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**Effects of Alternate Fuels
Report No. 3
Analysis of High-Duty Fireclay Refractories
Degraded by Residual Oil Combustion Products**

G. C. Wei
V. J. Tennery

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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 ~~\$5.25~~ 4.50; Microfiche \$3.00

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Contract No. W-7405-eng-26
METALS AND CERAMICS DIVISION

EFFECTS OF ALTERNATE FUELS
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ANALYSIS OF HIGH-DUTY FIRECLAY REFRACTORIES DEGRADED
BY RESIDUAL OIL COMBUSTION PRODUCTS

G. C. Wei and V. J. Tennery

Prepared for
Division of Industrial Energy Conservation
Department of Energy

Date Published: April 1978

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ABSTRACT.

This is the third of a series of reports on analyses of several types of refractories that have been used in industrial heating equipment with fuels alternative to natural gas. Refractory and insulation degradation and corrosion in high-temperature equipment become serious because of reactions between the alternate fuel impurities or their combustion products and the refractory linings. Our purpose is to better understand the refractory deterioration process and to provide viable means to retard the degradation.

We analyzed high-duty fireclay brick (~39 wt % Al_2O_3) used for only six months in the soot hopper of a residual-oil-fired steam boiler, where the refractory operated at about 1400°C . The refractory loss of this firebrick was about 30 mm and the reaction zone in the firebrick extended to a depth of 80 mm toward the brick cold end. The rate of the refractory material loss was 5 mm/month and the reaction zone front proceeded at a rate of 18 mm/month. In a natural-gas-fired boiler, this type of refractory has a typical service life of three years. The service time of the refractory was drastically shortened by reactions involving firebrick constituents with sodium and vanadium derived from the fuel oil plus calcium and magnesium from the fuel oil additives.

The unaltered or original refractory consists of large grog grains containing mullite crystallites bonded in a low cristobalite matrix. These grains are in turn dispersed in a matrix material consisting of mullite, quartz, low cristobalite, and a glassy phase. Hematite, rutile, and zircon are also present in small amounts in the cold end of the brick. The reaction zone in the hot end of the refractory consists primarily of a glass containing Na, K, V, Ca, Mg, Ti, Fe, Al, and Si. Aluminum vanadate, high cristobalite, corundum, mullite, zircon, and a titanium vanadium iron oxide are the crystalline phases dispersed in the glassy phase in the altered brick. The reaction zone contains significant amounts of Na, V, Ca, and Mg, which are not present in the original refractory.

We identified four principal reactions between the impurities derived from residual fuel oil and oil additives and the high-duty firebrick during service. The original quartz grains in the brick dissolve in the glassy phase in the

hot end of the brick. Mullite reacts with vanadium in the glassy phase to form aluminum vanadate and cristobalite during service. Mullite reacts with sodium in the slag to form corundum, while the silica content of the mullite enters the glassy phase. Hematite and rutile in the original brick react with vanadium to form a titanium vanadium iron oxide compound.

Both sodium and vanadium played an important role in the refractory degradation. The magnesia- and dolomite-based additives used in the fuel oil for retarding metal boiler tube corrosion did not impede the refractory corrosion.

A major conclusion of this study is that the use of any fuel oil additives to retard refractory deterioration and improve refractory performance needs to be carefully studied and their effectiveness evaluated.

Zircon and corundum phases in the firebrick appear inert to reactions with fuel oil impurities and additives. Zircon could perhaps be used as a protective coating on the working surfaces of refractories to give better performance if the differential expansion strains of the zircon and the refractory substrate due to boiler temperature fluctuation can be accommodated. Increasing the alumina content of the refractory may produce a more viscous glassy phase to reduce fuel oil impurity-refractory reaction rate and/or introduce more corundum into the refractory to increase its resistance to fuel oil impurity corrosion, and therefore improve the refractory performance. High- Al_2O_3 (>60 wt % Al_2O_3) refractories consistently exhibit better performance than simple fireclay based refractories (20-45 wt % Al_2O_3) when residual oil fuel is used.

INTRODUCTION

In recent years, the shortage and curtailments of natural gas in the United States have required conversion of many industrial furnaces to alternate fuels, such as distillate and residual oils, coal, and low-joule 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 Assuming that there will be a sufficient supply of fuel oils based on

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

both domestic and foreign sources, and that the pricing structure continues approximately as at present, distillate and residual oils will be the primary alternate fuels for industrial heating applications in the next five years. Currently industry uses distillate oils extensively as fuel. They are relatively clean, and the effects of their combustion on refractories are minor if the distillate oil combustion system is properly installed and operated. Residual oil may offer economic advantages over distillates; however, this fuel may contain substantial amounts of many impurities such as sodium, vanadium, sulfur, and others, which can be quite detrimental to furnace refractories. The impurity contents of residual oils vary over a wide range, depending on the crude source, refinery, and storage and transportation conditions. There is currently limited industrial refractory operating experience in the United States with residual oils. It is therefore instructive 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 selection and development of refractories that perform better in the presence of residual oil combustion.

The present report is an analysis of a high-duty fireclay brick used in the soot hopper of a utility steam boiler fired with residual oil. Approximately 30 mm (1 in.) of brick was lost at the hot working surface. The refractory service life was only six months, as opposed to the three-year typical service life in the same boiler using natural gas. Results presented in this report include chemical analysis, optical microscopy, scanning electron microscopy, electron microprobe analysis, and x-ray diffraction analysis plus an interpretation of the refractory degradation mechanism based on results from these analyses and other observations reported in the literature.

This is the third of a series of reports on analyses of several generic refractory types that have been used in industrial equipment

with either residual oil or coal as fuel.^{2,3} All the refractory samples were obtained with the cooperation of industrial firms.

SPECIMEN HISTORY

The sample analyzed is a high-duty fireclay brick, which had been used in the soot hopper of a residual-oil-fired utility steam boiler for six months. The boiler was fired with a No. 6 residual oil. Additives based on magnesia (MgO) and dolomite [Ca Mg (CO₃)₂] were used in the residual oil to inhibit the fuel oil impurity corrosion of the metal components on the fire side. The utility company who used this boiler for steam generation did not analyze the impurity content of the residual oil, and thus the amount of impurities in the fuel oil causing the observed reactions is unknown.

Fireclay refractories are typically made from mixtures of fireclay (a type of clay that is not white burning but free from fluxes such as iron, alkaline earths, alkalies, and excess silica), flint clay, and prefired or calcined fireclay grog. Most present-day fireclay bricks are manufactured either by dry pressing or by extruding in a column of clay, followed by repressing to give the desired shape. The raw material batch, which usually contains about 20 wt % prefired grog, is mixed with water, poured into press boxes, molded by means of mechanically or hydraulically applied pressure, and dried and fired to yield the final product.

