**Development,
Characterization and
Evaluation of Materials for
Open-Cycle MHD**

**Quarterly Report for The
Period Ending December 1980**

J. Lambert Bates
D. D. Marchant

January 1982

Prepared for the U.S. Department of Energy
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1.0 SUMMARY

The development and fabrication is continuing on a graded composite electrode with a refractory $\text{HfO}_2\text{-RE}_x\text{O}_y$ surface and a $\text{HfO}_2\text{-RE}_x\text{O}_y\text{-In}_2\text{O}_3$ current lead-out for testing. The electrical conductivity of some oxide current leadouts were measured, and some general conclusions made regarding effects of composition. Also measured was the electrical conductivity of some yttrium chromites doped with Mg and Ca.

The characterization and evaluation of Pt-coated Cu anodes tested in AVCO's Mark VI generator using K_2SO_4 as seed was completed. Potential mechanisms for enhanced corrosion of Cu and Pt in sulfate seed are discussed.

The characterization of slag removed from MSU No. 1 heat exchanger core was completed. Possible reasons for enhanced slag blocking of RFG core are considered.

2.0 OBJECTIVES AND SCOPE

The objectives of this program are to develop, test, characterize, and evaluate materials for open-cycle, coal-fired MHD power generators as part of the U.S. DOE Power Generation Program. The specific immediate goals emphasize electrode and insulator materials, and include: 1) testing and evaluating the enhanced effects of alkali seed on materials in a dc electric field; 2) developing and testing improved electrodes and insulators with controlled microstructures, compositions, and properties; and 3) characterizing and evaluating materials relating to MHD power generator systems including channel, combustor, and air preheater.

The scope of this program encompasses the following areas:

- developing and fabricating electrodes, insulators, and other related materials with controlled electrical, chemical, and physical properties, including evaluating materials from laboratory tests in U.S. MHD test facilities
- reproducible laboratory testing of both ceramic and metal electrode materials and insulator materials in alkali seed/slag under dc electric current and voltages as functions of temperature and seed/slag composition
- characterizing and evaluating materials, i.e., the measurement and analysis of structural, chemical, and thermophysical properties of electrodes, insulators, slag, and other related materials before and after testing.

3.0 TECHNICAL PROGRESS

3.1 MATERIALS DEVELOPMENT

3.1.1 Graded Composite Electrode Concept

The development of electrodes and insulators for open-cycle, coal-fired MHD at Pacific Northwest Laboratory (PNL) emphasizes hot electrodes and insulators. The basic approach is to develop a refractory oxide-oxide current leadout composite which will operate at surface temperatures above ~ 1800 K and be attached to metal (Cu) base near 400 K.

The concept assumes there are advantages in operating the electrode surfaces at high temperatures. The high-temperature electrode surfaces are expected to: 1) reduce heat losses; 2) eliminate arcing from the plasma to the electrode surface; and 3) most importantly, eliminate or minimize slag deposition on the electrode-insulator surfaces, thereby, reducing the interactions due to electrochemical corrosion. To accomplish this objective the electrode must be: 1) thermodynamically stable with a high melting point, no phase changes over a wide temperature range and a low vapor pressure; 2) electrically conducting over a wide temperature range; 3) electrochemically stable to seed, insulators and slag; 4) thermomechanically stable; and 5) fabricated reproducibly.

The electrode composite design, Figure 1, consists of a refractory stable oxide for the electrode plasma surface. This high-temperature, electrically conducting oxide (which generally does not exhibit high electrical conductivity at low temperatures) is graded into a current leadout, which has a high electrical conductivity at low temperatures, but may not exhibit the refractory stability required at the plasma surface. The example in Figure 1 indicates three compositions; however, only two may be required and more than three could be beneficial. As illustrated, the result is a composite electrode with the necessary electrical conductivity over the large temperature gradient from the plasma surface to the copper base. At the same time, the electrode surface will be thermodynamically stable and corrosion resistant to the high temperatures of the MHD plasma.

FIGURE 1. Concept of Graded Composite Electrode with Refractory Oxide and High Conducting Current Leadout

Two critical areas must be addressed to successfully develop this electrode concept. 1) The refractory oxides and oxide current leadout compositions must be thermomechanically and electrochemically compatible under MHD channel operating conditions. 2) The oxide current leadout must be attached to the cold copper base to accommodate the thermomechanical stresses due to thermal expansion mismatch and, at the same time, conduct heat and electrical current.

A major effort at PNL is devoted to the development and testing of this MHD electrode concept. The present electrode development is centered around the $\text{HfO}_2\text{-RE}_x\text{O}_y\text{-In}_2\text{O}_3$ oxide current leadout composite electrode. Methods for fabricating the graded composite electrode as an integral bar have been developed for some compositions. Two refractory oxide compositions (A and B) and two oxide current leadout compositions (LLL and MMM) are now being fabricated for testing in some MHD facilities. The compositions include:

Although these compositions have been selected for testing, they may not represent the best composition or design. However, they can be reproducibly fabricated and attached to Cu with a metal mesh. It is necessary to demonstrate within the near term this graded composite electrode concept using the best material presently developed and available.

3.1.2 Testing

Testing of these electrode materials and this concept is planned for the WESTF facility and in the Stanford University MHD Channel. Discussions are now under way regarding preliminary designs and schedules. Electrodes for testing are now being fabricated. Techniques for attaching the electrodes to copper are being developed using some preliminary techniques developed at Westinghouse Research Center.⁽¹⁾ The attachment between the ceramic electrode and the copper utilizes a metal mesh (Ni or Cu) to accommodate the thermomechanical stresses.

3.2 PROPERTY EVALUATIONS

3.2.1 Electrical Conductivity Oxide Current Leadouts

An understanding of the electrical conductivity of the oxide current leadouts is very important in evaluating the performance of the refractory oxide-oxide current leadout electrode and in improving compositions and properties. The initial part of this evaluation was to measure the dc electrical conductivity of a number of potential oxide current leadout compositions in air as a function of temperature.

