken from a slag sample. The peak height corresponding to each indicated element can, to first order, be taken as being proportional to the relative concentration of that element in the slag. The numbers

just above the symbols for the elements refer to the channel number in the multi-channel analyzer with which the data were recorded. For the unheated slag, we took the ratio of the potassium peak to that of the silicon peak as representative of the known proportion of K_2O (20 percent). After heating for times comparable to that necessary for performing the thermionic emission measurements, the same ratio was measured (the results are shown in Table II). It is clear that above about 1600 K, the potassium loss becomes large, at least within the first few microns of the surface, which is the depth to which the method can probe.

This observation lends weight to the supposition that the potassium concentration at the surface changes with temperature and that this change is responsible for the temperature dependence of the work function.

2. Thermionic Emission from Ceramics

The thermionic emission from strontium-doped lanthanum chromite ($La_{0.84}Sr_{0.16}CrO_3$) was measured over a temperature range of 1300 K to 1700 K. This ceramic remains solid at high temperatures and does not show any irreversible behavior. As a result, the measurements are more reproducible. Figure 8 shows a Richardson plot ($\ln j/T^2$ versus $1/T$, where j is the emission current density) of the measurements from this sample. For comparison, Figure 9 shows similar data for the aluminum- and magnesium-doped lanthanum chromite which had been taken previously. The effective work function is 3.28 ± 0.08 eV, which is an average of all the experimental points. This is a bit larger than the aluminum- and magnesium-doped sample, but the difference is not large enough to be significant.

3. Thermionic Emission at Higher Background Pressures

These experiments were conducted to determine if it is possible to measure the thermionic emission of slag or other materials in a non-vacuum environment when a gaseous atmosphere surrounds the emitting body. Two possible effects due to the surrounding medium were envisioned. The first is a reduction of the mean free path of the emitted electrons. This would act much like a resistor in series between the emitting cathode and the anode causing a reduction in the efficiency of collecting the emitting current and modifying the electric field distribution between the cathode and anode (which would tend to make the emission more space charge limited). To test these possible effects, argon was admitted into the measurement chamber at pressures up to one torr. The results showed that with argon present, the emission decreased by only a few percent, which might be attributed to a cooling effect on the slag due to the presence of the argon. The emission was found to recover completely when the argon was pumped out.

The other possibility was that of a chemical effect. An active gas might change the chemical nature of the emitting surface and

modify its work function. The same experiment was conducted with oxygen, and the effects were significant. When oxygen was admitted into the chamber at pressures higher than about 10^{-1} torr, the emission dropped by about two orders of magnitude and did not recover when the oxygen was removed. It appears that the oxygen had a significant and irreversible effect on the thermionic properties of the slag.

These results indicate that the composition of the gases in a channel can have a significant effect on the emission from the electrode.

4. Electrolysis and Mass Transport Effects in Slag during Electrical Conduction

Since slag is an ionic conductor, the drift of ions through the slag and their accumulation at the slag-electrode interface can have serious consequences for channel operation. The present experiments, which are as yet preliminary in character, were undertaken with the intent of determining the degree and kind of ionic motion in slag as a function of slag composition, temperature, and total charge which passes through the slag.

The following experimental procedures were used. A wafer of slag about 1mm thick was placed between platinum electrodes which made intimate contact with it, and the resulting structure was lowered into a furnace. When the temperature reached a prearranged value, an electric current was passed through it for a specified length of time. The slag then was quenched by drawing it out of the furnace and sectioned. The distribution of its component elements was determined by X-ray fluorescence or scanning Auger microprobe measurements. Since the latter instrument has been operational only a short time, the observations presented here were made with the X-ray fluorescence attachment on the scanning electron microscope.

Experiments were conducted on two slag samples. The first sample was K536, a high-silica synthetic slag with 30 weight percent K_2O ; the second sample was K517, a high-silica synthetic slag with no K_2O . Figure 10 shows the cross section of the sample with K_2O . The upper photograph is an SEM picture of the surface, and the lower one is a "dot map" on which the density of dots indicates the relative concentration of the particular element being measured--in this case, potassium. As can be seen, the potassium is more concentrated in the lower part of the sample, which was next to the negative electrode. Figure 11 shows the cross section of the sample without K_2O . The dot map (taken to show the presence of iron) indicates that the iron appears to be uniformly distributed throughout the sample despite the fact that the slag had obviously changed in appearance during the experiment. A light brown layer, approximately 0.2 mm thick, appeared at the positive electrode side; at the negative side, there was a much thinner dark brown layer.

No difference could be discerned between the composition of the light brown layer and the bulk of the sample utilizing the dot map technique. However, a close examination of the thin, dark brown layer showed that the relative concentration of calcium was twice as high as in the bulk of the sample, and the relative concentration of iron was about 50 percent higher. The nature of the light brown layer is not known at present, but it may be a region of excess oxygen. The X-ray fluorescence method is not sensitive to oxygen however, and measurements with the scanning Auger microprobe will be required to examine this possibility.

B. Discussion

The observations presented here show that potassium in coal slag lowers the work function by a significant amount, approximately 1 eV under the conditions of these experiments. The reason this result was not found for the high-silica slags measured previously is connected with the higher temperatures required to melt those slags and the higher temperatures at which the measurements were taken. These high temperatures result in an actual loss of potassium from the slag. In addition, the temperature dependence of the work functions of the low-silica slags indicates that the surface concentration of potassium is a function of temperature. The surface concentration of potassium depends on a balance between the diffusion to the surface and evaporation from the surface. Therefore, this is not an independent variable at the disposal of the investigator. In an actual channel, the concentration of potassium on the surface can be maintained at a higher level since it is being replenished continually from the surrounding plasma. It is anticipated that the data from these and subsequent experiments may be used eventually to develop a model which takes into account the replenishment process and which can be used to understand and predict the work function of a slag layer under a variety of conditions.

An extension of the experiments would entail the measurement of the emission under a controlled atmosphere of potassium. In this way the surface concentration of potassium would be more under the experimenter's control, since the flux of potassium atoms to the surface may be adjusted at will and calculated from kinetic theory. One of the problems connected with such an experiment is the possible influence of the presence of a dense atmosphere (relative to that of the vacuum measurements) between the emitting surface and the anode. The question of whether meaningful thermionic emission measurements are feasible under such conditions motivated the experiment with argon and oxygen described in the previous section. The results for argon suggest that such measurements are feasible, although it should be borne in mind that for a monatomic gas with a high ionization potential, the cross section for electron scattering should be quite low. Nitrogen, for instance, may provide a more severe test. The oxygen results are difficult to understand. The sharp decrease in the thermionic emission indicates a chemical change in the surface of the slag, but what this change might be and why it appears to be permanent cannot be speculated at present. The results of the thermionic emission measurements of the lanthanum chromite are straightforward and require little discussion. The measured work function, in

the range 3.1 eV to 3.3 eV, is low enough to sustain sufficient thermionic emission in a channel for electrode temperatures above 2000 K. Such a conclusion is, of course, conditional upon the absence of any possible effects due to interaction with the channel gases that might tend to increase the work function.

The electrolysis experiments are as yet preliminary in nature and were performed to work out the experimental methods and determine if such measurements will be fruitful. The results so far have been encouraging. Iron, calcium, and potassium cations have been observed to migrate through the slag under the influence of an electric field. We expect that further experiments along these lines will serve to characterize and quantify this behavior.

IV. CONCLUSIONS

The thermionic emission results from the low-silica slags show that potassium lowers the effective work function below that of the slag without potassium by approximately 1 eV. Under the conditions of the experiment, the effective work function was found to be temperature dependent, increasing with increasing temperature. The work function for the potassium-containing slag was found to range from about 3.2 eV at the lower measuring temperature of 1100 K to between 3.7 and 4.0 eV at 1550 K. The temperature dependence is tentatively attributed to a surface concentration of potassium which decreases with increasing temperature. This latter factor, as well as the loss of potassium at elevated temperatures, probably accounts for the relatively high work functions previously measured for the high-silica slags. Introducing argon and oxygen into the apparatus during the thermionic emission measurements indicates that the presence of a low-pressure (≈ 1 torr) atmosphere is in itself no impediment to measuring the thermionic emission, but thermal effects due to the interaction of the gas with the slag may have a drastic effect on the work function. The effective work function of strontium-doped lanthanum chromite is 3.28 ± 0.08 , slightly higher but close to that of aluminum- and magnesium-doped lanthanum chromite. Electrolysis experiments with coal slag indicate a drift of iron, calcium, and potassium cations under the influence of an electric field. The procedures for performing these experiments appear to be sound.

Table I.--Low-Silica Series (% by Weight)

<u>Slag #</u>	<u>SiO₂</u>	<u>Al₂O₃</u>	<u>Fe₃O₄</u>	<u>CaO</u>	<u>MgO</u>	<u>K₂O</u>
K492	38	14.25	14.25	19	9.5	5
K494	36	13.5	13.5	18	9	10
K510	32	12	12	16	8	20
K539	28	10.5	10.5	14	7	30
K488	40	15	15	20	10	0

Table II.--Potassium Content and Loss
From K510 After Heating
(20% K₂O Before Heating)

Maximum Temperature (°K)	K/Si Ratio	%K ₂ O After Heating	%K ₂ O Loss
1120° K	1.30 ± .11	17.4%	13%
1180° K	1.09 ± .11	14.8%	26%
1530° K	0.86 ± .06	12.0%	40%
1610° K	0.63 ± .01	9.1%	55%
1680° K	0.19 ± .09	3.7%	82%

Figure 1.--Effective work function measurements for slag #K488 containing no K_2O

Figure 2.--Effective work function for slag #K492, five percent K₂O

Figure 3.--Effective work function for slag #K494, ten percent K_2O

Figure 4.--Effective work function for slag #K510, 20 percent K₂O

Figure 5.--Effective work function for slag #K539, 30 percent K₂O

Figure 6.--Typical time dependence of effective work function for a potassium containing slab.

Figure 7.--Typical X-ray fluorescence spectrum for slag (The peak height for each element is to a first approximation proportional to the relative concentration of that element in the sample. The numbers listed for each element refer to the channel number of the pulse height analyzer at which X-ray quanta for the corresponding element were detected. The channel number is proportional to the X-ray energy and is plotted along the horizontal axis.)

Figure 8.--Richardson plot for $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3$

Figure 9.--Richardson plot for $\text{La}_{0.95}\text{Mg}_{0.05}\text{Al}_{0.25}\text{Cr}_{0.75}\text{O}_3$

Figure 10.--Top: SEM micrograph of cross section of slag sample K536 used in electrolysis experiment

Bottom: "Dot Map" showing the distribution of potassium after passing an electric current through the slag (Regions of higher density dots correspond to regions of higher density potassium. The negative electrode is at the bottom.)

Figure 11.--Top: SEM micrograph of cross section of slag sample K517 (no potassium) used in electrolysis experiment

Bottom: "Dot map" showing a fairly uniform distribution of iron throughout the sample

MILESTONE CHART

STATUS DATE Sept. 1978

TASK G

PROGRESS

MAJOR MILESTONES

ABSTRACT

Two computer models for the purpose of simulating MHD dynamic coal combustor performance currently are being evaluated. A model based upon the cycle analysis and control plug flow combustor model is being coded for the inclusion of devolatilization dynamics and to provide steady-state initial input boundary conditions for a more general dynamic model. Based upon the impulse response of the Navier-Stokes equations, a more general model also is under development.

Graphical routines have been incorporated into the general steady-state design/analysis program for the MHD topping cycle and the separate dynamic steam bottoming plant including heat capacitor.

All components necessary for a bench-scale, two-pole generalized inverter model have been received and tested with the exception of some capacitors.

Training of new personnel has been completed; one graduate student and four undergraduate students are assisting on the project.

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. 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 d-c to a-c 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.

II. SUMMARY OF PROGRESS TO DATE

Coding on improvements to the cycle analysis and control plug flow combustor model is progressing with the incorporation of a simplified model for devolatilization of Ubhayakar and Stickler.¹

The more general dynamic model is being coded by Johnson and Elhard. A trip to Thompson-Ramo-Wooldridge (TRW) and Rockwell Energy Systems Division (RESO) to review their ETF combustor work was made in mid-September.

The testing of all components for a two-pole generalized inverter system with microprocessor control has been completed.

Microprocessor software for control of the variable output power supplies has been completed sufficiently to test the supplies.

All work on hybrid programming simulation of MHD power plant cycles has been discontinued.

III. DETAILED SUMMARY OF TECHNICAL PROGRESS

Work on the dynamic combustor model for incorporation in the existing nozzle-channel-diffuser (NCD) dynamic model to produce a combustor-NCD (CNCD) model is progressing. The NCD model has been modified in the input phase to accept changes in mass flow rate, pressure, and temperature. The stability of convergence has been improved by the dissipative technique in the region of sonic shocks. Finally, an attempt to incorporate the steady-state determination of initial conditions into the dynamic model, rather than the usual steady-state model, is being made as the initial conditions are quite sensitive to changes in calculation algorithm, especially in the diffuser section.

Discussions with RESO, TRW, and AVCO indicate that the process of coal devolatilization may be extremely important relative to combustor sizing and the necessity for a second stage. In addition, opinions vary widely as to the necessity of coal pre-drying for successful combustor operation although it is generally agreed that higher flame temperatures will result from drying the coal if other volatile gases besides H₂O are not driven off in the process.

Based upon this information, the cycle analysis and control group is incorporating a time-dependent devolatilization calculation into their existing plug flow model.

1

D. B. Stickler and S. K. Ubhayakar, "Mechanistic Modeling of Pulverized Coal Combustion," 17th Symposium on Engineering Aspects of Magnetohydrodynamics, Stanford University, March 27-29, 1978.

The instrumentation and data acquisition group is approaching the simulation of the dynamic behavior of a combustor with the intention of incorporating a model which is as simple as possible but which will describe the combustor-nozzle-channel interaction adequately and emphasize the effects on the operation of the MHD channel. The purpose is not to improve combustor design but to describe CNCD behavior from a systems control standpoint.

To this end, the model currently being developed concentrates on analysis of combustor exit pressure variations as they affect combustor operation and eventually channel operation.

A truncated eigenfunction expansion of the Navier-Stokes Green's function response is coupled to the energy balance of individual fuel-gas one-dimensional slices to predict the fluid mechanics of the solution. Truncated solutions are used to reduce the computer execution time; it is expected that this will generate some error in the solution but the amount is unknown at present. The emphasis of the simulation is on the external behavior of the combustor as it affects the down-stream components of the MHD system. The simulation will provide information useful in combustor design indirectly (if at all).

A. Generalized Inverter Simulator

With the exception of a few capacitors, all components necessary to construct a two-pole inverter circuit driven by programmable power supplies have been received.

The Digital PDP11/03 computer has been interfaced to the Kepco power supplies to run the initial acceptance tests. All power supply units can be programmed satisfactorily over their specified output range. The 1 Kw units provide useful variation up to 1 kHz. The bipolar supply will function to 20 kHz. Interface connection in the connected system will be provided via optical isolation and eight-bit digital-to-analog converters. This interconnection is being constructed.

The construction of the gate control logic has been completed. Construction of the SCR gate pulse transformer interconnection board has been started. Preliminary testing of the AD converter components has been completed, and board construction has been started. This converter board will provide the analog data for the gate controller.

Heat sinks for the power diodes and SCR's have been constructed, and one inverter pole is under construction.

IV. CONCLUSIONS

The coal-fired combustor dynamic simulation program is behind schedule because of the training of new technical personnel and the need to incorporate a rapid devolatilization calculation in the plug flow combustion program as well as the dynamic model.

The inverter simulator is now under construction with the arrival and testing of all critical components. Computer control programs have been written and tested.