All but a few industrial heating processes make use of fireclay refractories. For example, linings of blast furnaces and stoves, roof, and side walls of soaking pits and reheating furnaces in the iron and steel industry; the subhearth of copper reverberatory furnaces in the nonferrous metals industry; linings, regenerators, and flues of pot

²G. C. Wei, V. J. Tennery, and L. A. Harris, *Effects of Alternate Fuels, Report 1. Analysis of High-duty Fireclay Refractories Exposed to Coal Combustion*, ORNL/TM-5909 (December 1977).

³G. C. Wei and V. J. Tennery, *Effects of Alternate Fuels Report 2. Analysis of Basic Refractories Degraded by Residual Oil Combustion Products*, ORNL/TM-6088 (February 1978).

furnaces and tank furnaces in the glass industry; walls, arches, and flues of boilers in utilities; cooler sections of rotary kilns in the cement industry; linings of catalytic reactors in the chemical and petrochemical industry; and incinerator linings in the waste disposal industry all employ fireclay refractories. The alumina content in fireclay refractories typically ranges from 20 to 45 wt %. Depending on their stability and properties at high temperatures, fireclay refractories are classified as low-duty, medium-duty, high-duty, and super-duty. The typical maximum recommended hot face working temperature for high-duty fireclay refractory is 1540°C (2800°F).

The particular type of high-duty fireclay brick examined in the present study has a reported as-received chemical composition shown in Table 1. The equivalent alumina content is 39 to 42 wt %. The

Table 1. Chemical Analyses of As-Received and Selected Zones from the High-Duty Firebrick

Oxide	Composition as Oxide Equivalent, wt %		
	As Received	Altered Brick	Unaltered Brick
Al ₂ O ₃	39-42	33.84	38.86
CaO	<1	1.68	0.09
Cr ₂ O ₃	<1	0.041	0.029
Fe ₂ O ₃	<1	1.74	1.98
K ₂ O	a	0.91	2.34
MgO	<1	4.87	0.35
Na ₂ O	a	8.10	0.26
NiO	<1	0.0154	0.0153
PbO	<1	0.01	<0.01
SO ₃	<1	0.58	0.02
SiO ₂	52-55	45.15	54.05
TiO ₂	<1	1.92	2.09
V ₂ O ₅	<1	1.34	0.0219

^aNa₂O + K₂O <3 wt %.

maximum temperature at the brick's hot face during service was reported as 1400°C (2550°F), which was 140°C (250°F) less than the recommended maximum hot-face working temperature for this particular type of firebrick. The service life, as stated earlier, was reduced by

conversion to residual fuel oil from gas from three years to only six months. The original dimensions of the high-duty firebrick were 230 by 110 by 64 mm (9.0 by 4.5 by 2.5 in.). Observed corrosion caused a loss of 30 mm at the brick's hot face. The total length of the used brick, including the altered and unaltered parts, is only 200 mm (8.0 in.). The temperature drop across the length of the brick was estimated to be 56°C (100°F) at the maximum hot face temperature. The service temperatures listed were estimated by the company who supplied the used boiler brick to us for analysis, and these temperatures were considered accurate to within $\pm 20^{\circ}\text{C}$.

RESULTS

Chemical, x-ray, optical microscopy, electron microprobe, and scanning electron microscopy analyses were performed on the firebrick. Experimental procedures were the same as those outlined in a report on the analysis of high-duty fireclay refractories exposed to coal combustion.²

Figure 1 shows a slice cut from the used brick. The hot face and the altered part of the brick had a greenish coloration. A better view of the hot face is shown in Fig. 2. The demarcation between the reaction zone and the unaltered part of the brick is rather irregular. The depth of the altered part or reaction zone varies from 10 mm in the center region of the brick hot face to 80 mm on one side of the brick hot face. Expressed in terms of rates, the firebrick lost its material at the hot face of the brick at a rate of 5 mm/month, and the reaction zone proceeded at a maximum rate of 18 mm/month. These values of material loss rate and reaction zone formation rate are extremely high. If the brick continued to be corroded at this rate, it would take only 13 months to convert the entire brick into a reaction zone. It should be noted, as stated earlier, that the present brick was anticipated to last three years with minimum alteration at the hot face if it were used in a natural gas combustion environment. A sampling plan for analyzing the brick is illustrated in Fig. 3. Selected areas in the used brick have been subjected to extensive analyses.

Fig. 1. A Section of the High-Duty Fireclay Brick Used in the Soot Hopper of a Residual-Oil-Fired Boiler for Six Months. Scale is 0.30 m.

Fig. 2. Hot Face of the High-Duty Fireclay Brick from Soot Hopper of Utility Steam Boiler Fired with Residual Oils for Six Months. Scale is in inches (1 in. = 25.4 mm).

Fig. 3. Sampling Plan of the Firebrick.

Chemical analyses of the altered and unaltered parts of the brick are shown in Table 1. A significant increase is seen in the equivalent contents of CaO , MgO , Na_2O , V_2O_5 , and SO_3 in the altered brick. Because of these increases the percentage contents of Al_2O_3 and SiO_2 decrease in the altered part compared with the unaltered part of the brick. Surprisingly, the K_2O content decreases sharply from 2.34 to only 0.91 wt %. The Fe_2O_3 and TiO_2 contents in the altered part of the brick remain pretty close to those in the unaltered brick. Other impurities, such as Pb, Ni, and Cr, were present in negligible amounts in the brick. In the altered part of the brick, the increase in the CaO and MgO contents is due to the magnesia and the dolomite additives used in the fuel oil for inhibiting the corrosion of metallic components in the boiler, whereas the increase in the Na_2O , V_2O_5 , and SO_3 contents is due to the presence of sodium, vanadium, and sulfur in the residual oil combustion products.

X-ray diffraction analyses were performed on four samples in the brick (BX1-BX4), located as shown in Fig. 3. In the unaltered part of the brick (sample BX4), the major crystalline phases are

mullite, α -quartz, low cristobalite, rutile (TiO_2), hematite (Fe_2O_3), and zircon (ZrSiO_4). Silica crystalline phases including α -quartz and low-cristobalite present in the unaltered brick disappear in the altered part of the brick (samples BX2 and BX3). The major crystalline phases in samples BX1, BX2, and BX3 taken from the brick reaction zone are mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), corundum (Al_2O_3), aluminum vanadate (AlVO_4), high cristobalite, and zircon. Table 2 lists the major crystalline phases identified in the four brick samples (BX1-BX4).