The electrical conductivity was determined in air using a four contact method, Figure 2. Samples were positioned in an Al_2O_3 muffle furnace with Pt and high purity Al_2O_3 hardware. The direct currents and voltages were measured in both directions at each measurement temperature and averaged to eliminate potential thermal emf effects. Measurements were generally made on both

FIGURE 2. Electrical Conductivity Four Probe Sample Holder

heating and cooling from room temperature to 1650 K after the oxides had been heat treated in air to 1850 K. Most measurements were made above 600 K.

The compositions of the oxide current leadouts are tabulated in Table 1. Duplicate samples of two compositions, B-4 and B-5 and LLL-40 and LLL-44, were measured to evaluate the reproducibility of the fabrication method.

Only two of the oxide current leadouts, MMM and LLL, have been characterized by X-ray diffraction and SEM-EDAX. The LLL from X-ray diffraction is a single phase, bcc structure with $a_0 = 10.20 \times 10^{-10} \text{ m}(\text{\AA})$. However, the SEM-EDX examination showed two phases, one high in In and Pr and low in Hf and one low in In and Pr while high in Hf. The MMM contained three phases, a major fcc fluorite phase with $a_0 = 5.17 \times 10^{-10} \text{ m}$ and high in In, a moderate bcc pyrochlore phase with $a_0 = 10.11 \times 10^{-10} \text{ m}$ and high in Tb and Hf, and a minor fcc phase with $a_0 = 5.29 \times 10^{-10} \text{ m}$ and a high In content. The characterization of these and other oxide current leadouts is continuing.

TABLE 1. Composition and Density of Oxide Current Leadouts

	Mole Percent						Density g/cm ³
	HfO ₂	In ₂ O ₃	Pr ₆ O ₁₁	Y ₂ O ₃	Yb ₂ O ₃	Tb ₄ O ₇	
BB	25	45	30	--	--	--	7.056
B-4	25	55	20	--	--	--	8.818
B-5	25	55	20	--	--	--	9.022
LLL-40	47	30	20	--	3	--	7.537
LLL-44	47	30	20	--	3	--	7.618
KKK	41	39	17	--	3	--	5.975
Z	25	55	--	20	--	--	7.557
Y	25	55	--	20	--	--	6.649
MMM	49	43	--	4	--	4	7.330
AA	25	45	--	--	30	--	7.207
EE	90	5	--	--	5	--	7.970
CC	46	51.5	--	--	2.5	--	8.998

The electrical conductivities for these various oxides are summarized in Figure 3. A wide variation in conductivities, up to six orders of magnitude, occur for the different compositions. The electrical conductivities can generally be represented by one, and often two, linear $\log_{10}\sigma$ versus K^{-1} relationship(s). The intersection of these two lines occurs between 800 and 900 K with the higher temperature conductivity having the larger activation energy. These data are summarized in Table 2.

The data fit these linear relationships with coefficients of determination better than 0.99 at the high temperatures and 0.95 at the low temperatures. The larger low temperature deviation may result because insufficient data were obtained below 600 K and some curvature occurred near the intercept of the two lines.

Some differences in conductivity were observed on heating and cooling for a few samples, i.e., LLL-40 and KKK. The values on heating exhibited a higher scatter and a 5 to 10% higher low temperature conductivity than on cooling.

FIGURE 3. Electrical Conductivity of Oxide Current Leadout

TABLE 2. Electrical Conductivity of Oxide Current Leadouts

Electrical Conductivity (S/M) $\text{Log}_{10}\sigma = A - B(K^{-1})$

	High Temperature				Low Temperature			
	A	B	eV	K	A	B	eV	K
BB	5.462	1.970×10^3	0.391	800-1434	4.1278	8.811×10^2	0.175	562-763
					3.005	2.498×10^3	0.050	299-562
B-4	5.160	1.904×10^3	0.378	895-1651 ^(a)	4.188	1.051×10^3	0.209	697-895
					2.8052	8.240×10^2	0.164	398-697
B-5	5.206	1.927×10^3	0.383	898-1649 ^(a)	--	---		(b)
LLL-40	5.273	2.840×10^3	0.564	997-1508	3.516	9.953×10^2	0.198	646-997 ^(a)
LLL-44	5.530	3.325×10^3	0.660	1151-1551	3.758	1.375×10^3	0.273	851-1052
KKK	6.496	3.120×10^3	0.620	950-1491	4.045	7.773×10^2	0.154	612-950 ^(a)
Z	7.289	7.616×10^3	1.51	940-1450	--	---		(b)
Y	7.289	5.798×10^3	1.15	940-1350	2.1517	8.410×10^3	0.167	720-940
MMM	5.275	2.038×10^3	0.405	829-1556	--	---		(b)
AA	7.207	9.034×10^3	1.79	900-1452	4.855	1.758×10^3	0.173	665-900
EE	4.908	5.060×10^3	1.00	697-1415	--	---		
CC	4.346	4.644×10^3	0.912	770-1538				

(a) Difference on heating and cooling.

(b) Data irregular at low temperatures, e.g. higher scatter at room temperature.

All measurements made after cooling confirm the cooling data, and are the data listed in Figure 1 and Table 2. The cause of these changes is not known.

The electrical conductivity data can be separated into two groups. One group has high conductivities, with high temperature activation energies of 0.38-0.66 eV. These compositions contain Pr_6O_{11} or Tb_4O_7 and In_2O_3 . These oxides contain little, if any, Yb_2O_3 or Y_2O_3 . The other group has lower electrical conductivities with high temperature activation energies between 1.00 and 1.79 eV. These oxides contain significant amounts of Y_2O_3 and/or Yb_2O_3 .

Assuming HfO_2 and In_2O_3 are necessary for high electrical conductivity, a number of general trends appear:

- Those oxides containing Pr_6O_{11} exhibit the highest electrical conductivity and the lowest high temperature activation energies, 0.38 to 0.60 eV. MMM exhibits similar electrical characteristics but does not contain Pr_6O_{11} ; however, it does contain Tb_4O_7 .
- Increases in In_2O_3 may increase σ when Yb_2O_3 and/or Y_2O_3 are not present. When Yb_2O_3 and/or Y_2O_3 are present, the electrical conductivity appears to decrease with increasing In_2O_3 .
- The presence of Yb_2O_3 and or Y_2O_3 appears to decrease the electrical conductivity.

