40
11/3/95 JS(2)

1	100	Program
2	100	Program
3	100	Program
4	100	Program
5	100	Program
6	100	Program
7	100	Program
8	100	Program
9	100	Program
10	100	Program
11	100	Program
12	100	Program
13	100	Program
14	100	Program
15	100	Program
16	100	Program
17	100	Program
18	100	Program
19	100	Program
20	100	Program
21	100	Program
22	100	Program
23	100	Program
24	100	Program
25	100	Program
26	100	Program
27	100	Program
28	100	Program
29	100	Program
30	100	Program
31	100	Program
32	100	Program
33	100	Program
34	100	Program
35	100	Program
36	100	Program
37	100	Program
38	100	Program
39	100	Program
40	100	Program
41	100	Program
42	100	Program
43	100	Program
44	100	Program
45	100	Program
46	100	Program
47	100	Program
48	100	Program
49	100	Program
50	100	Program
51	100	Program
52	100	Program
53	100	Program
54	100	Program
55	100	Program
56	100	Program
57	100	Program
58	100	Program
59	100	Program
60	100	Program
61	100	Program
62	100	Program
63	100	Program
64	100	Program
65	100	Program
66	100	Program
67	100	Program
68	100	Program
69	100	Program
70	100	Program
71	100	Program
72	100	Program
73	100	Program
74	100	Program
75	100	Program
76	100	Program
77	100	Program
78	100	Program
79	100	Program
80	100	Program
81	100	Program
82	100	Program
83	100	Program
84	100	Program
85	100	Program
86	100	Program
87	100	Program
88	100	Program
89	100	Program
90	100	Program
91	100	Program
92	100	Program
93	100	Program
94	100	Program
95	100	Program
96	100	Program
97	100	Program
98	100	Program
99	100	Program
100	100	Program

by S. H. D. Lee, K. Natesan,
and W. M. Swift

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Argonne National Laboratory, with facilities in the states of Illinois and Idaho, is owned by the United States government, and operated by The University of Chicago under the provisions of a contract with the Department of Energy.

DISCLAIMER

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

Reproduced from the best available copy.

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831
Prices available from (615) 576-8401

Available to the public from the
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

DISCLAIMER

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

ANL/FE-95-01

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, IL 60439

TESTING OF CANDIDATE MATERIALS FOR
THEIR RESISTANCE TO ALKALI-VAPOR
ADSORPTION IN PFBC AND GASIFICATION ENVIRONMENTS

FINAL REPORT

by

S. H. D. Lee, K. Natesan,[†] and W. M. Swift

Chemical Technology Division
[†]Energy Technology Division

August 1995

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
SUMMARY	1
1.0 INTRODUCTION	5
2.0 EXPERIMENTAL PROCEDURES	10
2.1 Candidate Materials and Their Preparation	10
2.1.1 Candidate Materials	10
2.1.2 Preparation of Specimen Coupons	11
2.2 Test Equipment and Procedures	12
3.0 RESULTS AND DISCUSSION	16
3.1 Tests in Baseline Simulated PFBC Off-Gas	16
3.2 Tests in Simulated PFBC Off-Gas Containing NaCl Vapor	21
3.2.1 304 SS	22
3.2.2 Hastelloy X	28
3.2.3 Hastelloy C-276	29
3.2.4 Haynes No. 188	29
3.2.5 Noble-Metal-Coated 304 SS	29
3.2.6 Aluminized 304 SS	30
3.2.7 ZrO ₂ -Coated 304 SS	30
3.3 Tests in Baseline Simulated Gasification Fuel Gas	31
3.4 Test in Simulated Gasification Fuel Gas Containing NaCl Vapor	32
3.4.1 Aluminized 304 SS	33
3.4.2 Haynes No. 188	35
4.0 CONCLUSIONS AND RECOMMENDATIONS	35
5.0 ACKNOWLEDGMENTS	38
6.0 REFERENCES	38