Table 2. Major Crystalline Phases in Four Samples from the Brick

Brick Zone	Sample ^a	Major Crystalline Phases
Altered	BX1	Mullite, corundum, aluminum vanadate, high cristobalite, zircon
Altered	BX2	Mullite, corundum, aluminum vanadate, high cristobalite, zircon
Altered	BX3	Mullite, corundum, aluminum vanadate, high cristobalite, zircon
Unaltered	BX4	Mullite, α -quartz, low cristobalite, zircon, rutile, hematite

^aFor zone and sample identification, see Fig. 3.

The original diffraction data expressed in terms of the crystal lattice spacings are presented in the Appendix. In the reaction zone of the brick, x-ray diffraction data verified the existence of corundum and aluminum vanadate, which were products from reactions of the residual oil impurities with the original refractory. The intensity of the diffraction peaks characteristic of mullite were lower for sample BX1 than for samples BX3 or BX2. This suggests that the residual oil impurities reacted with the mullite phase in the brick at a faster rate at the hot face than at brick zones just behind the hot face.

Three samples (BM1-BM3) from the brick were examined by optical microscopy. Zones from which these samples were taken are shown in Fig. 3. Microstructures of sample BM1 taken from the hot face

of the brick consist of a needle-shaped crystalline phase present around the periphery of the large fireclay grog particles consisting of very small mullite crystallites bonded together by cristobalite. The needles (N), and the grog (G) are shown in Fig. 4. In addition to such small needles, large needles are also observed to be distributed in an interlocking configuration in sample BM1. Figure 5 shows the large needle (AV) formation in a glassy matrix (M). Electron microprobe analysis on sample BM1 shows that both the small and the large needle crystals are rich in aluminum and vanadium. Since the x-ray diffraction analysis on sample BX1 taken from the hot face of the brick found aluminum vanadate crystals, the needle-shaped crystals observed optically are apparently this substance. Electron microprobe analysis of the glassy matrix material at the hot face of the brick indicated significant concentrations of many cation impurities, including Na, Mg, Al, Si, K, Ca, V, Ti, and Fe. The large needle-shaped aluminum vanadate crystals contain a precipitated phase (TVF) containing Ti, V, and Fe (see Fig. 5). The optically reflective phase(ZS) dispersed in the glassy matrix at the hot face of the brick contains silicon and zirconium, and is apparently zircon (ZrSiO_4).

Sample BM2, which was taken from the altered part of the brick and near the demarcation between the visual reaction zone and the unaltered part of the brick, has a typical microstructure as shown in Fig. 6. The microstructure of sample BM2 is very similar to the typical microstructure observed in fireclay-derived bricks. It consists predominantly of large grog (G) grains consisting of mullite crystallites. The large grog particles are bonded with quartz, cristobalite, and glassy bonding phases. However, it should be noted that the glassy bonding phase (B) in sample BM2 contains Al and Si as well as Na and V, which were revealed by the electron microprobe analysis. Apparently, the fuel oil impurities Na and V have reached the brick zone represented by sample BM2, and the effect of Na and V on this material in areas between the unaltered brick and the reaction zone consists largely of a reaction with the original glassy phase, probably reducing its viscosity.

Fig. 4. Reflected-Light Micrographs of Altered Brick. G = Grog. N = needle-shaped crystals. (a) 100 $\times$. (b) Central area of (a) at 500 $\times$, showing needle crystals in the periphery of the grog particle.

Fig. 5. Reflected-Light Micrograph Showing Large Needle-Shaped Aluminum Vanadate (AV) in a Glassy Matrix (M) and Crystal Precipitate (TVF) Containing Ti, V, and Fe Within Aluminum Vanadate Crystals Along with Zircon (ZS) in the Altered Part of the Brick. 500 $\times$.

Fig. 6. Reflected-Light Micrograph of the Altered Brick Near the Demarcation Between Reaction Zone and the Unaltered Brick. 100 $\times$. G = grog particle, B = glassy bonding phase containing Na and V, as well as Al, Si, and K.

The cold end of the brick has a microstructure typical of fireclay refractories. Large grog particles (G), which consist of mullite bonded with cristobalite, are bonded together by quartz, cristobalite, and glassy bonding phases. The typical microstructure of sample BM3, which was taken from the brick's cold end, is shown in Fig. 7.

Fig. 7. Reflected-Light Micrograph of Unaltered Brick. 100×.
G = grog particle.

Scanning electron microscopy of samples taken from the brick's hot face shows many interesting and important features. Scanning electron micrographs in Fig. 8 of the natural surface of the brick hot face show needle-shaped crystals (AV) growing from a matrix of fine mullite crystals (M) and residues (R) of a glassy phase on the needle-shaped crystals. Energy-dispersive x-ray analysis indicates the presence of aluminum and vanadium in these needles. This fact coupled with the findings from x-ray diffraction and optical microscopy on the hot face of the brick identifies the needles (AV) shown in Fig. 8(a) as aluminum vanadate. The residue of a glassy phase on the aluminum vanadate crystals is believed to be residues of an oxide melt

Fig. 8. Scanning Electron Micrographs of the Natural Surface of the Brick's Hot Face. (a) Needle-shaped aluminum vanadate crystals (AV) growing from a matrix of fine mullite crystals (M). 1000 $\times$. (b) Central area in (a), showing residues (R) of aluminum vanadate melt on the surface of the needle-shaped aluminum vanadate crystals (AV). 3000 $\times$.

originally rich in aluminum and vanadium at the refractory operating temperature. It should be noted that aluminum vanadate melts or crystallizes at 695°C, which is far below the estimated maximum refractory service temperature of 1400°C. Therefore, the aluminum vanadate crystals have formed during boiler cooldown.

In the altered part of the brick, we also observed aluminum vanadate crystals along with relatively large cristobalite crystals. Figure 9 is a scanning electron micrograph of the fracture surface in the altered part of the brick, showing aluminum vanadate crystals (AV) and cristobalite crystals (C). These phases were identified by energy-dispersive x-ray analysis plus the results of x-ray diffraction and optical microscopy. Another example of the microstructure of the altered part of the brick is shown in a scanning electron micrograph in Fig. 10. The crystals (C) having well-defined growth habits contain silicon, and we conclude that they are high-cristobalite

Fig. 9. Scanning Electron Micrograph of the Fracture Surface of the Altered Brick, Showing Needle-Shaped Aluminum Vanadate Crystals (AV) and Cristobalite Crystals (C). 2000 $\times$.

Fig. 10. Scanning Electron Micrograph of the Hot Face of the Brick, Showing the Formation of Cristobalite Crystals (C) as a Result of the Vanadium-Containing Slag Reaction with the Firebrick. 1000 $\times$.

from the results of energy-dispersive x-ray analysis plus x-ray diffraction. A direct conclusion is that the vanadium-containing slag reacted with the high-duty firebrick and formed aluminum vanadate and silica phases accompanied by decomposition of the original mullite.