The evaluation of the electrical conductivity for these oxide current leads is continuing. Studies will concentrate on the LLL and MMM compositions and efforts made to determine the degree of mixed ionic-electronic conduction.

3.2.2 Electrical Conductivity of Yttrium Chromites

The electrical conductivity of some selected yttrium chromites obtained from two different sources was measured. These included: 1) samples prepared by AT Research, Rolla, Missouri to evaluate a wide variety of compositions (C-101, C-102, C-103, C-110, C-112 and M-107); 2) samples prepared by TransTech, Gaithersburg, Maryland, for testing in a MHD facility (M-164A, M-165A and M-166A).

The preparation and properties of these chromites had been reported previously, including melting points^(2,3) thermal expansion,^(2,4) thermal

diffusivity^(2,5) and electrochemical corrosion.^(2,3,6) The yttrium chromites were doped with magnesium and calcium to increase the electrical conductivity.

The magnesium-doped yttrium chromites were generally multiphase with a second phase containing magnesium with small amounts of yttrium and chromium, Table 3. All of the structures, as determined by X-ray diffraction, were perovskite. The amount of second phase in the M-144A and M-145A chromites was substantially less but of the same compositions. The Ca-doped yttrium chromites were also two phase. The second phase of the 2% Ca containing chromite (M-146A) was a Cr-rich yttrium chromite.

The electrical conductivity was measured in air by using the technique described in the previous section of this report. Measurements were made on cooling after annealing in air above 1550 K. Measurements were made in air on heating on an as-fabricated chromite (C-101) before annealing to observe the large increase in conductivity as the chromite stoichiometry changes.

The compositions and electrical conductivities for the yttrium chromites are summarized in Table 4 and Figure 4. The $\log_{10}\sigma$ varies linearly with K^{-1} over the defined temperature ranges. Some deviation from these linear relationships may occur at lower temperatures since the near room temperature data are lower than that predicted by the equations. For $Y_{0.95}Mg_{0.05}CrO_3$ (C-112), a change in activation energy occurs near 800 K with a much lower activation energy and electrical conductivity at the higher temperatures.

The activation energies vary between 0.05 and 0.21 eV with the value for $YMg_{0.05}Cr_{0.95}O_3$ (C-101) of 0.207 eV. Those $YMg_xCr_{1-x}O_3$ compositions [with the exception of the laboratory prepared $YMg_{0.1}Cr_{0.9}O_3$ (C-102) and $YMg_{0.05}Cr_{0.95}O_3$ (C-101)] exhibit nearly the same activation energies, 0.075 to 0.082 eV. The reason for the very high energy of C-101 is not known.

The electrical conductivity in air of the fabricated yttrium chromites increases non-linearly as the temperature increases approaching that of the 1723 K air annealed samples, Figure 5. This increase is attributed to the changes in stoichiometry as the chromite prepared in 10^{-10} - 10^{-11} atmospheres of O_2 is heated in air.

TABLE 3. Composition of Yttrium Chromites

Sample	Chromite	Atom Percent Metal Elements						Comments
		Mg	Al	Si	Ca	Cr	Y	
M-164	$\text{YMg}_{0.02}\text{Cr}_{0.98}\text{O}_3$							Two phase with ~5% clusters
	overall	0	0.7	0.7	-	47.2	51.4	
	matrix	-	2.1	2.0		43.9	52.0	
		-	-	1.4		44.7	53.9	Cluster area
	2nd phase	90.7	-	0.9	-	4.1	4.3	
		94.2	-	1.0	-	4.5	0.3	Cluster area
M-165-A	$\text{YMg}_{0.05}\text{Cr}_{0.95}\text{O}_3$							Two phase
	Overall	5.6	-	0.7	-	42.5	51.2	
	Matrix	-	-	0.7	-	46.1	53.2	
	2nd Phase	91.9	-	0.8	-	4.0	3.3	
M-166-A	$\text{YCa}_{0.02}\text{Cr}_{0.98}\text{O}_3$							Some 10% as porous clusters - Second phase
	Overall	-	1.1	1.6	0.7	46.6	49.9	
	Matrix	-	0.7	1.0	1.4	47.3	49.6	only in clusters
	2nd Phase	-	0.5	1.0	0.7	58.2	39.6	

TABLE 4. Electrical Conductivity of Yttrium Chromites

Sample	Composition	Electrical Conductivity ^(a)		Activation Energy, eV	Temperature Range, K	Log ₁₀ ^σ at Room Temp, S/m
		Log ₁₀ ^σ = A - B(K ⁻¹)				
		A	B(10 ⁻²)			
M-107	YCrO ₃	1.882	4.121	0.082	918-1527	-0.185
C-101	YMg _{0.05} Cr _{0.95} O ₃	2.821	10.460	0.207	696-1667	(b)
C-102	YMg _{0.1} Cr _{0.9} O ₃	2.583	5.374	0.107	764-1549	0.125
C-103	YMg _{0.2} Cr _{0.8} O ₃	2.403	4.009	0.080	923-1567	(b)
C-110	Y(Mg _{0.05} Cr _{0.95} 0.75Al _{0.25} O ₃	2.569	5.694	0.113	820-1527	-0.053
C-112	Y _{0.95} Mg _{0.05} CrO ₃	2.188	2.684	0.053	813-1429	(b)
M-164A	YMg _{0.02} Cr _{0.98} O ₃	2.0967	3.839	0.076	852-1545	(b)
M-165A	YMg _{0.05} Cr _{0.95} O ₃	2.0506	3.794	0.075	835-1565	(b)
M-166A	Y _{0.98} Ca _{0.02} CrO ₃	2.6256	3.398	0.067	821-1562	(b)

(a) S/m

(b) Not Measured

FIGURE 4. Electrical Conductivity of Yttrium Chromite

The electrical conductivities of the $\text{YMg}_x\text{Cr}_{1-x}\text{O}_3$ are two to four times lower than that reported for similar compositions of the analogous $\text{LaMg}_x\text{Cr}_{1-x}\text{O}_3$,⁽¹⁾ Figure 4. The latter has an activation energy in this temperature range of ~ 0.07 eV and also exhibits a near room temperature conductivity of $\log_{10}\sigma \cong 0.9$. Although the conductivity of the yttrium chromite is lower, the conductivity is still more than enough for use as an MHD electrode. This lower conductivity is more than offset by the much superior electrochemical corrosion resistance in an MHD slag environment and the superior resistance to hydration.

