MASTER

**Effects of Alternate Fuels
Report No. 2
Analysis of Basic Refractories Degraded
by Residual Oil Combustion Products**

G. C. Wei
V. J. Tennery

OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION · FOR THE DEPARTMENT OF ENERGY

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy \$6.50; Microfiche \$3.00

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, contractors, subcontractors, or their employees, makes any warranty, express or implied, nor assumes any legal liability or responsibility for any third party's use or the results of such use of any information, apparatus, product or process disclosed in this report, nor represents that its use by such third party would not infringe privately owned rights.

Contract No. W-7405-eng-26

METALS AND CERAMICS DIVISION

EFFECTS OF ALTERNATE FUELS

REPORT NO. 2

ANALYSIS OF BASIC REFRACTORIES DEGRADED BY RESIDUAL OIL COMBUSTION PRODUCTS

G. C. Wei and V. J. Tennery

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Prepared for
Division of Industrial Energy Conservation
Department of Energy

Date Published: February 1978

NOTICE This document contains information of a preliminary nature. It is subject to revision or correction and therefore does not represent a final report.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

CONTENTS

LIST OF FIGURES	v
LIST OF TABLES	vi
ABSTRACT	1
INTRODUCTION	3
SPECIMEN HISTORY	4
RESULTS	8
Port-Side Chrome-Magnesite Brick	9
Target-Wall Chrome-Magnesite Brick	36
High-MgO Checker Brick	43
DISCUSSION OF RESULTS	48
Port-Side Chrome-Magnesite Brick	48
Target-Wall Chrome Magnesite Brick	53
High-MgO Checker Brick	56
CONCLUSIONS	59
REFERENCES	61
APPENDIX	67

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

LIST OF FIGURES

Figure		Page
1	Typical Side Port Glass Tank Melting Furnace	7
2	Port-Side Chrome-Magnesite Brick	9
3	Top View of the Hot Face of the Port-Side Chrome-Magnesite Brick	10
4	Sampling Plan for Analyses of the Port-Side Chrome- Magnesite Brick	10
5	One Area of the Nonexpanded Region of the Port-Side Chrome-Magnesite Brick	14
6	Second Area of the Nonexpanded Region of the Port-Side Chrome-Magnesite Brick	15
7	Third Area of the Nonexpanded Region of the Port-Side Chrome-Magnesite Brick	16
8	Fourth Area of the Nonexpanded Region of the Port-Side Chrome-Magnesite Brick	17
9	Samples (a) PM2 and (b) PM1 from the Port-Side Chrome- Magnesite Brick	18
10	Samples (a) PM4 and (b) PM3 from the Port-Side Chrome- Magnesite Brick	19
11	Sample PM5 from the Port-Side Chrome-Magnesite Brick	20
12	Typical Point Scan by an Electron Microprobe of Bright Particles in an Area A of Fig. 9	21
13	Typical Point Scan by an Electron Microprobe of Matrix Phase in an Area A of Fig. 9	22
14	Typical Point Scan by an Electron Microprobe of Bright Particles in an Area B of Fig. 9	22
15	Typical Point Scan by an Electron Microprobe of Matrix Phase in an Area B in Fig. 9	23
16	Typical Point Scan by an Electron Microprobe of an Area C in Fig. 9	23
17	Typical Point Scan by an Electron Microprobe of an Area D in Fig. 9	24
18	Cross Section Through a Part of the Hot Face in the Port- Side Chrome-Magnesite Brick	25
19	Area 1 in Fig. 18 Showing Cracks in the Forsterite and Monticellite	26
20	Higher Magnification of Areas (a) A and (b) B in Fig. 19 Showing Cracks in the Chrome Ore Spinel and Complex Phases Generated by Reactions of Impurity Phases Originally Present Within the Chrome Ore Grains	27
21	Areas 2 and 3 in Fig. 18	28
22	The Expanded part of the Port-Side Chrome-Magnesite Brick Showing Complex Phases Within the Forsterite and Monticellite	30
23	Scanning Electron Fractography of the Expanded Part of the Port-Side Chrome-Magnesite Brick	32

Figure		Page
24	Scanning Electron Fractography of the Expanded Part of the Port-Side Chrome-Magnesite Brick	33
25	Scanning Electron Fractography of the Expanded Part of the Port-Side Chrome-Magnesite Brick, Showing the Dendritic Phase	34
26	Scanning Electron Fractography of the Expanded Part of the Port-Side Chrome-Magnesite Brick	35
27	The Target-Wall Chrome-Magnesite Brick	37
28	Sampling Plan for the Target-Wall Chrome-Magnesite Brick	38
29	Sample TM1 of the Target-Wall Chrome-Magnesite Brick	39
30	Sample TM2 of the Target-Wall Chrome-Magnesite Brick	40
31	Sample TM3 of the Target-Wall Chrome-Magnesite Brick	41
32	Sample TM4 of the Target-Wall Chrome-Magnesite Brick	42
33	The High-MgO Checker Brick	44
34	Sampling Plan for the High-MgO Checker Brick	45
35	Sample CM1 of the High-MgO Checker Brick	46
36	Sample CM2 of the High-MgO Checker Brick	47
37	Scanning Electron Fractographs of a Sample from Zone A of the High-MgO Checker Brick Subjected to EDXA	49

LIST OF TABLES

Table		
1	Chemical Analysis of Chrome-Magnesite and High-MgO Brick	6
2	Chemical Analysis of the Mortar Residue on the Surface of the Target-Wall Chrome-Magnesite Brick	55
3	Thermodynamic Functions Involved in the Formation of Sulfates in Refractory Bricks	58
A1	X-Ray Diffraction Data of Sample PX1 from the Port-Side Chrome-Magnesite Brick	66
A2	X-Ray Diffraction Data of Sample PX2 from the Port-Side Chrome-Magnesite Brick	68
A3	X-Ray Diffraction Data of Sample PX3 from the Port-Side Chrome-Magnesite Brick	70
A4	X-Ray Diffraction Data of Sample PX4 from the Port-Side Chrome-Magnesite Brick	72
A5	X-Ray Diffraction Data of Sample PX5 from the Port-Side Chrome-Magnesite Brick	74
A6	X-Ray Diffraction Data of Sample PX6 from the Port-Side Chrome-Magnesite Brick	76
A7	X-Ray Diffraction Data of Sample TX1 from the Target-Wall Chrome-Magnesite Brick	78

EFFECTS OF ALTERNATE FUELS
REPORT NO. 2
ANALYSIS OF BASIC REFRACTORIES DEGRADED BY RESIDUAL OIL COMBUSTION PRODUCTS

G. C. Wei and V. J. Tennery

ABSTRACT

Industrial conversion in the U.S. to alternate fuels from natural gas is presently under way and will accelerate rapidly as a result of gas curtailments and National policy considerations. Currently the prime alternate fuels are distillate and residual oils and coal. Conversion to residual oils or coal for high-temperature process heat applications is anticipated to result in accelerated refractory and insulation corrosion and degradation due to reactions between fuel impurities and the ceramic linings of high-temperature equipment. Understanding the nature of such reactions and identification of means for preventing or retarding them will be of considerable assistance to both refractory manufacturers and users as well as a significant contribution to energy conservation.

This report is the second of a series that will be issued covering analyses of several generic types of refractories that have been used in industrial equipment with alternate fuels.

This report presents analyses of chrome-magnesite and magnesite refractories used in the port area and regenerator checkers, respectively, of a commercial 200 metric ton/day container glass furnace fired with residual oil for 3.5 years. The chrome-magnesite refractories analyzed were used in the port side and target wall of the furnace, while the magnesite refractory was from the 18th level checker in the regenerator. Maximum service temperature for the chrome-magnesite refractory was in the range 1500-1600°C (2800-2900°F), while for the magnesite refractory it was about 1100°C (2012°F). The chrome-magnesite refractory from the port side and the magnesite from the regenerator exhibited considerable degradation, which macroscopically appeared as swelling and cracking. The chrome-magnesite refractory used in the target wall showed evidence of gross fluxing. Both chrome-magnesite specimens had a visible slag or reaction layer on the surfaces exposed to the combustion atmosphere. The magnesite specimen exhibited gross swelling and cracking throughout the volume exposed to the combustion product gas stream, but had little swelling in other zones protected from the gas stream by the checkerwork structure. Analyses of

the port-side specimen of chrome-magnesite indicated that nickel impurity from the fuel oil reacted with the forsterite and monticellite bonding phases in the refractory to form a magnesium nickel silicate compound, and this was accompanied by a significant expansion. Vanadium impurity from the fuel oil reacted with the original monticellite phase to form a liquid phase. The chrome ore spinel appeared to be the most resistant phase to reaction with the fuel oil impurities. Analysis of the chrome-magnesite target wall specimen indicated that the forsterite and monticellite bonding phases react with both glass batch carryover and fuel oil impurities. This resulted in the formation of a significant amount of a relatively nonrefractory liquid phase, which dissolved the major chrome ore spinel phase. Significant reactions with nickel-bearing species did not occur in this furnace location, and gross swelling of the refractory was minimal during service.

In the magnesite refractory originally containing about 93 wt % MgO, swelling and cracking during service was primarily due to the formation of Na_2SO_4 within the periclase (MgO) grains as well as to some MgSO_4 formation. The sulfates form within the periclase grains with a particular geometric relationship to the crystallographic orientation of the MgO. Specific details of this orientation relationship were not identified. Swelling of this refractory appears to be related to specific molar volume difference between the MgO and the sulfate reaction products. The specific mechanisms for sodium and sulfur transport within this refractory were not identified.

These analyses have clearly shown that identification of a critical alternate fuel impurity for a given refractory system depends on where the refractory is used in the furnace. This is apparently related to not only the refractory hot-face service temperature but also the chemical potential of various impurity species in the combustion gas streams where the combustion gas contacts the refractory.

This work indicates that chrome-magnesite refractories can be made more resistant to degradation by alkali, nickel, and vanadium fuel impurities by reducing the content of the forsterite and monticellite bonding phases as much as possible. Magnesite refractories, on the other hand, are most susceptible to degradation by sodium and sulfur entering the refractory, either as gaseous species or by solid-state diffusion with subsequent formation of Na_2SO_4 and MgSO_4 . Identification of the sodium and sulfur transport mechanisms in high-magnesia refractories will be necessary to determine if the rate of transport can be sufficiently reduced to permit better refractory performance.

INTRODUCTION

Recently, natural gas curtailments in the U.S. have required conversion of many industrial furnaces to alternate fuels such as distillate and residual oils, coal, and low-Btu gases or other forms of energy such as electricity. Among these possible choices, distillate and residual oils were recently identified as industrially favored near-term alternate fuels.¹ Coal is expected to have a major role in the long term, as petroleum-based fuels are gradually depleted and coal becomes the only fuel available to industries. The combustion, fuel handling, and ash problems associated with coal firing for most process heat applications are not now considered solved. If we assume a sufficient supply of fuel oils based on domestic and foreign sources, distillate and residual oils will be the primary alternate fuels for industrial heating applications in the next five years. Distillate oils are relatively clean, and the effects of distillate oil combustion on refractories are minor if the distillate oil combustion system is properly installed and operated. Industrial usage of distillate oils as fuel is currently practiced extensively. Residual oils, however, may contain substantial amounts of many impurities such as sodium, vanadium, and sulfur, which can be quite detrimental to furnace refractories. The impurity contents of residual oils vary over a wide range depending on the crude source and storage and transportation conditions. There is currently limited industrial refractory operating experience in the U.S. with residual oils. It is therefore useful to analyze refractories that have been exposed to residual oil combustion in industrial furnaces and exhibit accelerated degradation when compared with the anticipated performance in a natural gas or distillate oil combustion environment. The analysis results will provide insight into the process of refractory deterioration due to residual oil impurities and provide guidance to U.S. industries as to selection and development of refractories having improved performance in the presence of residual oil combustion.

Basic refractories are an important class of refractory materials that are widely used in the iron and steel, nonferrous metal, glass,

and cement industries. The construction of furnace components including sidewalls, roofs, and regenerators in these industries typically employs basic refractories because of their outstanding high-temperature mechanical and chemical properties and good resistance to slag attack. Based on the chemical composition, basic refractories are classified into: magnesite, magnesite-chrome, chrome-magnesite, chrome, and dolomite types. The particular types of basic refractories that were analyzed in the present study are chrome-magnesite and high-MgO magnesite refractory bricks.

The refractory samples were used bricks collected from an industrial glass melting furnace. Chrome-magnesite bricks were obtained from the port side and the target wall, and the high-MgO refractory from the 13th-course checker of the regenerator of a glass furnace fired with residual oil for 3.5 years. This furnace was melting glass for commercial production of container glass at a rate of 200 metric tons per day. Results presented in this report include chemical, optical microscopy, scanning electron microscopy, and x-ray diffraction analyses plus an interpretation of the refractory degradation mechanism based on results from these analyses and other observations reported in the literature.

This report is the second of a series of reports on analyses of several generic refractory types that have been used in industrial furnaces fired with residual oil or coal. All the refractory samples were obtained with the cooperation of industrial firms. The objective of the present work is to identify the basic physical and chemical changes underlying the degradation processes operative in chrome-magnesite and high-MgO refractories exposed to residual oil combustion. The present report will explain the effects of residual oil use on these two important types of basic refractories at use temperatures typical of actual industrial processes.

SPECIMEN HISTORY

As-received chrome-magnesite bricks before use in the port side or the target wall of the glass furnace regenerator have a reported

chemical composition expressed in terms of weight percent oxide equivalents as shown in Table 1. This terminology for expressing the chemical composition of refractories is conventional in the industry and will be employed in this report. Basically, the amount of a given chemical element present in the refractory is presented as the most stable oxide of that element under standard conditions. This does not imply that a particular element is present in the refractory in the form of the stated oxide. For example, by this terminology, the compound mullite with a formula $\text{Al}_6\text{Si}_2\text{O}_{13}$ or $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ has a composition of 72 wt % Al_2O_3 and 28 wt % SiO_2 on an oxide equivalent basis. In chrome-magnesite bricks, the MgO equivalent content is 50 wt %, while the Cr_2O_3 equivalent content is 20 wt %. These bricks are of the direct-bonded type, having a microstructure consisting of chrome ore spinel $[(\text{Mg},\text{Fe})(\text{Al},\text{Cr})_2\text{O}_4]$ grains bonded together by a periclase (MgO) phase. This type of refractory has a minimal amount of silicate phase around the chrome ore or periclase (MgO) grains. The maximum temperature at the hot face of the bricks during their service life of 3.5 years was in the range 1538 to 1593°C (2800–2900°F).

The chemical composition expressed in terms of oxide equivalents of the original high-MgO bricks that were used in the 18th-course checker of the glass furnace regenerator is also shown in Table 1. The MgO equivalent content is 93 wt %. These high-MgO bricks are described by the vendor as chemically bonded. The CaO-to-SiO₂ ratio of 0.25 suggests that the bonding material in the original high-MgO bricks consisted of forsterite (Mg_2SiO_4) and montecellite ($\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$). During the 3.5-year service life of this refractory, the maximum temperature at the hot face of the brick was in the range 1093 to 1149°C (2000–2100°F).

