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**Effects of Alternate Fuels
Report No. 5
Analysis of Fused Cast AZS Refractory,
Silica Refractory, and High-MgO Refractory
Degraded by Residual Oil Combustion Products**

G. C. Wei
V. J. Tennery

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METALS AND CERAMICS DIVISION

EFFECTS OF ALTERNATE FUELS

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ANALYSIS OF FUSED CAST AZS REFRACTORY, SILICA REFRACTORY,
AND HIGH-MgO REFRACTORY DEGRADED BY RESIDUAL OIL COMBUSTION PRODUCTS

G. C. Wei and V. J. Tennery

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ABSTRACT

This study is the fifth of a series of reports on analyses of several types of refractories that have been used in industrial furnaces with fuels considered to be alternates to natural gas. The objective of this study is to better understand the subject refractory degradation process and to provide viable means to retard the deterioration. We analyzed fused cast AZS tuckstone brick, silica crown skew brick, and high-MgO checker brick used for only six months in a glass melting furnace fired with a residual oil that contained 175 ppm V and 2-3% S as major impurities. During the furnace campaign, the maximum hot face temperatures of the AZS refractory, the silica refractory, and the high-MgO refractory were 1530, 1530, and 1430°C, respectively.

The original microstructure of the fused cast AZS tuckstone, which consisted of zirconia, corundum, and mullite crystalline phases in a siliceous glass matrix, was altered at the hot face of the brick. The new microstructure, which consisted of crystalline zirconia in a sodium-rich, low-viscosity glass phase, resulted from reactions of batch carryover with the refractory in the presence of fuel oil combustion products. Such reactions caused the observed fast corrosion in the AZS refractory. Spinel was formed from reactions of magnesia carryover with corundum in the hot-face region of the refractory. Adding spinel to the AZS refractory or increasing the ZrO_2 content while maintaining the ratio of Al_2O_3/SiO_2 greater than or equal to the original ratio of 4 should improve the refractory performance for applications involving corrosive environments similar to the present case.

The silica crown skew brick reacted with batch carryover to form a low-viscosity soda-lime-silica glass, which constantly drained from the silica brick into the glass batch. Such reactions apparently were enhanced by the presence of fuel oil combustion products. The possibility of overheating on the hot face of the silica brick due to incorrect burner operation was ruled out because of the lack of an elongated morphology of the silica grains and pores. The observed severe corrosion in the silica refractory was primarily caused by reactions of the calcium silicate bonding phases in the silica refractory with batch carryover in the presence of

vanadium- and sulfur-bearing species derived from fuel oil combustion products. Adding to the silica refractory mineralizers that are not lime-based and resist reactions with batch carryover and removing the calcium-containing phases after firing should improve the corrosion resistance of the silica refractory or retard reactions of the refractory with batch carryover and fuel oil combustion products.

The refractoriness and the high-temperature load-bearing capability of the high-MgO checker brick were degraded because the original forsterite bonding phase transformed to monticellite by reactions with lime and silica carryover. The monticellite phase, in turn, reacted with vanadium from the fuel oil to form low-melting liquid phases at operating temperatures. Decreasing the CaO content in the high-MgO refractory, using a forsterite bond, or using a direct bond in the high-MgO refractory should improve its performance in a corrosive environment similar to the present case.

INTRODUCTION

In recent years, the shortage and curtailments of natural gas in the United States as well as the increasing concern for industrial energy conservation have required conversion of many industrial furnaces to alternate fuels, such as distillate and residual oils, coal, low-joule gases, and other forms of energy, such as electricity. Among these possible choices, distillate and residual oils have been identified as the primary alternate fuels for industrial heating applications in the near term,¹ assuming there will be a sufficient supply of fuel oil from both domestic and foreign sources and that oil prices do not increase drastically. Distillate oils are relatively free of impurities, and the effects of distillate oil combustion on refractories are minor if the combustion system is properly installed and operated. Residual oils may offer economic advantages over distillates. However, residual fuel oils may contain substantial amounts of many impurities such as sodium, vanadium, and sulfur, which can be quite detrimental to furnace refractories and insulations. Currently industrial refractory operating experience in the United States with residual oils is limited. It is therefore

instructive to analyze refractories that have been exposed to residual oil combustion in industrial furnaces and exhibit greater degradation than they would in a natural gas or distillate oil combustion environment.

The present report is an analysis of a fused cast AZS tuckstone brick, a silica crown skew brick, and a high-MgO checker brick used in a glass melting furnace fired with residual oil. Chemical, optical microscopy, x-ray diffraction, scanning electron microscopy, and electron microprobe analyses were performed on the used refractories to determine the cause for the observed severe corrosion or the accelerated degradation in the refractories.

This is the fifth of a series of reports on analyses of several generic refractory types that have been used in industrial furnaces with either residual oils or coal as fuel.²⁻⁵

SPECIMEN HISTORY

The three refractory bricks examined in this study were taken from a continuous glass melting furnace that was fired with natural gas for approximately 36 months, then with residual oil for six months. After six months operation with the residual oil, severe corrosion of the fused cast AZS ports and the silica crown at the skew line was observed. Figure 1 illustrates the locations of the tuckstone and the crown skew. The location of regenerator checker brick was shown in a previous report.³ The glass furnace operator can inspect the refractory wear from a viewport on the outside of the furnace wall. The excessive wear of the fused cast AZS tuckstone brick and the silica crown skew brick threatened to collapse the entire furnace after firing with residual oil for six months. Although typical service life for this type of glass melting furnace is three to five years when fired with natural gas, it had to be shut down for repairs 12 months earlier than planned. When the glass furnace was disassembled, the high-MgO checker bricks of the first four courses of the regenerator were found to be badly degraded.

The furnace was a 76.5-m², four-port, side-port furnace, which held a 1.47-m-deep glass melt and had a production rate of 300 metric tons/day. It was used for melting soda-lime-silica batches for container glass

Fig. 1. Locations of Tuckstone and Crown Skew in a Typical Side-Port Glass Melting Furnace.

manufacturing. The burners for residual oil firing were located above the ports. The No. 6 oil used contained 175 ppm V, 6 ppm Na, and 2 to 3% S by weight.

The fused cast AZS block (Monofrax* S-3) examined in this study was used at the tuckstone of the furnace. As shown in Table 1, the as-received Monofrax S-3 AZS brick contained 34.20 wt % ZrO_2 , 50.13 wt % Al_2O_3 , and 14.25 wt % SiO_2 in terms of oxide equivalents.

Fused cast AZS refractories are usually fabricated by casting a melt of oxides and minerals from an electric arc furnace into a refractory grain mold. When feeding ceases, the mold is stripped and the block immersed in a thermal insulation to slow down the rate of cooling and thus minimize internal stress and to obtain as uniform a crystallite size as possible. During solidification of the fused cast material, the crystal nucleation at the surface of the mold is rapid, and a large number of

* Monofrax: product of Carborundum Co., Falconer, N. Y.