Our observation of the presence of aluminum vanadate is solid evidence for reaction of vanadium from the residual oil with this refractory. This observation shows that vanadium can definitely play a major role in fireclay refractory degradation. This contrasts a previously expressed apprehension of some industrial refractory specialists that alkalis are the source of the main problems of fuel oil corrosion with this type of refractory. This report apparently gives the first direct observation of the existence of aluminum vanadate at the hot face of fireclay refractories exposed to residual oil combustion.

Although x-ray diffraction data detect corundum at the brick hot face, we could not identify it in our optical microscopy, electron microprobe, and scanning electron microscopy analysis. The reason is presumably the small size of corundum crystals in the reaction zone in the brick. The electron beam in our electron microprobe or scanning electron microscope has a 3- μm diameter, and therefore corundum crystals smaller than 3 μm and distributed in a complex matrix material could not be resolved.

DISCUSSION

Refractory failures have been observed in the combustion chamber of residual oil fired boilers. One case was reported⁴ as early as 1952. In this section, we first review the investigations reported in the literature and then discuss the results and the implications of the present study in light of relevant previous work.

⁴M.C.K. Jones and R. L. Hardy, "Petroleum Ash Components and Their Effect on Refractories," *Ind. Eng. Chem.* 44(11): 2615 (1952).

Previous Work

Jones and Hardy studied the effect of residual oil impurities on refractories.⁴ They reported two modes of boiler firebrick degradation in an oil firing environment. Spalling could result from residual oil slag forming on the brick working surface. The differential expansion of the slag and the brick resulted in spalling as a result of temperature fluctuation common to the service environment. Another mode of refractory failure is fluxing. Impurities originating from residual oils can react with the refractory to form a low-melting material, which is molten during the refractory service life. These authors found vanadium and sodium in residual oils were particularly destructive to boilers in which the fireclay refractory hot face temperature was in the vicinity of 1540°C (2800°F). From measurements of the fusion point of various mixtures of ground refractory powders with vanadium pentoxide (V_2O_5) powder, sodium vanadate ($NaVO_3$) powder, and/or residual oil ash, Jones and Hardy concluded that for furnaces in which vanadium-bearing fuel oils were burned and the refractory hot face temperature was at least 1315°C (2400°F), fireclay refractories should not be used and that high-alumina (>60 wt % Al_2O_3) refractories would be suitable.

Palfreyman⁵ reported a failure of super-duty fireclay refractories (43 wt % Al_2O_3) in the combustion chamber of a steam boiler converted from coal to residual oil firing. In this case, the boiler refractory lasted only 12 days after conversion to oil and caused a costly boiler shutdown. The author attributed the drastically shortened refractory service life to two reasons; (1) fluxing by vanadium derived from residual fuel oil, and (2) fluxing by coal ash residues that had been deposited on boiler tubes during coal firing and had not been removed before conversion to oil firing. While the boiler was coal-fired, the side walls did have smooth surfaces and coal ash could not find a place to be physically trapped and thus passed readily into the ash pit.

⁵M. Palfreyman, "Investigation of Refractory Failure in a Boiler Combustion Chamber," *J. Can. Ceram. Soc.* 41: 103 (1972).

However, for the conversion to oil, the side walls were reconstructed with steps or ledges on the vertical walls. Furthermore, because of local overheating to temperatures greater than 1280°C (2340°F) by fuel oil combustion in the higher regions of the chamber, coal ash deposits remaining on the boiler tubes were loosened and became relocated on the steps in the boiler side wall. The fuel oil was analyzed and contained 242 ppm V. Such a vanadium content was not extremely high, but Palfreyman found that vanadium had lowered the fusion point of the ash deposit on the combustion chamber floor from 1427°C (2600°F) to 1371°C (2500°F). This change corresponded to a V₂O₅ content of only 0.61 wt % in the ash deposit. The refractory failure reported by Palfreyman indicated at least three important factors that should be considered in conversion of a boiler to oil firing. First, the vanadium content in the fuel oil should be kept low and preferably less than 200 ppm. Second, any design changes in the refractory linings of the combustion chamber brought about by the conversion to oil firing should not allow residual oil ash to be trapped, thereby increasing its physical contact with the refractories. Finally, any traces of ash on the boiler tubes should be removed before conversion to oil, because the ash could be loosened because of the generally hotter flame characteristic of oil compared with coal or natural gas.

The reaction of residual oil impurities on boiler tubes and refractories has been reviewed by Walls and Proctor.⁶ They suggested firing boilers with residual oils having a total metallic impurity content less than 400 ppm. The number "400 ppm" was determined on the basis of their own experience and was rather arbitrary. It should not be regarded as the impurity content threshold for the onset of refractory corrosion in a typical oil-fired steam boiler.

⁶W. A. Walls and W. S. Proctor, "Water Wash of Bunker C Retards Boiler Slag on Atlantic Tank," *Combustion* 32(4): 43 (1960).

Rigby and Hutton⁷ and McLaren and Richardson⁸ used solid-solid and solid-liquid reactions to study fuel oil ash corrosion of refractories. The experiments were essentially the same as that of Jones and Hardy.⁴ Samples consisting of mixtures of characteristic combustion product compounds such as Na_2SO_4 and V_2O_5 and the phases of the refractory system of interest such as Al_2O_3 and SiO_2 were heated to high temperatures, then quenched and examined to determine the resultant phase compositions. They found that sodium vanadate was a strong fluxing agent in the Al_2O_3 - SiO_2 system. The presence of both sodium and vanadium in a high-temperature oxidizing environment will result in sodium vanadate formation, and this compound will react with the aluminosilicate refractories at much lower temperatures and generate more liquid phase than either Na_2O or V_2O_5 will do alone. McLaren and Richardson found that, in contact with aluminosilicate refractories, V_2O_5 on its own was not a major slagging agent, but V_2O_5 together with Na_2O , in particular, formed numerous low-melting compounds. Mullite resisted reaction with V_2O_5 at temperatures up to 1700°C . In the presence of both Na_2O and V_2O_5 , mullite was converted to nepheline ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) at Na_2O contents higher than 30 wt % at temperatures higher than 1260°C (2300°F). Rigby and Hutton⁷ essentially confirmed the findings of McLaren and Richardson. Rigby and Hutton found that Na_2O first reacts with components in the Al_2O_3 - SiO_2 system to form sodium aluminate and sodium silicate. Mullite also was decomposed and formed nepheline, sodium aluminate, and β -alumina. The corrosion effect of Na_2O plus V_2O_5 was largely attributed to Na_2O , and the role played by V_2O_5 was thought to be as a mineralizer, enhancing the formation of other crystalline phases.

