SUBTASK 6.4 – IMPROVED CORROSION RESISTANCE FOR ALUMINA REFRACTORY

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INTRODUCTION

In order to increase the efficiency of advanced coal-fired power systems, higher working fluid temperatures must be reached. Some system surfaces will have to be protected by covering them with corrosion-resistant refractories. Corrosion is the degradation of the material surfaces or grain boundaries by chemical reactions with melts, liquids, or gases causing loss of material and, consequently, a decrease in the 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 attack. Earlier tests with several commercially available high-temperature castable refractories showed that the fused-alumina aggregate grains within the materials had the highest corrosion resistance of any of the castable materials. However, the cement holding the grains was easily attacked. Therefore, to improve the corrosion resistance and thermomechanical properties of alumina-based refractories, we attempted to change the cement to a more corrosion- and erosion-resistant bonding material through the addition of rare-earth oxides (REO).

Phase diagrams were used to identify stable high-melting-temperature materials within the lanthanide–alumina series that could modify the bonding phase of the alumina-based refractory. Two mechanisms of reducing corrosion were investigated. One was the formation of corrosion-resistant layers within the refractory. The other was increased sintering to increase strength and seal continuous pores that would reduce slag penetration. Garnets ($Re_3Al_5O_{12}$) and perovskites ($ReAl_2O_3$), where Re is the REO, are two of the stable high-melting-temperature materials identified that were believed could be formed in the refractory matrix to help reduce corrosion rates. For the base refractory, Plicast 99 made by Plibrico was chosen. It is a 99% alumina castable composed of fused alumina aggregate and a cement made primarily from Alphabond 100, produced by Alcoa.

The initial work involved designing a test matrix to study the effects of selected REOs on the corrosion resistance of the refractory. Three different processing methods were employed for fabricating the test samples. These included bulk mixing, impregnation, and surface coatings. Two different corrosion test methods were used to test the mixtures. The first was the static cup test that was used to screen the samples for the second corrosion test which used flowing slag. In addition to the corrosion tests, three-point modulus-of-rupture (MOR) tests were performed using the standard American Society for Testing and Materials (ASTM) C133 procedure to determine if the addition of an REO improved the strength of the refractory. A strength increase would show that the refractory was more resistant to erosion and also that sintering had occurred, which would imply a reduction in porosity.

ACCOMPLISHMENTS

The initial test matrix was developed to study the effects of three REOs on the corrosion resistance of the Plicast 99. Two levels of additives were used, 0.25% or 1% REO on a weight percent basis. Table 1 shows the permutations used.

TABLE 1

Test Matrix Design for REO Additions

Test	Lanthana	Neodymia	Yttria
1	0.25	0.25	0.25
2	1.0	0.25	0.25
3	0.25	1.0	0.25
4	0.25	0.25	1.0
5	1.0	1.0	1.0
6	0.25	1.0	1.0
7	1.0	0.25	0.25
8	1.0	1.0	0.25
9	0	0	0
10	1.0	0	0
11	0	1.0	0
12	0	0	1.0
13	0	1.0	1.0
14	1.0	0	1.0
15	1.0	1.0	0
16	0.25	0	0
17	0	0.25	0
18	0	0	0.25
19	0	0.25	0.25
20	0.25	0	0.25
21	0.25	0.25	0

Three processing methods were employed for fabricating the refractory test samples. The three types of processing methods are as follows:

- Bulk mix: The dry refractory castable material was mixed with the REO powders.

- Impregnation: The fabricated refractory test sample was impregnated or pressure-infiltrated with nitrate solutions of the REOs.

- Surface coating: Colloidal sols of the rare-earth sols were used to coat the surface of the fabricated test sample.

Figure 1 shows a graphical representation of the bond-phase modification methods for the refractory ceramic. Early tests showed that the impregnation and surface-coating methods did not work because the sols did not wet the fired refractories, so that method was discarded. The permutations shown in Table 1 were only done for the bulk oxide technique. Only the mixtures with 1% addition of a single REO were prepared for the impregnation method.

