Six zircon-containing brick were evaluated for steel ladle slag line application. The following physical properties were studied: density, porosity, creep, slag resistance, thermal expansion, thermal shock resistance, and thermal conductivity, and compared to a high-purity 70% Al₂O₃ containing ladle brick. The data, in particular a zircon refractory’s resistance to slag erosion, indicated they should give better performance than the presently used 70% Al₂O₃ refractories. Two field trials were run in steel ladle slag lines. Inspections of the ladles during and after service showed no difference in performance between zircon and 70% Al₂O₃-containing refractories.

**Theoretical Background**

Due to its refractory character, zircon, the mineral, has been studied since the early 1900s. Nevertheless, investigations of the phase diagram of the system ZrO₂-SiO₂ and of the thermal stability of zircon are very inconsistent as they report conflicting melting and dissociation temperatures.

The melting temperature of zircon under nonequilibrium conditions was determined by Zirnowa to be 2430°C. However, it should be remembered that zircon has no true melting point, but may be forced into such a state under very extreme conditions of pressure and temperature. Under equilibrium conditions zircon melts incongruently to form zirconia (ZrO₂) and silica (SiO₂). The confusing data cast a shadow on the temperature of initial dissociation. Barlet reported a dissociation temperature as low as 1450°C while Matignon found it to be 2000°C. Toropov and Galakhov, in their phase diagram study under equilibrium conditions, found the decomposition temperature to be 1550°C. However, Geller and Lang determined it to be 1775°C.

The discrepancies in experimental data could be attributed to the impurity content of the zircon. Stott and Hilliard found a 100°C difference in dissociation temperature between high and low purity zircon samples. Zircons always contain some hafnium; the HfO₂/ZrO₂ ratio varies, but is normally about 0.01 to 0.04. Some have been found to contain 22% to 24% HfO₂ (HfO₂/ZrO₂=0.6), although this is not the highest amount ever reported. Iron and rare earths have sometimes been shown to be present in considerable amounts.

Most of the published studies indicate that zircon will decompose at temperatures above 1504°C according to the following equation:

\[
\text{ZrSiO}_4 \rightarrow \text{ZrO}_2 + \text{SiO}_2
\]

From the available enthalpy and entropy data for ZrO₂, ZrSiO₄ and SiO₂ the equation for free energy of formation of ZrSiO₄ can be calculated:

\[
\Delta G_f = 15360 - 8.48T
\]

Under equilibrium conditions (\(\Delta G_f = 0\)) the decomposition temperature of \(\text{ZrSiO}_4\), as calculated from Eq. (2), is 1540°C. Curtis and Sowman indicated that ZrO₂ and SiO₂ will recombine to form \(\text{ZrSiO}_4\) again if sufficient time is allowed in the temperature range of 1425°C to 1540°C. This is expected as zircon is the stable phase at low temperature.

The practical significance of the kinetics of zircon decomposition will depend on two factors: 1) the partial pressure of oxygen, which will affect the vaporization of SiO₂ in the form of SiO and thus move the equilibrium of reaction (1) to the right; 2) the slag chemistry, which will affect the reaction and removal rate of SiO₂ from the hot face of the brick. Silica will rapidly react with high CaO/SiO₂ and Fe₂O₃ containing slags and thus move the equilibrium of reaction (1) to the right.

**Results and Discussion**

The reported results are a combination of manufacturer supplied data and special testing performed during the investigation covering those areas which were of particular interest for this application. Data were obtained from several experimental refractory mixes and some readily available zircon refractories.

Table I lists the compositions of all the refractories used in the experiments. It should be noted that the standard against which all of them were compared is the high purity 70% Al₂O₃ brick listed last in Table I. The bulk of the work was done on three of them. Based on these results, only one mix was considered promising enough to warrant a field trial.

This test consisted of measuring the cold modulus of rupture (ASTM C 133-81) of five 25.4 by 25.4 by 152.4 mm bars. Subsequently five other bars of the same refractory were put into a 1600°C kiln for 20 min, air cooled for 20 min and then cycled 4 more times between room and high temperature. Cold modulus of rupture values were obtained on these bars after treatment and the percentage of strength lost was calculated. Figure 1 shows diagrammatically the effect of the thermal shock treatment on the test specimens.