The calcium-doped chromite (M-166) exhibited the highest electrical conductivity being very close to that for $\text{LaMg}_{0.05}\text{Cr}_{0.95}\text{O}_3$.

FIGURE 5. Electrical Conductivity of Y Mg_{0.05} Cr_{0.95} O₃ (C-101) in Air Showing Nonlinear Increase in Conductivity During Heating of As-fabricated Sample

The electrical conductivities of the yttrium chromites are very nearly the same as those for the lanthanum chromites. The electrical conductivity of the yttrium chromites, even with the wide variations in composition and dopants, exhibit only small variations in electrical conductivity (within a factor of 10 at any one temperature) and activation energy (0.05 to 0.2 eV). In contrast, the highly conducting $\text{Re}_x\text{O}_y\text{-HfO}_2\text{-In}_2\text{O}_3$, discussed earlier, exhibit a wide variation in activation energies and electrical conductivities as a function of composition.

3.3 CHARACTERIZATION AND EVALUATION OF MHD MATERIALS

A platinum-coated copper anode tested in AVCO's Mark VII MHD generator was evaluated.⁽⁷⁾ The anode was tested for 7 hours with K_2SO_4 seed and BOW coal slag. The purpose of the test was to evaluate both copper and platinum in coal slag and K_2SO_4 seed, specifically, the nature and extent of the slag/seed reactions with Cu and Pt.

3.3.1 Evaluation of Platinum-Coated Copper Anode--AVCO Mark VII

The electrode was a Pt-coated copper extrusion brazed to a copper anode base^(a) (Figure 6). A 6.35-mm (0.250-in.) wide and 0.254-mm (0.010-in.) deep slot was milled along with entire length of the electrode, removing the 0.254-mm (0.010-in.) thick Pt coating and exposing the underlying Cu. The continuous Pt coating covered the upstream rounded side and corner of the anode. The test caps were quarter sections cut from the extrusions.

FIGURE 6. Schematic Cross Section of Pt-coated Copper Electrode (AVCO)

(a) The Pt-Cu extrusions were supplied by Argonne National Laboratory.

In comparison to previous tests which used K_2CO_3 ,⁽⁴⁾ the seed was dry K_2SO_4 with injected coal ash from the BOW New Hampshire power plant (Table 5). The test was continuous for 7 hours at power with heat fluxes of $1.3 \times 10^6 \text{ J/m}^2$, Hall voltages near 1200 V/m, and a current density of $6 \times 10^3 \text{ J/m}^2$.

After the anodes were received from AVCO they were impregnated and cast in a fluid resin to retain the slag/metal interfaces and to fill all open pores. Representative cross sections were made nearly equidistant along the length of the anode for metallographic, SEM, and EDAX evaluations.

General Appearance

After the test, the anode exhibited extensive cavitation of the Cu where the Pt had been removed (Figure 7). This rounded cavity, up to 3.2 mm deep, was partially filled with molten slag and had undercut the Pt coating on both sides of the slot, but to a greater degree on the upstream plasma side.

Cu-Cu Braze

The Cu-Cu braze which attached the Pt-Cu extrusion to the Cu cooling base did not appear to be altered during the test. About 50% of the brazed area was voids extending across the entire thickness of the contact (Figure 7). The well bonded areas showed no apparent degradation during the test. It could not be determined if these areas affected the heat transfer and the temperature of the cap.

The thickness of the brazing alloy between the copper surfaces was $\sim 0.009 \text{ mm}$ (0.003 in.). The braze thickness probably was a contributing factor in the formation of the large number of voids.

TABLE 5. Chemical Composition of Ash (BOW N.H.)

<u>Element</u>	<u>wt%</u>	<u>Element</u>	<u>wt%</u>
SiO ₂	36.73	Na ₂ O	1.43
Al ₂ O ₃	22.47	TiO ₂	1.11
Fe ₂ O ₃	21.11	P ₂ O ₃	0.63
CaO	6.68	SO ₃	3.10
MgO	1.40	Undetermined	3.42
K ₂ O	1.91

FIGURE 7. Cross Sections of Pt-coated Cu Anode Showing Slag-filled Cavities in Copper

Platinum-Copper Bond

The bonding between the Pt and Cu of the extruded electrode cap was very good with no evidence of separation either before or during the test. The diffusion bond of the extrusion varied between 0.0058 and 0.0076 mm with an average thickness of 0.0067 mm (2.6×10^{-4} in.). The copper appeared to have diffused into the platinum (Figure 8), leaving a line of 1.7×10^{-3} mm (6.7×10^{-5} in.) pores near the original Pt-Cu interface. The demarcation between the reaction layer and the Pt was very sharp. The small pores did not appear to be a significant problem.

Examination of untested samples indicated a wide variation in the Pt thickness and areas of unbonded Pt-Cu. These areas occurred in locations where Pt was the thinnest and were 3 to 4 mm long. Debonding occurred along the line of pores of the Cu-Pt bond.

Platinum Coating

The platinum coating remained attached to the copper but exhibited some corrosion and/or corrosion/erosion by the slag/seed/plasma during the test.

FIGURE 8. Diffusion of Copper Into Platinum Coating Containing Slag, Seed, and Sulfur

Thickness of the coating after the test was determined from optical micrographs, with a measurement made about every 0.5 mm on three different cross sections. These measurements were compared with average values measured from untested reference samples (Figures 9 and 10). The reference measurements were made from the as-extruded bars, before cutting into quarters. The corner of the reference bar was the upstream edge of the anode (Figure 10). The average

FIGURE 9. Platinum Coating Thickness Variations Along Width of Cu-Pt. Reference dashed lines represent thickness from the plasma surface of test anode.

