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**Effects of Alternate Fuels Report No. 4
Analysis of Soaking Pit Cover
Refractories Degraded by
Residual Oil Combustion Products**

G. C. Wei
V. J. Tennery

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METALS AND CERAMICS DIVISION

EFFECTS OF ALTERNATE FUELS^①
REPORT NO. 40¹¹
ANALYSIS OF SOAKING PIT COVER REFRACTORIES
DEGRADED BY RESIDUAL OIL COMBUSTION PRODUCTS

G. C. Wei and V. J. Tennery

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EFFECTS OF ALTERNATE FUELS
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ABSTRACT

This is the fourth of a series of reports on analyses of several types of refractories that have been used in industrial heating equipment with fuels alternate to natural gas. Refractory degradation problems arise because the alternate fuel impurities react with the refractory linings in high-temperature furnaces. The present study is an analysis of steel soaking pit cover refractories degraded by residual oil impurities. The objective of this study is to better understand the refractory deterioration process in a residual-oil-fired steel soaking pit and to provide viable means to retard the degradation.

We analyzed a superduty fireclay plastic refractory (45 wt % Al_2O_3) and a high-alumina refractory anchor (65 wt % Al_2O_3) that had been used for six months in the cover of a dual-fuel-fired soaking pit. Residual oil was used for firing the soaking pit for an accumulative time of 2 to 4 months and during the rest of the service time natural gas firing was employed. Reaction zones were obvious in both the plastic and anchor materials. The reaction zone in the plastic extended to a depth of about 20 mm toward the refractory cold end. In the anchor, the readily visible reaction zone had a total depth of 15 to 25 mm, of which an altered zone extended 5 to 13 mm from the hot face and was followed with a transition zone of about 10 mm toward the cold end of the anchor. In a natural-gas-fired environment, these two refractories have longer service life (one year) and smaller reaction zones than were observed with use of residual fuel oil. The reaction zones at the hot face of the plastic and the anchor were due to sodium and potassium impurities in the fuel oil and iron derived from the oxide scale on steel ingots reacting with the refractory constituents.

The principal reaction that causes the deterioration in the plastic refractory appears to be the dissolution of original quartz or cristobalite in a glass phase at the hot face. Sodium, potassium, and iron played an important role in degrading the plastic refractory. Increasing the alumina content of this material, especially in the bonding

phase of the plastic, should produce a more viscous glassy phase which will reduce the reaction rate with impurities. High-alumina (>60 wt % Al_2O_3) plastic refractories can exhibit better performance than fireclay-based plastics when used in a residual-oil-fired soaking pit according to this analysis.

The reactions between the refractory anchor and fuel oil impurities plus iron from steel ingot scale are more complex than those of the plastic. This is probably due to the relatively higher temperature in the anchor. Sodium, potassium, and calcium from the residual oil combustion products reacted with quartz, cristobalite, and the glass bonding phase in the original anchor to form a new glass melt in the altered and the transition regions of the anchor. Mullite in the transition region of the anchor reacted with sodium and potassium in the glass melt to form corundum, while the silica components of mullite entered the glass melt. Iron derived from the steel ingot scale in the soaking pit dissolved in the glass melt in the altered region of the anchor and reacted with mullite and corundum to form $(\text{Al,Fe})_2\text{O}_3 \cdot \text{TiO}_2$, hercynite, and iron aluminate. Increasing the alumina content of the anchor may introduce corundum to produce less of the alkali aluminosilicate melt and increase its viscosity at the service temperature as well. This will reduce the reaction rate of the anchor with fuel oil impurities and iron oxide scale and thus improve its performance.

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 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 oils 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. Currently industrial refractory operating experience in the United States with residual oils is limited. It is therefore instructive to analyze refractories that have been exposed to residual oil combustion in industrial furnaces and exhibit 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 under these conditions.

The present report is an analysis of residues of a superduty plastic and a high- Al_2O_3 anchor used in the cover of a steel soaking pit. Natural gas and residual oils were used in firing the soaking pit. The refractory service time was approximately six months, two to four months with residual oil firing and the rest with natural gas firing. Results presented in this report include chemical, optical microscopy, scanning electron microscopy, electron microprobe, and x-ray diffraction analyses. We interpret the refractory degradation mechanism on the basis of results from these analyses and other observations reported in the literature.

This is the fourth of a series of reports on analyses of several generic refractory types that have been used in industrial furnaces with either oil or coal as fuel.²⁻⁴ Refractory samples described in this report were obtained with the cooperation of industrial firms.

SPECIMEN HISTORY

The two samples analyzed in the present report are a superduty fireclay (45% Al_2O_3) plastic refractory and a high-alumina (65% Al_2O_3) refractory anchor. Both refractories had been used in the cover of a

dual-fuel-fired steel soaking pit. Natural gas and a residual fuel oil were used in heating this soaking pit. The service time of these two refractory samples was approximately six months; two to four months fired with No. 6 residual oil and the rest with natural gas. The residual oil was not analyzed for impurity content by the steel manufacturer.

A soaking pit is a furnace commonly used for heating steel ingots to a uniform desired temperature before the steel is rolled and formed into a finished shape. Although soaking pits could be eventually eliminated with the use of a continuous casting process, thousands of soaking pits exist in the U.S. iron and steel industry at present. In the long term, both the potential decline in domestic steel production and the increased anticipated conversion to continuous casting will result in less use of steel soaking pits. Because of the capital investment that they represent, however, soaking pits will still play an important role in the steelmaking process in the immediate future. Steel soaking pits in the United States presently use a variety of fuels, including natural gas, distillate oils, residual oils, coke oven gas, and blast furnace gas. The types of refractories used in soaking pits cover a broad range, including fireclay (20-45% Al_2O_3), high-alumina (45-90%), chrome-magnesite, chrome, and magnesite in brick or monolithic form. Plastic refractories ranging from superduty grade to 90% Al_2O_3 are widely used in the covers, walls, and floors of soaking pits.

