Development of Materials for Open Cycle MHD

**Quarterly Report for the Period
Ending March 1981**

**J. L. Bates
D. D. Marchant**

January 1982

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

The work centers around the development and fabrication of the $\text{HfO}_2\text{-RE}_x\text{O}_y$ electrodes and $\text{HfO}_2\text{-RE}_x\text{O}_y\text{-In}_2\text{O}_3$ current leadouts for testing in MHD facilities. The electrical conductivity of some potential $\text{HfO}_2\text{-RE}_x\text{O}_y$ refractory electrodes has been measured and preliminary results analyzed in relationship to structure and composition.

Six potential air preheater materials, tested in the Montana State University heat exchanger, were characterized and evaluated. The potential mechanisms for corrosion/erosion are discussed in this report.

Electrochemical corrosion of platinum in molten coal slag was also measured. Possible corrosion mechanisms are discussed.

— 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 emphasizing electrode and insulator materials 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 such as channel, combustor, and air preheater.

The scope of this program encompasses the following areas:

- 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
- developing and fabricating electrodes, insulators, and other related materials with controlled electrical, chemical, and physical properties, including evaluation of material tested in U.S. MHD facilities
- 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

The development of ceramic hot electrodes for coal-fired MHD channels has been directed toward the attachment of the ceramic electrode to the cold metal base. This attachment must: 1) conduct sufficient heat to permit a reasonable thickness of ceramic electrode at the high heat fluxes; 2) conduct the electrical current up to 1 to 2 amps/cm²; 3) be resistant to attack by the potentially corrosive potassium seed (either directly or as a hydrated form); and 4) accommodate any differences in the thermal expansions of the copper ($\sim 16 \times 10^{-6}/K$) and ceramic electrode ($\sim 9 \times 10^{-6}/K$).

The approach now being taken is to utilize a compressed metal mesh of either Cu or Ni as a compliant layer between the refractory oxide electrode and the oxide current-leadout.⁽¹⁾ This technique has been used previously with moderate success.⁽²⁾ The thermal conductivity of the Ni mesh at various densities has been measured previously,⁽³⁾ and the electrical conductivity is substantially greater than the oxide current leadout. The thermal conductivity of the Cu mesh is now being measured.

The selection of the type of mesh, (thickness, density, and metal) depends upon the heat flux of the MHD facility and the ability to bond the mesh to the oxide. Westinghouse Electric Corporation developed some initial procedures for some of the ceramic electrode materials,⁽²⁾ and these methods are now being used as the basis for further development. The major effort is to develop a bonding procedure to attach the mesh(s) to the $HfO_2-RE_xO_y-In_2O_3$ oxide current leadout materials. The immediate need is to fabricate electrodes with this attachment for testing in the Westinghouse MHD test facility (WESTF) and in the Stanford MHD channel.

3.2 ELECTROCHEMICAL TESTING - PLATINUM

The anodic and cathodic interactions of platinum with a representative Illinois No. 6 coal slag was evaluated using laboratory electrochemical testing methods.⁽⁴⁻⁶⁾ Platinum corrosion in a dc electrical field is important

because Pt is used as a coating for copper anodes in cold wall, MHD channels and as a voltage probe in our electrochemical tests of ceramic hot electrodes. Previous preliminary evaluations in molten K_2CO_3 and K_2SO_4 seed⁽⁷⁾ suggested a substantially higher corrosion rate of Pt in the sulfate seed with a different mechanism for the two salts. The purpose of these tests was to determine the possible electrochemical corrosion mechanisms and to estimate the corrosion rate in a molten coal slag containing alkali metal seed.

The test electrodes were rectangular platinum sheets 0.52 mm thick and 5.27 mm wide. Two parallel sheets 10 mm apart were immersed 8 mm into the molten coal slag electrolyte. The test was conducted in air at 1723 K with current densities of 0.7 and 0.6 A/cm² for the anode and cathode, respectively. The test ran for 25.16 hours with a total of 24,462 coulombs on the anode.

The synthetic molten coal slag^(a) was prepared by heating the oxide constituents at 1823 K to homogenize the melt. The slag was then cooled to the test temperature and the electrodes were inserted to the predetermined depth. A constant direct current was maintained using a galvanostat. Instabilities in the current transport were measured by monitoring the changes in the electric potential required to maintain a constant current. The present test was terminated when electrical fluctuations of 3 to 11 volts were observed. The fluctuations during the initial parts of the test were ± 1 volt.

The slag was cooled with the electrodes still immersed in the slag. The slag and electrodes were cut and prepared for optical and scanning electron microscopy. The compositions of the electrode-slag reaction areas were determined with energy dispersion X-ray analysis in conjunction with the SEM. The SEM-EDX was quantitative to elements with atomic number of 11 (Na) or greater with a sensitivity of ± 0.5 wt%. Oxygen was assumed to be the difference between the measured metal weight percent and total weight of sample. The

(a) The synthetic Illinois No. 6 slag contained 57.2% SiO_2 , 15.7% Al_2O_3 , 7.9% CaO , 11.5% Fe_2O_3 , 3.5% MgO , 1.0% TiO_2 , 0.8% Na_2O , 1.9% K_2O , and 0.6% P_2O_5 (in mol%).

probe can make a distinction between oxide and metal, but does not allow a quantitative evaluation of the oxidation state of the complex metal oxide slag.

The microstructures of the platinum anodes and slag adjacent to the anode varied from that of the cathode, Figures 1 and 2. The composition of the phases are tabulated in Table 1.

Cathode: The Pt cathode had extensively reacted with the iron component of the coal slag. Metallic iron was deposited as a coating on the Pt cathode surface and was present as small iron particles in the slag adjacent to the cathode, Figures 1 a,c. The iron had also reacted with the platinum surface forming a platinum-iron alloy solid solution. Phase equilibrium data⁽⁸⁾ show complete solid solution between iron and platinum over a wide composition range.

The composition of the alloy was approximately 60 at.% Pt-40 at.% Fe. The alloying on the cathode was greatest on the surface facing the anode causing the cathode to swell and bow, Figure 1a.

The slag adjacent to the cathode surface had also changed. The slag surface contained nearly spherical particles of iron of different sizes. For example, Figure 1c shows a large iron particle which appears to have formed and subsequently separated from the cathode surface. The slag adjacent to the cathode is partially depleted in iron (from 10 to 3 wt%), Table 1, and overall enriched in magnesium and potassium. The second phase with a composition near $K_2O \cdot Al_2O_3 \cdot SiO_2$ precipitated in the vitreous slag.

Assuming all of the current transfer to the cathode through the slag was due to the transport of iron and that the ferric iron ions were reduced to free metal at the cathode surface, 4.45 grams of metallic iron would have been produced during the test. Estimates based on metallographic examinations of the total Fe in the slag on the cathode surface and that as free iron alloyed with the platinum yield only 0.02 grams, or ~0.5% of the calculated value. This large difference is attributed to: 1) the possibly high electronic conductivity of the slag; 2) competing reactions in conduction near the slag surface by other ions such as K^+ ; and/or 3) the partial reduction of the Fe^{3+} ions to Fe^{2+} ions instead of free iron and the diffusion of FeO into the slag away from the reaction zone.

FIGURE 1. Structures of Platinum Cathode After Testing in Synthetic Illinois No. 6 Coal Slag

The reduction of iron from the slag adjacent to the cathode and its alloying interaction with the platinum may have some deleterious effects on the use of platinum as electrodes in MHD channels. 1) Alloying with Fe reduces the melting point of the Pt. 2) The platinum oxidation resistance is reduced. 3) Iron, which alloys with the platinum, decreases the corrosion resistance to siliceous slag. 4) The depletion of iron in the slag decreases the electrical conductivity of the slag.