The blocks used for the static tests were cubes 2 inches on a side with a 1-inch^3 hole, or slag cup, in one surface. The fabricated samples with the REO additions were fired at 2732°F (1500°C). For the static test, 11 grams of Illinois No. 6 coal slag were placed into the slag cup and fired at 2732°F (1500°C) for 100 hours. The blocks were then cross-sectioned vertically through the slag cup, and the depth of slag penetration and surface recession was measured. The depth of slag penetration into the blocks is defined as the maximum depth at which measurable concentrations of the primary slag constituents of Si, Ca, and Fe were found in the blocks as determined by elemental mapping using a scanning electron microscope (SEM).

Figure 2 illustrates the slag penetrations in the Plicast 99 samples modified with the bulk mixing technique. As the graph shows, the most successful mixture after the static cup slag tests was the sample containing 1% yttria by weight. Under static conditions, this mixture showed a reduction in the depth of slag penetration by approximately 27% when compared with an unmodified sample of the Plicast 99. However, the SEM photograph shown in Figure 3 illustrates that the yttrium aluminum garnet, or YAG ($Y_3Al_5O_{12}$), formed from the reaction between the yttrium additive and the alumina refractory, was seen as individual crystals and not as a continuous corrosion-resistant layer. Therefore, the reduction in slag penetration was, possibly, caused by a reduced rate of intergranular transport, not by the formation of a passive layer that acts as a barrier to slag penetration. Because of the reduction in slag penetration, this REO mixture was then tested using the dynamic corrosion test.

For the dynamic test, the test samples are exposed to a continuous fresh slag flow of about 51 grams an hour. Figure 4 shows a schematic representation of the experimental dynamic corrosion test equipment which is named the dynamic slag application furnace (DSAF). The DSAF is a modified double-chamber bench-scale furnace designed to simulate conditions of dynamic corrosion on the vertical walls of a refractory-lined slagging combustor. It can operate up to a maximum of 2910°F (1600°C) and is designed to handle up to four test blocks simultaneously. The blocks are 4 inches wide and deep by 9 inches tall. A slag well is molded in the top of the block, and a flow channel is molded from the well and down one side of the block to force the slag to flow in a specific path. The slag is fed to the wells in a granular form using a low-rate volumetric feeder employing a set of double intermeshing augers. The slag granules

