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**Task 6.7.2 - Improved Corrosion Resistance of Alumina
Refractories**

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TASK 6.7 – IMPROVED CORROSION RESISTANCE OF ALUMINA REFRACTORIES

1.0 INTRODUCTION

In order to increase the efficiency of advanced coal-fired power systems, higher working fluid temperatures must be reached. To protect some system surfaces, they are covered with corrosion-resistant refractories. Corrosion is the degradation of material surfaces or grain boundaries by chemical reactions with melts, liquids, or gases, causing loss of material and, consequently, a decrease in strength of the structure. In order to develop methods of reducing corrosion, the microstructure that is attacked must be identified along with the mechanism and rates of the attack. Once identified, methods for reducing corrosion rates can be developed.

In order to determine the reactivity of a refractory to a slag, several tests have been developed. The most common are the cup slag test, drip slag test American Society for Testing and Materials ([ASTM] C768), gradient slag test, rotary slag test (ASTM C874) and the dip-and-spin test. Among these tests, the cup slag test is the only static test method and the most commonly used. Previous static testing at the University of North Dakota Energy & Environmental Research Center (EERC) has shown that alumina-based castable refractories are among the least expensive and most corrosion-resistant materials for the highest-temperature coal-fired power system applications.

2.0 OBJECTIVES

The objectives of this work are to use recently developed bench-scale methods to determine the mechanisms and rates of corrosion of alumina-based castable refractories by coal slag and develop methods to reduce the corrosion rates. The initial focus is to improve the bond phase between the grains. Bonding phases normally have a lower melting point and lower corrosion resistance than does the bulk of the material. The best conventional high-alumina refractories are bonded by mullite or alumina itself.

To change the bond characteristics to a more corrosion-resistant material compatible with the alumina matrix, the use of phase diagrams is critical. It is a well-established fact that alumina forms a complete series of crystalline solutions with the lanthanide or rare-earth oxides (REO) group. Within the lanthanide–alumina ($\text{Ln}_2\text{O}_3\text{--Al}_2\text{O}_3$) phase diagrams, several compounds have been identified whose relative stability depend on which individual lanthanide or REO is present. For example, the perovskites, LnAl_2O_7 , where Ln is, for example, Y, La, Nd, Ce, Pr, Pm, Sm, or Eu, and the garnets, $\text{Ln}_3\text{Al}_5\text{O}_{12}$, where Ln can be, for example, Y, Tb, Dy, Er, Tm, Yb, or Lu, are all stable high-melting materials. It is the objective of this study to evaluate the use of these REOs to increase the resistance to corrosion of the bonding phase in castable alumina refractories.

3.0 ACCOMPLISHMENTS

Three processing methods were used for fabrication of the refractory test samples:

- Bulk mix: The raw refractory castable powder was mixed with oxide powders of the three REOs.
- Impregnation: The raw castable refractory powder was mixed with a nitrate solution of the REOs, then pressed into the molds.
- Surface coating: Colloidal sols of the rare-earth sols were used to coat the surface of the fired test sample.

Figure 1 shows a graphical representation of these three bond-phase modification methods. Early tests showed that the surface-coating method did not work because the sols did not wet the fired refractories, so that method was discarded.

A test matrix was developed to study the effects of the three REOs on the corrosion resistance of two experimental high-alumina castable refractories from the Plibrico Company, Illinois. The castables are named Plicast 98 and Plicast 99 for the percentage of alumina in each. Two levels of additive were used, 0.25% or 1 % REOs on a weight percent basis. Table 1 shows the permutations used for the bulk oxide mix technique. Only the mixtures with 1% addition of a single REO were prepared for the impregnation method. The total batch weight for each test sample was 800 g (1.76 lb). For the bulk mix samples approximately 5% water was added to each raw material, a Hobart mixer was used to mix, and then the mixture was poured into a cubic mold 2 inches on a side, with a 1-inch-square cavity centered on one side to hold the slag for the corrosion test. For the impregnation tests, the REO nitrate solution was used to wet the refractory powder.

All of the test samples were first air-dried then oven-dried at 110°C for at least 24 hours. After removing the green cast blocks from the molds, they were sintered at 1500°C following the firing procedure prescribed by the refractory manufacturer. For the static corrosion test, 11 g (0.024 lb) of Illinois No. 6 coal slag was placed into the refractory test sample and placed into the furnace at 1500°C for 100 hours. The most corrosion-resistant mixture from the static corrosion tests will be tested in the first quarter of 1998 by a dynamic corrosion test in which fresh refractory blocks are exposed to a continuous slag flow of about 51 g (0.11 lb) an hour through a 1-cm-diameter semicircular channel. Figure 2 shows a schematic representation of the experimental dynamic slag corrosion testing system.