FIGURE 2. Structures of Platinum Anode After Testing in Synthetic Illinois No. 6 Coal Slag

The voltage instabilities near the end of the test may be partially due to increased electrical resistivity of the slag and enhanced polarization.

On the opposite side of the cathode, the platinum experienced some grain boundary attack. The cause of this is not known.

TABLE 1. Composition of Phase in Pt-Slag Electronic Tests

Phase Features ^(a)	Atom Percent							
	Mg	Al	Si	K	Ca	Ti	Fe	Pt
<u>CATHODE</u>								
Cathode (Pt) (Overall)	3	-	2	-	-	-	6	88
Slag (Slag)	-	32	39	14	5	0.6	10	0.1
Slag Reaction Zone (Fe Depleted Slag)								
-Overall	1	32	35	22	6	0.6	3.1	0.1
-Vitreous Matrix	6	23	39	6	15	15	10	0.2
-Precipitate (K, Al Silicate)	-	35	34	29	0.7	0.1	0.5	0
Cathode Reaction Zone								
-Surface Phase	-	1	2	0.4	0.2	-	90	7
-0.26 mm from Surface (Pt-Fe Alloy)	3	-	2	-	0.3	-	39	55
-0.45 mm from Surface	-	-	2	-	0.7	0.3	39	58
-Metal in Slag	-	1	1	-	-	-	98	0.3
Deposit in Grain Boundary Opposite Anode	4	12	6	13	2	-	63	0.2
<u>ANODE</u>								
Anode (Pt)	-	-	2	0.8	0.3	0.6	0.6	96
Slag	1	32	40	11	5	0.6	11	0
Slag Reaction Zone								
-Matrix (Fe Depleted Slag)	-	29	47	13	5	0.5	6	0.1
-Precipitate ($\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$)	-	51	0.2	-	-	0.8	48	0.1
-Dendrites (Fe Rich Phase)	4	35	33	7	2	0.3	18	1
Precipitates near Porous Pt (Al_2O_3 s.s.)	-	91	-	0.4	0.1	-	8	0.1
Reaction Interface (Fe_2O_3 s.s.)	1	1	2	0.3	-	-	95	1

(a) See Figures 1 and 2.

Anode: The anode reacted with the slag with a loss rate of 3.64×10^{-7} $\mu\text{g}/\text{coulomb}$. The corrosion loss was uniform along the top surface with enhanced corrosion near the bottom tip of the platinum anode sheet, Figure 2. [Note the significant difference between the final thickness of the cathode and the anode.] The platinum at the anode tip became porous with a buildup of iron-rich corrosion products in the slag, Figure 2c. Surrounding the anode, the slag had undergone significant alteration, Figure 2b.

The platinum anode did not alloy with the slag constituents, even at the bottom tip. However, imbedded $\sim 10 \mu\text{m}$ below the platinum surface were iron oxide particles, approximately $50 \mu\text{m}$ in diameter. The platinum immediately surrounding these particles or in other areas of the anode did not contain iron or other slag constituents.

The slag adjacent to the anode contained aluminum and iron oxide solid solution phases, Figure 2a,c. These phases appear to be the result of the highly oxidizing conditions at the anode which can also result in the formation of oxygen gas bubbles. The reported phase equilibria⁽⁹⁾ for Fe_2O_3 (hematite) and Al_2O_3 (corundum) show a solid solution $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ spinel in oxidizing atmosphere (1 to 2 at.% O_2) between 1593 and 1753 K. Below 1593 K, the phase separates into hematite and corundum solid solutions.

3.3 ELECTRICAL CONDUCTIVITY RE_xO_y STABILIZED HfO_2

The rare-earth stabilized hafnium oxides have previously demonstrated electrochemical stability in the potassium seed and coal slag environments.⁽¹⁰⁾ These refractory oxides are also a critical part of the hot electrode, composite graded ceramic MHD electrode.⁽¹⁾ The selection of compositions for electrical conductivity studies was based upon electrochemical stability, fabricability, and rare earth oxide additives which were thought to provide the highest electrical conductivities, Table 2. Since there are only limited phase data for the $\text{HfO}_2\text{-RE}_x\text{O}_y$ systems, potential compositions and structures were often based on the better known and analogous $\text{ZrO}_2\text{-RE}_x\text{O}_y$ systems.

TABLE 2. Composition and Density of $\text{HfO}_2\text{-RE}_x\text{O}_y$ Electrode Materials

Electrode		Composition - Mole Percent						Density, g/cm ³
		HfO_2	$\text{Er}_{2/3}\text{O}_3$	$\text{Pr}_{6/11}\text{O}_{11}$	$\text{Tb}_{4/7}\text{O}_7$	$\text{Y}_{2/3}\text{O}_3$	$\text{Yb}_{2/3}\text{O}_3$	CeO_2
O	a,b	91.4		8.6				8.44
Q	a,b	80		20				8.94
A-17	a,b	66		29			5	8.80
A-273-1	c	66		29			5	8.34
A-273-2	c	66		29			5	8.39
F	a,b	77.6		17.5			2.9	8.54
V	a,b	89.5		5.3			9.2	9.14
120-3	c	80	10	10				8.59
C-4	a,b	80	10		10			8.36
100-2	c	90			10			7.02
101-2	c	85		5	5		5	6.73
P	a,b	94.5			5.5			8.05
P-202	a,b	94.5			5.5			8.37
B-1	a,b	88			6	6		8.97
B-272-1	c	88			6	6		8.13
R	a,b	80				20		6.24
I	a,b	82				8		7.93
B	a	89					11	9.43
D	a,b	80					20	7.43

(a) Sintered in 2.67×10^{-2} Pa vacuum at 2225 to 2275 K for 4 to 5 hours.

(b) Annealed in air between 1375 and 1475 K for 8 hours.

(c) Sintered in air at 1875 to 1925 K for 20 hours.

A four contact technique⁽¹⁾ was used to measure the electrical conductivity in air from 544 to 1705 K. The oxide samples were prepared from coprecipitated powders which had been calcined at 1275 K and ball milled to break agglomerates. The powders were uniaxially pressed followed by isostatically pressing. The samples were sintered in two ways: 1) in 2.67×10^{-2} Pa (2×10^{-4} torr) vacuum at 2225 to 2275 K for 4 to 5 hours followed by an air anneal at 1475 K for 8 hours, or 2) in air at 1825 K for 20 hours. The sintered

densities are tabulated in Table 2. The microstructures were similar for all compositions, with small, 1 to 2 μm closed pores. Sample D had larger, irregular-shaped pores with a second phase present. Samples Q and O contained microcracks after measurements were completed. All others were single phase.

The electrical conductivities for most compositions could be represented by one or two straight ($\log_{10}\sigma$ versus K^{-1}) lines, one for the high temperature and one for the low temperature data, Figure 3, Table 3. The break in the curves generally occurred below 1000 K. Some data exhibited a change in slope at lower temperatures, but it was either nonreproducible or could not be resolved into two linear relationships. The data for D, R, P, 100-2 did not exhibit breaks in the $\log_{10}\sigma$ versus K^{-1} curves even though measurements were made to temperatures as low as 625 K. However, these oxides were approaching the lower conductivity values, which can be measured using this four-contact technique.

Two oxides, Q and V, exhibited a reproducible decrease in electrical conductivity above ~1620 K. The cause of this decrease is not known.

The lowest conductivity values for O and Q could possibly be attributed to sample cracking during the electrical conductivity measurements.

