**Effects of Alternate Fuels
Report No. 1
Analysis of High-Duty Fireclay Refractories
Exposed to Coal Combustion**

G. C. Wei
V. J. Tennery
L. A. Harris

MASTER

OAK RIDGE NATIONAL LABORATORY
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METALS AND CERAMICS DIVISION

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G. C. Wei V. J. Tennery L. A. Harris

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ABSTRACT

Anticipated conversion of industrial fuels from natural gas to coal and residual oils, among other fuels, leads to problems of accelerated refractory and insulation corrosion and degradation in high-temperature equipment. It is, thus, desirable to understand better the involved reactions between the fuel impurities and the ceramic linings and to learn how to reduce them.

Analyses were performed on high-duty firebrick, fashioned from calcined fireclay and used for 15 years in the crown of a coal-fired periodic kiln that underwent a thermal cycle to 1260°C (2300°F) once a week. The refractory loss of these bricks was approximately 1 in., a rate of approximately 0.07 in./year. A slag formed over the service end or hot face of the brick. The portion of the brick that was not exposed to the slag contained a microstructure of large grog grains interspersed in a fine matrix material. The grog grains consisted of mullite crystallites bonded in a matrix consisting primarily of low cristobalite and glass. Quartz, hematite (Fe_2O_3), and rutile (TiO_2) were also present in the cold face region of the brick.

The slag that covered the hot face of the brick during service is primarily glass containing some crystalline phases including grog fragments from the original brick microstructure. Iron oxide has apparently dissolved in this glass and imparted a brown-gold color to the glass. An iron titanium oxide, oligoclase feldspar, corundum, mullite, and high cristobalite were also identified as crystalline phases in the slag. It appears that the corundum is formed as a result of reactions of the slag with the original grog fragments. Quartz present in the original brick has also dissolved in the slag. Chemical analysis of the slag showed that it had a relatively high alkali content ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) of about 9.5 wt %, and slag penetration into the brick behind the hot face was minimal.

The principal reactions between the coal slag and this type of high-duty refractory brick appear to be (1) original quartz grains in the brick slowly dissolving in the liquid slag formed from fusion of the constituents of the coal ash and (2) mullite crystals present in the brick reacting with the slag. This reaction leads to the formation of corundum crystals while the silica component of the mullite is dissolved in the slag. Increasing the silica content of such slags typically increases the viscosity at a given temperature. High slag viscosity is conducive to the relatively low loss rate of the refractory on the hot face and is believed to provide a protective layer on the refractory. A major conclusion of this study is that high-duty fireclay refractories can perform satisfactorily in industrial furnaces fired with coal if the temperature is maintained low enough to maintain a highly viscous slag of the proper type on the hot face. In the case reported here, this condition was satisfied below temperatures of 1260°C (2300°F) for the particular coal used as a fuel.

This study is the first of a series on analyses of several types of refractories that have been used in industrial equipment with fuels alternative to natural gas.

1. INTRODUCTION

In the foreseeable future, there is expected to be a large amount of industrial activity in the United States toward conversion from natural gas fuels to alternate fuels in a variety of industries, because of the restricted use of natural gas.¹ The favored industrial alternate fuels in current plans are, in the order of decreasing interest, distillate and residual oils, coal, electricity, and low-Btu gases. Coal is expected to play a limited role in industrial fuel use in the immediate future because of problems with its combustion and ash handling as well as its tendency to contaminate some products. Coal must, however, play a major role in the long term, because it offers good long-term economics and eventually may be the only industrial hydrocarbon fuel candidate when natural gas and oil are not available. One obstacle to the wide use of coal as

¹G. C. Wei and V. J. Tennery, *Impact of Alternate Fuels on Industrial Refractories and Refractory Insulation Applications, An Assessment*, ORNL/TM-5592 (September 1976).

an industrial alternate fuel is the high percentage of noncombustible impurities present in typical coals that will result in significant ash deposits in the furnace. Fusion of the coal ash at temperatures above about 1150°C (2100°F) and subsequent slag deposition in the furnace followed by fluxing and cracking of refractories in the furnace walls and roof are presently significant impediments to direct substitution of coal for natural gas in many applications. Because the energy costs and eventual petroleum depletion will force many furnacing operations to convert to coal, it is expected that slagging problems associated with burning coals will result. A great amount of technical effort is currently directed at elucidating the reactions between refractories and coal ash slags.²⁻⁵ These important studies are designed to provide insight into the process of refractory deterioration in a coal-fired environment and to provide guidance to development of refractories more suitable for this application.

Fireclay refractories are widely used in many industrial heating applications (Table 1).

Table 1. Area summary of fireclay refractory (25 to 45% Al₂O₃) use

Industry	Installation	Location
Iron	Cupola	Linings
	Blast furnace	Linings
	Blast-furnace stoves	Linings and checkers
	Torpedo ladles	Linings
	Hot-metal mixers	Linings
Steel	Open-hearth furnaces	Subhearth, doors, checker chambers, and checkers
	Arc furnaces	Subhearth and doors
	Ladles	Linings
	Casting pit	All pouring-pit hollow ware
	Soaking pits	Roof and sidewalls
	Reheating furnaces	Hearth, roof, and sidewalls
Nonferrous	Copper reverberatory furnaces	Subhearth
	Lead dross furnaces	Hearth
Glass	Pot furnaces	Pots and furnace linings
	Tank furnaces	Regenerative system and flues
Carbonization	Coke ovens	Suboven section: flues and regenerators
Power	Boilers	Walls, arches, and flues
Cement	Rotary kilns	Cooler sections
Lime	Kilns	Most sections
Chemicals and petrochemicals	Reactors and stills	Linings
Waste disposal	Incinerators	Linings

²See, for example, B. Zanderer (ed.), *Proceedings of the 15th Symposium on the Engineering Aspects of Magnetohydrodynamics*, University of Pennsylvania, Philadelphia, May 1976.