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Scale Thickness and Intergranular Penetration Data for Bare Alloys after 500-h Exposure to Off-Gas Environment	5
2.	Scale Thickness and Intergranular Penetration Data for CaSO ₄ -Coated Alloys after 500- and 2000-h Exposures to Off-Gas Environment at Metal Temperatures of 704°C and 593°C	6
3.	Relative Corrosion Loss for Base Alloys in 1 vol% SO ₂ , 4 vol% O ₂ , and 5 wt% Alkali Sulfate	7
4.	Relationship Between Chromium Content of Alloys and Relative Corrosion Loss in 4 vol% O ₂ Off-Gas at 700°C	8
5.	Schematic of Pressurized NaCl-KCl-Vapor Generation Unit Integrated with Ames On-Line, Real-Time Alkali Analyzer	9
6.	Measured Sodium and Potassium Concentrations in the Gas Stream for Test of Type 304 Stainless Steel Sampling Line at 840-950°C and 9.2 atm Absolute	9
7.	Auger Electron Spectroscopy and Depth Profile Analysis for Pt-Coated 304 SS Specimen	12
8.	SEM Micrographs of Cross Sections of Aluminized 304 SS in the as-Aluminized Condition, and after Exposure to Air at 1000°C for 2 and 50 h.	13
9.	Elemental Concentration Profiles for Al, Cr, Fe, Ni, and O in the Near-Surface Regions of Aluminized 304 SS	14
10.	TGA Setup for Studying Alkali-Vapor Capture by Metallic Materials	15
11.	SEM Micrographs of Cross Sections of Test Specimens after Exposure to Baseline Simulated PFBC Off-Gas (No NaCl Vapor)	18
12.	EDX Analysis of Hastelloy X, Hastelloy C-276, and Haynes No. 188 after Exposure to Baseline Simulated PFBC Off-Gas (No NaCl Vapor)	19
13.	EDX Analysis of Scales of Pt-Coated 304 SS, Au-Coated 304 SS, and Ag-Coated 304 SS after Exposure to Baseline Simulated PFBC Off-Gas (No NaCl Vapor)	20

LIST OF FIGURES (contd)

<u>No.</u>	<u>Title</u>	<u>Page</u>
14.	Elemental Concentration Profiles for Al, Cr, Fe, Ni, and O in the Pretreated Aluminized 304 SS after Exposure to Baseline Simulated PFBC Off-Gas (No NaCl Vapor)	21
15.	SEM Micrographs of Surfaces and Cross Sections of 304 SS and Hastelloy X after Exposure to Simulated PFBC Off-Gas Containing NaCl Vapor	23
16.	SEM Micrographs of Surfaces and Cross Sections of Hastelloy C-276 and Haynes No. 188 after Exposure to Simulated PFBC Off-Gas Containing NaCl Vapor	24
17.	SEM Micrographs of Surfaces and Cross Sections of Pt-Coated, Au-Coated, and Ag-Coated 304 SS after Exposure to Simulated PFBC Off-Gas Containing NaCl Vapor	25
18.	SEM Micrographs of Surfaces and Cross Sections of Aluminized 304 SS and ZrO ₂ -Coated 304 SS after Exposure to Simulated PFBC Off-Gas Containing NaCl Vapor	26
19.	SEM Micrographs of Surface and Cross Section of Aluminized 304 SS after Exposure to Baseline Simulated Gasification Fuel Gas (No NaCl Vapor)	32
20.	EDX Spectra of the Surface of Aluminized 304 SS after Exposure to Baseline Simulated Gasification Fuel Gas (No NaCl Vapor)	33
21.	SEM Micrographs of Surface and Cross Section and EDX Spectra for Locations A and B on the Surface of Haynes No. 188 after Exposure to Baseline Simulated Gasification Fuel Gas (No NaCl Vapor)	34
22.	SEM Micrographs of Surface and Cross Section and EDX Spectra for Locations A, B, and C on the Surface of Aluminized 304 SS after Exposure to Simulated Gasification Fuel Gas Containing NaCl Vapor	36
23.	SEM Micrographs of Surface and Cross Section and EDX Spectra for Locations A and B on the Surface of Haynes No. 188 after Exposure to Simulated Gasification Fuel Gas Containing NaCl Vapor	37