The activation energies for the high temperature and low temperature conductivities vary between 0.85 and 1.38 eV and 0.24 and 0.98 eV, respectively. Some compositional factors appear to influence the high temperature activation energy. Generally, the results suggest that an increase in HfO_2 content and a decrease in Pr_6O_{11} content results in an increase in the activation energy. Those samples, A-17, A-273-1, and A-272-2, that have high Pr_6O_{11} concentrations exhibited higher high temperature activation energies than that expected simply by reducing the HfO_2 concentration. There appears to be a slight increase in activation energy with decreasing Yb_2O_3 . No patterns could be resolved for the effects of Tb_4O_7 , Er_2O_3 or Y_2O_3 . Those high HfO_2 oxides without Pr_6O_{11} (B, P-202, P and I) exhibited the lowest activation energies (0.83-0.86 eV).

FIGURE 3. Electrical Conductivities of $\text{HfO}_2\text{-RE}_x\text{O}_y$ Electrode Materials

TABLE 3. Electrical Conductivity of $\text{HfO}_2\text{-RE}_x\text{O}_y$ Electrode Materials

Electrode Material	High Temperatures					Low Temperatures			
	$\text{Log}_{10}\sigma = A-B/K, \text{ S/m}$		Energy, Temperatures,			$\text{Log}_{10}\sigma = A-B/K, \text{ S/m}$		Energy, Temperatures,	
	A	B(10 ³)	eV	K		A	B(10 ³)	eV	K
O	2.211	4.954	0.98	1019-1411		-1.438	1.205	0.24	800-1019
Q	3.184	6.073	1.21	1316-1620	(a)	-	-	-	-
A-17	5.300	6.912	1.37	1080-1451		3.550	4.918	0.98	806-1080
A-273-1	4.896	6.497	1.29	986-1532		1.587	3.220	0.64	813-986
A-273-2	4.644	6.087	1.21	1110-1493		2.775	3.973	0.79	834-1110
F	4.472	5.745	1.14	1007-1514		3.235	4.415	0.88	816-1007
V	4.625	5.266	1.05	863-1680	(a)	-	-	-	-
120-3	5.001	6.146	1.22	929-1665		-	-	-	(b)
C-4	3.822	5.011	1.00	1023-1539		0.160	1.458	0.29	544-911 (c)
100-2	4.631	5.460	1.08	753-1657		-	-	-	(d)
101-2	4.493	5.210	1.03	860-1664		-	-	-	-
P	3.557	4.328	0.86	619-1609		-	-	-	-
P-202	4.084	4.303	0.85	1149-1520		-	-	-	-
B-1	5.454	6.946	1.38	1000-1491		2.938	4.380	0.87	777-1000
B-273-1	4.625	5.891	1.17	1020-1553		3.305	4.191	0.83	862-1020
R	4.106	5.562	1.10	909-1705		-	-	-	-
I	4.048	4.345	0.86	807-1467		-	-	-	(b)
B	4.230	4.156	0.83	910-1515		0.284	1.996	0.40	794-910
D	4.789	6.585	1.31	808-1499	(e)	-	-	-	-

(a) Reproducible decrease in $\text{log}_{10}\sigma$ above 1620 K.

(b) A low temperature $\text{log}_{10}\sigma$ which could not be analyzed.

(c) Decreasing temperature data only. Some variations on heating.

(d) Indications of change in slope at lower temperatures.

(e) Some irregularities on heating.

Note: Some data are not illustrated on Figure 3.

A comparison of the magnitudes of the conductivities at 1000 K suggests that the conductivity increases with increasing HfO_2 content above 80 mol%, increases with increasing Yb_2O_3 content, and decreases slightly with increasing Y_2O_5 and Pr_6O_{11} content. The effects of Tb_4O_7 and Er_2O_3 were inconclusive.

The electrical conductivities of 2.8 and 0.43 S/m and activation energies of 1.12 and 1.4 eV for these rare-earth stabilized HfO_2 oxides are very near to the reported values for $0.08\text{Y}_2\text{O}_3 \cdot 0.92\text{HfO}_2$ and $0.20\text{Y}_2\text{O}_3 \cdot 0.80\text{HfO}_2$ at 1275 K, respectively.⁽¹¹⁾ The sample of $0.2\text{Y}_2\text{O}_3 \cdot 0.8\text{HfO}_2$ has values of 0.6 S/m at 1275 K and 1.1 eV. The reported values at 1275 K for $0.125 \text{ CaO} \cdot 0.875 \text{ ZrO}_2$ are 0.5 S/m and 1.83 eV.⁽¹²⁾

Compositions similar to $0.29\text{PrO}_{1.83} \cdot 0.05 \text{ Yb}_2\text{O}_3 \cdot 0.66\text{HfO}_2$ (A-273-1) and $0.06\text{Tb}_4\text{O}_7 \cdot 0.06 \cdot \text{Y}_2\text{O}_3 \cdot 0.88\text{HfO}_2$ (B-272-1) will be tested in MHD facilities. The phases present in these two compositions have been studied in detail using X-ray diffraction and SEM-EDX, Table 4. These results indicate that the A-273-1 is mainly a pyrochlore fcc structure (possibly $\text{Pr}_2\text{Hf}_2\text{O}_7$) with an fcc fluorite second phase. The unit cell values of 1.032 nm (10.32Å) are consistent with the 1.061 to 1.068 nm for low temperature reacted $\text{Pr}_2\text{Hf}_2\text{O}_7$. B-273-1 is a single phase fcc fluorite with a unit cell of 0.517 nm. This is very close to values reported for $\text{Tb}_2\text{Hf}_2\text{O}_7$ (0.5205 to 0.5216 nm) and for $\text{Yb}_2\text{Hf}_2\text{O}_7$ (0.5141 to 0.5143 nm).⁽¹³⁾

The compositions higher in Pr_6O_{11} are expected to be predominantly a pyrochlore structure⁽¹⁴⁾ with an anticipated lower electrical conductivity as the Pr_6O_{11} increases. Conversely, the additions of Er_2O_3 , Tb_4O_7 , Yb_2O_3 and Y_2O_3 are reported to stabilize the fluorite cubic phase^(13,14) resulting in a higher electrical conductivity. However, the conductivity of the pyrochlore is expected to be mainly electronic, while the fluorite phases will possibly be predominantly ionic or mixed; however, this has yet to be demonstrated.

These preliminary data represent only the start into a needed investigation of the effects of composition, structure, and oxygen partial pressure on the electrical conductivity and conductivity mechanisms for these MHD electrode materials. For high temperature MHD electrodes, an electronic conductor with a low activation energy/high electrical conductivity independent of oxygen pressure is desired.

