

# ornl

**OAK RIDGE  
NATIONAL  
LABORATORY**

**MARTIN MARIETTA**



3 4456 0137586 9

**ORNL/TM-9903**

## **Corrosion of Materials by High-Temperature Industrial Combustion Environments – A Summary**

J. I. Federer

OAK RIDGE NATIONAL LABORATORY

CENTRAL RESEARCH LIBRARY

CIRCULATION SECTION

4500N ROOM 111

**LIBRARY LOAN COPY**

DO NOT TRANSFER TO ANOTHER PERSON

If you wish someone else to see this  
report, send in name with report and  
the library will arrange a loan

NOV 1988 10 4 77

OPERATED BY  
MARTIN MARIETTA ENERGY SYSTEMS, INC.  
FOR THE UNITED STATES  
DEPARTMENT OF ENERGY

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  
NTIS price codes—Printed Copy: A04 Microfiche A01

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

METALS AND CERAMICS DIVISION

CORROSION OF MATERIALS BY HIGH-TEMPERATURE INDUSTRIAL  
COMBUSTION ENVIRONMENTS -- A SUMMARY

J. I. Federer

Date Published: February 1986

Prepared for the Assistant Secretary for Conservation and  
Renewable Energy, Office of Industrial Programs, Waste  
Energy Recovery Program, U.S. Department of Energy

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

Prepared by the  
OAK RIDGE NATIONAL LABORATORY  
Oak Ridge, Tennessee 37831  
operated by  
MARTIN MARIETTA ENERGY SYSTEMS, INC.  
for the  
U.S. DEPARTMENT OF ENERGY  
under Contract No. DE-AC05-84OR21400



3 4456 0137586 9



## CONTENTS

ABSTRACT . . . . .	1
INTRODUCTION . . . . .	2
LIMITATIONS OF EXPOSURE TESTS . . . . .	3
SUMMARIES OF EXPOSURE TEST REPORTS . . . . .	5
INDUSTRIAL FURNACES . . . . .	6
Coal-Fired Kiln . . . . .	6
Glass Furnace . . . . .	7
Soot Hopper of a Steam Boiler . . . . .	10
Steel-Soaking Pit . . . . .	11
Glass Furnace . . . . .	11
Oil-Fired Boiler . . . . .	13
Heat-Treating Furnace . . . . .	13
Oil-Fired Lime Kiln . . . . .	14
Glass Furnace . . . . .	15
Cement Kiln . . . . .	18
Aluminum-Remelt Furnace . . . . .	19
Glass Furnace . . . . .	21
Aluminum-Remelt, Steel-Forge, Steel-Reheat, and Steel-Soaking-Pit Furnaces . . . . .	21
Aluminum-Remelt Furnace . . . . .	25
TEST FURNACE BURNING INDUSTRIAL FUELS . . . . .	26
Refractory Test Facility . . . . .	28
Refractory Test Facility . . . . .	29
Refractory Test Facility . . . . .	30
Ceramic Recuperator Analysis Facility . . . . .	31
Ceramic Recuperator Analysis Facility . . . . .	32
Refractory Test Facility . . . . .	33
Ceramic Recuperator Analysis Facility . . . . .	36
LABORATORY FURNACES . . . . .	39
Synthetic Combustion Atmosphere . . . . .	39
Synthetic Combustion Atmosphere . . . . .	40
DISCUSSION . . . . .	40
DEGRADATION MECHANISMS IN CERAMIC MATERIALS . . . . .	43
Chemical Reactions . . . . .	43
Other Mechanisms . . . . .	45

DEGRADATION MECHANISMS IN METALLIC ALLOYS . . . . . 45  
    Breakaway Oxidation . . . . . 45  
    Intergranular Oxidation . . . . . 46  
    Sulfidation-Oxidation . . . . . 46  
SUMMARY OF DISCUSSION . . . . . 47  
ACKNOWLEDGMENTS . . . . . 47  
REFERENCES . . . . . 48  
Appendix. COMPOSITIONS OF CERAMIC MATERIALS AND ALLOYS . . . . . 51

CORROSION OF MATERIALS BY HIGH-TEMPERATURE INDUSTRIAL  
COMBUSTION ENVIRONMENTS -- A SUMMARY

J. I. Federer\*

ABSTRACT

During the past 9 years, 23 reports issued by Oak Ridge National Laboratory described the effects of high-temperature industrial flue-gas environments on ceramic materials and metallic alloys. This document summarizes those reports in a simple format for easy perusal. Materials involved in these exposures include commercially available alumina, silica, and magnesia refractories; alumina and aluminosilicate refractory fiber insulations; silicon carbide ceramics; sialons; alumina ceramics; cordierite; and various iron-, nickel-, and cobalt-based alloys. Exposures occurred in industrial furnaces of the following types: coal-fired kiln, glass furnace, utility boiler, steel-soaking pit, heat-treating furnace, lime kiln, cement kiln, aluminum-remelt furnace, and steel-reheat furnace. In these furnaces metallic and ceramic materials were exposed to high-temperature environments containing numerous chemical species derived from the fuels, materials being processed, and furnace refractories. Materials were also exposed to the combustion environment of a test furnace burning industrial fuels and to synthetic combustion atmospheres containing selected corrodents in laboratory furnaces.

Various chemical, thermal, and thermal-mechanical degradation mechanisms were identified or indicated by analysis of exposed materials. Degradation mechanisms in refractory oxides and oxide ceramics involved reactions with species in the combustion products, slags, and other deposits. Formation of new liquid, glassy, and solid phases resulted in loss of structural integrity. Destructive stresses associated with volume changes in the case of new solid phases were sometimes increased by thermal cycling. Oxides of Fe, K, Na, Ni, Si, and V were the principal species involved in these reactions. In the case of silicon carbide ceramics the viscosity of the normally protective oxide film was lowered by reaction with alkali oxides, which resulted in enhanced oxygen diffusion and active oxidation. Silicon carbide was also attacked by halide-containing atmospheres. Degradation of ceramic materials was also caused by excessive temperatures, thermal cycling, and stresses caused by adhering slags and other materials.

Several types of degradation mechanisms were observed in metallic alloys, including breakaway oxidation associated with excessive temperature, intergranular oxidation, and sulfidation-oxidation.

---

\*Research sponsored by the Waste Energy Recovery Program, Office of Industrial Programs, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

## INTRODUCTION

During the past decade the U.S. Department of Energy (DOE) has promoted and supported investigations of the behavior of refractory materials in high-temperature industrial combustion environments. This interest was associated with the possible degradation of refractory materials, such as furnace linings, because of the use of fuels other than natural gas.<sup>1,2</sup> A shortage of natural gas during the 1970s resulted in use of alternate fuels including No. 2 distillate oil, No. 6 residual oil, and coal in various industrial processes. The impurity contents of the latter two fuels in particular were thought to be involved in accelerated degradation of furnace refractories, which caused unplanned furnace shutdowns and loss of production. As a result, refractories from various high-temperature processes were analyzed under a program sponsored by DOE to reveal the cause of degradation and to indicate a solution to the problem.

At about the same time DOE began supporting various heat-recovery projects. The goal of these projects was to develop heat exchangers to recover heat from the high-temperature flue gases of industrial furnaces. Unrecuperated furnaces in the steel, nonferrous, glass, and other industries exhaust hot flue gases into the atmosphere, thereby losing a large portion of the heat content of the fuels being used. Processing costs can be lowered by recovering this heat and using it to preheat charge material or combustion air and to produce steam. Use of structural ceramics in these heat exchangers received considerable attention during this period because of the need to recover heat at higher temperatures than might be possible with metallic equipment. An assessment of recuperator materials by Tennery and Wei discusses critical materials problems associated with development of high-temperature heat recovery devices.<sup>3</sup> One of these problems is materials degradation in corrosive/fouling flue gases. The principal reason, therefore, to investigate the behavior of refractory materials in flue gas environments was to understand degradation mechanisms and to identify materials suitable for heat exchanger components.

The purpose of this document is to review and condense all of the reports of materials exposure tests in which Oak Ridge National Laboratory (ORNL) had an active role into a single document for easier access to the information. A summary of each report presented herein includes a brief discussion of materials tested, exposure conditions, results, and conclusions. Much more detail, of course, can be found in the original reports. This document includes only work presented in ORNL reports. The work in these reports was sponsored by DOE through the Office of Industrial Programs and the Pittsburgh Energy Technology Center.

#### LIMITATIONS OF EXPOSURE TESTS

Exposure tests provide information concerning oxidation, corrosion by flue gases and particulates, and response to thermal treatments of materials exposed to specific environments. These tests are conducted for two reasons: to compare the behavior of several candidate materials and to monitor materials in service. The exposure variables -- flue gas composition, particulate types and concentrations, maximum temperature, mean temperature, frequency and severity of thermal cycles, and duration of exposure -- act in various combinations to affect materials behavior. Even for furnaces of the same type, the value of these variables probably differs from furnace to furnace. In general, the composition of flue gases and particulates is not well known. Results of exposure tests, therefore, are specifically related to a particular furnace. Extension of the results to another furnace, even the same type, involves considerable uncertainty because of lack of knowledge concerning some of the variables.

Industrial furnaces are production facilities, so conditions within them are affected by production requirements. When exposure tests are being conducted, conditions may change because of several factors including type of fuel, raw materials, and processing schedules. Such variations are not welcomed by those conducting materials testing, but they occur often in some furnaces. The results of the exposure then are valid for the actual conditions, but the interpretation of materials behavior is complicated and use of the results to predict materials behavior in other furnaces is more difficult.

The compositions of flue gases and particulates are directly related to the type of fuel, materials being heated, and furnace refractories. Analyses of deposits or reaction layers on specimens exposed to furnace environments reveal flue gas constituents. For example, the composition of deposits on SiC ceramics exposed to the environments of two aluminum-remelt furnaces and a steel-soaking pit (Table 1) indicates that product carryover (Al in the former, Cr and Fe in the latter) is an important source of flue gas constituents. The actual concentration of any element in the flue gases, however, might be significantly different from the concentration in the deposit, because compounds with high vapor pressures tend to escape as gases rather than reacting with or condensing on specimens.

Table 1. Characteristics of deposits on specimens exposed to industrial furnace environments

Content <sup>a</sup> (ppm)	Aluminum-remelt No. 1	Aluminum-remelt No. 2	Steel-soaking pit No. 2
	Composition		
Major <sup>b</sup>	Al, Si	Al, K, Na, Si	Cr, Fe, Si
1000-3000	Fe, K, Na, Zn	Ba, Ca, Cu, Fe, Zn	Cu, K, Mn
500-1000	Ca, Ti	Cl, Mg	Ca, Na, Ni
100-500	B, Ba, Bi, Cr, Cu Mg, Mn, Ni, P, Pb, S, Sn	Mn, S, Sr	P, S, Ti, Zn
<100	Ce, Cl, Co, Mo, Sc, V, Zr	B, Co, Cr, F, La, Mo, Ni, P, Rb, Ti, V, Zr	As, B, Cl, Co, Ga, Ge, Mg, Mo, Rb, V, Zr
	Crystalline compounds		
	Al <sub>2</sub> O <sub>3</sub>	(Ca, Mg, Fe, Al) silicate	<sup>c</sup>
	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>		
	Melting range (°C)		
	1200-1300	1150-1300	1250-1300

<sup>a</sup>Determined by semiquantitative spectrographic analysis.

<sup>b</sup>5 to 20%.

<sup>c</sup>Not determined.

Knowledge of the thermal history of specimens to be analyzed is very important to an understanding of materials behavior. Often specimens are either provided with thermocouples or placed in a location where furnace temperature-monitoring thermocouples exist. On the other hand, exposure tests also have been conducted without accurate measurements of maximum temperature or temperature vs time relationships. In those cases only best estimates are available.

The uncertainties concerning flue gas constituents and temperature in industrial furnaces have resulted in use of special test facilities at ORNL to supplement tests in industrial furnaces. Small laboratory furnaces have been used to study the effects of specific chemical species on metallic and ceramic materials. Testing has also been conducted in a much larger furnace in atmospheres resulting from combustion of natural gas, distillate oil, residual oil, and coal-oil mixtures. Because these are dedicated test facilities, the exposure conditions can be selected, monitored, and controlled during the experiments.

#### SUMMARIES OF EXPOSURE TEST REPORTS

Summaries of reports describing exposure tests are presented in this section. The reports summarized herein described exposure tests in three types of furnaces: industrial furnaces, a test furnace burning industrial fuels, and laboratory furnaces containing synthetic combustion atmospheres. Each summary is structured in the same format for easy perusal: author(s), title, number, and date of the report; material(s); exposure conditions; results; discussion (for some); and conclusions.

The materials discussed in the summarized reports are conventional refractories, refractory fiber insulations, and structural ceramics. The former include many compositions based on alumina, magnesia, or silica manufactured into bricks, mortar, castable, and other forms. Their properties vary considerably as a result of differences in raw materials and processing methods. The conventional refractories are used in diverse applications for thermal insulation, furnace lining, erosion resistance, molten metal containment, etc. Fiber insulations have much better insulating properties than conventional refractories but are not capable of

supporting a significant load. Structural ceramics, on the other hand, are designed to provide specific properties such as high strength, toughness, or thermal conductivity and to vary less in characteristics and properties because of closer control of manufacturing variables. Structural ceramics are considered for use in more demanding applications than those of conventional refractories, such as diesel engine components, turbine rotors, and some heat-exchanger tubes.

Compositions of oxide ceramics and fuel ash are presented in terms of equivalent oxide contents for convenience. For example, mullite is a compound in the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system containing 72 wt %  $\text{Al}_2\text{O}_3$  and 28 wt %  $\text{SiO}_2$  equivalent oxide contents. The compound, however, has the elemental formula  $\text{Al}_6\text{Si}_2\text{O}_{13}$  (or  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) and contains neither  $\text{Al}_2\text{O}_3$  nor  $\text{SiO}_2$  in their pure, uncombined form.

## INDUSTRIAL FURNACES

Exposure tests have been conducted in a wide variety of industrial furnaces: coal-fired kiln, glass furnace, utility boiler, steel-soaking pit, refractory-metal heat-treating furnace, lime kiln, cement kiln, aluminum-remelt furnace, and steel-reheat furnace.

In these furnaces metallic and ceramic materials have been exposed to environments containing many chemical species derived from the fuels, materials being processed, and furnace refractories. We suspect that these species included oxides, sulfates, and halides in various proportions.

### Coal-Fired Kiln

G. C. Wei, V. J. Tennery, and L. A. Harris, *Effects of Alternate Fuels Report No. 1, Analysis of High-Duty Fireclay Refractories Exposed to Coal Combustion*, ORNL/TM-5909, December 1977 (ref. 4).

Material. The material investigated was fireclay brick containing 55 to 58 wt %  $\text{SiO}_2$ , 36 to 39 wt %  $\text{Al}_2\text{O}_3$ , and balance as  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$ .

Exposure Conditions. The bricks were used in the crown of a downdraft periodic kiln fired with coal. A typical coal-ash composition

was 44 wt % SiO<sub>2</sub>, 30 wt % Al<sub>2</sub>O<sub>3</sub>, 16 wt % Fe<sub>2</sub>O<sub>3</sub>, 3 wt % CaO, 1 to 2 wt % each K<sub>2</sub>O, MgO, Na<sub>2</sub>O, and TiO<sub>2</sub>, 0.1 to 1 wt % B<sub>2</sub>O<sub>3</sub>, BaO, P<sub>2</sub>O<sub>5</sub>, and SrO, and many other elements in lesser concentrations. The kiln cycled once each week from room temperature to 1260°C, then down to room temperature. This type of operation continued for 15 years, at which time some bricks were removed for examination. The ash (slag) was at least partially liquid at 1260°C.

Results. The slag layer plus the altered zone of brick was about 5 mm thick. Major crystalline phases in unaltered brick were mullite, low cristobalite, and  $\alpha$ -quartz. Major crystalline phases in the slag layer were mullite, corundum, oligoclase, hematite, and high cristobalite.

Conclusions. Quartz grains in the brick dissolved in the liquid slag. Mullite crystals reacted with the slag resulting in formation of corundum crystals while the silica component dissolved in the slag. The high-SiO<sub>2</sub> slag was viscous enough at 1260°C to provide a protective layer. High-duty fireclay refractories perform satisfactorily in industrial furnaces fired with coal if the temperature is low enough to maintain a highly viscous slag of the proper type on the hot face.