MILESTONE CHART

STATUS DATE Sept. 1978

TASK H-1

PROGRESS

MAJOR MILESTONES

STATUS DATE _____

ABSTRACT

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 sub-systems.

Recent papers that describe the work were published in Energy Conversion (Vol. 18, No. 2, 1978), the 13th Intersociety Energy Conversion Engineering Conference (August 20-25, 1978), the Second International Symposium on Large Engineering Systems (May 15-16, 1978), and the 17th Symposium on Engineering Aspects of MHD, March 1978. Methods for forming dynamic component models are being developed, as is a multi-input, multi-output model of the combustor, nozzle, channel, and diffuser. First-principle dynamic models of plant components are being embedded in the latest simulation.

I. OBJECTIVE AND SCOPE OF WORK

We are developing system component models which are suitable for control system simulations 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 as 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 set 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 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 OF PROGRESS TO DATE

During the past two years, the cycle analysis and control task has produced seven papers (References 1 through 7) which were accepted for publication. Four of these papers were published in 1978. These papers and associated technical reports have contributed to the characterization of MHD components and system performance with particular emphasis on the combustor. Also, a relatively new MHD component, the heat capacitor, has been examined with regard to its effectiveness in smoothing the temperature ripple in the preheated air and, therefore, its effect on power output fluctuations in the controlled combined-cycle MHD system. Detailed computer programs have been developed to simulate the controlled system.

Under development at this time is a control system simulation based on first principles. Included in this simulation are dynamic models for steam-bottoming plant components. Appendix A contains descriptions of these models and ways of incorporating compressor control, boiler feedwater control, and superheat attemperation in the combined-cycle simulation. The overall control will be of the coordinated type with control of air, fuel, seed, feedwater, superheat attemperator, turbine valve area, inverter characteristics, and air preheater firing in the case of separately fired high-temperature air heaters. The MHD combustor, nozzle, channel, and diffuser sections are being modeled in terms of a multi-variable input-output model which also is described in Appendix A.

The original efforts of the cycle analysis and control task were directed at commercial-size MHD systems. Now, however, many of the results are being modified to apply to the CDIF and the ETF. A combustor computer code was delivered to MERDI for use in its CDIF studies. The ETF conceptual design studies of Avco, GE, and Westinghouse have been examined and are being used to define an ETF system upon which control system models will be superimposed in our current control system simulation.

In connection with work on input-output models of various components and subsystems, a set of curves showing sensitivities of combustor output states to variations of input conditions has been constructed and is given in Appendix B. The steady-state, plug-flow model was used to generate the data base. Briefly, an operating point was selected and inputs were varied one at a time about this operating point. Several output states were plotted as a function of this single variation, giving a one-dimensional representation of an input-output combustor model. Appendix B is basically the body of a paper presented at the 17th MHD Symposium.⁶ Full-blown input-output models are multidimensional surfaces constructed as curve fits to many input variations. The impracticality of such a representation in print is the reason for showing a restricted set of results in Appendix B.

A set of routines describing the heating, devolatilization, and ignition processes of pulverized coal is in progress. These routines will improve the existing steady-state combustor routine and will be even more useful in the time-dependent combustor model being developed in conjunction with other MHD researchers at MSU. The sequence of pulverized coal combustion involves the two processes of 1) heating, devolatilization, and ignition and 2) solid-gas reaction to convert solid carbon to gaseous combustion products. Ash fusion and vaporization also occur during the solid-gas reaction phase. While the two processes overlap in time to some extent, this is the most logical major division of coal combustion.

The current steady-state combustor model has a very satisfactory portion dealing with solid-gas reactions, in which we feel no changes are necessary. However, it does treat heating, devolatilization, and ignition as instantaneous occurrences at the input point. To the degree that output states such as temperature, percent carbon reacted, total heat loss, etc. are affected by this assumption, the steady-state model has a correctable error.

The principal internal differences between behavior assuming instantaneous coal particle heating, devolatilization, and ignition and behavior based on a specific particle time history (dependent on particle size) appear in the internal temperature profile generated in the fraction of carbon reacted and in the total mass fraction of volatile matter driven off. Instantaneous availability and combustion of volatiles give an immediate, sharp temperature rise, followed by rapid reaction of the first 40 to 70 percent of the remaining solid carbon (depending on oxygen availability--see Figures B-2 and B-3). This is clearly unrealistic as is the assumption that a fixed mass fraction of volatiles is driven off (usually assumed to be the ASTM mass fraction). Temperature and heat loss errors are related principally to variations in heat loss stemming from this too high temperature. Errors in carbon reacted occur as a result of the temperature aberration (carbon reaction rate has a positive temperature dependence) and also as a result of errors in mass fraction of coal remaining after devolatilization (total mass fraction of volatile matter is not fixed but depends strongly on particle heating rate^{14,15}). While we do not expect significant differences in output states to occur by putting details of devolatilization, heating, and ignition into the steady-stage combustor model, the change is being made. We expect a few degrees of output temperature variation, a slightly decreased heat loss fraction, and two or three percentage points change in carbon reacted.

The main utility of detailed dynamics of particle heating, devolatilization, and ignition is associated with the time-dependent combustor model. In that respect, it is important to predict behavior regarding combustion stability, i.e., the effect of pressure and flow rate transients on energy release rate and subsequent combustor performance. Flow rate transients may appear at the input due to momentary plugging and unplugging of the pulverized-coal carrier-gas feed line. Pressure transients can occur from the same cause, from variations in the preheated oxidant feed, or as a result of coupling from the channel back through the nozzle to the combustor (in subsonic channels). It is important that this degree of detail be incorporated into the combustor model to render it consistent with the degree of detail present in other channels and balances of plant models produced at Montana State University.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Overall Control System Models

Control system models vary widely in regard to the amount of detail they incorporate. MHD control system results that have been published by the cycle analysis and control task to date have been based on a combined-cycle simulation in which dynamic relationships for power flow have been modelled, and active feedback control of fuel feed and turbine valve area have been studied. While these past developments have been useful from the standpoint of understanding overall system operation, they lack the detail that is required to determine the effect of various control strategies on the operation of many plant subsystems. Thus, a more detailed combined-cycle MHD/steam control system simulation model (System Model IV) is being developed from first principles. System Model IV contains an order of magnitude more detailed than System Model III. The new control model makes use of important physical parameters (steam temperature, feedwater flow rate, superheater pressure and temperature, etc.) as feedback and feedforward signals. Appendix A contains a detailed description of some of the more important component models.

Initial simulation runs will be for a specific ETF-size plant. The methods of forming first-principle dynamic models of key plant components is highlighted in the work so that the models can be converted readily to other plant sizes and configurations. The dynamics of each component of the bottoming plant are governed by conservation equations for mass, momentum, and energy. The overall control model is of the coordinated type with control for air, seed, coal, feedwater, superheat attemperator, inverter parameters, and turbine valve area. To accomplish these objectives, many dynamic models for boiler-turbine and related topics have been studied and compared.

The introduction of recirculated gas and gas tempering to control gas and steam temperature is attractive, but it complicates the problem formulation. Recirculated gas may be used in the seed condenser; the flow rate of this recirculated gas must be controlled to minimize temperature variations in the seed condenser.

B. Compressor Characteristics

The simulation of System Model IV contains dynamic control characteristics of the air compressor and the boiler feed pumps. Static characteristics of compressors and boiler feed pumps are well-documented in engineering handbooks, but dynamic characteristics are not. The high-pressure, high-volume compressor (either centrifugal or axial) must supply air at some ten times the mass flow rate of the coal and at pressures from five to nine atmospheres. The dynamic operating range of these units is limited by surge phenomena: flow must be maintained above limiting values (typically 75 percent of design flows) in order to avoid unstable pulsating flow; and therefore, the method of controlling flow is of concern. In general, flow control by throttling the inlet air stream is not advisable. More reliable control is obtained by using a variable speed drive, such as an auxiliary steam turbine drive. In System Model IV, coupled dynamics of a steam turbine driving an associated air compressor are included.

From the standpoint of reliability, large MHD plants undoubtedly will employ a bank of compressors operating in parallel. When reduced load operation is required, some of the units will be shut down and isolated from the remainder by appropriate valves. The active compressor units will be operated well above respective surge lines. Maintenance and repair work will be performed on out-of-service units without requiring plant shutdown. For the same reason, a battery of high-pressure boiler feed pumps will operate in parallel to supply the feedwater.

C. Multi-Variable CNCD Input-Output Models

A key subsystem of System Model IV is a new input-output model of the combustor/nozzle/channel/diffuser (CNCD). This model will be produced on the basis of the latest results in coal-combustor modelling, and a quasi one-dimensional channel model will be used. The approach being used to form this model is described in Appendix A. Inputs to the model include fuel feed, air feed, oxygen enrichment, seed feed, preheat air temperature, and inverter voltage characteristics. Outputs include combustion pressure, exit gas enthalpy, electrical power output, total mass flow rate, and feedwater heating

from each CNCDD subunit. Distinct dynamic controllers are to be developed for each of the feed systems. The seed feed controller will be implemented as a ratio controller, with air feed as the basis variable and with adjustments in seed level established by an optimizing program. Air and coal feed control will be coordinated on the basis of the CO/CO_2 ratio out of the channel, with overall feed rate dictated by megawatt load demand and steam plant operating conditions.

During the contract period, work was performed to develop a multi-variable input-output model for the combustor, and the MHD channel program was updated. A detailed two-stage combustor model already has been used to study the sensitivities of outputs to the variation of a single input about a design center point. The results of this study were presented at the 17th Symposium on Engineering Aspects of MHD (March 1978) in a paper entitled "Sensitivities of Outputs to Variations of Inputs in MHD Combustors." The present work extends that study to multi-dimensional inputs in which up to seven inputs are allowed to vary simultaneously. Because of the large number of inputs, the "brute force" approach of calculating outputs for every input condition results in excessive computer run times (e.g., seven inputs with five values allowed per input with a 2-1/2 minute run time would require over 135 days to complete). Therefore, strategies are being studied which would allow fewer combinations of inputs to be calculated while still providing an accurate prediction of actual behavior. A related problem involves defining functions (e.g., polynomial, exponential, logarithmic) which will fit the data well without an excessive number of parameters. Again, the large number of inputs increases the complexity of this problem. Present work is aimed at solving these problems so that different input-output models of the combustor with multi-dimensional inputs can be produced easily.

The MHD channel program has been modified to accept the above curve fits. The program will be used with the results of the combustor input-output model to produce the CNCDD input-output model to be used in the overall combined-cycle power plant. This will be a great improvement over past CNCDD input-output models.

D. Need for Expanded Details of Combustion

The lack of coal particle heating, devolatilization, and ignition description is a far more serious problem in the time-dependent combustor model than is the steady-state plug-flow model that we have been operating. In the steady-state model, one expects errors in outlet temperature, heat loss, and overall carbon conversion as discussed in Section III. While these are worth consideration in their own right, they pose no problems in the stability of the model since the steady-state has no instability by definition. In a real combustor (and hence in the time-dependent model), the complex set of interactions between heat release, pressure, and temperature of the solid-gas mixture may allow either periodic or non-periodic instabilities to occur. Therefore, it is essential that a reasonable model for the heat release process of coal particles be established. This process entails the heating, devolatilization, and ignition of coal particles.

E. Model Selection for Combustion

It is well recognized that conversion of coal particles to combustion products involves two stages: a devolatilization and ignition sequence followed by a heterogeneous reaction of carbonaceous char and gaseous oxidants. There is some overlap of these stages as the flame sheet settles inward to the particle surface, which can be accommodated by a judicious choice of equations and parameters. The solid-gas reaction model will be described first. It is the shrinking, unreacted sphere model controlled by combined diffusional effects and chemical surface reaction rate.^{8,9,10}

The complete equation for burning rate is

$$q = \frac{P}{\frac{1}{K_{\text{diff}}} + \frac{1}{K_s}} \text{ gm/cm}^2\text{-sec} \quad (1)$$

where q = burning rate, $\text{gm/cm}^2\text{-sec}$,

P = partial pressure of oxidant in free stream, atmospheres,

K_{diff} = diffusion controlled reaction rate, $\text{gm/cm}^2\text{-sec-atm}$, and

K_s = chemical controlled reaction rate, $\text{gm/cm}^2\text{-sec-atm}$.

Following Hirschfelder, Curtis, and Bird,²⁰ the expression for diffusion resistance is

$$K_{\text{diff}} = \frac{24\phi D}{xRT_s} \text{ gm/cm}^2\text{-sec-atm} \quad (2)$$

where x - particle diameter, microns,

R = gas constant, $82.06 \text{ atm-cm}^3/\text{gm mole} \cdot \text{K}$,

T_s = particle surface temperature, K,

ϕ = mechanistic factor = 1 if product being transported from surface

to bulk is CO_2 ;

2 if product is CO, and

$D = 0.207 \left(\frac{T_s}{300}\right)^{1.68}$, diffusion coefficient for $\text{O}_2 - \text{N}_2$ mixture, giving

$$K_{\text{diff}} = .08346 (T_s^{0.68})/x. \quad (3)$$

This result is quite well known and used.

Surface reaction resistance is a less agreed upon topic. The model selected has a two-part expression for reaction rate, given as K_{s1} and K_{s2} below. Evidence exists showing that coal particles become porous upon heating and devolatilization,^{9,10} making a means of accommodating differences between coal rank necessary. The general behavior is that coal particle porosity after devolatilization decreases as its rank increases (going from subbituminous through bituminous to anthracite). This results in a decreased surface/volume ration with the net effect that chemical surface resistance increases with coal rank. Thus, higher rank coals burn slower when chemical resistance is significant compared to diffusion resistance.

The best single line fit equation for surface reaction has been given as^{8,12}

$$K_{s1} = 8710 \exp (-35,700/RT_s) \text{ gm/cm}^2\text{atm sec} \quad (4)$$

where

$$R = 1.986 \text{ cal/g-mole K (gas constant) and}$$

$$T_s = \text{carbon surface temperature.}$$

This expression agrees well with experimental data up to about 1300 to 1400 K and is independent of coal rank. Above those temperatures, the surface reaction rate tends to fall below the single line fit,⁸ the extent of disparity being dependent on the coal rank. To accommodate this tendency, a second surface reaction rate, effective at high temperatures, has been combined with the first given above. The added reaction rate has surface reaction rate constants and activation energies that depend on the coal rank. It has the usual form

$$K_{s2} = A_2 \exp (-E_2/RT_s) \text{ gm/cm}^2\text{-sec-atm} \quad (5)$$

where

$$A_2 = \begin{cases} 1.180 \text{ gm/cm}^2\text{-sec-atm for bituminous coal} \\ 0.310 \text{ gm/cm}^2\text{-sec-atm for anthracite coal} \end{cases}$$

and

$$E_2 = \begin{cases} 6347 \text{ for bituminous coal} \\ 7589 \text{ for anthracite coal} \end{cases}$$

with R and T_s as given above. Both K_{s1} and K_{s2} behave analogously to electrical admittances so their reciprocals behave as electrical resistances. When $\frac{1}{K_{s1}}$ and $\frac{1}{K_{s2}}$ are combined as resistances in series, $\frac{1}{K_{s2}}$ reduced the steep increase of surface reaction rate of chars at high temperatures (predicted by $\frac{1}{K_{s1}}$ alone) to values in general agreement with the BCURA studies.⁸

When combined with a resistance representing the diffusion-controlled reaction rate, $\frac{1}{K_{\text{diff}}}$, the result is that of three non-linear (temperature and particle size dependent) electrical resistances in series, driven by a voltage source (partial pressure of oxidant in the free stream), with the burning rate of $\text{gm/cm}^2\text{-sec-atm}$ carbon reacted being analagous to the resultant current.