TABLE 4. Phase Analysis of Powders and Sintered Compacts

Electrode	X-Ray Diffraction		SEM-EDX
	Calcined Powders	Sintered	
A-273	Two Phase (Poorly Crystallized)	Two fcc Phases	Two Phases
	- Major Cubic 0.66HfO ₂ •0.33Pr ₆ O ₁₁ a ₀ = 5.22 Fluorite or a ₀ = 10.44 Pyrochlore	- Low Pr Phase (0.28 Pr ₆ O ₁₁) a ₀ = 5.33 - High Pr Phase	- fcc Cubic Fluorite (Pr ₆ O ₁₁ rich) - fcc Fluorite (HfO ₂ rich)
	- Minor bcc a ₀ = 10.42 (Yb ₂ O ₃)	(0.36 Pr ₆ O ₁₁) a ₀ = 10.32	- bcc a ₀ = 5.16 for Pyrochlore
B-272	Single Phase Fluorite a ₀ = 5.157	Single Phase Fluorite a ₀ = 5.17	Single Phase
a ₀ (Å) or nm(x10)			

3.4 EVALUATION AIR PREHEATER MATERIALS

A series of six refractory oxides with potential use in directly coal-fired MHD air preheaters were tested in Montana State University's heat exchanger. A Western "Rosebud" slag without seed was used for the tests. The six refractories tested were:

HM-8	Monofrax A ^(a)	99% Al ₂ O ₃ , 0.4% Na ₂ O ^(b)
HM-9	Monofrax E	79.7% Cr ₂ O ₃ , 4.7% Al ₂ O ₃ , 6.1% Fe ₂ O ₃ , 1.8% SiO ₂ , 8.1% other
HM-10	Monofrax K-3	60.4% Al ₂ O ₃ , 27.3% Cr ₂ O ₃ , 4.2% Fe ₂ O ₃ , 1.8% SiO ₂ , 0.3% Na ₂ O, 6.0% other
HM-11	Corhart X-317 ^(c)	64% MgO, 34% Al ₂ O ₃ , 1% SiO ₂ , 1% other
HM-12	Monofrax L(S)	71% Al ₂ O ₃ , 29% MgO
HM-13	Monofrax L(E) ^(d)	52% Al ₂ O ₃ , 48% MgO

-
- (a) Monofrax is a trade name of Carborundum
(b) Weight percent as reported by manufacturer
(c) Trade name of Corhart Refractories
(d) Eutectic composition

Samples of these as-received refractories were characterized as structural and compositional references. These results are included with the characterization and evaluation results for the tested samples of each refractory.

The refractories were tested for a total of 200 hours under thermal cycling conditions with 6-minute heating and 4-minute cooling cycles. The maximum and minimum temperatures were 1811 and 1755 K for the first 100 hours and 1866 and 1811 K for the second 100 hours. The simulated MHD combustion gas contained 0.1% Western Montana "Rosebud" ash, with nominal composition of SiO₂ (53.3%),^(a) MgO (9.9%), Al₂O₃ (18.5%), CaO (14.5%), Fe₂O₃ (3.7%), P₂O₃ (0.7%), Na₂O (0.4%) and K₂O (0.2%).

(a) Weight percent.

The six refractories were tested in a hexagonal configuration. Full size bricks were cut into six pie-shaped pieces, one from each kind of refractory and were fitted together to make one hexagonal-shaped core brick. Holes were matched to adjacent bricks and underlying RFG bricks to allow gas flow. The segments were impregnated with resin and examined by optical and scanning electron microscopy coupled with quantitative EDAX. Sections transverse and parallel to the gas flow were examined. No significant differences were observed between the two samples and/or the orientation of each refractory.

3.4.1 General Appearance

A general visual and optical microscopic examination, Figure 4 and Table 5, revealed that the slag penetrated extensively into the pores and grain boundaries of the Monofrax A (HM-8), Monofrax K-3 (HM-10), Monofrax L(S) (HM-12) and Monofrax L(E) (HM-13). The Monofrax E (HM-9) and Corhart X-317 (HM-11) exhibited only slight slag penetration; however, the Corhart X-317 exhibited substantial erosion.

The relative corrosion and erosion can best be illustrated by comparing the change in the shape of the original round holes in the refractory. Only the Monofrax E retained the smooth cylindrical surface, Figure 4. All the other refractories exhibited varying degrees of erosion/corrosion with the Monofrax A (HM-8), Monofrax L(E) (HM-13) and Corhart X-317 (HM-11) exhibiting the greatest changes. Both Monofrax K-3 (HM-10) and Monofrax L(S) (HM-12) exhibited some intermediate erosion/corrosion changes. Monofrax K-3, Monofrax L(S), and Monofrax L(E) were also fractured.

3.4.2 Microstructural Evaluation

Monofrax A (99 wt% Al_2O_3 , 0.4 wt% Na_2O)

The untested Monofrax A (HM-19) was made up of large (~0.5 mm) dense Al_2O_3 grains (see A, Table 6), with somewhat irregular shapes, Figure 5. Separating the grains and comprising ~10% of the sample was a darker crystalline phase shown by SEM and EDAX to be $\text{Al}_2\text{O}_3(\text{B})$, Table 6. The only apparent difference between these two Al_2O_3 phases was a small (0.8 to 0.4 at.%) difference in Si.

FIGURE 4. Microstructures of Refractories After Testing. All cross sections were cut from same location near the opex of the larger test pieces.

TABLE 5. Physical Appearance of Refractories After Testing

	<u>Color</u>	<u>Slag Penetration</u>	<u>Erosion</u>	<u>Fractured</u>
Monofrax A (HM-8)	White to Brown	Yes	Moderate	No
Monofrax E (HM-9)	Black	No	No	No
Monofrax K-3 (HM-10)	Black	Yes	Some	Yes
Corhart X-317 (HM-11)	White to Brown on Surface	Yes	Yes	Yes
Monofrax L(S) (HM-12)	White to Grey	Yes	Yes	Yes
Monofrax L(E) (HM-13)	White	No	Moderate	No

At the grain boundaries between these two Al_2O_3 phases was a crystalline phase (C) with a composition near $\text{Na}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (plus some Ca). Associated with this phase were metal particles (up to 3 μm) of 72 wt% Zr, 12 wt% Al and 5.5 wt% Na; (D) weight differences measured by SEM-EDX indicate these particles may be partially oxidized.

The erosion and corrosion by the slag was extensive, Figure 6. The original holes in the brick could not be defined and slag penetrated into all the open pores and along grain boundaries. The grains were still Al_2O_3 (G and J) with only minor traces of Si but were larger and of a higher porosity than those of the untested sample. The second phase (H and K) was uniformly distributed along the grain boundaries and was of a different composition than that in the original refractory. The phase at the grain boundaries and in the pores throughout the entire sample was a Ca-depleted $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ composition with a Si/Ca atom ratio of ~2.6.

The major Al_2O_3 grains (G, J), which contacted similar Al_2O_3 grains, were separated by small cracks free of second phase (K, E, H), Figure 6. Spherical pores were found also in these Al_2O_3 grains.

FIGURE 5. Microstructure of Monofrax A (HM-19) Before Testing

TABLE 6. Compositions of Microstructural Phases in Monofrax A
Before (HM-19) and After (HM-8) Testing

		Al ^(a)	Si	Ca	Mg	Fe	Na	Other	Phases
<u>PRETEST (HM-19)</u>									
<u>Matrix</u>									
A ^(b)	Major (Light)	99.2	0.8	---	---	---	---	---	Al ₂ O ₃
B	Major (Dark)	99.2	0.4	---	---	---	---	0.4	Al ₂ O ₃
<u>Grain Boundary</u>									
C	Matrix	49.2	11.6	1.0	---	---	26.9		Na ₂ O•2Al ₂ O ₃ •2SiO ₂
D	Particles	26.9	9.3	7.3	---	---	14.5	49.0 (Zr)	Metallic
<u>POST-TEST (HM-8)</u>									
<u>Slag (Surface)</u>									
E	Matrix	38.2	42.9	16.3	1.0	1.3	---	0.3	CaO•Al ₂ O ₃ •2SiO ₂
F	2nd Phase	44.4	2.0	0.2	50.6	21.8	---	0.4	Mg(Al,Fe) ₂ O ₄
<u>Matrix (Surface)</u>									
G	Major	99.2	0.3	---	---	0.4	---	0.1	Al ₂ O ₃
H	Pores, g.b.	39.4	41.1	17.0	---	1.4	---	0.6	CaO•Al ₂ O ₃ •2SiO ₂
<u>Matrix (Center)</u>									
J	Major	98.8	1.2	---	---	---	---	---	Al ₂ O ₃
K	Pores, g.b.	40.5	42.7	15.7	---	0.8	---	0.3	CaO•Al ₂ O ₃ •2SiO ₂

(a) Atom percent.