#### Glass Furnace

G. C. Wei and V. J. Tennery, *Effects of Alternate Fuels Report No. 2, Analysis of Basic Refractories Degraded by Residual Oil Combustion Products*, ORNL/TM-6088, February 1978 (ref. 5).

Materials. Chrome-magnesite bricks and high-MgO bricks obtained from an industrial glass furnace and regenerator had the following approximate compositions:

<u>Material</u>	<u>Compositions (wt %)</u>	
	<u>Chrome Magnesite</u>	<u>High-MgO</u>
MgO	50.0	93.0
Cr <sub>2</sub> O <sub>3</sub>	20.0	<0.1
Al <sub>2</sub> O <sub>3</sub>	17.5	1.0
Fe <sub>2</sub> O <sub>3</sub>	9.0	1.0
SiO <sub>2</sub>	2.5	4.0
CaO	1.0	1.0

Exposure Conditions. Chrome-magnesite bricks (Fig. 1) were obtained from the port and target walls of an industrial glass furnace (Fig. 2), where the maximum hot-face temperature was 1540 to 1595°C. The high-MgO brick was obtained from the regenerator, where the maximum hot-face temperature was 1095 to 1150°C. The furnace was fired with No. 6 residual oil of unknown composition. Bricks in the regenerator experienced numerous thermal cycles and variations in oxygen potential as a result of alternating flow of combustion air and exhaust gases. The exposure time for the bricks was 3.5 years.

Results. Chrome-magnesite brick expanded about 43% and cracked. The composition changed considerably —  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  decreased while  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{NiO}$  increased.

The high-MgO brick lost material from the hot face, which exhibited an expansion of about 20%. The composition changed as in the case of the chrome-magnesite brick except that there was no increase in  $\text{NiO}$  and a substantial increase in  $\text{SO}_3$ .

Discussion. Composition changes apparently resulted from depletion of volatile components, such as  $\text{Cr}_2\text{O}_3$ , and from addition of components of the glass batch, particularly  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$ . The  $\text{NiO}$  and  $\text{SO}_3$  were apparently derived from the No. 6 fuel oil.

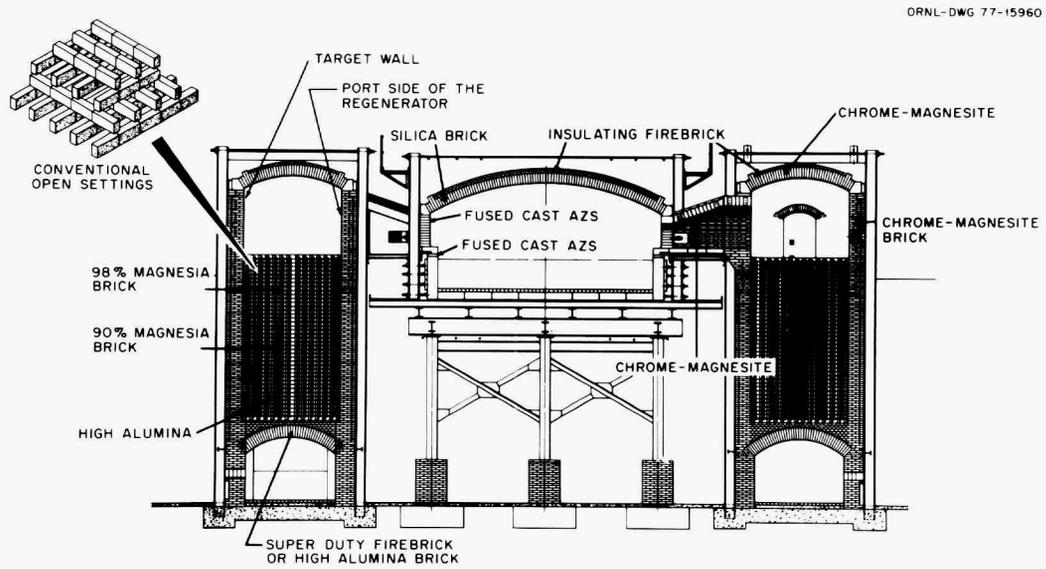
Several degradation mechanisms in the chrome-magnesite brick probably occurred:

1. Reaction of  $\text{NiO}$  with periclase ( $\text{MgO}$ ) to form  $\text{Mg}_{0.5}\text{Ni}_{0.5}\text{O}$  resulted in volume shrinkage of about 1% and generation of stress at the boundary between periclase and neighboring grains.
2. Reaction of  $\text{NiO}$  with forsterite ( $2\text{MgO}\cdot\text{SiO}_2$ ) to form  $\text{MgNiSi}_2\text{O}_6$  resulted in a volume expansion of 188%.
3. Reaction of  $\text{SiO}_2$  (carryover from the glass batch) with periclase to form forsterite resulted in a volume expansion of 6%.
4. Evidence exists for other reactions resulting in less-refractory phases or volume increases.

Degradation in the high-MgO brick was mostly attributed to  $\text{Na}_2\text{SO}_4$  by a mechanism not well understood. The evidence suggests that sodium and



Fig. 1. Port-side chrome-magnesite brick after exposure to glass-furnace environment at 1540 to 1595°C for 3.5 years.



ORNL-DWG 77-15960

Fig. 2. Typical side-port glass tank melting furnace and regenerators.

sulfur diffused into periclase grains at high temperatures, and then precipitation of  $\text{Na}_2\text{SO}_4$  at lower temperatures disrupted the brick. Another possible mechanism involves formation of  $\text{MgSO}_4$  and the considerable swelling associated with that reaction.

Conclusions. NiO, a fuel impurity, was mostly responsible for degradation of chrome-magnesite bricks by formation of new phases having higher specific volumes than those of the reactants. Degradation of high-MgO bricks was caused by the periodic freezing and melting of  $\text{Na}_2\text{SO}_4$  and by crystallization of that compound within periclase grains.

#### Soot Hopper of a Steam Boiler

G. C. Wei and V. J. Tennery, *Effects of Alternate Fuels Report No. 3, Analysis of High-Duty Fireclay Refractories Degraded by Residual Oil Combustion Products*, ORNL/TM-6184, April 1978 (ref. 6).

Material. The material investigated was high-duty fireclay brick with nominal composition of 39 to 42 wt %  $\text{Al}_2\text{O}_3$ , 52 to 55 wt %  $\text{SiO}_2$ , and small amounts of other compounds such as CaO,  $\text{Fe}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$ .

Exposure Conditions. The brick was used in the soot hopper of a utility steam boiler fired with No. 6 residual oil of unknown composition. Additives based on magnesia ( $\text{MgO}$ ) and dolomite ( $\text{MgCO}_3 \cdot \text{CaCO}_3$ ) were used in the residual oil to inhibit corrosion of steam tubes by combustion products. The maximum recommended hot-face temperature for the brick is  $1540^\circ\text{C}$ . In this application the maximum hot-face temperature was reported to be  $1400^\circ\text{C}$ . The duration of exposure was 6 months.

Results. The service life of the brick (6 months) was reduced from the normal period of 3 years by changing from natural gas to residual oil fuel. The hot face lost about 30 mm of material. The composition of the hot face was altered by increases in CaO, MgO,  $\text{Na}_2\text{O}$ ,  $\text{SO}_3$ , and  $\text{V}_2\text{O}_5$ .

Conclusions. The refractoriness of the brick was substantially altered by composition changes in the hot-face region. Alkali oxides from the fuel reacted with silica phases (low cristobalite and  $\alpha$ -quartz) to form a silicate melt containing Na, K, V, Ca, Mg, Ti, Fe, and Al. Reaction of mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), a major phase in the brick, with the glass resulted in formation of corundum ( $\text{Al}_2\text{O}_3$ ) while the  $\text{SiO}_2$  portion of the mullite dissolved in the glass. Reaction of  $\text{V}_2\text{O}_5$ , another fuel

impurity, with mullite produced relatively low-melting (695°C) aluminum vanadate ( $\text{AlVO}_4$ ), with the  $\text{SiO}_2$  portion entering the glass. Higher-alumina refractories would be more stable in a residual-oil combustion environment.

#### Steel-Soaking Pit

G. C. Wei and V. J. Tennery, *Effects of Alternate Fuels Report No. 4, Analysis of Soaking Pit Cover Refractories Degraded by Residual Oil Combustion Products*, ORNL/TM-6204, April 1978 (ref. 7).

Materials. The materials were a superduty fireclay refractory with nominal composition of 47 wt %  $\text{Al}_2\text{O}_3$  and 50 wt %  $\text{SiO}_2$ , and a high-alumina refractory containing 66 wt %  $\text{Al}_2\text{O}_3$  and 29 wt %  $\text{SiO}_2$ .

Exposure Conditions. Both refractories were used in the cover of a steel-soaking pit. The pit was fired for 2 to 4 months with a No. 6 residual oil (impurity content not determined) and with natural gas the remainder of the time. Because of obvious degradation the bricks were removed for analysis after about 6 months. During this period the bricks were exposed to combustion products and process carryover. A maximum hot-face temperature of 1290°C was attained during numerous thermal cycles.

Results. Each brick had a reaction zone extending about 20 mm in from the hot face. The amount of reaction was much greater than the same type of bricks exhibited after 1 year in a soaking pit fired with natural gas. The reaction zone in each brick consisted of crystalline phases in a glass matrix containing fuel impurities, principally  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , and  $\text{Fe}_2\text{O}_3$  from ingot scale.

Conclusions. Silica-containing phases in the bricks reacted with alkali oxides from the fuel, resulting in a glass of lower melting point than that of the original phases. Increasing the alumina content of the bricks should produce a more viscous glassy phase, which would reduce the reaction rate with fuel impurities.

#### Glass Furnace

G. C. Wei and V. J. Tennery, *Effects of Alternate Fuels Report No. 5, Analysis of Fused Cast AZS Refractory, Silica Refractory, and High-MgO Refractory Degraded by Residual Oil Combustion Products*, ORNL/TM-6278, April 1978 (ref. 8).

Materials. The materials were AZS refractory (Monofrax S-3) with nominal composition of 50 wt %  $\text{Al}_2\text{O}_3$ , 14 wt %  $\text{SiO}_2$ , and 34 wt %  $\text{ZrO}_2$ ; silica refractory (Vega superduty) with nominal composition of 96 wt %  $\text{SiO}_2$  and 3 wt %  $\text{CaO}$ ; and high-MgO refractory (P-95) with nominal composition of 95 wt %  $\text{MgO}$ , 1 wt % each  $\text{CaO}$  and  $\text{Cr}_2\text{O}_3$ , and 2 wt %  $\text{SiO}_2$ .

Exposure Conditions. Refractory bricks of the three materials were used in a continuous soda-lime-silica glass furnace, which was fired with natural gas for 36 months and then with residual oil for 6 months. Excessive degradation of the AZS tuckstone and silica skew bricks threatened to collapse the entire furnace at least 12 months before normal shutdown (if fired with natural gas only). The high-MgO bricks in the first courses of the regenerator were also badly degraded. The No. 6 residual oil contained approximately 175 ppm V, 6 ppm Na, and 2 to 3 wt % S. The maximum hot-face temperatures for AZS and silica bricks was  $1530^\circ\text{C}$ . The high-MgO bricks thermally cycled between  $1230$  and  $1430^\circ\text{C}$  and were also subjected to oxygen partial pressure cycling. In addition to V and S from the No. 6 fuel oil, the furnace atmosphere also contained  $\text{Na}^-$ ,  $\text{Ca}^-$ ,  $\text{Mg}^-$ , and Si-containing compounds that originated in the glass batch.

Results. The hot face of the AZS brick was converted to a glassy material. Four other distinct zones were present in succession between the hot face and the interior portion. The hot face of the silica brick contained many pores. Two other distinct zones parallel to the hot face were present. The high-MgO brick was extensively cracked. Material loss, if any, was not measured.

Conclusions. Degradation of the AZS brick was caused by reactions with components of the glass batch and with vanadium from the fuel oil, resulting in dissolution of all crystalline phases except  $\text{ZrO}_2$  and formation of an extensive silicate glass phase.

Glass batch carryover reacted with the calcium silicate bonding phase in the silica brick. The resulting liquid-phase product drained from the brick, resulting in loss of materials.

Glass batch carryover including  $\text{CaO}$  and  $\text{SiO}_2$  reacted with the forsterite bonding phase in the high-MgO brick, resulting in formation of less-refractory monticellite (the original bonding phase was a mixture of forsterite and monticellite). A low-melting liquid formed as a result

of reaction between vanadium and monticellite. Stresses induced by thermally cycling the reaction products caused extensive cracking and loss of load-bearing capability.

#### Oil-Fired Boiler

G. C. Wei and V. J. Tennery, *Effects of Alternate Fuels Report No. 6, Analysis of Low-Alumina Castable Refractory Degraded by Residual Oil Combustion Products*, ORNL/TM-6334, July 1978 (ref. 9).

Material. The material investigated was a low-alumina castable with nominal composition (equivalent oxide adjusted for loss of plasticizer and water) of 37 wt %  $\text{Al}_2\text{O}_3$ , 13 wt %  $\text{CaO}$ , 6 wt %  $\text{Fe}_2\text{O}_3$ , 38 wt %  $\text{SiO}_2$ , and small concentrations of  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ , and others.

Exposure Conditions. The castable refractory was used for only 2 months in the roof of a boiler fired with No. 6 oil. The maximum hot-face temperature was  $1255^\circ\text{C}$ , somewhat lower than the vendor-quoted maximum service temperature of  $1300^\circ\text{C}$ . The impurity content of the No. 6 oil was not known.

Results. The castable exhibited gross deterioration due to fluxing by species in the combustion environment, which resulted in lowered refractoriness and material loss. Concentrations of Fe, Ni, and Na (probably impurities in the fuel oil) were significantly increased in the degraded castable compared with those in the unaltered material.

Conclusions. Silicon-containing phases in the original castable (quartz, cristobalite, and mullite) reacted with fuel-oil impurities including Fe, Ni, and Na to form a glass phase of lower refractoriness.

#### Heat-Treating Furnace

G. W. Weber and V. J. Tennery, *Analysis of Cordierite (MAS) Recuperator from a Molybdenum Heat-Treating Furnace*, ORNL/TM-6794, May 1979 (ref. 10).

Material. Cordierite ( $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$ ) was the material investigated. The stoichiometric composition is 13.8 wt %  $\text{MgO}$ , 34.9 wt %  $\text{Al}_2\text{O}_3$ , and 51.4 wt %  $\text{SiO}_2$ .

Exposure Conditions. A cordierite recuperator was installed for demonstration on a natural-gas-fired furnace heating tungsten and molybdenum billets. Flue gases entered the recuperator at temperatures ranging

between 1100 and 1400°C. A brief overheating to 1550°C damaged the recuperator and terminated the demonstration after 2200 h. The flue gases contained tungsten and molybdenum oxides.

Results. The recuperator heated air to about 800°C at an effectiveness of about 0.6. Unsupported leading edges on the gas inlet side deformed; however, supported portions did not deform even during the brief overheating to 1550°C. Some portions exhibited extensive reaction with molybdenum and tungsten oxides but retained structural integrity except for deformation. Some flue gases leaked into air channels.

Conclusions. The recuperator performed satisfactorily for 2200 h at gas inlet temperatures of 1100 to 1400°C. Although some deformation and reaction occurred, the test showed that cordierite recuperators can survive brief overheating to 1550°C. Molybdenum and tungsten were incorporated into the cordierite structure at temperatures as low as 700°C. Flue gases leaked into air channels, but the effect on performance was not determined.

#### Oil-Fired Lime Kiln

J. I. Federer and V. J. Tennery, *Effects of Alternate Fuels Report No. 7: Analysis of Failure of a Mullite-Based Refractory Brick in an Industrial Oil-Fired Burner*, ORNL/TM-6878, July 1979 (ref. 11).

Material. The material investigated was refractory brick with nominal composition of 73 wt %  $\text{Al}_2\text{O}_3$ , 23 wt %  $\text{SiO}_2$ , and smaller amounts of  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ , etc. The major crystalline phase was mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ).

Exposure Conditions. The brick was used as the refractory lining in an oil-fired burner used to calcine  $\text{CaSO}_4$  in a lime kiln. The brick was in contact with less refractory aluminosilicate castable and mortar. The burner heated the kiln 8 h a day for 6 months. The estimated maximum hot-face temperature for the three refractories was 1750°C.