The original dimensions of the chrome-magnesite bricks used in the port side and the target wall of the glass furnace regenerator were 230 by 110 by 76 mm (9.0 by 4.5 by 3.0 in.) and 310 by 110 by 76 mm (12 by 4.5 by 3.0 in.), respectively. The original dimensions of the high-MgO bricks used in the 18th-course checker of the glass furnace regenerator are 230 by 110 by 76 mm (9.0 by 4.5 by 3.0 in.).

Table 1. Chemical Analysis of Chrome-Magnesite and High-MgC Brick

Oxide	Equivalent Content, wt %							
	Original Chrome- Magnesite Brick	Port-Side Brick		Target Wall Brick		Original High MgO Brick	Checker Brick	
		Expanded Part (Region A)	Nonexpanded Part (Region B)	Altered Part (Region A)	Unaltered Part (Region B)		Expanded Part (Region A)	Nonexpanded Part (Region B)
MgO	50.00	50.09	46.03	47.83	53.31	93.00	88.76	88.11
Cr ₂ O ₃	20.00	2.89	17.14	16.29	21.08	<0.10	0.208	0.158
Al ₂ O ₃	17.50	1.18	18.39	14.95	14.18	1.00	0.92	1.01
Fe ₂ O ₃	9.00	2.83	8.47	7.90	8.55	1.00	0.792	0.535
SiO ₂	2.50	38.10	8.11	9.88	1.95	4.00	4.03	3.79
CaO	1.00	1.59	4.71	2.29	0.36	1.00	1.65	1.63
TiO ₂	<0.10	0.109	0.327	0.218	0.109	<0.10	0.084	0.083
Na ₂ O	<0.10	0.43	0.25	0.13	0.10	<0.10	1.06	1.56
K ₂ O	<0.10	0.12	0.13	0.15	0.04	<0.10	0.06	0.06
SO ₃	<0.10	<0.01	0.06	0.02	0.01	<0.10	2.34	2.89
V ₂ O ₅	<0.10	<0.002	<0.002	0.022	0.056	<0.10	0.040	0.054
NiO	<0.10	3.29	0.189	0.121	0.121	<0.10	0.008	0.008

At this point, it will be helpful to review the configuration and the operation of a glass furnace regenerator. A schematic of a typical side port glass melting furnace is shown in Fig. 1. One set of two regenerators is connected to each of the two sides of the furnace. In the regenerator, the checker bricks, which are packed in a conventional open setting configuration or other arrangement, are first heated by the furnace exhaust gas. Air for the burners is then subsequently passed over the checkers to recover the heat stored in the checker refractories. The preheated air flows from the regenerator to the side ports and provides the secondary air for the burners located above the furnace side ports. While one set of regenerators is supplying preheated combustion air, the other set is being heated by the burner exhaust. The location of the side of the regenerator is indicated in Fig. 1. Furnace exhaust gas passes over this area and impinges on the target wall. Checker bricks examined in the present study were arranged in a conventional open setting configuration (shown in Fig. 1) in the regenerator.

ORNL-DWG 77-15960

Fig. 1. Typical Side Port Glass Tank Melting Furnace.

The refractory bricks in the regenerator experience numerous thermal cycles. The oxygen potential in the gas stream also cycles, as that of the exhaust gas is considerably lower than that of the incoming combustion air. Thus, regenerator refractories also experience an oxidation-reduction cycling process. Thermal cycling and oxidation-reduction cycling are important features of the history of the regenerator refractories analyzed in the present study. However, quantitative information about the thermal cycling and oxidation-reduction cycling, including cycling period, minimum temperature, and partial pressure of oxygen, was not acquired by the glass company during the furnace campaign. Only the maximum temperatures at the hot face of the bricks are known, and these are considered accurate to within $\pm 20^{\circ}\text{C}$. The temperature drop across the 230-mm (9.0-in.) length of the chrome-magnesite brick used in the regenerator port side was estimated by the furnace engineer to be 56°C (100°F) at the maximum hot face temperature. In the case of the target wall, the hot face consisted of the 114 by 76-mm (4.5 by 3.0-in.) end surface of the brick. The temperature varied from the maximum hot-face temperature of 1538 to 1593°C (2800 – 2900°F) to the maximum cold-face temperature of 1510 to 1566°C (2750 – 2850°F) along the 305 mm (12 in.) length of the chrome-magnesite brick. The high-MgO bricks that were used in the 18th-course level of the regenerator had a temperature difference of about 28°C (50°F) between their hot and cold surfaces at the maximum hot-face temperature.

A No. 6 residual oil was used in firing this glass melting furnace. Unfortunately, the glass company did not analyze the residual oil, and therefore the specific impurity input in the combustion products from this source is unknown.

RESULTS

Chemical, x-ray, optical microscopy, electron microprobe, and scanning electron microscopy analyses were performed on the previously described basic refractories. Experimental procedures were the same as those outlined in a report on the analysis of high-duty fireclay

refractories exposed to coal combustion.² In this section, results of the present analyses are categorized according to refractory types and usage.

Port-Side Chrome-Magnesite Brick

Fig. 2 shows the used chrome-magnesite brick (regenerator port side). A striking feature is the large expansion at the hot face of the brick, equivalent to a linear expansion of about 43%. The hot face of the brick has a mottled green color. A direct view of the hot face is shown in Fig. 3. The holes in the brick resulted from the glass company's sampling for its own analysis.

A sampling plan for the brick in Fig. 2 is illustrated in Fig. 4. The hot face, the cold end, and areas between them were subjected to extensive analyses, including metallographic and x-ray diffraction

Fig. 2. Port-Side Chrome-Magnesite Brick. Scale is 305 mm.

Fig. 3. Top View of the Hot Face of the Port-Side Chrome-Magnesite Brick. Scale is 102 mm.

Fig. 4. Sampling Plan for Analyses of the Port-Side Chrome-Magnesite Brick. Regions A and B represent the expanded and nonexpanded parts of the brick. Samples designated by PM and PX are optical microscopy and x-ray diffraction samples, respectively. Scale is 25 mm.

plus chemical analysis of various selected zones. Chemical analysis results of the expanded (region A) and the nonexpanded part (region B) of the brick are shown in Table 1. The Cr_2O_3 and Fe_2O_3 equivalent contents of the used chrome-magnesite refractory are less than those present in the original brick because of the volatility of refractory constituents containing these oxide equivalents. In contrast, the equivalent contents of SiO_2 and CaO are greater than their original values. The increases in the silicon and calcium contents in the used refractory resulted from depletion of the more volatile components during high-temperature service in addition to batch carryover from the glass melting process. In comparing the chemical compositions of the swelled (A) and nonswelled (B) regions of the brick, the SiO_2 equivalent content of region A is almost five times that of region B, while the Al_2O_3 and Cr_2O_3 equivalent contents decrease as one proceeds from region B to A. The Na_2O , K_2O , SO_3 , and V_2O_5 equivalent contents of the used brick are relatively low (i.e. <0.50 wt %), but the NiO equivalent content in region A (3.29 wt %) is over 17 times that in region B. The presence of a significant amount of nickel at the hot face of the brick is unexpected, and since nickel was not a significant component of the glass or refractories, it apparently was an impurity in the residual oil fuel. An example of nickel contamination of basic refractories of an industrial glass melting furnace fired with residual oil was reported³ by a European glass firm in 1970.

X-ray diffraction analyses were done on six samples of the refractory (PX1-PX6) corresponding to locations proceeding from the hot face to the cold end of the brick. The Appendix gives the detailed data. These samples were removed from various zones of the brick as shown in Fig. 4. At the cold end of the brick, major crystalline phases were chrome ore spinel, $(\text{Mg},\text{Fe})(\text{Al},\text{Cr})_2\text{O}_4$; periclase, MgO ; forsterite, Mg_2SiO_4 ; monticellite, $\text{CaO}\cdot\text{MgO}\cdot\text{SiO}_2$; magnesioferrite, MgFe_2O_4 ; and aluminum chromite, $(\text{Fe},\text{Al},\text{Cr})_2\text{O}_3$. X-ray diffraction data from all six samples indicated the presence of these six crystalline phases. Sample PX1 at the hot face of the brick contained two additional crystalline phases, namely $\text{MgNiSi}_2\text{O}_6$ and $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{O}$. X-ray

diffraction peak intensities of the monticellite and forsterite crystalline phases increased steadily from the cold end to the hot face of the brick. This can be explained as partially due to silica carryover to the refractory from the glass melting furnace, with resultant reaction of silica and the original periclase in the refractory to produce a large volume concentration of forsterite. Nickel impurity from the fuel oil present in the combustion gas stream apparently also reacted with the periclase and the forsterite in the refractory and produced $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{O}$ and $\text{MgNiSi}_2\text{O}_6$. Magnesium oxide and nickel oxide have a rock-salt structure, and their lattice spacings are 0.420 nm (4.20 Å) and 0.41769 nm (4.1769 Å), respectively. The lattice parameter of $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{O}$ is 0.41926 nm (4.1926 Å).⁴ Thus, a volume shrinkage of about 1.0% is expected with the formation of $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{O}$ from a reaction between MgO and nickel-bearing vapor species. Such shrinkages in the material will lead to high stresses and crack generation along the boundary between the periclase and neighboring phases. The crystal symmetry of both forsterite and $\text{MgNiSi}_2\text{O}_6$ is orthorhombic. Expansion will occur as a result of the reaction between nickel (from fuel oil combustion products) and forsterite (in the brick). The densities of Mg_2SiO_4 and $\text{MgNiSi}_2\text{O}_6$ are 3.222 and 3.749 Mg/m^3 , respectively. The molecular weights of Mg_2SiO_4 and $\text{MgNiSi}_2\text{O}_6$ are 140 and 235, respectively. Consequently, the volume change per mole of Mg_2SiO_4 associated with the formation of $\text{MgNiSi}_2\text{O}_6$ is about 188%. The reaction causing the observed expansion in the brick hot face is possibly the following:

Another possibility is the diffusion of a nickel oxide vapor species into the forsterite. Upon reaching the solid solubility limit, a crystalline phase containing nickel, such as $\text{MgNiSi}_2\text{O}_6$, is precipitated. If the nickel diffuses into the forsterite and is followed by precipitation of nickel-bearing phases, appreciable dilation of the host phase plus the volume constraint from the phases surrounding the forsterite

will generate high stresses in both the forsterite phase and the neighboring phases and thus produce significant cracking.

We also examined by optical microscopy a series of samples taken from different brick zones ranging from the cold end to the hot face; that is, from the nonexpanded part to the expanded part of the brick. These samples were labeled as PM1 through PM5, with the sequencing of the last digit corresponding to samples taken from the hot face to the cold face of the brick. Brick zones from which these samples were taken are shown in Fig. 4.

Microstructures from region B are shown in Figs. 5 through 8, in which the light phase is chrome ore spinel (C), the light gray phase is periclase (P), the gray phases are forsterite (F) and monticellite (M), and the dark area is the porosity (PR). These photomicrographs were taken on sample PM5, which was close to the cold end of the brick. Microstructures clearly show that in region B, chrome ore spinel and periclase or periclase and periclase are in direct contact. A minimum amount of the forsterite and monticellite phases is present as the bonding material, as shown in Fig. 6, and the bonding between chrome ore spinel and periclase or between periclase grains largely involves direct contact of these phases. The formation of the direct bond between the chrome ore and periclase is believed⁵ to result from an interdiffusion of these two phases. Magnesioferrite precipitate (MF) having a lamellar morphology is present within the periclase grains and is clearly visible in Figs. 5(b) and 7. Globular inclusions in the periclase grains shown in Fig. 7 are a chrome ore spinel. Large chrome ore spinel grains contain an aluminum chromite precipitate $(\text{Fe,Al,Cr})_2\text{O}_3$, designated by AC in Fig. 8. These phases were identified with the aid of an electron microprobe, by which elements of atomic number at least 11 (Na) can be detected in an area $3\text{ }\mu\text{m}$ in diameter, in addition to literature data⁶⁻¹⁷ on direct-bonded chrome-magnesite refractories.

Typical microstructures of samples PM1 to PM5 are presented in Figs. 9 through 11. It is worthwhile to note that chrome ore spinel grains are fragmented, as indicated by the arrow in Fig. 9(a), in

Fig. 5. One Area of the Nonexpanded Region of the Port-Side Chrome-Magnesite Brick. Features identified are C, chrome ore spinel; P, periclase; F, forsterite; M, monticellite; PR, porosity; MF, magnesioferrite. (a) 500 $\times$. (b) 100 $\times$.

Fig. 6. Second Area of the Nonexpanded Region of the Port-Side Chrome-Magnesite Brick. Features identified are C, chrome ore spinel; P, periclase; F, forsterite; M, monticellite; PR, porosity; MF, magnesio-ferrite. (a) 500 $\times$. (b) 100 $\times$.

Fig. 7. Third Area of the Nonexpanded Region of the Port-Side Chrome-Magnesite Brick. Features identified are C, chrome ore spinel; P, periclase; F, forsterite; M, monticellite; PR, porosity; MF, magnesioferrite. (a) 500 $\times$. (b) 100 $\times$.

Fig. 8. Fourth Area of the Nonexpanded Region of the Port-Side Chrome-Magnesite Brick. Features identified are C, chrome ore spinel; P, periclase; F, forsterite; M, monticellite; PR, porosity; MF, magnesioferrite; AC, aluminum chromite. (a) 1000 $\times$. (b) 100 $\times$.

Fig. 9. Samples (a) PM2 and (b) PM1 from the Port-Side Chrome-Magnesite Brick. 100 $\times$. F, forsterite; M, monticellite; P, periclase; C, chrome ore spinel. Larger letters on the micrographs refer to areas scanned by electron microprobe. Arrow in (b) shows fragmentation in chrome ore spinel grain.

Fig. 10. Samples (a) PM4 and (b) PM3 from the Port-Side Chrome-Magnesite Brick. 100 $\times$. F, forsterite; M, monticellite; P, periclase; C, chrome ore spinel.

Fig. 11. Sample PM5 from the Port-Side Chrome-Magnesite Brick. 100×. F, forsterite; M, monticellite; P, periclase; C, chrome ore spinel; MF, magnesioferrite.

regions close to the hot face of the brick. A large number of chrome ore spinel grains in the swelled part of the brick (samples PM1, PM2, and PM3) were fragmented, whereas chrome ore spinel grains in the non-swelled part of the brick (samples PM4 and PM5) remained intact. Forsterite and monticellite, which are identified by F and M in Figs. 9 through 11, also increase from a minor amount in the nonswelled part of the brick to major phases in the sections exhibiting large swelling. Extensive networks of cracks are present in the gray area (the forsterite and monticellite) of the swelled refractory. Results of elemental analyses by electron microprobe point scans of different areas in Fig. 9 are presented in Figs. 12 through 17. Nickel was found in the periclase, forsterite, and monticellite, but not in the chrome ore spinel. Apparently nickel impurity from the residual oil used in firing the glass melting furnace has reacted with periclase, forsterite, and monticellite at the hot face of the brick. This conclusion agrees with chemical analysis results for the refractory, which showed a nickel oxide equivalent content of 3.29 wt % in the swelled refractory

ORNL-DWG 77-15968

Fig. 12. Typical Point Scan by an Electron Microprobe of Bright Particles in an Area A of Fig. 9(a).