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Chemical Compositions of Candidate Materials	10
2.	Experimental Conditions for Atmospheric TGA Tests of Candidate Materials in Simulated PFBC Environment	15
3.	Total Weight Change of Candidate Materials Tested in Baseline Simulated PFBC Off-Gas (No NaCl Vapor)	17
4.	Total Weight Change of Candidate Materials Tested in Simulated PFBC Off-Gas Containing NaCl Vapor	22
5.	AES Surface Concentrations in Coupon Specimens Exposed to Simulated PFBC Off-Gas Containing NaCl Vapor	27
6.	AES Surface Concentrations at a Depth of 2700 Å in Coupon Specimens Exposed to Simulated PFBC Off-Gas Containing NaCl Vapor	28
7.	Total Weight Gain of Aluminized 304 SS and Haynes No. 188 under Baseline Simulated Gasification Fuel Gas (No NaCl Vapor)	31
8.	Total Weight Gain of Aluminized 304 SS and Haynes No. 188 under Simulated Gasification Fuel Gas Containing NaCl Vapor	35

TESTING OF CANDIDATE MATERIALS FOR THEIR RESISTANCE TO ALKALI-VAPOR ADSORPTION IN PFBC AND GASIFICATION ENVIRONMENTS

Final Report

by

S. H. D. Lee, K. Natesan, and W. M. Swift

ABSTRACT

Under the auspices of the U.S. Department of Energy through Morgantown Energy Technology Center, laboratory-scale studies were performed to identify metallic material(s) having no, or limited, affinity for alkali vapors in an environment of either the off-gas from pressurized fluidized-bed combustion (PFBC) or the fuel gas from coal gasification. Such materials would be potential candidates for use as components in advanced coal-utilization systems. The following materials were tested for adsorption of NaCl vapor at 870-875°C and atmospheric pressure in a simulated PFBC off-gas (oxidizing) doped with 80 ppmW NaCl vapor: iron-based Type 304 stainless steel (304 SS), nickel-based Hastelloy C-276 and Hastelloy X alloys, cobalt-based Haynes No. 188 alloy, noble-metal-coated 304 SS, aluminized 304 SS, and ZrO₂-coated 304 SS. The Haynes No. 188 alloy and the aluminized 304 SS were also tested for their NaCl-vapor adsorption in a simulated gasification fuel gas (reducing) under the same test conditions as in the PFBC off-gas test. After 100 h of testing, the specimens were analyzed with a scanning electron microscope equipped with an energy dispersive X-ray analyzer, and by an Auger electron spectrometer. The test materials showed various degrees of NaCl-vapor adsorption after exposure to the PFBC off-gas. The aluminized 304 SS had the least tendency to adsorb NaCl vapor, as well as an excellent resistance to corrosion as a result of the formation of a protective layer of Al₂O₃ on its surface. In the reducing environment, however, the aluminized 304 SS was badly corroded by H₂S attack. The Haynes No. 188 showed virtually no NaCl-vapor adsorption and only limited H₂S attack. Based on these results, we recommend further long-term parametric studies to quantitate alkali-vapor adsorption as a function of operating variables for (1) the aluminized 304 SS in the PFBC off-gas environment and (2) the Haynes No. 188 in the gasification fuel gas environment.

SUMMARY

Alkali vapors (chlorides, hydroxides, and sulfates of sodium and potassium) are present in the high-temperature/high-pressure (HTHP) off-gas of advanced coal utilization systems, such

as direct coal-fired turbines, pressurized fluidized-bed combustion (PFBC) systems, and integrated coal gasification combined-cycle systems. These vapors are a source of concern because of their deleterious effects on components of the HTHP process; for example, they cause hot corrosion of fire-side boiler tubes and gas turbine hardware. The objective of this study is to identify non-alkali-adsorbing material(s) (if any) that may be suitable components for advanced coal-utilization systems. One specific use for such a material is in the gaseous sampling line for an on-line alkali analyzer. An inert sampling line is needed to ensure analytical accuracy.