Results. The brick severely degraded after 6 months (~1000 h of service). Detached pieces of brick, castable, and mortar, which collected at the bottom of the burner, could be differentiated only by chemical analysis

Conclusions. Failure of the mullite-based brick was initiated by melting of adjacent castable and mortar. The liquid phases attacked the

brick, which was severely contaminated with CaO from the kiln and  $V_2O_5$  from the fuel oil. Two new compounds, anorthite ( $CaO \cdot Al_2O_3 \cdot 2SiO_2$ ) with melting point of  $1550^\circ C$  and aluminum vanadate ( $AlVO_4$ ) with melting point of  $640^\circ C$ , were identified. These and other molten phases advanced into the brick, causing major disruption of the structure.

#### Glass Furnace

G. W. Weber and V. J. Tennerly, *Materials Analyses of Ceramics for Glass Furnace Recuperators*, ORNL/TM-6970, November 1979 (ref. 12).

Materials. The compositions of the following materials are shown in Table A.1 of the appendix: SiC ceramics (sintered alpha, NC-400, NC-430, KT, CVD); silicon oxynitride; alumina ceramics (Vistal, AD-998, AD-94, AD-85); mullite; cordierite; zirconia; and reaction-bonded silicon nitride ( $Si_3N_4$ ).

Exposure Conditions. Specimens were located in the flue of a glass furnace (Fig. 3). The combustion atmosphere contained dust and evaporated species from the soda-lime glass charging and melting operations. The glass composition was approximately 66 wt %  $SiO_2$ , 14 wt % each CaO and  $Na_2O$ , 2 wt % each  $Al_2O_3$  and MgO, 0.5 wt % each  $B_2O_3$  and BaO. The glass also contained 0.6 wt % F. Materials were exposed to temperatures of 1150 to  $1550^\circ C$ , depending on location in flue, for periods of 4 to 117 days.

Results. SiC ceramics and silicon nitride exhibited surface recession inversely dependent on temperature. For example, sintered alpha SiC had a recession rate of  $6.3 \mu m/h$  after 430 h at  $1225^\circ C$ , but only  $1.1 \mu m/h$  after 408 h at  $1550^\circ C$ . Specimens had a glassy surface layer (Fig. 4).

Corrosion of alumina ceramics decreased with increasing alumina content. The reaction caused alteration of the crystalline structure to a glassy structure, rather than surface recession. Vistal, the highest purity alumina ceramic, was not significantly corroded. All alumina ceramics deformed by creep.

Mullite and cordierite deformed by creep and reacted to form glassy structures in a manner similar to that of the alumina ceramics.

Silicon oxynitride and zirconia were not specifically discussed.

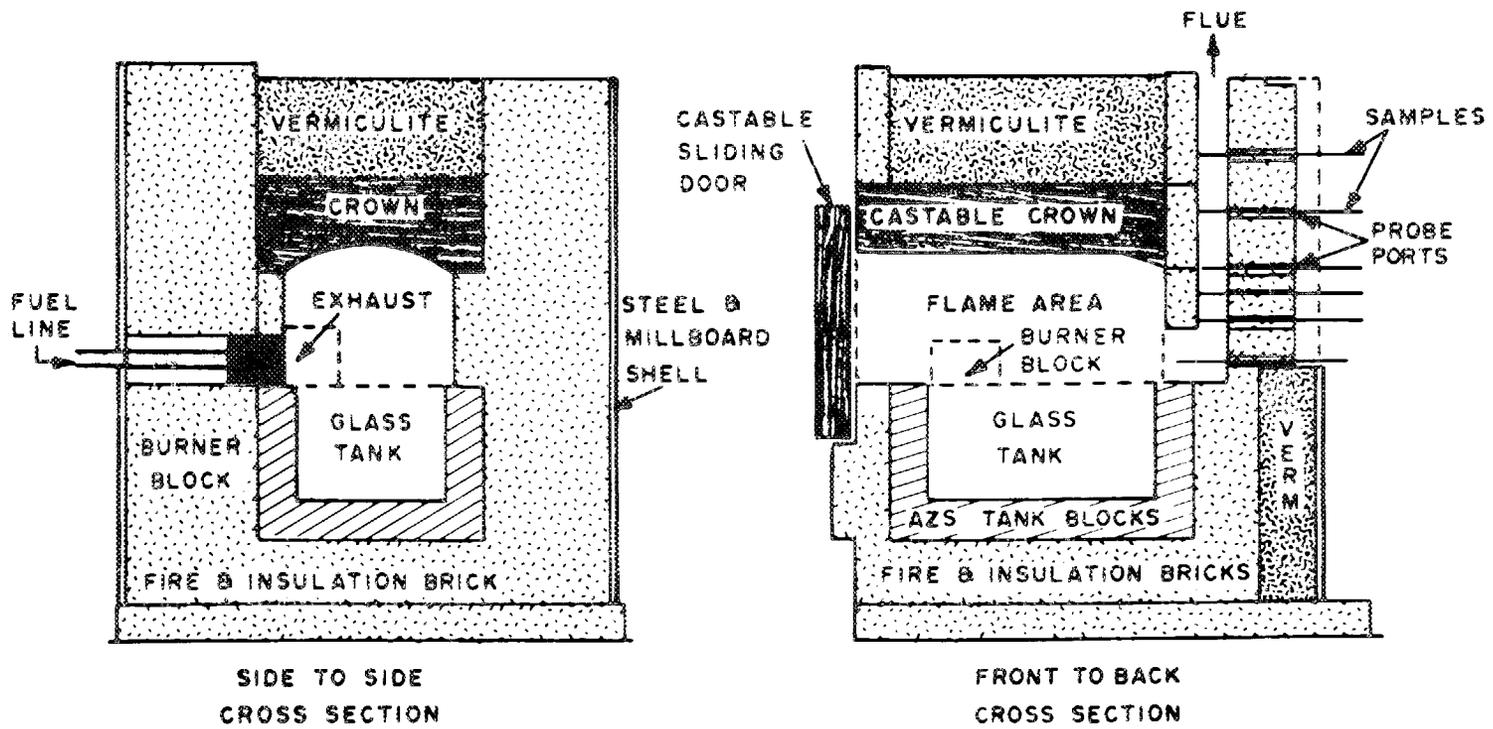
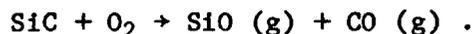


Fig. 3. Special day tank glass furnaces used for exposure tests.



Fig. 4. Sintered alpha SiC exposed to glass furnace environment.

Discussion. The observed increase in corrosion rate with decreasing temperature in SiC and Si<sub>3</sub>N<sub>4</sub> was attributed to a lowering of the viscosity of the normally protective silica film by condensation of alkali and iron oxides. The lowered film viscosity allowed active oxidation at the interface between the SiC (or Si<sub>3</sub>N<sub>4</sub>) and the film under low oxygen partial pressure conditions via the reaction



At higher temperatures where less condensation of alkali and iron oxides occurred, the higher film viscosity limited oxidation. The silicate bonding phase of mullite, cordierite, and the alumina ceramics (except Vistal) was fluxed by the alkali oxides, which resulted in extensive glass formation.

Conclusion. Materials that rely on a protective silica film or contain an extensive silicate bonding phase are subject to severe corrosion by the fluxing action of alkali and iron oxides. High-purity alumina (Vistal), which exhibited essentially no surface recession or reaction, performed better than any other material included in this test.

#### Cement Kiln

J. I. Federer and V. J. Tennery, *Effects of Alternate Fuels Report No. 8: Analysis of Degradation of Magnesia-Based Refractory Bricks from a Residual Oil-Fired Rotary Cement Kiln*, ORNL/TM-7165, May 1980 (ref. 13).

Materials. Magnesia-based bricks with nominal composition of 55 wt % MgO, 20 wt % CaO, 11 wt % SiO<sub>2</sub>, 5 wt % Fe<sub>2</sub>O<sub>3</sub>, 4 wt % Al<sub>2</sub>O<sub>3</sub>, and 3 wt % Cr<sub>2</sub>O<sub>3</sub> were investigated.

Exposure Conditions. The bricks were part of the refractory lining in the hot zone or clinkering zone of a rotary cement kiln, where the hot-face temperature was about 1500°C. The bricks were coated with cement clinker, which spalled periodically and removed a thin layer of brick. The major impurities in the fuel oil were Ca, Fe, Mg, Na, Ni, P, S, and V.

Results. Approximately 10 cm of the bricks (measured from the original hot face) were lost during 6 to 9 months of service. The bricks also had many cracks. The kiln operators, however, stated that the amount of

degradation was not more than occurred previously when natural gas was used as the fuel. The hot face of the bricks did not contain high concentrations of fuel impurities or new crystalline phases.

Conclusions. Degradation was normal for cement kiln operation and was not related to fuel impurities.

#### Aluminum-Remelt Furnace

J. I. Federer and V. J. Tenney, *Corrosion of a Stainless Steel Waste Heat Recuperator*, ORNL/TM-7166, June 1980 (ref. 14).

Material. The composition of the type 309 stainless steel used is shown in Table A.2 of the Appendix.

Exposure Conditions. A radiant recuperator constructed of type 309 stainless steel was exposed to flue gases from an aluminum-remelt furnace burning No. 2 oil (Fig. 5). A flux consisting of NaCl-45% KCl-5% Na<sub>3</sub>AlF<sub>6</sub> was charged along with aluminum scrap. The flue gases probably contained many chemical species derived from oil combustion, furnace refractories, impurities in the scrap metal, and the flux. Some constituents likely present are N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, SO<sub>2</sub>, NaCl, KCl, NaF, and AlF<sub>3</sub>. The flue gas temperature at the inlet to the recuperator was about 950°C except during a temperature excursion lasting about 3 days when the temperature was probably 1100 to 1200°C. The exposure time was 30 days of normal operation and 3 days during which excessive temperature occurred.

Results. The recuperator was severely damaged on the gas inlet end. A type 309 reradiant insert, originally about 5 mm thick, was completely corroded in some locations and less than 1 mm thick in other locations (Fig. 6). The alloy exhibited extensive intergranular attack beneath a thick scale of iron and chromium oxides. The scale contained Cl, K, Na, and S, and the corroded grain boundaries contained Cl, K, and S.

Conclusions. The corrosion mechanism was primarily sulfidation-oxidation in which low-oxygen, high-sulfur atmospheres resulted in formation of sulfides under conditions in which the steel could not maintain a normally protective oxide film. Chlorides in the flue gases contributed to corrosion by further reducing the ability of the steel to form a protective oxide film. Excessive temperatures caused extensive oxidation during the final 3 days of operation.

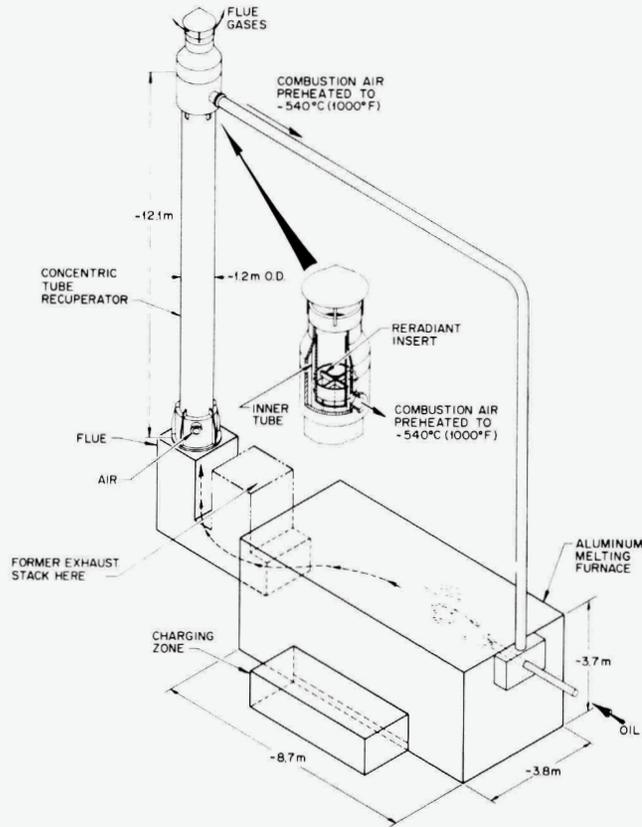


Fig. 5. Stainless steel recuperator on an aluminum-remelt furnace.

Y163944

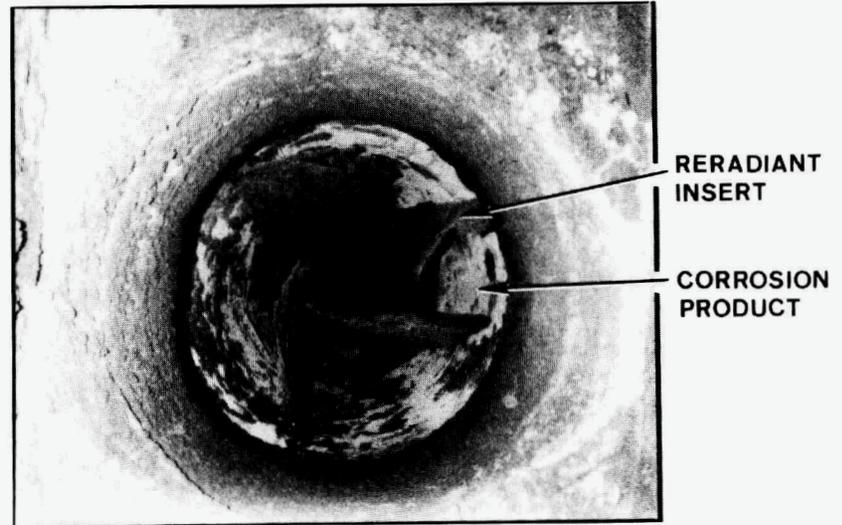


Fig. 6. Corroded partition wall and reradiant inserts at the bottom of the recuperator after exposure to aluminum-remelt furnace flue gases for 30 days at 950°C and 3 days at 1100 to 1200°C.

### Glass Furnace

J. I. Federer and V. J. Tennery, *Analysis of a Corroded Stainless Steel Recuperator Used on a Glass Melting Furnace*, ORNL/TM-7553, November 1980 (ref. 15).

Material. The composition of the type 321 stainless steel used is shown in Table A.2 of the Appendix.

Exposure Conditions. A radiant recuperator constructed of type 321 stainless steel was exposed to flue gases from a borosilicate glass furnace. The furnace burned natural gas containing about 0.1% sulfur. The charge to the furnace included cullet (scrap glass), sand ( $\text{SiO}_2$ ), borax (approximate composition  $\text{NaB}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ ), anhydrous borax (96%  $\text{B}_2\text{O}_3$ -2.5%  $\text{Na}_2\text{O}$ ), calcined alumina ( $\text{Al}_2\text{O}_3$ ), nitre ( $\text{KNO}_3$ ), and sodium chloride ( $\text{NaCl}$ ). Some sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) might have been included in the charge also. A partition-wall thermocouple indicated  $650^\circ\text{C}$  early in the campaign, but then it failed. The total exposure time was 5760 h.

Results. The partition wall was severely corroded. Approximately 30% (1.5 mm) of the original thickness of 4.0 mm had been converted to corrosion product or subjected to intergranular attack. The corrosion product, which consisted of Fe, Cr, and Ni oxides, contained 0.1 wt % Cl, 0.7 wt % S, >0.5 wt % Si, and various other elements.

Discussion. The oxide scale was about 1.5 mm thick after 5760 h at a reported temperature of  $650^\circ\text{C}$ . This thickness was about 30 times the thickness to be expected for oxidation of type 321 at  $925^\circ\text{C}$  in air. This result suggests either that the actual temperature was significantly higher than  $650^\circ\text{C}$  or that oxidation was accelerated by constituents of the flue gases.

Conclusions. The most probable cause of accelerated corrosion was sulfidation-oxidation, because sulfur was identified at various locations in the corrosion product and in the region of grain boundary attack of the alloy. Corrosion may have been further enhanced by chlorides.

### Aluminum-Remelt, Steel-Forge, Steel-Reheat, and Steel-Soaking-Pit Furnaces

J. I. Federer, T. N. Tiegs, D. M. Kotchick, and D. Petrak, *Analysis of Candidate Silicon Carbide Recuperator Materials Exposed to Industrial Furnace Environments*, ORNL/TM-9697, July 1985 (ref. 16).

Materials. The compositions of the following SiC ceramics are shown in Table A.1 of the Appendix: sintered alpha (Hexoloy SA), sintride, NC-400, NC-430, SC-X, KT, C/75, and CN-178. Alumina AD-998 and mullite were also included in one furnace exposure.