Table 1. Chemical Composition of Fused Cast AZS Tuckstone Refractory

Equivalent Oxide	Content, wt %					
	As Received	Zone A	Zone B	Zone C	Zone D	Zone E
Al ₂ O ₃	50.13	37.83	55.29	57.73	64.50	55.48
B ₂ O ₃	0.15	0.23	0.80	0.34	0.24	0.81
CaO	<0.01	3.44	1.22	0.15	0.10	0.11
Cr ₂ O ₃	<0.01	0.0031	0.0017	0.0010	0.0003	0.0003
Fe ₂ O ₃	0.12	0.062	0.059	0.080	0.047	0.050
K ₂ O	<0.01	0.13	0.11	0.19	0.01	0.01
MgO	<0.01	2.07	0.22	0.03	0.01	0.01
Na ₂ O	1.10	5.63	3.16	1.98	1.58	1.56
NiO	<0.01	0.023	0.0064	0.0042	0.0040	0.0042
PbO	<0.01	a	a	a	a	a
SO ₃	<0.01	0.05	0.03	0.07	0.03	0.05
SiO ₂	14.25	33.24	15.15	17.69	14.63	14.42
TiO ₂	<0.01	0.087	0.132	0.175	0.125	0.087
V ₂ O ₅	<0.01	a	a	a	a	a
ZrO ₂	34.20	17.35	23.79	21.56	18.83	27.38

^aNot detected.

crystals of different orientations form a rim around the mold interface. These crystals tend to be oriented to form large columnar crystals growing perpendicular to the face of the casting during subsequent cooling. Because of the fast growth of these columnar crystals and the long cooling time required to minimize internal stress and prevent cracking, a large grain size inevitably develops in fused-cast materials. Large grains can result in lowered corrosion and erosion resistance to slags or molten glasses. The volume of these refractory compositions decreases 10 to 25% during the liquid-solid transition. This causes the formation of shrinkage voids, contraction cavities, or "pipes" in the casting. This formation must be controlled by suitable mold design. The voids or cavities are often disconnected from surface openings because the low thermal conductivity of the melt allows the formation of a solid surface layer. At present, fused cast AZS refractories are primarily manufactured as individual large blocks, which can be cut into smaller ones with a diamond saw, as required.

Monofrax S-3 AZS refractory has a porosity of 0.46% and has a microstructure consisting of lath-shaped corundum crystals mottled with included zirconia crystallites in a siliceous glass matrix. Zirconia dendrites are intergrown with corundum crystals. According to the manufacturer, the noncrystalline siliceous phase makes up some 18% of the AZS refractory. The maximum hot-face service temperature in the used AZS refractory analyzed in the present study was about 1530°C.

The silica refractory brick (Vega superduty*) was taken from the crown skew of the glass melting furnace. The SiO_2 content was 96.4% and the CaO content was 2.9%. The chemical composition of as-received Vega superduty silica brick is shown in Table 2. The apparent porosity was 20 to 24%. Silica bricks are generally manufactured from ground ganister rock (quartzite) containing about 97–98% SiO_2 , to which is added some 2–3 wt % CaO as a mineralizer during firing. As-received

* Vega superduty: product of Harbison-Walker Refractories, Pittsburgh, Pa.

Table 2. Chemical Composition of Silica Crown Skew Refractory

Equivalent Oxide	Content, wt %			
	As-Received	Zone A	Zone B	Zone C
Al_2O_3	0.20	0.50	0.44	0.35
CaO	2.9	1.15	2.25	4.85
Cr_2O_3	<0.01	a	a	a
Fe_2O_3	0.50	0.196	0.351	0.686
K_2O	b	0.03	0.02	0.02
MgO	<0.01	0.39	0.37	0.18
Na_2O	b	1.27	1.02	0.93
NiO	<0.01	0.0125	0.0062	0.0081
PbO	<0.01	a	a	a
SO_3	<0.01	0.01	0.01	0.01
SiO_2	96.40	96.24	95.30	92.70
TiO_2	0.02	0.043	0.086	0.084
V_2O_5	<0.01	a	a	a

^a Not detected.

^b $\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Li}_2\text{O} = 0.04$.

silica refractory brick consists of quartz grains that have been almost completely transformed into cristobalite in a matrix of fine tridymite, cristobalite, and glass. Small amounts of unconverted quartz (about 10%) are present with nearly equal amounts of cristobalite and tridymite. Lime is added to the SiO_2 content of the silica refractory to form a bonding material and to enhance the formation of tridymite from quartz and cristobalite. The latter two are subject to polymorphic transformation changes at 575 and 250°C, respectively. The hot face of the used silica brick had a maximum service temperature of 1530°C. According to the CaO-SiO₂ binary system,⁶ the 97% SiO₂-3% CaO mixture is about 9% liquid at 1530°C. Under typical conditions, this liquid is highly viscous because of its high silica content, and it tends to stay in place on the refractory at typical service temperatures.

The high-MgO refractory brick examined in the present study is a P-95 unburned brick*. It contains 94.9% MgO, 2.1% SiO₂, and 1% CaO. The chemical composition of an as-received P-95 is shown in Table 3. The high-MgO brick analyzed in this study was used as a checker brick in the fourth course from the top in the regenerator. The high-MgO checker brick experienced temperature cycling of approximately $\pm 100^\circ\text{C}$ about an average temperature of 1330°C as well as oxygen partial pressure cycling during its use. Specific information on the temperature cycling and the oxygen partial pressure cycling for this refractory is unknown. The original high-MgO brick consisted of periclase grains bonded by a silica-lime mixture, which was supposedly gradually transformed into the forsterite and monticellite bonding phases when the brick was heated during service.

The temperatures at the hot face of the bricks reported in this section were estimated by the glass company's furnace operators and based on their past experiences. These temperatures are considered to be accurate to $\pm 30^\circ\text{C}$.

*P-95: product of Kaiser Refractories, Pleasanton, Calif.

Table 3. Chemical Composition of High-MgO Checker Brick

Equivalent Oxide	Content, wt %			
	As-Received	Zone A	Zone B	Zone C
Al ₂ O ₃	0.5	0.65	0.60	0.63
CaO	1.0	4.89	4.91	5.22
Cr ₂ O ₃	1.0	0.20	0.25	0.15
Fe ₂ O ₃	0.5	0.55	0.65	0.84
K ₂ O	<0.01	0.001	0.001	0.001
MgO	94.9	87.37	86.85	86.44
Na ₂ O	<0.01	0.34	0.32	0.32
NiO	<0.01	0.02	0.05	0.25
P ₂ O ₅	<0.01	0.027	0.031	0.027
SO ₃	<0.01	0.15	0.025	0.034
SiO ₂	2.1	5.80	6.31	6.08
TiO ₂	<0.01	<0.001	<0.001	<0.001
V ₂ O ₅	<0.01	0.005	0.003	0.01

RESULTS

The fused cast AZS tuckstone brick, the silica crown skew brick, and the high-MgO checker brick were examined with chemical, x-ray diffraction, optical microscopy, electron microprobe, and scanning electron microscopy (SEM) analyses. The experimental procedures were the same as those outlined in a previous report.² Analysis results are presented in this section for each type of refractory.

Fused Cast AZS Tuckstone Brick

Figure 2 shows the fused cast AZS tuckstone brick. What was formerly the hot face of the brick was covered with a layer of glassy material. Visual inspection of a section cut through the brick indicated that the refractory consisted of five apparent zones when traversed from the hot face toward the cold end. These five zones were named A, B, C, D, and E for the convenience of reference during analysis. A sampling plan for analyzing the AZS brick is shown in Fig. 3. Zone A is a thin light pink layer (≈ 1 mm) of glassy slag on the hot face followed by zone B (≈ 5 mm deep, pink rose coloration), zone C (≈ 5 mm deep, light pink rose coloration),

TOWARD COLD END

Fig. 2. Cross Section of a Fused Cast AZS Refractory After Six Months Service in a Residual-Oil-Fired Environment. Scale is 102 mm long.

