Reduction in Corrosion of Refractories Using Encapsulated Glass Additives*

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Objective

- To characterize the corrosion behavior of refractories in molten borax glass.
- To evaluate the effect of pelletization on the corrosion behavior of refractories.

Experimental Procedure

Three brands of refractories, two from North American Refractories Company and one from L. E. Smith Glass Company, were evaluated to estimate their corrosion resistance in molten glass. North American refractories included VISION TILE and RESERV® 70. Primary constituents of VISION TILE and L. E. Smith refractories were alumina, zirconia, and silica, while the primary constituents of RESERV® 70 were chromic oxide and alumina. These refractories were in the shape of rectangular bricks. Two batches of anhydrous borax glass (sodium tetraborate, $Na_2B_4O_7$) were received from Kopp Glass, Inc., to characterize their effect on refractory corrosion. Among the two glass batches, one was prepared using powdered cadmium sulfide (unpelletized), while the other was prepared using pelletized cadmium sulfide.

The three refractory bricks were machined to form cube specimens 2 in. (≈5.1 cm) on a side. Subsequently, a cylindrical cavity [0.5 in. (≈1.3-cm) diameter x 0.75 in. (≈1.9-cm) deep] was machined at the top center in the cubes, as shown in Fig. 1. This cavity was filled with 2.2 g of the borax glass for the corrosion experiments; this amount was sufficient to fill ~95% of the cavity. The corrosion experiments consisted of heating the refractory cubes (filled with glass) in a box furnace (air atmosphere) to different temperatures, holding the cubes at pre-selected temperatures for a specific period of time, and subsequently cooling to room temperature. Corrosion testing for each refractory was performed with both pelletized and unpelletized glasses. The test temperatures were selected as 1371 and 1460°C. The time of exposure at these temperatures was varied

from 10 to 100 h. The furnace was heated and cooled at a rate of 300°C/h. After each experiment, the refractory cubes were visually inspected and subsequently cross-sectioned at the center cavity to evaluate the extent of corrosion. The extent of corrosion was estimated by measuring the depth of glass penetration/corrosion into the refractory at the glass/refractory interface. Further, small samples of the corroded area were machined from the cross-sectioned region and were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Results and Discussion

Experiments conducted at 1371°C for 10 to 50 h using unpelletized glass exhibited no visible corrosion damage in the three refractories. Similarly, no corrosion was visible for the three refractories tested at 1460°C for 10 to 50 h. However, when tested at 1460°C for 100 h, the three refractories exhibited varying degrees of corrosion. Figure 2 shows cross-sectional views of the three refractories exposed to unpelletized glass at 1460°C for 100 h. It is apparent that the VISION TILE (Fig. 2a) exhibits the maximum corrosion, while the L. E. Smith refractory (Fig. 2c) shows insignificant or no corrosion. Figure 2c indicates that the glass was unable to penetrate into L. E. Smith refractory even after a long exposure.

Cross-sectional evaluation of the three refractories exposed to pelletized glass at 1460°C for 100 h showed corrosion damage similar to that observed in Fig. 2. The average depth of corrosion in the two refractories, VISION TILE and RESERV® 70, is approximately 10 mm and 3 mm, respectively, as shown in Fig. 3. It is also clear from Fig. 3 that the corrosion depth for each refractory is similar in the unpelletized and pelletized glasses.

XRD analysis was performed on the corroded surface along the penetration depth in VISION TILE and RESERV® 70 refractories exposed to 1460°C for 100 h. The XRD profiles for VISION TILE before and after exposure to glasses are shown in Fig. 4. Figure 4a shows diffraction peaks corresponding to Al_2O_3, SiO_2, and ZrO_2, confirming the composition of the as-received refractory. The X-ray profile for the corroded surface after exposure to unpelletized glass (Fig. 4b) shows the formation of different sodium compounds such as sodium silicate and sodium zirconium oxide. From Fig. 4b, a small quantity of aluminum silicate is also formed. This material probably appears because of

reactions between the refractory constituents (alumina, silica), which apparently become unstable in the presence of molten glass. Possible corrosion reactions are

$$Na_2B_4O_7 + \left.\begin{matrix} SiO_2 \\ Al_2O_3 \\ ZrO_2 \end{matrix}\right] \longrightarrow \begin{matrix} Na_4SiO_4 \\ Al_2(SiO_4)O \\ ZrSiO_4 \\ Na_2ZrO_3 \end{matrix}$$

(Glass) (R fræcto :rVISyIO TNLE)

Note that the above reaction does not reflect the refractory constituents that are less than 5%, and the "Na" in glass is the most reactive species.