Exposure Conditions. Six industrial furnaces were used for exposure tests: two aluminum-remelt furnaces (Fig. 7), a steel-forge furnace, a steel-reheat furnace, and two steel-soaking pits. All six furnaces burned natural gas. The combustion products contained constituents of the materials and refractories being heated. Deposits on the specimens in the aluminum-remelt furnaces (Fig. 8) contained substantial amounts of Al, Fe, K, Na, Si, and Zn and other elements in lesser amounts. The combustion products probably also contained halide species, which were derived from fluxes. Deposits on specimens in a steel-soaking pit contained major amounts of Cr, Fe, and Si and substantial amounts of Ca, Cu, K, Mn, Na, and Ni. These elements evidently derived from the steel billets and topping compounds. No substantial deposits formed on specimens exposed to the steel-forge furnace, steel-reheat furnace, and the other steel-soaking pit. Either the atmospheres were cleaner in those three furnaces or the specimens were in protected locations. Exposure temperatures and times were:

<u>Furnace</u>	<u>Temperature (°C)</u>	<u>Duration (h)</u>
Aluminum-remelt No. 1	1040	5545
Aluminum-remelt No. 2	1150	530
Steel-forge	1175	4440
Steel-reheat	1150	1455
Steel-soaking pit No. 1	925	2280
Steel-soaking pit No. 2	1250	3460

Results. Aluminum-remelt furnaces — SiC ceramics:

1. Glassy and loosely adhering coating in No. 1, glassy coating only in No. 2.
2. Surface recession in SiC ceramics of 0.1 to 0.6 mm/year linearly projected from 0.6-year exposure.
3. Flexural strength decreases of sintered alpha SiC and NC-430, the only materials tested, attributed to corrosion and/or thermal history.

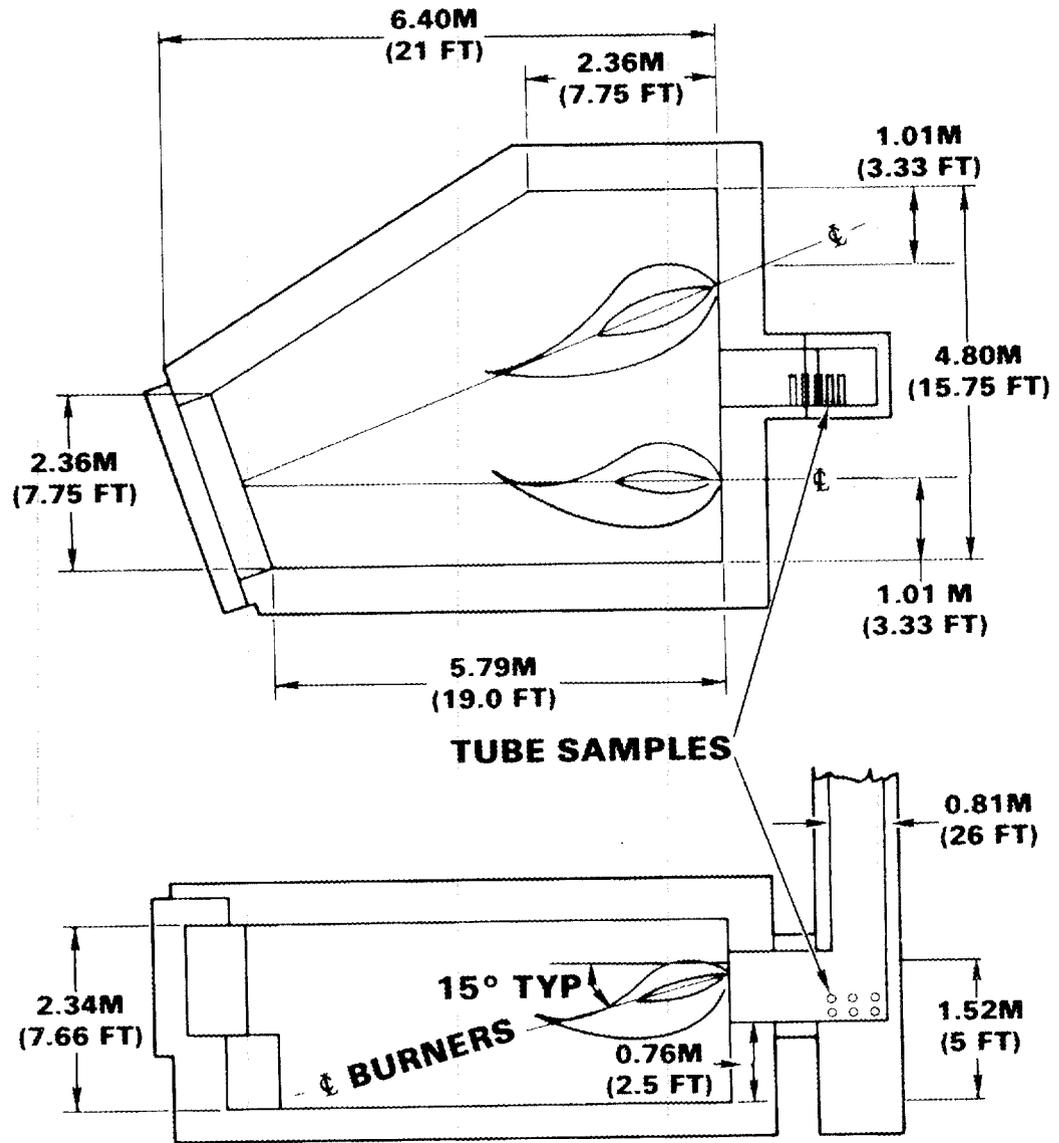


Fig. 7. Aluminum-remelt furnace used for exposure test.

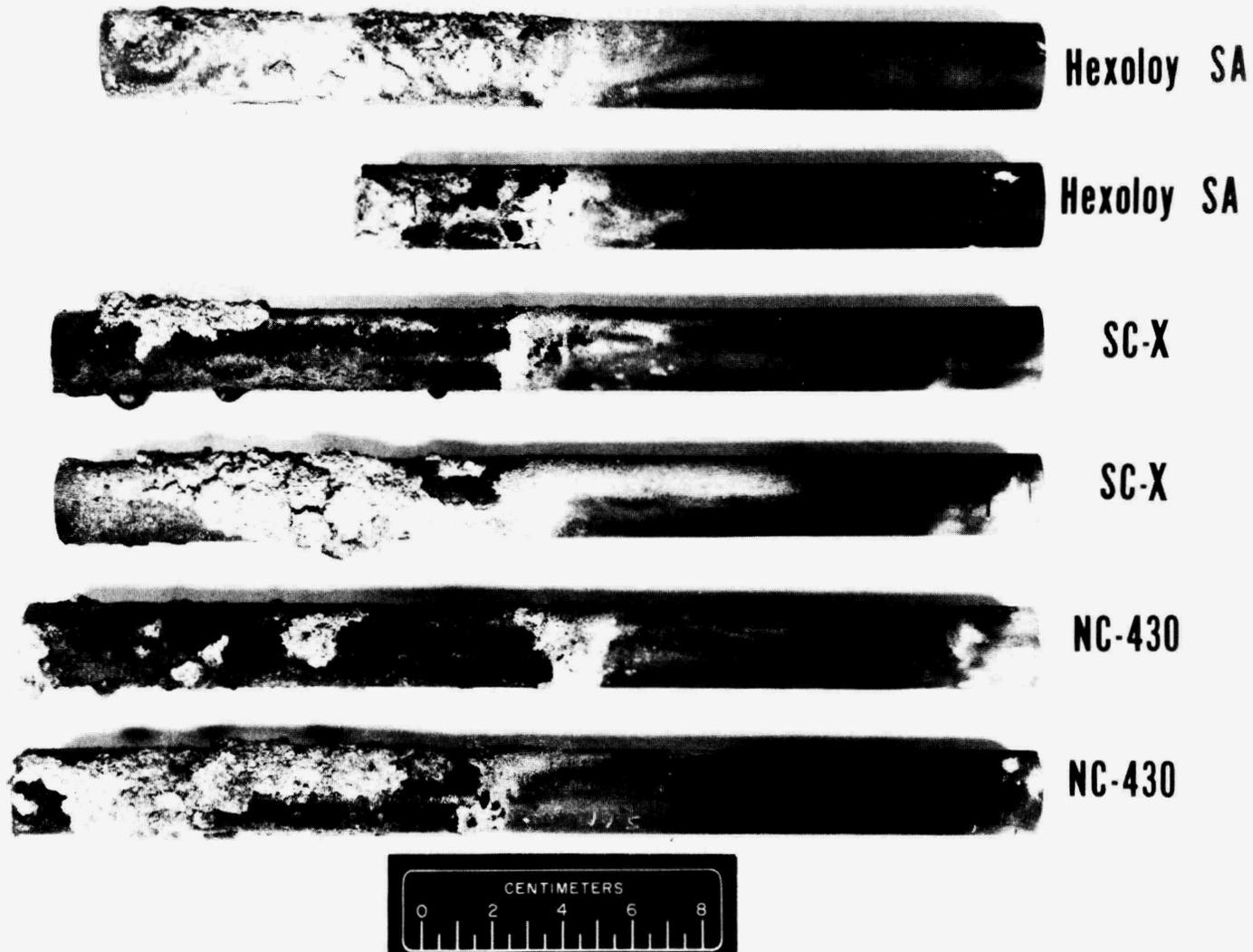


Fig. 8. SiC ceramics exposed to aluminum-remelt furnace environment for 5545 h at a maximum temperature of 1040°C.

4.  $\text{Si}_3\text{N}_4$ -bonded SiC ceramics (C/75 and CN-178) cracked, deformed, and had significant surface recession.

Aluminum remelt furnace No. 1-oxide ceramics:

1. Alumina AD-998 broke during the exposure, apparently because of thermal shock.
2. Neither alumina nor mullite was significantly corroded.

Steel-forge and steel-reheat furnaces — SiC ceramics:

1. No deposits on specimens.
2. Little or no surface recession except for NC-430 in steel-reheat furnace.

Steel-soaking pits — SiC ceramics:

1. No deposits or surface recession in No. 1.
2. Extensive slag deposits and surface recession (3.5–6.8 mm/year) in No. 2.  
Evidence was found for participation of iron and nickel in the corrosion process.

Conclusions. Environments in the aluminum-remelt furnace were very corrosive to SiC ceramics. Halide attack was suspected to be the corrosion mechanism. Alumina and mullite, however, were almost unaffected.

The environments in the steel-forge and steel-reheat furnaces did not significantly affect SiC ceramics.

SiC ceramics were not corroded by exposure to flue gases in one soaking pit, possibly because of a protected location. Extensive corrosion in the other soaking pit was caused by a combination of high temperature and particularly aggressive silicate slag containing iron and nickel.

#### Aluminum-Remelt Furnace

J. I. Federer and P. J. Jones, *Oxidation/Corrosion of Metallic and Ceramic Materials in an Aluminum Remelt Furnace*, ORNL/TM-9741, December 1985 (ref. 17).

Materials. The compositions of the following materials are shown in Tables A.1 and A.2 of the Appendix.

1. Metallic alloys:
  - a. type 316 stainless steel,

- b. type 310 stainless steel,
  - c. type 446 stainless steel,
  - d. Alloy 800,
  - e. Inconel 601,
  - f. Inconel 625,
  - g. Hastelloy X,
  - h. Hastelloy N,
  - i. Alloy 214,
  - j. Haynes 25,
  - k. Haynes 188.
2. Coatings:
- a. aluminum coatings on some of the above alloys,
  - b. SiO<sub>2</sub> coatings on some of the above alloys.
3. SiC ceramics:
- a. sintered alpha,
  - b. NC-430,
  - c. Refel,
  - d. Refrax 20.
4. Oxide ceramics:
- a. alumina AD-998,
  - b. mullite.

Exposure Conditions. Conditions included air at 1000 and 1100°C for about 1000 h (alloys only), and aluminum-remelt furnace flue gases and particulates containing Al, Ca, Cl, Fe, K, Na, Ni, S, Si, Ti, Zn, and other elements at 1000 to 1150°C for up to 4400 h.

Results. For the alloys, air oxidation caused surface scales, sub-surface porosity (or oxidation), and intergranular attack in some alloys. Aluminum coatings generally protected the alloys against oxidation, but SiO<sub>2</sub> coatings detached and were not protective. Uncoated Inconel 625 corroded by intergranular attack at a projected rate of 2.6 mm/year in an aluminum-remelt furnace (Fig. 9). Aluminum-coated Inconel 625 corroded more slowly (1.2 mm/year) in an aluminum-remelt furnace. Aluminum coatings did not consistently protect alloys in an aluminum-remelt furnace; SiO<sub>2</sub> coatings detached and provided no protection.

For the ceramic materials, SiC ceramics corroded at a projected rate of about 0.5 mm/year in an aluminum-remelt furnace. Alumina was

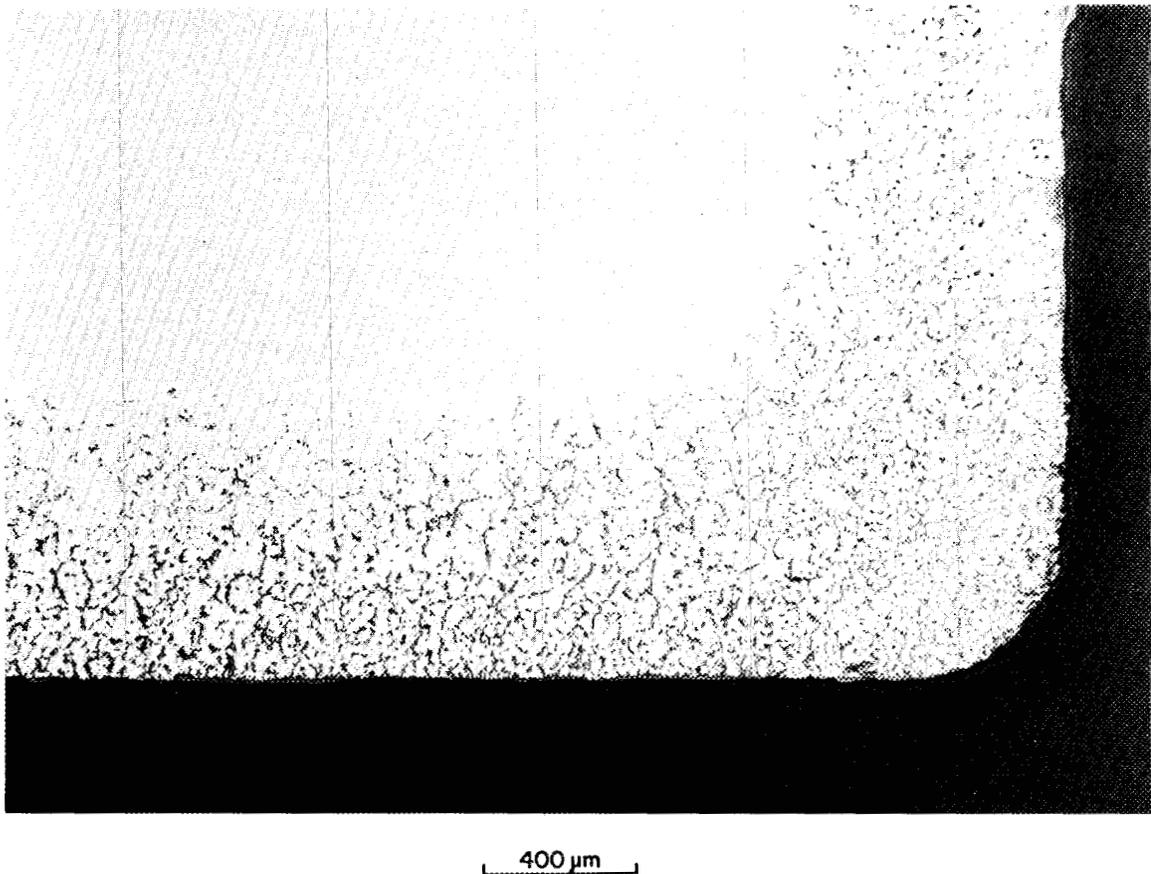


Fig. 9. Uncoated Inconel 625 exposed to aluminum-remelt furnace flue gases for 2250 h at a maximum temperature of 1000 to 1150°C. As polished.

essentially unaffected, but millite had a thin reaction layer (0.2mm/year) as a result of exposure to an aluminum-remelt furnace.