The superduty (45% Al_2O_3) fireclay refractory analyzed in the present study is a type commonly referred to as a plastic. It consists of a mixture of prefired or calcined fireclay grog grains and fireclays plus a minimum amount of water. Plastic refractories can be pressed, rammed, or plastered onto a supporting reinforcing structure in a furnace. After being placed, this refractory will bond or cure upon furnace heating and form a monolithic structure. This material is widely used in furnace application areas that have intricate shapes or geometries and need flexibility in refractory construction. Plastic refractory construction offers flexibility of design to obtain maximum furnace and fuel efficiency. A typical recommended hot-face working temperature for

a superduty fireclay plastic refractory is 1700°C (3100°F). The maximum service temperature at the hot face of the plastic refractory analyzed in this report was 1290°C (2350°F).

In a natural-gas-fired soaking pit lined with plastic refractories with compositions ranging from superduty to 90% Al₂O₃, the life expectancy of the upper walls ranges from four to eight years. The lower walls and floors are constantly subjected to molten slag attack and abrasion and thus have a service life as short as 12 to 18 months. The exhaust system of a soaking pit — including the recuperator, flues, and stacks — usually uses a combination of plastics, castables, and firebrick construction and usually has a service life of several years. The cover of a soaking pit is subjected to mechanical vibration, cyclic temperatures, and atmosphere changes due to the constant opening and closing of the pit. In a natural gas or distillate oil combustion environment, the cover has a typical service life of 12 months or more. As noted previously, the superduty plastic refractory we analyzed had a service life of six months. The second refractory analyzed in the present study is a high-alumina (65% Al₂O₃) ceramic anchor, which was used to hold the previously described plastic (45% Al₂O₃) refractory in place in the cover. The anchor is a corrugated dense part with a particular shape for supporting the monolithic plastic refractory structure and is fastened to a metal casing on the cold side. The hot face of the ceramic anchor during service had a maximum reported temperature of 1290°C (2350°F).

RESULTS

Chemical, x-ray, optical microscopy, electron microprobe, and scanning electron microscopy analyzes were performed on the plastic and on the ceramic anchor. 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, the analysis results will be presented for both types of refractory.

Superduty Plastic Refractory

Figure 1 shows a remnant of the used superduty plastic refractory. The hot face and the altered zone of the refractory had a dark or black coloration. The reaction zone in the refractory extends from the hot face to a maximum depth of 20 mm toward the cold end.

Expressed in terms of reaction zone boundary movement, the visible boundary moved at an average rate of 3 mm/month (note that the service time was six months, of which two to four months were residual oil firing). The sampling plan for analyzing the refractory specimen in Fig. 1 is shown in Fig. 2. Selected areas were subjected to extensive analyses. Chemical analysis results for the altered and unaltered parts of the refractory specimen are shown in Table 1. The equivalent contents of Fe_2O_3 , K_2O , and Na_2O have significantly increased in the altered refractory. Because of these increases, the percentage contents of Al_2O_3 and SiO_2 decrease. The SiO_2 content dropped significantly in the altered plastic. Other impurities such as Ca, Cr, Mg, Ni, S, and V were found in negligible amounts in the plastic refractory. The increase in the Fe_2O_3 content in the altered part is apparently from the iron oxide scale on steel ingots, whereas the increase in the Na_2O and K_2O contents is caused by the presence of sodium and potassium in the residual oil combustion products.

X-ray diffraction analyses were performed on four samples in the plastic refractory. The locations of refractory zones from which these samples (PX1-PX4) were taken are shown in Fig. 2. The major crystalline phases in the unaltered plastic refractory are mullite, β -quartz, and low and high cristobalite. These phases persist through sample PX2. Crystalline silica phases start to disappear as one proceeds from the cold face into the altered zone, and the only major crystalline phase in the altered plastic refractory (sample PX1) is mullite. Grog particles (sample PX4) in the unaltered zone of the plastic refractory consist of the crystalline phases mullite, β -quartz, and high and low cristobalite. Table 2 summarizes the major crystalline phases identified in samples PX1 through PX4. The original x-ray diffraction data for samples PX1 through PX4 are presented in the Appendix.

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Fig. 1. Superduty Plastic Refractory Used in the Cover of a Residual-Oil-Fired Steel Soaking Pit.

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SIDE VIEW OF THE PLASTIC REFRACTORY

Fig. 2. Sampling Plan of the Superduty Plastic Refractory.

Table 1. Chemical Analyses of Selected Areas in the Superduty Plastic Refractory and the High-Alumina Ceramic Anchor

Oxide	Content, wt % Equivalent Oxide				
	Superduty Plastic		High-Alumina Ceramic Anchor		
	Altered Part	Unaltered Part	Altered Part	Transition Part	Unaltered Part
Al ₂ O ₃	44.77	46.56	55.02	59.34	66.02
CaO	0.21	0.14	1.51	0.18	0.08
Cr ₂ O ₃	0.024	0.025	0.025	0.025	0.029
Fe ₂ O ₃	9.66	1.12	15.24	1.07	1.03
K ₂ O	3.25	0.30	2.06	1.19	0.20
MgO	0.13	0.13	0.26	0.09	0.10
Na ₂ O	2.76	0.18	1.86	1.16	0.22
NiO	0.0414	0.008	a	a	a
SO ₃	0.02	0.01	<0.01	<0.01	<0.01
SiO ₂	37.73	50.08	22.88	33.31	29.19
TiO ₂	1.40	1.53	1.45	3.25	2.95
V ₂ O ₅	0.0068	<0.002	a	0.0089	0.0022

^aNone detected.