(b) Denotes label designation on Figures 5 and 6.

FIGURE 6. Microstructure of Monofrax A (HN-8) After Testing

The slag that covered the refractory surface was two phase. In addition to the Ca depleted $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ phase (E), Al and Fe-rich $\text{Mg}(\text{Al},\text{Fe})_2\text{O}_4$ (F) particles low in Ca with Al/Fe atom ratio of 2 (possible oxygen depleted) were found in the slag adjacent to the untreated Al_2O_3 refractory. Large pores near the surface also contained these spinel crystalline particles.

The corrosion of the Al_2O_3 by the Montana "Rosebud" slag appears to result from: 1) the reaction of the Mg and Fe in the slag with the Al_2O_3 forming $\text{Mg}(\text{Al},\text{Fe})_2\text{O}_4$ spinel, and 2) the change in the slag composition forming the Ca-depleted $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Since there is a nearly complete removal of the Mg (0.4 at.%) and Fe (0.5 at.%) from the slag, the limiting factor for the corrosion appears to be the amount of Mg in the slag which is available to form the spinel. The Fe appears to form a wide solubility with the Al in the spinel and may be involved only in a minor way with the reaction, if at all, since the formation of the spinel is limited by the Mg available in the slag. The near constant Si/Ca ratio in the original slag (2.70) and that in and on the Al_2O_3 (2.6) suggest that Ca does not play an important role in the corrosion.

Monofrax E (79.7 wt% Cr_2O_3 , 4.7 wt% Al_2O_3 , 6.1 wt% Fe_2O_3 , 1.8 wt% SiO_2 and 8.1 wt% other)

This high chromium oxide refractory (HM-14) was made up of large grains (0.2-0.3 mm) of $\text{Mg}(\text{Cr},\text{Al},\text{Fe})_2\text{O}_4$ spinel (A) with long crystallites (0.1 to 0.3 mm) of nearly pure Cr_2O_3 (B) containing ~3 at.% Al scattered throughout the spinel, Figure 7 and Table 7. The spinel grains were generally separated by a porous, glass-like silicate phase containing Al_2O_3 and CaO (C), Table 7. Small (2 to 5 μm) metallic iron particles (D) were also found in the grain boundaries. About 2-5 at.% sodium was present in all phases except the Cr_2O_3 phase.

The microstructure of the chromium refractory (HM-9) during testing had changed very little during the test and retained the $\text{Mg}(\text{Cr},\text{Al},\text{Fe})_2\text{O}_4$ (E and G), the acicular Cr_2O_3 (F and H), and the grain boundary slag structure, Table 7 and Figure 8. However, the Cr/Al/Fe and $(\text{Cr},\text{Al},\text{Fe})/\text{Mg}^{(a)}$ ratios were changed

(a) The analysis for Mg is not absolute, but the variations in ratios are precise.

FIGURE 7. Microstructure of Monofrax E (HM-14) Before Testing

TABLE 7. Composition of Microstructure Phases of E Before (HM-14) and After (HM-9) Testing

		Cr	Al	Fe	Mg	Na	Other	Cr/Al/Fe Ratio(a,b)	(Cr,Al,Fe)/Mg Ratio(b)
<u>PRETEST (HM-14)</u>									
A ^(c)	Spinel	58.0	7.0	6.2	24.2	5.4	0.2	9/1/1	3
B	Cr ₂ O ₃	90.2	8.2	--	--	--	1.6	--	--
C	Grain boundary phase	3.4	18.2	--	0.5	5.7	73.0 ^(d)		
D	Metal phase	8.9	2.7	77.0	4.0	5.8	1.6		
<u>POST-TESTING (HM-9)</u>									
<u>Center</u>									
E	Spinel	55.9	1.3	8.4	27.4	--	1.0	7/1/1	2.6
F	Cr ₂ O ₃	89.7	7.1	1.2	--	--	2.0	--	--
<u>Near Surface (0.13 mm)</u>									
G	Spinel	44.9	10.8	12.5	30.3	--	1.6	4/1/1	2.0
H	Cr ₂ O ₃	87.0	8.2	2.2	--	--	2.6	--	--
J	(Minor)	69.4	14.2	10.3	2.3	--	3.8	--	--
<u>Surface</u>									
K	Spinel	39.1	8.9	21.8	28.6	--	1.5	4/1/2	2.3
		47.2	8.6	12.3	29.9	--	2.0	12/2/3	2.4

(a) Approximate whole numbers.

(b) Atom percent; ratios using Mg are not absolute.

(c) Denotes label designation for Figures 7 and 8.

(d) 63.4% Si and 8.6% Ca.

FIGURE 8. Microstructure of Monofrax E (HM-9) After Testing

from the original composition, and varied from the center and the surface (9/1/1 to 4/1/1 or 4/1/2 and 3 to 2.0 or 2.3, respectively), Table 7.

The Cr_2O_3 phase was approximately the same before and after testing, except near the surface where it had apparently reacted with the Mg, Al, and Fe of the slag to form a $\text{Mg}(\text{Cr},\text{Al})_2\text{O}_4$ spinel. Compare Phase A with Phases G and H, Table 7.

The Cr contents of the $\text{Mg}(\text{Cr},\text{Al},\text{Fe})_2\text{O}_4$ and the Cr/Al/Fe and (Cr,Al,Fe)/Mg atom ratios increased from the surface to the sample center, but were less than in the original spinel. Sodium found in the original spinel was not observed in any phases of the sample after testing.

The slag penetrated into the cracks and grain boundaries of the spinel grains but had not penetrated into the smaller closed pores. The siliceous material at the grain boundaries near the center of the sample was substantially higher in Al and Cr than that in the untested Monofrax E, Table 8. The slag, which had penetrated along the grain boundaries, also varied in composition from the surface to the center of the sample and apparently had reacted with the Na. Only limited Na (<0.8 at.%) remained in the grain boundaries after testing, Table 8. The Mg and Si increased toward the center while the Al, Cr, and Fe decreased. The siliceous phase was generally associated with and surrounded the Cr_2O_3 phase similar to that in the untested refractory; however, the composition was different, Table 8.

The Monofrax E surface reacted with the slag and resulted in the formation of a single phase spinel layer approximately 50 μm thick. The atom ratios of spinels found near the surface varied in compositions, with Cr/Al/Fe varying from 4/1/2 to 12/2/3 but with the (Cr,Al,Fe)/Mg ratio unchanged, Table 7. The high chromium containing spinel and absence of Cr_2O_3 appeared to result from the reaction of the Cr_2O_3 with slag components. This surface was covered with a thin slag layer, approximately 80 μm thick. The layer contained a dendritic-like second phase with a composition near $2\text{MgO} \cdot 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ plus iron, Table 3. The continuous phase was Mg and Si depleted and Al rich when compared to the reported composition of the ash. Neither phase contained Cr.

TABLE 8. Slag Composition^(a) In Monofrax E (HM-5) After Testing

		<u>Mg</u>	<u>Al</u>	<u>Si</u>	<u>Ca</u>	<u>Fe</u>	<u>Cr</u>	<u>Other</u>
	<u>SURFACE (HM-9)</u>							
L ^(b)	Coating	2.5	29.9	42.6	18.5	5.7	0.4	0.5
	Reaction Layer	3.8	23.1	48.2	12.6	3.1	8.5	0.7
		4.2	25.4	53.2	13.9	3.4	-- ^(c)	--
	Cracks	4.0	17.9	60.4	14.9	1.2	0.9	0.8
	<u>PRETEST (HM-14)</u>							
	Grain Boundaries	0.5	18.0	65.8	8.9	--	2.1	6.6 Na
	<u>COAL ASH</u>							
	As Reported	15.2	11.3	55.3	16.2	1.4	--	0.5

(a) Atom percent

(b) Denotes label designation in Figure 8.