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Fig. 3. Sampling Plan of the Fused Cast AZS Tuckstone Brick.

zone D (≈ 20 mm deep, light pink rose coloration), and zone E (pink rose coloration) in that sequence when traversed toward the cold face. The boundaries between the five zones were based on the brick's appearance and coloration. The variation in color was later found to be due to the variation of the ZrO_2 content, with a lower ZrO_2 content being associated with the light pink rose coloration.

The results of chemical analysis are shown in Table 1. The SiO_2 , CaO , MgO , and Na_2O contents increased significantly in zones A and B, causing the Al_2O_3 and ZrO_2 contents in these zones to decrease sharply from their values in the original brick. Impurities common to residual oils — such as V, S, K, and Ni — are present in negligible amounts. The high Na_2O content in the hot face region of the brick apparently originated from the batch material in the glass melting furnace.

X-ray diffraction analysis of zones C, D, and E (see Appendix) showed the presence of corundum, baddileite (ZrO_2), and mullite. Mullite was not observed in zone A or B. Corundum was absent from zone A. The major crystalline phases in zones A to E are listed in Table 4. Baddileite (ZrO_2) was observed in all five zones and appears to be the most stable crystalline phase in this refractory under the service conditions cited previously.

Figure 4(a) is a photomicrograph of a top view of the microstructure of the hot face region, which consists of zirconia crystallites (the bright phase) dispersed in a siliceous glass matrix containing Na, Al, Mg, and Ca. The dark areas are pores. Figure 4(b) is a photomicrograph of zone A from the direction normal to the temperature gradient and shows basically the same features illustrated in Fig. 4(a). Both photomicrographs indicate that the pores in zone A are quite rounded. The rounded morphology of

Table 4. Major Crystalline Phases in Selected Zones of the Three Used Refractories

Zone	Crystalline Phases
<u>Fused Cast AZS Tuckstone Brick</u>	
A	Zirconia
B	Zirconia, corundum
C	Zirconia, corundum, mullite
D	Zirconia, corundum, mullite
E	Zirconia, corundum, mullite
<u>Silica Crown Skew Brick</u>	
A	Tridymite
B	Tridymite, cristobalite
C	Tridymite, cristobalite, $\alpha\text{-CaSiO}_3$ (pseudo-wollastonite)
<u>High-MgO Checker Brick</u>	
A	Periclase, monticellite
B	Periclase, monticellite
C	Periclase, monticellite

Fig. 4. Reflected-Light Micrographs of the AZS Brick, Showing Zirconia Distributed in a Glass Phase. 100 $\times$. (a) Polished section of the hot face, viewed perpendicular to the hot face. (b) Zone A, viewed perpendicular to the direction of temperature gradient.

these pores indicated that the temperature gradient through the refractory was not exceedingly high and also suggested that the hot face of the refractory did not overheat. In zone B, spinel (MgAl_2O_4) as well as zirconia and corundum was observed. The microstructure of zone B is presented in Fig. 5. It consists of spinel (S) crystallites together with zirconia (Z) and corundum (C) distributed in a siliceous glass matrix containing Na, Mg, Al, and Ca. Spinel (S) was observed in the interface of zones A and B. Zones C, D, and E have the microstructure typically characteristic of fused cast AZS refractories, as shown in Figs. 6 and 7. It consists of long corundum crystallites mottled with small zirconia crystallites together with intergrowing chainlike zirconia dendrites in a siliceous glass matrix containing aluminum and sodium. Various phases in optical micrographs were identified by the observed well-developed

Fig. 5. Reflected-Light Micrograph of Zone B of the AZS Brick Showing Zirconia (Z), Spinel (S), and Corundum (C) Distributed in a Glass Phase. 100 $\times$.

Fig. 6. Typical Microstructure of Zone C, D, or E of the AZS Brick, Showing Corundum (Light Gray) Mottled with Zirconia (White) Crystallites, White Rounded Zirconia Granules, and Long Mullite Needles in a Siliceous Glass Matrix. 100 $\times$.

morphology of the crystalline phases, electron microprobe analysis, and x-ray diffraction analysis. It should be noted that phases containing impurities such as V, S, K, and Ni commonly found in residual oils were not detected by optical microscopy or electron microprobe analysis.

However, scanning electron microscopy (SEM) analysis did reveal the presence of a small amount of vanadium in zirconia and the glass matrix of zone A. Figure 8 is a scanning electron micrograph of the fractured surface of zone A. Energy dispersive x-ray analysis identified zirconium and vanadium in area Z, which has many cleavage steps and a rough appearance. Area G has a smooth appearance, and it contains the elements Na, Al, Si, Mg, Ca, and V. These findings together with the x-ray diffraction results of zone A indicate that area Z is zirconia and area G

Fig. 7. Typical Microstructure of Zone C, D, or E of the AZS Brick, Showing Zirconia (Z), Corundum (C), and Mullite (M) in a Siliceous Glass Matrix. 500 $\times$.

Fig. 8. Scanning Electron Micrograph of the Fractured Surface of Zone A of the AZS Brick. Both the zirconia phase (Z) and the glass phase (G) have slight vanadium contents.

is a glass phase, and both contain a small amount of vanadium. Analysis by SEM of zones B, C, D, and E showed typical microstructures of fused cast AZS refractories, and no vanadium was observed.

Silica Crown Skew Brick

The silica crown skew brick was about 180 mm long as received. The sample shown in Fig. 9 is about one half of the whole piece, with the cold end broken off. Visual inspection indicated three zones in the brick.

Fig. 9. A Silica Crown Skew Brick After Six Months Service in a Residual-Oil-Fired Environment.

The hot face was white and appeared rough with many rounded pores. Brick zone A extending from the hot face to a depth of 50 mm toward the cold end was also white. From a depth of 50 to 100 mm the brick appeared light gray, and this zone was designated B. At a depth of 150 mm from the hot face, the brick was light brown. This zone (designated C) extended from 100 to 180 mm toward the cold end. A sampling plan based on the zone distinction described above is shown in Fig. 10.

Fig. 10. Sampling Plan of the Silica Crown Skew Brick.

Chemical analyses of zones A, B, and C are listed in Table 2. The SiO_2 and Na_2O contents in zones A and B are significantly greater than in zone C. Notable are the smaller CaO and Fe_2O_3 contents in zone A or B compared with zone C. The MgO and Al_2O_3 contents are essentially the same in all three zones. The contents of V_2O_5 , SO_3 , K_2O , and NiO in all three zones are negligible.

The major crystalline phases in the three zones are listed in Table 4. In zones A and B, tridymite and cristobalite are major crystalline phases. Zone C, which is close to the cold end of the

brick, contains pseudo-wollastonite (α - CaSiO_3) in addition to tridymite and cristobalite. The x-ray diffraction data expressed in terms of lattice spacings are presented in the Appendix.