Table 2. Major Crystalline Phases in the Used
Superduty Fireclay Plastic Refractory

Phase	Contained in Samples
Mullite	PX1, PX2, PX3, PX4
β -Quartz	PX2, PX3, PX4
High-crystobalite	PX2, PX3, PX4
Low-crystobalite	PX2, PX3, PX4

With optical microscopy, we examined samples in the altered and unaltered parts of the refractory. Microstructures of the altered zone of the plastic refractory consist of mullite crystals containing a small amount of Fe_2O_3 in solid solution distributed in a glassy phase containing Na, K, Al, Si, Ti, and Fe. In contrast, the unaltered plastic refractory consists of mullite crystallites in a glassy matrix material containing Al, Si, Ti, and Fe. The differences in the microstructures of the altered and the unaltered plastic refractory are that the crystalline size of mullite is much larger (with Fe_2O_3 in solid solution) in the altered part than in the unaltered part of the refractory, and the glassy matrix material in the altered part contains Na and K, which are absent in the unaltered refractory. The microstructures of both the altered and the unaltered plastic are shown in Fig. 3. Typical microstructures of the altered and the unaltered plastic refractory are presented in Figs. 4 and 5, respectively. The bright phase in the altered zone [Fig. 4(b)] is a titanium-iron-aluminum-silicon oxide. At the hot face, hercynite is observed. Figures 4 and 6 show the microstructure of the hot face region. In addition to hercynite, long mullite needles and pyramidal diamond-shaped mullite crystals with Fe_2O_3 in solid solution are also observed within the glassy slag at the hot face.

Scanning electron microscopy was performed on samples taken from the altered (Fig. 7) and the unaltered (Fig. 8) plastic. In the altered plastic, mullite crystals with some Fe_2O_3 in solid solution are bonded together with a glass phase that contains Na, K, Ti, Fe, Al, and Si. Extremely long needles ($\approx 200 \mu\text{m}$) of mullite with some Fe_2O_3 in solid

Fig. 3. Reflected-Light Micrograph Showing Microstructure of the Altered Part and the Unaltered Part of the Plastic.

Fig. 4. Reflected-Light Micrographs of the Altered Zone of the Plastic Refractory. (a) Section through hot face, 100 $\times$. The temperature gradient is horizontal, with the hot face at the left. The light crystals at the left are hercynite. The light gray is mullite with Fe_2O_3 in solid solution, distributed in the darker gray matrix, which contains Na, K, Fe, Ti, Al, and Si. Large dark spots are pores. Needle-shaped mullite crystals can be seen in the lower left. (b) Region away from hot face, 500 $\times$. In addition to the mullite distributed in the darker glassy phase, a very fine light-colored Fe-Ti-Al-Si oxide can be seen.

Fig. 5. Reflected-Light Micrographs of the Unaltered Zone of the Plastic Refractory. (a) Large grog particle in relation to neighboring particles, 50 $\times$. (b) Interior of grog particle, 500 $\times$. Mullite is seen distributed in the darker glassy material containing Si, Al, Fe, and Ti.

Fig. 6. Hot-Face Region of the Plastic Refractory. 500 $\times$. The hot face is toward the left. (a) Hercynite crystals near the hot face are surrounded by highly reflective Fe-Ti-Al-Si oxide. Mullite (with Fe_2O_3 in solid solution) is seen at the right. (d) Dendritic Fe-Ti-Al-Si oxide is interspersed with prismatic mullite (with dissolved Fe_2O_3) crystals.

MULLITE (WITH Fe_2O_3 IN SOLID SOLUTION)

Fig. 7. Scanning Electron Micrographs of the Altered Plastic Refractory, Showing the Mullite- Fe_2O_3 Solid Solution in a Glassy Phase Containing Na, K, Fe, Ti, Al, and Si. (a) Fractured surface, 1000 $\times$. (b) Natural surface, 300 $\times$. Mullite needles are seen on the surface of a large pore.

Fig. 8. Scanning Electron Micrograph of the Unaltered Plastic Refractory, Showing Mullite Bonded by a Matrix Material Containing Si, Al, Fe, and Ti. 200 $\times$.

MULLITE

solution are also observed on the surface of pores in the altered zone, as shown in Fig. 7(b). In the unaltered zone, a microstructure typical of a fireclay-based refractory is observed. Figure 8 shows this microstructure, consisting of mullite needles distributed in an oxide glass matrix material containing Al and Si with minor amounts of Ti and Fe.

In summary, the mullite phase in the original plastic was converted to a solid solution of mullite and Fe_2O_3 with an accompanying expansion in the reaction zone of the plastic. Quartz and cristobalite in the original plastic apparently reacted with sodium and potassium derived from the residual oil impurities to form a glass phase. Iron, originating from the ingot scale, dissolved in the glassy phase and subsequently reacted with the mullite phase to form a mullite- Fe_2O_3 solid solution and hercynite.

High-Alumina Refractory Anchor

The high-alumina refractory anchor is shown in Fig. 9. The reaction zone in the used anchor extends 15 to 25 mm deep, of which the altered part is 5 to 13 mm and the transition part is 10 to 13 mm. The region referred to as the altered part is dark gray, while the transition part is light gray. The average reaction zone formation rate was approximately 5 mm/month. That is to say, the demarcation between the transition part and the unaltered part of the anchor moved at a rate of about 5 mm/month. Such a high rate of reaction zone formation is caused by reactions involving the refractory constituents in the anchor with the residual oil combustion products and iron oxide scale. The sampling plan for the analyses of the high-alumina ceramic anchor is shown in Fig. 10. Selected sections of the refractory were analyzed extensively.

Chemical analysis results of the altered, transition, and unaltered parts of the used refractory anchor are presented in Table 1. The contents of Fe_2O_3 , CaO, Na_2O , and K_2O in the altered and the transition regions are significantly increased over the unaltered part of the anchor. The SiO_2 content increases in the transition region and then decreases in the altered part relative to the unaltered part. Because of the increases in the Fe_2O_3 , Na_2O , K_2O , and CaO contents, the Al_2O_3 content

Fig. 9. The Used High-Alumina Ceramic Anchor.