In this study, nine candidate materials were tested for their NaCl-vapor adsorption in a simulated PFBC off-gas environment, namely, an iron-based Type 304 stainless steel (304 SS), two nickel-based Hastelloy C-276 and Hastelloy X alloys, a cobalt-based Haynes No. 188 alloy, a platinum-coated 304 SS, a gold-coated 304 SS, a silver-coated 304 SS, an aluminized 304 SS, and a ZrO₂-coated 304 SS. Haynes No. 188 and aluminized 304 SS were also tested for their NaCl-vapor adsorption in a simulated gasification fuel gas. Tests of the metallic materials were conducted using prepared coupons. Those of 304 SS, Hastelloy X, Hastelloy C-276, and Haynes No. 188 were finished by polishing with 4000-grit SiC paper, cleaned in an ultrasonic water bath, and finally rinsed with alcohol. For coupons of Pt-, Au-, and Ag-coated 304 SS, a finished 304 SS coupon was sputter-deposited with Pt, Au, or Ag. The deposited layers were approximately 1 μm thick. To prepare the aluminized specimen, a finished 304 SS coupon was aluminized by a commercial vendor (Alon Processing, Inc., PA). The ZrO₂-coated 304 SS coupon was prepared by depositing (1) a bond coat of (Ni, Co) Cr Al Y and (2) an external ceramic coating of ZrO₂ by use of a thermal spray process. The bond layer was about 100 μm thick, and the ZrO₂ coating, about 500 μm .

For experimental testing, specimen coupons were suspended in a thermogravimetric analyzer (TGA) setup and exposed to the simulated PFBC off-gas, or the gasification fuel gas, at 870-875°C and atmospheric pressure for 100 h. The simulated PFBC off-gas contained 3.1% O₂, 14.7% CO₂, 2.0% H₂O vapor, 880 ppmV SO₂, either 0 or 80 ppmW NaCl vapor, and the balance N₂. The simulated gasification fuel gas contained 20% H₂, 19% CO, 5% CH₄, 0.2% H₂S, 12% CO₂, 2% H₂O vapor, either 0 or 80 ppmW NaCl vapor, and the balance N₂. At the end of the test period, coupons were analyzed by scanning electron microscopy (SEM) using a microscope equipped with an energy dispersive X-ray (EDX) analyzer to examine corrosion of the candidate materials and NaCl-vapor adsorption. Near-surface regions of selected specimens were also analyzed by Auger electron spectroscopy (AES).

A set of all coupons (except the ZrO₂-coated specimen) was first tested in a baseline PFBC off-gas containing no NaCl vapor. At the end of the test, all the originally shiny coupon specimens (304 SS, Hastelloy X, Hastelloy C-276, Haynes No. 188, Pt-coated 304 SS, Au-coated 304 SS, and Ag-coated 304 SS) had formed black scales. The scale was predominantly Cr₂O₃ in the 304 SS, Hastelloy X, and Haynes No. 188 specimens, whereas the oxide scale in Hastelloy C-276 contained Cr, Fe, and Ni. The lower concentration of chromium (15.5 wt%) in Hastelloy C-276 is not sufficient to form pure chromia scale at temperatures of 870-875°C. In the case of the Pt-, Au-, and Ag-coated 304 SS coupons, the sputter deposit of the noble metals did not prevent outward diffusion of substrate elements (Cr and/or Fe) and subsequent oxidation of these elements. The oxide scale on the Pt-coated 304 SS was almost pure Cr₂O₃, that on the Au-coated 304 SS was (Cr, Fe) oxide, and that on the Ag-coated sample was iron oxide. The as-received

aluminized 304 SS specimen was pretreated in air at 1000°C for 50 h to form a continuous Al_2O_3 scale on the surface before exposure to the simulated PFBC off-gas for 100 h. This scale remained intact throughout exposure. No sulfur was detected in the scale or the alloy substrate in any of the coupons.

The second set of coupon specimens was tested in the simulated PFBC off-gas containing 80 ppmW NaCl vapor. Black scales formed on the specimens as in the baseline experiment. The black scales of the 304 SS, Hastelloy X, Haynes No. 188, Pt-coated 304 SS, and Au-coated 304 SS specimens appeared visually firm and smooth; however, the Hastelloy C-276 and Ag-coated 304 SS specimens became severely corroded when exposed to the NaCl vapor, with the black scales peeling off the specimens.