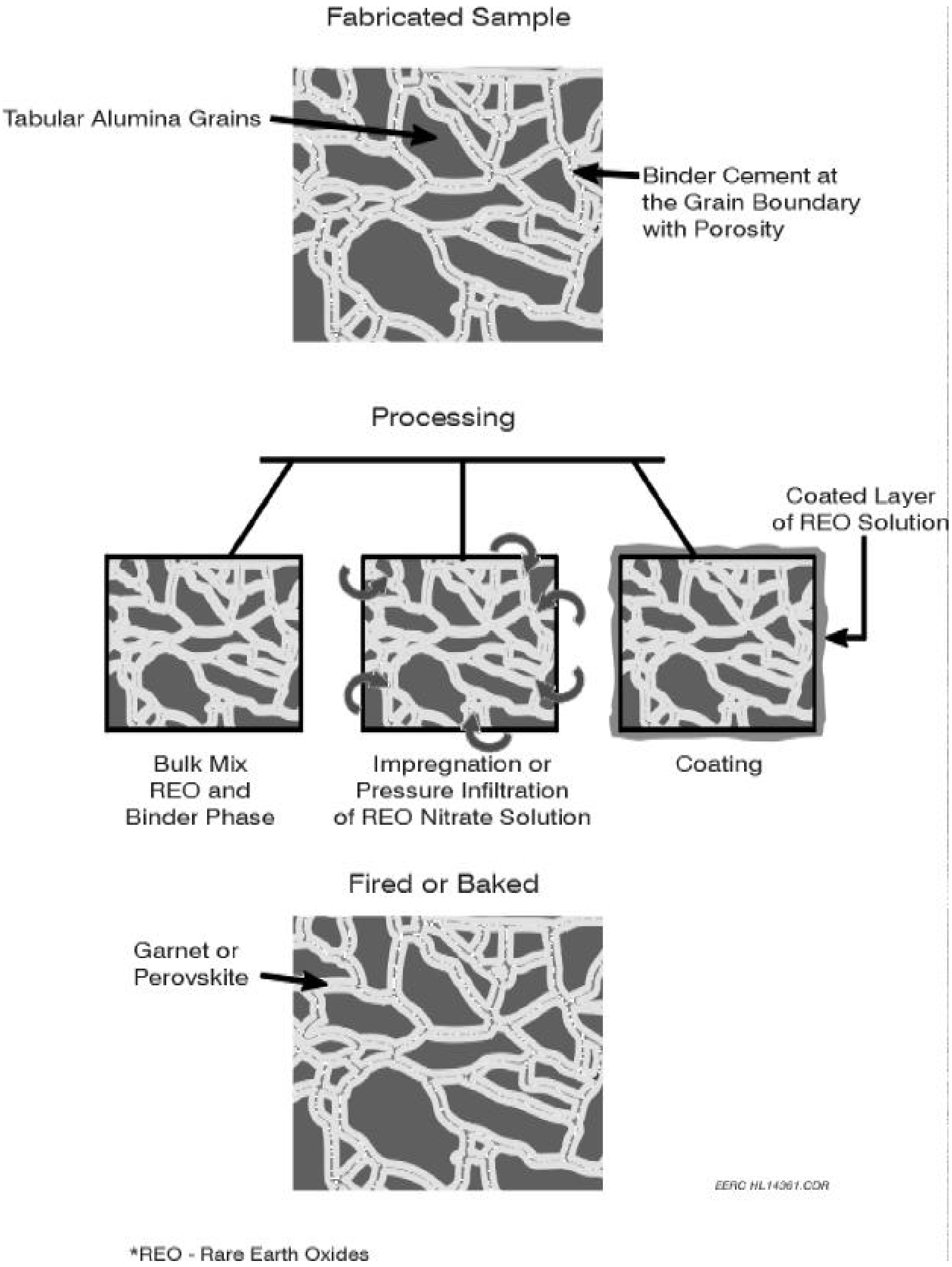

Figure 1. Illustration of the three techniques for adding REOs to castable refractories.

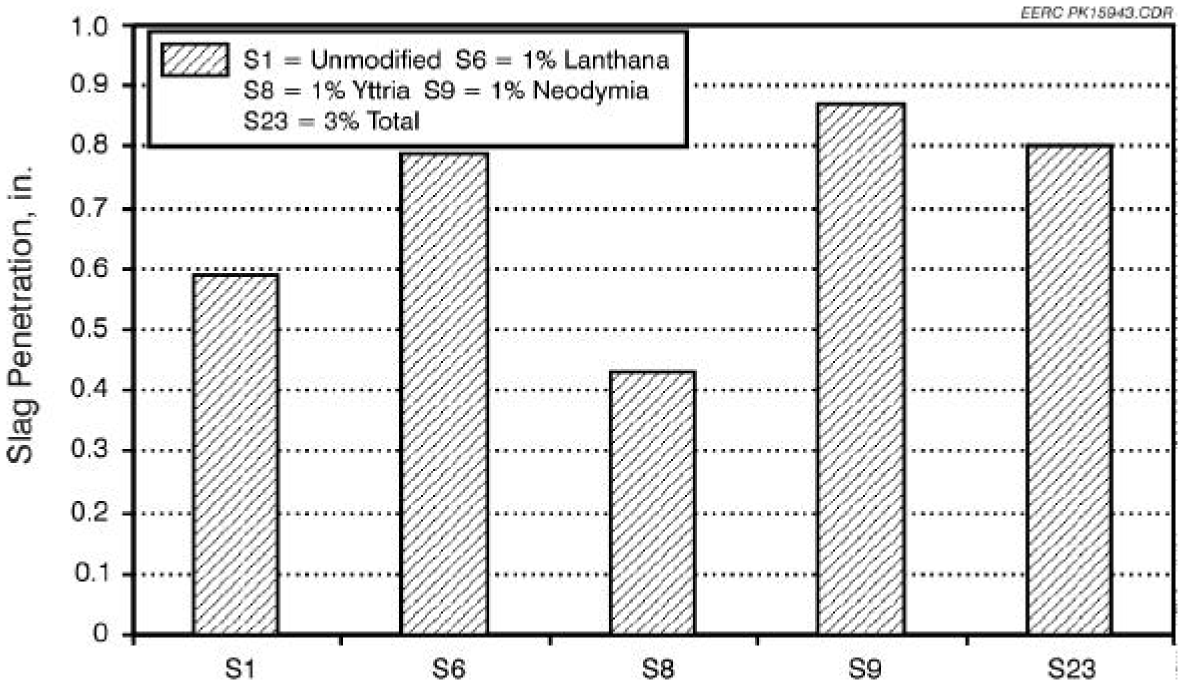

Figure 2. Slag penetration depths for static corrosion test measured by SEM.