Conclusions. Concerning use of materials in an aluminum-remelt furnace, uncoated metallic alloys are only marginally suitable for high-temperature use because of scale formation and intergranular corrosion. Aluminum coatings, which provided variable protection against corrosion, need to be optimized for performance. SiC ceramics, which corroded less than the alloys, are better candidate materials for high-temperature applications. Oxide ceramics, which corroded even less than SiC ceramics, are also good candidates.

#### TEST FURNACE BURNING INDUSTRIAL FUELS

Exposure tests have been conducted in a Refractory Test Facility (RTF), a furnace designed to burn industrial fuels such as natural gas,

No. 2 distillate oil, No. 6 residual oil, and coal-oil mixtures. Most exposure tests have been conducted with the latter two fuels because of their relatively high ash content. The RTF and Integral Ceramic Recuperator Analysis Facility (CRAF) have been used to conduct exposure tests of a wide variety of furnace refractories (bricks, mortars, and castables), refractory fiber insulations, and structural ceramics for recuperator applications.

#### Refractory Test Facility

A. E. Pasto and V. J. Tennery, *Effects of Alternate Fuels Refractory Test Facility (RTF) Test 1, Analysis of Selected Aluminosilicate Refractory Bricks, Mortars, and Fibrous Insulations Degraded by Domestic Residual Oil Combustion Products*, ORNL/TM-6351, June 1978 (ref. 18).

Materials. The materials tested were high-alumina and aluminosilicate bricks, mortars, and fibrous insulations containing 46 to 97 wt %  $\text{Al}_2\text{O}_3$  as shown below.

<u>Material</u>	<u>Nominal composition (wt %)</u>		
	<u><math>\text{Al}_2\text{O}_3</math></u>	<u><math>\text{P}_2\text{O}_5</math></u>	<u><math>\text{SiO}_2</math></u>
High-alumina brick	90		9
Phosphate-bonded mortar	Major	5	10
Mullite-based brick	46		50
Mullite-based mortar	Major		Major
High-alumina fiber	97		1.5
Medium-alumina fiber	54		45

Exposure Conditions. The materials were exposed to the combustion products of residual oil for 500 h at 1375°C. The fuel oil impurities included Fe, Ca, Zn, Ni, Pb, and S in concentrations from tens to hundreds of weight ppm.

Results. Significant reactions between the materials and several fuel impurities occurred. A mixed layer of crystalline and glassy reaction products formed on original surfaces. The more reactive impurities were Fe, Ca, and Zn. These impurities reacted with the major silicate phases in the materials to form glassy silicate phases and with alumina and mullite to form Fe-Zn-Al oxide spinel and hercynite ( $\text{FeAl}_2\text{O}_4$ ).

Conclusions. Alumina, both pure and combined with silica as mullite, reacts with iron and zinc to form spinels. Calcium reacted with silica and alumina to form a glassy phase. Materials with high  $\text{Al}_2\text{O}_3/\text{SiO}_2$  ratios did not perform better than materials with low ratios in this environment.

#### Refractory Test Facility

J. I. Federer and V. J. Tennery, *Effects of Alternate Fuels Refractory Test Facility (RTF) Test 2: Evaluation of Magnesia-Based Bricks and Mortar and Alumina-Based Bricks, Castables, and Fibrous Insulations Exposed to Residual Oil Combustion Products*, ORNL/TM-6840, March 1980 (ref. 19).

Materials. Bricks, mortar, castables, and fiber insulations with the nominal compositions shown below were tested:

<u>Material</u>	<u>Nominal composition (wt %)</u>					
	<u><math>\text{Al}_2\text{O}_3</math></u>	<u>CaO</u>	<u><math>\text{Cr}_2\text{O}_3</math></u>	<u><math>\text{Fe}_2\text{O}_3</math></u>	<u>MgO</u>	<u><math>\text{SiO}_2</math></u>
MgO-based brick	20	0.6	24	11	41	3
MgO-based brick	10	0.6	12	6	69	2
High-MgO brick	0.2	0.8	0.1	1	91	6
MgO-based mortar	2	1	<0.1	1	79	15
Spinel brick	69	0.2	<0.1	<0.1	29	1
High-alumina brick	>99	<0.1	<0.1	0.2	<0.1	0.2
High-alumina castable	96	3	<0.1	<0.1	<0.1	0.2
Alumina-based castable	60	3	<0.1	0.7	0.5	34
High-alumina fiber	97	<0.1	<0.1	<0.1	<0.1	3
Alumina-based fiber	60	<0.1	<0.1	<0.1	<0.1	40

Exposure Conditions. Specimens were exposed to the combustion products of No. 6 residual oil at 1375°C for 510 h. The oil contained high concentrations of V, Si, Ni, P, Na, Fe, Mg, and S.

Results. MgO-based bricks and mortar were extensively cracked and had an increase in NiO and  $\text{V}_2\text{O}_5$  contents. No new compounds were identified.

Alumina-magnesia spinel brick had an increase in Fe, Ni, and V contents.  $\text{NiAl}_2\text{O}_4$  and possibly  $\text{FeAl}_2\text{O}_4$  were identified as new phases.

High-alumina castable had an increase in Fe, Ni, and V contents.  $\text{AlVO}_4$  was identified as a new phase.

Alumina-based castable had an increase in Na, Ni, and V contents.  $\text{AlVO}_4$  and  $\text{CaAl}_2\text{Si}_2\text{O}_8$  were identified as new phases.

High-alumina fiber insulations had an increase in Ca, Fe, K, Mg, Na, Ni, and V contents.  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ,  $\text{AlVO}_4$ ,  $\text{NiAl}_2\text{O}_4$ ,  $\text{MgAl}_2\text{O}_4$ , and  $\text{FeAl}_2\text{O}_4$  were identified as new phases.

Alumina-based fiber insulation had an increase in Ca, Fe, Mg, Na, Ni, Ti, and V contents.  $\text{FeAl}_2\text{O}_4$  was identified as a new phase.

Conclusions. None of the refractories were seriously degraded by fuel-oil combustion products in this test; however, because new compounds containing combustion products formed in the alumina refractories and insulations, a longer exposure time might result in serious degradation. Extensive cracking of MgO-based refractories and some cracking in  $\text{Al}_2\text{O}_3$ -containing refractories were caused by thermal shock.

#### Refractory Test Facility

J. I. Federer and V. J. Tennery, *Effects of Alternate Fuels Refractory Test Facility Test 3: Part 2. Analysis of Magnesia- and Alumina-Based Dense Refractories Exposed to the Combustion Products of No. 6 Residual Oil*, ORNL/TM-7284, July 1980 (ref. 20).

Materials. Bricks, mortar, and castables with the following nominal compositions were tested.

<u>Material</u>	<u>Nominal composition (wt %)</u>					
	$\text{Al}_2\text{O}_3$	CaO	$\text{Cr}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	MgO	$\text{SiO}_2$
Low-MgO brick	20	0.6	24	11	41	3
Medium-MgO brick	10	0.6	12	6	69	2
High-MgO brick	0.2	0.8	0.1	1	91	6
Chrome mortar	29	0.9	31	16	15	
Alumina brick	>99	<0.1		0.2	<0.1	0.2
High-alumina brick	91	<0.1		0.2	<0.1	9
Low-alumina brick	42	0.6		1	0.3	52
Calcia-bonded castable	97	2		0.2	0.1	0.6
Calcia-bonded castable	93	5		0.1	0.2	1
Silica-bonded castable	66	5		0.7	0.1	26

Exposure Conditions. Specimens were exposed to the combustion products of No. 6 residual oil for 500 h at 1375°C. The oil contained 1.3 wt % S, 37 ppm Na, 27 ppm Mg, 23 ppm V, 21 ppm P, 17 ppm Fe, 16 ppm Ni, and 11 ppm Ti.

Results. MgO-based bricks were discolored, had obvious cracks and a network of fine cracks, and had an increase in nickel and vanadium contents. Chrome mortar had several cracks and an increase in nickel content. Al<sub>2</sub>O<sub>3</sub>-based bricks and castables were discolored and had an increase in nickel content. There was no significant degradation of any of the materials.

Conclusions. The combustion products did not significantly degrade any of the refractories because of the relatively low concentrations of impurities in the No. 6 oil.

#### Ceramic Recuperator Analysis Facility

G. C. Wei and V. J. Tennery, *Evaluation of Tubular Ceramic Heat Exchanger Materials in Residual Oil Combustion Environment*, ORNL/TM-7578, March 1981 (ref. 21).

Materials. The compositions of the following materials are shown in Table A.1 of the Appendix.

1. SiC ceramics:
  - a. Refel,
  - b. KT,
  - c. NC-430,
  - d. sintered alpha,
  - e. CVD SiC,
  - f. CVD SiC on NC-400,
  - g. Carbofrax M,
  - h. Carbofrax A,
  - i. Refrax 20.
2. Oxide ceramics:
  - a. alumina AD-998,
  - b. mullite,
  - c. zirmul,
  - d. cordierite MAS 8200,
  - e. cordierite MAS 8400.

Exposure Conditions. Tubular specimens were exposed to the combustion products of No. 6 residual oil derived from Venezuelan crude oil. The specimens were tested as heat exchanger elements with air flowing through the inside and flue gases flowing perpendicular to the long axes of the tubes. The major impurities in the No. 6 oil were approximately 2.7 wt % S, 80 ppm each Na and V, 45 ppm each P and S, 10 ppm Ni, and 1 to 5 ppm each Ca, Fe, K, Mg, and Zn. The total amount of oil used was about 36 m<sup>3</sup> (9800 gal or 35 Mg). The temperature was approximately 1200°C with five cycles to about 400°C. The test duration was 500 h.

Results. SiC ceramics had smooth nodules 5 to 20 mm in size on the upstream side. Major elements in the nodules were 1 to 3 wt % each Al, Ba, Fe, La, Na, Ni, Si, and V and 30 to 49 wt % O.

Although SiC ceramics were not obviously degraded, some effects of the exposure were found. KT was deformed and CVD SiC was cracked. Helium permeability increased several orders of magnitude in some types. Flexural strength at room temperature increased in some types, decreased in others. Fe and Ni in the combustion products reacted with the siliconized SiC materials to form Fe-Ni-Si compounds. Active oxidation probably occurred at the interface between SiC and nodule due to the low oxygen partial pressure, which favors formation of volatile SiO.

Oxide ceramics had thin dark deposits and were cracked. Major elements in the deposits were Mg, Al, Si, Ca, V, Fe, and Ni. Helium permeability increased substantially as a result of cracks. Hercynite (FeO·Al<sub>2</sub>O<sub>3</sub>) typically formed at the surface.

Conclusions. Sintered alpha and siliconized SiC ceramics and high-purity alumina (AD-998) are suitable materials for heat exchanger applications where corrosion by No. 6 oil combustion products and thermal shock are involved. Mullite, cordierite, and zirmul are less suitable because of extensive cracking.

#### Ceramic Recuperator Analysis Facility

M. K. Ferber and V. J. Tennery, *Evaluation of Tubular Ceramic Heat Exchanger Materials in Acidic Coal Ash from Coal-Oil-Mixture Combustion*, ORNL/TM-7958, December 1981 (ref. 22).

Materials. The compositions of the following materials are shown in Table A.1 of the Appendix: sintered alpha, KT, and CVD SiC ceramics; alumina AD-998; and sialon.

Exposure Conditions. Tubular specimens were exposed to the combustion products of a test furnace burning a coal-oil mixture (Fig. 10). The specimens were tested as heat exchanger elements with air flowing through the inside and flue gases flowing perpendicular to the long axes of the tubes. The coal ash had the following approximate composition in equivalent oxides: 51 wt % SiO<sub>2</sub>, 24 wt % Al<sub>2</sub>O<sub>3</sub>, 16 wt % Fe<sub>2</sub>O<sub>3</sub>, 2.7 wt % CaO, 1.7 wt % SO<sub>3</sub>, 1.6 wt % K<sub>2</sub>O, 0.7 wt % MgO, 0.6 wt % TiO<sub>2</sub>, 0.5 wt % Na<sub>2</sub>O, 0.3 wt % P<sub>2</sub>O<sub>5</sub>, and a base/acid ratio of 0.29. The slag (ash) that deposited on specimens was evidently fluid at the exposure temperature of about 1200°C. The exposure time was 496 h.

Results. All samples were covered with slag (Fig. 11). A difference in coefficient of thermal expansion between the strongly bonded slag and the alumina and sialon specimens apparently caused extensive cracking in those materials, preventing any posttest flexural testing.

The SiC specimens were not significantly degraded. Flexural strengths decreased slightly in the case of CVD SiC and sintered alpha SiC. An 11% increase in flexural strength of KT SiC was attributed to flaw blunting.

Conclusions. SiC ceramics are excellent candidates for heat exchanger materials exposed to acidic coal ash (slag). Alumina and sialon are lesser candidates because of cracking associated with the tightly adhering slag.

#### Refractory Test Facility

J. I. Federer, *Analysis of Refractory Fiber Insulations and Hot Face Coatings Exposed to Coal-Oil Mixture Combustion Products*, ORNL/TM-8243, July 1982 (ref. 23).

Materials. The materials tested were aluminosilicate fiber insulations containing 42 to 77 wt % Al<sub>2</sub>O<sub>3</sub>; aluminosilicate hot-face coatings containing 43 to 78 wt % Al<sub>2</sub>O<sub>3</sub>; phosphate-bonded hot-face coatings containing approximately 85 wt % Al<sub>2</sub>O<sub>3</sub>, 8 wt % Cr<sub>2</sub>O<sub>3</sub>, and 5 wt % P<sub>2</sub>O<sub>5</sub>; and a zirconium silicate hot-face coating containing 62 wt % ZrO<sub>2</sub>.

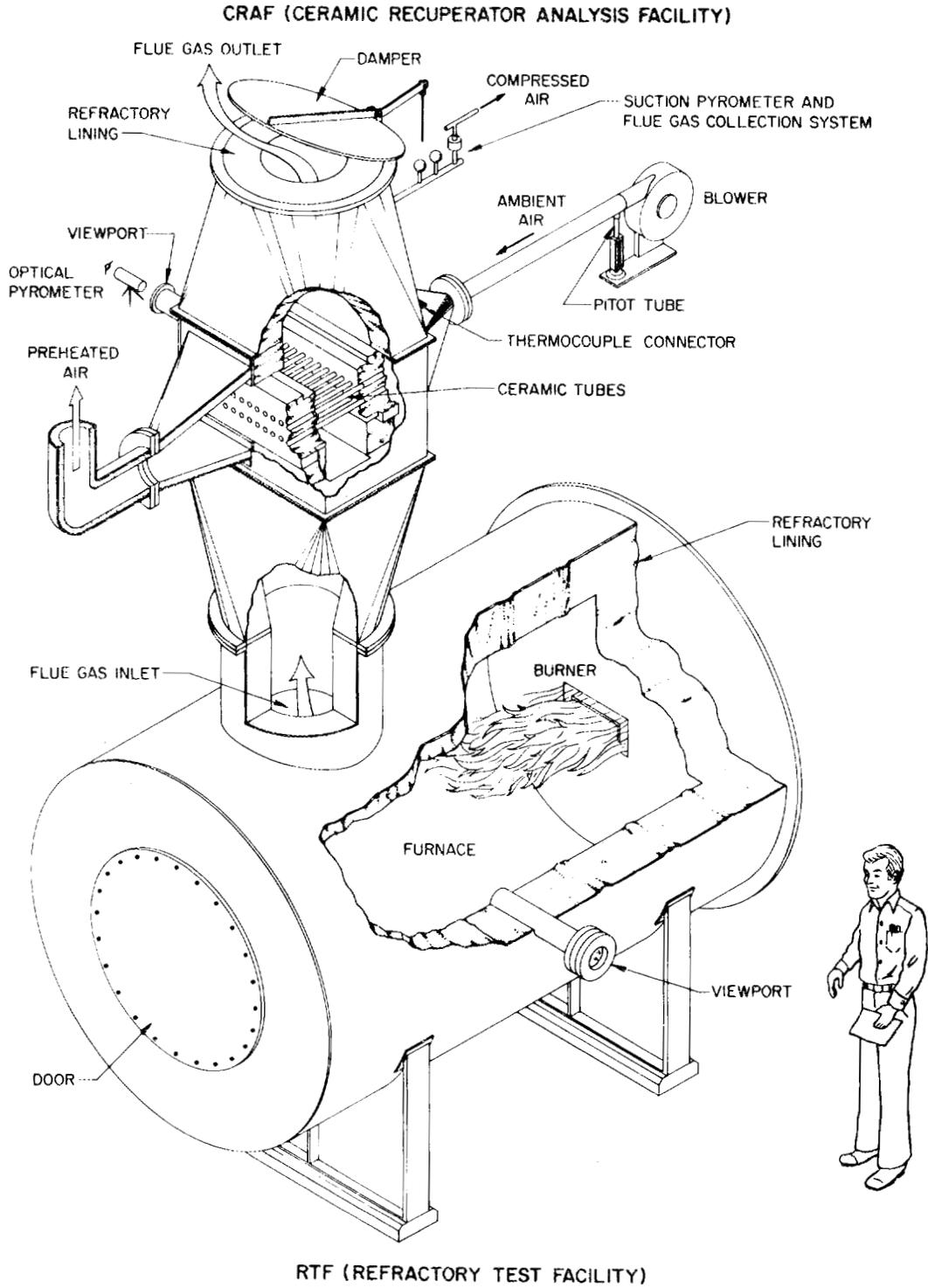


Fig. 10. Refractory Test Facility (furnace) and Ceramic Recuperator Analysis Facility.