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SIDE VIEW OF THE CERAMIC ANCHOR

Fig. 10. Sampling Plan of the Used High-Alumina Refractory Anchor.

is lower in the altered and the transition zones than in the unaltered anchor. The TiO_2 content also decreases as one proceeds from the unaltered to the altered part.

X-ray diffraction analyses of the altered zone indicated two iron-bearing crystalline phases, namely iron aluminate (FeAlO_3) and hercynite (FeAl_2O_4), as well as corundum and mullite. Electron microprobe analysis of this region indicated a compound containing Al, Ti, and Fe with a rather well-defined crystalline morphology and believed to be the $(\text{Al,Fe})_2\text{O}_3 \cdot \text{TiO}_2$ phase (ATFT). The ATFT phase was reported by Crouch⁵ and by Caldwell, Hayburst, and Webster.⁶ In the transition area, corundum and mullite were present. The unaltered refractory anchor consists of the following crystalline phases: mullite, β -quartz, and low cristobalite. Table 3 summarizes the major crystalline phases in the three regions: x-ray diffraction data expressed in terms of lattice spacings are presented in the Appendix.

Table 3. Major Crystalline Phases in the Used High-Alumina Refractory Anchor

Phases Present		
Altered Part	Transition Part	Unaltered Part
Corundum	Corundum	Mullite
ATFT [(Al,Fe) ₂ O ₃ •TiO ₂]	Mullite	β-quartz
Iron aluminate (FeAlO ₃)		Low-cristobalite
Hercynite (FeAl ₂ O ₄)		
Mullite		

Optical microscopy was performed on samples taken from the various parts of the anchor. Microstructures of both the altered and the transition regions are shown in Fig. 11. Iron-bearing phases are extensively distributed in a glass matrix in the altered area. Electron microprobe analysis identified Na, K, Ca, Ti, Fe, Al, and Si in this glass matrix. The ATFT phase and iron aluminate (FeAlO₃) are distributed in a relatively thin section extending about 1 mm from the hot face (Fig. 12). Immediately below this section [Fig. 12(a)] is a second zone 2 mm deep containing iron aluminate and hercynite. Corundum (Al₂O₃) and mullite are observed (Figs. 13 and 14) along with hercynite in a third 1-mm-thick zone behind the zone containing hercynite and iron aluminate. Thus, the distribution of iron-bearing phases — including ATFT, iron aluminate, and hercynite — in the altered anchor are sharp and distinct. In other words, these iron-bearing phases are most abundant in certain sections of the altered anchor and their distributions are quite localized. The formation of the ATFT phase has a particular crystallographic relationship with iron aluminate. Apparently, it was formed as a result of a reaction between iron aluminate and the glassy matrix. Iron aluminate dissolution in the matrix material is indicated by the rounded morphology of the crystals in Fig. 12(b). Hercynite also reacted with the matrix material, as evidenced by the irregular surfaces of the hercynite phase in Fig. 13(b).

Fig. 11. The Altered and Transition Parts of the Anchor.

Fig. 12. Microstructure Near the Hot Face in the Altered Region of the Anchor. (a) 100 $\times$. The hot face is toward the top. The upper half of the micrograph shows largely ATFT $[(\text{Al},\text{Fe})_2\text{O}_3 \cdot \text{TiO}_2]$ and FeAlO_3 dispersed in a glassy matrix containing Na, K, Ca, Fe, Ti, Al, and Si. Midway down the micrograph (about 1 mm in from the hot face) the dispersoid becomes the darker hercynite (FeAl_2O_4). The large black area on the left is a pore. (b) Higher magnification — 500 $\times$ — and altered contrast permits distinguishing the lighter ATFT from FeAlO_3 in the region nearer the hot face.

Fig. 13. Microstructure of the Altered Region of the Anchor About 4 mm Behind the Hot Face. Principally hercynite (FeAl_2O_4), the blocky particles, is dispersed in the glassy phase containing Na, K, Ca, Fe, Ti, Al, and Si. (a) 100 $\times$. In the lower half corundum (Al_2O_3), the fine needle-like particles, becomes more prominent. Large dark areas are pores. (b) 500 $\times$. Some of the corundum needles in the lower left are viewed end-on.

Fig. 14. Microstructure of the Altered Zone of the Anchor Near the Transition Zone. 100 $\times$. Along with the small blocky hercynite and needle-like corundum, rounded mullite is distributed in the glassy phase containing Na, K, Ca, Fe, Ti, Al, and Si.

The microstructure of the transition zone (Fig. 15) consists of mullite and corundum distributed in a glass matrix material containing Na, K, Ca, Ti, Fe, Al, and Si. The unaltered anchor (Fig. 16) consists of large grog particles (consisting of fine mullite crystallites) bonded by a matrix material consisting of mullite, quartz, cristobalite, and a glass phase. No Na, K, or Ca was observed in the unaltered anchor by electron microprobe analyses.

Figures 17, 18, and 19 are scanning electron micrographs of the altered part, the transition part, and the unaltered part of the anchor, respectively. In the altered and the transition regions crystalline phases are surrounded by an oxide glass matrix material containing Na, K, Ca, Ti, Fe, Al, and Si. In the unaltered anchor, mullite needles are bonded in an oxide matrix material containing Si, Al, Ti, and Fe.

Fig. 15. Microstructure of the Transition Part of the Anchor, Showing Globular Mullite and Angular and Needle-Like Corundum Distributed in a Glassy Matrix Phase Containing Na, K, Ca, Fe, Ti, Al, and Si. 500 $\times$.