In equation form

$$q = \frac{P}{\frac{1}{K_{\text{diff}}} + \frac{1}{K_{s1}} + \frac{1}{K_{s2}}} \text{ gm/cm}^2\text{-sec} \quad (6)$$

Calculations show that for 2500 K, particles larger than 100 microns diameter are in a basically diffusion-controlled mode of reaction, those between 30 microns and 100 microns diameter are controlled by both diffusion and surface reaction rate, while those particles below 30 microns diameter are strongly controlled by surface reaction rates. At lower temperatures, surface reaction rate control becomes more significant for any particle size.

The results of simulation runs were interesting. Using the conditions of tests 44A (bituminous coal) and 82B (anthracite coal) in Reference 13, runs were made for 1) diffusion control only, 2) for combined diffusion and single-equation surface rate control (K_{s1} only), and 3) for combined diffusion and dual-equation surface rate control. Table 1 shows that results for diffusion control only and results for combined diffusion and single-equation surface rate control are only slightly different, showing about 2 K drop in Test 44A and less than 1 K in 82B, respectively. Coal conversion is nearly identical in each case, running 99.4 and 94.3 percent.

When the second surface rate control relation is introduced, giving combined diffusion and dual-equation surface rate control, output temperatures drop by 53 K and 15.5 K in tests 44A and 82B, while the respective carbon conversions drop to 98.8 and 92.8 percent. Since the latter values are in better agreement with test values, it is clear that the dual-mode surface rate control, which grossly takes account of diminished particle size and varying porosity of bituminous and anthracite coal, is preferable to simple diffusion control or diffusion control with medium-temperature surface rate control only.

F. Heating and Devolatilization Model

A devolatilization and ignition sequence is requisite for the time-dependent combustor model being developed in conjunction with other tasks and is desirable for more accurate prediction of steady-state behavior via the current steady-state plug flow combustor model. Generally, we sought the simplest model that could manifest the following characteristics of devolatilization and ignition:

1. The extent of devolatilization is dependent upon coal rank and heating rate, giving the ASTM volatiles mass fraction as a lower bound;
2. The mixing rate of incoming oxidant and the coal carrier-gas flow is variable, thereby reflecting injector and mixing chamber geometry; and
3. The char remaining after devolatilization may change in size from the original particle size. (It is composed of a uniform mixture of solid carbon ash and possibly hydrogen; all other fractions having volatilized.)

Some models or discussions of coal particle devolatilization exist in the literature.^{8,14,17,18,19} It was judged that the simplest one meeting criteria is the two-competing-reaction-rate model introduced by Kobayashi¹⁴ and since described elsewhere.^{15,16} Briefly, it proposes that two competing, parallel processes describe coal devolatilization: one that has a low activation energy and gives a hydrogen atom to carbon atom ratio of about two in the volatiles, and a second process that has a high activation energy and gives a hydrogen atom to carbon atom ratio of about one. This pair of reactions has been modified to reflect other volatiles (oxygen, nitrogen, and sulfur) being driven off with the hydrogen and carbon, leaving a residual char of unreacted solid carbon, ash, and possibly hydrogen when devolatilization is complete. In equations, the coal converts to chars (R_1 and R_2) and volatiles (V_1 and V_2) according to the mass fraction relations

where $k_n = B_n \exp(-E_n/RT_c(r_i, t))$, $n = 1, 2$, are two rate functions and α_n , $n = 1, 2$, are the mass stoichiometry constants. One of the rate functions, say $n = 1$, has a low frequency factor, B_1 , and a low activation energy, E_1 , thus representing a low-temperature process that characterizes ASTM volatile mass fractions. The other rate function has both B_2 and E_2 quite high and represents limiting devolatilization under extremely high heating rates. This allows the process to simulate observations that under conditions of extremely rapid heating (about 10^5 K/sec), volatile yields approaching twice the ASTM values have been achieved.¹⁶ This is not to say that Relations 7 and 8 actually describe the physical processes occurring but only that they explain the appearances. We have modified the original presentation by assuming that 1) the dry ash-free coal is characterized by the equivalent formula $\text{CH}_x\text{O}_y\text{N}_z\text{S}_w$, 2) the formula of remaining char is

CH_{x_{R,n}}, n = 1, 2, and 3) the formula of volatiles released is CH_{x_{V,n}}
 $\hat{y} = \hat{y} \left(\frac{x_{V,n} - x_{R,n}}{x - x_{R,n}} \right)$ and similarly for $\hat{z}$ and $\hat{w}$.
 Then the volatile mass fractions, α_1 and α_2 , are

$$\alpha_n = \frac{\left(\frac{x - x_{R,n}}{x_{V,n} - x_{R,n}} \right) (12 + x_{V,n}) + 16y + 14z + 32.1w}{12 + x + 16y + 14z + 32.1w}, \quad n = 1, 2 \quad (9)$$

The actual mass fraction devolatilized will lie between α_1 and α_2 , depending on the heating rate of the particle. This expression for α_n is similar to that given in References 8, 10, and 11 but includes mass fractions of oxygen, nitrogen, and sulfur in addition to carbon and hydrogen. If $y = z = w = 0$, it becomes the expression for α_n given in the references. It describes a process in which all oxygen, nitrogen, and sulfur is devolatilized, leaving a carbonaceous char with perhaps some hydrogen.

Inclusion of oxygen, nitrogen, and sulfur usually requires an adjustment of $x_{V,1}$ to a value other than 2 to achieve the ASTM volatiles mass fraction result. Selecting a typical Montana Rosebud seam coal as an example and assuming it is dried to 5 percent ASTM moisture, we get an equivalent formula of CH_{.79502} O_{.17848} N_{.01253} S_{.00564} Ash_{.04348} (H₂O)_{.05574}. When converted to a d.a.f. basis, and using $x_{R,1} = x_{R,2} = 0$, $x_{V,1} = 2$ and $x_{V,2} = 1$, we find $\alpha_1 = .5483$ and $\alpha_2 = .8463$. When converted back to the as-received basis, the value of α_1 becomes .4374, significantly higher than the observed value of .3725 volatile matter by ASTM procedures for the Rosebud coal cited. Adjustment of $x_{V,1}$ to 2.75 given ASTM results for Equation 7 exclusively. A few runs of the program should indicate the sensitivity of total volatiles released with respect to $x_{V,1}$ and $x_{V,2}$.

The remainder of relations follows closely that given by References 15 and 16. The salient equations are those for the production of coal volatiles, for coal particle temperature, and for mixing rate of carrier gas and oxidant.

Mass rate production is given by

$$\dot{m}_{V,n}(r_i, t) = \alpha_n \dot{m}_{cu}(r_i, t) k_n, \quad n = 1, 2 \quad (10)$$

where $\dot{m}_{cu}$ is the unreacted mass at time t of a coal particle having initial radius r_i .

Temperature and hence k_n ($n + 1, 2$) is determined by a rather complex expression for $\dot{q}(r_i, t)$

$$\begin{aligned} \dot{q}(r_i, t) = & \left[T_g(t) - T_c(r_i, t) \right] \left[\left\{ \dot{m} c_c / \left[\exp\left(\frac{\dot{m} c_c}{4 \pi r_i \lambda_g} \right) - 1 \right] \right\} \right. \\ & \left. + 0.6 \pi r_i \lambda_g \text{Re}(r_i, t)^{0.6} \right] \left[1 - \left\{ 1 + 0.17/\text{Kn}(r_i) \right\}^{-1} \right] \quad (11) \\ & + \sum_n \dot{m}_{V,n} \Delta h_n, \end{aligned}$$

where $T_g(t)$ is the local gas temperature, $\dot{m} = \sum_n \dot{m}_{V,n}$, c_c is the specific heat of coal + char, λ_g is the gas thermal conductivity, $\text{Re}(r_i, t)$ is the Reynolds number of relative flow for each particle, $\text{Kn}(r_i)$ is the Knudsen number, and Δh_n are the specific heats of reaction associated with Equations 7 and 8, $n = 1, 2$. The Reynolds number is written as $\text{Re}(r_i, t) = 2 u_i(t) r_i / \nu_g$, where the relative velocity $u_i(t) = u_0 \exp(-t/t_{d,i})$, the characteristic drag time $t_{d,i} = (2 \pi r_i^2 \rho_c) / (9 \nu_g \rho_g)$, ν_g the gas kinematic viscosity and ρ_c , ρ_g , the densities of coal particle (assumed constant and equal to ρ_{c0} , its initial value) and gas phase, respectively. The Knudsen number $\text{Kn}(r_i) = L/2 r_i$, where L is the gas mean free path. The gas density $\rho_g(t)$ is computed from equation of state at $T_g(t)$.

Note that this expression for heat transfer is conductive and convective dependent only, contrasting with radiative transfer postulated by others.¹⁹ The authors of the model adapted here have affirmed, upon personal contact, the conductive-convective heat transfer mechanism in relatively dense-phase coal-gas mixtures under consideration.

An exponential expression for the mixing of oxidant and coal carrier gas has a specifiable mixing time parameter (t_{ch}) so that gross characteristics of injector mechanisms and mixing chambers can be simulated. This model gives the elemental composition of the local gas phase in terms of mass fractions at any time t as

$$X_j = [X_{j,mix} + X_{j,V}] / f_g(t) \quad (12)$$

where $f_g(t)$ is the gas phase mass fraction.

The contribution by mixing is

$$X_{j,mix} = (f_o + f_k) X_{j,k} \exp(-t/t_{ch}) + (f_o X_{j,o} + f_k X_{j,k})(1 - \exp(-t/t_{ch})) \quad (13)$$

in which f_o and f_k are mass fractions of the original hot gas and coal carrier gas, respectively, and $X_{j,o}$ and $X_{j,k}$ are gas phase mass fractions of the j th element in the original hot gas and coal carrier gas, respectively, for $j = C, H, O, N, S$. The contribution by volatiles is given by

$$X_{h,v} = \sum_n f_n(t) X_{j,n} \quad n = 1, 2 \quad (14)$$

The remainder of calculations consist of relations between enthalpy and temperature of the local gas phase. The relations are quite straightforward and will not be repeated here.

IV. CONCLUSIONS

Methods of coordinated control of combined-cycle MHD/steam power plants are being investigated. Results of this work are being disseminated to the MHD power system community in several ways: presentation and publication of papers on various aspects of the modelling and control; discussion of results with MHD personnel from other locations in the USA; and attendance at MHD and Energy conferences.

Control system models of combined-cycle MHD/steam power plants have been developed. Most of the reported results to date have been obtained on the basis of System Model III, which is structured on the basis of a dynamic power flow model. A more desirable form of combined-cycle control simulation is one in which detailed process variables (e.g., steam temperature, pressure, and flow rate) appear in the simulation, and simulated control actions are based on the available system outputs and command signals. During the year, advances have been made in modelling key components of such an overall dynamic system simulation. The component models and the associated variables are being formulated in a way which will enable them to be linked together in System Model IV. To show the utility of System Model IV, the following steps will be taken: first, the various subsystem models will be completed (the combustor-nozzle-channel-diffuser model requires the most effort); second, a reference ETF-size plant will be established on the basis of the conceptual design studies by Avco, GE, and Westinghouse; third, model parameters associated with the reference plant will be derived; and fourth, control system simulation runs will be made to establish which of the many possible coordinated control strategies leads to satisfactory performance of the plant over transient conditions.

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APPENDIX A

Subsystem Models for MHD/Steam Plants

INTRODUCTION

The subsystem models described in this appendix are time-dependent models to be incorporated in an overall control system model of a combined-cycle MHD system. The overall model is to be simulated on a digital computer and is to be used to examine the relative merits of different coordinated control strategies and to determine controller parameter values that yield smooth, stable, and relatively fast response to changes in reference inputs and load disturbances.

The component models described are based on physical laws and are, therefore, so-called first-principle models and are lumped-parameter models in contrast to more intractable distributed-parameter models. The models can be used to predict time varying changes in combustion gas temperature and enthalpy and changes in water-steam pressure, density, enthalpy, and temperature within each major component of the combined-cycle system.

CONDENSER TO DEAERATOR MODEL

We are considering a system in which the water from the steam condenser has known physical properties--the dynamics of the condenser cooling water are not included in the model. The feed water from the condenser is boosted in pressure by a condensate pump and is preheated by passage through the MHD channel cooling tubes. The water then enters the deaerator storage tank and is purified. The water density in the storage tank is essentially constant. The boiler feed pump draws water from the tank.

Of interest is the variation of the enthalpy h_{dst} of the water in the tank as a function both of feed water flow rate w_{bfp} and of the thermal power Q_τ from the MHD channel which heats the water. Q_τ is given by an equation of the form

$$\tau_1 \frac{dQ_\tau}{dt} = \eta Q_{chan} - Q_\tau \quad (A-1)$$

where Q_{chan} is obtained from the input-output model of the combustor-nozzle-channel-diffuser, τ_1 is an appropriate time constant for heat transfer through the channel walls, and $\eta \approx 0.95$ is an efficiency factor to account for power lost to ambient. An energy balance for the tank gives

$$\frac{dh_{dst}}{dt} = \frac{1}{\rho_{dst} V_{dst}} (Q_\tau + w_{bfp} h_{cond} - w_{bfp} h_{dst}) \quad (A-2)$$

where V_{dst} is the storage volume. The condensate pump is assumed to be controlled to maintain a constant level in the tank; therefore, w_{bfp} is used as both the input and the output flow rate in the right-hand member of Equation A-2.

The pressure p_{dst} in the tank is much smaller than the pressure out of the boiler feed pump; p_{dst} is assumed constant without noticeable loss of accuracy.

BOILER FEED PUMP

The water intake for the boiler feed pump is from the deaerator storage tank. The enthalpy h_{dst} and the pressure p_{dst} of the compressed water in the tank are available from the deaerator tank model, and temperature T_{dst} and density ρ_{dst} are known as functions of h_{dst} and p_{dst} . The boiler feed pump is equipped with its own controller to drive pump output pressure to a regulated set-point value; this set point value is generated by a cascade controller (not shown) which responds to errors in the pressure at the high-pressure turbine inlet. For purposes of system modelling, Figure A-1 given the assumed form that relates effective pumping power r to the error in boiler-feed-pump pressure. Gain K and time constants τ_1 and τ_2 are dependent on system size, η_1 is an efficiency factor, and s is the Laplace variable.

Figure A-1.--Block diagram relating effective pumping power r to pressure error

The enthalpy h_{bfp} of the water out of the pump is given by

$$h_{bfp} = h_{dst} + \frac{\Gamma}{w_{bfp}} \quad (A-3)$$

and pressure out p_{bfp} is

$$p_{bfp} = p_{dst} + k \rho_{dst} \frac{\Gamma}{w_{bfp}} \quad (A-4)$$

With SI units used in Equation A-4, the constant k is slightly less than 1 and ideally is 1 for frictionless and noncompressible pumping. Curve fits can be used to obtain ρ_{bfp} and T_{bfp} as functions of h_{bfp} and p_{bfp} .

The output flow of the boiler feed pump is divided into two streams,

$$w_{bfp} = w_{ecin} + w_{spray} \quad (A-5)$$

where w_{spray} is controlled by the spray attemperator (superheat steam temperature controller) and is small relative to the input flow rate w_{ecin} to the economizer. The economizer input flow rate is obtained from the economizer model as

$$w_{ecin} = c \left[\rho_{econ} (p_{bfp} - p_{econ}) \right]^{1/2} \quad (A-6)$$

where c is an appropriate constant, and p_{econ} is the economizer output pressure which has a direct relationship to the state-variable outputs of the economizer model. Note that w_{ecin} and, therefore, w_{bfp} also is dependent on p_{bfp} in Equation A-6, but p_{bfp} is dependent on w_{bfp} in Equation A-4. The three equations A-4, A-5, and A-6 in terms of unknowns w_{bfp} , w_{ecin} , and p_{bfp} can be reduced to the following equation in terms of p_{bfp} :

$$p_{bfp} = p_{dst} + \frac{k \rho_{dst} \Gamma}{w_{spray} + c \left[\rho_{econ} (p_{bfp} - p_{econ}) \right]^{1/2}} \quad (A-7)$$

which must be solved iteratively for p_{bfp} at each time step. Equations A-6, A-5, and A-3 can then be used to obtain w_{ecin} , w_{bfp} , and h_{bfp} .