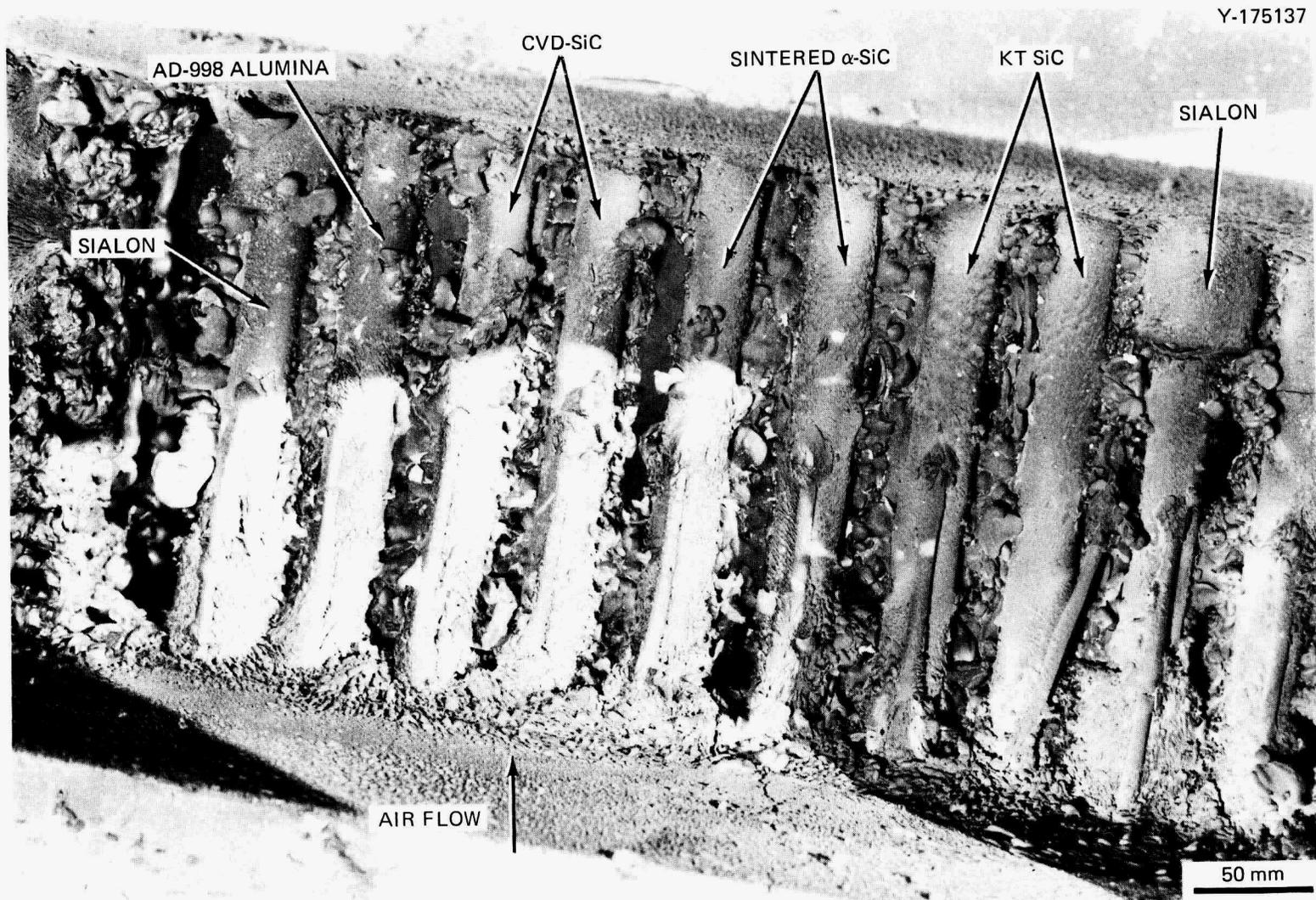


Fig. 11. Downstream surfaces of ceramic tubes after exposure to combustion products of a coal-oil mixture for 496 h at 1200°C.

Exposure Conditions. Fiber insulation modules with and without hot-face coatings were exposed to the combustion products of a coal-oil mixture for 500 h at 1375°C. Major impurities in the coal-oil mixture were Al, Si, Fe, P, K, and S, and minor impurities were Mg, Na, Ni, Ti, and V.

Results. For the aluminosilicate fiber insulations (uncoated), the reaction layer on the hot face was about 1 mm thick and consisted mostly of a glassy phase containing Al, K, Ca, Ti, Fe, and Si. The  $\text{Al}_2\text{O}_3$  content in the reaction layers decreased, but the  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{NiO}$ , and  $\text{TiO}_2$  contents generally increased. No new crystalline phases were detected.

For the hot-face coatings, aluminosilicate coatings had higher concentrations of  $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ , and  $\text{MgO}$ . Phosphate-bonded alumina coatings had higher concentrations of  $\text{Fe}_2\text{O}_3$  and  $\text{K}_2\text{O}$ . The zirconium silicate coating had higher concentrations of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{K}_2\text{O}$  and lower  $\text{ZrO}_2$ . All hot-face coatings (except the zirconium silicate) consisted of crystalline phases associated with a glass phase containing fuel impurities.

Conclusions. Serious degradation of fiber insulations did not occur. Uncoated fiber insulations degraded no more than coated insulations. Microstructural changes and compositional changes occurred in the hot face of uncoated insulations and in the hot-face coatings; those changes might result in more serious degradation during longer exposures.

#### Ceramic Recuperator Analysis Facility

M. K. Ferber and V. J. Tennery, *Evaluation of Tubular Ceramic Heat Exchanger Materials in Basic Coal Ash from Coal-Oil-Mixture Combustion*, ORNL/TM-8385, October 1982 (ref. 24).

Materials. The compositions of the following materials are shown in Table A.1: sintered alpha, KT, SC-2, NC-430, CVD, and CVR SiC ceramics; alumina AD-998; and GE-128, GE-129, and GE-130 sialons.

Exposure Conditions. Tubular specimens were exposed to the combustion products of a test furnace burning a coal-oil mixture. The specimens were tested as heat exchanger elements with air flowing through the inside and flue gases flowing perpendicular to the long axis of the tubes. The slag resulting from combustion had the following approximate composition of equivalent oxides: 46 wt %  $\text{SiO}_2$ , 19 wt %  $\text{CaO}$ , 14 wt %  $\text{Al}_2\text{O}_3$ ,

11 wt % Fe<sub>2</sub>O<sub>3</sub>, 7 wt % MgO, 1 wt % Na<sub>2</sub>O, 0.5 wt % each K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, and NiO, 0.13 wt % TiO<sub>2</sub>, 0.2 wt % SrO plus BaO, 0.06 wt % SO<sub>3</sub>, 0.03 wt % V<sub>2</sub>O<sub>5</sub>, and a base/acid ratio of 0.63. The slag was fluid at the exposure temperature, approximately 1200°C. The exposure time was 240 h.

Results. All specimens were covered with a slag deposit, which was generally thicker on the upstream side (Fig. 12).

The GE-128 and one of the SC-2 specimens were broken as a result of the exposure. The CVD SiC had a crack traversing almost the full length of the specimen.

All specimens exhibited surface recession, the maximum amount usually on the upstream side, as shown below. The room-temperature fracture strength of all materials tested was lower after the exposure as shown below.

<u>Material</u>	<u>Surface recession (mm)</u>	<u>Mean fracture strength decrease (%)</u>
CVR SiC	0.33	16
CVD SiC	0.43	
Sintered alpha SiC	0.52	3
SC-2 SiC	0.95	61
KT SiC	1.04	47, <sup>a</sup> 60 <sup>b</sup>
NC-430 SiC	1.29	38
Alumina AD-998	0.41	28
Sialon GE-128	2.99	
Sialon GE-129	2.37	
Sialon GE-130	0.91	

<sup>a</sup>Thin wall.

<sup>b</sup>Thick wall.

Discussion. Corrosion of SiC ceramics was attributed to formation of iron and nickel silicides at the slag-ceramic interface. The silicides subsequently detached from the SiC and eventually dissolved in the fluid slag. The AD-998 alumina corroded by formation of iron-nickel aluminate, which subsequently dissolved in the slag. Corrosion of SiC ceramics and AD-998 alumina produced microscopically rough surfaces, which contributed to reductions in room-temperature fracture strengths.

Conclusions. On the basis of surface recessions on the upstream side of the tube specimens, none of the materials have sufficient corrosion resistance to serve as heat-exchanger elements under high-temperature fluid basic coal slag conditions, unless very thick sections are used.

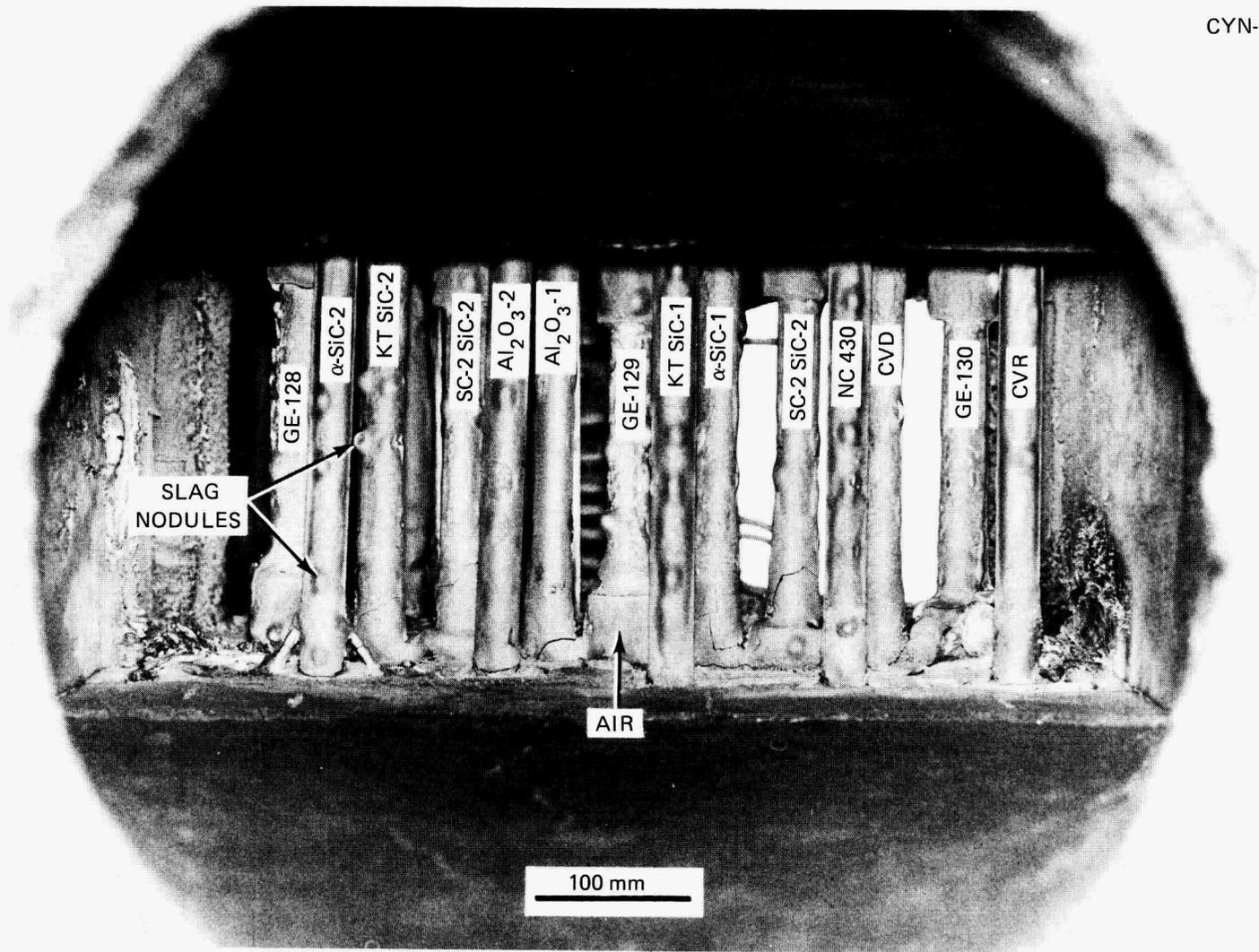


Fig. 12. Upstream surfaces of ceramic tubes after exposure to combustion products of a coal-oil mixture for 240 h at 1200°C.

## LABORATORY FURNACES

A few exposure tests have been conducted in laboratory furnaces for the purpose of studying the effects of specific potential corrodents on materials. Specimens were exposed to synthetic combustion atmospheres containing unknown concentrations of potential corrodents at temperatures of interest to heat exchangers. The advantages of this type of test, compared with tests in an industrial furnace, are that exposure conditions are well known and corrosion mechanisms are more easily identified.

### Synthetic Combustion Atmosphere

J. I. Federer, *Corrosion of Fluidized-Bed Boiler Materials in Synthetic Flue Gas*, ORNL/TM-8819, November 1983 (ref. 25).

Materials. The compositions of the following materials are shown in Table A.2 of the Appendix: plain carbon steel, type 405 stainless steel, type 316 stainless steel, and Alloy 800.

Exposure Conditions. A gas mixture containing approximately 79 vol % N<sub>2</sub>, 17 vol % O<sub>2</sub>, 2 vol % each CO<sub>2</sub> and H<sub>2</sub>O, and 0.01 vol % each Cl<sub>2</sub> and HCl was used. Specimens were exposed to different temperatures depending on their composition and intended application:

<u>Material</u>	<u>Exposure temperature (°C)</u>
Plain carbon steel	240-560
Type 405	220-560
Type 316	625-660
Alloy 800	605-665

Results. Specimens had oxide scales that increased in thickness with increasing exposure temperature. The scales on the carbon steel and type 405 stainless steel contained hematite (Fe<sub>2</sub>O<sub>3</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>), and those on type 316 and Alloy 800 contained hematite, chromia (Cr<sub>2</sub>O<sub>3</sub>), and chromite (FeCr<sub>2</sub>O<sub>4</sub>).

Corrosion rates projected from the 3000-h exposure were:

<u>Material</u>	<u>Corrosion rate (mm/year)</u>	<u>Exposure temperature (°C)</u>
Plain carbon steel	0.04 - 0.59	240-560
Type 405	0.03 - 0.08	220-560
Type 316	0.17 - 0.22	625-660
Alloy 800	0.08 - 0.13	605-665

Conclusions. Corrosion was caused by air oxidation. Halides in the environment were not directly related to corrosion.

Synthetic Combustion Atmosphere

J. I. Federer, J M Robbins, P. J. Jones, and C. Hamby, Jr., *Corrosion of SiC Ceramics in Synthetic Combustion Atmospheres Containing Halides*, ORNL-6258, December 1985 (ref. 26).

Materials. The SiC ceramics tested were sintered alpha (>99 wt % SiC), NC-430 (~90 wt % SiC, 10 wt % Si), and RSSC (~88 wt % SiC, 12 wt % Si).