Figure 4c shows the XRD profile for the VISION TILE refractory surface exposed to pelletized glass. This profile shows the formation of identical corrosion products as in Fig. 4b, suggesting no significant difference in the corrosion behavior of the refractory exposed to pelletized versus unpelletized glass. XRD profiles obtained at various locations along the depth of penetration indicated the same corrosion products, suggesting uniformity of corrosion along the depth of penetration. This finding was also confirmed by the X-ray dot-mapping obtained by energy dispersive spectroscopy. Figure 5(a, b) represents elemental dot-maps for Na and Si, which are constituents of the glass and VISION TILE refractory, respectively. Figure 5c represents a composite of the two maps, which clearly shows an overlapping of the locations of the two elements, suggesting the formation of complex corrosion products. Similar results were obtained for other refractory constituent elements such as Al and Zr.

Figure 6 represents the XRD profile for RESERV® 70 before and after exposure to unpelletized and pelletized glasses. Figure 6a shows the presence of Cr_2O_3 and Al_2O_3, corresponding to the composition of the as-received refractory. The XRD profile of the corroded surface after exposure to unpelletized glass, shown in Fig. 6b, indicates the formation of complex sodium chromium oxide and sodium aluminum oxide compounds.

Possible reactions are

$$\underset{\text{(Glass)}}{Na_2B_4O_7} + \left.\begin{matrix} Al_2O_3 \\ Cr_2O_3 \end{matrix}\right] \longrightarrow \begin{matrix} NaAlO_2 \\ Na_{1.5}Al_{11.83}O_{17} \\ Na_{0.74}CrO_2 \\ Na_{0.5}CrO_2 \end{matrix}$$

Refra tory: RESERV® 70

Note that the reaction does not show the refractory constituents that are less than 5%.

Figure 6c shows the XRD profile of the RESERV® 70 refractory exposed to the pelletized glass. This profile shows the formation of the same corrosion products as in Fig. 6b, suggesting no significant difference in the corrosion behavior of the refractory exposed to pelletized versus unpelletized glass.

Summary

Corrosion testing of VISION TILE, RESERV® 70, and L. E. Smith refractories in pelletized and unpelletized glasses was performed in air at 1371 and 1460°C for 10 to 100 h. The following observations were made:

1. No corrosion damage occurred for the three refractories tested at 1371°C for 10 to 50 h. However, refractories tested at 1460°C for 100 h exhibited varying degrees of corrosion.

2. For testing performed at 1460°C for 100 h, VISION TILE exhibited the maximum corrosion, while the L. E. Smith refractory exhibited little or no corrosion.

3. Corrosion depth was ~10 mm for the VISION TILE and ~3 mm for the RESERV® 70 refractory.

4. The depths of corrosion for each refractory was observed to be similar in both pelletized and unpelletized glasses, suggesting that there is no significant effect of pelletization on the corrosion behavior of the refractories exposed to the two glasses.