(c) Percent not considering Cr.

The reaction of the Monofrax E with the coal slag appeared to result from the reaction the MgO in the slag with the Cr₂O₃ forming a (1-x)MgO·x(Cr,Al,Fe)₂O₃ spinel high in Cr. This combined with the original spinel phase to form a single phase spinel. Iron in the slag readily combined with the spinel solid solution, but its role in the reaction is not known.

In addition, the slag penetrated the cracks and grain boundaries which originally contained a siliceous material. This MgO containing siliceous phase then reacted with the Cr₂O₃ of the Monofrax E. However, because of the limited amount of Mg in the slag in the grain boundaries and the limited mobility of the Mg through these thin layers of slag along the grain boundaries, only limited reaction occurred. The reaction was greatest nearest the surface and less as the distance from the surface increased. Because the reaction resulted in the formation of a stable spinel at the reaction interface, reaction rates were low because of required reactant transport from and to the slag.

Improvement in the degradation resistance of the Monofrax E composition might result by: 1) eliminating the Cr₂O₃ phase and forming a single phase

chromium spinel; 2) by eliminating the spinel and using pure Cr_2O_3 which appears to have the better corrosion resistance; 3) eliminating the siliceous and Na phase present in the grain boundaries which provides a path for the reaction products; and 4) improving the bonding between the grains, thereby reducing the open cracks and pores.

Monofrax K-3 (60.4 wt% Al_2O_3 , 27.3 wt% Cr_2O_3 , 4.2 wt% Fe_2O_3 , 1.8 wt% SiO_2 , 6.3 wt% other)

The Monofrax K-3 alumina-chromia refractory was composed originally of large (0.1 mm) grains of $(\text{Al,Cr})_2\text{O}_3$ which varied in Al and Cr within the same grain (A and B), Figure 9 and Table 9. The bright centers of the larger grains (A) have an Al/Cr atom ratio of ~1, while the darker outer volume (B) has an Al/Cr atom ratio of ~5. Intermixed with these $(\text{Al,Cr})_2\text{O}_3$ grains were smaller (50 to 75 μm) grains of $\text{Mg}(\text{Al,Cr})_2\text{O}_4$ (C) with an Al/Cr atom ratio of ~2 (plus some iron). The separation along the grain boundaries was extensive and contained small (5 to 10 μm) particles of impure metallic iron (80 at.%) (D). The Monofrax K-3 reacted extensively with the slag components, with the slag penetrating through the entire sample (H and L), Figure 10.

With the exception of the infrequent coating on the surface, the slag at the grain boundaries was the same throughout the sample, being very high in aluminum (~40 at.%) and containing little chromium. The grain boundaries were substantially enlarged after testing, and the metallic iron particles were no longer observed.

The grains of $(\text{Al,Cr})_2\text{O}_3$ had reacted extensively with the slag, forming the less reactive $\text{Mg}(\text{Cr,Al})_2\text{O}_4$ spinel. This is evident from the rounded shape of the $(\text{Al,Cr})_2\text{O}_3$ grains near the reaction surface with relatively small changes in the shape and size of the spinel inside the sample. The composition of the $(\text{Al,Cr})_2\text{O}_3$ grains in the sample center retained a similar two-composition structure, although it had reacted slightly with the slag. Al/Cr atoms ratios were very similar to pretest ratios, Table 9. However, near the surface, the $(\text{Cr,Al})_2\text{O}_3$ was nearly homogeneous with a composition more near that of the original edge composition.

FIGURE 9. Microstructure of Monofrax K-3 (HM-15) Before Testing

TABLE 9. Composition of Microstructural Phases in Monofrax K-3 Before and After Testing

		<u>Cr(a)</u>	<u>Al</u>	<u>Si</u>	<u>Ca</u>	<u>Fe</u>	<u>Mg</u>
<u>PRETEST</u>							
<u>(Al,Cr)₂O₃</u>							
A ^(b)	Grain Center	50.7	44.7	0.5	0.2	0.7	2.9
B	Grain Edge	16.1	83.2	0.5	0.2	0.2	--
C	Mg(Al,Cr) ₂ O ₄	21.3	42.5	0.4	--	5.1	30.7
D	G.B. Phase	3.6	10.1	1.1	--	81.7	2.7 (metal)
<u>POST-TEST</u>							
<u>Sample Center^(b)</u>							
<u>(Al,Cr)₂O₃</u>							
E	Grain Center	50.5	47.7	1.0	0.3	0.5	--
F	Grain Edge	23.0	74.3	0.5	0.2	1.7	
G	Mg(Al,Cr) ₂ O ₄	22.3	41.1	0.9	--	7.8	27.7
H	G.B. Phase	1.6	40.1	42.2	15.0	0.8	--
<u>Sample Surface</u>							
J	(Al,Cr) ₂ O ₃	18.8	79.0	0.75	--	1.3	--
K	Mg(Al,Cr) ₂ O ₄	21.0	42.0	0.2	--	7.8	28.8
L	G.B. Phase	0.3	40.0	42.5	16.3	0.5	--

(a) Atom percent

(b) Denotes label designation for Figures 9 and 10.

In contrast, the Mg(Al,Cr)₂O₄ phase remained approximately the same throughout the sample with only slight increase in Fe (5 to 8 at.%) from that of the untested sample.

The corrosion of the Monofrax K-3 apparently resulted as the slag reacted with the (Al,Cr)₂O₃ phase, with penetration of slag along the cracks and grain boundaries. The aluminum was dissolved into the silicate as evidenced by the higher Al content in the grain boundary slag. The Mg in the slag reacted with

FIGURE 10. Microstructure of Monofrax K-3 (HM-10) After Testing

the Cr and Al to form the $\text{Mg}(\text{Al},\text{Cr})_2\text{O}_4$ spinel as evidenced by the absence of Mg in the grain boundary slag. The Ca in the slag does not appear to be a contributing factor in the corrosion of the Monofrax K-3.

These results suggest that Monofrax K-3 is unsuitable for air preheater applications because of the high $(\text{Al},\text{Cr})_2\text{O}_3$ content which reacts to form more of the stable and corrosion-resistant $\text{Mg}(\text{Al},\text{Cr})_2\text{O}_4$ spinel.

Monofrax L(E) (52 wt% Al_2O_3 , 48 wt% MgO)

The pretest, eutectic, magnesium aluminate spinel (HM-16) consisted of large, irregularly shaped dense grains (0.4 to 0.5 mm) of Mg-rich MgAl_2O_4 which appeared to be oxygen deficient (approximately 20%) (A), Figure 11 and Table 10. The grains were surrounded by a multiphase mixture of NaAlO_2 (B and C) with minor phases of impure MgO (D) and impure (Si and Ca) sodium magnesium aluminate (F), Table 10. Stringers of this phase mixture were also found in the spinel grains.

This eutectic, stoichiometric spinel eroded extensively, with slag penetrating into the open pores and most grain boundaries, Figure 12. The matrix of the siliceous phase at the grain boundaries was a near-anorthite phase, $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. The grain boundaries no longer contained Na or the NaAlO_2 phase. The second phase at the grain boundaries was a Mg silicate containing significant amounts of Al and some Ca (H). The silicate composition was very near that of $0.43\text{MgO} \cdot 0.57\text{SiO}_2$, very close to the clinoenstatite ($0.45\text{MgO} \cdot 0.55\text{SiO}_2$) but containing Al and Ca, Table 10. The melting point of clinoenstatite (-1816 K) is close to the temperature during the test.