Results of the SEM/EDX analyses of the exposed 304 SS coupon suggested that a layer of Na_2SO_4 was distributed on a thin oxide scale. The captured sodium could also have reacted with the base metal to form complex (Na, Cr, Mn, Fe) oxides as reaction products. The AES analyses indicated sodium concentrations of 26.7 and 11.8 at.% on the surface and 21.1 and 4.2 at.% at a depth of 2700 Å for two specimens exposed for 100 and 90 h, respectively. Chlorine (2.8 at.%) was also detected on the surface of one specimen, indicating the adsorption of NaCl vapor on the Cr_2O_3 . It is possible that NaCl vapor was initially adsorbed on the surface and then gradually reacted with adsorbed SO_2 , O_2 , and H_2O vapor to form the Na_2SO_4 layer that was observed by SEM.

The SEM/EDX analyses of the Hastelloy X coupon also suggested that a Na_2SO_4 layer was deposited on the oxide scale. The AES analyses of the specimen showed similarly high sodium concentrations on the surface (28.6 at.%) and at 2700 Å (20.3 at.%) as were measured for the 304 SS specimen. The AES analysis also detected 2.2 at.% chlorine on the surface of the specimen. In contrast to Hastelloy X, the Hastelloy C-276 coupon was severely corroded and showed evidence of substantial internal sulfidation after exposure. This enhanced corrosion can be attributed to the lower chromium content (15.5 wt%) of the alloy compared to the Hastelloy X (22.0 wt%). As in the 304 SS and the Hastelloy X specimens, a layer of Na_2SO_4 was observed on the oxide scale surface of the Haynes No. 188 coupon, but the AES analysis showed lower sodium concentrations, both on the surface (19.0 at.%) and at 2700 Å (11.6 at.%), than those measured in 304 SS and the Hastelloy X. A trace amount (0.8 at.%) of chlorine was also detected on the surface of the Haynes No. 188 specimen.

The SEM/EDX analyses of the Pt-, Au-, and Ag-coated 304 SS coupons showed that the Pt-coated specimen developed a thin, predominantly Cr_2O_3 scale, whereas the scale on the Au- and Ag-coated specimens was mainly iron oxide. Substantial segregation of Au and Ag was observed at the scale/alloy interface, indicating that these coatings do not act as barriers to outward diffusion and subsequent oxidation of iron from the bulk alloy. Some sulfides were observed in the interior of all three coupons. The AES analyses showed sodium concentrations of 20.2, 16.1, and 15.3 at.% on the surfaces of the Pt-, Au-, and Ag-coated specimens, respectively, and lower concentrations (10.6, 7.8, and 7.7 at.%) at 2700 Å.

As in the baseline PFBC tests, SEM/EDX analyses of two aluminized 304 SS specimens after 100- and 150-h exposures to the NaCl-vapor-bearing PFBC environment showed that the

continuous Al_2O_3 scale developed during the pretreatment remained intact. No sulfur was detected in the scale or the alloy substrate. The AES analyses of the two specimens showed sodium concentrations of 6.1 and 8.5 at.% on the surface, and 14.3 and 10.0 at.% at a depth of 2700 Å, after 100 and 150 h, respectively. For the ZrO_2 -coated 304 SS specimen, the SEM/EDX analyses indicated a fairly uniform deposit layer of Na_2SO_4 , with a globular shape 30 µm in diameter. The deposit exhibited some porosity accompanied by chipping and cracking of the coating in a few areas. In agreement with the SEM/EDX analyses, the AES analysis of the specimen showed relatively high sodium concentrations, i.e. 26.7 at.% on the surface and 24.0 at.% at 2700 Å.