FIGURE 10. Platinum Coating Thickness Variations Along Length of Cu-Pt. The reference dashed line represents the thickness from the plasma surface of test anode.

values for the tested anodes for both the sides and plasma surface are shown as the dotted line. The Pt coating on the top surface was significantly thinner, varying from 0.166 to 0.171 mm (0.0064 to 0.0070 in.). The upper rounded corner of the anode retained a thicker Pt coating of approximately 0.34 mm (0.013 in.). The thickness on both sides of the milled slot was the same, although there was some distortion and thinning on the Pt which overhung the cavity in the Cu.

Because the thicknesses of the Pt were not measured before the test, and because there was a substantial variation both along the length of each cap and between caps from different extrusions, it is difficult to estimate the corrosion loss of the Pt. However, assuming that the Pt on the sides adjacent to the insulator that were not exposed directly to the plasma did not change during the test, an estimate can be made of the corrosion loss of the Pt on the plasma surface. This estimate can be made by: 1) Comparing the average value of the reference Pt width measurements with the corresponding side measurements of the tested anode. These ratios can then be compared to the variations of the measured Pt thickness at the plasma surface relative to the average thickness of the reference measurements. The difference in these ratios would then represent the corrosion loss. 2) Comparing the actual thicknesses of the Pt on the sides and on the plasma surface of the tested cap with a selected reference cap which had the same corresponding width measurements and comparing the relative differences in the Pt exposed to the plasma. Both procedures gave similar values indicating a loss of 0.01 ± 0.005 mm of Pt. This corresponds to a loss of 1.4 ± 0.7 $\mu\text{g}/\text{coulomb}$ which is similar to loss reported by others.^(4,8,9)

The top surface of the Pt was generally free of any reaction products and slag, except in some small surface depressions. These irregularly-shaped depressions contained thin siliceous deposits. This deposit was an oxide composed principally of Si (49 wt%), Cu (17 wt%), Fe (11 wt%), K (8 wt%), with a high sulfur content (15 wt%). Substantial Pt was also detected in this deposit; however, the very thin nature of this coating precluded an analytical determination of Pt and was not included in the weight percent values. The concentration of sulfur in the slag coating was 50 to 100 times higher than the sulphur content in the slag coating. This suggests that the presence of sulfur may have contributed significantly to the corrosion of the Pt coating of the anode.

The very thin nature of the slag in these depressions, and the presence of Cu from upstream corrosion, also suggests that the slag was molten when deposited. The absence of slag or similar reaction products on the smooth Pt surface could be attributed to continuous erosion and removal by the high velocity slag containing plasma. Such erosion could have continually exposed new surfaces, except in the surface depressions where flow velocity was reduced.

The formation of these depressions in the Pt surface and the coating with an apparent melted oxide slag could possibly have resulted from higher localized temperatures due to arc concentration. Such increases in temperature, and the presence of slag, sulfur, and seed, could have resulted in the higher corrosion rates compared to those using K_2CO_3 seed. The presence of Cu in this very thin coating suggests that at some time the slag had covered and reacted with the copper from upstream electrodes. The copper also could have contributed to the corrosion of the platinum. It is not known why the slag in these cavities does not contain Al_2O_3 or CaO .

Copper

The corrosion rate of the copper, which is estimated to vary between 120 and 180 $\mu g/coulomb$, is 10 to 20 times greater than corrosion in K_2CO_3 seed and slag and agrees with other reported rates for copper using K_2SO_4 seed/slag.^(8,9) This estimate assumes the current density to be the same for both the copper and the platinum.

Slag was found in the cavity formed in the area from which the Pt coating was removed (Figure 7). The thickness varied from nearly complete filling to a relatively thin layer covering the sides and bottom of the cavity. The composition and structure of the slag varied across its thickness (Figure 11). However, a number of common features were observed in the different cross sections examined, which provided some insight into the possible cause for corrosion of the Cu.

The slag in all but a few areas had separated from the copper at the Cu-slag interface leaving a clean Cu surface (Figure 11). In a few small areas, the slag coating had fractured above the Cu-slag interface, leaving small islands of slag still attached to the Cu. However, the detached slag surfaces matched the adjacent copper surfaces. The copper surface showed no evidence of reaction except for its irregular surface. No seed, sulfur or elements in the slag had diffused into the copper within resolution of the SEM (~ 1 nm).

In localized areas, the slag immediately adjacent to the Cu was composed of nearly pure CuO , Figures 12, 13 and Table 6.^(a) This layer, up to 0.1 mm

FIGURE 11. Microstructure of Slag (M-157-3) From Plasma Surface to Copper (See Figure 3)

FIGURE 12. Microstructure of Slag Attached to the Cu Showing Formations of CuO with CuSO_4 in the Pores

FIGURE 13. Microstructures of Slag (M-157-1) From Areas A and B (See Figure 12 and Table 11 for Compositions)

TABLE 6. Composition of Phases in Slag, at.%(a)

Phase	Si	Al	Mg	Ca	Fe	Cu	K	S	Probable Phases
C	0.6	-	-	-	-	98.7	0.2	0.5	CuO
D E+F	2.2	0.6	-	-	11.2	85.1	0.2	-	Two phase of E and F from eutectic
E	1.8	5.1	-	-	28.0	62.8	0.2	-	0.64CuO+0.18CuFe ₂ O ₄ or 0.82CuO•0.18Fe ₂ O ₃ spinel
F	1.3	-	-	-	3.7	94.4	0.2	0.3	0.97CuO•0.03Fe ₂ O ₃
G	32.7	23.4	-	1.4	8.8	23.7	9.2	-	Vitreous
H	35.4	24.9	0.9	0.3	9.1	14.4	14.2	0.4	Two phase (I+J)
I	20.7	30.0	2.7	-	22.6	16.1	6.9	-	2nd phase in H
J	43.7	24.7	0.7	0.3	5.5	7.3	17.2	0.2	Matrix of H
K	34.6	31.9	1.1	0.3	3.3	0.5	98.3	-	K ₂ O•Al ₂ O ₃ •2SiO ₂
L	36.1	12.3	3.4	20.0	10.7	9.3	5.9	-	Vitreous--near CaO•(Al,Fe) ₂ O ₃ •2SiO ₂
M	1.4	5.7	15.1	0.8	65.5	9.6	0.2	0.2	Crystallites MgO•2Fe ₂ O ₃
N (wt%)	35.9	27.4	2.4	6.5	11.3	0.4	11.0	0.2	Vitreous; original
(wt%)(b)	43.0	28	1.9	7.2	18.0	0.5	-	0.2	Slag + K
P	6.7	4.9	-	0.4	6.5	1.7	6.4	2.8	CuSO ₄

(a) These compositions determined by quantitative EDAX.