³A. D. Shaefer et al., *A Program to Discover Materials Suitable for Service Under Hostile Conditions Obtaining in Equipment for the Gasification of Coal and Other Solid Fuel*, FE-1784-12, The Metal Properties Council, Inc., New York (Jan. 1976).

⁴S. J. Schneider, *Materials Research for Clean Utilization of Coal* (Quarterly Report), FE-1749-8, National Bureau of Standards, Washington, D.C. (July 1976).

⁵R. B. Snow, *The Effect of Chemical Attack and Operational Parameters on the Wear of Blast Furnace Refractories*, FE-3731-1, private consultant, Pittsburgh (1976).

Many of these processes involving use of these refractories, such as soaking pits and reheating furnaces in the steel industry, melters and regenerators in the glass industry, boilers and incinerators in utilities, rotary kilns in the cement industry, and process heaters and catalytic reactors in the chemical industry, are being converted from natural gas to fuel oils or coal. In some cases, the conversions have already been made for some time. One concern frequently mentioned¹ by refractory users and producers is whether standard fireclay refractories that performed satisfactorily in a natural gas combustion chamber can perform as well when fired with residual oil or coal.

The present study is an analysis of high-duty fireclay refractory brick that has been used for 15 years in the crown of a round downdraft periodic kiln fired with coal. This kiln was used in firing face bricks in commercial production. Results presented in this report include chemical, petrographic, optical microscopy, and x-ray diffraction analyses plus an interpretation of the refractory corrosion mechanism based on results from these analyses. Interpretation and discussion of the results are based on known thermochemical equilibrium relationships, along with the limited reaction kinetics data available in the literature.

The objective of this work was to identify the basic physical and chemical changes underlying the corrosion process operative in high-duty fireclay refractories in a coal-fired environment. Different coals have different average ash contents and compositions; therefore, two processes or furnaces that appear identical may perform very differently when different coals are used. It is hoped that the results of the present work can be useful in understanding the coal ash slagging of this important class of refractories in the relatively low temperature regime employed during use of these bricks: $T \leq 1370^{\circ}\text{C}$ (2500°F).

This report is the first of a series on analyses of several types of refractories that have been used in industrial equipment with either residual oil or coal as fuel (Table 2).

Table 2. Refractory, fuel, and furnace applications

Refractory type	Fuel	Furnace application
Crume-magnesite	Residual oil	Glass tank port and target wall
Magnesite	Residual oil	Glass tank and regenerator
Fireclay	Residual oil	Boiler and soot hopper
Aluminosilicate	Residual oil	Steel soaking pit roof anchor
Plastic, aluminosilicate	Residual oil	Steel soaking pit cover
Silica	Residual oil	Glass tank and crown
Alumina/zirconia/silica (AZS)	Residual oil	Glass tank and port floor
Magnesite	Coal	Glass tank and regenerator
Silica	Coal	Glass tank and crown

2. HISTORY OF FIREBRICKS EXPOSED TO COAL COMBUSTION

2.1 As-Received Firebricks

The refractory bricks that were investigated in this study are PCP high-duty firebricks.⁶ According to the manufacturer, the clay used in making these bricks is an Ohio fireclay. Major phases in as-received

⁶Product of A. P. Green Co., Mexico, Mo.

PCP high-duty firebricks are mullite, quartz, cristobalite, tridymite, and a glass phase. The reported chemical composition of PCP high-duty firebrick is:

<i>Oxide</i>	<i>Oxide equivalent concentration (wt %)</i>
SiO ₂	55 to 58
Al ₂ O ₃	36 to 39
Fe ₂ O ₃	1.0 to 2.5
CaO	0.01 to 0.06
MgO	0.1 to 0.6
TiO ₂	2 to 3
Na ₂ O + K ₂ O	1.0 to 2.0

Major impurities are titanium, iron, sodium, potassium, calcium, and magnesium. The original dimensions of these bricks are standard size: 9.0 × 2.5 × 1.5 in. (23 × 6.4 × 3.8 cm). The bulk density of new brick is in the range 2.10 to 2.20 g/cm³ and the porosity is 16 to 20%.

2.2 Thermal History of Used Firebricks

These firebricks were used in the crown of a round downdraft periodic kiln fired with coal. The service life was 15 years. The frequency of thermal cycling imposed on these firebricks was one cycle per week. The temperature at the hot face of the firebrick crown was increased from room temperature to about 1260 to 1316°C (2300 to 2400°F) during each thermal cycle. The temperature drop across the 9-in. length of the brick at the maximum firing temperature was approximately 56°C (100°F).

2.3 Coal

The coal used in this periodic kiln was a West Virginia coal. Coal contains several extraneous minerals such as pyrites or marcasite, plus clays such as kaolinites and illites, mica, sand, and alkaline earth carbonates or silicates. These impurities usually are not homogeneously distributed, and consequently coal ash composition varies widely. The coal ash composition for a typical West Virginia coal⁷ is:

<i>Oxide</i>	<i>Average concentration (wt %)</i>	<i>Oxide</i>	<i>Average concentration (wt %)</i>	<i>Oxide</i>	<i>Average concentration (wt %)</i>
Li ₂ O	0.075	Ag ₂ O	0.0010	La ₂ O ₃	0.030
Na ₂ O	1.78	As ₂ O ₃	<0.07	MnO	0.046
K ₂ O	1.60	B ₂ O ₃	0.12	MuO ₃	0.016
Rb ₂ O	0.030	BcO	0.008	NiO	0.047
CaO	2.76	Bi ₂ O ₃	<0.004	P ₂ O ₅	0.35
SiO	0.38	U ₂ O ₅	0.010	PbO	0.048
BaO	0.22	CoO	0.010	Sb ₂ O ₃	<0.005
MgO	0.98	Cr ₂ O ₃	0.023	SnO ₂	0.020
Al ₂ O ₃	29.9	CuO	0.061	V ₂ O ₅	0.050
SiO ₂	43.9	GaO	0.022	WO ₃	<0.01
Fe ₂ O ₃	15.9	GeO ₂	0.011	ZnO	0.053
TiO ₂	1.52	HgO	0.011	ZrO ₂	0.029

⁷H. F. Yancey and M. R. Geer, *Coal Preparation*, American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., New York, 1968.