Fig. 13. Typical Point Scan by an Electron Microprobe of Matrix Phase in an Area A of Fig. 9(a).

Fig. 14. Typical Point Scan by an Electron Microprobe of Bright Particles in an Area B of Fig. 9(b).

ORNL-DWG 77-15965

Fig. 15. Typical Point Scan by an Electron Microprobe of Matrix Phase in an Area B in Fig. 9(b).

ORNL-DWG 77-15966

Fig. 16. Typical Point Scan by an Electron Microprobe of an Area C in Fig. 9.

Fig. 17. Typical Point Scan by an Electron Microprobe of an Area D in Fig. 9.

near the hot face. The spinel phase from the original chrome ore was not affected by the presence of nickel-bearing impurities. Expansions of the refractory due to the generation of forsterite, the diffusion of nickel into forsterite and monticellite, and the formation of new nickel-bearing phases caused the large swelling and the mechanical weakening of the refractory brick zones close to the hot face.

A montage of a cross section (from the hot face toward brick interior) of sample PML is shown in Fig. 18. Selected areas have been examined at higher magnifications and are presented in Figs. 19 through 21. It should be pointed out that the swelled part of the brick has substantially higher porosity (~40%) compared with the cold end (~4%). This is clearly indicated in Fig. 18. Large pores (indicated by LP in Fig. 18) at the hot face of the brick have diameters up to 1 mm, and the porosity is continuous in several areas. Small fragments of the original phases present in the swelled part of the brick are located in these large pores and are also distributed with the new major phases, as shown in Fig. 21(b). Except chrome ore spinel remnants, all these grains contain sodium. In some grains, vanadium is present

THIS SIDE DIRECTLY EXPOSED TO ATTACK
BY RESIDUAL OIL IMPURITIES

Fig. 18. Cross Section Through a Part of the Hot Face in the Port-Side Chrome-Magnesite Brick. Areas 1, 2, and 3 are selected for examination at higher magnification.

Fig. 19. Area 1 in Fig. 18 Showing Cracks in the Forsterite and Monticellite. 100×.

Fig. 20. Higher Magnification (500×) of Areas (a) A and (b) B in Fig. 19, Showing Cracks in the Chrome Ore Spinel and Complex Phases Generated by Reactions of Impurity Phases Originally Present Within the Chrome Ore Grains. Gray area, G; light gray area, LG; light gray weblike area, LGW.

Fig. 21. Areas 2 and 3 in Fig. 18. (a) Complex phases developed along cracked spaces in the forsterite and monticellite of area 2. 100 $\times$. (b) Remnants of various fractured phases distributed about the nickel-containing forsterite phase in area 3. 500 $\times$.

in addition to other elements, including Na, Al, Si, Ca, Cr, and Fe. Sodium, which came from the fuel oil and batch carryover, appears to have played a major role in the reaction of crystalline phases at the hot face of the brick.

Chrome ore spinel grains in chrome-magnesite refractories usually contain some forsterite, monticellite, and merwinite inclusions, depending on the source. In the case at hand, new phases have formed extensively within the chrome ore spinel grains during refractory service. Volume increases associated with the formation of these phases have generated extensive arrays of cracks in the grains. Typical crack lines caused by this mechanism are shown in Fig. 20(a). The reaction in the inclusion phases within the chrome ore grains produced a liquid phase and several complex crystalline phases, as deduced from the microstructure. Some of these inclusions are shown in Fig. 20. Electron microprobe analysis indicated that the light gray phase identified as LG included the elements Ca, Mg, Si, Cr, and Fe (note that our electron microprobe does not detect elements of atomic number <11). In addition to these elements, aluminum was also present in the light gray web phase identified as LGW. The gray phase identified as G in Fig. 20 contained Ca and Cr in addition to Na, Al, Si, and Fe. It should be noted that nickel was not detected in either the chrome ore spinel crystals or the inclusion phases.

Two other areas in the refractory shown in Fig. 18 were studied, and typical areas are shown in Fig. 21. Figure 21(a) shows complex phases present at the sites of cracks within the forsterite and monticellite, and Fig. 21(b) shows a large number of particles dispersed along the boundary of the main phase. The phases within the crack sites in the forsterite and montecellite were analyzed with an electron microprobe. Figure 22 shows the microstructure of complex phases at crack sites in the forsterite and monticellite. A phase having a dendritic morphology is present in an extensive dark gray matrix phase (see arrow DG). Another light gray phase is also present (see arrow LG). The microprobe analyses showed Na, Al, Si, Ca, and Fe in the matrix phase, while Mg, Al, Si, Ca, and Fe were detected in the dendritic phase. The light gray phase (LG) contains chromium in

Fig. 22. The Expanded part of the Port-Side Chrome-Magnesite Brick, Showing Complex Phases Within the Forsterite and Monticellite. C, chrome ore spinel; M, monticellite; DG, dark gray area; LG, light gray area. (a) 500 $\times$. (b) 1000 $\times$.

addition to the elements detected in the dendrites. The gray phase that surrounds this whole area is monticellite (M), which contains some iron and nickel. The more reflective phase identified as C in Fig. 22 is chrome ore spinel.

Scanning electron microscopy was used to further characterize the brick structure near region A in Fig. 4. Figure 23 shows that a liquid phase (L) existed along the grain boundaries at the service temperature. The reason that the phase L was liquid is the absence of a well-defined crystalline morphology or habit. Microprobe analyses of the phase L in Fig. 23 indicated the presence of Ca, Mg, Si, V, Cr, and Fe. Vanadium impurity from the fuel oil apparently formed a low-melting liquid by reaction with the monticellite. Small spherical crystals (SC) grew in this liquid phase, and analyses showed that they contained Ca, Mg, Si, Fe, and Ni. Figure 24 obtained from fracture surfaces near region A indicate a microstructure consisting of a phase (W) distributed in a weblike pattern within a matrix phase (M). The weblike phase has a geometry characteristic of surfaces produced by brittle fracture and contains Ca, Mg, Cr, Fe, V, and Ni. The matrix phase contains Ca, Mg, Si, and Ni, but not V; thus the vanadium has effectively partitioned between these phases. Dendritic crystals (D), which probably are forsterite, are also present in this region of the refractory, and examples are shown in Fig. 25.

Figure 26, which is another scanning electron micrograph of the fracture surface near region A of Fig. 4, shows the fracture morphology of forsterite, monticellite, and chrome ore spinel, represented respectively, by F, M, and C. Using the energy-dispersive analysis of x rays (EDAX) mode of SEM, we determined that nickel is present in the forsterite and monticellite but not in the chrome ore spinel. This agrees with the findings obtained by optical microscopy and the electron microprobe analysis on samples from the same zone in the refractory.

Fig. 23. Scanning Electron Fractography of the Expanded Part of the Port-Side Chrome-Magnesite Brick. (a) Spherical crystals (SC) growing from a liquid phase (L). (b) Liquid phase at higher magnification.

Fig. 24. Scanning Electron Fractography of the Expanded Part of the Port-Side Chrome-Magnesite Brick. (a) Weblike phase (W) distributed in a matrix phase (M). (b) Fracture river patterns in the matrix phase.

Fig. 25. Scanning Electron Fractography of the Expanded Part of the Port-Side Chrome-Magnesite Erick, Showing the Dendritic Phase (D).

Fig. 26. Scanning Electron Fractography of the Expanded Part of the Port-Side Chrome-Magnesite Brick. C, chrome ore spinel; F, forsterite; M, monticellite.

Target-Wall Chrome-Magnesite Brick

Figure 27 shows the chrome-magnesite brick used in the target wall of a glass furnace regenerator and analyzed in this section. Although the brick hot face became mechanically weak and friable, it expanded only slightly during service compared with the specimen in Fig. 2. Nominal chemical analysis of the original brick in Table 1 is the same as that of the chrome-magnesite refractory used in the port side of the glass-furnace regenerator. A sampling plan used for analysis of this chrome-magnesite brick is shown in Fig. 28. Chemical analysis results for brick zones near the hot face (region A in Fig. 28) and near the cold end (region B in Fig. 28) are presented in Table 1. The chemical composition of the brick sample from region B, which is about 0.23 m (9 in.) from the hot face of the brick, is similar to that of the original brick. However, the chemical composition of the brick sample from region A, located about 25 mm (1 in.) from the hot face of the brick, shows significant increases in the SiO_2 and CaO equivalent contents. The increases in the SiO_2 and CaO equivalent contents were probably caused by batch carryover from the glass melting operation. The alkali oxide ($\text{Na}_2\text{O} + \text{K}_2\text{O}$), V_2O_5 , and NiO equivalent contents in regions A and B are rather low (<0.5 wt %).

X-ray diffraction data for three segments in the brick are presented in the appendix. These three samples for x-ray analysis were designated as TX1, TX2, and TX3. Figure 28 shows the locations in the brick from which these samples were taken. All three samples contain six crystalline phases; namely, chrome ore spinel, periclase, forsterite, aluminum chromite, magnesioferrite, and diopside ($\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$). The relative intensities of the diopside diffraction peaks increase as one proceeds from the cold end to the hot end of the brick. Monticellite also appears present in sample TX1, the sample closest to the brick hot end.

The locations of the samples in the original brick selected for optical microscopy are represented by the symbols TM1 through TM4 in Fig. 28. Typical microstructures of these samples are shown in

PHOTO 5964-76

HOT FACE →

CHROME-MAGNESITE BRICK FROM TARGET WALL
OF LEFT REGENERATOR No. 2 PORT (No. 6 OIL
FIRED FURNACE)

Fig. 27. The Target-Wall Chrome-Magnesite Brick. Scale is 305 mm.

Fig. 28. Sampling Plan for the Target-Wall Chrome Magnesite Brick. Scale is 51 mm.

Figs. 29 through 32. Samples TM1 and TM2, which were located close to the hot face of the brick, contain chrome ore spinel, periclase, forsterite, and diopside.

A phase (L) that was liquid at the service temperature and contains lamellar precipitate (LP) surrounds some of the chrome ore spinel grains (C) in Fig. 29(b). Electron microprobe analysis showed Ca, Mg, Al, Si, Ti, and Fe in the lamellar precipitate and Na, Ca, Al, Si, K and Fe in the matrix. Nickel was also present in periclase grains in samples TM1 and TM2. The microstructure of sample TM3 (Fig. 31) consisted of angular chrome ore spinel crystals dispersed in a matrix (L) containing the elements Na, Al, Si, K, Ca, Ti, V, Cr, and Fe. At the colder end of the brick, sample TM4 has a microstructure typical of that for direct-bonded chrome-magnesite refractories, which contain chrome ore spinel (C) and periclase (P) as major phases plus only a minor amount of silicate phases.

In summary, the data indicate that at the furnace operating temperature the refractory hot face consisted of a significant amount of liquid phase containing Na, Ca, Al, Si, K, Fe, in which a lamellar

Fig. 29. Sample TM1 of the Target-Wall Chrome-Magnesite Brick. LP, lamellar precipitate; C, chrome ore spinel; P, periclase; L, liquid phase. (a) 100 $\times$. (b) 500 $\times$.

Fig. 30. Sample TM2 of the Target-Wall Chrome-Magnesite Brick. C, chrome ore spinel; P, periclase; L, liquid phase. (a) 100 $\times$. (b) 500 $\times$.

Fig. 31. Sample TM3 of the Target-Wall Chrome-Magnesite Brick. C, chrome ore spinel; L, liquid phase. (a) 500 $\times$. (b) 100 $\times$.

Fig. 32. Sample TM4 of the Target-Wall Chrome-Magnesite Brick. C, chrome ore spinel; P, periclase. (a) 100 $\times$. (b) 500 $\times$.

precipitate formed. Sodium and potassium apparently played major roles in the formation of this liquid phase. Nickel impurity from the fuel oil also reacted with the major periclase phase at the hot face of the brick. About 0.13 m (5 in.) behind the hot face the microstructure consists of partially dissolved angular chrome ore spinel grains dispersed in a liquid phase containing Na, Al, Si, K, Ca, Ti, V, Cr, and Fe. At the relatively cold end of the brick, the microstructure is typical of direct-bonded chrome-magnesite refractories. The microstructure was significantly changed in approximately 70% of the length of the refractory brick along the temperature gradient.

High-MgO Checker Brick

A high-MgO ($\sim 93\%$ MgO) brick used in the 18th level checker, as measured from the top of the regenerator of a 200 metric ton/day glass furnace fired with No. 6 oil for a period of 3.5 years, is shown in Fig. 33. In the regenerator, these checker bricks were placed in an open setting configuration in which preheated air passed upward or flue gas passed downward alternately through the channels in the brickwork. Accordingly, the checker brick temperatures fluctuate over a range of about 200°C (360°F). The high-MgO brick showed a large expansion in the portion that was not under the mechanical constraint of the adjacent courses of checker bricks, as shown in Fig. 33.

Chemical analysis results of the expanded part and nonexpanded part of this high MgO brick is listed in Table 1. A sampling plan used for analysis of the brick is illustrated in Fig. 34. Chemical analysis indicated that both the portion showing swelling (region A) and the nonswelled (region B) part of the brick had the equivalent contents of MgO, SiO_2 , Al_2O_3 , Fe_2O_3 , and CaO all very close to the reported values of the original brick (see Table 1). The V_2O_5 , NiO, and K_2O equivalent contents in both zones A and B were very low (<0.06 wt %). However, the portion showing about 20 vol. % swelling and the nonswelled part of the brick contained significant amounts of sodium and sulfur. Indeed, x-ray diffraction data confirmed the existence of sodium sulfate as a crystalline phase in both the expanded and the nonexpanded parts of the used brick.

Fig. 33. The High-MgO Checker Brick.

ORNL-DWG 77-15961

Fig. 34. Sampling Plan for the High-MgO Checker Brick. Scale is 25 mm.

Designations for x-ray diffraction samples of this refractory are shown in Fig. 34. Samples taken from region A, region B, and the transition area between the above two zones are designated as CX1, CX3, and CX2 respectively. X ray diffraction data for these three samples are given in the appendix. Five crystalline phases — namely periclase, forsterite, merwinite, sodium sulfate, and magnesium sulfate — are present in all three samples. The intensities of diffraction peaks characteristic of sodium sulfate and magnesium sulfate showed no appreciable variation from zone CX1 to CX3.