TYPICAL STEAM/WATER PATH LUMPED UNIT MODEL

Let k be the index for the given unit and its outputs, j be the index for the input fluid to unit k , and i be the index of the hot-gas input (that is, the hot gas coming from Unit i).

The continuity equation gives

$$\frac{d\rho_k}{dt} = \frac{1}{V_k} (w_j - w_k) \quad (\text{A-8})$$

where w 's are mass flow rates, V_k is the volume of heated fluid in the k^{th} unit, and ρ_k is the fluid density out of the k^{th} unit.

The energy balance equation gives

$$\frac{d}{dt} (\rho_k h_k) = \frac{1}{V_k} (w_j h_j + Q_k - w_k h_k) \quad (\text{A-9})$$

where the h 's are enthalpies, and Q_k is the power in the form of heat supplied to the heated fluid.

The heat balance equation gives

$$\frac{dh_{mk}}{dt} = \frac{1}{M_k} (Q_{gk} - Q_k) \quad (\text{A-10})$$

where h_{mk} is the enthalpy of the metal that separates the hot gas from the fluid, M_k is the mass of the metal, and Q_{gk} is the power from the hot gas to the metal. The temperature T_{mk} of the metal is determined from h_{mk} by means of a curve fit.

At any given instant of time, ρ_k and $\rho_k h_k$ are available as state variables from Equations A-8 and A-9. Both p_k and T_k are directly obtainable from ρ_k and h_k (e.g., via steam-table curve fits).

The mass flow rate w_j at the input to the k^{th} unit is

$$w_j = c_{1k} \left[\rho_j (p_j - p_k) \right]^{1/2} \quad (\text{A-11})$$

where constant c_{1k} is determined on the basis of design-center operating conditions.

The heat flow Q_k is given by

$$Q_k = c_{2j} w_k^{0.8} (T_{mk} - T_k) \quad (\text{A-12})$$

and the heat flow Q_{gk} is given by

$$Q_{gk} = c_{3k} w_g^{0.6} (T_{gi} - T_{mk}) + c_{4k} (T_{gi}^4 - T_{mk}^4) \quad (A-13)$$

where w_g is the hot gas mass flow rate, T_{gi} is the temperature of the hot gas into the K^{th} unit, and the constant c_{4k} is zero if heating by radiation is negligible within the unit. The use of the 0.6 and 0.8 exponents in the above equations is fairly standard.^{A.1}

The output gas temperature T_{gk} is obtained from

$$T_{gk} = T_{gi} - \frac{Q_{gk}}{w_g c_{5k}} \quad (A-14)$$

Inputs into the subsystem are ρ_j , h_j , p_j , T_j , and w_k . State variables in the subsystem are ρ_k , $\rho_k h_k$, and h_{mk} from which h_k , ρ_k , and T_k are obtainable algebraically. Output quantities of interest include ρ_k , h_k , p_k , T_k , w_j , T_{gk} , T_{mk} , Q_k , and Q_{gk} .

Typical steam/water path units include economizers, radiant boilers, and convective super heaters. Some of the low-temperature air-preheater units can be modeled in a similar way. The water-side combustor and the diffuser models are similar, except that Equations A-12, A-13, and A-14 are deleted, and Q_k is obtained on the basis of the combustor-nozzle-channel-diffuser input-output model; the appropriate Q_k of the input-output model is passed through a first-order lag to obtain the Q_k used in Equation A-9. For radiant boilers that have refractory linings, more complicated models may be used to find Q_k .

FEEDWATER CONTROL AND DRUM LEVEL

The drum feedwater is regulated by a valve in the input water line. When this drum input line is from the diffuser, input water mass flow rate is given by

$$w_{in} = A_v \sqrt{\rho_{in} (p_{dif} - p_{dr})} \quad (A-15)$$

where the A_v valve characteristic is controlled on the basis of three signals: drum level l , steam mass flow rate w_{out} , and input water mass flow rate w_{in} . Figure A-2 illustrates an appropriate block diagram.

Figure A-2.--A three-element drum-level controller

Two mass balance equations are required for the drum: one for steam and the other for water. The steam mass balance gives

$$\frac{d}{dt} (V_{drs} \rho_{drs}) = x w_{cww} - w_{out} - w_{cond} \quad (A-16)$$

where V_{drs} is the volume of drum steam, x is the dryness fraction of the controlled water-wall flow rate w_{cww} , and w_{cond} is the condensation rate at the steam-water interface.

$$w_{cond} \approx c(T_{drs} - T_{drw}) \quad (A-17)$$

For the water mass balance,

$$\frac{d}{dt} (V_{drw} \rho_{drw}) = w_{in} + (1-x) w_{cww} + w_{cond} - w_{cww} = w_{in} + w_{cond} - x w_{cww} \quad (A-18)$$

Note that the water-wall flow rate w_{cww} is assumed to be controlled, rather than the result of natural convection as in other models.^{A.2} The volume of water V_{drw} in the drum is variable, but

$$V_{drw} + V_{drs} = V_{dr} \quad (A-19)$$

where V_{dr} is a constant. The water level ℓ in the drum is approximated by

$$\ell = V_{drw}/A_{dr} \quad (A-20)$$

Energy balances for both water and steam are required. For drum steam,

$$\frac{d}{dt} (V_{drs} \rho_{drs} h_{drs}) = x w_{cww} h_{wws} - w_{out} h_{drs} - w_{cond} h_{drs} \quad (A-21)$$

and for drum water,

$$\frac{d}{dt} (V_{drw} \rho_{drw} h_{drw}) = w_{in} h_{in} + (1-x) w_{cww} h_{www} - w_{cww} h_{drw} + w_{cond} h_{drs} \quad (A-22)$$

Note that there are five enthalpies of interest: h_{in} of the input water; h_{drs} of the steam in the drum; h_{wws} of the saturated steam from the riser tubes in the water wall; h_{drw} of the water in the drum; and h_{www} of the saturated water from the riser tubes.

The dryness fraction x is determined on the basis of an energy balance for the water/steam mixture in the heated riser tubes, as follows:

$$(1-x) w_{cww} h_{www} + x w_{cww} h_{wws} = Q_{ww} + w_{cww} h_{drw} \quad (A-23)$$

The heat rate Q_{ww} into the boiling water is characterized by^{A.3}

$$Q_{ww} = c(T_{wwm} - T_{www})^3 \quad (A-24)$$

where c is an appropriate constant, T_{wwm} is a spatial average temperature of the water-wall metal, and T_{www} is a spatial average temperature of the water-wall water. Equation A-23 is solved for x by

$$x = \frac{Q_{ww} + w_{cww}(h_{drw} - h_{www})}{w_{cww}(h_{wws} - h_{www})} \quad (A-25)$$

where $0 < x < 1$ for realistic operation. Because h_{wws} and h_{www} represent steam and water, respectively, under saturated conditions, they can be determined directly from the pressure p_{dr} in the drum. Let $p_{dr} \triangleq p_{drs}$; it is reasonable to assume that $p_{drw} = p_{dr}$ even though the average drum water pressure is slightly greater than the average drum steam pressure.

The hot gas to water-wall surface heat transfer is approximated by an equation of the form in the Equation A-12, and the temperature of the hot gas after the transfer is given by an equation of the form in Equation A-14. The heat balance equation for the water-wall is

$$M_{wm} \frac{dh_{wm}}{dt} = Q_g - Q_{ww} \quad (A-26)$$

and the T_{wwm} to be used in Equation A-24 is a known function of h_{wm} .

There are several ways of using the above equations in the model. A suggested way is indicated in Figure A-3. Careful examination of Figure A-3 will show that a value of ρ_{drw} is used in a sequence of algebraic calculations to determine many values of interest including a new value of ρ_{drw} . This approach appears to be reasonable in this case because the density of the water in the drum changes only slightly over a wide range of operating conditions.

Figure A-3.--An arrangement of key equations for the drum model

SPRAY ATTEMPERATOR MODEL

The temperature of superheated steam at the entrance to the high-pressure turbine must be maintained within prescribed bounds for safe turbine operation. The spray attemperator supplies a controlled amount of feedwater to mix with steam at a point in the steam path that is at least one superheat stage away from the turbine control valve. Figure A-4 describes the control loop.

Figure A-4.--Pictorial description of superheat steam temperature control

The mass flow rate w_i of the steam into the attemperator is

$$w_i = w_o - w_a \quad (\text{A-27})$$

where w_o is the output steam flow rate and w_a is the flow rate of spray water.

An energy balance gives

$$w_o h_o = w_i h_i + w_a h_a \quad (A-28)$$

from which

$$h_o = \frac{w_i h_i + w_a h_a}{w_o} \quad (A-29)$$

is evaluated. The pressure of the steam at the exit of the attemperator is assumed to be essentially the same as that at the entrance. Thus, with p_o and h_o known, steam-table curve fits are used to obtain ρ_o and T_o , and the subsystem is readily incorporated in the overall system simulation.

STEAM TURBINE CONTROL VALVES AND MODELS

In MHD-steam systems, steam turbines are used to drive the air compressor in addition to the electrical generators. Several models for control valves and steam turbines are available in the literature. A particularly elementary model is given by Chou and Davis.^{A.4} The mass flow rate w_v through the control valve is characterized by

$$w_v = k_t A_v \frac{p_s}{p_{so}} \quad (A-30)$$

where K_t is the valve flow coefficient, A_v is the valve opening (which is controlled) normalized to 1 at rated conditions, p_s is the steam throttle pressure, and p_{so} is the design-center throttle pressure. The effective mass flow w_t through the turbine is given by

$$\tau \frac{dw_t}{dt} = w_v - w_t \quad (A-31)$$

where the time constant τ is on the order of 0.5 second for a high-pressure turbine and 5.0 seconds for intermediate and low-pressure turbines. When the turbine is connected to an electrical generator, output electrical power is assumed to be proportional to w_t .

A more basic model^{A.5} of the control valve is as follows:

$$w_i = k A_v \frac{p_s}{T_s^{1/2}} \quad (A-32)$$

where w_i is the inlet mass flow rate to the high-pressure turbine. An appropriate continuity equation is

$$V_t \frac{d\rho_o}{dt} = w_i - w_o \quad (A-33)$$

where w_o is the output mass flow rate of the turbine, ρ_o is the output steam density, and V_t is the volume of pipes, etc. from the throttle valve to the high-pressure turbine. The energy balance equation that applies is

$$V_t \frac{d}{dt} (\rho_o h_o) = w_i h_i - w_o h_o - \Gamma \quad (A-34)$$

in which the mechanical output power Γ is assumed to be proportional to w_i .

When two turbines are driven from the same high-pressure steam source (as in an AVCO ETF design where the electrical generator and the air compressor are driven by high-pressure steam turbines), two sets of equations are used, and w_{i1} and w_{i2} mass flow rates defined to give a total high-pressure steam mass flow rate $w = w_{i1} + w_{i2}$.

Low-pressure steam turbines generally have wet steam outputs and require more detailed models that account for the dryness fraction x of the output steam.

More detailed models of the steam control valve may be used if the model is to be applied over an extremely wide range of operating conditions. Such models are available. ^{A.6}

COMPRESSOR MODEL

In base-load plants, power will be delivered to the air compressor by a steam turbine. The amount of power delivered is controlled by a control valve in the steam supply line; the characterization of the valve and turbine are given in preceding sections. Let $\Gamma_1 = c_1 w_s$ be the power to the turbine.

Effective power Γ_2 to compress air is governed by an equation of the form

$$\tau \frac{d\Gamma_2}{dt} = \eta \Gamma_1 - \Gamma_2 \quad (A-35)$$

The temperature T_{ao} of the air out of the compressor is given by

$$T_{ao} = T_{ai} + \frac{\Gamma_2}{w_{ao} c_p} \quad (A-36)$$

where T_{ai} is the input air temperature, w_{ao} is the air mass flow rate out of the compressor, and c_p is an average specific heat of air. The ratio p_{ao}/p_{ai} of output air pressure to input air pressure can be derived from basic principles^{A.7} as follows:

$$\frac{p_{ao}}{p_{ai}} = [1 + \eta_c (\frac{T_{ao}}{T_{ai}} - 1)]^{3.5} \quad (A-37)$$

where η_c is compressor efficiency. Enthalpy out h_{ao} is

$$h_{ao} = c_p T_{ao} \quad (A-38)$$

and output air density follows from an equation of state

$$\rho_{ao} = 0.003462 (p_{ao}/T_{ao}) \quad (A-39)$$

which applies for air and SI units.

In the above equations, power Γ_1 is a controlled input, and w_{ao} is used to determine T_{ao} in (A-36); T_{ao} is used in turn to determine p_{ao} in (A-39). However, w_{ao} itself is a function of p_{ao} , that is

$$w_{ao} = c \sqrt{\rho_h (p_{ao} - p_h)} \quad (A-40)$$

where p_h and ρ_h characterize the air that flows from the low-temperature air heater which follows the compressor. An iterative method therefore must be used at each integration step to solve for w_{ao} and p_{ao} in terms of specific values of Γ_2 , T_{ai} , ρ_h , and p_h . The equations can be reduced to

$$p_{ao} = p_{ai} \left\{ 1 + \frac{\eta_c \Gamma_2}{c c_p T_{ai} [\rho_h (p_{ao} - p_h)]^{0.5}} \right\}^{3.5} \quad (A-41)$$

from which p_{ao} may be determined numerically by use of an appropriate iterative procedure.

MHD COMPONENT MODELS

The overall dynamic system simulation will contain a comprehensive input-output model of the combustor, nozzle, channel, and diffuser. We refer to this as a CNCD input-output model. Inputs to the model are as follows: fuel feed rate, seed feed rate, air feed rate, oxygen feed rate, preheat air temperature, and two parameters that characterize the interaction between inverter voltages and channel power extraction. Outputs of the CNCD model are combustor pressure, electrical power, peak current density in the channel, peak Hall electric field, combustion gas flow rate, exit gas enthalpy, thermal power to combustor and nozzle walls, thermal power to channel walls, and thermal power to diffuser walls.

To generate the input-output model, more detailed steady-state models are being used. Each steady-state solution for the CNCD supplies specific numerical outputs that correspond to a particular set of inputs, and each steady-state solution is obtained by the use of a plug-flow combustor model (Appendix B) coupled with a quasi-one-dimensional characterization of the nozzle, channel, and diffuser. A two-point boundary-value problem must be solved to obtain each steady-state solution. The input-output data that are generated in the above way are used as the data base from which multi-variable curve fits will be generated. A curve fit is to be made for each CNCD output; each output will be expressed as a nonlinear algebraic function of relevant inputs.

The approach used to generate the CNCD input-output model can be separated into several stages.

Stage One

In stage one, five gas properties (molecular weight, enthalpy, electron mobility, conductivity, and emissivity) are curve fit as functions of several independent variables: pressure (from 1 to 10 atmospheres); temperature (from 2000 K to 2800 K); potassium percentage (0.5 to 1.5 percent); and the percentages of air, oxygen enrichment, and coal. The gas enthalpy and emissivity are strong functions of pressure and temperature but are independent to a large extent of seed and air feed rates if oxygen enrichment is not used. For this case, therefore, enthalpy and emissivity were fitted using functions dependent only on pressure and temperature. Molecular weight, conductivity, and electron mobility are functions of all independent input variables.