Fig. 16. Microstructure of the Unaltered Part of the Anchor. Large grog particles, consisting primarily of mullite, are bonded by a fine material consisting of mullite, quartz, cristobalite, and a glassy phase containing Fe, Ti, Al, and Si. 100 $\times$.

Fig. 17. Scanning Electron Micrograph of the Altered Part of the Anchor, Showing Crystalline Phases Engulfed in a Glassy Matrix Phase Containing Na, K, Ca, Ti, Fe, Al, and Si.

Fig. 18. Scanning Electron Micrograph of the Transition Part of the Anchor, Showing Mullite in a Glassy Matrix Phase Containing Na, K, Ca, Ti, Fe, Al, and Si.

Fig. 19. Scanning Electron Micrograph of the Unaltered Anchor Showing Mullite as the Predominant Phase. 150 $\times$.

MULLITE

In summary, sodium, potassium, and calcium derived from the residual oil combustion products reacted with quartz, cristobalite, and the glass bonding phase in the original anchor to form a new glass melt in the altered and transition regions of the anchor. Iron from the steel ingot scale in the soaking pit dissolved in the glassy phase and reacted with mullite to form the ATFT phase, hercynite, iron aluminate, and corundum, which were identified by x-ray diffraction, optical microscopy, and electron microprobe analyses.

DISCUSSION

Superduty Plastic Refractory

A striking feature in the altered plastic refractory compared with the unaltered material is the 9- to 15-fold increase in the Fe_2O_3 , K_2O , and Na_2O equivalent contents. The ratio of the weight percentage of

Al_2O_3 to SiO_2 changed from 0.48 to 0.54. Mullite grew in the altered plastic by the formation of solid solution with Fe_2O_3 and possibly by the increase in the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio. Mullite in the original refractory appears to be a stable phase in the presence of the various impurities except at the surface of the hot face region. Sodium and potassium from the residual oil combustion products plus iron from the oxide scale reacted primarily with the bonding phases, including quartz, cristobalite, and a glass phase.

The reactions of sodium and potassium with aluminosilicate refractories have been reported. Okawara and Yamaguchi⁷ reported that mullite reacts with Na_2CO_3 vapor to form carnegieite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), corundum, sodium silicate, and nepheline ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). Rigby and Hutton⁸ investigated the reactions between Na_2O and aluminosilicate refractories. First Na_2O reacts with alumina and silica to form sodium aluminate and sodium silicate, and mullite decomposes to form nepheline, sodium aluminate, and β -alumina. McCune et al.⁹ studied the reactions between K_2O and aluminosilicate refractories. Quartz and cristobalite react with K_2O at 1200°C (2200°F).¹⁰ Leucite ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$) and kaliophilite ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) form at 930°C (1700°F). At 1200°C (2200°F), mullite remains stable until the K_2O content reaches 12%. The formation of leucite is observed where the K_2O content is greater than 7%. The final phase relations at equilibrium can be calculated from the Na_2O content and the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ phase diagram¹⁰ or the K_2O content and the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ phase diagram.¹¹

Sodium- or potassium-containing crystalline phases that had been reported as products of the reactions between Na_2O or K_2O with aluminosilicate refractories were not observed in the superduty plastic. The reason for this could be (1) the altered plastic was not in an equilibrium state and thus could not be predicted by simple ternary phase diagrams, or (2) another major impurity such as Fe_2O_3 had important effects on phase equilibrium of the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system such that no sodium- or potassium-bearing crystalline phases were generated.

At the surface of the hot face region of the refractory, hercynite is observed in the glass matrix material. From the study on reactions between iron oxide and aluminosilicate refractories by Muan,¹² hercynite

will be present only at temperatures above 1385°C up to the liquidus temperatures in the $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ system in air. The maximum temperature at the hot face of the plastic during service was reportedly 1290°C (2350°F), which is about 100°C lower than the reported temperature required for hercynite generation.¹³ The fact that hercynite was observed at the hot face of the used plastic indicates that the $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ system cannot be applied to the present case, that the impurities such as Na_2O or K_2O have significant effects on the $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ system, or that the actual service temperature was somewhat higher than reported by the steel manufacturer. Performance of this refractory in this type of application could be improved by increasing the Al_2O_3 content in the grog particles of the plastic refractory, as this would result in a higher concentration of mullite, which is relatively stable with respect to reactions with impurities such as those observed in this case. A fireclay or other bonding material of a higher Al_2O_3 content will be especially helpful in terms of improving resistance of this type of refractory to corrosion by sodium, potassium, and iron. The present study showed clearly that the bonding phases in the plastic refractory are more prone to reactions with fuel and process-derived impurities than are the grog particles. Increasing the Al_2O_3 content of the bonding system will increase the viscosity of any glass phase that is produced from reactions of the bond material with sodium, potassium, and iron impurities. Increased viscosity in the glassy phase will reduce the dissolution rate of the original crystalline phases in the glass phase and reduce the transport rate of detrimental species such as Na, K, and Fe through the glassy phase to the solid crystalline refractory components.

High-Alumina Refractory Anchor

Reactions of the anchor with impurities in the soaking pit atmosphere were more complex than those in the plastic refractory. One explanation for this may be the relatively higher average service temperature in the anchor. The unaltered anchor consisted largely of mullite with minor amounts of quartz, cristobalite, and glassy bonding phases. In the

transition zone of the specimen, chemical analyses indicate a significant increase in the sodium, potassium, and silicon contents. The iron concentration in the transition zone was essentially identical to that in the unaltered zone.