Exposure Conditions. Three different test atmospheres were used. In each case a halide species was added to a synthetic combustion atmosphere (SCA) representing combustion of natural gas: 77 wt % N<sub>2</sub>, 13 wt % CO<sub>2</sub>, 11 wt % H<sub>2</sub>O, and 2 wt % O<sub>2</sub>. The test atmospheres were designated SCA-HCl (0.6 wt % HCl), SCA-NaCl (0.1 wt % NaCl), and SCA-NaF (0.1 wt % NaF). Specimens were exposed to these atmospheres at 1200°C for approximately 1000 h in the apparatus shown schematically in Fig. 13.

Results. Specimens exposed to SCA-HCl were not significantly degraded.

Specimens exposed to SCA-NaCl and SCA-NaF had a glassy coating and were corroded (Fig. 14). The glassy coating contained approximately 48 wt % Si, 3 wt % Na, 2 wt % Al, and the balance mostly O; the principal crystalline phase was SiO<sub>2</sub> (tridymite). Projected corrosion rates were approximately 1.2 mm/year.

Flexural strengths were not significantly decreased by exposure to any of the atmospheres. In fact, some increased.

Conclusions. SiC is not corroded by HCl in an oxidizing combustion atmosphere. SiC is corroded by NaCl and by NaF in an oxidizing combustion atmosphere. Corrosion by SCA-NaCl and SCA-NaF involved formation of a volatile Si species.

## DISCUSSION

The summaries that have been presented describe the results of exposure of a wide variety of commercially available refractories, refractory

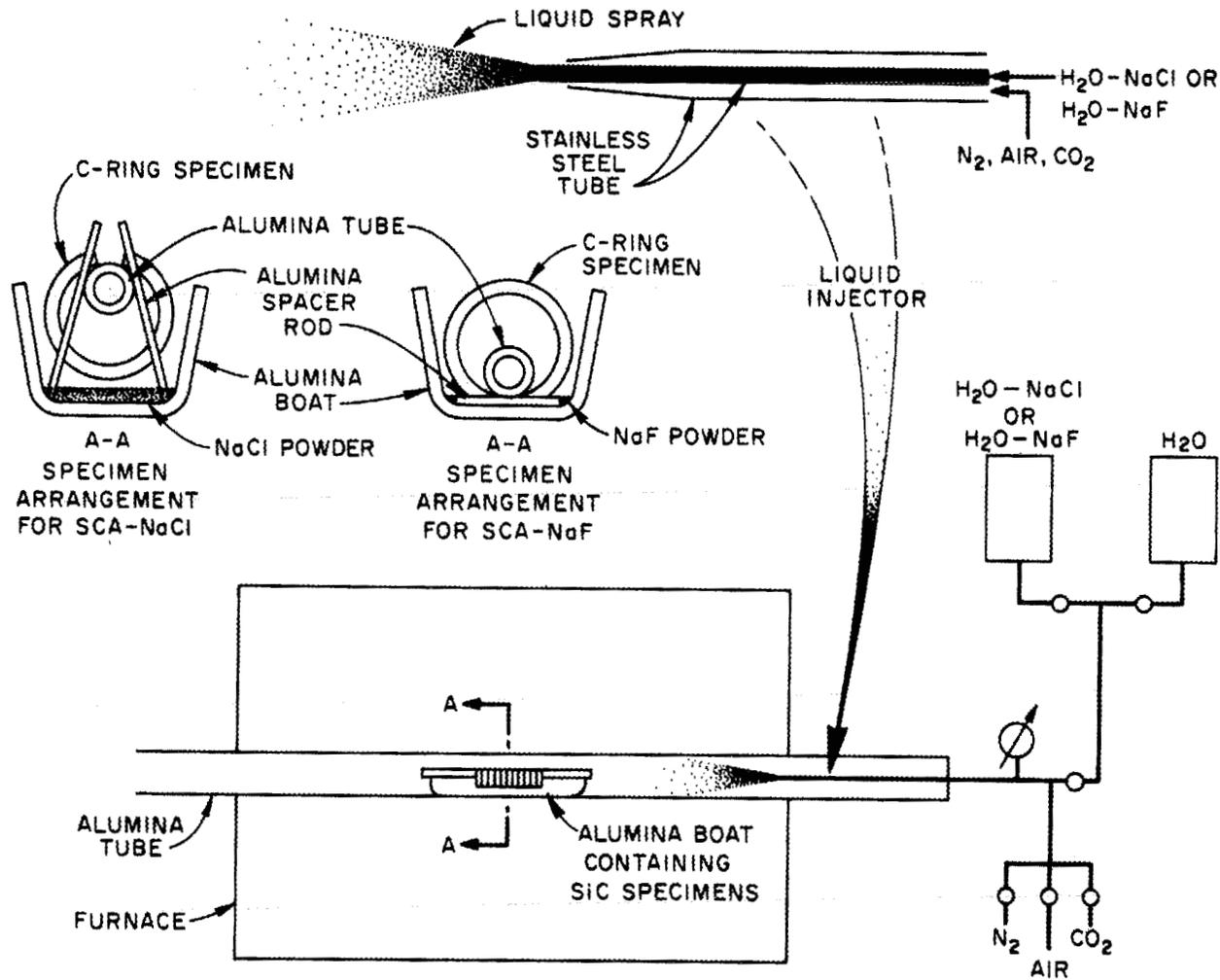


Fig. 13. Apparatus for exposing C-ring specimens of SiC ceramics to synthetic combustion atmospheres.

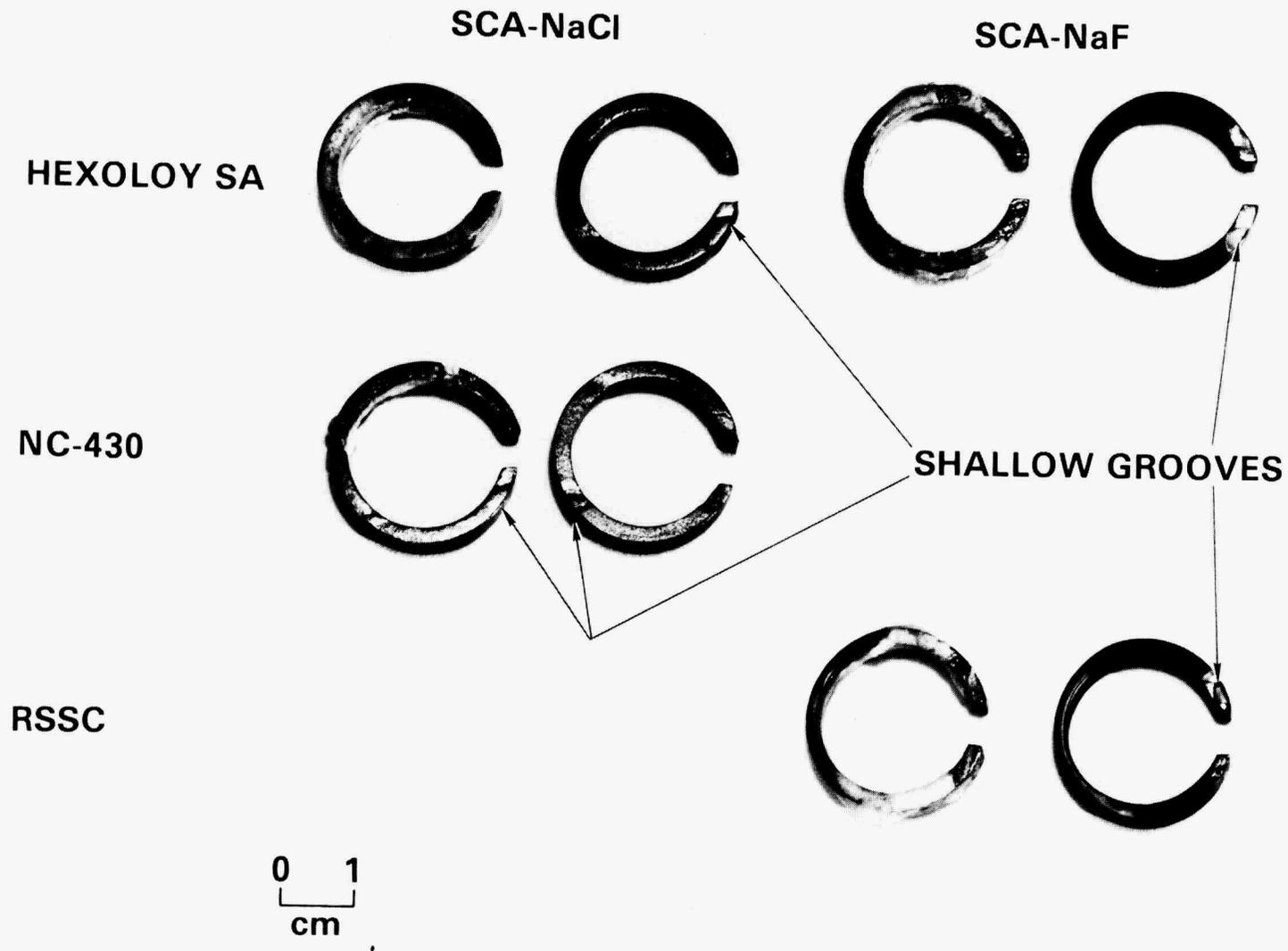


Fig. 14. SiC ceramics after exposure to SCA-NaCl and SCA-NaF for 1000 h at 1200°C.

fiber insulations, structural ceramics, and metallic alloys to flue gas constituents. Many different reactions between materials and constituents of combustion environments have been identified or suggested by analysis of exposed specimens. In addition, several degradation mechanisms were observed that did not involve chemical reactions. A brief description of the degradation mechanisms described in the summarized reports is presented below. Other degradation mechanisms, not described herein, might also exist; their exclusion from this discussion simply means that they were not identified in the various analyses. The term degradation, as used here, refers to mechanisms that would eventually destroy the material or prevent the material from providing the intended function.

## DEGRADATION MECHANISMS IN CERAMIC MATERIALS

### Chemical Reactions

Deposition of flue gas constituents on materials and their subsequent reaction with constituents of the materials can cause significant structural changes, loss of integrity, change in thermal conductivity, or gradual loss of material. The type and extent of reaction is time and temperature dependent. Examples of typical degradation mechanisms of this type follow.

Formation of Liquid Phases. Reaction of alkali oxides ( $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ) and  $\text{V}_2\text{O}_5$  with silica-based materials and aluminosilicates can cause formation of liquid phases and loss of structural integrity. Several low-melting compounds occur in the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ,  $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3-\text{V}_2\text{O}_5$  systems.<sup>27</sup> Formation of liquid phases was identified in several tests.<sup>6,7,8,11</sup>

Formation of Glassy Silicate Phases. Silica-based materials and aluminosilicates react with  $\text{SiO}_2$  and alkali oxides in the flue gases to form glassy silicate phases.<sup>8,9,18,23</sup> This reaction is similar to that described above except that the concentration of alkali oxides is insufficient to form liquid phases. The ceramic material gradually restructures as the glassy phase dissolves components such as mullite. The resulting structure has a lower melting point and is more susceptible to fluxing by alkali oxides.

Reaction of Components of Basic Slags with SiC. Slags with a base/acid ratio of 0.63 caused extensive surface recession of SiC, apparently by a dissolution process involving  $\text{Fe}_2\text{O}_3$  and NiO flue gas constituents.<sup>16,24</sup> Reaction of  $\text{Fe}_2\text{O}_3$  and NiO with SiC resulted in formation of iron and nickel silicides and possibly CO or other gases at the slag-SiC interface. The silicides eventually detached from the SiC and dissolved in the slag, possibly reforming  $\text{Fe}_2\text{O}_3$  and NiO to continue the process.

Lowered Viscosity of  $\text{SiO}_2$  film on SiC. Reaction of alkali oxides with the normally protective  $\text{SiO}_2$  film lowers the viscosity of the film. Enhanced oxygen diffusion through the altered film allows active oxidation to occur at the film-SiC interface by formation of gaseous SiO and CO, thereby causing surface recession of the SiC.<sup>12</sup>

Halide Attack. Halide fluxes and  $\text{Cl}_2$  gas are used to purify aluminum in scrap-remelting furnaces. Significant corrosion of SiC ceramics has been observed in these furnaces.<sup>16,17</sup> Laboratory experiments using NaCl or NaF in synthetic combustion atmospheres have shown that SiC ceramics are corroded by both halides in a manner similar to that in aluminum-remelt furnaces. The mechanism apparently involves formation of volatile silicon halides because the silicon content of the glass reaction layer was much less than the amount of SiC lost by reaction.<sup>26</sup>

Disruption by New Phases. Reaction of flue-gas constituents with ceramics often produces new phases. A new phase can cause stress and mechanical disruption of the affected region if its specific volume and coefficient of thermal expansion are significantly different from those of the original ceramic material. An example of this mechanism is the reaction of NiO fuel impurity with forsterite ( $2\text{MgO}\cdot\text{SiO}_2$ ) to form  $\text{MgNiSi}_2\text{O}_6$ , which involves a volume expansion of 188%. This mechanism caused mechanical disruption of chrome magnesite bricks.<sup>5</sup> High-MgO bricks were disrupted by precipitation of  $\text{Na}_2\text{SO}_4$ . The sodium and sulfur flue gas constituents diffused into MgO grains at high temperatures and subsequently precipitated as  $\text{Na}_2\text{SO}_4$  at lower temperatures.<sup>5</sup>

### Other Mechanisms

These mechanisms cause serious degradation of ceramic materials in the absence of any chemical reactions. Combination of one or more of these mechanisms with chemical reactions complicates interpretation of results of analysis of exposed materials.

Excessive Temperature. Excessive temperature can result in formation of liquid phases and loss of structural integrity. An example of this mechanism was the failure of mullite-based bricks in an oil-fired burner, the failure being initiated by formation of liquid phases in adjacent mortar and castable materials of lesser refractoriness.<sup>11</sup>

Thermal Cycling. Stresses induced by thermal cycling can cause severe mechanical disruption of ceramic materials. An exposure test in a furnace burning No. 6 fuel oil resulted in disintegration of MgO-based bricks. The bricks, which experienced several severe thermal cycles, exhibited a pattern of cracks perpendicular to surfaces.<sup>19</sup> This pattern is typically associated with failure by thermal shock.

Mechanical Stress Caused by Slags or Product. Slags or product in process, which adhere to ceramic materials, cause mechanical disruption during temperature changes. Differences in coefficient of thermal expansion between ceramic materials and the adhering materials generate stresses at the interface. Cracks were produced in oxide ceramics by adhering acid slag derived from combustion of a coal-oil mixture.<sup>22</sup> Clinker material, alternately depositing on and spalling from the surface of MgO-based bricks in a cement kiln, gradually "eroded" the bricks.<sup>13</sup>

### DEGRADATION MECHANISMS IN METALLIC ALLOYS

Reaction of flue gas constituents with metallic alloys causes severe degradation. As with ceramic materials, the reactions are time and temperature dependent. Oxygen and other oxidizing species in the flue gases are usually involved in the degradation mechanisms. Examples of degradation of metallic alloys described in the summarized reports follow.

#### Breakaway Oxidation

Most metallic alloys used for high-temperature applications in oxidizing environments contain chromium for oxidation resistance. A

temperature regime of passive oxidation exists in which a protective oxide film (typically containing a high chromium content) inhibits oxygen diffusion to the metal constituents of the alloy and also inhibits diffusion of the metal constituents to the interface between the film and the environment. Increasing temperature results in increasing diffusion rates. A regime of active oxidation occurs wherein metal is consumed at a predictable, and perhaps tolerable, rate. At still higher temperatures the oxide film is no longer protective, and rapid destructive oxidation occurs. This mechanism probably resulted in destruction of the type 309 stainless steel radiant inserts in a metallic recuperator on an aluminum-remelt furnace, even though sulfidation-oxidation was also identified as a corrosion mechanism.<sup>14</sup>

#### Intergranular Oxidation

As described above, oxidation of metallic alloys increases with increasing temperature. Some alloys exhibit grain boundary oxidation simultaneously with active oxidation. Diffusion along grain boundaries is inherently faster than diffusion through the grains. Oxidation of elements that have precipitated at grain boundaries, or that diffuse there during service, further weakens those regions. As a result the effective load-bearing cross section of the alloy can be substantially reduced. This mechanism was observed in type 310, Incoloy 800, Inconel 601, and Haynes 25 alloys after an exposure to air at 1100°C (ref. 17). Inconel 625, Inconel 601, Haynes 188, and Alloy 214 also exhibited extensive intergranular oxidation as a result of exposure to aluminum-remelt furnace flue gases.<sup>17</sup> The attack might have been accelerated by halides in the flue gases; however, this possibility was not verified.