3. ANALYTICAL PROCEDURES

3.1 X-Ray Diffraction

Crystalline phases were identified with the use of standard x-ray diffraction techniques. To minimize the x-ray background, samples were mounted on a silicon single crystal oriented so that no x rays from silicon planes were diffracted to the x-ray detector. The diffraction data were collected at a scan rate of $1/8^\circ/\text{min}$ (rate of scan of 2θ , where θ is the diffraction angle) with 6 sec integrating time. The final output was in the form of a plot of diffraction intensity versus 2θ .

3.2 Optical Microscopy

Reflected and transmitted light microscopy were used in the examination of the brick and slag. The former method employs polished sections, whereas the latter technique uses thin sections and powdered samples. Both bright field and polarized light conditions were used in these analyses.

A polarizing microscope in conjunction with immersion oils was used to identify several of the phases in the powdered samples, and refractive indices were determined by matching the appropriate immersion oil to the phase. The Bertrand lens with conoscopic light was used in the observation of interference figures and optical signs to aid crystalline phase identification.

3.3 Metallographic Preparation

The entire sample was placed in a hollow cylindrical mounting mold. The specimen was then covered with a catalyzed epoxy resin (Shell Epon No. 815⁸), and the mold and specimen were placed in a vacuum chamber to impregnate the sample with epoxy.

The mounted specimen was ground to remove fractured material resulting from the curing operation with the use of successively finer silicon carbide abrasive papers (180, 320, 400, and 600 grit) and water as a coolant.

The ground specimen was placed on a vibratory polishing bowl using a Pellon⁹ cloth with a slurry of alumina (Linde-A,¹⁰ 0.3 μm) and water. A time of 6 to 8 hr was usually required to remove the scratches from the grinding operation.

Final polishing started with vibratory polishing with the use of 0- to 1- μm diamond paste on a nylon cloth with water as a vehicle. Usually a time of 6 to 8 hr was required for this step. The polished specimen was washed with ethyl alcohol and dried by warm air. After drying, the specimen was examined with the use of a reflected-light metallurgical microscope or a metallurgical metallograph.

4. RESULTS

4.1 Unaltered Part in the Firebrick

Figure 1 is a photograph of one of the high-duty firebricks. A coal-derived slag (see arrow) has formed over the service end of the brick. The sampling plan of this brick is shown in Fig. 2. The first number, the second letter, and the third number of the identification symbol (e.g., 2B1) represent the brick number, the zone in the brick, and the segment within that zone, respectively. The letter F identifies the brick end farthest from the hot face. This region has been selected as being representative of the original brick. Chemical analyses for the slag and different brick zones are listed in Table 3.

Optical and x-ray analyses of brick zones B, C, D, E, and F are revealed the same microstructural features and crystalline phases and therefore considered as unaltered parts of the brick. Figure 3 shows a

⁸Product of Shell Oil Co., New York, N.Y.

⁹Pellon: Product of Pellon Co., New York, N.Y.

¹⁰Linde-A: Product of Union Carbide Corp., New York, N.Y.

Fig. 1. Photograph of a high-duty firebrick after 15 years' service in a coal-fired environment.

Fig. 2. Sampling plan of firebrick.

typical microstructure of the unaltered brick with large grog grains interspersed in a fine matrix material. Separate analyses of the grog grains were accomplished by physically extracting them from the brick and subjecting them to x-ray and optical analyses.

The indexed x-ray diffraction data for the grog grains are presented in Table 4. Two crystalline phases were identified as the major constituents: mullite and low cristobalite. The displacement d of the lattice spacing for the (1 0 1) reflection at 4.04 Å of low cristobalite suggests that the clay used in producing the grog consisted primarily of kaolinite. A study by Flörke¹¹ showed that cristobalite formed from kaolinite contains this expanded lattice spacing, which was claimed to be indicative of a disordered structure.

¹¹D. W. Flörke, *Silic. Ind.* 23(10), 497, (1958).

Table 3. Chemical analyses of slag and selected zones from firebricks^a

Firebricks were used in crown of coal-fired round downdraft kilns.

Oxide	Zone composition as oxide equivalent ^b (wt %)				
	2A1—slag (hot face)	2B1	2C1	2D1	2E1
SiO ₂	54.20	62.00	62.13	62.79	62.57
Al ₂ O ₃	27.33	31.39	31.29	30.95	30.95
Fe ₂ O ₃	4.55	1.96	1.97	2.06	3.00
TiO ₂	1.64	1.75	1.73	1.73	1.73
Cr ₂ O ₃	0.045	0.026	0.026	0.025	0.024
P ₂ O ₅	0.60	0.06	0.09	0.05	0.08
CaO	1.20	0.32	0.28	0.21	0.26
MgO	0.75	0.58	0.55	0.53	0.52
Na ₂ O	5.46	0.43	0.35	0.27	0.28
K ₂ O	3.95	1.40	1.50	1.35	1.51
B ₂ O ₃	0.23	0.12	NF	NF	NF
SO ₃	0.13	0.03	0.02	0.02	0.14

^aFor zone identification, see Fig. 2.^bNF = none found.

Table 4. X-ray diffraction data from grog particles in firebrick

Grog particles are in unaltered part of firebrick used in a kiln crown and exposed to coal combustion for 15 years.

Displacement of lattice spacing (Å)		
Grog	Mullite	Low cristobalite
5.355	5.39	
4.095		4.04
3.765	3.774	
3.421	3.428	
3.381	3.390	
3.13		3.138
2.883	2.886	
2.851		2.845
2.691	2.694	
2.541	2.542	
2.510		2.49
2.427	2.428	
2.383	2.393	
2.308	2.308	
2.290	2.292	
2.206	2.206	
2.120	2.121	
2.026	2.106	2.024
1.968	1.969	
1.884	1.887	
1.841	1.841	
1.795	1.795	
1.713	1.712	
1.700	1.700	
1.692	1.694

Reflected-light micrograph showing microstructure of unaltered brick. G = grog particle; M = matrix material. (Actual magnification of this illustration: 22X.)