Optical microscopy samples taken from the swelled and the nonswelled parts of the brick and designated as samples CM1 and CM2 had the microstructures shown in Figs. 35 and 36. The gray phase is periclase, identified as P, the dark gray material is the forsterite and merwinite bond phases, identified as F/M, and the dark areas are pores. Electron microprobe scans over the surfaces of samples CM1 and CM2 did not reveal the presence of elements characteristic of fuel oil impurities, such as nickel and vanadium, which were routinely detected in the chrome-magnesite refractories.

Fig. 35. Sample CM1 of the High-MgO Checker Brick. F/M, forsterite and monticellite. P, periclase. (a) 100×. (b) 500×.

Fig. 36. Sample CM2 of the High-MgO Checker Brick. F/M, forsterite and monticellite. P, periclasite. (a) 100 $\times$. (b) 500 $\times$.

Sodium and sulfur were not detected by the microprobe on the surface of the metallographic samples. The reason for this was determined to be leaching of these elements from the sample surfaces during metallographic polishing. The voids in periclase grains visible in Fig. 35(b) and 36(b) and indicated by the arrows are the spaces originally occupied by sodium sulfate, which had dissolved in the metallographic polishing liquid vehicle (water). Scanning electron fractography and EDXA of other specimens clearly indicated the presence of a phase containing sodium and sulfur, a phase containing magnesium and sulfur, and another phase containing Na, Mg, Ca, and S indicated by an arrow in Fig. 37(b). These phases are identified on a fracture surface of this refractory in Fig. 37.

DISCUSSION OF RESULTS

Port-Side Chrome-Magnesite Brick

An established refractory practice is to use chrome-magnesite refractories in the port side and the target wall of furnace regenerators for large continuous glass melting tanks. This refractory has good resistance to reaction with alkaline species such as sodium and potassium. It also has good high-temperature mechanical strength in the corrosive environment typical of a glass furnace regenerator. Swelling at the hot face has been observed for this material even in a natural gas firing environment and has been referred to as "the cauliflowering effect."¹⁸ Swelling has also been observed on the working surfaces of chrome-magnesite refractories in contact with slags containing iron.¹⁹ Various explanations offered for this swelling have been based upon expansion due to the formation of phases containing iron. One proposed mechanism is based on the idea that the volume increase results from porosity generated as a result of unequal diffusion rates of chromium and iron during the interdiffusion of the elements in the chrome ore spinel and the iron oxide impurity within the chrome ore.²⁰ Another proposed mechanism is based on a model involving the vaporization of the iron oxide existing in the

RICH IN Na,
Mg, Ca, S

Fig. 37. Scanning Electron Fractographs of a Sample from Zone A of the High-MgO Checker Brick Subjected to EDXA. (a) Sulfur-bearing areas: S, sodium sulfate; M, magnesium sulfate; P, periclase. (b) Arrow shows area containing Na, Ca, Mg, and S.

brick and subsequent reaction of this vapor with chrome ore spinel grains to form magnetite (Fe_3O_4). This reaction results in an expansion due to the greater volume occupied by the magnetite.²¹ Still another proposed mechanism takes into account the oxidation and reduction cycling in glass furnace regenerators.²² During the more oxidizing portion of the regenerator cycle, the ferrous iron present in the chrome ore is oxidized to ferric iron, and a consequence is the decomposition of the ferrous chromite ($\text{FeO}\cdot\text{Cr}_2\text{O}_3$) phase originally present. It results in a solid solution of ferric oxide and chromium oxide ($\text{Fe,Cr})_2\text{O}_3$. During the subsequent portion of the regenerator cycle, the solid solution of ferric oxide and chrome oxide is decomposed, and ferrous chromite $\text{FeO}\cdot\text{Cr}_2\text{O}_3$ is again formed. As much as 10% expansion is associated with the latter reaction.

If these expansion mechanisms are operative, chrome-magnesite refractories will swell during use regardless of the type of fuel used in firing the glass melting furnace. One necessary condition required by the redox type of volume expansion mechanism is that a crystalline phase, Fe_3O_4 or $\text{FeO}\cdot\text{Cr}_2\text{O}_3$, must be present in the brick during service. However, x-ray diffraction analyses of the expanded part of the brick reported on here did not reveal any diffraction peaks characteristic of Fe_3O_4 or $\text{FeO}\cdot\text{Cr}_2\text{O}_3$. They could have been present at the use temperature but reacted with other phases in the brick during cool-down of the furnace and, therefore, were not present in the analyzed brick. In any case, the abnormal expansion (43%) at the hot face of the brick does not seem to be totally explained by the above mechanisms. Alternative degradative mechanisms involving reactions of refractory constituents with batch carryover and fuel oil combustion products can explain the abnormal swelling in a more satisfactory way. Silica carried to the refractory hot face as batch carryover from the tank will react with periclase in the brick to produce forsterite at the service temperature, and the resulting expansion leads to cracking and fracturing of the bricks.²³ Forsterite has a density of 3.22 Mg/m^3 , which is less than the density of periclase (3.58 Mg/m^3).²⁴ There is a 6% volume increase for the formation of

one mole of forsterite from silica and periclase according to the reaction,

It has also been reported²³ that the forsterite bond in this type of refractory will under some conditions migrate to the cooler region of a brick and thereby leave the hotter regions devoid of silicates, thus rendering the hot face of the brick friable. This work has shown that nickel-bearing species derived from fuel oil combustion products may react with the forsterite and monticellite phases at the brick hot face. We pointed out previously that the molar volume of the reaction product, $\text{MgNiSi}_2\text{O}_6$, is 188% larger than that of forsterite. Consequently, the generation of $\text{MgNiSi}_2\text{O}_6$ will result in drastic expansion. X-ray diffraction lines characteristic of $\text{MgNiSi}_2\text{O}_6$ were observed in the brick hot face. Electron microprobe and scanning electron microscopy analyses indicated clearly the existence of a material containing Ni, Mg, and Si. Chemical analysis results also confirmed the presence of a significant amount of NiO equivalent content (3.29 wt %) in the swelled part of the brick. Our conclusion is that nickel from the fuel oil definitely played a major role in the abnormal swelling at the hot face of this refractory brick.

Nickel is a relatively common impurity in residual oils. The nickel content in No. 6 fuel oil varies depending on the crude source, refinery, and the transportation and storage conditions. Oil users do not ordinarily determine the nickel content in the oil used in firing industrial equipment such as glass melting furnaces. Therefore, we do not know the nickel content in the fuel oil used in the glass melting furnace from which these refractories were obtained. If we assume the concentration of nickel in the fuel oil is 100 ppm and the furnace consumes about 9500 m³ (25×10^5 gal) of fuel oil per year, about 950 kg of nickel per year would be delivered to the furnace. At the end of a three and a half year long furnace campaign, this would represent 3325 kg of nickel. This amount of nickel would be sufficient to convert periclase and forsterite in the 25-mm (1-in.)

zone at the brick hot face, 76×114 mm (3.0×4.5 in.) surface, to $(\text{Mg},\text{Ni})\text{O}$ and $\text{MgNiSi}_2\text{O}_6$ if the total amount of chrome-magnesite bricks in the regenerator is 50 metric tons and periclase plus forsterite account for about 50% of the weight of chrome-magnesite refractories at the hot face. This estimate that about 25 mm (1 in.) of the brick hot face will be affected by nickel conforms with what has been observed is the used brick.

The large expansion and the large amount of porosity generated near the hot face of the brick obviously are not desirable. The modulus of rupture and the tensile strength of chrome-magnesite refractories drop drastically with increasing porosity.¹⁸ Thus, attention should be addressed to ways to reduce the deleterious effects.

One conclusion based on the data was that chrome ore spinel in the present brick did not react with silica batch carryover. Electron microprobe point scans did not detect sodium, vanadium, or nickel within the chrome ore spinel grains. Of all the original phases, the chrome ore spinel phase appears to be the most volume-stable component in the chrome-magnesite refractories according to this analysis. Our observation agrees with that reported by Wilson,²⁵ that chrome ore spinel is resistant to reaction with fuel oil ash under conditions similar to those existing in the present glass furnace. This fact suggests that increasing the chrome ore content of chrome-magnesite refractories should result in better volume stability and better corrosion resistance in a residual oil combustion environment.

Forsterite is thermodynamically stable with respect to reaction with vanadium up to its melting point, 1890°C (3434°F).^{26,27} This agrees with our results. On the other hand, our results show that monticellite reacted with vanadium to form a liquid phase at the hot face temperature. Periclase in the present brick did not react significantly with vanadium impurity from the oil. In summary, the effect of vanadium impurity from fuel oils is one of reacting with the monticellite phase in this type of refractory to produce a lower melting liquid, thus, decreasing the refractoriness of the brick.

Our results indicate that nickel from the fuel oil has reacted with periclase, forsterite, and monticellite in the refractory. Magnesioferrite will react with nickel from fuel oil ash to form a $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{O}\cdot\text{Fe}_2\text{O}_3$ spinel phase.³ Although the reactions mentioned above involving nickel do not reduce the refractoriness of the brick, the appreciable swelling associated with these reactions will cause cracking and other mechanical failure of the bricks.

The data also suggest that sodium from glass batch carryover to the ports and regenerators and the fuel oil impurities reacted with the calcium-aluminum silicate phases in the present brick to form a less refractory phase, which was liquid at the furnace operating temperature. Because electron microprobe analysis in the present work has shown that the residual phases distributed in large pores at the hot face of the brick all contain sodium, it appears that sodium has also reacted with phases such as forsterite, monticellite, periclase, magnesioferrite, and aluminum chromite at the brick hot face to form new crystalline phases. However, the amounts of these sodium-containing crystalline phases are rather small, and therefore x-ray diffraction data do not show these phases. Reactions with sodium fragment the original phases — forsterite, monticellite, periclase, magnesioferrite, and aluminum chromite — at the very end of the hot face. The fragmentation generates cracks or spaces, which allow more fuel oil impurities to enter the brick and thus facilitate reaction of nickel and vanadium from the fuel oil with original phases in the brick.

Target-Wall Chrome-Magnesite Brick

The expansion in the hot face of the brick employed in the regenerator target wall was much less severe than that observed in the chrome-magnesite brick used in the port side of the same glass furnace regenerator. In this case, the expansion was primarily caused by (1) the reaction of silica in batch carryover with periclase in the brick to form forsterite, and (2) the reaction of nickel impurity from the fuel oil with forsterite in the brick. The reaction involving

nickel was determined in the present analyses to be rather localized. Only a few regions in the forsterite at the hot end of the brick contained nickel. Chemical analysis indicated negligible nickel in this region of the refractory, and x-ray diffraction data also revealed negligible nickel-rich crystalline phases such as $(\text{Mg},\text{Ni})\text{O}$ or $\text{MgNiSi}_2\text{O}_6$.

The most significant changes in the chemical composition of the hot end of the brick as compared with the cold end were increases in the silicon and calcium concentrations. The weight ratio of CaO to SiO_2 equivalent contents changed from the original value of 0.40 to 0.23 and 0.18 in the hot and cold ends of the brick, respectively. The bonding phases in the brick corresponding to all these ratios at phase equilibrium are forsterite and monticellite.²⁰ However, monticellite was not present in the cold end of the analyzed brick. In the altered and unaltered parts of the brick, forsterite and diopside were present in significant amounts. The structural integrity of chrome-magnesite bricks behind the working surface can be reduced significantly by reaction with CaO in service.²⁹ In the present brick, mechanical integrity in areas close to the brick hot face was maintained by keeping the CaO/SiO_2 weight ratio less than unity. Under this condition, the equilibrium bonding phases in the refractory are forsterite, monticellite, and diopside as in the original refractory. The CaO/SiO_2 ratio was reduced during service, thus favoring the existence of the desired phases in this region of the refractory.

Literature³⁰ on the analysis of chrome-magnesite refractories used in the checkers of glass furnace regenerators reported the presence of sodium-potassium chromate crystals in the refractories. This material was not observed in the present brick, probably because it was used in the target wall where the temperatures are higher than for the checker bricks of the regenerator. The alkalis (sodium and potassium) observed in this refractory originated from batch carryover and/or fuel oil impurities. The analyses indicate that the alkalis reacted with all the original phases in the present brick except the chrome ore spinel to form a liquid phase at the operating temperatures at the refractory hot face. A crystalline phase having lamellar

morphology containing the cations Ca, Mg, Si, Al, Fe, and Ti was present in this matrix phase after it was cooled to room temperature.

Chemical analysis of the remnants of the mortar on the surfaces of the brick is shown in Table 2. The mortar contained appreciable titanium (0.98 wt % TiO_2 equivalent). In addition, the alkali oxide ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) equivalent content was relatively high at 6.68 wt %. Perhaps the mortar that was used between the chrome-magnesite bricks in the target wall provided the titanium for the formation of titanium-rich lamellar crystals found in the zone A of the brick. It also appears that this mortar has been fluxed by the sodium and potassium impurities from the residual oil and the glass furnace batch carryover.

Table 2. Chemical Analysis of the Mortar Residue on the Surface of the Target-Wall Chrome-Magnesite Brick

Oxide	Equivalent Content (wt %)	Oxide	Equivalent Content (wt %)
SiO_2	30.72	MgO	10.82
Al_2O_3	19.55	Na_2O	6.17
Fe_2O_3	9.41	K_2O	0.51
TiO_2	0.979	SO_3	0.12
Cr_2O_3	20.91	NiO	0.152
CaO	0.37	V_2O_5	<0.002

One outstanding feature of the liquid phase, which was a liquid located 25 mm (1 in.) back from the brick hot face (zone TM2 in Fig. 27), was the presence of significant amounts of the cations V, Na, and K. In contrast, the liquid phase at the hot face of the brick contained the elements Na and K, but no V. We speculate that vanadium from the fuel oil has greatly decreased the viscosity of the silicate melt or, equivalently, increased the mobility of the melt, and promoted the preferential migration of vanadium-containing melt to the cooler brick interior under the thermal gradient. Also, vanadium might evaporate from the hot surface of the brick.

High-MgO Checker Brick

In the original high-MgO brick, the equivalent contents of MgO, SiO₂, and CaO were 93, 4, and 1 wt %, respectively (see Table 1). These have been changed to 88, 3.7, and 1.6 wt % in the brick after service. The CaO/SiO₂ and MgO/SiO₂ ratios for both the original and the used refractory are consistent with a bonding phase system consisting of forsterite and monticellite if the composition is in phase equilibrium.²⁸ X-ray diffraction results for the used brick showed the presence of forsterite and merwinite, but no monticellite. The absence of monticellite in the refractory suggests that either the phases in this material are not in equilibrium or one or more of the impurities present has had a significant effect on the equilibrium phase composition.