(b) K not included in percent determination.

thick, contained 0.6 at.% Si and 0.5 at.% S with a S/K ratio of ~ 2.5 , both in the attached and unattached oxide. This ratio was substantially higher than that of the deposited slag (< 0.02).

The CuO immediately adjacent to the Cu was porous and was free of sulfur and contained only very small quantities of K (Figure 12). However, the pores contained what appeared to be CuSO_4 with 7 wt% K, undoubtedly resulting from the reaction of copper with sulfur.

The role of the sulfur in the electrochemical corrosion of Cu appears complex and may involve the presence of potassium. A number of potential reactions could be involved. For example, it could be very similar to the patination process common in atmospheric and synthetic surface finishes of copper. The Cu reacts with oxygen to form Cu_2O , which subsequently reacts with sulfur (either as H_2SO_4 or SO_2) and H_2O to form either CuSO_4 or basic sulfate $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$.

Copper exposed to air containing SO_2 undergoes extensive reactions when high humidity ($> 70\%$) is present.⁽¹⁰⁾ The absorbed SO_2 can collect sufficient water for catalytic oxidation to sulfuric acid, which, in the presence of oxygen (the anode is highly oxidizing), reacts readily with either Cu or Cu_2O to form CuSO_4 ; i.e.:

The higher temperature possibly generated by ohmic heating or arcing, as discussed later, can revert CuSO_4 above 926 K to CuO, i.e.,

with decomposition complete at 1009 K. Such reactions can be enhanced in temperature gradient and electrical field. In addition, regeneration of SO_2 and/or SO_3 can result, which then can contribute to further H_2SO_4 formation.

(a) See Table 4 for composition of phase in Figures 12 and 13.

Other reactions may also be operative and the role of potassium, if any, is not known. Similar reactions involving CuCO_3 can occur, as would be the case with K_2CO_3 seed; however, reactivity is significantly less.

As discussed earlier, whether attached or separated, the slag immediately adjacent to the Cu was composed of nearly pure CuO. This CuO was concentrated in localized areas and was mixed with the slag which had a composition and structure substantially different from the injected ash and the slag nearer the plasma surface. These localized areas of the Cu-slag interface could have been at a higher temperature than anticipated during the test.

The slag immediately adjacent to this CuO layer (~ 0.1 to 0.25 mm thick) was a multiphase eutectic structure, suggesting locally higher temperature in excess of 1275 K. The matrix of this eutectic-type structure (Area G, Figures 12 and 13 and Table 6) was a copper-aluminum silicate with substantial amounts of Fe and K but free of S. Dispersed in this matrix were two phase, spherical particles (Area D) composed of nearly equal amounts of stringer-like phases. These phases appear to result from the solidification of a eutectic composition of CuO and CuFe_2O_4 ⁽¹⁰⁾ with an Fe (28 wt%)-Cu (63 wt%) oxide spinel or CuFe_2O_4 stringers (Area F) surrounded by CuO containing 3.7 wt% Fe (Area E). The grain boundaries often contained residual slag with substantial $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. These compositions are consistent with the CuO- CuFe_2O_4 eutectic⁽¹¹⁾ which melts between 1278 and 1343 K and a CuO- Cu_2O composition which melts near 1473 K. It thus appears that the CuO-slag mixture within 5×10^{-2} to 16×10^{-2} mm (2×10^{-3} to 6.1×10^{-3} in.) of the Cu surface had been molten, reaching temperatures near 1278 - 1373 K during the test. Such temperatures could have resulted in increased reaction rates between Cu, sulfur and oxygen. Because of the localized nature of these formations, these temperatures could have occurred during arcing across the Cu-slag interface and/or ohmic heating of the slag from current channeling.

At higher temperatures in the slag, a mottled two-phase structure was formed (Area H, ~ 0.2 to 0.6 mm above the copper). The darker matrix was a vitreous calcium-aluminum-potassium silicate (Area J) with some Fe, Cu and ~ 0.2 wt% S. The brighter second phase was also a complex mixture high in Fe and Cu. This structure also suggests possible melting.

As the distance from the Cu-slag interface increased, the overall slag composition became more like that of the injected ash and the concentration of Cu and Fe decreased. In contrast, the potassium tended to increase, forming a crystalline $K_2O \cdot Al_2O_3 \cdot 2SiO_2$ phase (Area K) that contained varied amounts of Ca, Mg, and Cu. This phase was generally surrounded by vitreous silicates of varied compositions. Additional phases such as bright crystals of $MgO \cdot 2Fe_2O_3$ (plus Al and Cu impurities) (Area M) and a vitreous matrix of $CaO \cdot (Al, Fe)_2O_3 \cdot 2SiO_2$ (Area L) were also present which undoubtedly formed in the deposited slag depending upon the temperature and the time at temperature.

The surface layer was vitreous (Area H) with a composition near that of the starting ash but substantially higher in K, ~12 wt%. The Si was slightly higher and the Fe and S slightly lower. Some Pt-metal particles were found in the vitreous slag surface, which suggests that some surfaces of the Pt had melted either from the surface or, more probably, from the Pt coating which extended over the edge of the copper cavity.

Conclusions

The characterization and evaluation of a platinum-coated copper anode tested in AVCO's Mark VII MHD generator by using K_2SO_4 seed and coal slag leads to the following conclusions for MHD cold wall anodes.