Additional x-ray diffraction data are presented in Table 5, which presents the total data from a segment of the unaltered brick. Three major crystalline phases were identified, namely, mullite, low cristobalite, and α -quartz with minor amounts of hematite and rutile. The quartz grains appear as separate crystals, indicating that they were probably added to the clay mixture before the firing operation to form the brick.

Optical examination of the crushed grog in selected immersion oils showed mullite crystallites ($<2\ \mu\text{m}$ diam) bonded in a matrix material, probably consisting of low cristobalite and some glass. Positive optical identification of these small crystals was not possible because of the limit of resolution of the microscope system.

The presence of the quartz in the unaltered brick can readily be seen in a thin section sample as large birefringent crystals (Fig. 4) whereas the hematite particles form discrete patches in the unaltered brick as seen in a reflected-light micrograph (Fig. 5).

Table 5. X-ray diffraction data from unaltered part of high-duty firebrick
Firebrick was used in a kiln crown and exposed to coal combustion for 15 years.

Displacement of lattice spacing (Å)					
Unaltered brick	Mullite	α -Quartz	Rutile	Hematite	Low cristobalite
5.355	5.39				
4.24		4.26			
4.08					4.04
3.76	3.774				
3.65				3.66	
3.421	3.428				
3.381	3.390				
3.34		3.343			
3.25			3.25		
3.13					3.138
2.883	2.886				
2.85					2.845
2.691	2.694			2.69	
2.541	2.542				
2.510				2.51	2.49
2.49			2.487		
2.44		2.456			
2.427	2.428				
2.385	2.393				
2.311	2.308				
2.294	2.292	2.281	2.297		
2.234		2.236			
2.206	2.206			2.20	
2.119	2.121	2.127			
2.103	2.106				
2.049			2.054		2.024
1.977		1.979			
1.967	1.969				
1.841	1.841			1.84	
1.815		1.817			
1.794	1.795	1.801			
1.713	1.712				
1.700	1.700				
1.693	1.694		1.687	1.69	
1.672		1.671

Fig. 4. Transmitted-light micrograph of thin section of unaltered brick, taken with polarized light, showing birefringent quartz (SiO_2) grains (QTZ). (Actual magnification of this illustration: 320X.)

Fig. 5. Reflected-light micrograph showing patches of hematite (Fe_2O_3) in unaltered brick, along with grog grains. *H* = hematite. (Actual magnification of this illustration: 140X.)

4.2 Slag

The slag forms a relatively thin coating (0.2 to 0.3 cm thick) on the service face of the firebrick (Fig. 6). Macroscopic examination of the slag/brick interface showed color gradations within the slag, continuing into the brick. The outer slag surface had a rust color and appeared to contain fragments of ash adhering to its surface. Slightly below this surface there was a dark glassy-looking material, which graded into a light brown in the direction of the brick. The color variation probably results from more and more unreacted grog and brick being incorporated into the slag as the distance from the unaltered refractory decreases. The slag plus altered brick zone extended to a depth of approximately 0.5 cm below the slag surface.

A reflected-light micrograph of a polished section of the slag is shown in Fig. 7. Note the profusion of highly reflecting crystals and the spherical pores. An elemental analysis of this high-reflectivity phase by

Fig. 6. Photograph of slag face.

Fig. 7. Reflected-light micrograph of slag surface of Zone A, showing highly reflecting iron-rich phase dispersed throughout. (Actual magnification of this illustration: 310X.)

the electron microprobe suggests that the crystals may be an iron titanium oxide. In addition, grog fragments may also be seen within the slag by viewing with polarized light as shown in Fig. 8. In this figure, the large birefringent areas are associated with the crystalline phases in the grog particles. The slag/brick interface is rather sharply defined. Arrows in Fig. 9 indicate the boundary between the slag and the brick. It is also shown in Fig. 9 that grog grains (*G*) in the original brick were dispersed in the slag. Figure 10 is a micrograph at a higher magnification of grog grain (*G*) in Fig. 9.

Petrographic examination of the crushed slag using immersion oils revealed the presence of an isotropic (probably amorphous) matrix phase with crystalline phases, including grog fragments from the brick. The slag glass, when examined in thicker sections, has a slightly brown-gold appearance, probably due to some

Fig. 8. Reflected-light micrograph taken with polarized light, showing the birefringent grog fragments (*G*) within the slag. (Actual magnification of this illustration: 67X.)

Fig. 9. Reflected-light micrograph of a polished section of the slag/brick interface. Arrows indicate the boundary between the slag and the brick. *G* is a grog grain in the slag. (Actual magnification of this illustration: 29X.)

Fig. 10. Reflected-light micrograph of higher magnification of area *G* in Fig. 9. (Actual magnification of this illustration: 67X.)

Fig. 11. Transmitted-light micrograph showing euhedral crystals (C) within the glass matrix of slag in Zone A. (Actual magnification of this illustration: 400X.)

iron oxide being incorporated into the glass. In Fig. 11, a fragment of the slag glass is shown in which crystals of the iron titanium oxide previously mentioned are present.

Large birefringent crystals (refractive index of 1.538) are embedded in the glass. They were identified as the plagioclase feldspar oligoclase, having the formula $[(\text{NaSi})_{0.9-0.7}(\text{CaAl})_{0.1-0.3}] \text{AlSi}_2\text{O}_8$, based upon the indexing of the x-ray diffraction data (Table 6). The measured refractive index of these crystals also agrees with the reported value (1.549) of the oligoclase. Figure 12 shows these feldspar crystals as the birefringent species in polarized light. The plagioclase feldspar crystals observed in the slag were untwinned, whereas these crystals formed in geologic processes are usually twinned. The reason for this untwinned character was not identified, but it may be due to inclusion of other elements from the melt within the crystal.