⁷G. R. Rigby and R. Hutton, "Action of Alkali and Alkali-Vanadium Oxide Slags on Alumina-Silica Refractories," *J. Am. Ceram. Soc.*, 45(2): 68 (1962).

⁸J. R. McLaren and H. M. Richardson, "The Action of Vanadium Pentoxide on Aluminosilicate Refractories," *Trans. Br. Ceram. Soc.* 58(9): 188 (1959).

Because the total amounts of Na_2O and V_2O_5 used in the previously reported investigations all exceeded 10 wt %, which was high compared with levels more typical of combustor concentrations, Busby⁹ used samples containing less than 5 wt % V_2O_5 and Na_2O . He concluded that only 2 wt % Na_2O could lower by about 20°C the maximum use temperature of fireclay refractories, but 2 wt % of V_2O_5 caused only a minor change in refractory properties. If the total concentration of V_2O_5 was less than 0.5 wt %, the effect on properties of the Al_2O_3 - SiO_2 system was negligible.

From the above review, it is obvious that, while one school of thought⁴⁻⁶ views vanadium as the most detrimental impurity in the fuel oil, another school of thought⁷⁻⁹ strongly disagrees with this and views alkalis and especially sodium as detrimental, while vanadium is considered as less detrimental to refractories. The disagreement is due to a lack of similarity between some of these experiments and the actual conditions in a combustor, and a lack of understanding of the refractory degradation process in a residual oil combustion environment.

Boiler Refractory Failures and Fuel Oil Additives

Even though the refractory community knows that residual oil impurities can corrode boiler refractories, and various means have been demonstrated to improve the refractory corrosion resistance, refractory failures in residual-oil-fired boilers are still frequently reported, especially in cases where conversion is made from natural gas to residual oils. Examples of these means include increasing the alumina content or using magnesia,¹⁰⁻¹² dolomite,¹⁰⁻¹²

⁹T. S. Busby, "A Study of the Effects of Fuel Oil Ash on Glass Tank Refractories," *Glass Technol.* 4(1): 18 (1963).

¹⁰J. A. Bonar, "Fuel Ash Corrosion," *Hydrocarbon Processing* 51(8): 76 (1972).

¹¹R. J. Zoschak and R. W. Boyers, "An Experimental Investigation of Fuel Additives in a Supercharged Boiler," *J. Eng. Power* 82(7): 168 (1960).

¹²W. D. Niles and H. R. Sanders, "Reactions of Magnesium with Inorganic Constituents of Heavy Fuel Oil and Characteristics of Compounds Formed," *J. Eng. Power* 84(4): 178 (1962).

alumina,¹³ and silicon carbide¹³ additives in residual oils. The reasons for the occurrence of such unexpected refractory failures are many. The major reason is the lack of a detailed understanding of the deterioration or corrosion process of refractories used in a well-characterized residual oil combustion environment. Another important fact is that commercially available residual oils have a wide range of impurity contents depending on the crude source, storage and transportation conditions, and the refinery operational parameters. There is strong evidence¹⁴ that the impurity content of residual oils has increased significantly in recent years because of the increasing demand for the higher grade gasoline and distillate fuel oils. The users usually do not specify the impurity content when they buy residual oils. Specifying the oil impurity content is desirable from the viewpoint of refractory corrosion, but it is difficult or impractical because such specification may increase the residual oil price, and compliance with such specifications is not routine to many residual oil suppliers. The wide impurity content range observed in residual oils usually makes it difficult to obtain successive shipments of this fuel with relatively constant and predictable impurity content. Another important consideration is that the boiler refractory design changes required as a result of conversion to residual oils often create new locations in the refractory hot face for entrapment of residual oil slag. The generally hotter and longer flame typical of oil combustion can also result in local overheating in the elevations of the combustion chamber such as the roof. Magnesia or dolomite additives to residual oils have been proven effective as inhibitors for corrosion in boiler tubes, and their addition to the fuel oil before use is an established practice.^{11,12} Although additives are useful in retarding metal corrosion, their effectiveness in retarding refractory corrosion is not at all established. The refractory performance in boilers fired

¹³H. Kirsch, "Einige Aspekte Zur Verhinderung der Hochtemperatur-Korrosionen durch Additive und Schutzschichten in Konventionellen Kraftwerken," *High Temp. High Pressures* 6: 545 (1974).

¹⁴R. W. Marshall, "An Introduction to the Use of Today's Fuel Oils," *Bull. Am. Ceram. Soc.* 54(9): 774 (1975).

with residual oils treated with corrosion-inhibiting additives has never been systematically studied, and quantitative effects of such additives are unknown at present. In fact, our study strongly suggests that such additives do not retard the refractory corrosion. They might even have a detrimental effect on refractory life by playing an active role in fluxing the refractory.

In the slagged end of the used high-duty firebrick, the CaO and MgO contents are, respectively, 18 and 14 times the contents in the unaltered part of the brick. These high contents are due to additives used in the residual oil. We anticipated that MgO or CaO may react with the residual oil combustion product V_2O_5 and form relatively refractory vanadium-containing compounds, thereby making less vanadium available for reactions with the boiler tube and ceramic linings. According to the equilibrium phase diagrams of the $MgO-V_2O_5$ ¹⁵ and $CaO-V_2O_5$ ¹⁶ systems, the eutectic temperature of MgO with V_2O_5 and CaO with V_2O_5 are 604 and 618°C respectively. Magnesium oxide and calcium oxide also form low-melting intermediate compounds with V_2O_5 :

Compound	$MgO \cdot V_2O_5$	$2MgO \cdot V_2O_5$	$3MgO \cdot V_2O_5$	$CaO \cdot V_2O_5$	$2CaO \cdot V_2O_5$	$3CaO \cdot V_2O_5$
mp, °C	750	940	1150	778	1015	1380

All these compounds melt incongruently, namely, they melt to a V_2O_5 -rich liquid and a higher melting compound richer in the second oxide. Addition of Na_2O into the V_2O_5 -MgO system results in a region of liquidus temperatures (which is dependent upon the oxygen partial pressure)¹⁷ and also yields several compounds, one eutectic, and four peritectics, with the lowest one at 470°C. In the present case, we

¹⁵E. M. Levin, C. R. Robbins, and H. F. McMurdie, *Phase Diagrams for Ceramists, 1969 Supplement*, American Ceramic Society, Columbus, Ohio, 1969, p. 89.