The microstructure of the hot face consists of rounded silica grains and a glassy phase composed of soda, lime, and silica. A photomicrograph of a polished section of the hot face (view in the direction perpendicular to the hot face) is shown in Fig. 11. The microstructure of zone A viewed in a direction perpendicular to the temperature gradient is illustrated in Fig. 12. From Figs. 11 and 12, we can conclude that the silica grains are rounded and little elongation had occurred. The lack of elongation of silica grains indicated no overheating at the hot face of the silica refractory during service. The direct bonding of silica grains was still present, but the original calcium silicate bonding phase had been changed

Fig. 11. Reflected-Light Micrograph of a Polished Section of the Hot Face (Zone A) of the Silica Brick (Top View of the Hot Face), Showing the Network of a Glass Phase Connecting Spheroidal Silica Grains. 100 $\times$.

Fig. 12. Typical Microstructure of Zone A or B of the Silica Brick, Showing the Infiltration of the Glass Phase into the Silica Brick Structure and the Silica Grains of the Silica Brick. (View in the direction perpendicular to the direction of the temperature gradient.) 100 $\times$.

to a continuous glassy phase containing soda, lime, and silica. A similar microstructure was observed in zone B. A typical microstructure of zone C, shown in Fig. 13, consists of large silica grains and calcium silicate bonding phases consisting of wollastonite and a glassy phase containing soda, lime, and silica.

Scanning electron microscopy analysis of the fractured surfaces of zones A, B, and C revealed microstructures shown in Figs. 14 and 15. In zone A or B, silica grains and a soda-lime-silica bonding phase were observed. Large silica grains and a bonding phase containing calcium and silicon, as shown in Fig. 15, were observed in zone C. This observation coupled with the x-ray diffraction results of zone C indicated that the needle dendrites in zone C were pseudo-wollastonite (α - CaSiO_3).

Fig. 13. Reflected-Light Micrograph of Zone C of the Silica Brick, Showing Silica Grains and Calcium Silicate Bonding Phases. 100 $\times$.

Fig. 14. Scanning Electron Micrograph of the Fractured Surface of Zone A or B in the Silica Brick, Showing the Glass Phase (G) and the Silica Grains (S).

Fig. 15. Scanning Electron Micrograph of the Fractured Surface of Zone C in the Silica Brick, Showing Silica Grains (S) and Pseudo-Wollastonite (α -CaSiO₃) (C).

High-MgO Checker Brick

About half of the high-MgO checker brick is shown in Fig. 16. Visual inspection indicated cracks throughout the brick, and the entire brick section had a brown coloration. For analysis, the brick was divided into three zones (Fig. 17): A, B, and C, each approximately 50 mm thick, starting from the broken end of the brick.

Chemical analyses of zones A, B, and C (Table 3) indicated that the compositions of the three zones were essentially the same, with a significant increase in the CaO and SiO₂ contents compared with the original brick, whereas the Na and S contents were negligible. Other impurity concentrations — including V₂O₅, K₂O, and NiO — were also negligible. The Fe₂O₃ and Al₂O₃ contents are close to the reported original composition (0.5 wt %).

X-ray diffraction analyses of zones A, B, and C showed periclase (MgO) and monticellite (CaO•MgO•SiO₂) to be the major crystalline phases (Table 4). The original x-ray diffraction data expressed in terms of lattice spacings are presented in the Appendix.

Fig. 16. A High-MgO Brick After Six Months Service in a Residual-Oil-Fired Environment.

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SIDE VIEW

Fig. 17. Sampling Plan of the High-MgO Checker Brick.

The microstructures of zones A, B, and C appeared similar. A typical microstructure of the brick is shown in Fig. 18. Periclase (P) grains are bonded together by monticellite (M), the bonding phase. Electron microprobe analysis on the polished sections of zones A, B, and C revealed no significant amounts of V, Na, or S.

The energy dispersive x-ray analyses with the SEM of zones A, B, and C revealed the presence of vanadium. It was found along with Ca, Mg, and Si in small particles (V), which appeared to form from the original monticellite phase. Figures 19 and 20 show vanadium-containing phases along with periclase (P) or monticellite (M). Vanadium distribution in the high-MgO brick was rather localized and was always associated with Ca, Mg, and Si. It should be noted that vanadium was easily detected in the small particles described above by energy dispersive x-ray analysis. The reason why vanadium was found by EDXA of SEM, but not by chemical analysis or electron microprobe analysis was not identified.

Fig. 18. Typical Microstructure of Zone A, B, or C of the High-MgO Brick, Showing Periclase Grains (P) Bonded with Monticellite (M). 100 $\times$.

Fig. 19. Scanning Electron Micrograph of the Fractured Surface of Zone A in the High-MgO Checker Brick, Showing Vanadium-Bearing Particles (V) Along with Monticellite (M).

Fig. 20. Scanning Electron Micrograph of the Fractured Surface of Zone A in the High-MgO Checker Brick, Showing the Vanadium-Containing Area (V) and Periclase (P).

DISCUSSION

Fuel Oil Combustion Products

According to the glass company who supplied the used refractories for analysis, the particular No. 6 oil used contained vanadium and sulfur as major impurities: 175 wt ppm V, 2 to 3 wt % S. The glass melting furnace had an output of 300 metric tons of glass per day and consumed about 34.1 m^3 of No. 6 oil daily. After six months use of residual oil, the cumulative quantity of vanadium and sulfur discharged from the residual oil were 1.07 and 153 Mg, respectively. Expressed in terms of oxides, these would correspond to $5.88 \times 10^3 \text{ mol}$ of V_2O_5 and $2.39 \times 10^6 \text{ mol}$ of SO_2 . Part of this would escape from the furnace stack, but appreciable amounts were available to react with furnace and regenerator refractories. The reactions that occurred during refractory service were solid-vapor,

solid-liquid, or solid-solid reactions, depending on the local temperature and oxygen partial pressure. The reaction products could be in the form of solid, liquid, or vapor.

Vanadium was observed in the AZS tuckstone brick and the high-MgO checker brick by SEM and EDXA. However, sulfur was not observed in either the AZS, the silica, nor the high-MgO brick, and vanadium was not found in the silica brick. A plausible explanation is that the high temperatures at the brick surfaces that were exposed to the furnace atmosphere prevented the condensation of sulfur-bearing species on the refractories. The absence of vanadium in the silica crown skew brick was possibly due to the constant dripping and draining of the vanadium-containing reaction products from the surface of the brick into the glass melt in the furnace.

In addition to V and S, which originated from the fuel oil, Na, Ca, Mg, and Si were also present in the furnace atmosphere from the raw material used in the glass furnace including soda, lime, dolomite, and silica. The batch carryover including Na-, Ca-, Mg-, and Si-containing species reacted with furnace and regenerator refractories regardless of the type of fuel used. The rapid deterioration observed in the three refractories reported here was due to fuel oil combustion products coupled with the batch carryover reacting with the refractories. A possibly higher flame temperature with residual fuel oil than with natural gas could also have contributed to the refractory degradation, but this possibility was ruled out by the analyses, as discussed in the following section.

Refractory Deterioration Mechanisms

AZS Refractory

In this section, the mechanisms of the observed degradation in the fused cast AZS tuckstone brick, the silica crown skew brick, and the high-MgO checker brick will be discussed sequentially in terms of the chemical, structural, and microstructural changes that occurred in the refractories during their service life in the glass furnace.