Additional phases including corundum, mullite, and high cristobalite were also identified in the x-ray diffraction data for the hot face of the brick (Table 6). The corundum is believed to be a consequence of reactions of the slag with the original grog fragments. No growth of mullite crystals was observed in the slag, and the regions surrounding the grog show reaction zones on their surfaces containing birefringent material that probably consists of optically unresolvable plagioclase feldspar crystals. There was very little free quartz present in the slag.

The physical demarcation between the slag layer and the bulk refractory was very distinct with the transition from one region to the other occurring over a distance of approximately 10^{-3} m (0.1 cm) within the refractory along the normal to the hot face surface.

5. DISCUSSION

The slag composition given in Table 3 contained a high percentage of alkali, Na_2O (5.46%) and K_2O (3.95%), on an oxide equivalent weight basis. From the analysis presented in the previous section, it appears that during refractory use, quartz and cristobalite grains from this firebrick are slowly dissolved in

Table 6. X-ray diffraction data from slag from hot face of high-duty firebrick

Slag formed on high-duty firebrick that had been used in kiln crown and exposed to coal combustion for 15 years.

Displacement of lattice spacing (Å)					
Slag	Mullite	Corundum	Oligoclase	Hematite	High cristobalite
5.37	5.39				
4.90					
4.15					4.15
4.05			4.03		
3.90			3.88		
3.75	3.774		3.75		
3.66			3.63	3.66	
3.46		3.479	3.47		
3.427	3.428		3.42		
3.38	3.390		3.37		
3.21			3.21		
3.18			3.18		
3.14			3.13		
3.02			3.02		
2.95			2.95		
2.93			2.93		2.92
2.885	2.886				
2.84			2.84		
2.69	2.694			2.69	
2.55	2.542	2.552			2.53
2.51			2.518	2.51	
2.455					
2.386	2.393	2.379			
2.290	2.292				
2.211	2.206			2.20	
2.16		2.165			2.17
2.145					
2.122	2.121				
2.088	2.085				2.07
1.840	1.841			1.84	
1.834			1.829		
1.800	1.795				
1.744		1.740			
1.693	1.700			1.69	
1.689	1.694				
1.641					1.639
1.605	1.599	1.601			
1.525	1.524				
1.481				1.48	1.471
1.439	1.44				
1.377					1.379
1.375		1.374			

the slag. Simultaneously, mullite crystals dissociate in the slag resulting in the formation of corundum crystals with concurrent dissolution of SiO_2 in the slag glass. Because the slag contains sodium and potassium, the different roles of sodium and potassium in the slagging process can be best discussed by use of the ternary systems, $\text{K}_2\text{O}/\text{Al}_2\text{O}_3/\text{SiO}_2$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3/\text{SiO}_2$.

In the ternary system, $\text{K}_2\text{O}/\text{Al}_2\text{O}_3/\text{SiO}_2$, the addition of the K_2O content from the slag to the unaltered brick (62% SiO_2 , 31% Al_2O_3 , and 1.5% K_2O) results in a new composition that has 3.95% K_2O equiv-

Fig. 12. Transmitted-light micrograph of the slag made with the use of polarized light reveals the birefringent feldspar crystals (*F*). (Actual magnification of this illustration: 400X.)

alent and that falls within the composition triangle, mullite-silica-feldspar ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 / \text{SiO}_2 / \text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$).¹² At 1260°C (2300°F), the equilibrium phases are mullite and one liquid phase. When cooled to room temperature, the final phases present in equilibrium should be mullite, silica, and potash feldspar ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$). However, the presence of potash feldspar in the slag was not observed. Instead, a complex feldspar called oligoclase was observed in the slag. The system therefore does not appear to be in equilibrium, at least during the cooling process. This condition is not surprising because the slag/refractory system was cooled from the maximum temperature of 1260°C (2300°F) to room temperature 25°C (77°F) in about 24 hr; equilibrium would not be expected in such a short period.

McCune¹³ *et al.* studied the reactions between K_2O and high-duty, super-duty, and high- Al_2O_3 (70% Al_2O_3) fireclay refractories. It was found that quartz and cristobalite were attacked by K_2O at 1204°C (2200°F). They observed the formation of leucite ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$) and kaliophilite ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) at temperatures below 927°C (1700°F) when the K_2O content was greater than 7.5%. At 1204°C (2200°F), mullite remained stable until the K_2O content reached 12%. The formation of leucite was observed where the K_2O content was greater than 7%. In the present study, the K_2O equivalent content in the slag is 3.95%, and leucite does not exist in the slag. This agrees with McCune's findings.¹³ Because the K_2O equivalent content in the slag (3.95%) is less than the 12% K_2O equivalent required to decompose mullite at 1204°C (2200°F), it appears that the potassium in this slag did not have much effect on the mullite phase. The generation of corundum is probably due to the sodium in the slag. However, potassium in the slag did react with cristobalite and quartz grains in the brick.

Examination of used firebricks from blast furnace¹³ linings where a high content of potassium contamination is present also reveals the nature of the reactions between potassium and aluminosilicate

¹²E. M. Levin, C. R. Robbins, and H. F. McMurdie (eds.), *Phase Diagrams for Ceramists*, American Ceramic Society, Columbus, Ohio, 1964.

¹³S. E. McCune, T. G. Greaney, W. C. Allen, and R. B. Snow, *J. Am. Ceram. Soc.* 40(6), 187 (1957).

refractories. In firebricks containing 7% K_2O equivalent, leucite and mullite were major phases, whereas cristobalite was present in a lesser amount. If the K_2O equivalent is higher than 12%, kalsilite (a mineral similar to kaliophilite but with a small amount of CaO in solid solution) is produced along with leucite and mullite. In some cases in which the K_2O equivalent content is about 8%, the potash feldspar is present.