Of the nine candidate materials tested in the simulated PFBC off-gas (oxidizing), the aluminized 304 SS and the Haynes No. 188 showed both good resistance to corrosion and low sodium capture; therefore, these two materials were selected for further testing in the simulated gasification fuel gas (reducing). In the baseline test (no NaCl vapor), the Al_2O_3 scale that originally formed on the aluminized 304 SS during pretreatment (in air at 1000°C for 50 h) showed evidence of H_2S attack in isolated regions, forming (Cr, Mn, Fe) sulfides. By contrast, the Haynes No. 188 specimen formed a continuous, uniform black scale on the surface. The EDX analysis of the specimen indicated that the scale consisted of chromium-rich (Cr, Mn, Fe) oxides containing a trace amount of sulfur.

Finally, the aluminized 304 SS and the Haynes No. 188 specimens were tested together at 870-875°C for 70 h in the simulated gasification fuel gas containing 80 ppmW NaCl vapor. The aluminized 304 SS specimen became badly corroded, and EDX analysis of the specimen clearly showed the formation of (Cr, Mn, Fe) oxides and sulfides in isolated areas of the surface. The formation of these corrosion products undermined the Al_2O_3 scale originally developed on the surface, causing it to spall off. The EDX analysis also showed the presence of sodium along with sulfur on the surface of the Al_2O_3 scale, suggesting the affinity of the Al_2O_3 for sodium adsorption. By contrast, a continuous, uniform black scale of chromium-rich (Cr, Mn, Fe) oxides was formed on the surface of the Haynes No. 188 specimen. Some sulfur was shown in isolated locations, but virtually no sodium was found, indicating a lack of sorption affinity of the oxide scale for NaCl vapor. This is in contrast to the Cr_2O_3 scale developed in the oxidizing PFBC off-gas, on which NaCl vapor adsorbed and gradually converted to Na_2SO_4 .

1.0 INTRODUCTION

In advanced coal-utilization systems, such as direct coal-fired turbines, pressurized fluidized-bed combustion (PFBC), and integrated coal gasification combined-cycle systems, the high-temperature/high-pressure (HTHP) off-gas is expanded through a gas turbine to recover thermal energy for improved system efficiency. Alkali vapors (chlorides, hydroxides, and sulfates of sodium and potassium) are present in the HTHP off-gas of these systems¹⁻³ and are known to cause hot corrosion of fire-side boiler tubes and gas turbine hardware.^{4,5} Because of their deleterious effect on the HTHP process component materials, alkali vapors have been a cause of concern and their removal from the HTHP off-gas of advanced coal-utilization systems has been the subject of many studies.^{2,6-9}

A literature review revealed information about the effect of alkali on metallic materials. Corrosion of structural materials exposed to the effluent from fluidized-bed combustion (FBC) can occur by gas phase oxidation/sulfidation or deposit-induced liquid-phase corrosion. The former can be minimized by using materials that are oxidation resistant at service temperatures of interest. The FBC effluent is generally oxidizing and has PO_2 values in the range of 10^{-2} - 10^{-4} atm. Under these conditions, the sulfur in the gas phase will be present predominantly in the form of SO_2 at concentrations of 100-2000 ppmV. Extensive studies have been conducted on the corrosion performance of structural alloys exposed to SO_2 -containing gas atmospheres, and the results of two such studies^{10,11} are shown in Figs. 1 and 2. Figure 1 shows the scale thickness and alloy penetration data for carbon steel, low-alloy ferritic steels, and high-chromium

Fig. 1.

Scale Thickness and Intergranular Penetration Data for Bare Alloys after 500-h Exposure to Off-Gas Environment.^{10,11} The numbers 310 and 800 correspond to Type 310 Stainless Steel and Alloy 800. C Steel and 9 Cr-1Mo Steel were not tested at 840°C.

austenitic alloys when exposed to an oxidizing environment containing approximately 1700 ppmV of SO_2 at temperatures of 593, 704, and 840°C (1100, 1300, 1544°F, respectively). Figure 2 shows the scale thickness and penetration data for the $CaSO_4$ -coated alloys exposed to the SO_2 -containing gas mixture. The results show that the scaling rates for the high-chromium alloys are in the range of 2-8 mils per year, based on parabolic kinetics.