The degradation of Monofrax L(E) undoubtedly resulted from the penetration of the slag along the grain boundaries and reaction of the slag with the grain boundary impurities, most probably the NaAlO_2 and MgO phases. The Ca and Si in the slag then reacted with the MgO phase (if present) in the grains to form the Ca,Mg silicate phase in the slag. The Al combined with the MgO to form MgAl_2O_4 . The reaction along the grain boundaries resulted in the separation of the grains at the surface which probably allowed the flowing gas and slag to quickly erode the Monofrax L(E).

FIGURE 11. Microstructure of Monofrax L(E) (HM-16) Before Testing

TABLE 10. Composition of Microstructural Phases in Monofrax L(E)
Before and After Testing

		Mg ^(a)	Al	Na	Si	Ca	Fe	Other	Al/Mg	Phases
<u>PRETEST (HM-16)</u>										
A ^(b)	Mg Al ₂ O ₄	35.7	61.3	3.0	--	--	--	--	1.72	
F		37.3	38.3	7.7	6.6	9.7	0.2	0.2	1.03	
<u>Grain Boundary Phases</u>										
B	Major		49.2	39.4	4.2	6.3	0.2	0.7	--	
E		48.6	46.3	4.7	0.2	--	--	0.2	--	
C	Minor	18.9	29.1	33.1	11.4	7.4	--	0.1	--	
D	Minor	85.8	7.2	5.8	1.0	--	0.2	--	--	
<u>POST-TEST (HM-13)</u>										
<u>Center</u>										
G	Grains	33.9	65.1		0.5	--	0.5	--	1.92	
<u>Grain Boundaries</u>										
H	Matrix	0.7	39.8		41.6	17.6	0.2	0.1		CaO·Al ₂ O ₃ ·2SiO ₂
J	2nd Phase	30.1	18.4		43.0	6.9	0.5	1.1		3MgO·Al ₂ O ₃ ·4SiO ₂
<u>SURFACE</u>										
<u>Grains</u>										
G		32.8	64.3		--	--	0.29	0.3	1.96	
G		32.0	64.5		--	--	0.33	0.2		MgAl ₂ O ₄
<u>Grain Boundaries</u>										
H	Matrix	--	39.0		42.7	16.5	1.7	0.1		CaO·Al ₂ O ₃ ·2SiO ₂
J	Stringers	32.1	10.4		42.3	0.9	5.2	0.9		
K	Particles	20.9	20.0		18.1	3.2	33.2	4.6		

(a) Atom percent.

(b) Denotes labels designation for Figures 11 and 12.

Monofrax L(S) (71 wt% Al₂O₃ - 29 wt% MgO)

The pretest, near-stoichiometric, magnesium aluminate spinel (HM-17) was made up of large grains (0.5 to 0.8 mm) of MgAl₂O₄ (A), Figure 13 and Table 11, containing long parallel stringers, 2 to 5 μm wide, in the grains. These were

FIGURE 12. Microstructure of Monofrax L(E) (HM-11) After Testing

FIGURE 13. Microstructure of Monofrax L(S) (HM-17) Before Testing

TABLE 11. Composition of Microstructural Phases in Monofrax L(S)
Before and After Testing

		Mg ^(a)	Al	Si	Ca	Fe	Na	Al/Mg	Phases
<u>PRETEST (HM-17)</u>									
<u>Grains</u>									
A ^(a)		34.7	62.0	0.4	--	--	2.7	1.79	MgAl ₂ O ₄
<u>Grain Boundaries</u>									
B	Major(b)	11.3	43.8	4.5	0.2	0.2	40.2	--	MgO
C	Major	90.6	2.1	0.8	--	0.1	6.3	--	
B	Major(b)	--	50.7	4.5	0.6	0.2	44.0		
D	Major	72.6	13.1	1.8	0.9	0.3	11.4		
E	Minor	2.7	26.6	15.8	21.3	0.2	33.3		
<u>POST-TEST (HM-12)</u>									
<u>Center</u>									
<u>Grains</u>									
F		35.7	64.0	0.2	0.1	--	--	1.79	
<u>Grain Boundaries</u>									
G	Matrix	41.0	1.1	32.9	24.8	--	--		3CaO•5MgO•4SiO ₂
H	Second Phase	99.0	--	--	0.1	--	--		MgO
<u>Surface</u>									
<u>Grains (Near-Surface)</u>									
J		34.5	60.7	0.7	0.1	3.0	--	1.72	
J		34.5	61.7	0.9	--	2.6	--	1.72	
J		34.0	58.6	0.8	0	3.8	--	1.79	
<u>Grain Boundaries</u>									
K	Stringer	28.1	21.6	40.8	7.2	1.8	--		3MgO•Al ₂ O ₃ •6SiO ₂
L	Matrix	2.8	40.1	41.7	13.9	1.0	--		2CaO•3Al ₂ O ₃ •6SiO ₂

(a) Atom percent

(b) Denotes label designations for Figures 10 and 11.

multiphase containing particles of MgO (C and D) in an impure NaAlO₂ matrix. Similar phases were found in the grain boundaries.

The tested spinel (HM-12) had eroded extensively and had reacted with the slag, Figure 14. The slag had penetrated along the grain boundaries, forming a

FIGURE 14. Microstructure of Monofrax L(S) (HM-12) After Testing

(Ca,Mg)O·SiO₂ (forsterite) (G) around the MgAl₂O₄ spinel grains (F) in the sample center, Figure 14. Small MgO particles (H) (25 μm) were also observed with this boundary phase, Table 11.

At the slag-refractory surface, the spinel phase (J) was nearly the same as that observed in the sample center and close to that of the pretest spinel but with 2.5 to 3.0 at.% Fe and other impurities. No Na was found in any of the spinel grains after testing. These grains were surrounded at the grain boundaries by a two-phase matrix of Ca,Al silicate (L) (Ca-depleted anorthite) with stringers of Mg,Al silicate (K).

The Ca was concentrated in the grain boundary slag phases. The iron, however, varied uniformly through the spinel phase with highest concentration at the slag-refractory surface, and uniformly decreased toward the center. The darkening of the surface also suggests a diffusion of iron into the spinel.

The degradation of the Monofrax L(S) appeared to result as the slag reacted with the high Mg- and Na-containing phases at the grain boundaries forming 2(Mg,Ca)O·SiO₂ and other siliceous phases. This resulted in the debonding of the individual grains at the surface, allowing them to be eroded by moving gas and/or slag apparently with only minor corrosion of the spinel itself.

The slag probably reacted slowly with the spinel phase. In addition to the diffusion of iron into the spinel, which did not appear to significantly alter the spinel, the Si and Ca had reacted with the spinel. By comparing the compositions of the siliceous phases at the grain boundaries in the different parts of the sample, it appears that both Mg and Al are reacting. The Ca of the slag may be indirectly involved because of its concentration in the grain boundary slag and the formation of the Ca,Mg,Al silicates phases.