It is also worthwhile to mention the slagging tests performed on mullite and alumina for coal-fired magnetohydrodynamic (MHD) preheater material applications¹⁴ and their possible relevance to the present work. In the MHD case, the corrosion agent is coal ash slag plus potassium seed. It was found that the α -alumina was preferentially attacked, whereas mullite showed relatively good corrosion resistance. This was explained to be due to the high potassium content of that slag. In this study, the K_2O equivalent content in the slag is 3.95%, and the α -alumina appears stable with respect to the high potash melt. The slag dissolved the silica phases (quartz and cristobalite) and dissociated the mullite phase. The reason for a difference in behavior between the MHD case and the present one is not clear, but it may be due to the different potassium levels in the two slags.

The slag/refractory system may also be viewed in terms of the ternary system $Na_2O/Al_2O_3/SiO_2$.¹⁵ The addition of the Na_2O content from the slag to the unaltered brick (62% of SiO_2 , 31% of Al_2O_3 , and 0.43% of Na_2O) results in a new composition that has 5.46% Na_2O content and that falls within the composition triangle mullite/silica/albite ($3Al_2O_3 \cdot 2SiO_2/SiO_2/Na_2O \cdot Al_2O_3 \cdot 6SiO_2$). At 1260°C (2300°F), the equilibrium phases are mullite and one liquid phase. Upon cooling to room temperature, the final equilibrium phases are mullite, silica, and albite. Albite was not observed in the slag. The absence of albite in the slag indicates that this ternary system was not representative of the actual slag/refractory system, the actual system was not in equilibrium during cooling and, possibly, the slag/refractory reaction process was not representative of equilibrium conditions either.

The corrosion of mullite by Na_2CO_3 vapor was reported by Okawara and Yamaguchi.¹⁶ They found that mullite first reacts to form carnegieite ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$) and corundum. The corundum subsequently slowly reacts and sodium silicate and nepheline ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$) form. Rigby and Hutton¹⁷ investigated the reactions between Na_2O and aluminosilicate refractories. Na_2O first reacts with alumina and silica to form sodium aluminate and sodium silicate, and mullite decomposes and forms nepheline, sodium aluminate, and β -alumina ($Na_2O \cdot 11Al_2O_3$). In this study, we observed the presence of the feldspar oligoclase, but no evidence of the existence of nepheline, sodium aluminate, or β -alumina.

In the unaltered brick, x-ray analysis showed the existence of low cristobalite. However, only high cristobalite was found in the slag (Table 6). The transformation of low cristobalite to high cristobalite was either enhanced because of the presence of the impurities such as Na in the slag,¹⁸ or the high-temperature phase was stabilized by impurities.

Our results indicate that mullite crystallites in the grog particles that were dispersed in the slag are surrounded with reaction shells or zones of the feldspar oligoclase. As a result of the reaction between the slag and mullite, corundum crystals are formed in the melt. The consequence of these reactions is expected to be an increase in the viscosity of the glass phase of the slag due to the addition of silica to the glass phase.¹⁹

¹⁴H. P. R. Frederickse, T. Negas, and S. J. Schneider, *Quarterly Report for the Period October-December 1975*, National Bureau of Standards, Washington, D.C., pp. 42-4.

¹⁵E. M. Levin, C. R. Robbins, and H. F. McMurdie (eds.), *Phase Diagram for Ceramists*, p. 181, American Ceramic Society, Columbus, Ohio, 1969.

¹⁶S. Okawara and A. Yamaguchi, *J. Ceram. Assoc. Jpn. (Yogyo Kyokai Shi)* 77, 208 (1969).

¹⁷G. R. Rigby and R. Hutton, *J. Am. Ceram. Soc.* 45(2), 68 (1962).

¹⁸A. V. Morsanyi, *Glass Technol.* 4(1), 23 (1963).

¹⁹W. F. Ford, *Glass Technol.* 1(1), 17 (1960).

Mass transport through the viscous glass phase will be slower as the viscosity increases. Because the liquid content at temperatures above 1260°C (2300°F) in the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3/\text{SiO}_2$ system or the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3/\text{SiO}_2$ system for a composition corresponding to the unaltered brick plus the alkali content in the slag decreases with increasing alumina content,¹⁸ the addition of silica to the glass phase of the slag will generate more liquid if the system is at equilibrium. The solubility of the aluminosilicate refractory in the liquid phase will also increase as a result of the dissolution of silica and dissociation of mullite in the glass phase of the slag.¹⁹ This process will continue to proceed until all free silica is dissolved and all mullite crystallites are dissociated. It thus seems that the solubility of the aluminosilicate refractory is not a limiting factor in the process of the corrosion of this refractory in the slag. The presence of a reaction zone around the grog particles dispersed in the slag suggests that the refractory degradation process is probably controlled by chemical reactions at the slag/refractory interface.

The corrosive role of iron oxide or rutile in the slag is probably minor. At 1380°C (2516°F), no liquid phase would be developed in the $\text{Al}_2\text{O}_3/\text{SiO}_2$ binary containing more than 35% SiO_2 if less than 5% of iron oxide is present.²⁰ It is expected that there is no liquid phase formation at 1260°C (2300°F) if the iron oxide content is less than 5%. However, the viscosity of the liquid phase in the slag might be decreased, and crystallization of oligoclase feldspar might be enhanced, as iron oxide is dissolved in the glassy phase of the slag.

Sulfur in the coal ash can react with sodium to form sodium sulfate, which does not dissociate readily and could contribute to slag attack on the refractory. This sulfate can react with alumina to form a sodium aluminate liquid, while sulfur is released as gaseous sulfur oxide.²¹ The large number of bubbles observed in the slag were probably generated by this mechanism.