Fused cast AZS material is currently used widely in the United States as glass furnace refractory. The observed dissolution of the original corundum and mullite phases in the newly formed glass phase at and near the hot face in zones A and B of the AZS brick was not surprising and had been known to glass refractory specialists for many years.⁷ However, the observation of spinel at the interface of zones A and B was unexpected. There was reportedly no spinel phase in the original AZS brick. The spinel phase must therefore be formed by reaction of the original refractory, the furnace batch carryover, and the residual oil combustion products. The reaction probably involved corundum in the original refractory with MgO derived from the batch carryover. The reaction can be described by:

The morphology of the resultant spinel phase was not elongated, so the hot-face temperature of the AZS block was not extremely high. The possibility of overheating on the AZS refractory surfaces due to the conversion to fuel oil was thus ruled out.

Analysis results indicated extensive reactions of Na, Ca, Si, and Mg carryover with the original refractory in zones A and B. The relatively high rate of these reactions was probably due to the presence of such fuel oil combustion impurities as vanadium, which was observed in minor amounts in zone A. In this case, vanadium most likely was in the form of V_2O_5 vapor, which reacted with the refractory and/or enhanced the reactions between batch carryover material and the refractory. A mechanism involving vanadium-containing vapor could account for the minor amounts of vanadium detected in zone A. Among the crystalline phases present in the original refractory, zirconia was the most stable in this application.

The chemical composition of zone E (14.4 wt % SiO_2 , 55.5 wt % Al_2O_3 , and 27.4 wt % ZrO_2) is very close to that of the ternary eutectic of the ZrO_2 - Al_2O_3 - SiO_2 system⁹ (17 wt % SiO_2 , 53 wt % Al_2O_3 , and 30 wt % ZrO_2) with a liquidus temperature slightly below 1800°C. In fact, the chemical compositions of zones B, C, D, and E are all close to the ternary eutectic composition of the ZrO_2 - Al_2O_3 - SiO_2 system. Minor variations of the ZrO_2

content caused the observed variation in the coloration of the refractory zones. The change in the ZrO_2 content of zone A or B can be explained by reactions with batch carryover, but the variation of the ZrO_2 contents in zones C, D, and E is still unexplained. The Al_2O_3/SiO_2 ratio is about 4 in zones B, C, D, and E. In zone A, the Al_2O_3/SiO_2 ratio was 1.2, with the silica increase being due to the available silica batch carryover. The drastically decreased ratio of Al_2O_3/SiO_2 in zone A also agrees with the observed large amount of glass phase present in zone A.

In summary, the degradation in the AZS tuckstone brick was primarily caused by the reactions of the refractory with batch carryover in the presence of vanadium in the fuel oil combustion products. The reaction product was a glass phase, which at the service temperature dissolved all the original crystalline phases except zirconia. A new spinel phase also crystallized from the melt on the surface of the refractory.

Silica Refractory

Silica brick is widely used in sprung arches as roofs for glass tanks because of its outstanding high-temperature load-bearing capability and its characteristic of not adversely contaminating the glass melt, although dripping or draining does occur on silica refractories at the hot face. It is well known that glass batch carryover such as soda, lime, and silica can flux the silica brick and cause an increased amount of glass melt to drain from the silica brick into the tank.⁷ The thermal conductivity of a silica refractory probably decreases as a result of the chemical and microstructural changes in the silica brick, and thus produces a higher temperature at the hot face. One possible mechanism for the observed accelerated corrosion in the silica crown skew brick was overheating at the hot face of the brick because of the different flame characteristics of residual oil as well as the lowered thermal conductivity of the brick during service. The lack of the normally observed elongated silica grains and/or elongated pores in the used silica brick characteristic of this refractory following long-term high-temperature service⁸ rules out the possibility of overheating as the solitary cause for the observed accelerated corrosion.

Fuel oil combustion products such as vanadium and sulfur were not observed in the used silica brick, probably because the high hot-face temperature prevented physical deposition of vanadium- or sulfur-bearing solid phases from vapor species present in the furnace atmosphere. The constant draining of the resultant liquid phase in the hot end of the silica brick away from the refractory limits the amount of residual glass phase. This mechanism can also explain the relatively low alkali and vanadium contents in the hot-face region. Although vanadium is essentially absent from the used brick, it could have been present in the dynamically draining melt phase and in a vapor phase at the hot-face region of the brick during service. However, the glass product and the furnace atmosphere were not analyzed for vanadium during this campaign. The degradation mechanism of this refractory then appears to have consisted of batch carryover reacting with the calcium silicate bonding phase of the silica refractory in the presence of fuel oil combustion products. These reactions occurred much faster than they would in a combustion environment where natural gas fuel is used.

The reported effect of vanadium on silica refractories is based on analyses of quenched mixtures of powders of vanadium compounds and silica refractories that had been heat-treated at high temperatures. Two such studies^{10,11} concluded that vanadium did not increase the corrosion rate of silica refractories up to 1600°C. However, this type of experiment did not truly simulate the environment in a glass-melting furnace, and thus the results would not be directly related to the present case.

It is obvious from the analyses that the calcium silicate bonding phase present in the refractory is prone to reaction with batch carryover. Calcium silicate is traditionally added to the silica refractory before firing as a mineralizer to enhance the transformation of quartz into the more desirable cristobalite or tridymite.

In summary, batch carryover reacted with the calcium silicate phase in the silica brick at an accelerated rate because fuel oil combustion products were present in the furnace. The resultant liquid phase drained from the original refractory body.

MgO Refractory

The high-MgO checker brick reacted with batch carryover, including CaO and SiO₂, so that bulk chemical analyses of zones A, B, and C in the sample showed a significant increase in the silica and lime contents relative to the original brick. The ratio of CaO/SiO₂ changed from 0.48 in the original refractory to 0.83 in the used refractory. This change agrees with the findings that the bonding phase in the used brick consists largely of monticellite instead of a combination of forsterite and monticellite reported by the manufacturer to be the bonding phases in the original brick. It should be noted that monticellite (mp 1490°C) has a considerably lower melting point than forsterite (mp 1900°C).¹² The predominance of monticellite as the bonding phase in the used high-MgO brick therefore reduces its refractoriness. Accompanying the conversion of the bonding phases from a mixture of forsterite and monticellite to only monticellite was the reaction of monticellite with vanadium derived from the fuel oil.

Analysis results indicated unambiguously that some small particles in the used high-MgO brick contained V in addition to Ca, Mg, and Si. The lack of a well-defined crystalline habit for these particles suggests that they are amorphous or glassy phases. Since the presence of these vanadium-containing phases was always associated with Ca, Mg, and Si (see Figs. 19 and 20), we believe that vanadium reacted with monticellite to form a low-melting liquid phase, which resulted in the observed small vanadium-containing particles upon refractory cooldown.

Reaction of vanadium with monticellite in basic refractories has been reported.³ Indeed, thermochemical calculations suggested that monticellite is unstable while forsterite is stable in the presence of vanadium¹³ under conditions typical for the sample reported on here. Although vanadium was identified in the used high-MgO checker brick by SEM and energy dispersive x-ray analysis, bulk chemical analysis showed rather small amounts of vanadium (<0.1 wt % V₂O₅). The Na₂O and SO₃ contents are also small in the used high-MgO brick. These results were probably due to the relatively high temperatures at the refractory surfaces that were exposed to batch carryover and residual oil combustion products

during use. At such temperatures, most of the sodium-, sulfur-, and vanadium-bearing species are in vapor form. Thus, little of these impurities was condensed onto the external and accessible internal surfaces of the brick even though the brick had an apparent porosity of about 20%.