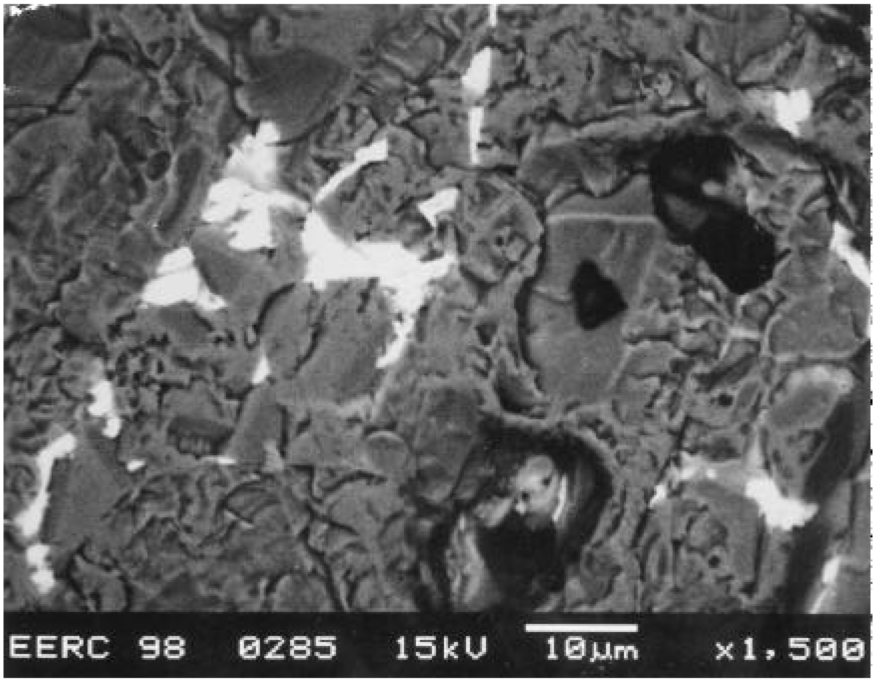

Figure 3. SEM photograph of crystals of yttrium aluminum garnet that formed in the refractory material.