The critical deflection under load was used as an alternate method to check the thermal shock resistance of the specimens. Brezny developed the method to correlate the numbers so obtained with the thermal shock resistance of the refractory. Figure 1 also shows the results obtained through this approach. It can be...
### Table I. Chemistry and Physical Properties of Refractories Studied

<table>
<thead>
<tr>
<th>Property</th>
<th>A*</th>
<th>B*</th>
<th>C*</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>70% Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry (wt%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrO₂</td>
<td>48.8</td>
<td>24.8</td>
<td>55.9</td>
<td>67</td>
<td>16.3</td>
<td>19.2</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>35.5</td>
<td>42.8</td>
<td>35.1</td>
<td>33</td>
<td>27.0</td>
<td>10.2</td>
<td>24.4</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13.85</td>
<td>29.87</td>
<td>8.5</td>
<td>55.8</td>
<td>70.0</td>
<td>71.5</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.77</td>
<td>1.28</td>
<td>0.48</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>0.45</td>
<td>0.31</td>
<td>0.05</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.53</td>
<td>0.84</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alk</td>
<td>0.1</td>
<td>0.1</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>3.22</td>
<td>2.86</td>
<td>3.47</td>
<td>3.7</td>
<td>2.89</td>
<td>3.15</td>
<td>2.62</td>
</tr>
<tr>
<td>App. porosity (%)</td>
<td>17</td>
<td>13</td>
<td>17</td>
<td>18</td>
<td>12</td>
<td>16</td>
<td>18</td>
</tr>
<tr>
<td>Linear reheat change after 1600°C (%)</td>
<td>-0.3</td>
<td>+0.3</td>
<td>-0.17</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>+1.33</td>
</tr>
<tr>
<td>Creep (%) (20–50 h at 1400°C)</td>
<td>1.31</td>
<td>1.28</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>1.30</td>
</tr>
<tr>
<td>Thermal expansion at 1500°C (%)</td>
<td>-1.071</td>
<td>-0.901</td>
<td>-1.018</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>-0.269</td>
</tr>
<tr>
<td>Thermal conductivity (W/mK)</td>
<td>3.16</td>
<td>2.44</td>
<td>4.10</td>
<td>4.38</td>
<td>3.17</td>
<td>3.55</td>
<td>2.22</td>
</tr>
</tbody>
</table>

*Experimental mixes. †Provided by supplier.

seen that the critical deflection method is a good indicator of the thermal shock resistance of the refractory. Overall, the zircon refractories have relatively poor thermal shock resistance, especially sample A which broke mostly on contact.

The thermal conductivity of the samples was established using the hot wire method at room temperature (Table I). Sample preparation consisted in cutting a clean surface with a saw. The results obtained are in close agreement with those published by Kawakami, et al., as they show the same dependence of thermal conductivity to zirconia content as long as the matrix is clay. No published data is available for an alumina matrix.

The percent thermal expansion was obtained for samples A, B, and C (Table I). The samples consisted of small (6.3 by 6.3 by 50.8 mm) bars which were heated in air to 1500°C at a rate of 2.6°C/min.

Creep data were obtained for samples A and B following DIN 51053/II specifications. The subsidence was measured between the 20th and 50th hour at 1400°C and under a load of 196 kPa. Table I shows the percent creep obtained.

The bulk density and apparent porosity were determined following ASTM C 830-79 procedures. The numbers obtained correlate well with the zirconia levels in the brick. The same trend was observed by Kawakami, et al.

Double cup gradient tests were run at 1593°C under oxidizing conditions using a very basic slag (CaO:SiO₂ = 3.6). The test samples were kept at temperature for 3 h. The experimental setup consisted of brick size samples 225 mm long which were placed in the door of a kiln. Two 50-mm diam. cups were core drilled 25 mm behind the future hot face of each brick (Fig. 2). Both cups were filled with predetermined amounts of test slag. The samples were then placed in the door of the kiln in such a manner as to achieve a particular thermal gradient (Fig. 2) when exposed to temperature. It was attempted to duplicate expected service conditions. The thermal gradient was measured with a set of Pt-Rh thermocouples placed in 25 mm increments behind the hot face of the test samples.

After the test, the samples were split longitudinally and the extent of brick erosion and slag penetration was observed. Single cup slag tests were also run. The test temperature was 1650°C and the samples were exposed to it for 2 h. Table II lists the slag chemistries. They were chosen to closely reflect the different environments the brick would be exposed to in service. Figures 3 and 4 illustrate the test setup.
slag A

Erosion

70% Al₂O₃

Zircon A

Penetration

Penetration

No Erosion

Penetration Only

slag B

Erosion

70% Al₂O₃

Zircon B

Penetration

slag C

Erosion

70% Al₂O₃

Zircon C

Penetration

Fig. 3. Double-cup gradient test results.