In summary, batch carryover including CaO and SiO₂ reacted with the analyzed high-MgO brick to change the bonding phases to predominantly monticellite. Vanadium as a fuel oil impurity aggravated the situation by reaction with monticellite to form a low-melting liquid phase during refractory use. Upon thermal cycling in the regenerator, these reaction products caused the extensive cracks, loss of refractoriness, and consequent degradation in the load-bearing capability of the high-MgO brick.

The degradation mechanism of the present high-MgO brick is quite different from that of a high-MgO checker brick³ that showed gross swelling in brick portions not under the constraint of neighboring checker bricks. The swelling and the extensive cracking in that high-MgO brick were due to the formation of Na₂SO₄ liquid and solid, and MgSO₄ solid in the refractory, where sodium and sulfur were derived from fuel oil combustion products. The observed different degradation mechanisms of the same type high-MgO brick cited here indicate that refractory degradation depends strongly on the particular type of fuel oil used and its impurities.

Refractory Composition Recommendations

AZS Refractory

The fused cast AZS refractory composition had an original ratio of Al₂O₃/SiO₂ of about 4. Increasing or decreasing the ratio of Al₂O₃/SiO₂ while keeping the ZrO₂ content constant probably will not improve the corrosion resistance of the AZS refractory in the present application because both corundum and mullite were dissolved in the liquid phase at the hot face. Since ZrO₂ is the most stable crystalline phase under such severe corrosion condition, increasing the ZrO₂ content while keeping the ratio of Al₂O₃/SiO₂ at least 4 will improve the corrosion resistance of

the fused cast AZS refractory used in a corrosive environment similar to the present case. Increasing the ZrO_2 content while keeping the ratio of Al_2O_3/SiO_2 greater than 4 is also in line with the direction of moving away from the ternary eutectic in the $ZrO_2-Al_2O_3-SiO_2$ system.

Silica Refractory

Lime is used as a mineralizer in the fabrication and firing of silica refractories. Since the resultant calcium silicate bond phases are prone to reaction with batch carryover, in the presence of residual fuel oil combustion products, to form relatively low-melting liquid phases, it is advisable either to use some other mineralizer in place of lime in the fabrication of silica refractories or to somehow remove the calcium-bearing phases after firing of lime-bonded silica refractories. Alternate bonding systems to the lime include forsterite, iron oxide, alkali, titania, and phosphate. Iron oxide and titania bonds are generally considered not acceptable because of possible discoloration of the glass product. Alkali and phosphate bonds are probably less corrosion resistant than the lime bond in silica refractory for application in a glass furnace. Since forsterite is relatively stable with respect to reactions with fuel oil impurities such as vanadium,¹³ silica refractories bonded with forsterite are a possible alternative to provide better corrosion resistance. However, the technology of forsterite-bonded silica refractories is apparently not well established at present.

MgO Refractory

The analyses showed that the forsterite and monticellite bonding phases in the high-MgO checker brick were easily converted largely to monticellite by reaction of the refractory with lime and silica carryover during service. Decreasing the original lime and silica contents in the high-MgO brick or using a direct bond system will result in formation of less monticellite in the high-MgO brick and thus better maintain the refractoriness and the load-bearing capability during a typical glass furnace campaign. The monticellite phase also reacted with vanadium

fuel oil impurities to form a low-melting liquid in the high-MgO refractory at the service temperature. Since forsterite is stable with respect to reactions with vanadium,^{3,13} we thus recommend that forsterite-bonded high-MgO refractories or direct-bonded high-MgO compositions be used as regenerator checker bricks in glass furnaces employing residual oil combustion.

CONCLUSIONS

1. The cold end of the fused cast AZS refractory (zones C, D, and E) consisted of interlocking zirconia and corundum phases along with some mullite in a siliceous glass matrix. Glass batch carryover including soda, lime, and silica reacted with the AZS refractory, in the presence of vanadium- and sulfur-bearing species derived from the fuel oil combustion products, to form a new and less refractory glass phase in zones A and B. The microstructure of zone A (located at the hot face) consisted of zirconia dispersed in this glass phase. The formation of this sodium-rich, relatively low-viscosity melt and the flow of this melt from the fused cast AZS refractory to the glass batch contributed to the fast corrosion and the drastically shortened service life. Zone B consisted of zirconia and corundum crystals dispersed in the modified glass phase. Spinel (MgAl_2O_4) formed as a result of the reaction of magnesia in the batch carryover with corundum at the interface region of zones A and B. Increasing the ZrO_2 content while keeping the ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ equal to or greater than 4 or incorporating spinel into the refractory should improve its corrosion resistance for such applications.

2. The calcium silicate bond of the silica crown skew brick was seriously fluxed by batch carryover. The presence of vanadium- and sulfur-containing vapor species appreciably enhanced the reaction rate of the lime-bonded silica brick with materials in the batch carryover. These reactions produced a high-sodium, low-viscosity glass melt, which infiltrated the brick structure at the hot-face region and constantly drained from the hot face of the silica brick. This accelerated the corrosion and degradation of the silica refractory. Removing the calcium silicate from the silica refractory after fabrication or using mineralizers

(other than lime) that are resistant to reactions with batch carryover and fuel oil combustion products should improve the corrosion resistance of silica refractories for applications such as the present case.

3. The original forsterite and monticellite bonding phases of the high-MgO checker brick were altered to a bonding system consisting largely of monticellite by reactions of the refractory with lime and silica in the batch carryover. Vanadium from the fuel oil reacted with monticellite to form a low-melting liquid phase during refractory use. The formation of these phases, including monticellite and the vanadium-containing liquid phase, caused the observed rapid degradation in the refractoriness and the load-bearing capability of the high-MgO brick. Decreasing the lime content of the bonding system or using forsterite bond or direct bond should improve the chemical stability of the high-MgO refractory for use in regenerator checkers such as the present case.

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APPENDIX

X-RAY DIFFRACTION DATA

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Table A1. Zone A of the Fused Cast AZS Brick

Lattice Spacing (nm)	
Observed	Zirconia
0.50848	0.5079
0.36776	0.3694
0.36332	0.3636
0.36187	
0.31534	0.3162
0.28312	0.2839
0.26143	0.2621
0.25960	
0.25342	0.2498
0.22116	0.2213
0.21870	
0.21709	
0.20144	
0.19873	
0.18448	0.18472
0.18156	0.18179
0.18005	0.18026
0.17793	0.1780
0.16922	0.16931
0.16894	
0.16562	
0.16534	
0.16404	
0.16084	
0.15441	
0.15395	0.1541
0.15360	
0.14946	0.14950
0.14188	0.14191
0.13607	0.13604
0.13259	0.13249
0.13243	
0.12632	

Table A2. Zone B of the Fused Cast AZS Brick

Lattice Spacing (nm)		
Observed	Zirconia	Corundum
0.50447	0.5079	
0.36776	0.3694	
0.36187	0.3636	
0.34636		0.3479
0.31490	0.3162	
0.28295	0.2839	
0.26143	0.2621	
0.25425		0.2552
0.24907	0.2498	
0.24295		
0.23726		0.2379
0.23266	0.2332	
0.22064	0.2213	
0.20795		0.2085
0.20161		
0.18434	0.18472	
0.18153	0.18179	
0.17998	0.18026	
0.17796	0.178	
0.17362		0.1740
0.16905	0.16931	
0.16556	0.1656	
0.16433	0.16425	
0.16073		0.1601
0.15992		
0.15951		
0.15436	0.15410	
0.15395		
0.15088		
0.14953	0.14950	
0.14754	0.14771	
0.14269		
0.14235		
0.14034		0.1404
0.13729		0.1374
0.10427		0.10426
0.099761		0.09976