For the case of zero oxygen enrichment, the data of the above curve fits has been obtained using the combustor programs described in Appendix B. This combustor program has been modified slightly as follows: for each data point, the combustor program is run for varying seed rates and stoichiometry. At the end of the combustor program, a section has been added which varies the pressure and temperature over a range that we expect to exist in the channel. Available subroutines and gas chemistry are used to calculate the desired gas properties. For every combination of seed and stoichiometry, 30 combinations of temperature and pressure were used--this complicated the curve fitting procedure.

The molecular weight data was fitted using a function of the form

$$MW = f(T,P)*f(SEED,\phi) \quad (A-42)$$

Both factors in the product used a two-variable quadratic, i.e.,

$$f(T,P) = x_1 + x_2 *T + x_3 *P + x_4 *T^2 + x_5 *P^2 + x_6 *T*P \quad (A-43)$$

All fits were made in a least squares manner using an optimization routine. Quadratics were used where possible. For conductivity, however, wide variations required the use of a function of the form

$$f(T,P) = x_1 \cdot \exp(-x_2/T) \cdot P^{-x_3} \quad (A-44)$$

The curve fits were held to be within several percent of the data.

Stage Two

Several combustor outputs must be curve fit. These are as follows: combustion gas output temperature, mass flow rate, stoichiometry, and combustor heat loss. Combustor inputs are seed rate, air rate, oxygen enrichment rate, coal rate, pressure, and air preheat temperature. It is impractical to generate output data for every combination of the six inputs (for example, if each input has a range of five values and the program run time is two minutes, the total run time for all 6^5 input combinations would be 10.8 days). Instead, a reduced set of combinations is chosen to define a unique quadratic surface in the appropriate hyperspace. This surface fits the reduced set of data points exactly. Other data points deviate more or less from the surface, depending on how close the entire data set approximates a quadratic in six variables.

The data to be fit is smooth with no rapid changes so that this method should produce the desired results.

The above method has already been used to fit the output temperature of a combustor with good results. The reduction in computation was significant; less than an hour of computer time was required.

Stage Three

The nozzle-channel-diffusor has electrical power, outlet gas temperature and enthalpy, and heat loss as outputs for each section. Input conditions that control these outputs are inlet mass flow rate and gas temperature, and voltage level and slope for inverters. An additional "output" is the pressure at the nozzle inlet. For each set of input conditions, this pressure will be determined by an iterative solution of the nozzle-channel-diffusor equations to satisfy the required diffusor outlet pressure of approximately one atmosphere. Gas properties within the nozzle-channel-diffusor are calculated using the curve fits found in Stage One.

Inverter voltages are specified as inputs and are used to determine the channel electrical loading. This will enable the control of such quantities as peak current density and Hall field. A linear increase (or decrease) is imposed on the inverter voltage distribution down the channel; both the entrance voltage level and the slope of the voltage distribution are specified as input parameters. The channel electrodes are assumed to be connected in the segmented Faraday configuration.

A channel program A.8 that was written several years ago has been modified to accept the curve fits of Stage One. This is a significant improvement because the equations used before included carbon and hydrogen as the only constituents of the fuel, and oxygen and nitrogen as the only constituents of the oxidant. The equations being developed here consider all chemical constituents that appear in any significant amount.

Stage Four

The results of Stages One, Two, and Three will be combined to form the overall CNCD input-output model. This model will be an order of magnitude better than the previously developed model. A.8 The new model will exhibit the following:

1. An input set expanded to seven adjustable parameters as compared with two in the previous model;
2. Gas and combustion properties derived from a detailed coal combustor program; and
3. The possibility of improved control through the adjustment of inverter voltages in real time.

The coupling of the CNCD input-output model to the air feed system is accomplished as follows. The air pressure in the high-temperature air heater is slightly greater than the combustion pressure. The air pressure in the high-temperature air heater is a state-related quantity and is known at any instant of time from the high-temperature air-heater model. For a given high-temperature air pressure p_{ht} , combustor air input mass flow rate w_{ci} is governed by

$$w_{ci} = c [\rho_{ht} (p_{ht} - p_c)]^{1/2} \quad (A-45)$$

An iterative solution is required. Step 1, a p_c value is selected judiciously and is used in Equation A-45 to generate a w_{ci} value. Step 2, the w_{ci} value of Step 1 is used with other inputs to the CNCD model to obtain a p_c CNCD output value. Step 3, the p_c value of Step 2, is compared with that of Step 1. The steps are repeated if the p_c 's differ by any significant amount; otherwise, the correct p_c and w_{ci} values have been determined, and all outputs of the CNCD at that time instant can be evaluated.

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APPENDIX B

Sensitivities of Outputs to Variations of Inputs in MHD Combustors

INTRODUCTION

As a first step in control policy synthesis, identification of input-output characteristics of system components is necessary. This appendix describes predictions obtained from one of those component models, an internally adiabatic, steady-stage, plug-flow combustor model^{B.1} designed to predict operating states of single-stage or two-stage, pulverized-coal-fired combustors operating in the 1800 K to 3000 K range, which is appropriate for MHD generators. The specific studies are of sensitivities of outputs to variations of inputs in MHD combustors. Results are given for combustors having 45 MW_t total input and 356 MW_t total input. Output temperature, char burnout, electrical conductivity, and heat loss are shown as functions of a wide variety of input variations.

The program is intended as an aid in system analysis and control policy synthesis. It is a tool for predicting behavior of already designed combustors rather than for analysis of detailed internal behavior as a part of the combustor design process. A rigorous treatment would call for information on ignition and devolatilization^{B.2}, fluid flow and swirl patterns, on slag particle size distribution and trajectories in the first stage^{B.3}, and on kinetics of ash vaporization.^{B.4} None of these are embodied in the model used for the analysis at hand, but the features of ash vaporization, ignition, and devolatilization are being incorporated in an improved combustor model as described in Section III.

The program is related to a single-stage model which was originated by the Chemical Engineering Department at MIT.^{B.5} It is considerably more extensive, particularly with respect to thermochemistry, multi-stage operation, and great variability of operating conditions. The fundamental operating assumptions are given in the following list.

1. Plug flow exists with perfect mixing in the radial direction and with no significant mixing in the axial direction.
2. Devolatilization of coal particles is instantaneous.
3. Char particles are carbon spheres perfectly entrained in the combustion gas and at the same temperature as the combustion gas. They burn out according to combined diffusion and surface rate control. Reacting species are O₂, O, and OH.
4. Chemical equilibrium exists at every point in the combustor. Principal species are O₂, O, CO, CO₂, OH, N₂, H₂, H, S, NO, NO₂, SO₂, K₂CO₃, K₂SO₄, KOH, K, K⁺, e, OH⁻, and O⁻.
5. Sidewall temperatures are uniform throughout each combustor stage.

6. Gases conform to the perfect gas law.
7. Velocities are low so that the difference between actual pressure and stagnation pressure is insignificant.
8. A gas temperature gradient exists in the axial direction only.
9. Specified slag rejection occurs uniformly along the first stage only. Non-rejected slag consists of a vapor-droplet mixture and is perfectly entrained in the combustion gas.
10. Heat loss is due to slag rejection and to both radiative and convective effects to the sidewalls from each slice. Slices are isolated from each other giving an internally adiabatic heat loss model.

The input-output response of this fairly detailed model has been analyzed; the results for a single input variable changing are shown graphically in this paper. It is emphasized that absolute values of outputs are not of prime importance in such input-output models. Rather, it is the sensitivity of outputs to inputs that is important. In a properly designed feedback control system, automatic regulation of set points is intrinsic. But proper design of a feedback system to meet required set points without instability, excessive settling time, or other undesirable behavior demands knowledge of component transfer functions, i.e., component sensitivities.

OPERATING CONDITIONS

Combustors in the 30 MT_t coal input range (CDIF-sized) and the 235 MW_t coal input range (possibly ETF-sized) were analyzed. When preheated air is accounted for, total thermal inputs become 45 MW_t and 356 MW_t, respectively. Complete specifications for design center operation are given in Tables B-1 and B-2.

Table B-1.--Center Operating Point of Both Combustors

First Stage Sidewall Emissivity	.60
Second State Sidewall Emissivity	.60
First Stage Sidewall Temperature	1750 K
Second Stage Sidewall Temperature	1750 K
First State Stoichiometric Ratio	.55
Second Stage Stoichiometric Ratio	.95
First Stage Nominal Residence Time	70 ms
Second Stage Nominal Residence Time	45 ms
Sidewall Convection Coefficient	200 w/m ² - K
Seed Type	K ₂ CO ₃ dry feed
Potassium Seeding by Mass Fraction	.01
Air Preheat Temperature	1750 K
Ambient Pressure	.90 atm
Ambient Temperature	276 K

Table B-1.--Center Operating Point of Both Combustors (Continued)

Relative Humidity	50%
Slag Fraction Removed	.90
Raw Coal Temperature	278 K
Seed Input Point	Beginning of Second Stage
Coal Density	1362 Kg/m ³
Coal Heating Value (as fired)	23.46 MJ/Kg

Table B-2.--Center Operating Points of Specific Combustors

	<u>45 MT_t</u>	<u>356 MW_t</u>
First State Diameter,m	.85	1.7
First Stage Length,m	.75	1.5
Second Stage Diameter,m	.60	1.7
Second Stage Length,m	1.5	1.55
Coal Feed Rate,Kg/sec	1.263	10.047
Coal Thermal Input (approx.)	29.6	235.5
First Stage Air Thermal Input,Mw	8.80	70.0
Second Stage Air Thermal Input,Mw	6.40	50.8
Total Thermal Input,Mw	44.80	356.3
First Stage Gas Velocity,m/sec	9.7	20
Second Stage Gas Velocity,m/sec	34	35
First Stage Residence Time,m/sec	70	70
Second Stage Residence Time,m/sec	45	45

The coal is typical Montana Rosebud dried to 5 percent ASTM moisture with an ash having equivalent molecular weight of 70.27. Its analysis is given in Table B-3. It is assumed to be pulverized to fit a Rosin-Rammler distribution^{B.6} of $\bar{x}$ = 52 microns and s = 1.2, parameters which characterize typical pulverized fuel.^{B.7} Twenty geometrically spaced discrete sizes are used to represent the continuous distribution with the resulting mass fraction of coal in each size bin as shown in Figure B-1.

Table B-3.--Coal Analysis

Carbon	.59802
Hydrogen	.03962
Oxygen	.14231
Nitrogen	.00874
Sulfur	.00903
Moisture	.05000
Ash	.15288

Equivalent Coal Formula

CH_{.79502}O_{.17848}N_{.01253}S_{.00564}Ash_{.094348}(H₂O)_{.05574}

Figure B-1.--Coal mass fraction distribution

Rosin-Rammler parameters: $x = 52$ microns, $s = 1.2$

RESULTS

A set of axial profiles of temperature, char particle burnout, and heat loss for both combustors, and concentration of selected compounds for the 45 MW_t combustor are shown first. A second and larger set of results shows the sensitivities of first- and second-stage output temperature, electrical conductivity, char particle burnout, and heat loss as functions of input variations about the center operating values (given in Tables B-1 and B-2). A complete set of sensitivities were established for a 1704 MW_t combustor; but due to space limitations and the fact that its sensitivities are very similar to those of the 356 MW_t combustor, the results are not presented here.

Figure B-2.--Axial variations of temperature, char burnout, and heat loss for 45 MW_5 combustor.

Figure B-3.--Axial variations of selected species for 45 MW_t combustor.

Mole fraction scaling of first stage same as second stage.

Figure B-4.--Axial variations of temperature, char burnout, and heat loss for 356 MW_t combustor.

Figure B-5.--Output temperature variations vs. air preheat temperature, first- and second-stage stoichiometry, combustion pressure, and seed mass fraction.

Figure B-6.--Output temperature variations vs. ambient temperature, relative humidity, coal particle screening, mass flow rate, and coal moisture content.

Figures B-5 and B-6 show the variation of output temperature as inputs are changed. In these and subsequent figures, curves are identified by codes for combustor size and input that is varied, e.g., in Figure B-5, 45 A refers to the 45 MW_t combustor as air preheat is varied from 1650 K to 1850 K; and 356 C refers to the 356 MW_t combustor as overall stoichiometry is varied from .85 (fuel rich) to 1.05 (excess air). In Figure B-5, all curves pass through

design center at their midpoint. Air preheat temperature shows a near-linear effect, producing about 0.35 K output/1.0 K input for either combustor. This is a very significant sensitivity, indicating that some means of reliably minimizing preheat air variations, such as a heat capacitor^{B.8}, is desirable. Increased first-stage stoichiometric ratios have a generally negative effect on output temperature, with some recovery of output temperature when first-stage stoichiometry exceeds 0.60. By comparison, overall stoichiometry results in a concave downward curve having a broad peak in the .95 to 1.0 range for the 45 MW_t combustor and in the .90 to .95 range for the 356 MW_t combustor. This is the range of operation commonly considered appropriate, a conclusion supported by these results. Combustion pressure shows a near-linear positive slope of about 12.5 K/atm. Seed concentration (K₂CO₃ dry feed) causes a near-linear negative slope of -26.0 K/0.01 mass fraction, due almost entirely to the dissociation energy of the seed.

In Figure B-6, curves for ambient temperature, relative humidity, and mass flow rate pass through design center at their midpoints, while curves for coal particle size screening and coal moisture content do not reach design center until the extreme end of their variation. Ambient temperature is seen to cause a decline of output temperature of about -.29 K output/1.0 K ambient variation. This is entirely due to holding relative humidity fixed at 50 percent as temperature varies, thereby greatly changing absolute humidity of the oxidant. A similar, but lesser, effect occurs with varying relative humidity at fixed ambient temperature, giving a slope of about -.067 K/percentage point relative humidity.

Variation of mass flow rate (fixed stoichiometry) gives a gently concave-downward curve with an average sensitivity of 1.2 K/percent mass flow change for the 45 MW_t combustor and 0.70 K/percent mass flow change for the 356 MW_t combustor.

The effect of screening coal particles to permit passage of only those under a specific size shows that progressive elimination of larger particles results in higher output temperature. The smaller particles burn more rapidly. This lowers the combustion gas emissivity which in turn decreases heat loss and increases combustion temperature. Particle screening occurs at 40, 70, 100, and 150 microns, giving a correspondingly truncated version of the mass fraction distribution shown in Figure B-1. The new mass fractions are adjusted to give a total of unity, preserving all mass flow values. The point at the extreme left in Figure B-6 is 40 micron screening, progressing linearly along the points indicated to the unscreened (240 micron maximum particle size) on the right, which is design center. This is an interesting curve, exhibiting no linearity--only a general trend.

The other non-centered curve is that showing the effect of coal moisture on output temperature. It has values of 5 percent ASTM moisture on the left (design center), increasing in 5 percent steps to 25 percent moisture at the far right. It also is non-linear but has a general slope of -5.2 K/percent coal moisture for both combustors, thereby quantifying the preferability of dry coal.

Figures B-7 and B-8 show the effect of the same set of variables on electrical conductivity. Conductivities are less in the combustor than they will be in the MHD channel because the combustor operates at a higher pressure.

In Figure B-7, three of the curves (air preheat, first stage stoichiometry, and overall stoichiometry) tend to follow the same behavior pattern as previous output temperature curves. Air preheat temperature increases provide .0064 mhos/m/K for the 45 MW combustor and .0096 mhos/m K for the 250 MW combustor. First-stage stoichiometry has little effect in the 45 MW combustor and a mild positive slope of .009 mhos/m/percentage point of stoichiometry in the 356 MW combustor.