A striking feature of this refractory is the swelling of about 20% and the microcracking accompanying this swelling. Large expansions in high-MgO bricks used in regenerators of glass furnaces fired with residual oils have been observed and known for many years.³¹ This phenomenon has been attributed to the formation of a Na₂SO₄ crystalline phase inside the brick, but a detailed understanding of swelling mechanism is still lacking. The origins of sodium and sulfur are believed to be batch carryover and residual fuel oil combustion products, respectively. Local blockage of gas passages in regenerators has been caused by such swelling, and in many cases the blockage has spread along the setting in a horizontal zone some four to six courses deep, until total collapse occurred in the regenerator, requiring shutdown of the furnace.³¹

Sodium sulfate boils at 1750°C at standard conditions,²⁴ but under certain conditions it may dissociate to form Na₂O and SO₃. The equilibrium SO₃ pressure over sodium sulfate is very low at conventional glass-forming temperatures (10⁻⁵ Pa at 1350°C and 10⁻¹² Pa at 900°C).³² The SO₃ partial pressure in the furnace atmosphere derived from the sulfur in the fuel is likely to be much higher than these dissociation pressures. Therefore, Na₂SO₄ will not dissociate in the furnace or the regenerator. Also, Na₂SO₄ is reported not to react with the phases

present in this type of refractory.³³ Many refractory users in the glass industry hold the view that, with temperature cycling occurring in glass furnace regenerators, alternate freezing-melting of Na_2SO_4 disrupts the brick structure. The melting point²⁴ of Na_2SO_4 of 884°C is in the range anticipated within the regenerator. The molar volume ratio of liquid and solid Na_2SO_4 at or near the liquidus temperature could not be found in the literature.

In the present brick, sodium sulfate is located in the cracks within periclase grains and also at their grain boundaries. One mechanism that may account for the presence of sodium sulfate within periclase grains is the percolation of sodium sulfate liquid to cracks within periclase grains. The viability of this possible mechanism could not be quantitatively evaluated because the relative surface energies of liquid sodium sulfate and solid periclase are not available to permit an assessment of the ability of the liquid sulfate to fill previously generated cracks. Furthermore, there is no direct experimental evidence in the present case of molten sulfate melt flowing in the brick during service. Cracks in periclase grains were probably caused by the relatively poor thermal shock resistance of periclase and the resultant cracking during thermal cycling in the brick during service. However, the regular geometry and the preferred orientation of the sodium sulfate deposits observed in the present case suggests a process of sodium and sulfur diffusion into periclase grains and sodium sulfate precipitation during the cooling cycle of the regenerator operation. The conjecture that sodium sulfate recrystallizes from the sodium and sulfur dissolved in periclase is by necessity speculative because the solubilities and diffusivities of sodium and sulfur in periclase are presently unknown.

A ternary eutectic between MgSO_4 , CaSO_4 , and Na_2SO_4 has been shown³⁴ to occur at 650°C . Evidence of the existence of such a material was observed by SEM and EDAX studies of fractured surfaces within the swelled zone of this refractory. The formation of solid MgSO_4 within an MgO refractory can also be detrimental because of the accompanying expansion. The density²⁴ of MgSO_4 is 2.66 Mg/m^3 , whereas the density of MgO is 3.58 Mg/m^3 . The molar volume change for the

reaction $\text{MgO}(s) + \text{SO}_3(g) \rightarrow \text{MgSO}_4(s)$ is 125% at room temperature. The melting point²⁴ of MgSO_4 of 1125°C is above the service temperature of the high-MgO refractory, so MgSO_4 should be present as a solid phase. Our SEM and EDAX results have indicated that most of sulfur is present in the form of Na_2SO_4 . This agrees with the fact that the standard free energy change $[-543.506 + 0.159T \text{ (K)} \text{ (kJ/mol)}]$ for the reaction $\text{Na}_2\text{O}(s) + \text{SO}_3(g) \rightarrow \text{Na}_2\text{SO}_4(l)$ is more negative than that $[265.279 + 0.197T \text{ (K)} \text{ (kJ/mol)}]$ of the reaction $\text{MgO}(s) + \text{SO}_3(g) \rightarrow \text{MgSO}_4(s)$. The above standard free energy changes were calculated from the standard enthalpy and entropy changes for the formations of the compounds involved, shown in Table 3. The amount of free SO_3 in the regenerator atmosphere would therefore be expected to have a critical effect on the formation of Na_2SO_4 and MgSO_4 .

Table 3. Thermodynamic Functions Involved in the Formation of Sulfates in Refractory Bricks

Process	ΔH_{298}° , Standard Enthalpy Change (kJ/mol)	ΔH_{298}° , Standard Entropy Change (kJ/mol K)
Formation		
$\text{Na}_2\text{O}(s)$	-418.181	-0.130
$\text{Na}_2\text{O}(l)$	-373.023	-0.113
$\text{SO}_3(g)$	-395.581	-0.080
$\text{MgO}(s)$	-601.528	-0.109
$\text{Na}_2\text{SO}_4(l)$	-1357.269	-0.368
$\text{Na}_2\text{SO}_4(s)$	-1387.868	-0.398
$\text{MgSO}_4(s)$	-1262.389	-0.385
$\text{Na}_2\text{O}(s) + \text{SO}_3(g) \rightarrow \text{Na}_2\text{SO}_4(l)$	-543.506	-0.159
$\text{MgO}(s) + \text{SO}_3(g) \rightarrow \text{MgSO}_4(s)$	-265.279	-0.197

Mörtl³³ calculated that a furnace fired with a typical residual oil and having an output of 87 metric tons per day would discharge about 400 metric tons of sulfur into the furnace atmosphere each year.

If this number is right, the total amount of sulfur discharge in the 200 metric ton per day glass furnace in which the present refractory was used would be about 920 metric tons per year. In general, SO_3 appears to constitute 1 to 4% of the total sulfur oxides in the furnace flue gases.³² Even with such a low conversion ratio of SO_2 to SO_3 , there still will be 14 to 55 metric tons of SO_3 per year in the furnace flue gases, assuming that all the sulfur is present either as SO_2 or as SO_3 and that all SO_3 is present in the furnace atmosphere. In container glass furnaces, the loss of soda from the batch and glass melt is reported to be 0.04 to 0.23% of the total glass weight.³² For a glass furnace of 200 metric tons per day output, some 51 metric tons of SO_3 will be required to convert the estimated soda loss to Na_2SO_4 , based on a 0.04 wt % figure. Following the consumption of the soda to produce Na_2SO_4 , there will still be about 4 metric tons of SO_3 per year available for reactions with MgO . This amount of free SO_3 in the regenerator atmosphere could be sufficient to convert as much as 10% of six courses of high- MgO bricks (assuming total weight is 28 metric tons) to MgSO_4 in the regenerator over a period of two years. Furthermore, the formation³² of MgSO_4 is accelerated by the presence of Na_2SO_4 . The maximum rate of formation of MgSO_4 occurs at about 800°C , which coincides with that for the condensation of Na_2O vapor and the formation³³ of Na_2SO_4 . This availability of SO_3 in the regenerator appears to have been sufficient to produce enough Na_2SO_4 and MgSO_4 to explain the swelling observed in the high- MgO refractory.

CONCLUSIONS

1. The chrome-magnesite refractory used in the port side of the regenerator of a glass melting furnace fired with No. 6 oil for three and a half years had a large expansion in areas within a few inches of the brick hot face. Nickel impurity from the fuel oil reacted with the forsterite and monitcellite originally present in the refractory and contributed to the expansion by the formation of magnesium nickel silicate. Vanadium impurity from the fuel oil reacted with the monticellite originally present in the refractory to form a liquid phase

at the service temperature. The original chrome ore spinel present in the refractory appeared to have the greatest stability of any phase originally present in the brick. Increasing the chrome ore content and decreasing the forsterite and monticellite contents in a chrome-magnesite brick will reduce the sensitivity of this type of refractory to the degradation observed in the furnace port-side application.

2. The chrome-magnesite brick used in the target wall of the regenerator of a glass melting furnace also fired with No. 6 oil for three and a half years reacted with sodium, potassium, and vanadium originating from glass batch carryover and fuel oil combustion products. A phase that was liquid at the operating temperature and contained significant amounts of sodium and potassium was present within the brick and very close to its hot face. A second phase containing the Ca, Mg, Si, Al, Fe, and Ti and having lamellar morphology was distributed in this phase when the refractory was cooled to room temperature. Zones in the brick located within 0.13 m (5 in.) behind the hot face had a microstructure consisting of angular chrome ore spinel dispersed in a second phase that was liquid at the operating temperature and also contained significant concentrations of Na, K, and V. Nickel impurity from the fuel oil was present in the periclase, forsterite, and monticellite but did not produce new phases causing severe swelling. A recommendation for increasing the corrosion resistance of the chrome-magnesite refractory used in this environment is to decrease the concentration of forsterite and monticellite and to increase the chrome ore content, the same as for port-side applications discussed previously.

3. The swelling and accompanying cracking of about 20% in a high-MgO brick from the 18th course regenerator of the same furnace were caused primarily by formation of crystalline Na_2SO_4 within the periclase (MgO) grains in the refractory, with resultant disruption of the brick structure. The mechanism apparently involved periodic freezing and melting of Na_2SO_4 due to the temperature cycling characteristic of glass furnace regenerators. An improved understanding is needed of the mechanism of the transport of sodium and sulfur in the high-MgO refractory and the formation of sodium sulfate in the periclase phase in the high-MgO refractory. Understanding these basic transport

mechanisms may then indicate specific options to impede sodium and sulfur transport into the high-MgO refractory or to retard the formation of sulfate within the refractory. Also, SO_3 in the regenerator atmosphere reacted with the periclase to form MgSO_4 . Expansions of about 125% are associated with this reaction. Resistance to degradation of this refractory by sodium and sulfur can perhaps be increased by use of some chromia because the free energy change for the reaction $\text{Cr}_2\text{O}_3(s) + 3\text{SO}_3(g) \rightarrow \text{Cr}_2(\text{SO}_4)_3(s)$ is positive, and $\text{Cr}_2(\text{SO}_4)_3$ would therefore not be formed between 600 and 1100°C.

4. Routine analyses of the impurity content of residual fuel oil used in firing industrial furnaces would be very useful in improving the understanding of refractory behavior associated with use of this fuel. If the fuel oil to be used contains high levels of impurities such as alkali, vanadium, nickel, and sulfur, caution should be directed to the selection and specification of the refractories in the furnaces. In the case of chrome-magnesite bricks and high-MgO bricks used in the regenerator, increasing the chrome ore content and decreasing the silicate content in the refractory can give better resistance to the type of fuel oil impurity attack observed. Routine oil analyses would be a good investment for establishing a better data base on refractory performance in the presence of residual oil combustion products. The additional cost for routine chemical analysis of fuel oils being used is no more than the cost of 50 pieces of standard shape basic bricks.

REFERENCES

1. G. C. Wei and V. J. Tennery, *Impact of Alternate Fuels on Industrial Refractory and Refractory Insulation Application*, ORNL/TM-5592 (September 1976).
2. G. C. Wei, V. J. Tennery, and L. A. Harris, *Analysis of High-duty Fireclay Refractories Exposed to Coal Combustion*, ORNL/TM-5509 (in press).
3. P. Robijn and W. L. DeKeyser, "Changes in Basic Checker Bricks of Glass Furnaces due to the Heavy Elements of Fuel," *Trans. Br. Ceram. Soc.* 69: 169 (1976).

4. *Powder Diffraction File Search Manual, Alphabetical Listing and Search Section of Frequently Encountered Phases, Inorganic* 1976, Published by the Joint Committee on Powder Diffraction Standards, Swarthmore, Pa., 1976.
5. B. Davies and F. H. Walther, "Direct Bonding of Basic Brick," *J. Am. Ceram. Soc.* 47(3): 116-22 (1964).
6. G. R. Rigby, R. F. Hutton, and B. G. Hamilton, "Reactions Occurring in Basic Brick," *J. Am. Ceram. Soc.* 46(7): 332-42 (1963).
7. D. H. Hubble and W. H. Powers, "High-Fired Basic for Open-Hearth Roofs," *Bull. Am. Ceram. Soc.* 42(7): 409-13 (1963).
8. H. M. Mikami, W. E. Brown, and V. Gilbert, "Direct Bonded Basic Brick in Open Hearth Roofs," *Bull. Am. Ceram. Soc.* 44(5): 433-38 (1965).
9. M. L. Van Dreser and W. H. Boyer, "High-Temperature Firing of Basic Refractories," *Bull. Am. Ceram. Soc.* 46(6): 257-64 (1967).
10. P. E. Scheerer, H. M. Mikami, and J. A. Tauber, "Microstructure of Chrome-Periclase at 1650°C to 2310°C," *J. Am. Ceram. Soc.* 47(6): 297-305 (1964).
11. R. H. Herron and W. J. Smothers, "Fine-Grained Magnesite-Chrome Refractories," *Bull. Am. Ceram. Soc.* 48(5): 544-48 (1969).
12. H. M. Richardson, K. Fitchett, and M. Lester, "Bond Structure and the Behavior of Basic Bricks at High Temperatures," *Trans. Br. Ceram. Soc.* 59: 483-504 (1960).
13. B. Jackson, W. F. Ford, and J. White, "The Influence of Cr_2O_3 and Fe_2O_3 on the Wetting of Periclase Grains by Liquid Silicate," *Trans. Br. Ceram. Soc.* 62: 577-601 (1963).
14. A. Hayhurst and J. Laming, "The Structure of Chrome-Magnesite Refractories at High Temperatures," *Trans. Br. Ceram. Soc.* 62: 989-1005 (1963).
15. V. S. Stubican and I. deMenezes, "Grain-Boundary Reactions in Magnesia-Chrome Refractories - Application of the Electron Probe I," *J. Am. Ceram. Soc.* 49(10): 535-40 (1966).
16. I. deMenezes and V. S. Stubican, "Grain-Boundary Reactions in Magnesia-Chrome Refractories - Application of the Electron Probe II," *J. Am. Ceram. Soc.* 49(11): 609-12 (1966).