- The Cu-Cu braze was wide and not continuous. The development of improved brazing procedures should continue.
- The Pt-Cu bond of the extruded platinum-coated Cu cap was very good in most areas. There was, however, significant localized areas of Pt coating thinning and debonding observed in reference Pt-Cu caps. Deterioration of the bond during the test was not observed. The original coating varied significantly in thickness from 0.050 to 0.40 mm.
- The estimated corrosion rate ($\sim 1.4 \pm 0.7$ $\mu\text{g}/\text{coulomb}$) of the Pt in BOW slag containing K_2SO_4 seed appeared to be greater than for similar tests using K_2CO_3 as seed. The wide unknown variation in the original Pt coating thickness precluded accurate measurements.

- The corrosion rate of Cu (120 to 180 $\mu\text{g}/\text{coulomb}$) in BOW slag containing K_2SO_4 was 10 to 20 times greater than reported erosion rates using K_2CO_3 seed. Corrosion of Cu is attributed to oxidation of Cu and reaction with sulfur resulting from localized high temperatures due to arcing or ohmic heating of slag near the Cu-slag interface.
- Sulfur appears to have a specific role in the corrosion of Cu as evidenced by a high S concentration at the Cu-slag interface. The corrosion may be attributed to oxidation of the Cu; formation of H_2SO_4 from SO_2 and H_2O via catalyzed oxidation; and reaction of the Cu, Cu_2O and/or CuO with H_2SO_4 to form CuSO_4 . The latter may then decompose to form CuO and SO_3 in the localized high temperature areas formed by arcs and/or ohmic heating in the electrical field. CuO and CuSO_4 are the primary reaction products observed at the Cu-slag interface. Potassium does not appear to be involved in these reactions.
- Localized areas ~ 0.1 mm from the Cu-slag interface exceeded 1275 K, resulting in the formation of a molten eutectic of $\text{CuO-CuFe}_2\text{O}_4$.
- Slag held at high temperatures resulted in the formation of some relatively stable crystalline forms containing potassium, i.e., $\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ (feldspar).

3.3.2 Characterization of Slag From MSU Heat Exchanger RFG Core No. 1

During the operation of Montana State University's heat exchanger (core No. 2, runs 8 and 9), large amounts of slag (Table 7) were discharged through the ceramic core.⁽¹²⁾ Representative slag samples were provided to PNL for characterization and evaluation using optical ceramography and quantitative SEM-EDX. The objective was to provide additional insight into the performance of the RFG oxide core (Table 8) during these heat exchanger tests and into the role that slag might have in air preheater performance.

The slag samples were recovered from the slag trap below the downward gas flowing core during deslagging operation at temperatures that exceeded the nominal operating temperatures. The bottom core temperature was increased during deslagging from ~ 900 K to 1450 K for 12 hours (run No. 9). Most pres-

TABLE 7. Composition of Slags, wt%

	<u>Analysis #6^(a)</u>	<u>Overall Runs</u>
P ₂ O ₃	0.75	0.65
SiO ₂	53.5	53.25
MgO	9.14	9.85
Na ₂ O	0.51	0.40
K ₂ O	0.18	0.19
Al ₂ O ₃	17.3	18.53
CaO	18.66	14.54
Fe ₂ O ₃	4.06	3.68

(a) Taken from near top of bed.

TABLE 8. RFG Nominal Compositions, wt%

	<u>As Reported</u>	<u>SEM-EDX</u>
MgO	55-56%	63
Cr ₂ O ₃	20%	16
Al ₂ O ₃	8.0	6
FeO	11.0	11
SiO ₂	2.5	3
CaO	0.5	1
TiO ₂	1.5	1
Density:	3.26 g/cm ³	
Porosity:	14%	
Thermal Expansion Coefficient:	10.8 x 10 ⁻⁶ , K ⁻¹	

sure drop was reduced after the first 2 hours of deslagging when bottom core temperature was ~1200 K. There was little change in the top core temperature of ~1775 K during this deslagging period.

General Appearance

The slag samples varied in size, shape and surface characteristics. The slag particles were classified and separated into five groups according to their

general shape, color and surface characteristics. Representative samples from each group were selected for metallographic and SEM examination. The general characteristics of these five groups are summarized in Table 9. These samples were up to ~40 mm long and ~16 mm diameter. The maximum diameter was close to, but less than, the hole diameter of the core.

Microstructure Evaluation

Although there are substantial differences in the microstructure characteristics of the slag, there were a number of significant similarities in the microstructures and phases and only SS-4-C varied significantly, Figure 14 and Table 9.

All structures were multiphase with a vitreous slag matrix, modified in composition from the original slag. The amount of vitreous slag and crystalline phases varied as did the composition of the slag (see Table 10).

- $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (anorthite, mp 1826 K) is a major crystalline phase in the slags (a minor phase in SS-4-C).
- $\text{Mg}(\text{Al}, \text{Cr}, \text{Al})_2\text{O}_4$, a spinel solid solution, occurs as a minor crystalline phase, especially near the particle surfaces. The Al:(Cr,Fe) ratio is close to 2:1 with the Cr:Fe varying substantially, but generally from 1:2 to 2:1.
- $2\text{MgO} \cdot \text{SiO}_2$, (forsterite, mp 2165 K) occurs generally as a minor phase in most samples, but as a major phase in the sample that had apparently melted, SS-4-F.
- The surfaces of some particles, especially those of SS-4-C which contained residual RFG refractory, were coated with a siliceous layer (~0.25 mm thick) with phase compositions nearly the same as SS-4-A but with fine grain structure.
- The composition of the slag appeared to change with different microstructures. With a decrease in Si, there was also a decrease in Al and increases in Ca, Mg, and Fe.