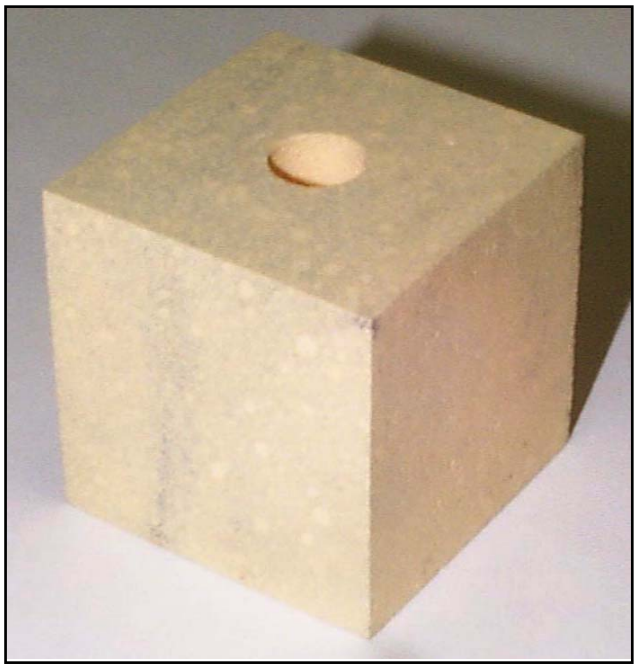

Fig. 1. Picture showing a typical cube specimen (2 in. on a side) machined from the refractory bricks. A cylindrical cavity (0.5 in. diameter and 0.75 in. deep) in the center of the cube is also apparent.