17. B. Jackson and W. F. Ford, "A Quantitative Study of Bonding in Basic Refractories, *Trans. Br. Ceram. Soc.* 65: 19-39 (1966).
18. J. H. Chester, *Refractories Production and Properties*, Iron and Steel Institute, London, 1973.
19. K. Shaw, *Refractories and Their Uses*, Wiley, New York, 1972.
20. G. R. Rigby, "Some Properties of the Spinels Associated with Chrome-Ore," *Trans. Br. Ceram. Soc.* 45: 137 (1946).
21. J. H. Chester and T. R. Lynam, "Chrome-Magnesite Brick for Open-Hearth Furnaces," *J. Am. Ceram. Soc.* 22: 97 (1939).
22. G. R. Rigby, "Mechanical Properties of Basic Bricks, 1. A Survey of the Magnesia-Chrome System," *Trans. Br. Ceram. Soc.* 69: 189 (1970).
23. G. Evans and J.F.E. Cholerton, "Mechanism of Attack on Upper Course Checker Bricks in Glass Tank Regenerators," *Glass Technol.* 13(4): 117-21 (1972).
24. *Handbook of Chemistry and Physics*, 57th ed., CRC Press, Cleveland, Ohio, 1976.
25. J. R. Wilson, "Understanding and Preventing Fuel Ash Corrosion," Paper 12 presented at National Association of Corrosion Engineers 1976 Annual Meeting, Houston, Texas, 1976.
26. M. Eke and N. H. Brett, "Phase Equilibria in the System $\text{CaO-MgO-SiO}_2\text{-V}_2\text{O}_5$: Their Relevance to Refractory Usage in Glass Tank Regenerators I. The Partial Systems $\text{MgO-C}_2\text{S-V}_2\text{O}_5$ and $\text{MgO-C}_3\text{S-V}_2\text{O}_5$ at 1500°C ," *Trans. Br. Ceram. Soc.* 72(5): 195-202 (1973).
27. M. Carter and N. H. Brett, "Phase Equilibria in the System $\text{CaO-MgO-SiO}_2\text{-V}_2\text{O}_5$: Their Relevance to Refractory Usage in Glass Tank Regenerators II. The Partial Systems $\text{MgO-M}_2\text{S-V}_2\text{O}_5$, $\text{MgO-C}_2\text{S-V}_2\text{O}_5$, $\text{MgO-C}_2\text{S-C}_3\text{S}$ and $\text{MgO-50 wt \% C}_3\text{S-V}_2\text{O}_5$ at 1450°C ," *Trans. Br. Ceram. Soc.* 72(5): 203-07 (1973).
28. T. Hatfield, C. Richmond, W. F. Ford, and J. White, "Compatibility Relationships Between the Periclase and Silicate Phases in Magnesite Refractories at High Temperatures," *Trans. Br. Ceram. Soc.* 69: 53-58 (1970).

29. G. D. Pickening and W. F. Ford, "The Effect of Absorbed Lime on the Cohesive Strength of Chrome-Magnesite Refractories at High Temperatures," *Trans. Br. Ceram. Soc.* 63: 487 (1964).
30. P. Elroy, M. Jaupain, and E. Plumet, "The Behavior of Basic Refractories in Atmospheres Rich in Alkaline Vapors," *Glass Technol.* 1(40): 162-73 (1960).
31. C. F. Fisher and M. L. Maberry, *Ceram. Ind. (Chicago)* 83(5): 46 (1964).
32. T. S. Busby and M. Carter, "The Conversion of MgO to $MgSO_4$ in Glass Furnace Regenerators," *Glass Technol.* 12(5): 113-16 (1971).
33. G. Mörtl, " SO_3 -beständige, feuerfeste Steine für die Zerstellung der unteren Lagen von Regeneratorgitterungen," *Radex Rundsch.* 4-5: 315 (1968).
34. S. M. Mikimov and Z. I. Filippova, *Dokl. Akad. Nauk Uzb. SSR* 2: 131 (1949).

Table

Page

A8	X-Ray Diffraction Data of Sample TX2 from the Target-Wall Chrome-Magnesite Brick	80
A9	X-Ray Diffraction Data of Sample TX3 from the Target-Wall Chrome Magnesite Brick	82
A10	X-Ray Diffraction Data of Sample CX1 from the High-MgO Checker Brick	84
A11	X-Ray Diffraction Data of Sample CX2 from the High-MgO Checker Brick	85
A12	X-Ray Diffraction Data of Sample CX3 from the High-MgO Checker Brick	86

Table A1. X-Ray Diffraction Data of Sample PX1 from
the Port-Side Chrome-Magnesite Brick

$d, \text{\AA} (10^{-10} \text{ m})$								
Observed	Chrome Ore	Periclase	Forsterite	CMS	Magnesioferrite	(FeAlCr) ₂ O ₃	MgNiSi ₂ O ₆	MgNiO ₂
5.0618				5.54				
4.7652	4.76			4.41	4.84			
3.8584				3.84				
3.6987				3.62				
3.4742								
3.4596							3.30	
3.3155								
3.2067								
2.9804				3.15			3.15	
2.9775					2.96			
2.9270	2.92			2.929				
2.7557				2.656			2.86	
2.5014			2.509	2.534	2.525		2.524	
2.4880	2.49					2.48		
2.4493		2.431	2.457	2.391		2.462		
2.3400				2.346				
2.2648								
2.2593								
2.2421				2.204				
2.1565			2.160					
2.1511				2.150				
2.0997		2.106			2.094			
2.0781				2.082				
2.0735	2.07							
2.0446								
2.0344								
2.0264			2.030	3.011			2.017	
1.9430			1.940				1.979	
1.9379							1.959	
1.8704			1.874					
1.8668								
1.8075				1.811				
1.7867								
1.7454				1.744				
1.7353					1.709		1.725	
1.6684	1.687			1.680				
1.6343								
1.6151					1.612			
1.6009				1.593			1.609	
1.5871	1.593			1.589		1.584	1.584	
1.5694								
1.5102							1.516	
1.5016								
1.4974				1.499				
1.4935		1.489						
1.4775					1.481			1.4827
1.4670	1.466					1.464	1.464	
1.4353				1.416				

Table A1. (Continued)

$d, \text{\AA} (10^{-10} \text{ m})$								
Observed	Chrome Ore	Periclase	Forsterite	CMS	Magnesioferrite	(FeAlCr) ₂ O ₃	MgNiSi ₂ O ₆	MgNiO ₂
1.3954								
1.3930								
1.3894							1.388	
1.3858				1.385				
1.3822								
1.3572								
1.3494								
1.3460								
1.3420								
1.3147					1.324			
1.2905					1.277		1.287	
1.2578								1.2640
1.2445								
1.2413								
1.2240								
1.2226								
1.2222		1.216			1.208			1.2103
1.1884	1.197							
1.1858								
1.1695								
1.652								
1.1597								
1.1550								
1.1389								
1.1363								
1.1345								
1.1333								
1.1248								
1.1162	1.108				1.119			
1.0985								
1.0985								
1.0958					1.090			
1.0808	1.081							
1.0733								
1.0706								
1.0633								
1.0510		1.0533			1.047			1.0482
1.0357	1.038							
1.0330								
1.0204								
1.0182								
1.0069								
1.0015								
0.98592								
0.97934								
0.97182								
0.96942		0.9665			0.967			0.9620
0.96229								
0.95119		0.9419			0.936			

Table A2. X-Ray Diffraction Data of Sample PX2 from
the Port-Side Chrome-Magnesite Brick

$d, \text{\AA} (10^{-10} \text{ m})$						
Observed	Chrome-ore	Periclase	Forsterite	CMS	Magnesioferrite	(FeAlCr) ₂ O ₃
1.1081						
5.0532						
4.7399	4.76				4.84	
4.7175						
4.2064				4.41		
4.1520						
3.8833						
3.8534				3.84		
3.7002				3.62		
3.4769						
3.2503						
3.0511				3.15		
2.9912					2.96	
2.8901	2.92			2.929		
2.8426						
2.7598				2.658		
2.5054	2.49		2.509	2.534	2.525	2.48
2.4682		2.431	2.457	2.391	2.418	
2.2703				2.346		
2.2637						
2.2475						
2.2421				2.204		
2.1526			2.160	2.150		
2.0997	2.07	2.106		2.082	2.094	
2.0490						
2.0290			2.030	2.011		
1.9403			1.940			
1.8769						
1.8744			1.874			
1.8122			1.874			
1.7887						
1.7485				1.744	1.709	
1.6695	1.687			1.680		
1.6404						
1.6367						
1.6319						
1.6187				1.593	1.612	
1.5789	1.593			1.587		1.584
1.5750						

Table A2. (Continued)

$d, \text{\AA} (10^{-10} \text{ m})$						
Observed	Chrome Ore	Periclase	Forsterite	CMS	Magnesioferrite	(FeAlCr) ₂ O ₃
1.5711						
1.5104						
1.4959				1.499		
1.4929						
1.4868		1.489			1.481	
1.4796						
1.4760						
1.4564	1.466					1.489
1.4515						
1.4037				1.416		
1.3958						
1.3870						
1.3802				1.385		
1.3507						
1.3477						
1.3460						
1.3167						
1.3137					1.324	
1.2960						
1.2930						
1.2524	1.265	1.270			1.277	
1.2493	1.249					
1.2383		1.216			1.208	
1.1860	1.197					
1.1837						
1.1701						
1.1552						
1.1523						
1.1502						
1.1371						
1.1244						
1.1257						
1.1000	1.108				1.119	
1.0956						
1.0866	1.081				1.090	
1.0699						
1.0670		1.0533				
1.0372	1.038				1.047	
1.0347						
1.0275						
1.0027						

Table A3. X-Ray Diffraction Data of Sample PX3 from the Port-Side Chrome-Magnesite Brick

$d, \text{\AA} (10^{-10} \text{ m})$						
Observed	Chrome-ore	Periclase	Fosterite	CMS	Magnesioferrite	(FeAlCr) ₂ O ₃
5.0618				5.54		
4.7100	4.76			4.41	4.84	
3.8700				3.84		
3.7983						
3.7231						
3.6987						
3.6821				3.62		
3.4759						
3.2398						
3.0552				3.15		
2.9902					2.96	
2.8828	2.92			2.929		
2.8356						
2.7549				2.658		
2.5081				2.534	2.525	
2.5047	2.49		2.509			
2.4668		2.431	2.457			2.48
2.3787				2.391		
2.3726						
2.3429				2.346		
2.2648						
2.2485						
5.2432				2.204		
3.1531			2.160	2.150		
2.0969	2.07	2.106		2.082	2.094	
2.0429						
2.0385			2.030			
2.0273			1.948	2.011		
1.9403						
1.8762			1.874			
1.8112				1.811		
1.8082						
1.7893						
1.7488						
1.7457				1.744		
1.7390					1.709	
1.6701	1.687			1.680		
1.6356						
1.6319				1.593	1.612	
1.5767	1.593			1.587		1.584
1.4972		1.489		1.499		
1.4800					1.481	
1.4523	1.466					1.464
1.4493				1.416		

Table A3. (Continued)

$d, \text{\AA} (10^{-10} \text{ m})$						
Observed	Chrome-ore	Periclase	Fosterite	CMS	Magnesioferrite	(FeAlCr) ₂ O ₃
1.3963						
1.3927						
1.3876						
1.3847				1.385		
1.3504						
1.3467						
1.3182					1.324	
1.3140						
1.2972						
1.2937						
1.2669	1.265	1.270			1.277	
1.2637						
1.2571						
1.2510						
1.2480	1.249					
1.2367						
1.2148		1.216			1.208	
1.1846	1.197					
1.1501						
1.1363						
1.1333						
1.1176					1.119	
1.1010	1.108					
1.0989						
1.0977						
1.0969					1.090	
1.0688	1.081					
1.0661		1.0533				
1.0373	1.038				1.047	
1.0283						
1.0258						
1.0227						
1.0201						
0.98170						
0.96768	0.9665				0.967	
0.94809						
0.94620						
0.94549						
0.94183	0.9419				0.936	

Table A4. X-Ray Diffraction Data of Sample PX4 from the Port-Side Chrome-Magnesite Brick

$d, \text{\AA} (10^{-10} \text{ m})$						
Observed	Chrome-ore	Periclase	Fersterite	CMS	Magnesioferrite	(FeAlCr) ₂ O ₃
5.0503				5.54		
4.6780	4.76					
4.2643				4.41	4.84	
4.1635				4.18		
3.8551				3.84		
3.6821				3.62		
3.4636						
3.0480				3.15		
2.9882						
2.9698	2.92			2.929	2.96	
2.8819						
2.8356						
2.7516				2.658		
2.5000	2.49		2.509	2.534	2.525	
2.4616			2.457			2.48
2.4461		2.431		2.391	2.418	
2.3388			2.344	2.346		
2.2583			2.267			
2.2410			2.246	2.204		
2.1501			2.160	2.150		
2.0932	2.07	2.106		2.082	2.044	
2.0420						
2.0273			2.030			
2.0230				2.011		
1.9430			1.948			
1.9372			1.940			
1.8719			1.874			
1.8675						
1.8062				1.811		
1.7867						
1.7454				1.744	1.709	
1.6667	1.687			1.680		
1.6353						
1.6171						
1.6130				1.593	1.612	
1.5769	1.593			1.587		1.584
1.4965		1.489		1.499		
1.4792					1.481	
1.4754	1.466					1.464
1.4487						
1.4459						
1.3952				1.416		
1.3917						

Table A4. (Continued)

$d, \text{\AA} (10^{-10} \text{ m})$						
Observed	Chrome-ore	Periclase	Fosterite	CMS	Magnesioferrite	(FeAlCr) ₂ O ₃
1.3858				1.385		
1.3822						
1.3491						
1.3457						
1.3175					1.324	
1.3131						
1.2985						
1.2969						
1.2948						
1.2653	1.265	1.270			1.277	
1.2507	1.249					
1.2477						
1.2375						
1.2363						
1.2244						
1.2136	1.197	1.216			1.208	
1.1882						
1.1846						
1.1839						
1.1828						
1.1710						
1.1678						
1.1491						
1.1362						
1.1261						
1.1232	1.108				1.119	
1.0974						
1.0942					1.090	
1.0747	1.081					
1.0693						
1.9667						
1.0522		1.0533				
1.0377	1.038					
1.0351						
1.0268						
1.0244						
0.98149					0.967	
0.95047		0.9665				
0.94856		0.9419				
0.94673						
0.94573					0.936	

Table A5. X-Ray Diffraction Data of Sample PX5 from
the Port-Side Chrome-Magnesite Brick

$d, \text{\AA} (10^{-10} \text{ m})$						
Observed	Chrome-ore	Periclase	Forsterite	CMS	Magnesioferrite	(FeAlCr) ₂ O ₃
5.0762				5.54		
4.7150	4.76			4.41	4.84	
4.1329				4.18		
3.8800				3.84		
3.6245				3.62		
3.6014						
3.1491				3.15		
2.9902					2.96	
2.002	2.92			2.929		
2.7798						
2.7698				2.762		
2.6742						
2.6352				2.658		
2.5636	2.49			2.578		
2.5136	2.49		2.509	2.534	2.525	
2.4714			2.457			2.48
2.4232		2.431			2.418	
2.3811				2.391		
2.3769						
2.3488			2.344	2.346		
2.2692			2.267			
2.2523						
2.2464			2.246	2.204		
2.1001		2.106	2.160	3.150		
2.0534	2.07		2.030	2.082		
1.9473			1.948	2.011		
1.9418			1.940			
1.8166			1.874	1.811		
1.7579						
1.7529				1.744		
1.7065				1.716	1.709	
1.6757	1.687			1.697		
1.6255				1.680		
1.6218				1.593	1.612	

Table A5. (Continued)