Table A3. Zone C of the Fused Cast AZS Brick

Lattice Spacing (nm)			
Observed	Zirconia	Corundum	Mullite
0.53530			0.539
0.50790	0.5079		
0.50446			
0.36776	0.3694		
0.36245	0.3636		
0.34662		0.3479	
0.34140			0.3428
0.33759			0.3390
0.31534	0.3162		
0.28312	0.2839		
0.26158	0.2621		
0.25439		0.2552	
0.23738		0.2379	
0.23266	0.2332		
0.22064	0.2213		0.2206
0.21834			
0.21759			
0.20813		0.2085	
0.20166			
0.19873			
0.18455	0.18472		
0.18427			0.1841
0.18156	0.18179		
0.18022	0.18026		
0.17776	0.178		
0.17368		0.1740	
0.16922	0.16931		0.1694
0.16543	0.1656		
0.16502	0.16425		
0.16078			
0.16002		0.1601	
0.15406	0.15410		
0.15395			
0.15088			
0.15011			
0.14950	0.14950		
0.14786			
0.14754	0.14771		
0.14691			
0.14192			
0.14041		0.1404	
0.13733		0.1374	
0.12960			
0.12945			
0.12930			
0.12914			
0.12899			
0.12863			
0.12847			
0.12795			
0.12589			
0.12578			
0.12552			
0.12538			
0.12521			
0.12486			
0.12388			
0.12356			
0.10429			
0.10402		0.10426	
0.10398			
0.09979		0.09976	

Table A4. Zone D of the Fused Cast AZS Brick

Lattice Spacing (nm)			
Observed	Zirconia	Corundum	Mullite
0.51493			0.539
0.50675	0.5079		
0.50475			
0.36776	0.3694		
0.36216	0.3636		
0.34716		0.3479	0.3428
0.31534	0.3162		
0.28312	0.2839		
0.26165	0.2621		0.2694
0.25439		0.2552	0.2542
0.24947	0.2498		
0.23751		0.2379	
0.23295	0.2332		
0.22095	0.2213		0.2206
0.21885			
0.20804		0.2085	
0.20144			
0.19877			
0.18448	0.18472		0.1841
0.18139	0.18179		
0.18039	0.18026		
0.18005			
0.17809	0.1780		
0.17374		0.1740	
0.16911	0.16931		0.1694
0.16543	0.1656		
0.16420	0.16425		
0.15992		0.1601	
0.15441			
0.15406	0.15410		
0.14935	0.14950		
0.14764	0.14771		
0.14211			
0.14192			
0.14041		0.1404	
0.13729		0.1374	
0.12383		0.1243	
0.12354			
0.12333			
0.11897		0.11898	
0.11471		0.11470	
0.10986			

Table A5. Zone E of the Fused Cast AZS Brick

Lattice Spacing (nm)			
Observed	Zirconia	Corundum	Mullite
0.54147			0.539
0.52002			
0.51463			
0.50906	0.5079		
0.47500			
0.47199			
0.46903			
0.46707			
0.36956	0.3694		
0.36405	0.3636		
0.34795		0.3479	
0.33885			0.339
0.31644	0.3162		
0.28400	0.2839		
0.26254	0.2621		0.2694
0.25467		0.2552	0.2542
0.25034	0.2498		
0.23799		0.2379	
0.23382			
0.23324	0.2332		
0.22116	0.2213		0.2206
0.21910			
0.20867		0.2085	
0.20242			
0.20195			
0.19968			
0.19901			
0.18466	0.18472		0.1841
0.18344			
0.18193	0.18179		
0.18039	0.18026		
0.17848			
0.17809	0.1780		
0.17405		0.1740	
0.16945	0.16931		0.1694
0.16606			
0.16570	0.1656		
0.16420	0.16425		
0.16017		0.1601	
0.15839			
0.15479			
0.15441			
0.15413	0.1541		
0.15111			
0.14989			
0.14950	0.14950		
0.14786	0.14771		
0.14231			
0.14208			
0.14052		0.1404	
0.13747		0.1374	
0.13367			
0.13278			
0.13084			
0.12397		0.1239	
0.12367			
0.12346			
0.11487			
0.11474			
0.11261			
0.11056			
0.10998			
0.10433		0.10426;	
0.10395			
0.10341			
0.10326			
0.10309			
0.10301			
0.099977			
0.099819			
0.099681			
0.099583			

Table A6. Zone A of the Silica Brick

Lattice Spacing (nm)		
Observed	Low Cristobalite	Tridymite
0.40527	0.405	0.4107
0.31447	0.314	
0.28488	0.2841	0.2776
0.24913	0.2485	0.2500
0.24714	0.2465	0.24900
0.21217	0.2118	0.2117
0.20230	0.2019	0.2049
0.19317	0.1929	
0.19279		
0.18740	0.1870	0.1874
0.16940	0.1690	0.1695
0.16143	0.1612	
0.16104	0.1600	0.1600
0.15357	0.1533	0.1534
0.14972	0.1494	
0.14338	0.1431	0.1434
0.14221	0.1429	
0.14004	0.1398	0.1402
0.13671	0.1365	
0.13479	0.1352	
0.13354	0.1346	
0.13011	0.1299	
0.12829	0.1281	
0.12346	0.1233	
0.12252	0.1223	
0.12075	0.1206	
0.11898	0.1188	
0.11852	0.1183	
0.11767		
0.10989		
0.10974		
0.099041		

Table A7. Zone B of the Silica Brick

Lattice Spacing (nm)		
Observed	Low Cristobalite	Tridymite
0.49552		
0.47855		0.4328
0.40437	0.405	0.4107
0.31361	0.314	0.3171
0.28426	0.2841	0.2975
0.24893	0.2485	0.2500
0.24682	0.2465	0.2490
0.21184	0.2118	
0.20208	0.2019	0.2049
0.19302	0.1929	
0.18722	0.1870	
0.17601		0.1783
0.17286		0.1715
0.16922	0.1690	0.1695
0.16353		0.1635
0.16130	0.1612	
0.16027	0.1600	0.1600
0.15743		
0.15691		
0.15348	0.1533	0.1534
0.14961	0.1494	
0.14328	0.1431	0.1434
0.14215	0.1429	
0.13995	0.1398	0.1402
0.13671	0.1365	
0.13541	0.1352	
0.13507		
0.13474	0.1346	
0.13347		
0.13006	0.1299	
0.12824	0.1281	
0.12343	0.1233	
0.12221	0.1223	
0.12071	0.1206	
0.11848	0.1188	
0.11822	0.1183	
0.11762		
0.11730		
0.11645		
0.10987		
0.10969		
0.099027		