Within the transition zone mullite decomposes into corundum while its silica content becomes part of the glass bonding phase. This amorphous oxide glass contains Na, K, Ca, Ti, Fe, Al, and Si. The increase in the SiO_2 content in the transition zone of the specimen could be due to the migration of the glassy phase in the altered zone to the transition part of the anchor. In the altered part, the Al_2O_3 and SiO_2 contents decreased significantly compared with either of the other two sample zones. The reduction of the Al_2O_3 and SiO_2 contents in the altered zone is due to the significant increase in the Fe_2O_3 , Na_2O , K_2O , and CaO contents. The increase in the Fe_2O_3 content is significantly higher in the altered anchor than in the altered plastic even though these two refractories presumably were exposed to similar environments. The CaO content in the altered anchor is particularly notable since there is a negligible amount of CaO in the altered plastic refractory. The reason for the high CaO content in the altered anchor but negligible amounts of CaO in the altered plastic was not identified during this investigation. The generation of corundum from mullite in the transition part of the anchor is primarily caused by the presence of sodium and potassium in the glass phase. These alkalis came from fuel oil impurities. A similar reaction has been reported on a high-duty firebrick exposed to coal combustion.² No sodium- or potassium-containing crystalline phases are present in the transition region or the altered part of the anchor, which is similar to what was observed in the altered plastic. Again, since the expected sodium- and potassium-bearing crystalline phases were not observed, the phase equilibrium in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system or the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system appears to have been altered by the presence of significant amounts of iron-, titanium-, and calcium-bearing phases. A high level of iron (15 wt % Fe_2O_3 equivalent) is present in the altered zone of the anchor. The Fe_2O_3 , Al_2O_3 , and SiO_2 equivalent contents normalized to 100% in the altered anchor correspond to a composition that falls in the field of

hematite (Fe_2O_3), iron aluminate (FeAlO_3), and mullite in the Fe_2O_3 - Al_2O_3 - SiO_2 system¹⁴ at 1378°C in air. Hercynite will be present at somewhat higher temperatures ($>1385^\circ\text{C}$) according to the Fe_2O_3 - Al_2O_3 - SiO_2 system.¹⁴ However, in the altered anchor, which had experienced a reported maximum hot face temperature of 1290°C , we observed hercynite, iron aluminate, corundum, and mullite, but no hematite.

According to the phase diagram of the Fe_2O_3 - Al_2O_3 - SiO_2 system, the iron aluminate (FeAlO_3) phase is unstable below 1318°C in air. At temperatures below 1318°C , the iron aluminate converts to hematite and corundum. This reaction is reported to be sluggish under typical conditions. The iron aluminate phase observed in the anchor was produced from reactions of mullite and corundum with Fe_2O_3 in the presence of other impurities. The presence of these impurities probably stabilizes iron aluminate without transformation to hematite at the hot-face region of the anchor.

The cyclic atmosphere changes due to the opening and closing operation of the soaking pit cover may have important effects on the reactions of the anchor with the residual fuel oil impurities and iron oxide in the soaking pit. It is known that as the oxygen partial pressure increases hercynite will transform to hematite or iron aluminate in certain temperature intervals. These transformations are caused by an oxidation of the ferrous iron of hercynite to ferric iron, which is the only form of iron accommodated into the crystal structure of hematite and iron aluminate. The iron aluminate observed at the hot face of the anchor might have been produced from hercynite as the oxygen partial pressure increased when the soaking pit cover was opened and exposed to air.

The reactions that generated hercynite, iron aluminate, and ATFT [$(\text{Al},\text{Fe})_2\text{O}_3 \cdot \text{TiO}_2$] in the altered anchor apparently depend strongly on temperature and the Fe_2O_3 concentration. During service, the temperature and the iron, sodium, and potassium concentrations decrease in the direction from the hot face to the cold end of the anchor. The temperature and impurity distributions together were apparently responsible for the confinement of the iron-bearing crystalline phases to the altered zone.

It should be noted that the iron-bearing phases in the altered zone as ATFT, iron aluminate, and hercynite, have relatively high melting points. The generation of these iron-bearing compounds will not decrease

the refractoriness of the high- Al_2O_3 anchor. However, the volume changes associated with these reactions may cause swelling, spalling, and cracking, which damage the refractory. In the anchor analyzed here, the formation of a significant volume fraction of a liquid containing substantial amounts of Fe, Na, K, and Ca was the principal cause of refractory degradation.

CONCLUSIONS

The unaltered superduty fireclay plastic refractory consisted of large grog grains dispersed in a fine matrix material. The grog grains consisted primarily of mullite. The matrix material consisted of mullite, quartz, and cristobalite. In the altered zone of the plastic following service in the steel soaking pit, the original mullite phase had reacted with iron oxide from the steel ingot scale to form a solid solution of mullite with Fe_2O_3 , which was distributed in an oxide glass phase containing Si, Al, Fe, Ti, Na, and K. Quartz and cristobalite originally present in the plastic were apparently dissolved in the molten glass at the service temperature, primarily as a result of the fluxing effect of sodium and potassium fuel-derived impurities in the glass phase. Iron oxide from the ingot scale dissolved in the glass phase, which also resulted in a lower viscosity melt at a specific temperature, and thus enhanced the refractory corrosion rate. A small amount of hercynite was observed at the hot face of the plastic. The presence of hercynite was a consequence of reactions of the melt with mullite at the hot face. Increasing the Al_2O_3 content in this refractory would increase the viscosity of the glass phase at a given temperature and thus improve the resistance of this material to corrosion by sodium and potassium from residual fuel oil plus iron from the ingot scale.