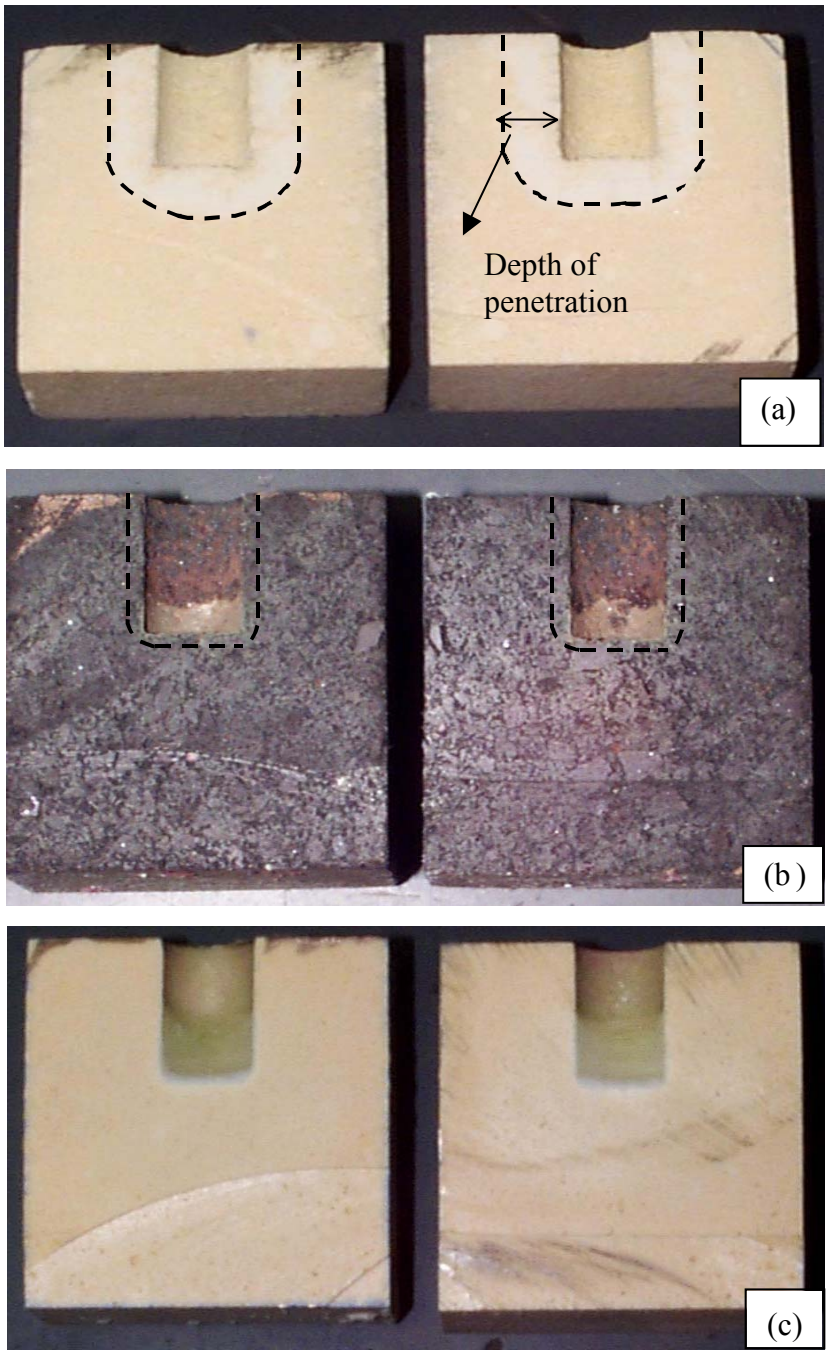

Fig. 2. Cross-sectional views of the refractories exposed to unpelletized glass at 1460°C for 100 h.: (a) VISION TILE, (b) RESERV® 70, and (c) L. E. Smith. VISION TILE and RESERV® 70 show measurable corrosion depth, while L. E. Smith shows no corrosion reaction with glass.

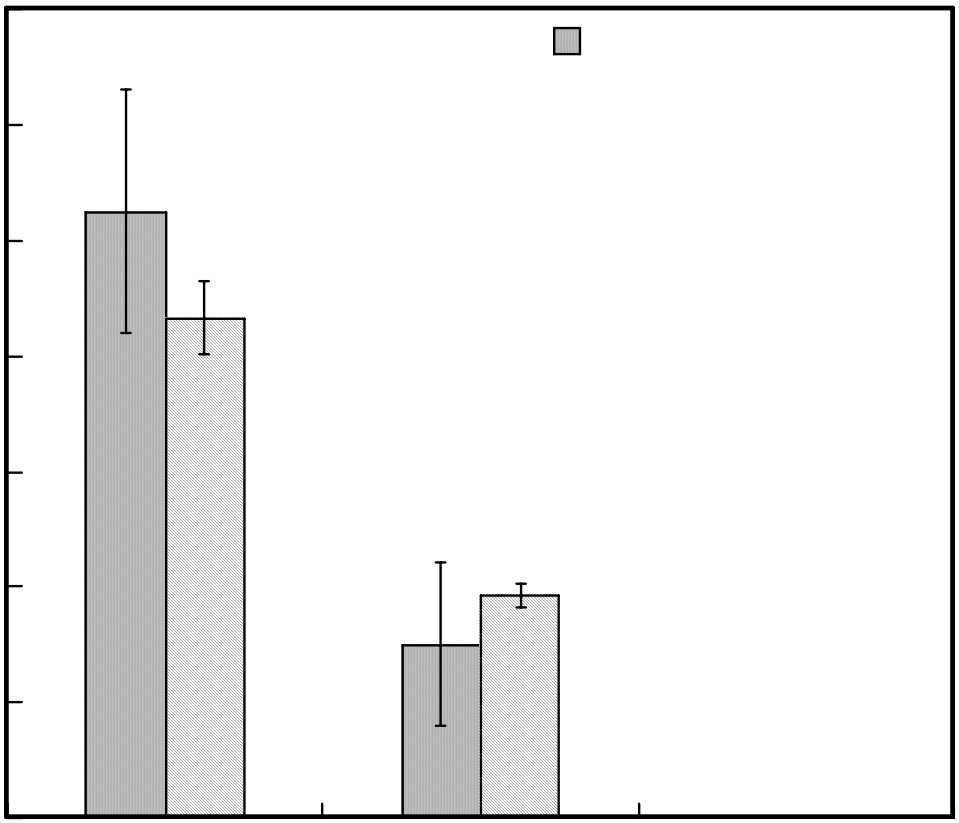

Fig. 3. Observed corrosion depths in VISION TILE, RESERV® 70, and L. E. Smith refractories after exposure to unpelletized and pelletized glasses at 1460°C for 100 h.