$d, \text{\AA} (10^{-10} \text{ m})$						
Observed	Chrome-ore	Periclase	Fosterite	CMS	Magnesioferrite	(FeAlCr) ₂ O ₃
1.5831	1.593			1.587		1.584
1.5821						
1.5031						
1.4877		1.489		1.499		
1.4843					1.481	
1.4527	1.466			1.416		1.464
1.3883				1.385		
1.2997					1.324	
1.2969						
1.2686	1.265	1.270		1.277		
1.2547	1.249					
1.2388						
1.2152		1.216			1.208	
1.1887	1.197					
1.1869						
1.1837						
1.1822						
1.1533						
1.1521						
1.1507						
1.1441						
1.1006	1.108				1.119	
1.0996						
1.0969					1.090	
1.0717	1.081					
1.0708						
1.0694						
1.0529		1.0533			1.047	
1.0280	1.038					
0.45083		0.9665			0.967	
0.94910					0.936	
0.94212		0.9419				

Table A6. X-Ray Diffraction Data of Sample PX6 from
the Port-Side Chrome-Magnesite Brick

$d, \text{\AA} (10^{-10} \text{ m})$						
Observed	Chrome ore	MgO	Mg ₂ SiO ₄	(FeAlCr) ₂ O ₃	MgFe ₂ O ₄	CMS ₂
4.1367	4.76			4.76		
3.9205						
3.8833						
3.7154						3.66
3.5942						
3.4970						3.35
3.1534						3.23
3.0339						
2.9961					2.96	2.99
2.9011	2.92			2.91		2.952
2.8550						2.893
2.7715						2.839
2.7673						
2.6442						
2.5643						2.566
2.5163			2.509		2.525	2.518
2.4734	2.49		2.457	2.48		
2.4263		2.431			2.418	
2.3823						2.392
2.3535			2.344			
2.2736			2.267			2.304
2.2529			2.246			2.218
2.1034		2.106	2.160		2.094	2.109
2.0534	2.07		2.030	2.05		2.077
2.0449			1.940			2.043
1.8075			1.874			1.832
1.7516			1.861			1.755
1.7485						
1.7436						
1.7089					1.709	
1.6774	1.687					1.685
1.6740				1.67		1.674
1.6402						
1.6359					1.612	1.625
1.5814	1.593			1.58		1.588
1.5782						1.565
1.5020						
1.4881		1.489			1.481	
1.4517	1.466			1.46		

Table A6. (Continued)

Observed	$d, \text{\AA} (10^{-10} \text{ m})$				
	Chrome ore	MgO	Mg ₂ SiO ₄	(FeAlCr) ₂ O ₃	MgFe ₂ O ₄
1.3995					
1.3885					
1.3867					
1.3535					
1.3502					
1.3460					
1.3270					1.324
1.3207					
1.3015					
1.2994					
1.2699		1.270			1.277
1.2609	1.265			1.26	
1.2538					
1.2524					
1.2493	1.249				
1.2389					
1.2154		1.216			
1.2128				1.21	1.208
1.1881	1.197			1.19	
1.1852					
1.1519					
1.1490					
1.1462					
1.1031	1.108				1.119
1.1000					
1.0991					
1.0982					
1.0960					1.090
1.0704	1.081				
1.0699				1.07	
1.0681					
1.0663					
1.0529		1.0533			1.047
1.0271	1.038				
0.96974					0.987
0.96781		0.9665			0.967
0.94987					
0.94898		0.9419			

Table A7. X-Ray Diffraction Data of Sample TX1 from
the Target-Wall Chrome-Magnesite Brick

$d, \text{\AA} (10^{-10} \text{ m})$							
Observed	Chrome Ore	MgO	Mg ₂ SiO ₄	(FeAlCr) ₂ O ₃	MgFe ₂ O ₄	CMS ₂	CMS
5.0906							5.54
4.7525	4.76			4.76	4.84	4.69	
4.3093						4.41	4.41
4.1635							4.18
3.8750							3.84
3.8176							
3.7369						3.66	3.62
3.4957							
3.4782						3.35	
3.2573						3.23	3.18
2.9902					2.96	2.991	3.15
2.9038	2.92			2.91		2.893	2.929
2.7648							2.762
2.7590							2.685
2.4880	2.49		2.509	2.48	2.525	2.528	2.578
2.4590			2.457				2.534
2.4525		2.431	2.344		2.418		2.341
2.2670			2.267			2.304	2.346
2.2621							
2.2518							
2.2442			2.246			2.218	2.204
2.1560			2.160			2.157	2.150
2.0601		2.106			2.094	2.109	2.082
2.0552				2.05			
2.0420						2.043	
2.0363							
2.0307			2.030				
2.0268			1.940			2.016	2.011
1.8729			1.874			1.862	1.828
1.7488			1.861			1.755	1.811
1.7448					1.709	1.730	1.744
1.6836	1.687					1.685	1.716
1.6723				1.67		1.674	1.697
1.6681						1.659	1.680
1.6335						1.625	
1.6153						1.618	
1.6114					1.612		
1.5896	1.593						1.593
1.5871						1.588	1.587
1.5826				1.58			
1.5774							

Table A7. (Continued)

$d, \text{\AA} (10^{-10} \text{ m})$							
Observed	Chrome Ore	MgO	Mg ₂ SiO ₄	(FeAlCr) ₂ O ₃	MgFe ₂ O ₄	CMS ₂	CMS
1.5706						1.565	
1.4879		1.489			1.481		1.499
1.4771							
1.4588	1.466		1.46				
1.4566							
1.4527							1.416
1.3921							1.386
1.3477							
1.3457							
1.2144					1.324		
1.3117							
1.2933							
1.2609	1.625	1.270		1.26	1.277		
1.2592							
1.2568							
1.2547							
1.2471	1.249						
1.2460							
1.2452							
1.2445							
1.2150		1.216					
1.2139			1.21	1.208			
1.1936	1.197						
1.1924							
1.1906							
1.1900				1.19			
1.1882							
1.1847							
1.1548							
1.1335					1.119		
1.0980	1.108				1.090		
1.0765	1.081						
1.0756							
1.0739							
1.0737							
1.9727							
1.0716							
1.0715				1.07			
1.0523		1.0533			1.047		

Table A8. X-Ray Diffraction Data of Sample TX2 from the Target-Wall Chrome-Magnesite Brick

$d, \text{\AA} (10^{-10} \text{ m})$						
Observed	Chrome Ore	MgO	Mg ₂ SiO ₄	(FeAlCr) ₂ O ₃	MgFe ₂ O ₄	CMS ₂
4.1367	4.76			4.76		3.66
3.9205						
3.8833						
3.7154						3.66
3.5942						
3.4970						3.35
3.1534						3.23
3.0339						
2.9961					2.96	2.99
2.9011	2.92			2.91		2.952
2.8550						2.893
2.7715						2.839
2.7673						
2.6442						
2.5643						2.566
2.5163			2.509		2.525	2.518
2.4734	2.49		2.457	2.48		
2.4263		2.431			2.418	
2.3823						2.392
2.3535			2.344			
2.2736			2.267			2.304
2.2529			2.246			2.218
2.1034		2.106	2.160		2.094	2.109
2.0534	2.07		2.030	2.05		2.077
2.0449			1.940			2.043
1.8075			1.874			1.832
1.7516			1.861			1.755
1.7485						
1.7436						
1.7089					1.709	
1.6774	1.687					1.685
1.6740				1.67		1.674
1.6402						
1.6359					1.612	1.625
1.5814	1.593			1.58		1.588
1.5782						1.565
1.5020						
1.4881		1.489			1.481	

Table A8. (Continued)

$d, \text{\AA} (10^{-10} \text{ m})$						
Observed	Chrome Ore	MgO	Mg ₂ SiO ₄	(FeAlCr) ₂ O ₃	MgFe ₂ O ₄	CMS ₂
1.4517	1.466			1.46		
1.3995						
1.3885						
1.3867						
1.3535						
1.3502						
1.3460						
1.3220					1.324	
1.3207						
1.3015						
1.2994						
1.2699		1.270			1.277	
1.2689	1.265			1.26		
1.2538						
1.2524						
1.2493	1.249					
1.2389						
1.2154		1.216				
1.2128				1.21	1.208	
1.1881	1.197			1.19		
1.1852						
1.1519						
1.1490						
1.1462						
1.1031	1.108				1.119	
1.1000						
1.0991						
1.0982						
1.0960					1.090	
1.0704	1.081					
1.0699				1.07		
1.0681						
1.0663						
1.0529		1.0533			1.047	
1.0271	1.038					
0.96974					0.987	
0.96781		0.9665			0.967	
0.94987						
0.94898		0.9419				

Table A9. X-Ray Diffraction Data of Sample TX3 from the Target-Wall Chrome-Magnesite Brick

Observed	$d, \text{\AA} (10^{-10} \text{ m})$					
	Chrome-ore	MgO	Mg ₂ SiO ₄	(FeAlCr) ₂ O ₃	MgFe ₂ O ₄	CMS ₂
6.1211						
4.7399	4.76			4.76		
3.9171						
3.8900						
3.8750						
3.7462						
3.7185						
3.6230						
2.9863					2.96	3.66
2.9029	2.92			2.91		2.99
2.7706						2.893
2.6468						2.837
2.5156					2.525	
2.5088			2.509			2.518
2.4780	2.49		2.457	2.48		
2.4270		2.431			2.418	
2.3860						2.392
2.3738			2.344			2.304
2.2670			2.267			2.218
2.1010		2.106	2.246		2.094	2.104
2.0521	2.07		2.160	2.05		2.077
2.0468			2.030			2.043
2.8099			1.940			1.832
1.7507			1.861			1.755
1.7464						
1.7430						
1.7098					1.709	1.713
1.6851	1.687					1.685
1.6822						
1.6779				1.67		1.674
1.5951	1.591				1.612	
1.5826				1.58		1.588
1.5806						
1.4881	1.466	1.489			1.481	
1.4592				1.46		
1.4531						
1.3894						
1.3492						
1.3457					1.324	
1.3035						
1.3009						
1.2983						
1.2696		1.270			1.277	
1.2678						
1.2663						
1.2649	1.265					
1.2613						
1.2599						
1.2578						
1.2547						
1.2542						
1.2314						
1.2500	1.249					
1.2423						
1.2408						

Table A9. (Continued)

Observed	$d, \text{\AA} (10^{-10} \text{ m})$				
	Chrome-ore	MgO	Mg ₂ SiO ₄	(FeAlCr) ₂ O ₃	MgFe ₂ O ₄
1.2390					
1.2157		1.216			
1.2139					
1.2126				1.21	1.208
1.1931	1.197			1.19	
1.1911					
1.1894					
1.1882					
1.1863					
1.1831					
1.1525					
1.1510					
1.1493					
1.1018	1.108				1.119
1.1003					
1.0987					
1.0977					1.090
1.0753	1.081				
1.0743					
1.0722					
1.0710					
1.0722					
1.0703				1.07	
1.0538					
1.0530					
1.0319					
1.0513					
1.0507					
1.0498					
1.0297	1.038				
1.0285					
1.0273					
1.0260					
1.0247					
0.96877				0.987	
0.96832					
0.96691				0.967	
0.96640		0.9665			
0.96583					
0.96526					
0.95500					
0.95370					
0.95311					
0.95251					
0.95071					
0.95011					
0.94898					
0.94744					
0.94690					
0.94632					
0.94503					
0.94427					
0.94005					
0.93907					

Table A10. X-Ray Diffraction Data of Sample
CX1 from the High-MgO Checker Brick

$d, \text{\AA} (10^{-10} \text{ m})$					
Observed	MgO	Mg ₂ SiO ₄	3CaO•MgO•2SiO ₂	Na ₂ SO ₄	MgSO ₄
5.0964				5.04	
4.6707			4.70	4.63	4.65
4.2562					
3.9171					3.97
3.8800			3.88	3.83	3.66
3.4930				3.50	3.55
3.3510				3.37	
3.3362			3.32		3.33
3.1655			3.16	3.17	3.21
2.7756				2.77	
2.7648			2.75		2.65
2.5115		2.509	2.67	2.63	2.55
2.4577		2.457			2.463
2.4263	2.431				
2.1020	2.106	2.160	2.221	2.327	
1.8136		1.861			
1.8099				1.835	
1.7498				1.797	1.776
1.7386				1.768	
1.7353					
1.6712				1.676	
1.5616				1.551	
1.4879	1.489			1.490	
1.2694	1.270			1.278	
1.2154	1.216				
1.2127				1.211	
1.0529	1.0533			1.064	
1.0504				1.039	
0.96628	0.9665				
0.96418					
0.94316	0.9419				

Table A11. X-Ray Diffraction Data of Sample
CX2 from the High-MgO Checker Brick

$d, \text{\AA} (10^{-10} \text{ m})$					
Observed	MgO	Mg ₂ SiO ₄	3CaO·MgO·2SiO ₂	Na ₂ SO ₄	MgSO ₄
5.3179				5.23	
5.0790				5.04	
4.6610			4.70	4.63	
4.2282			4.33		4.65
4.0693					
4.0565			3.88		3.97
3.4153				3.50	3.55
3.3759				3.37	
3.3264			3.32		3.33
2.8828					
2.8621				2.86	
2.7648			2.752	2.77	
2.6842			2.674	2.63	2.650
2.5411				2.559	2.547
2.5095		2.509	2.515		
2.4920					
2.4787					
2.4519		2.457	2.452		2.463
2.4244	2.431				
2.2880		2.364	2.282	2.33	
2.2736		2.316			
2.2670		2.267	2.262		
2.2064		2.160	2.211		
2.1015	2.106	2.030	2.171	2.047	
1.8153		1.874	1.874	1.797	
1.7377					1.776
1.7341					
1.6911			1.659		
1.6027				1.607	
1.5981				1.587	
1.5250				1.551	
1.4873	1.489			1.490	
1.4455				1.459	
1.4435					
1.3807					
1.3768					
1.3748					
1.3701				1.372	
1.3392					
1.3377				1.321	
1.2789	1.270			1.278	
1.2689					
1.2657				1.257	
1.2152	1.216				
1.2130					
1.0528	1.0533			1.211	
1.0513				1.064	
1.0503				1.039	
0.96640	0.9665				
0.96596					
0.96481					
0.96406					
0.96324					
0.94993					
0.94744					
0.94316	0.9419				

Table A12. X-Ray Diffraction Data of Sample CX3 from the High-MgO Checker Brick

$d, \text{\AA} (10^{-10} \text{ m})$					
Observed	MgO	Mg ₂ SiO ₄	3CaO·MgO·2SiO ₂	Na ₂ SO ₄	MgSO ₄
5.0993					
5.0704				5.04	
4.6780			4.70		4.65
4.6561				4.63	
4.6130					
3.9205					3.97
3.8733			3.88	3.83	
3.7047			3.74		3.66
3.6014					3.55
3.4769				3.50	
3.4662				3.37	3.42
			3.16	3.17	3.21
2.9941				2.91	2.966
2.7615			2.752	2.77	
2.6780			2.674		
2.6480			2.652	2.63	2.650
2.5095		2.509	2.515		2.547
2.4551	2.431	2.457	2.452		2.463
2.4219		2.344			
2.0987	2.106	2.160	2.061	2.047	
1.7479				1.768	1.776
1.7464					
1.7417					
1.7402					
1.7124				1.707	
1.6726				1.676	
1.6369			1.659		
1.6205				1.607	
1.5913					
1.5893					
1.5876				1.587	
1.5621					
1.5597				1.551	
1.4873	1.489			1.490	
1.2689	1.270			1.278	
1.2153	1.216			1.211	
1.0526	1.0533			1.064	
1.0501				1.039	
0.96628	0.9665			1.023	
0.96456					
0.94200	0.9419				