#### Sulfidation-Oxidation

This corrosion mechanism is controlled by the thermodynamic stability of oxides and sulfides of elements of the alloy and by fluctuations in partial pressures of oxygen and sulfur. High-temperature alloys generally have a chromium-containing protective oxide film. Under certain conditions of temperature and partial pressures of oxygen and sulfur, diffusion of sulfur through the oxide film results in formation of metal

sulfides beneath the oxide film. In severe cases sulfides form ahead of the oxidation front and prevent formation of a continuous protective oxide film. As a result, the alloy oxidizes. A self-perpetuating situation develops when oxidation of the sulfides releases sulfur, which diffuses further into the alloy and forms more sulfides. This mechanism was identified in stainless steel radiant recuperators.<sup>14,15</sup>

#### SUMMARY OF DISCUSSION

Materials exposed to flue gas environments have exhibited various degradation mechanisms. Some mechanisms are easily recognized, while others are revealed only by extensive analysis. A point made earlier is worth repeating. Materials behavior in a particular industrial furnace should be used only as a guide to behavior of the same material in another industrial furnace of the same type. The environment in industrial furnaces of the same type can vary as the result of production requirements. Differences in fuels, raw materials, furnace refractories, heating schedules, and other furnace practices can result in different temperatures and concentrations of flue gas species.

#### ACKNOWLEDGMENTS

The authors of the reports summarized in this report are especially acknowledged: M. K. Ferber, C. Hamby, Jr., L. A. Harris, P. J. Jones, D. M. Kotchick, A. E. Pasto, D. Petrak, J M Robbins, V. J. Tennery, T. N. Tiegs, G. W. Weber, and G. C. Wei. Their descriptions of the effects of various combustion environments on materials form the basis for this report. Thanks are extended to others who assisted in the preparation of this report: Mary Upton and Debbie Northern for typing the draft; J M Robbins and E. L. Long, Jr., for technical review; A. J. Moorhead for many helpful suggestions; O. A. Nelson for editing; and Mary Upton and Alma McDonald for final preparation of the manuscript.

## REFERENCES

1. G. C. Wei and V. J. Tennery, *Impact of Alternate Fuels on Industrial Refractories and Refractory Insulation Applications: An Assessment*, ORNL/TM-5592, September 1976.
2. *Impact of Alternate Fuels on Refractories and Refractory Insulations*, ORNL/TM-5895, proceedings of a seminar held in Washington, D.C., Sept. 21, 1976, Energy Research and Development Administration, Division of Industrial Energy Conservation, May 1977.
3. V. J. Tennery and G. C. Wei, *Recuperator Materials Technology Assessment*, ORNL/TM-6227, February 1978.
4. G. C. Wei, V. J. Tennery, and L. A. Harris, *Effects of Alternate Fuels Report No. 1, Analysis of High-Duty Fireclay Refractories Exposed to Coal Combustion*, ORNL/TM-5909, December 1977.
5. G. C. Wei and V. J. Tennery, *Effects of Alternate Fuels Report No. 2, Analysis of Basic Refractories Degraded by Residual Oil Combustion Products*, ORNL/TM-6088, February 1978.
6. G. C. Wei and V. J. Tennery, *Effects of Alternate Fuels Report No. 3, Analysis of High-Duty Fireclay Refractories Degraded by Residual Oil Combustion Products*, ORNL/TM-6184, April 1978.
7. G. C. Wei and V. J. Tennery, *Effects of Alternate Fuels Report No. 4, Analysis of Soaking Pit Cover Refractories Degraded by Residual Oil Combustion Products*, ORNL/TM-6204, April 1978.
8. G. C. Wei and V. J. Tennery, *Effects of Alternate Fuels Report No. 5, Analysis of Fused Cast AZS Refractory, Silica Refractory, and High-MgO Refractory Degraded by Residual Oil Combustion Products*, ORNL/TM-6278, April 1978.
9. G. C. Wei and V. J. Tennery, *Effects of Alternate Fuels Report No. 6, Analysis of Low-Alumina Castable Refractory Degraded by Residual Oil Combustion Products*, ORNL/TM-6334, July 1978.
10. G. W. Weber and V. J. Tennery, *Analysis of Cordierite (MAS) Recuperator from a Molybdenum Heat-Treating Furnace*, ORNL/TM-6794, May 1979.

11. J. I. Federer and V. J. Tennery, *Effects of Alternate Fuels Report No. 7: Analysis of Failure of a Mullite-Based Refractory Brick in an Industrial Oil-Fired Burner*, ORNL/TM-6878, July 1979.

12. G. W. Weber and V. J. Tennery, *Materials Analyses of Ceramics for Glass Furnace Recuperators*, ORNL/TM-6970, November 1979.

13. J. I. Federer and V. J. Tennery, *Effects of Alternate Fuels Report No. 8: Analysis of Degradation of Magnesia-Based Refractory Bricks from a Residual Oil-Fired Rotary Cement Kiln*, ORNL/TM-7165, May 1980.

14. J. I. Federer and V. J. Tennery, *Corrosion of a Stainless Steel Waste Heat Recuperator*, ORNL/TM-7166, June 1980.

15. J. I. Federer and V. J. Tennery, *Analysis of a Corroded Stainless Steel Recuperator Used on a Glass Melting Furnace*, ORNL/TM-7553, November 1980.

16. J. I. Federer, T. N. Tiegs, D. M. Kotchick, and D. Petrak, *Analysis of Candidate Silicon Carbide Recuperator Materials Exposed to Industrial Furnace Environments*, ORNL/TM-9697, July 1985.

17. J. I. Federer and P. J. Jones, *Oxidation/Corrosion of Metallic and Ceramic Materials in an Aluminum Remelt Furnace*, ORNL/TM-9741, December 1985.

18. A. E. Pasto and V. J. Tennery, *Effects of Alternate Fuels Refractory Test Facility (RTF) Test 1, Analysis of Selected Aluminosilicate Refractory Bricks, Mortars, and Fibrous Insulations Degraded by Domestic Residual Oil Combustion Products*, ORNL/TM-6351, June 1978.

19. J. I. Federer and V. J. Tennery, *Effects of Alternate Fuels Refractory Test Facility (RTF) Test 2: Evaluation of Magnesia-Based Bricks and Mortar and Alumina-Based Bricks, Castables, and Fibrous Insulations Exposed to Residual Oil Combustion Products*, ORNL/TM-6840, March 1980.

20. J. I. Federer and V. J. Tennery, *Effects of Alternate Fuels Refractory Test Facility Test 3: Part 2. Analysis of Magnesia- and Alumina-Based Dense Refractories Exposed to the Combustion Products of No. 6 Residual Oil*, ORNL/TM-7284, July 1980.

21. G. C. Wei and V. J. Tennery, *Evaluation of Tubular Ceramic Heat Exchanger Materials in Residual Oil Combustion Environment*, ORNL/TM-7578, March 1981.
22. M. K. Ferber and V. J. Tennery, *Evaluation of Tubular Ceramic Heat Exchanger Materials in Acidic Coal Ash from Coal-Oil-Mixture Combustion*, ORNL/TM-7958, December 1981.
23. J. I. Federer, *Analysis of Refractory Fiber Insulations and Hot Face Coatings Exposed to Coal-Oil Mixture Combustion Products*, ORNL/TM-8243, July 1982.
24. M. K. Ferber and V. J. Tennery, *Evaluation of Tubular Ceramic Heat Exchanger Materials in Basic Coal Ash from Coal-Oil-Mixture Combustion*, ORNL/TM-8385, October 1982.
25. J. I. Federer, *Corrosion of Fluidized-Bed Boiler Materials in Synthetic Flue Gas*, ORNL/TM-8819, November 1983.
26. J. I. Federer, J M Robbins, P. J. Jones, and C. Hamby, Jr., *Corrosion of SiC Ceramics in Synthetic Combustion Atmospheres Containing Halides*, ORNL-6258, December 1985.
27. E. M. Levin, C. R. Robbins, and H. F. McMurdie, *Phase Diagrams for Ceramists*, M. K. Reser, ed., American Ceramic Society, Columbus, Ohio, 1964.

Appendix

COMPOSITIONS OF CERAMIC MATERIALS AND ALLOYS



Table A.1. Compositions of SiC and oxide ceramics

Ceramic materials	Nominal composition (wt %)						
	SiC	Si	Si <sub>3</sub> N <sub>4</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	AlN	MgO
Sintered alpha SiC	>99						
Sintridge	>99						
NC-400	>99						
CVD	>99						
CVR	>99						
NC-430	90	10					
KT	84	16					
Refel	90	10					
SC-2	88	12					
SC-X	88	12					
Carbofrax A	90			9			
Carbofrax M	89			6			
Refrax 20	73		21	3	3		
C/75	75		23				
CN-178	75		23				
Sialon GE-128			64	0.9	26	8	0.6
Sialon GE-129			83	0.9	12	2	0.6
Sialon GE-130			87	0.9	10	1	0.6
AD-998				<0.1	99.8		
AD-94					94		
AD-85					85		
Mullite				28	70		
Cordierite				51	35		14

Table A.2. Compositions of alloys

Alloy	Nominal composition (wt %)								
	Al	Co	Cr	Fe	Mo	Nb	Ni	Ti	W
Plain carbon steel				~99					
Type 405 stainless steel	0.2		13	bal.					
Type 309 stainless steel			24	bal.	0.4		14		
Type 310 stainless steel			25	bal.			21		
Type 316 stainless steel			17	bal.	3		12		
Type 321 stainless steel			17	bal.			10	0.4	
Type 446 stainless steel			25	bal.					
Alloy 800	0.4		22	bal.			33		
Inconel 601	1.5		23	bal.			60		
Inconel 625			22	5	10	3.7 <sup>a</sup>	58	0.4	
Hastelloy X		1.5	22	19	10		bal.		0.5
Hastelloy N	0.5 <sup>b</sup>	0.2	7	5	17		bal.		0.5
Alloy 214	5		16	4			bal.		
Haynes 25		bal.	20	3			10		15
Haynes 188		bal.	22	3			22		15

<sup>a</sup>Nb + Ta.

<sup>b</sup>Al + Ti.

## INTERNAL DISTRIBUTION

- |        |                               |        |                             |
|--------|-------------------------------|--------|-----------------------------|
| 1-2.   | Central Research Library      | 32.    | J. F. Martin                |
| 3.     | Document Reference Section    | 33.    | P. J. Maziasz               |
| 4-5.   | Laboratory Records Department | 34.    | H. E. McCoy                 |
| 6.     | Laboratory Records, ORNL RC   | 35.    | A. J. Moorhead              |
| 7.     | ORNL Patent Section           | 36.    | A. R. Olsen                 |
| 8.     | R. A. Bradley                 | 37.    | R. E. Pawel                 |
| 9.     | C. R. Brinkman                | 38.    | J. M. Robbins               |
| 10.    | A. J. Caputo                  | 39.    | M. L. Santella              |
| 11.    | R. S. Carlsmith               | 40-49. | A. C. Schaffhauser          |
| 12.    | P. T. Carlson                 | 50.    | G. M. Slaughter             |
| 13.    | J. A. Carpenter, Jr.          | 51.    | D. P. Stinton               |
| 14.    | J. V. Cathcart                | 52.    | R. W. Swindeman             |
| 15.    | F. C. Chen                    | 53.    | V. J. Tennery               |
| 16.    | R. M. Davis                   | 54-56. | P. T. Thornton              |
| 17.    | J. H. DeVan                   | 57.    | T. N. Tiegs                 |
| 18-23. | J. I. Federer                 | 58.    | D. B. Trauger               |
| 24.    | R. L. Graves                  | 59.    | J. R. Weir                  |
| 25.    | D. O. Hobson                  | 60.    | R. J. Charles (Consultant)  |
| 26.    | M. A. Janney                  | 61.    | G. Y. Chin (Consultant)     |
| 27.    | R. R. Judkins                 | 62.    | H. E. Cook (Consultant)     |
| 28.    | J. R. Keiser                  | 63.    | Alan Lawley (Consultant)    |
| 29.    | C. T. Liu                     | 64.    | W. D. Nix (Consultant)      |
| 30.    | E. L. Long                    | 65.    | J. C. Williams (Consultant) |
| 31.    | T. S. Lundy                   |        |                             |

## EXTERNAL DISTRIBUTION

- 66-67. AEROJET ENERGY CONVERSION COMPANY, P.O. Box 13222, Sacramento, CA 95813  
 L. Hoffman  
 H. W. Williams
- 68-69. AIRESEACH MANUFACTURING COMPANY, 2525 W. 190th Street, Torrance, CA 90509  
 M. G. Coombs  
 D. M. Kotchick
70. BABCOCK AND WILCOX, P.O. Box 239, Lynchburg, VA 24505  
 D. Petrak  
 W. P. Parks, Jr.
71. C&H COMBUSTION, 1104 E. Big Beaver Road, Troy, MI 48083  
 R. G. Graham

72. CABOT CORPORATION, 1020 West Park Avenue, Kokomo, IN 46901  
M. F. Rotham
73. COMBUSTION ENGINEERING, INC., 911 West Main Street, Chattanooga,  
TN 37402  
C. H. Sump
74. CONSOLIDATED NATURAL GAS, 11001 Cedar Avenue, Cleveland, OH 44106  
J. Bjerklie
- 75-77. COORS PORCELAIN COMPANY, 600 Ninth Street, Golden, CO 80501  
C. Dobbs  
R. Kleiner  
D. Roy
78. GAS RESEARCH INSTITUTE, 8600 West Bryn Mawr Avenue, Chicago,  
IL 60631  
W. W. Liang
- 79-80. GTE PRODUCTS CORPORATION, Hawes Street, Towanda, PA 18848  
J. L. Ferri  
J. Gonzalez
81. HAGUE INTERNATIONAL, 3 Adams Street, South Portland, MA 04106  
S. B. Young
- 82-83. IDAHO NATIONAL ENGINEERING LABORATORY, P.O. Box 1625, Idaho Falls,  
ID 83415  
F. W. Childs  
D. J. Landini
- 84-85 IIT RESEARCH INSTITUTE, 10 West 35th Street, Chicago, IL 60616  
J. W. Adams  
D. C. Larsen
- 86-87. NORTON COMPANY, Worcester, MA 01606  
B. D. Foster  
M. L. Torti
88. PENNSYLVANIA STATE UNIVERSITY, 201 Steidle Building, University  
Park, PA 16802  
R. E. Tressler
- 89-90. SOLAR TURBINES INCORPORATED, P.O. Box 8537, San Diego, CA  
92138-5376  
C. E. Smeltzer  
M. E. Ward

91. SOHIO ENGINEERED MATERIALS COMPANY, Structural Ceramics Division,  
P.O. Box 10549, Niagara Falls, NY 14302  
J. Halstead
- 92-94. THERMO ELECTRON CORPORATION, P.O. Box 459, Waltham, MA 02254  
W. E. Cole  
R. DeSaro  
K. Patch
95. UNIVERSITY OF ILLINOIS AT CHAMPAIGN-URBANA, 105 W. Goodwin Ave.,  
Urbana, IL 61801  
M. K. Ferber
96. UNIVERSITY OF ILLINOIS AT CHICAGO, P.O. Box 4348, Chicago, IL 60680  
M. J. McNallan
- 97-98. DOE, IDAHO OPERATIONS OFFICE, 550 Second Street, Idaho Falls, ID  
83401  
R. N. Chappell  
W. H. Thieldbar
99. DOE, MORGANTOWN ENERGY TECHNOLOGY CENTER, P.O. Box 880, Morgantown,  
WV 26505  
J. M. Hobday
100. DOE, OAK RIDGE OPERATIONS OFFICE, P.O. Box E, Oak Ridge, TN 37831  
Office of Assistant Manager for Energy Research and Development
- 101-118. DOE, OFFICE OF INDUSTRIAL CONSERVATION, 1000 Independence Ave.,  
Forrestal Building, Washington, DC 20585  
J. Euctis  
S. L. Richlen  
J. R. Rossmeissl  
W. B. Williams, Director (15)
- 119-145. DOE, TECHNICAL INFORMATION CENTER, Office of Information Services,  
P.O. Box 62, Oak Ridge, TN 37831  
For distribution by microfiche as shown in DOE/TIC-4500,  
Distribution Category UC-95 (Energy Conservation).