TABLE 9. Characteristics and Structure of Slag - MSU Heat Exchange Core

Designation	General Appearance		Micro Structure Phases	
	Macro	Micro	Major	Minor
SS-4-A	-Oval in shape with smooth to irregular glassy surface -Black and dark brown	-Dense -Multiphase	- $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ -Slag	- $\text{MgO} \cdot \text{CaO} \cdot 2\text{SiO}_2$ $2\text{MgO} \cdot \text{SiO}_2$ - $\text{Mg}(\text{Al}, \text{Cr}, \text{Fe})_2\text{O}_4(\text{a})$
SS-4-B,E ^(b,d)	-Round with irregular glassy surface -Multicolor-brown, gray, tan	-Dense with some pores -Multiphase	- $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	- $\text{MgO} \cdot \text{CaO} \cdot 2\text{SiO}_2$ - $2\text{MgO} \cdot \text{SiO}_2$ - $\text{Mg}(\text{Al}, \text{Cr}, \text{Fe})_2\text{O}_4$
SS-4-C	-Elongated-pointed one end -Fibrous, rough surface -Dark brown matrix with light brown fibers	-Dense with round pores -Multiphase -Large variation across samples	-Residual RFG -Slag	- $\text{Mg}(\text{Al}, \text{Cr}, \text{Fe})_2\text{O}_4$ - $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$
SS-4-D ^(b)	-Elongated, porous with partially glassy surface -Fibrous-woody -Dark brown and black	-Very porous -Multiphase	- $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ -Slag	- $\text{Mg}(\text{Al}, \text{Cr}, \text{Fe})_2\text{O}_4(\text{a})$
SS-4-F	-Molten-like globules and stringers ^(c) -Glassy, rough surface -Light tan to dark brown	-Porous (irregular) -Multiphase	- $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ - $2\text{MgO} \cdot \text{SiO}_2$ -Slag	- $\text{Mg}(\text{Al}, \text{Cr}, \text{Fe})_2\text{O}_4(\text{a})$

(a) The Al:(Cr+Fe) ratio is ~2:1 with Cr:Fe ratio varying from 2:1 to 1.2.

(b) Very similar to SS-4-C but open fibrous as if phase between fibers had been removed.

(c) The particles showed evidence of melting, flow and solidification.

(d) SS-4-E was a large, broken sample with the same general features as the SS-4-B group samples.

FIGURE 14. Representative Microstructures of SS-4-A Slag

TABLE 10. Composition of Slag Phases

Phase	Mg	Al	Si	Ca	Cr	Fe
A - Slag						
1-L	6.7	31.2	37.9	19.8	0.1	2.7
1-T	16.5	18.8	40.4	18.3	0.0	3.8
2	9.9	24.6	38.7	22.0	0.1	2.9
3	17.8	15.8	36.9	22.4	0.0	5.2
B - $\text{Mg}(\text{Al,Cu,Fe})_2\text{O}_4$ (Spinel)						
1-L	32.8	54.8	1.6	0.2	5.6	4.6
1-T	33.3	48.1	2.6	1.0	4.4	10.4
2	35.8	42.7	1.0	0.2	12.6	7.1
C - $2\text{MgO}\cdot\text{SiO}_2$ (Forsterite)						
1-L	-	-	-	-	-	-
1-T	66.5	0.0	31.9	0.5	0.0	0.8
2	-	-	-	-	-	-
4	68.5	0.0	30.2	0.4	0.0	0.7
D - $\text{MgO}\cdot\text{CaO}\cdot 2\text{SiO}_2$ (Diopside)						
1-L	-	-	-	-	-	-
1-T	20.6	11.0	40.5	22.1	0.1	4.7
2	-	-	-	-	-	-
4	-	-	-	-	-	-
E - $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ (Anorthite)						
1-L	0.0	40.0	42.4	16.9	0.1	0.5
1-T	0.0	38.4	43.4	16.6	0.0	1.1
2	0.0	40.8	40.6	17.8	0.0	0.6
4	0.0	39.0	40.9	18.5	0.0	1.4
A, C and E	Major Phases					
B	Crystalline Second Phase					
D	Minor Second Phase					
1,2,3,4	Samples					
T	Transverse Section					
L	Longitudinal Section					

- Little or no Cr was found in any phase, including the slag, except in the $\text{Mg}(\text{Al},\text{Cr},\text{Fe})_2\text{O}_4$ spinel and the residual RFG. Assuming that the slag temperatures on removal from the core for SS-4-F>SS-4-D>SS-4-A, the phase formations are consistent, including the formation of $2\text{MgO}\cdot\text{SiO}_2$.

Conclusions and Discussion

The results of this characterization and evaluation can provide some insight into the performance of the RFG refractory and the MSU heat exchanger. The following conclusions, although based on this indirect evidence, are suggested.

- The solids that were retained in the holes of the core during operation and subsequently released on deslagging were not the original slag but were reaction products between the slag and RFG refractory. The formation of crystalline phases [i.e., $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$, $2\text{MgO}\cdot\text{SiO}_2$ and $\text{Mg}(\text{Al},\text{Cr},\text{Fe})_2\text{O}_4$] and alteration of the vitreous phase composition resulted in an increased viscosity of the slag and required higher temperatures for removal.
- Removal of the material blocking the holes of the core probably resulted when increased temperatures during reslagging heated the material surfaces, which became partially or entirely liquid, allowing particle flow and removal.
- The compositions of siliceous materials, in particular the crystalline phases, are the same as those found on the surface of the RFG during the characterization of the MSU heat exchanges, Core No. 1, reinforcing the conclusion that these materials are RFG-slag reaction products.
- Larger RFG particles, which had partially reacted with the slag may become the nuclei for slag the formation of the particles, as evidenced by the presence of some residue RFG in the slag.
- The shape, color, and surface character give some indication of the source of the particles. 1) The regular oval-shaped, fibrous and

woody material (SS-4-C) contains large amounts of residual RFG, which had partially reacted with the slag. 2) The very dense, rounded, glassy particles are mostly vitreous, modified slag with $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ being the major crystalline phases. 3) The obviously molten particles, SS-4-F, are highly crystalline, with major quantities of $2\text{MgO} \cdot \text{SiO}_2$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ in addition to the slag. These different phases probably represent three distinctly different temperatures during testing, with the number-1 type the highest and number 3 the lowest temperatures.

It is concluded that if the RFG had not reacted with slag and changed its properties, the extensive blocking of holes within the core may not have occurred.

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