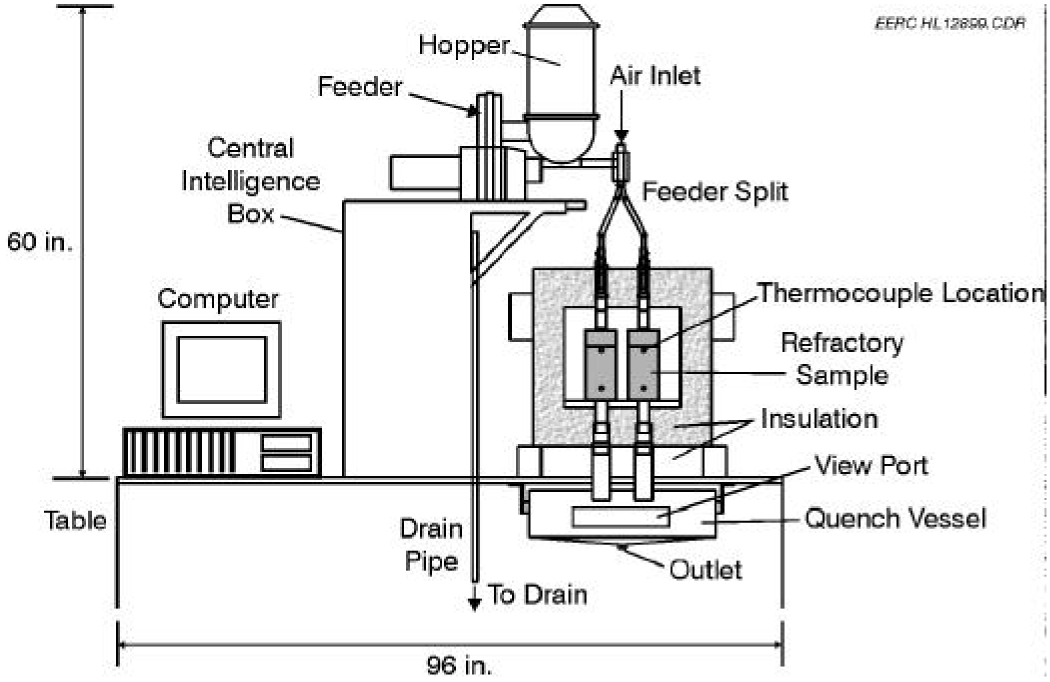

Figure 4. Schematic of the experimental dynamic slagging corrosion testing system.

enter the furnace through four slag injector feed ports located on the top of the furnace, melt in the well, flow down the channel, and exit the furnace through two ports at the bottom of the furnace. The spent slag is collected in a water quench vessel.

An unmodified sample of the Plicast 99 refractory and a fresh test block composed of the 1% yttria mixture was subjected to the dynamic corrosion test using Illinois No. 6 slag at 2732°F (1500°C). After 47½ hours of slag feed, the test was stopped because the recession measurements, shown in Figure 5, indicated that the 1% yttria addition did not reduce the surface recession during the dynamic corrosion test enough to justify continuing the 100-hour test.

In an effort to determine whether the formation of a passive YAG layer would reduce corrosion rates, a bar of dense YAG was tested for its corrosion resistance to Illinois No. 6 slag at 2732°F (1500°C). The bar measured ¾ in. × ¾ in. × ¼ in. It was placed on its side vertically in a platinum crucible, and enough slag was poured into the crucible to cover the bottom half of the bar. The crucible was heated slowly to 2732°F (1500°C), where it was held for 100 hours, then slowly cooled to room temperature. Visual observations indicated that the bar had completely dissolved into the slag. Therefore, it was decided to abandon the attempts to form a passive corrosion-resistant YAG layer in the refractory material.

The focus of the experiments then turned to improving the sintering of the refractory, which would increase the strength and decrease the porosity of the material. Because of the reduction in slag penetration during the static corrosion tests of the yttria-treated refractory blocks, blank, and two concentrations of yttria, 0.5 wt% and 2.0 wt%, were tested for the effects