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

INTERNAL DISTRIBUTION

1-2. Central Research Library	38. D. L. McElroy
3. Document Reference Section	39. C. J. McHargue
4-5. Laboratory Records Department	40. J. P. Nichols
6. Laboratory Records, ORNL RC	41. A. E. Pasto
7. ORNL Patent Office	42. H. Postma
8. M. Baker	43. M. W. Rosenthal
9. D. A. Canonico	44. A. C. Schaffhauser
10. R. S. Carlsmith	45. G. M. Slaughter
11. J. E. Cunningham	46-55. V. J. Tennery
12. J. H. DeVan	56. D. B. Trauger
13-28. R. G. Donnelly	57-66. G. C. Wei
29. W. P. Eatherly	67. J. R. Weir, Jr.
30. W. Fulkerson	68. C. S. Yust
31. T. G. Godfrey	69. R. W. Balluffi (Consultant)
32. L. A. Harris	70. P. M. Brister (Consultant)
33-35. M. R. Hill	71. W. R. Hibbard (Consultant)
36. R. T. King	72. N. E. Promisel (Consultant)
37. T. S. Lundy	

EXTERNAL DISTRIBUTION

73. D. Allen
Southern Portland Cement Co.
P. O. Box 937
Victorville, CA 92305	86. S. Banerjee
General Refractories Co.
P. O. Box 1673
Baltimore, MD 21203
74-83. R. W. Anderson
Division of Buildings and
Industry
Energy Research and Develop-
ment Administration
20 Massachusetts Ave., NW
Washington, DC 20545	87. I. Baumer
Owens-Illinois, Inc.
P. O. Box 1035
Toledo, OH 43666
84. B. H. Baker
ARMCO Steel Corp.
Res. Center South
Middletown, OH 45043	88. N. Bernoth
C-E Refractories Co.
Box 828
Valley Forge, PA 19482
85. W. T. Bakker
Fossil Energy Div.
U.S. Energy Research and
Development Administration
20 Massachusetts Ave., NW
Washington, DC 20545	89. J. M. Revilacqua
The Carborundum Co.
P. O. Box 808
Niagara Falls, NY 14302
	90. D. R. Bissell
Drexel Refractories Co.
Box 50
Kittanning, PA 16201

91. J. A. Bonar
Carborundum Co.
Niagara Falls, NY 14302
92. A. Brown
General Motors Corp.
GM Technical Corp.
Manufacturing Development
Warren, MI 48090
93. B. R. Brown
E.I. duPont de Nemours & Co.,
Inc.
1007 Market St.
Wilmington, DE 19898
94. David Brown
Transco Inc.
700 Melvin Ave., Suite 2
Annapolis, MD 21401
95. C. E. Burley
Reynolds Metal Co.
P. O. Box 27003
Richmond, VA 23261
96. F. Campbell
Babcock and Wilcox Co.
Box 923
Old Savanna Rd.
Augusta, GA 30903
97. A. N. Copp
Basic Refractories
(Sub. of Basic, Inc.)
845 Hanna Bldg.
Cleveland, OH 44115
98. J. A. Crookston
A. P. Green Refractories Co.
Green Blvd.
Mexico, MO 65265
99. M. S. Crowley
Standard Oil Co. (Indiana)
Naperville, IL 60540
100. L. J. Davies
Canadian Refractories Div.
Dresser Industries Canada LTD.
P. O. Box 1750, Station B
Montreal, Quebec, Canada
113B3L3
101. W. J. Englert
PPG Industries Corp.
Melting and Forming Lab.
Ferry St.
Creighton, PA 15030
102. C. R. Enoch
Resco Products, Inc.
Box 108
Norristown, PA 19404
103. W. X. Fay
General Refractories Co.
50 Monument Rd.
Bala-Cynwyd, PA 19004
104. A. D. Fentzke
Emhart Corp.
Hartford Div.
Box 2809
Hartford, CT 06101
105. L. E. Ferreira
Interpace Corp.
Corporate Headquarters
Box 1111
Parsippany, NJ 07054
106. R. E. Ferris
Kaiser Res. Center
Box 870
Pleasanton, CA 94566
107. H. H. Greene
Ohio Lime Co.
128 E. Main St.
Woodville, OH 43469
108. Richard Grekila
Res. Center
Westinghouse Electric Corp.
Beulah Rd.
Pittsburgh, PA 15235
109. F. Hamel
Gulf Research and Development Co.
P. O. Box 2038
Pittsburgh, PA 15230
110. R. S. Harris
Anchor Hocking Co.
Lancaster, OH 43135

111. Douglas Harvey
Energy Research and Development
Administration
20 Massachusetts Ave., NW
Washington, DC 20545
112. S. P. Hepburn
ICI Fiber Materials
Concord Pike and New Murphy Rd.
Wilmington, DE 19849
113. J. P. Holt
Valley Minerals Products
915 Olive St.
St. Louis, MO 63101
114. A. V. Illyn
Babcock and Wilcox
P. O. Box 923
Augusta, GA 30903
115. H. L. Johns
Zircoa Products
31501 Solon Rd.
Solon, OH 44139
116. K. K. Kappmeyer
Applied Res. Lab.
United States Steel Corp.
Monroeville, PA 15146
117. R. V. Kilgore
Gunning Refractories Co.
(Sub. of BMI, Inc.)
Box 38
Pedro, OH 45659
118. W. D. Kingery
Dept. of Materials Science and
Engineering
M.I.T.
Cambridge, MA 02139
119. L. Krietz
Plibrico Co.
1800 N. Kingsburg St.
Chicago, IL 60614
120. L. J. Kuhlman
Monsanto Co.
800 N. Lindbergh Blvd.
St. Louis, MO 63166
121. R. G. LaBar
Alcoa Res. Labs.
Aluminum Co. of America
Alcoa Center, PA 15069
122. J. Langensiepen
Brockway Glass Co.
Central Lab.
Brockway, PA 15824
123. D. H. Larson
Inst. of Gas Technology
3424 S State Street
IIT Center
Chicago, IL 60616
124. F. A. Layne
Gem Refractories Co.
16th and Georgia St.
Sebring, OH 44672
125. R. Limes
Republic Steel Corp.
1441-T Republic Bldg.
P. O. Box 6778
Cleveland, OH 44101
126. C. Lindsay
Tennessee Valley Authority
303 Union Bldg.
Knoxville, TN 37902
127. D. E. McBride
Zircoa
31501 Solon Rd.
Box 39217
Cleveland, OH 44139
128. J. R. McGaughey
Bickley Furnaces, Inc.
550 State Road
Philadelphia, PA 19114
129. T. D. McGee
Iowa State University
Materials Science and Engineer-
ing Dept.
Ames, IA 50010
130. R. W. Marshall
North American Manufacturing Co.
4455 E 71st St.
Cleveland, OH 44105

131. F. M. Maupin
A.P. Green Refractories Co.
Green Blvd.
Mexico, MO 65265
132. W. Mead
Temtek-Allied Div.
Ferro Corp.
One Erieview Plaza
Cleveland, OH 44114
133. E. D. Miller
Lava Crucible-Refractories Co.
1045 Oliver Bldg.
Pittsburgh, PA 15222
134. J. I. Moates
General Shale Products Corp.
P. O. Box 3547, C.R.S.
Johnson City, TN 37601
135. R. J. Moffat
Pullman-Swindell
(Div. of Pullman, Inc.)
441 Smithfield St.
Pittsburgh, PA 15222
136. J. E. Moore
Kaiser Refractories Co.
(Div. of Kaiser Aluminum and
Chemical Corp.)
P. O. Box 47
Columbiana, OH 44408
137. A. Moser
A. Moser, Inc.
5700 SW 7th St.
Plantation, FL 33317
138. J. E. Neal
Johns-Manville Corp.
Box 5108, Greenwood Plaza
Denver, CO 80217
139. R. Neeley
Chattanooga Glass Co.
400 W 45th St.
Chattanooga, TN 37410
140. J. A. Nelson
University of Illinois
Urbana, IL 61801
141. R. E. Nelson
C-E Minerals Co.
901 E 8th Ave.
King of Prussia, PA 19406
142. D. Olenchut
Jones and Laughlin Steel Corp.
3A, Gateway Center
Pittsburgh, PA 15230
143. H. Orr
Trane Thermal Co.
Brook Rd.
Conshohocken, PA 19428
144. P. Papa
Cornhart Refractories Co.
1600 W Lee St.
Louisville, KY 40210
145. J. D. Parsons
Chicago-Wellsville Fire Brick Co.
1467 Elston Ave.
Chicago, IL 60622
146. G. Passell
AFC Corp.
Canfield, OH 44406
147. C. M. Pelanne
Johns-Manville Corp.
Box 5108
Denver, CO 80217
148. S. C. Porter, Jr.
Globe Refractories Co.
(Div. of C-E Refractories Co.)
Box D
Newell, VA 26050
149. G. V. Prible
C-E Refractories Co.
(Div. of Combustion Engineering,
Inc.)
Box 828
Valley Forge, PA 19482
150. C. J. Ranhke
Power Train and System Research
Ford Motor Co.
20,000 Rotunda Drive
Dearborn, MI 48121
151. P. H. Reed
New Castle Refractories Co.
Box 471
New Castle, PA 16103
152. R. Reed
John Zink Co.
4401 S. Peoria St.
Tulsa, OK 74105

153. D. M. Rice
Davis Fire Brick Co.
Box 235
Oak Hill, OH 45456
154. R. Rose
H. K. Porter Co.
Porter Bldg.
601 Grant St.
Pittsburgh, PA 15219
155. R. B. Rosenberg
Inst. of Gas Technology
3424 State Street
IIT Center
Chicago, IL 60616
156. R. P. Ross
Glasrock Products, Inc.
2210 Marietta Blvd., NW
Atlanta, GA 30318
157. G. R. Rowland
Hartford Refractories, Emhart
Corp.
P. O. Box 2809
Hartford, CT 06101
158. C. K. Russell
Res. Center
United States Steel Corp.
125 Jamison Lane
Mail Stop 43
Monroeville, PA 15146
159. E. C. Sargent
Kolb Refractories Co.
Box 95
East Greenville, PA 18041
160. M. Savitz
Energy Research and Development
Administration
20 Massachusetts Ave., NW
Washington, DC 20545
161. B. L. Schmidt
Anchor Hocking Co.
Lancaster, OH 43130
162. F. E. Schmidt
E.I. duPont de Nemours & Co.,
Inc.
Experimental Station
Bldg. 304
Wilmington, DE 14898
163. W. E. Scruggs
Monsanto Co.
300 N. Lindbergh Blvd.
St. Louis, MO 63166
164. R. L. Shultz
Armco Steel Corp.
Research Center South
Middletown, OH 45043
165. H. D. Smith
Wellsville Fire Brick Co.
Highway 19W
Wellsville, MO 63384
166. T. E. Smith
Southern Div.
Martin-Marietta Cement Co.
1800 Daniel Bldg.
Birmingham, AL 35223
167. W. J. Smothers
Homer Res. Labs.
Bethlehem Steel Corp.
Bethlehem, PA 18016
168. R. R. Smyth
Fluidyne Engineering Co.
5900 Olson Memorial Highway
Minneapolis, MN 55422
169. I. Snyder
Dow Chemical Co.
2020 Dow Center
Midland, MI 48640
170. D. Stefl
Freeport Brick Co.
Drawer F
Freeport, PA 16229
171. D. F. Stock
Harbison-Walker Refractories Co.
Dresser Industries, Inc.
Two Gateway Center
Pittsburgh, PA 15222
172. W. E. Swearingen
Koppers Co., Inc.
Pittsburgh, PA 15219
173. Larrie H. Sweet
Manager Technical Development
Carborundum Co.
P. O. Box 808
Niagara Falls, NY 14302

<p>174. C. A. Taylor
Shell Oil Co.
1 Shell Plaza, Box 2463
Houston, TX 77001</p> <p>175. C. H. Taylor
National Crucible Co.
Queen St. and Mermaid Lane
Philadelphia, PA 19118</p> <p>176. E. A. Thomas
Charles Taylor Div.
NL Industries, Inc.
8361 Broadwell Road
P. O. Box 44040
Cincinnati, OH 45244</p> <p>177. C. J. Thompson
Bartlesville Energy Res. Center
P. O. Box 1398
Bartlesville, OK 74003</p> <p>178. L. J. Trostel, Jr.
Norton Co.
One New Bond St.
Worcester, MA 01606</p> <p>179. B. S. Tucker
The Refractories Inst.
1102 One Oliver Plaza
Pittsburgh, PA 15222</p> <p>180. R. Van der Linden
Johns-Manville Products Corp.
Box 5108
Denver, CO 80217</p> <p>181. M. L. Van Dreser
Center for Technology
Kaiser Aluminum and Chemical
Corp.
Box 870
Pleasanton, CA 94566</p> <p>182. Theodore Vojnovich
Res. Labs.
Westinghouse Electric Corp.
Beulah Rd.
Pittsburgh, PA 15235</p> <p>183. R. L. Walter
H. J. Heinz Co.
P. O. Box 57
Pittsburgh, PA 15230</p> | <p>184. Alvin Weinberg
Inst. for Energy Analysis
Oak Ridge Associated Universities
Oak Ridge, TN 37830</p> <p>185. R. F. Whitford
North American Refractories Co.
1012 National City E 6th Bldg.
Cleveland, OH 44114</p> <p>186. R. D. Whiting
Coors Porcelain Co.
600 9th St.
Golden, CO 80401</p> <p>187. R. Wilcox
Chevron Res. Center
225 Bush St.
San Francisco, CA 94120</p> <p>188. J. R. Wilson
Shell Development Co.
Box 1380
Houston, TX 77001</p> <p>189. J. Wosinsky
Corning Glass Works
Box 432
Corning, NY 14830</p> <p>190. S. Young
Babcock and Wilcox Refractories
Co.
Old Savanna Rd.
Box 923
Augusta, GA 30903</p> <p>191. C. E. Zimmer
Babcock and Wilcox Co.
Lynchburg, VA 24505</p> <p>193. Research and Technical Support
Division
Oak Ridge Operations Office
Energy Research and Development
Administration
P. O. Box E
Oak Ridge, TN 37830</p> <p>194-220. Technical Information Center
P. O. Box 62
Oak Ridge, TN 37830</p> |
|--|--|