In the smaller combustor, conductivity peaks at an overall stoichiometry of 0.95, while the larger combustor shows the peak moved down to a ratio of 0.90. (This downward shifting continued in the 1704 MW combustor for which it occurred at a ratio of 0.85.)

Combustion pressure shows almost no effect on conductivity. This is initially surprising since a positive effect on output temperature was noted. But conductivity is negatively influenced by pressure, and it appears that the two effects mutually cancel. The strongest and expected variation of conductivity is caused by seed concentration. It is also a highly non-linear effect.

Figure B-7.--Electrical conductivity vs. air preheat temperature, first- and second-stage stoichiometry, combustion pressure, and seed mass fraction.

Figure B-8.--Electrical conductivity vs. ambient temperature, relative humidity, coal particle screening, mass flow rate, and coal moisture content.

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Figure B-9.--First-stage char burn-out vs. air preheat temperature, coal particle screening, first-stage stoichiometry, mass flow rate, and combustion pressure.

Figure B-10.--Second-stage char burnout vs. air preheat coal particle screening, second-stage stoichiometry, mass flow rate, and combustion pressure.

The most dramatic effects are those of coal particle screening and stoichiometric ratio. Little can be said about them to enhance their graphical depiction. Again, design center values are reached at the extreme right point of the coal particle screening curve rather than at the midpoint of the curve.

Figures B-11 and B-12 show the dependence of heat loss on various inputs. It is interesting to note that air preheat and first-stage stoichiometry give similarly shaped curves with sensitivities of roughly 0.01 percent loss/ K air pre-heat and 0.05 percent loss/percent change of stoichiometry. Overall stoichiometry causes a heat loss change of about -0.13 percent loss/percent change of stoichiometry in the 45 MW_t combustor and -0.06 percent loss/percent change of stoichiometry in the 356 MW_t combustor. Coal moisture is very effective in reducing heat loss, principally as a result of depressing the overall internal temperature profile. This does not infer that high coal moisture is desirable. The sensitivities are -0.24 percent loss/percentage point coal moisture for the 45 MW_t combustor and -0.15 percent loss/percentage point coal moisture for the 356 MW_t combustor. Combustion pressure influences heat loss by -0.33 percent loss/atm and -0.21 percent loss/atm in the respective combustors. The effect of coal particle screening is highly non-linear, with the smallest heat loss occurring for the 40 μ m screening. This is because the smaller particles burn out more rapidly, causing the combustion gas emissivity to be lower.

Figure B-11.--Heat loss vs. air pre-heat temperature, mass flow rate, and first- and second-stage stoichiometry.

Figure B-12.--Heat loss vs. coal particle screening combustion pressure, and coal moisture content.

The most important factor affecting heat loss is the decrease of the surface-to-volume ratio and is implicit in the design center heat losses for the two combustors.

Figures B-13 and B-14 show the effects of oxygen enrichment on output temperature, conductivity, first-stage char burnout, and heat loss. With the exception of heat loss, all of the curves are concave downward. This does not necessarily indicate a decreased sensitivity of the outputs to oxygen enrichment in a properly sized combustor. As much as anything, they indicate that the original combustor is increasingly oversized for the decreased mass flows associated with oxygen enrichment.

Figure B-13.--Output temperature and electrical conductivity vs. oxygen mole fraction of oxidant.

Figure B-14.--First-stage char burnout and heat loss vs. oxygen mole fraction of oxidant.

CONCLUSIONS

Several variables have been seen to have a significant effect on combustor operations. One of these, varying temperature at fixed relative humidity, is one over which we have no control. (As a matter of interest, ambient pressure variations from 0.8 atm to 1.0 atm showed almost no effect.) The most significant aspect of fuel preparation was coal moisture content. The great sensitivity of electrical conductivity with respect to coal moisture suggests that an economic analysis of coal drying processes may be advisable. There is also some benefit from smaller coal particle distribution, indicating that an economic analysis of pulverization methods may also be warranted.

Operationally, it is clear that air preheat temperature should be closely controlled and that any preheat system improvements would be beneficial. Stoichiometric control is also important. It has a broad effect on output temperature and conductivity, showing a tendency to peak at lower overall ratios as combustor size increases. First-stage stoichiometry has less effect on output temperature and electrical conductivity than does overall stoichiometry. This indicates that first-stage stoichiometry variations may be used to control gasifier operation with respect to slag rejection, heat loss, NO_x formation, etc. Other conclusions are that potassium concentrations of about .01 mass fraction are appropriate and that the highest reasonable pressures should be used in the combustor.

Finally, it must be emphasized that results discussed here pertain to only one component of a complex system and that operating conditions which maximize some important output of the combustor, e.g., electrical conductivity, may not be the optimal set of operating conditions for the combined-cycle MHD-steam turbine plant. Only a thorough analysis of the complete system subject to operational constraints can establish optimal control policies and operating points.

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MILESTONE CHART

STATUS DATE Sept. 1978

TASK H-3

PROGRESS

MAJOR MILESTONES

O N D J F M A M J J A S

DEVELOP MULTIVARIABLE INPUT-OUTPUT
MODEL OF ETF-SIZE COMBUSTOR

DEVELOP DYNAMIC MODELS OF ETF SYSTEM
COMPONENTS

DEVELOP TIME-DEPENDENT COMBUSTOR
MODEL

535

STATUS DATE _____

Slag Physical Properties:
Electrical and Thermal Conductivity
R. Pollina

ABSTRACT

Electrical conductivity data for seeded and unseeded coal slags from eastern, mid-western, and western coals are presented in this report. Above approximately 1675 K, the composition differences between these slags have little effect on electrical conductivity, a fact which is significant for generator operation. Below about 1400 K, large differences in electrical conductivity are observed which can be explained in part by differences in their composition.

Data is presented for Rosebud ash electrical conductivity as a function of seed content to 1723 K. Again, seed content has only a small effect on conductivity at high temperatures.

Calculations of slag surface layer conductivity were done for the Faraday direction (normal to the slag layer) and for the Hall direction (interelectrode gap resistance). For metal electrodes, these were determined by the metal-slag and the slag-plasma interface temperatures, respectively. These calculations agree with slag layer measurements at AVCO. As yet, we are not in a position to explain the cathode shorting effects observed by AVCO, but further work on this effect is planned.

The thermal expansion of vitreous, natural Rosebud ash was measured and found to be $6.4 \pm 0.3 \times 10^{-6} \text{K}^{-1}$ between 300 and 95 K. In its crystalline form, an increase of 11 percent in the thermal expansion was evidenced.

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 d-c and two lead a-c 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. Thermal conductivity measurements can be made in solid materials to 1000 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.

II. SUMMARY OF PROGRESS TO DATE

Progress has been made in many areas this year. Electrical

conductivity studies of Rosebud and other slags as a function of chemical composition, temperature, and oxygen pressure have been continued, and additional programs to study the nature of the conduction species in slags have been initiated. An experimental arrangement using water-cooled copper electrodes has been tested successfully and will be used to study the electrolysis of molten slags.

A system for measuring the thermal expansion under load is nearing completion and will be used to study the mechanical properties of refractory materials. Some creep work also may be performed on this system in cooperation with the studies of MHD preheater materials being conducted at Montana Tech. To study time-dependent effects, an on-line data acquisition system is being installed.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

In an MHD generator channel, the conductivity of the slag layer adhering to the walls of the generator must be in a range appropriate for the slag to act as a good conductor for the generator output current and yet low enough to prevent shorting of the axially directed Hall current. The mathematical analysis of the current flow indicates that opposing demands are made upon the slag conductivity. However, the criterion has not been determined yet by which the suitability of a given slag, with respect to the magnitude and character (ionic or electronic) of its electrical conductivity, is judged. The ultimate goal of this task is to supply design data necessary to model the output of the channel and to predict empirically the behavior of slag under any constraints which might occur when larger scale projects (such as the CDIF) become operational. Close cooperation with other groups engaged in MHD research is required and is being sought.

The Montana coal ash used in these experiments is from the Rosebud seam and was obtained from a local power company.² The combustor temperature was approximately 1900 K,³ and bottom and fly ash were supplied from the combustor and the base of the stack, respectively. The samples were received in the form of powder, and each was homogenized and melted in alumina or platinum crucibles in air at 1700 to 1750 K for one to 36 hours and then air quenched.

In the conductivity tests below 1750 K, samples were contained in alumina boats of 99.8 percent purity⁴ (interior dimensions 2 x 4 x 4 mm). The d-c conductivity was measured using the conventional four-lead technique because of its sensitivity, reproducibility, and ability to separate polarization effects from true conductivity. A two-lead technique and an a-c resistance bridge were used to measure a-c conductivity. Pulverized samples were placed in a crucible into which four leads had been suspended. A Type B thermocouple (platinum-6 percent rhodium versus platinum-30 percent rhodium), which was calibrated at the gold point, monitored the temperature. Above 1750 K, a two-lead technique was used to measure the electrical conductivity. Because of problems in d-c measurement associated with polarization charge buildup in ionically conducting coal slag when only two leads are used, a-c conductivity was measured above 1750 K, but d-c conductivity was not. For measurements

at temperatures above 1750 K, a small platinum-40 percent rhodium cup was used to contain the slag sample and served as one of the electrodes. A 20 mil Pt-40 percent Rh wire penetrating the slag surface served as the other electrode. The change to platinum-rhodium was dictated by corrosion problems with alumina at high temperatures.

Samples were raised to the maximum temperature, and data were taken from the highest temperature downward. During one run, the ceramic boats developed a web of cracks, indicating that the slag had a lower thermal expansion than alumina.

To determine the existence of any time-dependent effects in the d-c conductivity measurements, a sample was held under a d-c current for 25 hours, and both the conductance of the sample and the charge buildup at the current electrode were monitored. This charge buildup was measured by the compliance voltage necessary to maintain constant current through the sample. The sample, a Rosebud ash with 20 percent K_2CO_3 equivalent of added potassium seed, was chosen because of its strong ionic effects and strong charge buildup on the electrodes. The compliance voltage between the outer two electrodes varied from 2.5 to 135 volts, while the conductance between the inner two drifted slowly which was insufficient to affect the data. Typically, the conductivity follows the Arrhenius law, and even an error as large as 50 percent is not enough to affect the temperature dependence of the electrical conductivity in coal slag. Because the voltage and current leads were separated, the ionic charge buildup resulting from current flow did not affect the accuracy of the measurements.

Samples used for thermal expansion and thermal conductivity experiments were air-quenched from 1450°C to 750°C and cooled slowly from 750°C to room temperature. In this way, samples were produced which were free of gaseous inclusions and mechanical strains or fractures. After annealing, samples could be cut into any shape desired without fracturing.

A. Electrical Conductivity

Much of our work to date has been devoted to investigating the electrical conductivity of Rosebud ash and the effects of adding potassium seed (added as $K_2CO_3 \cdot 1\frac{1}{2} H_2O$) and iron (added as Fe_2O_3).

Seeded Rosebud ash has been studied in the temperature range of 973 K to 1723 K using the four-lead d-c technique with data taken isothermally at 50° temperature intervals. Conductivity data has been taken for the following K_2O percentages (natural Rosebud ash): 1.8%, 3.6%, 5.8%, 7.3%, 9.9%, 13.8%, 18.9%, and 30.1%. Iron-enriched Rosebud ash has been studied with total Fe concentrations (as wt.% Fe_2O_3) as follows: 4.5 wt.%

Fe_2O_3 (natural Rosebud ash), 10.4%, 15.3%, 17.2%, and 22.3%. The temperature range for measurements taken at 50° intervals was 1173 K to 1723 K. The effects of changes in oxygen partial pressure on electrical conductivity also were studied using controlled atmospheres. Controlled atmospheres were obtained by mixing air and argon, or CO_2 and CO, to give oxygen partial pressures of .17atm (air) to 10^{-10} atm.

Selected ashes also were studied at higher temperatures (up to 2025 K) using the two-lead d-c bridge technique. Figure 1 shows the electrical conductivity of some slags from the east, midwest, and west, including seeded New Hampshire (AVCO) slag (□), Illinois #6 slag (○), Montana Rosebud slag (●), seeded Montana Rosebud slag (+), and iron-enriched Montana Rosebud slag (▲). Their compositions are given in Table 1.

Figure 1 shows that at temperatures above approximately 1675 K, the composition differences between the slags have little effect on electrical conductivity. All of the ashes in this temperature region appear to be single-phase liquid solutions; conduction by the movement of various ionic species probably predominates. In the liquid state, the mobilities of the various ionic species may not differ greatly. The conductivity of a given liquid slag is probably more dependent upon the total ionic concentration than upon the ionic concentration of seed alone. The small differences in conductivity of liquid slags of different compositions also may be related to differing viscosities, as previously suggested by Bates.

The data represented in Figure 1 show large differences in electrical conductivity for the different ash compositions at temperatures below about 1400 K. At these lower temperatures, the slags are plastic or solid and contain some crystalline phases in addition to the glassy networks. The mobility of all ionic species which characterize the liquid slags is radically altered at lower temperatures. Conductance by ionic charge transport becomes sensitive to concentrations of the relatively mobile K^+ and Na^+ ions as well as to the composition of the glass network through which these ions must move. The conductivity of the seeded Rosebud ash (Figure 1) is about three orders of magnitude higher than natural Rosebud at temperatures below 1300 K.

Iron enrichment also radically improves the conductivity of Montana Rosebud slag. At $T = 750$ K, the conductivity of the enriched slag is four and one-half orders of magnitude greater than the conductivity of the natural slag. In Figure 1, the slag with the greatest conductivity (iron-enriched Montana Rosebud) is the one with the highest iron content. The slag with the second greatest conductivity, seeded New Hampshire (AVCO), is the one with the second highest iron content. Rosebud ash enriched with iron to 22.3 wt. % Fe_2O_3 has higher conductivity than Rosebud ash saturated with seed at 30.1 wt. % K_2O .

Ashes with Fe_2O_3 content greater than about five or six percent can exhibit some electronic contribution to conductivity in the lower temperature region. As previously reported, iron-enriched Rosebud ashes showed an oxygen sensitivity favoring conductivity in atmospheres which result in substantial concentrations of both ferrous and ferric iron. The fact that conductivity is enhanced by the presence of both oxidation states rather than the predominance of one or the other indicates a significant electronic contribution to conductivity in these ashes. Although little is known about the charge transport mechanism for this electronic contribution, it appears to involve the transfer of electrons between proximate iron atoms rather than simple ionic movement of

ELECTRICAL CONDUCTIVITY OF MHD SLAGS $P_{O_2} = 0.17 \text{ ATM}$

Figure 1.--Electrical conductivity of MHD slags
 $P_{O_2} = 0.17 \text{ ATM}$

TABLE 1.--Composition of the slags*

<u>Oxide</u>	<u>Rosebud Natural</u>	<u>Seeded Rosebud</u>	<u>Rosebud 20</u>	<u>Avco (N.H.)</u>	<u>Illinois</u>
SiO ₂	41.3%	31.6%	36.6%	34.9%	45%
Al ₂ O ₃	26.7	20.2	23.4	19.6	20
CaO	19.7	14.9	17.3	5.0	--
MgO	6.2	4.7	5.4	1.1	--
Fe ₂ O ₃	4.5	3.4	22.3	19.6	11.3
K ₂ O	0.5	30.1	0.4	15.1	12.6
Na ₂ O	0.5	0.4	0.4	1.3	--

*In some cases, composition is measured by elemental analysis and reported here as oxide. Since not all elements appear as oxides, this tends to give values higher than they actually are in the slag. As a result, some analyses add up to greater than 100 percent.