¹⁶E. M. Levin, C. R. Robbins, and H. F. McMurdie, *Phase Diagrams for Ceramists*, American Ceramic Society, Columbus, Ohio, 1964, p. 109.

¹⁷R. C. Kerby and J. R. Wilson, "Solid-Liquid Phase Equilibria for the Tenery Systems V_2O_5 - Na_2O - Fe_2O_3 , V_2O_5 - Na_2O - Cr_2O_3 , and V_2O_5 - Na_2O - MgO ," *Can. J. Chem.* 51: 1039 (1973).

found no evidence of the existence of magnesium vanadate or calcium vanadate in the altered zone of the brick. Either the combustion environment, such as the oxygen potential, did not favor a fast reaction of MgO or CaO with V_2O_5 , or the other impurities such as Na, K, and S had interfered with the CaO- V_2O_5 or MgO- V_2O_5 reactions to form even more complex compounds. Clearly, MgO- or CaO-based oil additives did not seem to reduce the refractory corrosion in the present case.

Reactions with Sodium and Potassium Contaminants

The K_2O content in the altered brick decreased when compared with the cold end. It dropped from 2.34 wt % in the cold end to only 0.91 wt % in the hot end. This is somewhat surprising and has not been reported in any other studies. We speculated that the residual oil probably did not contain a significant amount of potassium, and the original potassium content in the brick hot face was reduced as potassium evaporated because of its relatively high vapor pressure over such compositions. Sodium, which also has an appreciable vapor pressure at these temperatures, apparently was continuously replenished from the residual oil and, thus, had increased in the altered zone to almost 40 times its original content after the six month service time.

If we neglect other elements temporarily and focus only on the ternary system Al_2O_3 - SiO_2 - Na_2O , the relative ratio of the Al_2O_3 , SiO_2 , and Na_2O contents in the altered zone of the brick (33.84:45.15:8.10), if normalized to a 100% basis, gives a composition that falls in the compatibility triangle of albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$), mullite, and silica.¹⁸ This means that albite, mullite, and silica should be present in the hot end of the brick. However, albite was not detected and the mullite concentration was reduced in the altered zone as compared with the cold end of the brick. This implies that either the other

¹⁸E. M. Levin, C. R. Robbins, and H. F. McMurdie, *Phase Diagrams for Ceramists, 1969 Supplement*, American Ceramic Society, Columbus, Ohio, 1969, p. 181.

impurities — represented in the chemical analysis as V_2O_5 , CaO , MgO , TiO_2 , Fe_2O_3 , K_2O , and SO_3 — have interfered and changed the reactions involving Al_2O_3 , SiO_2 , and Na_2O to a situation totally different from the Al_2O_3 – SiO_2 – Na_2O ternary system, or the hot end of the brick was not in an equilibrium state at the service temperature ($1400^\circ C$) or during cooldown. Sodium is present as an element in the glassy phase along with other elements, including Mg , Al , Si , K , Ca , Ti , V , and Fe . Sodium is not observed to be present in any crystalline phases in either part of the brick. The commonly observed spalling due to the formation of nepheline or albite in aluminosilicate refractories exposed to Na_2O did not occur in the present case. The effect of sodium originating from the fuel oil on the firebrick was essentially a fluxing effect. That is to say, sodium reacted with the brick constituents and formed a relatively low-melting glassy phase at the brick hot face. The low viscosity glassy phase so formed would aid the transport of other detrimental species, such as vanadium, through the glassy material and thus favor reactions of vanadium with the major refractory constituent of the brick, namely, mullite.

Reactions with Vanadium

Vanadium clearly reacted with mullite in the present case, and based upon the data, this reaction can be represented by,

Unfortunately, the standard free energy of formation for $AlVO_4$ is presently unknown, so it is uncertain whether reaction (1) is thermodynamically favorable or not. Reaction (1) could account for the observed aluminum vanadate and cristobalite crystals at the brick hot end. The phase diagram¹⁹ of the Al_2O_3 – V_2O_5 system contains a compound, $AlVO_4$, with a melting point of $695^\circ C$. The maximum hot face

¹⁹E. M. Levin, C. R. Robbins, and H. F. McMurdie, *Phase Diagrams for Ceramists*, 1969 Supplement, American Ceramic Society, Columbus, Ohio, 1969, p. 124.

temperature of the firebrick during service, as stated previously, was 1400°C (2550°F), which was much higher than the melting point of AlVO_4 . Therefore the observed AlVO_4 crystalline phase was apparently formed only during boiler shutdown. Reaction (1) proceeded at the refractory service temperature (1400°C), and the reaction products, AlVO_4 and SiO_2 , were in a liquid and a solid state respectively. The solid AlVO_4 was then formed during cooldown. The mechanism described above explains the existence of AlVO_4 and cristobalite in the altered brick. Our finding of aluminum vanadate and cristobalite in the altered part of the brick is not consistent with the implications of the work reported by McLaren and Richardson²⁰ and Rigby and Hutton.²¹ These two papers did not report any reaction between V_2O_5 and mullite to form aluminum vanadate or cristobalite. These authors reported that mullite was quite resistant to reaction with V_2O_5 at the temperatures of interest. In the presence of both Na_2O and V_2O_5 , the aluminosilicate system at high temperature will result in nepheline and/or albite, but not aluminum vanadate or cristobalite. It is therefore possible that other impurities, including MgO and CaO , might have important effects on the reaction of Na_2O and V_2O_5 with high-duty firebrick. The presence of significant amounts of MgO and CaO probably retards the crystallization of sodium-bearing crystalline phases and enhances the formation of vanadium-bearing compounds and sodium-bearing amorphous phases. The net result of the presence of MgO , CaO , Na_2O , and V_2O_5 is then an extremely fast corrosion process in fireclay refractories, such as a refractory material loss rate of 5 mm/month reported in the present case.

We previously found²² that sodium can react preferentially with the silica component in the mullite phase to form a glassy phase and leave

²⁰J. R. McLaren and H. M. Richardson, "The Action of Vanadium Pentoxide on Aluminosilicate Refractories," *Trans. Br. Ceram. Soc.* 58(9): 188 (1959).

²¹G. R. Rigby and R. Hutton, *J. Am. Ceram. Soc.* 45(2): 68 (1962).