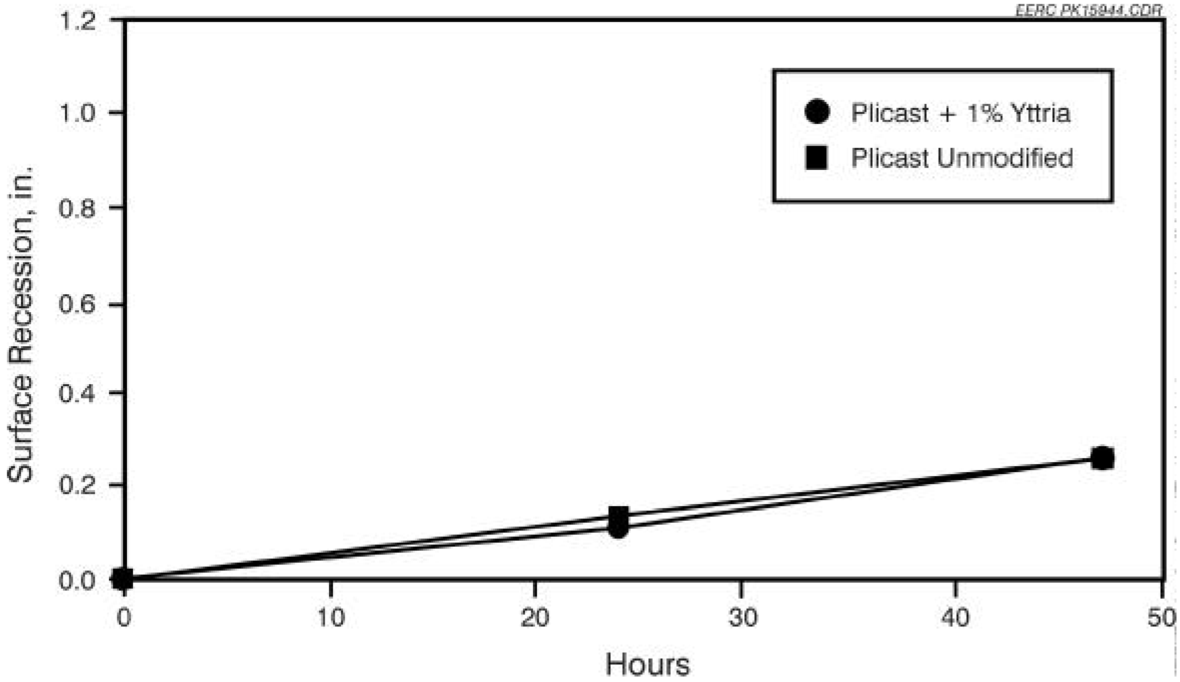

Figure 5. Comparison of recession measurements from DSAF test of Plicast 99 refractory modified with 1% yttria and an unmodified sample using Illinois No. 6 slag.

on the MOR of test bars. Four MOR bars for each wt% were made (total of 12 bars). The test bars were 2 × 2 × 9 inches. The first set of bars was fired to 2732°F (1500°C), held for 4 hours then cooled to room temperature, at which time a three-point MOR test was performed, using the ASTM C133 procedure. Figure 6 is a graph showing that for samples fired to 2732°F (1500°C), the greater the amount of yttria the lower the flexural strength. The average strengths were 2486, 2305, and 1976 psi for Plicast 99 unmodified, Plicast 99 + ½% yttria, and Plicast 99 + 2% yttria, respectively. Therefore, for blocks fired to 2732°F (1500°C), there was actually a disadvantage to adding yttria to the refractory mix.

Experiments were also carried out using the same amounts of yttria, but a higher firing temperature. The second set of blocks were fired to 2910°F (1600°C). The hope was that the higher temperature would increase the amount of sintering, and therefore the strength would increase. Figure 7 is a graph showing that the increased temperature did cause the strengths to increase, but as with the samples fired to 2732°F (1500°C), the unmodified sample strength was much higher than the modified samples. The average strengths were 3468, 3055, and 2168 psi for the unmodified Plicast 99, Plicast 99 + ½% yttria, and Plicast 99 + 2% yttria, respectively. These experiments did show us that an increase of 100°C in the firing temperature can make a significant difference in the strength and, therefore, the erosion resistance of the material, but that the yttria addition is not a good sintering aid.