The temperature gradient from the hot face to the cold end of the firebrick is estimated to be about 56°C (100°F). If the slag did penetrate through external and internal pores and was present in brick zones far behind the hot face, extensive slag/refractory reactions would have been expected even at the cold end of the brick if significant slag was present, because the maximum temperature at the cold end was approximately 1160°C (2120°F). However, the present case shows that there was very little penetration of the slag into the brick as determined optically and as shown in Fig 9. Because of the maximum service temperature, 1260°C (2300°F), the viscosity of the slag was obviously sufficiently high to inhibit melt migration.

In summary, the principal reactions between the coal slag and this type of high-duty refractory brick appear to be (1) quartz grains in the brick slowly dissolving in the slag glass phase, and (2) mullite crystallites in the brick reacting with the slag and corundum being formed while the silica content of the mullite is dissolved in the slag glass phase. The slag/brick reaction is, however, confined to the interface region and proceeds at a slow rate. The rate of refractory loss was approximately 0.07 in./year, an entirely satisfactory value. Higher service temperatures would be expected to result in much more rapid refractory corrosion due to the exponential decrease of slag viscosity with increasing temperature and the concomitant increase in diffusivities in the slag and in the resultant reaction rates.

6. CONCLUSIONS

The unaltered fireclay brick consists of large grog grains dispersed in a fine matrix phase. The grog grains consist primarily of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). The matrix material consists of mullite, low cristobalite, α -quartz, and minor amounts of hematite (Fe_2O_3) and rutile (TiO_2).

²⁰ A Muan, *J. Am. Ceram. Soc.* 41(8), 275 (1958).

²¹ T. D. McGee, "Slagging of Refractories by Ash from Alternate Fuels," paper given at the Meeting on the Impact of Alternate Fuels on Refractories and Refractory Insulation, Sponsored by ERDA, Division of Industrial Energy Conservation, Washington, D.C. (Sept. 21, 1976).

The solidified slag present on the hot face following disassembly of the kiln is primarily a glass with some grog grains from the brick dispersed in the glass. An iron titanium oxide, oligoclase feldspar, corundum, mullite, and high cristobalite were also identified as crystalline phases present in the slag. Iron oxide is apparently dissolved in the glass phase of the slag, results in a lower viscosity at a specific temperature, and enhances oligoclase feldspar crystallization. The slag/refractory interface was very discrete with very little slag penetration into the refractory behind the slag zone.

Quartz and cristobalite grains originally present in the brick were apparently slowly dissolved in the glassy phase of the slag during the service life of the refractory. The slag contains a relatively high alkali content. Both potassium and sodium present in the glass of the slag favored silica dissolution.

The presence of corundum is a consequence of reactions of the slag with mullite present in the grog grains of the original refractory. Also observed were reaction zones consisting of oligoclase feldspar surrounding the grog grains in the slag. It appears that sodium in the slag may play an important role in mullite reaction with the slag.

Sulfur found in the slag came from the coal and some of it was subsequently released, probably as gaseous sulfur oxide bubbles. Many bubbles whose diameter were small compared to the slag layer thickness were present throughout the slag.

The slag/brick reaction was confined only to the interface region and proceeds at a relatively slow rate as demonstrated by the performance of the refractory. The low reaction rate was apparently controlled by the viscous slag layer at the operating temperature.

High-duty fireclay refractories can perform satisfactorily in industrial furnaces fired with coal or converted from natural gas to coal, if the temperature at the hot face of the refractories is limited to a maximum of 1260°C (2300°F) during the refractory service life.

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(Div. of Pullman, Inc.)
441 Smithfield St.
Pittsburgh, Pa. 15222
156. J. E. Moore
Kaiser Refractories Co.
(Div. of Kaiser Aluminum & Chemical Corp.)
P.O. Box 47
Columbiana, Ohio 44408
157. J. Moskowitz
Philadelphia Electric Co.
2301 Market St.
Philadelphia, Pa. 19100
158. R. E. Muchow
Box 337
Niagara Falls, N.Y. 14302
159. J. E. Neal
Johns-Manville Corp.
Box 5108, Greenwood Plaza
Denver, Colo. 80217
160. R. Neeley
Chattanooga Glass Co.
400 W 45th St.
Chattanooga, Tenn. 37410
161. J. A. Nelson
University of Illinois
Urbana, Ill.
162. R. E. Nelson
C-E Minerals Co.
901 E 8th Ave.
King of Prussia, Pa. 19406
163. D. Olenchut
Jones and Laughlin Steel Corp.
3A, Gateway Center
Pittsburgh, Pa. 15230
164. P. Papa
Cornhart Refractories Co.
1600 W Lee St.
Louisville, Ky. 40210
165. J. D. Parsons
Chicago-Wellsville Fire Brick Co.
1467 Elston Ave.
Chicago, Ill. 60622
166. G. Passell
AFC Corp.
Canfield, Ohio 44406
167. C. M. Pelanne
Johns-Manville Corp.
Box 5108
Denver, Colo. 80217
168. N. V. Poer
Utility Relations and Conservation
General Motors Corp.
Detroit, Mich. 48202
169. R. B. Pool
Kaiser Aluminum and Chemical Corp.
300 Lakeside Dr.
Oakland, Cal. 94643
170. S. C. Porter, Jr.
Globe Refractories Co.
(Div. of C-E Refractories Co.)
Box D
Newell, Va. 26050
171. G. V. Prible
C-E Refractories Co.
(Div. of Combustion Engineering, Inc.)
Box 828
Valley Forge, Pa. 19482