The high-alumina (65 wt % Al_2O_3) refractory anchor used in the same soaking pit cover consisted of three relatively distinct zones. The cold end of the anchor consisted primarily of mullite with minor amounts of quartz, cristobalite, and a glass bonding phase. In the transition zone, located toward the hot face, the original quartz and cristobalite reacted with Na, K, and Ca residual oil impurities to form

a significant concentration of a glass phase. Iron oxide from the ingot scale also dissolved in the glass melt. Mullite reacted with sodium and potassium in this melt, with corundum being crystallized from the melt while the silica component in the mullite phase dissolved in the glass melt. In the altered zone, which is nearest to the hot face, corundum produced from previous mullite decomposition reacted with iron in the glass melt to form either iron aluminate or hercynite, depending on the local temperature and iron content. The distribution of iron aluminate and hercynite was sharply concentrated in the altered anchor. At the hot face of the anchor, the ATFT $[(\text{Al},\text{Fe})_2\text{O}_3 \cdot \text{TiO}_2]$ phase was formed as a result of reactions between corundum and the iron and titanium in the glass melt. The presence of Na, K, Ca, and Fe in the glass melt apparently played an important role in the deterioration process for this refractory. These impurities penetrated 15 to 25 mm into the anchor during its use. Increasing the Al_2O_3 content in the anchor above that presently used in its formulation would introduce corundum into the anchor as the Al_2O_3 content (65 wt %) in the original anchor is already similar to the composition of mullite (72 wt % Al_2O_3). Increased Al_2O_3 content in the anchor will cause an increase in the viscosity of the glassy phase since the viscosity of these silicate melts increases with the aluminum concentration. A higher viscosity would favor a slower dissolution of various crystalline phases dispersed in the glassy phase and a slower transport rate of detrimental species such as Na, K, and Fe through the glass phase.

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APPENDIX

X-RAY DIFFRACTION DATA

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Table A1. Sample PX1 of the Superduty
Fireclay Plastic Refractory

D Spacing, nm	
Observed	Mullite
0.82678	
0.72426	
0.53983	0.539
0.47907	
0.40547	
0.36836	0.3774
0.34903	
0.34347	0.3428
0.33974	0.3390
0.29478	
0.29317	
0.28938	0.2886
0.26991	0.2694
0.25594	0.2542
0.25102	
0.24314	0.2428
0.23872	0.2393
0.22981	0.2292
0.22131	0.2206
0.21250	0.2121
0.20932	0.2106
0.18960	
0.18448	0.1841
0.17457	
0.16972	0.17001
0.16066	0.15999
0.15295	
0.15270	0.15242
0.15160	0.15067
0.14691	0.14731
0.14670	0.14605
0.14487	0.14421
0.14086	0.14046
0.13782	
0.13400	0.13396
0.12952	
0.12675	
0.12426	
0.12385	
0.12364	
0.11951	
0.11512	
0.11310	
0.11026	
0.10812	
0.10468	
0.10097	
0.10008	

Table A2. Sample PX2 of the Superduty Fireclay Plastic Refractory

D Spacing, nm				
Observed	Mullite	β -Quartz	High-Cristobalite	Low-Cristobalite
0.43322		0.434		
0.42745			0.415	0.405
0.37697				
0.34205	0.3428	0.340		
0.33809	0.3390			
0.31545				0.314
0.28810	0.2886		0.292	0.2841
0.26889	0.2694			
0.25425	0.2542		0.253	
0.25081		0.250		0.2485
0.24257	0.2428			
0.23921				
0.23823				
0.22897	0.2292	0.231		
0.22064	0.2206	0.217	0.217	
0.21193	0.2121			0.2118
0.21034	0.2106		0.207	
0.20477				
0.20424				
0.20187		0.201	0.199	0.2019
0.19673				
0.19379				
0.19225				
0.18850	0.1887			
0.18604				0.1870
0.18575				
0.18399	0.1841	0.1837		
0.17933	0.17954		0.1795	
0.17133	0.17125			
0.17004	0.17001			
0.16931	0.16940	0.1696	0.169	0.1690
0.16255		0.1624	0.1641	
0.16007	0.15999			0.1600
0.15782	0.15786			0.1571
0.15665		0.1566		
0.15458				
0.15248	0.15242			
0.14604	0.14605	0.1477	0.1460	
0.14441	0.14421	0.1433		0.1431
0.14246	0.14240			0.1419
0.14052	0.14046			
0.14036				
0.13507				
0.13472	0.13462	0.1347		0.1346
0.13372	0.13356			
0.13306				
0.13283				
0.13191				
0.13140				
0.12783		0.1276		0.1281
0.12635			0.1266	
0.12409		0.1249		0.1242
0.12217				
0.11943				
0.11933				
0.11863				0.1188
0.10993			0.1090	

Table A3. Sample PX3 of the Superduty Fireclay Plastic Refractory

D Spacing, nm				
Observed	Mullite	β -Quartz	High-Cristobalite	Low-Cristobalite
0.43114		0.434		
0.41444			0.415	0.405
0.40456				
0.34217	0.3428	0.340		
0.33797	0.3390			
0.31732				0.314
0.28837	0.2886		0.292	
0.28488				0.2841
0.26905	0.2694			
0.25425	0.2542		0.253	
0.25014		0.250		
0.24880				0.2485
0.24270	0.2428			
0.22913	0.2292	0.231		
0.22074	0.2206	0.217	0.217	
0.21203	0.2121		0.207	0.2118
0.20255	0.2106	0.201	0.199	0.2019
0.18850	0.1887			0.1870
0.18406	0.1841	0.1837		
0.17962	0.17954		0.1795	
0.17133	0.17125			
0.17015	0.17001			
0.16934	0.16940	0.1696	0.169	0.1690
0.16894			0.1641	
0.16017	0.15999	0.1624		0.1600
0.15841	0.15786	0.1566		0.1571
0.15257	0.15242			
0.15220				
0.14613	0.14605	0.1477	0.1460	
0.14447	0.14421	0.1433		0.1431
0.14254	0.14240			0.1419
0.14049	0.14046			
0.13474	0.13462	0.1347		0.1346
0.13373	0.13356			
0.12790		0.1276	0.1266	0.1281
0.12637				
0.12419		0.1249		0.1242
0.11865				0.1188
0.10998			0.1090	
0.10080				
0.10060				
0.098592				
0.094898				