Fe^{2+} or Fe^{3+} through the glass network. It should be noted that the evidence for an electronic contribution to conductivity in some ashes does not preclude additional ionic contribution by iron in these ashes; in fact, in the liquid state, the strong oxygen sensitivity of these ashes disappears as the glass network is broken down. At the highest temperatures for which data was taken (1900 to 2000 K), conductivity in all of the slags studied may be considered entirely ionic.

Figure 2 shows some of the conductivity data generated from seeded Rosebud ash; the figure is plotted isothermally to illustrate the effects of seed concentration. The isotherm for liquid slag at 1723 K shows a gradual increase in conductivity with the addition of seed. As was noted for the high-temperature data in Figure 1, the effects of seed addition on the conductivity of liquid Rosebud slag are small and should not prove significant for MHD applications.

At lower temperatures, however, increased seed concentration produces dramatic changes in conductivity. As the isothermal plots show, conductivity response to increasing seed content in solid slag is not as regular as might have been expected. The anomalies in conductivity behavior with respect to potassium concentration at the lower temperatures shown are substantial and are yet to be explained. We plan to use X-ray diffraction studies to determine whether these anomalies are associated with crystalline phases in the seeded slags. Previously reported work has shown that composition can influence conductivity behavior indirectly by determining the crystalline phases which can occur in a given slag. The relationship between the crystallization of anorthite from liquid Rosebud ash at about 1650 K and the sharp drop in electrical conductivity as the slag is cooled below this temperature is an example of this kind of indirect compositional effect.

It also should be noted that the most heavily seeded ash (at 30.05 wt. % K_2O) suffered considerable loss of potassium during the course of conductivity measurements. Thus, the data points plotted at about 30 wt. % K_2O in Figure 2 actually represent conductivity of Rosebud slag with a somewhat lower seed content. This is particularly true at the lower temperatures. Additional measurements will be made with seed concentrations in the range of 20 to 30 wt. % K_2O to correct this deficiency in the data.

We have attributed the loss of potassium from heavily seeded slags to electrolysis of the slags during the course of measurements.⁹ Electrolysis of the slag layer in an MHD channel could have important effects on generator performance. We have begun experiments to investigate this and related aspects of ion movement through seeded slags. Water-cooled copper electrodes will be used in these experiments so that results can be correlated more easily with data and observations from the AVCO test channel.

B. Comparison of Slag Electrical Conductivity with AVCO Channel Results

To determine the usefulness of laboratory slag electrical conductivity measurements in predicting the behavior observed in an MHD

Figure 2.--Potassium concentration (wt. % as K_2O)

generator, we have calculated the Faraday and Hall path resistances due to the presence of a slag layer. These results will not take into consideration magnetohydrodynamic effects such as the cathode wall nonuniformities observed in AVCO tests.¹¹ We first must find the expression for the conductivity of a slag layer with a temperature gradient. This is the configuration for Faraday current normal to the slag surface.

Assuming that $V = j \int \frac{dl}{\sigma}$ (where j is the Faraday current density, σ is the slag conductivity, and l is the thickness of the slag layer) and assuming (for simplicity) that $\sigma = Ae^{-B/T}$ approximates the slag conductivity curve, the following equation results. We shall verify this assumption later.

$$V = j \int \frac{dl}{A} e^{B/T} = \frac{j}{A} \int e^{B/T} \frac{dl}{dT} dT,$$

The variables have been changed to make use of the fact that $\frac{dl}{dT}$ is approximately constant through a slag layer in an MHD generator and is given by $\frac{dl}{dT} = \frac{s}{T_s - T_m}$ where (following Rosa¹) s is the slag layer thickness, T_s is the temperature at the slag-plasma interface, and T_m is the temperature at the slag-electrode interface.

We can change variables to $x = \frac{B}{T}$ and obtain

$$V = -j \frac{dl}{dT} \frac{B}{A} \int_{x(T_m)}^{x(T_s)} \frac{e^x}{x^2} dx$$

$$V = j \frac{dl}{dT} \frac{B}{A} \left[\frac{e^x}{x} - \ln x - \frac{x}{1!} - \frac{x^2}{2 \cdot 2!} - \frac{x^3}{3 \cdot 3!} - \dots \right]_{x(T_m)}^{x(T_s)}$$

To determine the Faraday current, we obtain a conductivity of

$$\sigma_F = \frac{j s}{V} = \frac{A(T_s - T_m)}{B} \left[S_F \begin{matrix} x(T_s) \\ x(T_m) \end{matrix} \right]^{-1}$$

in which we have replaced the integral by S_F . Using the earlier

approximation for σ , $\sigma = Ae^{-\frac{B}{T}}$. We can fit the seeded N. H. data in Figure 1 to within experimental accuracy with the expression

$$\sigma = 0.80 e^{-0.47 \frac{10^4}{T} \frac{\text{mho}}{\text{cm}}}$$

Considering the vagaries of the material involved, this assumption is reasonably accurate. Thus,

$$A = 0.80, B = 0.47 \times 10^4, \text{ and we take } T_m = 480 \text{ K } \left(\frac{10^4}{T} \approx 21 \text{ K}^{-1} \right) \text{ and } T_s = 1818 \text{ K } \left(\frac{10^4}{T} = 5.5 \text{ K}^{-1} \right)$$

Before evaluating σ_F , the leakage conductivity σ_H and leakage resistance R_H between adjoining electrodes are calculated.

The average conductivity of a slag layer for current flow between electrodes is given by

$$\sigma = \int \sigma dl = \int \sigma \frac{dl}{dT} dT$$

Again, we take $\sigma = Ae^{-\frac{B}{T}}$, $\frac{dl}{dT} = \frac{s}{T_s - T_m}$ and by letting $x = \frac{B}{T}$, we obtain

$$\sigma_H = \frac{-BA}{T_s T_m} \int_{x(T_m)}^{x(T_s)} \frac{e^{-x}}{x^2} dx$$

$$\sigma_H = \frac{-BA}{T_s - T_m} S_H \Big|_{x(T_m)}^{x(T_s)}$$

$$\text{where } S_H(x) = \frac{e^x}{x} + \ln x - \frac{x}{1!} + \frac{x^2}{2 \cdot 2!} - \frac{x^3}{3 \cdot 3!} + \dots$$

The series parts of the sums S_F and S_H converge; the results for seeded New Hampshire slag are calculated for $T_s = 1818$ ($x=2.59$) and $T_m = 480$ ($x=9.79$) yielding $\sigma_F = 9.3 \times 10^{-4} \frac{\text{mho}}{\text{cm}}$ and $\sigma_H = 1.9 \times 10^{-2} \frac{\text{mho}}{\text{cm}}$. If we assume that the electrodes are 15cm long and one cm wide with an insulator separation of 0.2cm and a slag thickness of 0.2cm, then $R_F = 14.8\Omega$ and $R_H = 3.3\Omega$. The only available AVCO data with which to compare these

numbers appear in the proceedings of the last MHD engineering symposium.¹¹ Before the magnetic field was activated in a seeded and slagged channel, the resistance between two electrodes was found to be 5 to 10Ω. Since the current path between two neighboring electrodes is through the slag layer of one electrode, along the slag layer to the next electrode, and down through its slag layer, the actual inter-electrode resistance is approximated by $2R_F + R_H$.

Given the fact that the AVCO test was conducted at a higher seeding level than was used to find our conductivity data, the results are in excellent agreement. When the magnetic field in the generator is activated, the phenomenon of cathode shorting occurs which lowers the inter-electrode resistance by two orders of magnitude (except for the electrode immediately downstream of an arcing electrode). Between these two electrodes, the resistance remains of the order of 5 to 10Ω. Because of the high iron content of the New Hampshire slag, a high concentration of iron and potassium on the cathode wall is anticipated when the field is activated. This will lower the slag resistance considerably (two orders of magnitude is not unreasonable based upon our data). When the field is deactivated, the slag will return to its original composition and resistance--as observed at AVCO.

We now are studying this phenomenon with the use of water-cooled copper electrodes; results of this research will be presented in future reports.

C. Thermal Expansion of Rosebud Coal Ash

We have investigated the thermal expansion of both vitreous and crystalline unseeded Rosebud ash below its plastic point. Thermal expansion is measured with a differential dilatometer using sapphire push rods and a sapphire reference sample. For Rosebud Natural ash, we obtained the thermal expansion $\alpha = 6.4 \pm 0.3 \times 10^{-6} \text{ K}^{-1}$ between room temperature and the yield point of the slag $\approx 950 \text{ K}$. For crystalline slag, we found an increase of thermal expansion of about 11 percent.

The value of the thermal expansion below the slag softening point is important because it bears on the durability of porous materials used in the preheater and channel and other elements which come in contact with liquid slag. If a slag-containing body such as a porous firebrick or alumina laboratory crucible is cooled to room temperature, mechanical stresses will be expected because of the slag inclusions. These stresses will depend on the thermal expansion of the material in question. For example, if a firebrick has a thermal expansion smaller than slag, it contracts less than slag when cooled; depending on the adherence of the slag to the brick material, the slag might merely flake off the material when cold (as it appears to have done in the MSU preheater), or the brick may be fractured. Few high-temperature refractories meet the criterion of appropriate thermal expansion. The thermal expansion of boron carbide is close to that of Rosebud ash, and one would expect bonds between the two to be quite stable. Sapphire has a somewhat higher thermal

expansion than slag (8.17 vs. $6.4 \times 10^{-6} \text{ K}^{-1}$), and one would expect slag-containing alumina crucibles to crack on cooling--which they do. Spinel behaves similarly. Periclase has more than twice the expansion of slag and thus would crack severely on cooling if used as a crucible. Smooth, low-porosity walls of MgO may be scraped clean of slag on cooling because of the stress cracking which would be induced at the slag interface by the large differential expansion between the two materials (6.4 vs. $14 \times 10^{-6} \text{ K}^{-1}$). In addition to chemical attack at grain boundaries of porous MgO, one would expect the pores to be enlarged on cooling by the differential stresses produced by the slag. This is another reason why porous MgO is not suitable for use with slag. In the future, we plan to study other slags and perhaps correlate these results with deterioration observed in MHD test facilities which are thermally cycled to low, damage-inducing temperatures.

IV. CONCLUSIONS

Several conclusions can be drawn from this electrical conductivity work. Above approximately 1675 K , the electrical conductivity of slags becomes practically independent of composition; thus, little effort needs be devoted to this region. Secondly, the results of conductivity measurements may be used to predict the slag layer conductivity if the composition of the slag on the electrode walls when the generator is on is known. Finally, a crude estimate of the low-temperature (below about 1400 K) effect of composition of slag conductivity for Rosebud slag can be made for varying iron and potassium concentrations; that is, the effects of iron and seed to a first approximation are additive in the conductivity. If a percentage of iron raises the conductivity from 10^{-4} to 10^{-2} , it is reasonable to estimate the final conductivity of both the iron and seed addition as $10^{-3} + 10^{-2} \approx 10^{-2}$. Further work needs to be done in this area; the results would be very important for attaining a simplified understanding of slag conductivity for a given slag type.

The low-temperature thermal expansion of coal slag is often overlooked, but its value below the slag softening point is important. Impregnated refractory materials will be stressed severely on cool down if their thermal expansion does not match that of the slag. We have measured the thermal expansion of Rosebud slag at $6.4 \pm 0.3 \times 10^{-6} \text{ K}^{-1}$. Even if porous MgO firebrick resisted slag attack (which it does not), the mechanical stresses arising from its differential thermal expansion with coal slag would be severe.

MILESTONE CHART

STATUS DATE Sept. 1978

TASK J

PROGRESS

MAJOR MILESTONES

COMPLETE ELECTRICAL CONDUCTIVITY
STUDIED ON SEEDED ROSEBUD ASH FOR
SEED CONCENTRATIONS OF 5-20% K_2CO_3

COMPLETE MODIFICATIONS OF THERMAL
EXPANSION SYSTEM

COMPLETE ELECTRICAL CONDUCTIVITY
STUDIES ON SEEDED ROSEBUD ASH FOR
SEED CONCENTRATIONS OF 20-30% K_2CO_3

NUMERICALLY COMPARE ELECTRICAL
CONDUCTIVITY MEASUREMENTS WITH
RESULTS OF CHANNEL MEASUREMENTS
AT AVCO

COMPLETE MEASUREMENT OF QUENCHED
AND SLOW COOLED SAMPLES OF ROSEBUD
NATURAL ASH THERMAL EXPANSION BELOW
ITS SOFTENING POINT.

STATUS DATE _____

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Abstract

We present some electrical conductivity studies of a Montana coal ash (as obtained from the power plant) with and without the additions of potassium seed and iron oxide.

We have been able to show over a limited temperature range, that the slag electrical conductivity of Rosebud coal can be described by a closed-form mathematical expression to an accuracy of about ten percent as a function of temperature and iron content. Complications are posed by the occurrence of phase transitions within the material which are accompanied by anomalous variations in the conductivity. Seeded slag data indicates that similar curve fitting may be possible for this case also--again over a limited temperature range. X-ray analysis confirms the nature of the high temperature phase transition at 1650 K as the development of an anorthite crystalline phase. Rosebud ash has been simulated from basic oxide ingredients and its conductivity is quite close to the real ash.

The conductivity of natural Rosebud ash was found to be only weakly dependent upon oxygen partial pressure. Graded samples of bottom ash with additions of K_2CO_3 were studied to determine the effect of potassium seed addition on the conductivity of Montana coal ash. Large additions of K_2CO_3 produce relatively small changes in the electrical conductivity at temperatures above 1650 K, but important and substantial changes occurred at temperatures below this. The conductivity of coal ash with high iron content is very sensitive to oxygen partial pressure as might be expected.

I. Introduction

In an MHD generator channel the conductivity of the slag layer adhering to the walls of the generator must be in a range appropriate for the slag to act as a good conductor for the generator output current and yet must be low enough to prevent shorting of the axially directed Hall current. The mathematical analysis of this balance in seemingly opposing demands upon the slag conductivity has already been carried out. The ultimate goal of this work is to provide electrical conductivity data for coal slag in a form that can be utilized by designers in modeling the output of the channel and by operators in anticipating the conductivity behavior of slag in any thermal and chemical environment which might occur when larger scale projects such as the CDIF become operational.

II. Experiment

The coal ash used in these experiments is from the Rosebud seam and was obtained from a

local power company.² The combustor temperature was approximately 1900 K³ and bottom and fly ash were supplied from the combustor and the base of the stack respectively. The samples were received in the form of powder, and each was homogenized and melted in alumina or platinum crucibles in air at 1700-1750 K for 1 to 36 hours and then air quenched.

The bottom and fly ash compositions were essentially the same except for slightly higher concentrations of sulphur, potassium, and calcium in the bottom ash as seen in an intensity analysis⁴ of the proton induced x-ray spectrum (PIX) of each sample. The natural Rosebud ash used in this research contains approximately 41.6% SiO_2 , 26.6% Al_2O_3 , 19.6% CaO , 6.2% MgO , 4.5% Fe_2O_3 , 0.5% K_2O , 0.5% Na_2O , and 0.3% SO_2 .

In the conductivity tests below 1800 K, samples were contained in alumina boats of 99.8 percent purity⁵ (interior dimensions 28x6x6 mm). The d-c conductivity was measured using the conventional 4-lead technique because of its sensitivity, reproducibility, and ability to separate polarization effects^{6,7} from the true conductivity. For most d-c measurements four platinum wire leads were suspended into an alumina boat which was then filled with pulverized slag. For measurements on seeded slags with high potassium concentrations we have switched to plate electrodes for the outer, current carrying leads. This change has minimized experimental problems arising from the polarization of seeded slags and apparent arcing at the current carrying electrodes. A-C conductivity measurements were made by a two-lead technique using an a-c resistance bridge. For a-c measurements it was necessary to use plate electrodes cut to fit the interior cross-section of the sample boats. This ensured a uniform current path between the two electrodes for accurate calculation of cell constants. A type-B thermocouple (platinum-6 percent rhodium vs platinum-30 percent rhodium), which was checked at the gold point, monitored the temperature.