Corhart X-317 (64 wt% MgO, 34 wt% Al₂O₃, 1 wt% SiO₂, 1 wt% other)

The pretest Corhart X-317 (HM-18) was relatively porous with cracks separating many of the individual grains, Figure 15. The grains contained approximately equal volumes of a darker MgO phase (B) and a lighter MgAl₂O₄ phase (A), Table 12. The grain boundaries, especially at the triple points,

FIGURE 15. Microstructure of Corhart X-317 (HM-18) Before Testing

TABLE 12. Compositions of Microstructural Phases in Corhart X-317

		Mg ^(a)	Al	Si	Ca	Fe	Al/Mg	Phases
<u>PRETEST</u>								
<u>Grains</u>								
A ^(b)	Light	36.0	64.0	--	--	--	1.79	
B	Dark	99.5	--	0.5	--	--	--	
<u>Grain Boundaries</u>								
C		48.3	4.2	15.5	32.0	--		3MgO·2CaO·SiO ₂
D		60.0	28.3	5.7	5.9	--		2MgO·Al ₂ O ₄
<u>POST-TEST (HM-11)</u>								
<u>Sample Center Grains</u>								
E	Major	97.2	1.2	1.1	--	0.3	--	
F	Minor	44.2	54.1	1.0	--	0.6	1.22	
G	Matrix	35.7	63.6	0.5	--	0.1	1.78	
<u>Slag-Gas Surface</u>								
<u>Grains</u>								
H	Major	95.3	--	1.1	0.1	3.4	--	
J	Minor	37.5	54.8	1.1	0.1	6.3	1.46	
K	Matrix	35.2	62.7	--	--	1.2	1.78	
<u>Reaction Zone</u>								
L	Minor	67.2	--	30.8	0.4	0.4		2MgO·SiO ₂
		67.9	--	31.3	0.2	1.1	--	
M	Major	35.3	59.5	0.6	0.1	3.6	1.68	
		35.5	53.6	1.0	--	9.1	1.63	
N	Slag	29.9	20.0	39.3	8.9	1.5		2MgO·Al ₂ O ₃ ·4SiO ₂
N		21.8	14.6	41.4	17.1	4.2		3MgO·Al ₂ O ₃ ·CaO·3SiO ₂
N		20.9	12.3	42.6	17.7	4.9		
O		6.5	31.3	43.2	16.3	2.3		CaO·Al ₂ O ₃ ·3SiO ₂

(a) Atom percent

(b) Denotes labels designation for Figures 15 and 16.

contained a multiphase silicate with a matrix overall composition near $3\text{MgO} \cdot 2\text{CaO} \cdot \text{SiO}_2$ (C) and some Al. The stringer-like second phase was $2\text{MgO} \cdot \text{Al}_2\text{O}_3$ (D) eutectic magnesium, aluminum spinel. High-iron, magnesium, silicate particles were also found associated with the stringers near the surface.

The center of the post-test sample had reacted very little with the slag (Figure 16) and exhibited a different microstructure than that observed for the untested spinel. No slag penetrated into the interior of the sample and/or into the pores, and reactions occurred only at the slag-Corhart X-317 surface. However, the center portion of this sample was not representative of the original refractory and consisted of rounded grains (E and F) (0.1 mm) composed of MgO (E) (with some 1 to 3 at.% each of Al, Si, and Fe) with many (approximately 15 to 25 vol%) small second phase crystallites of Mg-rich (35 at.%) magnesium aluminate spinel (F), Figure 17 and Table 12. These rounded phases were surrounded by a single-phase MgAl_2O_4 (A) with an Al/Mg atom ratio very close to stoichiometric spinel. This structure and composition persists to the refractory slag gas reaction surface.

The Corhart X-317 corroded significantly as evidenced by the enlargement of the flow holes, Figure 4. However, slag did not penetrate into the matrix except where open porosity existed. The reaction was therefore limited to the areas where slag remained in contact with the spinel and resulted in a distinct reaction boundary, Figure 18. This layer varied in thickness from 50 to 100 μm on the surfaces with substantial gas-slag flow to 1 mm in the sheltered area. This flow of slag undoubtedly resulted in the continued erosion of some corrosion products.

The corrosion of the Corhart X-317 appeared to occur initially as the silica reacted with the MgO phase (E and H), Figure 17, forming $2\text{MgO} \cdot \text{SiO}_2$ (L) (forsterite). At the same time, some iron diffused into the unreacted spinel and MgO of these globules, and into the surrounding stoichiometric spinel forming $\text{Mg}(\text{Al},\text{Fe})_2\text{O}_4$ (K and M). This was evident by the higher Fe content of the spinels immediately adjacent to the reaction area. In addition, darkening of the surface due to Fe solution was also observed.

FIGURE 16. Microstructure of Corhart X-317 (HM-13) After Testing

FIGURE 17. Microstructure of Monofrax L(E) (HM-11) After Testing

The Mg-enriched slag near the reaction boundary contained the unreacted islands of spinel, Figure 18, in a multiphase slag containing $2\text{MgO}\cdot\text{SiO}_2$ (L) and 2 or 3 complex magnesium, aluminum, calcium silicates (O and N), Table 12. In the areas where the slag layer is thick, these silicates form long stringer structures with phase compositions near $3\text{MgO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{CaO}\cdot 3\text{SiO}_2$ and $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SiO}_2$.

Although some reaction of the spinel with the slag does occur in the reaction area, it was significantly less than for the MgO. Undoubtedly, much of the degradation occurred as the grains of spinel and reaction phases were entrapped in the slag and carried away by the combustion gases and flowing slag, exposing new surfaces to unreacted slag.

3.4.3 Conclusions

The evaluation of these six potential MHD air preheater refractories leads to the following conclusions:

- The high chromium Monofrax E exhibited the highest resistance to corrosion and erosion by the slag-combustion gases.
- Monofrax L(S) exhibited the next best resistance. The high alumina Monofrax A, eutectic magnesium aluminate Monofrax L(E) and magnesium chromium Corhart X-317 exhibited the greatest degradation.
- The reactions of the slag with these refractories occur by two general mechanisms.
 1. For refractories Monofrax A, Monofrax E and Monofrax K-3, which contain Al_2O_3 and/or Cr_2O_3 phases, the Mg and Fe in the slag reacts with the $(\text{Al,Cr})_2\text{O}_3$ phase forming $\text{Mg}(\text{Al,Cr,Fe})_2\text{O}_4$ which appears to be the most stable phase. Ca in the slag does not appear to be directly involved, but combines with the Al and Si to form stable calcium aluminum silicate phases in a modified siliceous slag.

2. For refractories with basic spinel structures, Monofrax L(E), Monofrax L(S) and Corhart X-317, the second phase of MgO reacts with the silican in the slag to form magnesium silicates, i.e., $2\text{MgO}\cdot\text{SiO}_2$ and/or $\text{MgO}\cdot\text{SiO}_2$. The $\text{Mg}(\text{Al,Cr})_2\text{O}_4$ remains relatively stable and unreacted, with only the combination of iron into the spinel.
- A major weakness of all the refractories appears to be the second phases which are present in the grain boundaries of the as-fabricated oxides. This includes second phases of NaAlO_2 , MgO and silicates. The elements in the slag readily attacks these phases and penetrates the refractory oxide. This contributes to: 1) enhanced reaction rates, 2) mobile paths for reaction products, and 3) weakening of grain boundaries and separation of grains. This weakening of the grain boundaries and separation of the grains enhances the erosion by the flowing slag and gases, and exposes new surfaces to the slag for further corrosion.
 - The stoichiometric magnesium aluminate spinel [Monofrax L(S)] exhibited a greater resistance to slag attack than the eutectic magnesium aluminate spinel [Monofrax L(E)] or the intermediate Corhart X-317 spinels. The enhanced corrosion of the eutectic spinel is attributed to the presence of the MgO phase which reacts with the silican in the slag.
 - Potential improvement in the corrosion and erosion of refractories for MHD air preheaters can possibly result by: 1) eliminating the reactive second phases and concentration of impurities at the grain boundaries; and 2) forming the single phase stoichiometric $\text{Mg}(\text{Al,Cr})_2\text{O}_3$ and eliminating the $(\text{Al,Cr})_2\text{O}_3$ and MgO phases which are readily attacked by the components in the slag.

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