Table A4. Sample PX4 of the Superduty Fireclay Plastic Refractory

D Spacing, nm				
Observed	Mullite	β -Quartz	High-Cristobalite	Low-Cristobalite
0.53659	0.539			
0.43093		0.434		
0.40657			0.415	0.405
0.34166	0.3428	0.340		
0.33759	0.339			
0.31534				0.314
0.28792	0.2886		0.292	0.2841
0.26873	0.2694			
0.25397	0.2542		0.253	
0.25081		0.250		
0.24238	0.2428			0.2485
0.22891	0.2292	0.231		
0.22043	0.2206	0.217	0.217	
0.21175	0.2121			0.2118
0.21010	0.2106		0.207	
0.20355		0.201		0.2019
0.19669	0.1969		0.199	
0.18835	0.1887			0.1870
0.18389	0.1841	0.1837		
0.17121	0.17125			
0.16980	0.17001	0.1696	0.169	
0.16922	0.16940			0.1690
0.15999	0.15999	0.1566		0.1600
0.15236	0.15242			0.1533
0.14413	0.14421	0.1433	0.1460	0.1431
0.13364	0.13462	0.1347		0.1346
0.12780				0.1299
0.12632				

Table A5. Altered Part of the High-Alumina Refractory Anchor

Observed	D Spacing, nm			
	Corundum	Mullite	Iron Aluminate	Hercynite
0.83930				
0.48399				
0.47855				
0.47601				
0.46829			0.463	0.469
0.41713			0.425	
0.40953				
0.40583				
0.36449				
0.34782	0.3479			
0.34321		0.3428		
0.34050				
0.33809		0.3390		
0.33386				
0.33252				
0.29214			0.2898	0.287
0.27271				
0.26873		0.2694		
0.26795			0.2657	
0.25509	0.2552	0.2542		
0.24947			0.2499	
0.24251		0.2428		0.245
0.23823	0.2379		0.2391	
0.22064		0.2206	0.2234	
0.21799			0.2180	
0.21236		0.2121	0.2120	
0.20872	0.2085			
0.20740				
0.20690				
0.20623			0.202	0.202
0.19597		0.1969		
0.19489			0.1935	
0.17430				
0.17417	0.1740			
0.17133		0.17125		
0.17086		0.17001		
0.16969		0.16940		
0.16873				0.164
0.16043	0.1601			
0.15612				0.156
0.15474	0.1546	0.15461		
0.15245		0.15242		
0.15139	0.1514			
0.15113	0.1510	0.15067		
0.14613		0.14605		
0.14094				0.143
0.14079	0.1404	0.14046		
0.13989		0.13932		
0.13764				
0.13740	0.1374			
0.13710				
0.13350	0.1337	0.13356		
0.12781	0.1276			
0.12422				
0.12383	0.1239			
0.12378				
0.12346	0.12343			
0.12313				
0.11906	0.11898			
0.11770				0.117
0.11282				
0.11270				
0.11259	0.11255			
0.11248	0.11246			
0.11006				
0.10991	0.10988			
0.10980				
0.10855				
0.10837	0.10831			
0.10826				0.108
0.10803				
0.10469				0.105
0.10444				
0.10422	0.10426			
0.10009				0.101
0.099819	0.09976			
0.098557	0.09857			

Table A6. Transition Part of the
High-Alumina Refractory Anchor

D Spacing, nm		
Observed	Corundum	Mullite
0.53885		0.539
0.34269	0.3479	0.3428
0.33936		0.3390
0.28983		0.2886
0.26968		0.2694
0.25474	0.2552	0.2542
0.24282	0.2379	0.2428
0.22958		0.2292
0.22116		0.2206
0.21231		0.2121
0.20950	0.2085	0.2106
0.18927		0.1887
0.18462		0.1841
0.18002		
0.17408	0.1740	
0.17151		0.17125
0.17047		0.17001
0.16989		0.16940
0.16027	0.1601	
0.15834		0.15786
0.15259	0.1546	0.15242
0.14650		0.14605
0.14459		
0.14423		0.14421
0.14266		0.14240
0.14069	0.1404	0.14046
0.13383		0.13396
0.13347	0.1337	
0.12799	0.1276	
0.12660		
0.12429	0.1239	
0.12250	0.12343	
0.11929		
0.11494	0.14470	
0.11021	0.10988	

Table A7. Unaltered Part of the High-Alumina Refractory Anchor

D Spacing, nm			
Observed	Mullite	β -Quartz	Low-Cristobalite
0.54913			
0.53951	0.539		
0.43176		0.434	
0.40878			0.405
0.40657			
0.37760	0.3774		
0.34205	0.3428	0.340	
0.33885	0.3390		
0.32514			
0.31743			0.314
0.28874	0.2886		0.2841
0.26968	0.2694		
0.25467	0.2542		
0.24282	0.2428		0.2485
0.22947	0.2292	0.231	
0.22100	0.2206		
0.21241	0.2121	0.217	
0.18916	0.1887	0.201	0.1929
0.18441	0.1841	0.1837	0.1870
0.17982	0.1795		0.1757
0.17145	0.1712		
0.16998	0.1694	0.1696	0.1690
0.15826	0.1599	0.1566	
0.15554	0.15644		0.1567
0.15273	0.15242		
0.14637	0.14605	0.1477	
0.14455	0.14421		
0.14266	0.14240	0.1433	0.1431
0.14250			
0.14086			
0.14064	0.14046		0.1398
0.13491	0.13494	0.1347	0.1346
0.13383	0.13396		0.1333
0.12792			0.1281
0.12762		0.1276	
0.12652			
0.12427		0.1249	0.1242
0.12232			0.1223
0.11953			0.1188
0.11498			
0.11199			
0.11056			
0.11016			
0.10190			
0.10163			
0.10158			
0.10088			
0.10063			
0.099754			
0.099562			

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