²²G. C. Wei, V. J. Tennery, and L. A. Harris, *Effects of Alternate Fuels, Report 1. Analysis of High-duty Fireclay Refractories Exposed to Coal Combustion*, ORNL/TM-5909, in press.

behind the corundum phase, in the case of a high-duty fireclay brick exposed to coal combustion at a maximum temperature of about 1260°C for 15 years in the crown of a periodic kiln. The same mechanism might have been operative in the present case and could account for the existence of corundum in the altered zone of the brick. Reaction of V_2O_5 with Al_2O_3 remaining from the mullite originally dissolved by reaction with Na_2O also is a possibility. The latter phase of this reaction sequence can be represented by the reaction,

Again, we are uncertain if reaction (2) would proceed because of the lack of the required thermodynamic data for $AlVO_4$. Reaction (2) could produce aluminum vanadate, but not cristobalite, which was also observed in the altered zone of the brick. One mechanism for the generation of cristobalite involves invoking the mineralizing effect of vanadium on quartz (present in the original brick) resulting in the transformation to cristobalite. Vanadium can act as a mineralizer for the quartz transformation to tridymite and cristobalite.²³ However, both tridymite and cristobalite are reportedly produced as a result of the mineralizing effect of vanadium on quartz. The x-ray diffraction data detected only cristobalite but no tridymite. This evidence and the well developed morphology of the cristobalite crystals as shown in Figs. 9 and 10 indicate that mullite and quartz originally present in the refractory were dissolved by a sodium- and vanadium-rich oxide melt, that the observed cristobalite crystallized and grew at a relatively high temperature, and that the $AlVO_4$ crystals grew rapidly from the slag during cooling of the refractory. Thus it appears that the mineralizing effect of vanadium was not operative in this slag, probably because of the presence of other constituents. In short, even though reaction (2) could also account for the existence of aluminum vanadate in the altered brick,

²³A. V. Morsanyi, "The Effect of Vanadium Compounds on Silica Refractories," *Glass Technol.* 4(1): 23 (1963).

our experimental results suggests that reaction (1) more properly describes what occurred. From the viewpoint of phase stability in the present case, mullite was more susceptible to reaction with vanadium-bearing species, while corundum is less prone to vanadium corrosion.

The conclusion that mullite reacted with vanadium-bearing components has some important implications. In the literature, many people have proposed or recommended the use of mullite refractories in residual oil combustion environments.²⁴ Our observations from this case indicate that such recommendation on refractory selection is not based on mullite resistance to residual oil impurity corrosion, but rather is based on the requirement of formation of a highly viscous liquid slag. The case reported here clearly shows that mullite can react with vanadium and form aluminum vanadate plus silica at temperatures up to 1400°C. A refractory containing primarily mullite or compositions of even higher Al_2O_3 content may produce a more viscous slag because of the resulting higher Al_2O_3 content of any resultant slag. Reduced transport rate of fuel impurity species within the slag would be accompanied by reduced degradation rates for the refractory. Results of this present work also indicate that increasing the Al_2O_3 content in the high-alumina refractories will obviously increase the concentration of corundum in the refractory, and this phase appears to be the most stable under residual oil slagging conditions like the present case.

We also observed zircon to be quite stable in the altered zone of the brick. Zircon was present as a minor impurity phase in the original brick. It probably could be added in the fireclay refractories or applied as a thin protective coating on the working face of the refractory to increase its service life in a residual-oil combustion environment at temperatures below 1400°C.

²⁴J. R. Bonar, "Choosing Refractories for Fuel Ash Corrosion Resistance," paper 11 presented at NACE 1976 Annual Meeting, March 22-23, Houston, Texas.

The hematite and rutile phases in the original brick apparently reacted with vanadium derived from residual oils to form a titanium-vanadium-iron oxide compound. This agreed with work reported by Crouch.²⁵ He found that V_2O_5 would react with $Fe_2O_3 \cdot TiO_2$ to form a $TiO_2-V_2O_5$ solid solution and $Fe_2O_3 \cdot V_2O_5$. The presence of minor amounts of TiO_2 and Fe_2O_3 in the brick seems to offer little advantage other than, perhaps, a moderate increase in the slag viscosity after their dissolution due to the formation of the Ti-V-Fe oxide liquid.

Estimate of Fuel Oil Impurity Delivery To Boiler

If we assume that the sodium and vanadium concentrations in the fuel oil used were 100 ppm and the boiler consumes about 0.125 m^3 (330 gal) of fuel oil per hour or equivalently 15.0 MW(t), about 540 kg of sodium and 540 kg of vanadium would be delivered to the furnace by the end of the six month service time. Expressed in terms of oxide, these would represent 718 kg of Na_2O and 961 kg of V_2O_5 . If half the oxide were assumed to have passed through the boiler and entered the stack exhaust, still 359 kg of Na_2O and 481 kg of V_2O_5 would be available in the boiler for reactions with boiler tubes and refractories. If we assume that, (1) there is 1000 m^2 total surface area of the refractory hot face and boiler tubes, of which a 500 m^2 total surface area of the refractory hot face reacts with sodium and vanadium, (2) the fireclay refractory has a bulk density of 2.0 Mg/m^3 , (3) the fireclay refractory has a porosity of 18%, and (4) the reaction zone in the refractory is 50 mm deep, the amount of Na_2O and V_2O_5 estimated above would result in concentrations of 0.78 wt % Na_2O and 1.05 wt % V_2O_5 in the reaction zone or the altered part of the brick. These assumptions, though approximate, show that the Na_2O and V_2O_5 in the boiler appears to have been sufficient to account for the observed concentrations of these elements in the firebrick.

²⁵A. G. Crouch, "The Corrosion of Bauxite-based Refractories by Products of Residual Fuel Oil Combustion," *Trans. Br. Ceram. Soc.* 68: 67 (1969).

CONCLUSIONS

The unaltered high-duty fireclay brick consisted of large grog grains bonded with a fine matrix phase. The grog grains consisted primarily of mullite. The matrix material consisted of mullite, low cristobalite, α -quartz, and minor amounts of hematite, rutile, and zircon.

The reaction zone in the refractory consisted primarily of a silicate glass containing Na, K, V, Ca, Mg, Ti, Fe, and Al, with some crystalline phases dispersed in it. Aluminum vanadate, high-cristobalite, corundum, mullite, zircon, and a titanium vanadium iron oxide were identified as crystalline phases present in the reaction zone of the brick.

Quartz and mullite originally present in the refractory were dissolved in the glass phase in the reaction zone. The alkali oxide content in the altered brick is very high (9.01 wt %). The alkali dissolved silica to form an alkaline silicate melt. Mullite reacted with vanadium in this melt, with aluminum vanadate and high-cristobalite being subsequently formed. The alkali in the glass phase also reacted preferentially with the silica component in the mullite phase and produced corundum in the altered part of the brick. Corundum as a product of residual oil impurity reactions with the fireclay refractory was relatively stable in the slagged region of the brick. The presence of both sodium and vanadium in the slag played an important role in the refractory deterioration process.