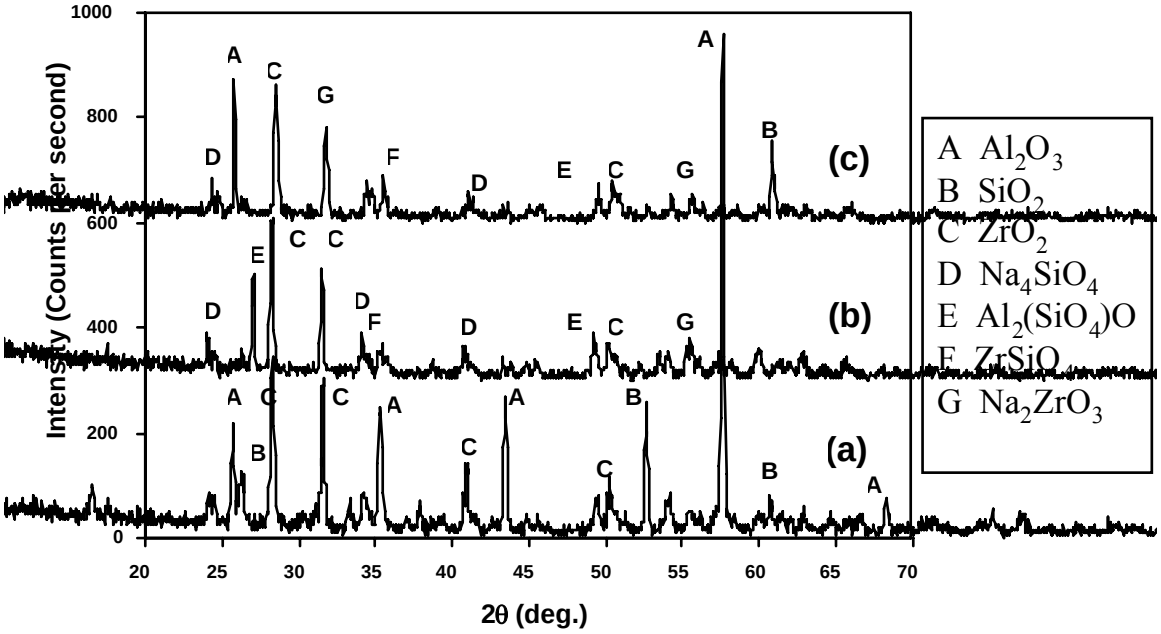

Fig. 4. XRD plots for VISION TILE refractory: (a) unexposed, (b) exposed to unpelletized glass, and (c) exposed to pelletized glass, at 1460°C for 100 h.