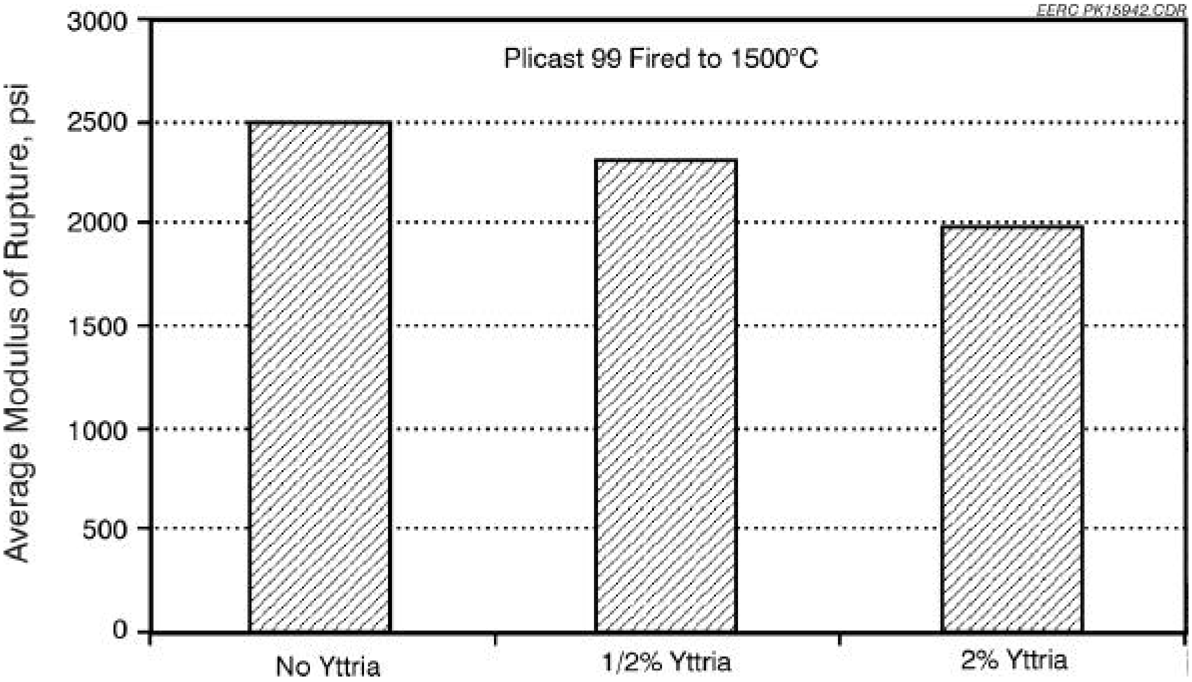

Figure 6. Modulus-of-rupture test results for Plicast 99 samples fired to 1500°C.

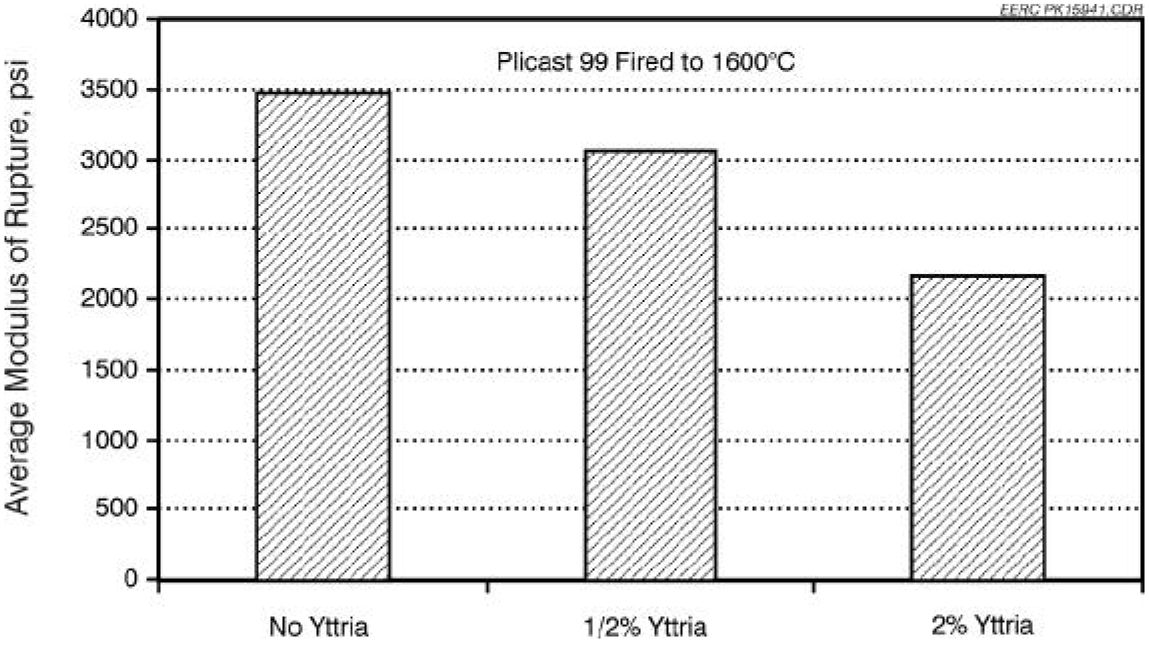

Figure 7. Modulus-of-rupture test results for Plicast 99 samples fired to 1600°C.

FUTURE WORK

The addition of REOs to castable alumina refractories did not improve the corrosion resistance or the sintering properties of the fired refractories. Therefore, we are stopping that area of research. In addition, for the next year, we will not pursue the development of refractories for use in fossil energy systems using funds from the base cooperative agreement. That work will be paid for from a separate project. Instead, we have proposed to begin addressing refractory problems in the glass and metal industries.