The magnesia- and dolomite-based additives used in the fuel oil for retarding boiler tube corrosion apparently did not impede the refractory corrosion and might have assisted residual oil impurity reaction with the fireclay refractory. Mullite is known to be susceptible to sodium and vanadium attack in the presence of CaO and MgO at 1400°C.

Zircon in the original refractory appeared inert to the residual oil impurities.

Hematite and rutile present in the original brick reacted with vanadium and a titanium vanadium iron oxide compound crystallized from the glass phase in the altered brick.

The interface between altered and unaltered brick was rather discrete on a macroscopic scale. The microstructure of the refractory zone at the interface region was similar to that of the unaltered part of the brick, except the glassy bonding phase contained sodium and vanadium as well as aluminum and silicon. These impurities were thus able to penetrate several centimeters into the refractory during its use.

Increasing the alumina content of fireclay refractories of the type analyzed here may produce more viscous glassy phases and reduce the residual oil impurity-refractory reaction rate. High- Al_2O_3 (>60 wt % Al_2O_3) refractories can perform better than fireclay refractories (20-45 wt % Al_2O_3) when used in a residual-oil-fired boiler that has a fuel oil impurity slagging or corrosion condition similar to the case reported here.

ACKNOWLEDGMENTS

The authors would like to acknowledge the Metals and Ceramics Division personnel who have contributed to this study; N. H. Rouse for the metallography, T. J. Henson for the scanning electron microscopy, R. S. Crouse for the electron microprobe analysis, and O. B. Cavin for the x-ray diffraction. We thank J. D. Holder, R. A. Perkins, and R. G. Donnelly for their review and comments on the text. This report was edited by S. Peterson and prepared for reproduction by Connie Harrison.

APPENDIX

X-RAY DIFFRACTION DATA

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Table A1. Data on Sample BX1

Lattice Spacing, nm					
Observed	Known for Various Phases				
	Mullite	Aluminum Vanadate	Corundum	High Cristobalite	Zircon
0.68836					
0.64214					
0.53434	0.539				
0.47424					0.443
0.40767				0.415	
0.38650					
0.37338					
0.34114	0.3428		0.3479		
0.33709	0.3390				
0.33264					0.330
0.32226					
0.31921					
0.29048				0.292	
0.28865	0.2886				
0.28810					
0.27199					
0.26842	0.2694				
0.25369	0.2542		0.2552	0.253	0.252
0.24813					
0.24461					
0.24219	0.2428	0.243			
0.23769	0.2292	0.237	0.2379		
0.22863					
0.22752					
0.22033	0.2206				
0.21555			0.2165	0.217	
0.21156	0.2121	0.212			
0.21020	0.2106				
0.20987					
0.20822				0.207	
0.20605					
0.20561	0.1969				
0.18375	0.1841				
0.18153					
0.18117					
0.17946	0.1795				
0.17841					
0.16934	0.1694				
0.16908					
0.16959					
0.16009				0.1639	
0.15992					
0.15236					
0.14582				0.1471	
0.14435					
0.14405					
0.13764				0.1379	
0.13743					
0.12767					

Table A2. Data on Sample BX2

Lattice Spacing, nm					
Observed	Known for Various Phases				
	Mullite	Aluminum Vanadate	Corundum	High Cristobalite	Zircon
0.81764					
0.68623					
0.63436					
0.56802					
0.53498	0.539				
0.47702					
0.47150					
0.44504					0.443
0.42202				0.415	
0.40730					
0.40583					
0.34076	0.3428		0.3479		
0.33696	0.3390				
0.33264					0.330
0.32491					
0.32352					
0.28783	0.2886			0.292	
0.28711					
0.26827	0.2694				
0.25383	0.2542		0.2552	0.253	0.252
0.25034					
0.24973					
0.24866					
0.24760					
0.24200	0.2428	0.243	0.2379		
0.22897	0.2292	0.237			
0.22057					
0.22023	0.2206		0.2165		
0.21165	0.2121	0.212		0.217	
0.21034	0.2106			0.207	
0.18375	0.1841				
0.17103	0.1712				
0.17024	0.1700				
0.16980					
0.16966	0.1694				
0.16899				0.1639	
0.15997					
0.15234					
0.14604				0.1471	
0.14578					
0.14557					
0.14503					
0.14467					
0.14437					
0.14411					
0.13357				0.1379	
0.13327					
0.13308					
0.13283					
0.13267					
0.12780					
0.12765					
0.12750					
0.12736					
0.12646					
0.12627					
0.12619					
0.12599					

Table A3. Data on Sample BX3

Lattice Spacing, nm					
Observed	Known for Various Phases				
	Mullite	Aluminum Vanadate	Corundum	High Cristobalite	α -quartz
0.71379					
0.64822					
0.57313	0.539				
0.41253				0.415	0.426
0.38850					
0.37509	0.3774				
0.37385					
0.35928					
0.34308	0.3428		0.3479		
0.33835	0.3390				
0.33386					0.3343
0.32433					
0.32124					
0.29717					
0.29650					
0.29122				0.292	
0.28919	0.2886				
0.27673					
0.26928	0.2694				
0.26202			0.2552	0.253	
0.24263	0.2428	0.243	0.2379		0.2456
0.23787		0.237			0.2281
0.22085	0.2206				0.2236
0.21639			0.2165	0.217	
0.21217	0.2121	0.212			0.2127
0.21066	0.2106			0.207	
0.17913	0.1795				0.1801
0.17887			0.1740		
0.15236					
0.14905				0.1471	
0.14451					
0.14069					
0.12787					

Table A4. Data on Sample BX4

Lattice Spacing, nm						
Observed	Known for Various Phases					
	Mullite	α -quartz	Low Cristobalite	Zircon	Hematite	Rutile
0.53700	0.539					
0.43575				0.443		
0.42482		0.426				
0.40878			0.404			
0.38305						
0.37744	0.3774					
0.37571					0.366	
0.34217	0.3428					
0.33809	0.3390					
0.33362		0.3343				
0.32974				0.330		
0.32433			0.3138			0.325
0.28938						
0.28865	0.2886		0.2845			
0.26921	0.2694				0.269	
0.25446	0.2542			0.252		
0.25129					0.251	
0.25054						
0.24886			0.249			0.2487
0.24564		0.2456				
0.24282	0.2428					
0.22924	0.2292	0.2281				0.2297
0.22095	0.2206				0.220	
0.21212	0.2121	0.2127				
0.21052	0.2106					0.2054
0.18413	0.1841					
0.18166		0.1817			0.184	
0.17004	0.1700					
0.16934	0.1694					
0.16902		0.1671			0.169	
0.16712						0.1687
0.16020						
0.15259						
0.14453					0.148	
0.14433						
0.13370						
0.12783						
0.12639						

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