Table A8. Zone C of the Silica Brick

Lattice Spacing (nm)			
Observed	Low Cristobalite	Tridymite	Pseudo-Wollastonite (α -CaSiO ₃)
0.57020			0.567
0.43239		0.4328	
0.40953	0.405	0.4107	
0.38733		0.3867	
0.38502			
0.38079		0.3818	
0.36362		0.3642	
0.34269			0.3419
0.33936		0.3396	
0.32468			
0.32375	0.314	0.3250	0.3235
0.30178		0.3017	0.3219
0.29698		0.2975	
0.28173	0.2841		0.2816
0.28087			
0.27883			0.2798
0.27765		0.2776	0.2784
0.26413			
0.25464		0.2540	
0.24500	0.2485	0.2490	0.2449
0.23860		0.2385	
0.23738			
0.23382			0.2345
0.23065		0.2308	
0.22930		0.2294	
0.21629			0.2180
0.21394		0.2137	
0.21151	0.2118	0.2117	0.2118
0.21071			
0.20817			
0.20525			
0.20481		0.2049	
0.20437			0.2044
0.20385	0.2019	0.2031	
0.19947			0.1998
0.19893			0.1984
0.19754	0.1929	0.1976	0.1970
0.16917	0.1690	0.1695	
0.16873			0.1681
0.16375			
0.16327		0.1635	
0.15360	0.1533	0.1534	
0.15321			
0.15298			
0.15252			0.1525
0.14598			0.1467
0.14387	0.1431		
0.14135			
0.14015			0.1403

Table A9. Zone A of the High-MgO Brick

Lattice Spacing (nm)		
Observed	Periclase	Monticellite
0.41463		0.418
0.38176		0.384
0.36129		0.362
0.32283		0.318
0.31589		0.315
0.29186		0.2929
0.28577		
0.27765		0.2762
0.26533		0.2658
0.25700		0.2578
0.25245		0.2534
0.24695		
0.24251	0.2431	
0.23848		0.2391
0.23476		0.2346
0.21006	0.2106	
0.20767		0.2082
0.18105		0.1811
0.17664		
0.17426		0.1744
0.17130		0.1716
0.16197		0.1697
0.16791		0.1680
0.15891		0.1587
0.15757		
0.15672		
0.15602		
0.14873	0.1489	
0.13863		0.1385
0.12686	0.1270	
0.12150	0.1216	
0.12037		
0.11954		
0.11931		
0.11903		
0.11655		
0.11635		
0.10611		
0.10528	0.10533	
0.10505		
0.10394		
0.10370		
0.10318		
0.10283		
0.096672	0.09665	
0.096532		
0.096324		
0.096129		
0.096004		
0.095732		
0.095640		
0.095402		
0.095239		
0.094999		

Table A10. Zone B of the High-MgO Brick

Lattice Spacing (nm)		
Observed	Periclase	Monticellite
0.54880		0.554
0.49634		
0.43851		0.441
0.42442		
0.41463		0.418
0.40492		
0.39776		
0.39256		
0.38192		0.384
0.37525		
0.36129		0.362
0.31556		0.315
0.29094		0.2929
0.28747		
0.28612		
0.28321		
0.27985		
0.27417		0.2762
0.26450		0.2658
0.25707		0.2578
0.24767		
0.24238	0.2431	
0.23811		0.2391
0.23470		0.2346
0.20992	0.2106	0.2082
0.18231		0.1828
0.18079		0.1811
0.17604		
0.17566		
0.17426		0.1744
0.17408		
0.17103		0.1716
0.16948		0.1697
0.16922		
0.16902		
0.16862		
0.16740		0.1680
0.15878		0.1587
0.15851		
0.15743		
0.15395		
0.14873	0.1489	0.1499
0.13868		0.1385
0.12688	0.1270	
0.12592		
0.12154	0.1216	
0.12096		
0.12017		
0.10859		
0.10529	0.10533	
0.10506		
0.10442		
0.10420		
0.10395		
0.097045		
0.09666	0.09665	

Table All. Zone C of the High-MgO Brick

Lattice Spacing (nm)		
Observed	Periclase	Monticellite
0.55494		0.554
0.54779		
0.44394		0.441
0.41367		0.418
0.38015		0.384
0.36000		0.362
0.31876		0.318
0.31523		0.315
0.30862		
0.29122		0.2929
0.29038		
0.28515		
0.28418		
0.28234		
0.27063		0.2762
0.26420		0.2658
0.25629		0.2578
0.25342		0.2534
0.25211		
0.24213	0.2431	
0.23799		0.2391
0.23738		0.2346
0.20950	0.2106	0.2082
0.18089		0.1811
0.17124		0.1711
0.17092		
0.16902		0.1697
0.16791		0.1680
0.15911		0.1593
0.15861		0.1587
0.14847	0.1489	0.1499
0.14310		0.1416
0.13854		0.1385
0.12675	0.1270	
0.12578		
0.12144	0.1216	
0.10886		
0.10518	0.10553	
0.096602	0.09665	
0.096488		
0.096374		
0.096261		

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Midland, MI 48640</p> <p>178. D. Stefl
Freeport Brick Co.
Drawer F
Freeport, PA 16229</p> <p>179. D. F. Stock
Harbison-Walker Refractories Co.
Dresser Industries, Inc.
Two Gateway Center
Pittsburgh, PA 15222</p> |
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180. W. E. Swearingen
Koppers Co., Inc.
Pittsburgh, PA 15219
181. Larrie H. Sweet
Manager Technical Development
Carborundum Co.
P. O. Box 808
Niagara Falls, NY 14302
182. C. A. Taylor
Shell Oil Co.
1 Shell Plaza, Box 2463
Houston, TX 77001
183. C. H. Taylor
National Crucible Co.
Queen St. and Mermaid Lane
Philadelphia, PA 19118
184. E. A. Thomas
Charles Taylor Div.
NL Industries, Inc.
8361 Broadwell Road
P. O. Box 44040
Cincinnati, OH 45244
185. C. J. Thompson
Bartlesville Energy Res. Center
P. O. Box 1398
Bartlesville, OK 74003
186. L. J. Trostel, Jr.
Norton Co.
One New Bond St.
Worcester, MA 01606
187. B. S. Tucker
The Refractories Inst.
1102 One Oliver Plaza
Pittsburgh, PA 15222
188. R. Van der Linden
Johns-Manville Products Corp.
Box 5108
Denver, CO 80217
189. M. L. Van Dreser
Center for Technology
Kaiser Aluminum and Chemical
Corp.
Box 870
Pleasanton, CA 94566
190. Theodore Vojnovich
Res. Labs.
Westinghouse Electric Corp.
Beulah Rd.
Pittsburgh, PA 15235
191. R. L. Walter
H. J. Heinz Co.
P. O. Box 57
Pittsburgh, PA 15230
192. Alvin Weinberg
Inst. for Energy Analysis
Oak Ridge Associated Universities
Oak Ridge, TN 37830
193. R. F. Whitford
North American Refractories Co.
1012 National City E 6th Bldg.
Cleveland, OH 44114
194. R. D. Whiting
Coors Porcelain Co.
600 9th St.
Golden, CO 80401
195. R. Wilcox
Chevron Res. Center
225 Bush St.
San Francisco, CA 94120
196. J. R. Wilson
Shell Development Co.
Box 1380
Houston, TX 77001
197. J. Wosinsky
Corning Glass Works
Box 432
Corning, NY 14830
198. S. Young
Babcock and Wilcox Refractories
Co.
Old Savanna Rd.
Box 923
Augusta, GA 30903
199. C. E. Zimmer
Babcock and Wilcox Co.
Lynchburg, VA 24505
- 200-201. Research and Technical Support
Division
Oak Ridge Operations Office
Department of Energy
P. O. Box E
Oak Ridge, TN 37830
- 202-228. Technical Information Center
P. O. Box 62
Oak Ridge, TN 37830