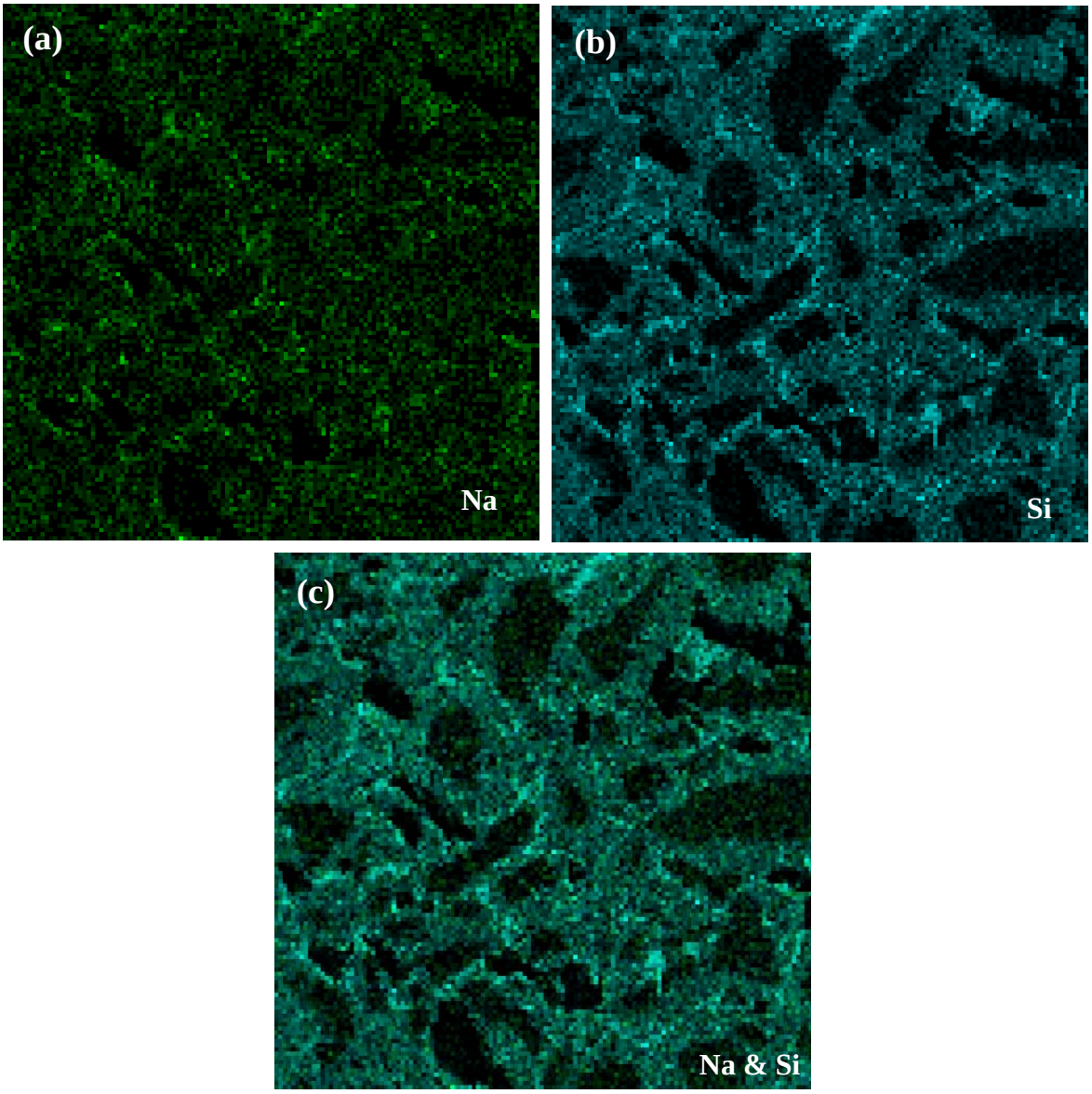

Fig. 5. X-ray elemental dot-maps for a randomly selected corroded region from VISION TILE refractory: (a) glass constituent Na (green color), (b) refractory constituent Si (blue color), and (c) overlapping of Na and Si maps indicating the formation of complex corrosion products.

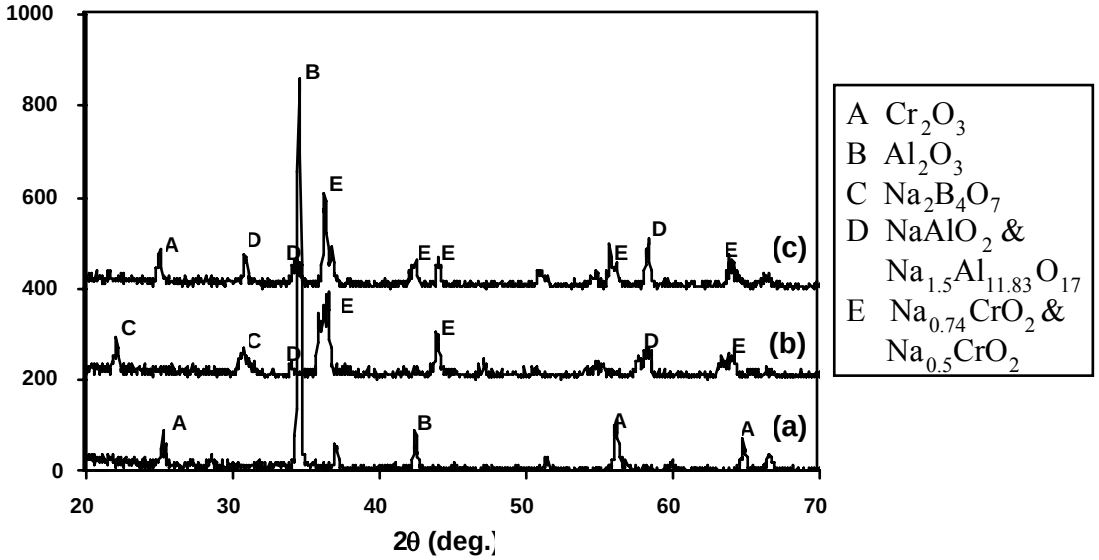

Fig. 6. XRD plots for RESERV® 70 refractory: (a) unexposed, (b) exposed to unpelletized glass, and (c) exposed to pelletized glass, at 1460°C for 100 h.