The procedure was that samples were raised to the maximum temperature and data was taken starting at the highest temperature and moving downwards. During a run the alumina boats developed a web of cracks⁸ indicating that the slag had a lower thermal expansion than alumina.

In an effort to determine whether or not there were any time-dependent effects in the d-c conductivity measurements, a sample was held under a d-c current for 24 hours and voltages were measured across both the inside and outside pairs of leads. The voltage across the outside leads is the compliance voltage necessary to maintain constant current through the sample. The inner lead voltage is inversely proportional to the sample conductance. The data shown in

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Figure 1 is for a Rosebud ash sample with 20 percent K_2CO_3 equivalent of added potassium seed. This sample was chosen because it showed strongly time-dependent compliance voltage buildup. The compliance voltage varies from 2.5 to 135 volts while the conductance drifts slowly and not by an amount sufficient to affect the data. The results indicate that because the voltage and current leads are separated in four lead measurements, time-dependent effects at the outside leads do not affect the accuracy of the sample conductivity measurements.

Any systematic effort to study empirically the physical properties of slags as a function of individual slag components should include not only additive variations but subtractive ones as well. Much can be learned about the contribution of a particular slag component to the conductivity of the slag by adding the appropriate oxide to a natural ash and measuring conductivity. However, to compliment the information gained from such additive variations, it should be very useful to measure conductivity in synthetic oxide mixtures where the component has been reduced or eliminated. The first attempts toward this end were to produce a simulated version of Rosebud ash which exhibited conductivity behavior similar to the natural ash. In addition to the usual precautions of avoiding phase separations and ensuring homogeneity, one must be especially concerned with the need for complete reaction of the constituents in the liquid state. One cannot merely mix oxides and assume that one has coal slag. Nor, on the other hand, does one have to raise the temperature of the mix beyond that of the highest melting point constituent. If one major component melts first it can act as a flux and dissolve the other components. At this point, all remaining crystalline phases will have disappeared and the chemical interactions should proceed to equilibrium sufficiently rapidly, provided no significant separation of liquid phases occurs. Figure 2 shows a comparison between the electrical conductivities of Rosebud ash and a simulated ash of comparable elemental composition produced in our laboratory. The desirability of producing a simulated coal ash has often been expressed but to the authors' knowledge this is the first attempt to reproduce with a simulated slag the conductivity behavior of a natural slag. Except for the conductivity anomalies that generally occur in Rosebud ash at about 1615 K and 1390 K (presumably due to the mode of devitrification taking place), which were not evident in the simulated sample, the conductivity of the synthetic closely follows that of the natural to within experimental error. Having been able to prepare a simulated slag, it may now be possible to measure the effects of reducing the concentration of a component. We plan to measure the conductivity of simulated slags with reduced CaO content to determine the contribution of calcia to the electrical conductivity.

III. MHD Slag Data

Figure 3 displays the electrical conductivity data for Rosebud coal ash with graded additions of K_2CO_3 as seed. Below approximately 1400 K there is a strong dependence of the conductivity on potassium content. This dependence increases with decreasing temperature. The potassium concentration dependence of conductivity above 1400

K is weaker; particularly at temperatures above 1650 K. For example, a 60% increase in potassium content leads to conductivity increases of approximately 8 X, 100 X, and 1600 X at temperatures of 1723 K, 1423 K, and 1123 K respectively. Much practical importance is placed on the strong low-temperature dependence of conductivity on potassium content since channel wall temperatures may be in this temperature region.

Elucidation of the details of slag conductivity behavior as a function of seed content will require additional data points within the seed concentration range as well as more complete information regarding charge carriers and their mobilities, activation energies, electrochemical effects, and phase transitions.

It should be noted that the potassium concentrations given in Figure 3 (expressed as weight percent K_2O) are based on elemental analysis of the seeded slags after initial melting and quenching, but before the conductivity measurements were taken. Previously⁹ we used the percent seed added to the ash before initial melting. Preliminary analysis of samples after the experimental runs indicated that slags containing less than 15 percent K_2O lose only about 1 to 5 percent of their initial potassium (perhaps by evaporation) during the course of measurements. Analysis of the most heavily seeded sample after conductivity measurements indicated a much greater reduction of potassium content from the initial 30 percent K_2O . The physical appearance of the sample, with large gas pockets at the d-c current carrying electrodes, and the non-uniform distribution of the remaining potassium in the sample suggest that electrolysis of the slag was taking place during d-c measurements. Such phenomena were not observed in slags with less than 15% K_2O . Further experiments to investigate these phenomena are planned but from this preliminary evidence we surmise that they can be explained by the evolution of gaseous potassium at the cathode with some other gas (probably oxygen) evolved at the anode.

Phase transitions in slags may account for some of the anomalies in electrical conductivity behavior observed with various slags, but accurate phase diagrams have not yet been established for these complex materials. We have done x-ray powder diffraction studies⁹ on four samples of Rosebud bottom ash with the same elemental composition but different thermal histories. The powder patterns indicate the onset of crystallization of anorthite from liquid Rosebud slag at about 1378°C (1651 K). This temperature coincides with one of the regularly observed anomaly regions in the conductivity behavior of Rosebud ash as a function of temperature. The crystallization of anorthite at this temperature and the relative concentrations of CaO, Al_2O_3 , and SiO_2 (approximately 22-30-48 percent respectively) are consistent with the phase diagrams for the system Ca-Al-Si-O.¹⁰ Two regularly observed anomaly regions are discernible in Figure 3. The first is the anorthite/liquid slag anomaly at a reduced temperature of approximately 6.1 K⁻¹ and the other occurs at a reduced temperature of 7.2 K⁻¹.

It is well known that iron plays a key role as a charge carrier in slag. It is presumably

charge transfer between double and triple valence states that makes the iron contribute substantially to the conduction in slag. The ratio of Fe^{2+} to Fe^{3+} depends upon slag composition, temperature, and oxygen partial pressure above the slag. Because of the role of iron as a major contributor to the conductivity, it is important that the nature and empirical behavior of its contribution be studied. There has been some recent work on this subject.¹¹

Figure 4 shows the electrical conductivity data as a function of temperature for four iron enriched samples of Rosebud bottom ash. The data shown were taken in air at an oxygen partial pressure, P_{O_2} , of 0.17 atm., but the general pattern of conductivity behavior with respect to temperature and iron content is similar to that observed at other oxygen partial pressures. Increased dependence of conductivity on iron content is observed at the lower temperatures similarly to the data for potassium enriched ash. It is also interesting to note that the conductivity of a high-seed slag is quite similar to the conductivity of a high-iron slag.

Figure 5 shows oxygen pressure isobars of the temperature dependence of the d-c conductivity of an iron enriched Rosebud ash sample with an iron content of 9.4 weight percent as Fe_2O_3 . Several facts become readily apparent from this figure. The strong low temperature oxygen dependence of the conductivity is quite substantially reduced above the anorthite/liquid phase transformation range. This comparison is most dramatic in the composition shown here. Other iron percentages do not show so dramatically such an almost complete independence of the conductivity to oxygen pressure above the phase transition range.

Figure 6 illustrates the same data plotted as isotherms of conductivity vs. P_{O_2} on a log-log scale. The isothermal plots display distinct maxima in conductivity near the oxygen partial pressure of 10^{-5} atm. The magnitudes of the maxima and the general dependence of conductivity on oxygen partial pressure in high-iron slags are greater at the lower temperatures. During the course of further measurements and data analysis we plan to investigate whether the shape and position of the maxima can be related to the ratio $R = a_{\text{Fe}^{3+}}/a_{\text{Fe}^{2+}}$, where $a_{\text{Fe}^{3+}}$ and $a_{\text{Fe}^{2+}}$ are the activities of iron in the two oxidation states. R is related to total iron content, oxygen partial pressure, and temperature by the thermodynamics of the slag mixture.

The electrical conductivity of coal ash can be considered a function of the following parameters: T , P_{O_2} , X_{Fe} , X_{K} , X_{G} where X_{K} is the mole fraction of alkali metals, X_{Fe} is the mole fraction of iron, and X_{G} is the remaining glass matrix composition of the slag (i.e., $X_{\text{G}} = 1 - (X_{\text{Fe}} + X_{\text{K}})$). In a typical coal seam the relative concentrations of the components which make up the matrix G-- SiO_2 , Al_2O_3 , CaO , MgO --do not vary sufficiently to make as significant a difference in the conductivity as do the normal variations of X_{Fe} , X_{K} , and of P_{O_2} in the channel itself. Thus, these studies are limited at present to the first four independent variables above,

$$\sigma = \sigma(T, P_{\text{O}_2}, X_{\text{Fe}}, X_{\text{K}})$$

With four independent parameters strongly affecting the conductivity behavior a given slag it is not practical to try to duplicate all the possible combinations of channel slag layer conditions in the laboratory. However, by systematically varying the most significant parameters and measuring conductivity at selected values for these parameters within the range of their expected values it should be possible to describe the probable response of slag conductivity to various channel environments. This systematic data will be useful to systems designers in predicting slag conductivity.

In order to express our laboratory results in a form more readily and generally useful for practical application we are attempting to obtain computer fits of our data on iron enriched slags using those parameters which most strongly affect conductivity. We have attempted to describe our results on the conductivity of unseeded Rosebud ash in a single equation for each oxygen partial pressure with temperature and X_{Fe} as independent parameters. Because the presence of phase transitions can produce anomalies in the conductivity at certain temperatures, the range of temperature over which such a fit of the conductivity to a single equation may be possible is sometimes limited to a small temperature region. However, at certain slag compositions these anomalies may be small and a useful fit will be possible over a comparatively large temperature range.

The log of the conductivity is easier to fit as a function of $X_{\text{Fe}_2\text{O}_3}$ than as a function of P_{O_2} . Because of this, T and X_{Fe} were chosen as the independent variables in a preliminary computer fit of the data. The data used was taken with samples at constant P_{O_2} and with a constant $X_{\text{K}}/X_{\text{G}}$ ratio. Thus the form to be analyzed is $\sigma = \sigma(T, X_{\text{Fe}}; \text{constant } P_{\text{O}_2}, \text{constant } X_{\text{K}}/X_{\text{G}})$. X_{Fe} instead of $X_{\text{Fe}_2\text{O}_3}$ is arbitrarily used because the oxidation state probabilities for iron in these samples are not known.

The data for the electrical conductivity of Rosebud ash at an oxygen partial pressure of 10^{-3} atm. is fit over a temperature range of 1223-1523 K for iron content between 2.6 and 6.9 mole percent Fe or 9.6-23.7 weight percent Fe_2O_3 . The equation of the fit in Kelvin temperatures is

$$\ln \sigma = a + \frac{10^4 b}{T} + \left[c + \frac{10^4 d}{T} \right] X_{\text{Fe}} + \left[e + \frac{10^4 f}{T} \right] \ln X_{\text{Fe}}$$

where $a = -6.778$; $b = 2.902$; $c = 55.74$; $d = -11.10$; $e = -1.390$; $f = 0.9794$.

This expression represents conductivity terms linear in charge carrier density with a cross term with temperature dependence. The linear terms for σ appear, of course, as log terms in our expansion of log σ . These terms are

$\left[e + \frac{10^4 f}{T} \right] \ln X_{\text{Fe}}$. The remaining terms, linear in log σ and exponential for σ , are an attempt to expand the activation energy in terms of mole fraction and temperature analogously to the pre-factor term before the exponential. These are the terms $\left[c + \frac{10^4 d}{T} \right] X_{\text{Fe}}$. For a direct, graphical reading of b from the log σ vs $\frac{10^4}{T}$ plot, b is the slope divided by log e .

Figure 7 shows the excellent fit of this equation (solid lines) to the data points plotted. Above 1523 K, the conductivity increases anomalously because of the onset of the anorthite phase transition and cannot be accounted for in a simple manner. Below 1223 K, the available data is limited and not sufficient for fitting purposes. Within the same temperature range we have obtained corresponding sets of coefficients for equations of fit in the above form at oxygen partial pressures of 0.17 , 10^{-2} , 10^{-4} and 10^{-10} atm. The equations fit the experimental conductivity data to within ten percent.

In future work we will extend the experimental range of mole fraction Fe, and we will attempt to fit our data with oxygen partial pressure as an independent variable. Emphasis will then be put on obtaining similar results for seed content. Such equations of fit to experimental conductivity data should be very useful in modeling programs. Until now, models have used only crude approximations to ash conductivity. It is hoped that this work will change that.

IV. Conclusions

We have been able to show that the slag electrical conductivity of Rosebud coal can be described over a limited temperature range by a closed-form mathematical expression to an accuracy of about 10 percent as a function of temperature and iron content. We intend to extend this work to wider temperature ranges and to include oxygen partial pressure as an additional parameter in this equation. We hope eventually, of course, to include seed as a variable.

Over the past three years there have been persistent recommendations for the use of iron¹² or iron-containing spinel electrodes such as hercynite.^{13,14} Iron enhances considerably the electrical conductivity of slag with some percentage, perhaps only ten percent, of this contribution being electronic.^{15,16} In spite of this low percentage of electronic contribution, these electrode materials may be compatible with ionic transfer through the slag. It still remains a problem, however, that there is a large amount of bulk transport of iron from the anode¹⁷ which puts a limit on the total accumulated charge transfer from these materials to the slag. Special designs might serve to bypass this problem. Current flow in slags will produce a loss of iron at the anode and a deposition of SiO_2 on the anode from current neutralization of SiO_2^{2n} anion complexes¹⁶ where $n=1,2$. It was observed recently by Perkins¹⁸ that silica did indeed coat a platinum anode in d-c conductivity experiments. This reduced the effective conductivity of the electrode-slag system and severely inhibited conductivity in the reverse direction (i.e., reverse polarity) after the SiO_2 had been coated electrolytically on the anode. This has not been observed heretofore since bulk conductivity measurements are normally either a-c or low current density d-c measurements. Although the bulk conductivity is not a function of current density, electrode slag interactions require a sufficient build-up of reaction products to be observable and this naturally requires high current densities or long time measurements.

In addition, the Lockheed group¹⁸ also observed a substantial amount of intermittent

arcing at the anode surface presumably caused by current punching its way through the silica barrier being deposited.

These observations have substantial and important implications for the operation of an MHD electrode assembly both in the choice of electrode and in generator operating conditions. Since precious metal electrodes cannot contribute iron to the slag, as iron is removed from the slag at the anode surface a silica layer is formed producing the effects described above. If iron electrodes are used, iron is continually transferred to the slag at the anode and this maintains the high conductivity of the slag near the slag-anode interface. At the interface itself, there would appear to be a low concentration of iron which will be discussed in a forthcoming report by Kent Koester.¹⁹ It remains to be seen what other electrodes will encounter the same problems with silica deposition. In the choice of operating conditions, the occurrence of crystallization-induced anomalies in the conductivity behavior of Rosebud ash will be very important and will affect the stability of electrode operation. Fluctuations in bulk conductivity over a narrow temperature range can lead to disruption of the character of the current transfer mode at the electrode surface. This is true in the arc mode and large variations in diffuse mode performance have been correlated well with a function of slag layer resistance.¹⁹ Stable operation of an electrode will be dependent upon maintenance of the current transfer mode for which it was designed. Diffuse mode electrodes would not withstand the severe deterioration which would occur from the thermal hot spotting characteristic of the arcing mode. Studies of the iron and seed dependence of slag electrical conductivity together with the results of electrode tests should help determine proper channel operating conditions as well as suitable electrode materials in future MHD generators.

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Figures

Figure 1

Figure 2

Figure 3