Figure 3 is a photograph of the cross sections of several of the test blocks which shows about a 50% reduction in the visible depth of slag penetration into the refractory for two of the REO-impregnated blocks as compared to the unmodified test sample. However, visible

*REO - Rare Earth Oxides

Figure 1. Illustration of the three techniques for adding the REOs to the castable refractories.

TABLE 1

Test Matrix Design for REO Additions, %

Test	Lanthana	Neodymia	Yttria
1	0	0	0
2	0.25	0	0
3	0	0.25	0
4	0	0	0.25
5	1.0	0	0
6	0	1.0	0
7	0	0	1.0
8	1.0	1.0	0
9	0	1.0	1.0
10	1.0	0	1.0
11	1.0	1.0	1.0
12	0.25	0.25	0
13	0	0.25	0.25
14	0.25	0	0.25
15	1.0	1.0	0.25
16	1.0	0.25	1.0
17	0.25	1.0	1.0
18	0.25	0.25	1.0
19	0.25	1.0	0.25
20	1.0	0.25	0.25

discoloration may not indicate the true depth of slag penetration. Therefore a scanning electron microscope (SEM) was used to determine the penetration depth and to look for structural changes which are the direct result of the compositional changes due to the contributions of the REOs. The depth of slag penetration into the blocks is defined as the maximum depth

Figure 2. Schematic of the experimental dynamic slag corrosion testing system.

at which measurable concentrations of the primary slag constituents of Si, Ca, and Fe were found in the blocks as determined by elemental mapping.

The SEM analyses show that the Fe, Ca, and Si tend to penetrate well beyond the visible discoloration in most cases. Figure 4 shows a representation of the results of the slag penetrations in the Plicast 99 samples modified with the bulk mixing technique. The samples presented include the unmodified (S1), the samples modified with 1% REO (lanthana [S6], yttria [S8], and neodymia [S9]), and the sample containing 1% of each of the three REOs (S23). Data for the samples modified by the impregnation technique were similar.

The SEM analyses show that in the samples modified with 1% of the REOs neodymia and lanthana, the silica from the slag combined with the REO to increase the slag diffusion into the refractory. There were similar effects when all three REOs were added in equal amounts (1% each) to the Plicast 99. A second problem with this mixture was that the block developed abnormal structural cracking. This is probably due to the formation of the mineral phase found along cracks shown in Figure 5. X-ray diffraction was used to determine the mineralogy of the modified samples. The new phases found in the modified samples include aluminum yttrium oxide garnet ($\text{Al}_5\text{Y}_3\text{O}_{12}$), lanthanum aluminum oxide ($\text{LaAl}_{11}\text{O}_{18}$), and calcium neodymium oxide phosphate silicate ($\text{Ca}_3\text{Nd}_7[\text{PO}_4][\text{SiO}_4]_5\text{O}_2$).

Plicast Cement-Free 99
Al₂O₃-based refractory

Plicast Cement-Free 99
Al₂O₃-based refractory + REO 1

Plicast Cement-Free 99
Al₂O₃-based refractory + REO 2

Figure 3. Cross sections of unmodified and modified refractory blocks corroded with Illinois No. 6 coal slag.

Figure 4. Illinois No. 6 coal slag penetration depths measured by SEM.

Figure 5. SEM photograph of crystals containing REOs that formed in the refractory cracks.

In contrast to the lanthana- and neodymia-modified samples, the Plicast 99 sample modified with 1% of yttria showed a reduction in the slag diffusion by approximately 27% when compared to the unmodified sample. However, the aluminum yttrium oxide garnet ($\text{Al}_3\text{Y}_3\text{O}_{12}$) was seen as individual crystals, not as a continuous coating. Therefore, the reduction in slag penetration is caused by a reduced rate of intergranular transport, not by the formation of a passive layer that acts as a barrier to slag penetration.

4.0 FUTURE WORK

During the next quarter, we will test blocks of unmodified Plicast 99 and yttria-modified Plicast 99 with flowing slag to determine if the slag penetration is still reduced with the yttria addition.