4 show how the different slag chemistries interacted with the refractories. It is obvious that the least amount of destruction was done to sample C while the 70% Al₂O₃ standard was partially dissolved. This information, coupled with the fact that zircon C also had acceptable shock resistance, made it a good candidate for a field test.

A thorough microscopic investigation of the zircon brick A, B, and C was undertaken in order to determine their failure mechanism. Figure 5 shows slag-free brick sections. Zircon A (Fig. 5(A)) is characterized by a bimodal distribution of rounded zircon grains bound together by a clay/mullite matrix. Zircon B has a very similar microstructure to zircon A. It consists of sharply angular zircon grains in a bimodal distribution to characterize it. Rounded mullite can also be seen. Some of the grains have titinates as inclusions. At high temperatures, the matrix clay recrystallized as mullite onto most existing grains and also formed a glass phase. Zircon C (Fig. 5(B)) has round zircon grains of a uniform size and minimal clay matrix.

Microscopic and X-ray evaluation indicate that all test brick were fired below 1550°C, since the decomposition of ZrSiO₄ to ZrO₂ and silica was not detected in the as received samples.

The mode of interaction between the slags and all three of these brick seemed to be the same with regard to zircon. The rate of penetration though, was controlled by the amount of glass in the matrix. Figure 6 depicts the slag A/brick interface of zircon C. The slag was at the top of the picture while the bottom extends towards unused brick. The slag attacks the zircon grains, dissolving them by preferential leaching of the silicate. The outlines of the former zircon grains are preserved well into the slag phase. The halo around the zircon is composed of zirconia (Fig. 7(A)) as determined on an electron microprobe. Further investigation showed that zirconium was concentrated in small, but distinct areas of the matrix glass (Fig. 7(B)) indicating the possibility of differential melting.

The phase diagram of the system ZrO₂-SiO₂ shows that zircon should decompose into zirconia and silica at 1540°C. In order to encourage this transformation and to be able to determine its rate 20 by 20 by 20 mm samples of refractory C were heated to 1500°, 1600°, and 1700°C and held for two hours at temperature. X-ray diffraction of these samples showed no zirconia at 1500°C, a minimal amount at 1600°C and an abundance at 1700°C. This is in good agreement with the theoretical decomposition temperature of 1540°C.

The application chosen was a steel ladle slag line where zircon refractories were supposed to replace the 70% Al₂O₃ brick currently in use. This steel ladle is in a shop where exposure to slags of variable lime/silica ratios (0.5 to 3.0) are common practice. Two field trials were run. One consisted of a side-by-side comparison

4 Cameca Electron Microprobe, with an EDAX attachment, Paris, France.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Slag A</th>
<th>Slag B</th>
<th>Slag C</th>
<th>Slag D</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>61</td>
<td>20</td>
<td>35</td>
<td>50</td>
</tr>
<tr>
<td>SiO₂</td>
<td>17</td>
<td>49</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12</td>
<td>10</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>MgO</td>
<td>10</td>
<td>6</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>FeO</td>
<td>12</td>
<td>12</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>MnO</td>
<td>2.3</td>
<td>4</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
</tbody>
</table>

Table II. Chemical Analysis of Slags

Fig. 4. Single-cup slag test results for (A) slag B, (B) slag C, and (C) slag D.
of the high purity 70% $\text{Al}_2\text{O}_3$ against the zircon C refractory in a split slag line. The other trial consisted of a full zircon C slag line. Inspections of the ladle during service and while waiting for tear-out showed absolutely no wear differences between the zircon and the 70% $\text{Al}_2\text{O}_3$ brick, neither did the slag line life improve when it was all zircon brick.

Conclusions

The lab testing of zircon containing refractories showed them to be slightly attacked by slags of high lime/silica ratios and of high iron oxide. In the same tests the high-purity 70% $\text{Al}_2\text{O}_3$-containing brick were heavily attacked. On the other hand, the zircon refractory selected for the steel ladle slag line test did not outperform the high-purity 70% $\text{Al}_2\text{O}_3$ brick in the field trials. In this application it was exposed to various steel grades with their concomitant range of slag compositions. The discrepancy between laboratory testing and field results can be attributed to the relatively small amount of slag used in the laboratory tests. This causes the original slag chemistry to change rapidly to reach equilibrium with the surrounding brick. In order for zircon brick to successfully compete against high-alumina refractories in steel ladle applications, it is necessary that their technical and price advantage be more clearly defined and improved.

Acknowledgment

The authors wish to thank Didier-Taylor, Harbison and Walker, and North American Refractories for their brick samples and experimental mixes.

References