172. C. J. Ranhke
Power Train and System Research
Ford Motor Co.
20,000 Rotunda Drive
Dearborn, Mich. 48121
173. P. H. Reed
New Castle Refractories Co.
Box 471
New Castle, Pa. 16103
174. R. Reed
John Zink Co.
4401 S. Peoria St.
Tulsa, Okla. 74105
175. D. M. Rice
Davis Fire Brick Co.
Box 235
Oak Hill, Ohio 45456
176. R. Rose
H. K. Porter Co.
Porter Bldg.
601 Grant St.
Pittsburgh, Pa. 15219
177. R. B. Rosenberg
Inst. of Gas Technology
3424 State Street
IIT Center
Chicago, Ill. 60616
178. R. P. Ross
Glasrock Products, Inc.
2210 Marietta Blvd, NW
Atlanta, Ga. 30318
179. G. R. Rowland
Hartford Refractories, Emhart Corp.
P.O. Box 2809
Hartford, Conn. 06101
180. C. K. Russell
Res. Center
United States Steel Corp.
125 Jamison Lane
Mail Stop 43
Monroeville, Pa. 15146
181. E. C. Sargent
Kolb Refractories Co.
Box 95
East Greenville, Pa. 18041
182. M. Savitz
Energy Research and Development Administration
20 Massachusetts Ave., NW
Washington, D.C. 20545
183. F. E. Schmidt
E.I. duPont de Nemours & Co., Inc.
Experimental Station
Bldg. 301
Wilmington, Del. 14898
184. W. E. Scruggs
Mosanto Co.
800 North Lindbergh Blvd.
St. Louis, Mo. 63166
185. R. L. Shultz
Armco Steel Corp.
Research Center South
Middletown, Ohio 45043
186. H. D. Smith
Wellsville Fire Brick Co.
Highway 19W
Wellsville, Mo. 63384
187. H. D. Smith
Res. Labs.
Westinghouse Electric Corp.
1310 Beulah Rd.
Pittsburgh, Pa. 15235
188. T. E. Smith
Southern Div.
Martin-Marietta Cement Co.
1800 Daniel Bldg.
Birmingham, Ala. 35223
189. W. J. Smothers
Homer Res. Labs
Bethlehem Steel Corp.
Bethlehem, Pa. 18016
190. R. R. Smyth
Fluidyne Engineering Co.
5900 Olson Memorial Highway
Minneapolis, Minn. 55422

191. I. Snyder
Dow Chemical Co.
2020 Dow Center
Midland, Mich. 48640
192. D. Stefl
Freeport Brick Co.
Drawer F
Freeport, Pa. 16229
193. T. D. Steinke
Kaiser Aluminum & Chemical Corp.
Center for Technology
Box 870
Pleasanton, Calif. 94566
194. D. F. Stock
Harbison-Walker Refractories Co.
Dresser Industries, Inc.
Two Gateway Center
Pittsburgh, Pa. 15222
195. W. E. Swearingen
Koppers Co., Inc.
Pittsburgh, Pa. 15219
196. S. J. Sweeney
Boston Edison Co.
800 Boylston St.
Boston, Mass. 02199
197. Larrie H. Sweet
Manager Technical Development
Carborundum Co.
P.O. Box 808
Niagara Falls, N.Y. 14302
198. C. A. Taylor
Shell Oil Co.
1 Shell Plaza, Box 2463
Houston, Tex. 77001
199. C. H. Taylor
National Crucible Co.
Queen St. and Mermaid Lane
Philadelphia, Pa. 19118
200. J. W. Tieman
Bituminous Coal Research, Inc.
350 Hochberg Rd.
Monroeville, Pa. 15146
201. E. A. Thomas
Charles Taylor Div.
NL Industries, Inc.
3044 Coral Park Drive
Cincinnati, Ohio 45211
202. C. J. Thompson
Bartlesville Energy Res. Center
P.O. Box 1398
Bartlesville, Okla. 74003
203. L. J. Trostel, Jr.
Norton Co.
One New Bond St.
Worcester, Mass. 01606
204. B. S. Tucker
The Refractories Inst.
1102 One Oliver Plaza
Pittsburgh, Pa. 15222
205. R. Van der Linden
Johns-Manville Products Corp.
Box 5108
Denver, Colo. 80217
206. M. L. Van Dreser
Center for Technology
Kaiser Aluminum and Chemical Corp.
Box 870
Pleasanton, Calif. 94566
207. Theodore Vojnovich
Res. Labs.
Westinghouse Electric Corp.
Beulah Rd.
Pittsburgh, Pa. 15235
208. R. L. Walter
H. J. Heinz Co.
P.O. Box 57
Pittsburgh, Pa. 15230
209. Alvin Weinberg
Inst. for Energy Analysis
Oak Ridge Associated Universities
Oak Ridge, Tenn. 37830
210. W. T. Wells
Gulf Oil Co.
P.O. Box 1357
Houston, Tex. 77001

<p>211. R. F. Whitford
North American Refractories Co.
1012 National City E 6th Bldg.
Cleveland, Ohio 44114</p> <p>212. R. D. Whiting
Coors Porcelain Co.
600 9th St.
Golden, Colo. 80401</p> <p>213. H. R. Wickenden
Goodyear Tire and Rubber Co.
1144 E Market St.
Akron, Ohio 44316</p> <p>214. R. Wigner
Res. Lab.
United States Steel Corp.
125 Jamison Lane
Mail Stop 43
Monroeville, Pa. 15146</p> <p>215. R. Wilcox
Chevron Res. Center
225 Bush St.
San Francisco, Calif. 94120</p> <p>216. J. R. Wilson
Shell Development Co.
Box 1380
Houston, Tex. 77001</p> <p>217. D. Wilty
Commonwealth Edison Co.
P.O. Box 767
Chicago, Ill. 60690</p> | <p>218. C. E. Winters
Union Carbide Corp.
270 Park Ave.
New York, N.Y. 10017</p> <p>219. J. Wosinsky
Corning Glass Works
Box 432
Corning, N.Y. 14830</p> <p>220. Neil Young
International Paper Co.
220 E. 42nd Street
New York, N.Y. 10017</p> <p>221. S. Young
Babcock and Wilcox Refractories Co.
Old Savanna Rd.
Box 923
Augusta, Ga. 30903</p> <p>222. C. E. Zimmer
Babcock and Wilcox Co.
Lynchburg, Va.</p> <p>223. Research and Technical Support Div.
Oak Ridge Operations Office
Energy Research and Development Admin-
istration</p> <p>224- Technical Information Center</p> <p>250. Energy Research and Development Admin-
istration</p> |
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