Fig. 2. Scale Thickness and Intergranular Penetration Data for CaSO_4 -Coated Alloys after 500- and 2000-h Exposures to Off-Gas Environment at Metal Temperatures of (a) 704°C and (b) 593°C^{10,11}

On the other hand, deposit-induced corrosion of materials by alkali is an accelerated type of attack, influenced by the vaporization and condensation of small amounts of impurities, such as Na, K, Cl, and S (or their compounds), that are present in the coal feedstock. Corrosion of metallic materials in the presence of liquid Na_2SO_4 , either by itself or in combination with NaCl, has been a problem in gas turbines; this corrosion process has been termed "hot corrosion" to differentiate it from gas-phase sulfidation attack. Two types of hot corrosion have been identified¹²⁻¹⁴; Type I, operative in the range 800-950°C, and Type II, operative over the range 600-750°C.

Type I hot corrosion can be split into an initiation (or incubation) stage and a propagation stage. The process, in general, requires the presence of liquid Na_2SO_4 (melting point 884°C) on the metal surface. In the initiation stage, the protective oxide scale dissolves by a basic fluxing mechanism and the corrosion rates are generally low. In the propagation stage, when the protective oxide has been destroyed and is not able to reform, the alloy is subjected to sulfidation by inward diffusion of sulfur, leading to accelerated corrosion rates.

Type II hot corrosion, also known as low-temperature hot corrosion, involves the eutectics of base metal sulfates and sodium sulfate and, therefore, occurs predominantly at lower temperatures, especially in the effluent of the FBC environment. For example, the eutectic temperature for sodium sulfate-cobalt sulfate is 565°C. In this type of corrosion, the transient oxides of cobalt or nickel (which nucleate in the early stage of oxidation in chromium- and aluminum-containing superalloys) react with sodium sulfate to form eutectic salts that prevent formation of protective chromia or alumina. The corrosion process is strongly dependent on the partial pressure of sulfur trioxide at the melt/scale interface, but the process occurs at much lower temperatures than the melting point of sodium sulfate.

Extensive studies¹²⁻¹⁴ were conducted to evaluate the hot-corrosion behavior of nickel-based superalloys and coatings in environments typical of gas turbines. The major thrust in these studies was to correlate the corrosion behavior of the alloys with various parameters, such as test temperature, the salt (Na_2SO_4) chemistry, salt film thickness, gas composition, and alloying element additions. The presence of NaCl in the environment can lead to formation of Na_2SO_4 via the reaction

which can contribute to hot corrosion. In general, it was found that high-chromium alloys exhibited better resistance to hot corrosion. In addition to chromium, elements such as Al, Ti, and W seemed to impart better resistance. Elements such as Mo and C had a deleterious effect on the corrosion resistance.

Although extensive studies have been conducted on hot-corrosion resistance of nickel-based superalloys, very little is known about the performance of iron-based heat-resistant alloys. Some corrosion studies were conducted on iron-based materials in the presence of synthetic coal ash with addition of Na_2SO_4 and/or K_2SO_4 , in support of material evaluation for superheaters and reheaters of coal-fired boilers.¹² The results, based on 100-h tests in simulated combustion atmospheres with synthetic coal ash deposits, showed increased corrosion resistance with increased chromium content of the alloys up to 20-25 wt%. Figures 3 and 4 show the relative corrosion loss data, and the relationship between chromium content and relative corrosion loss for several of the alloys tested.¹⁵

Fig. 3.

Relative Corrosion Loss for Base Alloys in 1 vol% SO_2 , 4 vol% O_2 , and 5 wt% Alkali Sulfate¹⁵

Predicting the evolution of alkalis from the combustion and gasification of coal has been the goal of many thermodynamic studies.^{1-3,16-19} Sodium and potassium chlorides are suggested to be major gaseous alkali carriers in PFBC off-gas.^{1,3,16} Alkali hydroxide vapors may exist to a

Fig. 4.

Relationship Between Chromium Content of Alloys and Relative Corrosion Loss in 4 vol% O₂ Off-Gas at 700°C¹⁵

lesser extent.³ These chlorides and hydroxides can substantially convert to condensed-phase sulfate by reacting with SO₂ in the off-gas forming sulfate aerosols, or by nucleating on entrained ash particles.^{2,3,17} Thermodynamic calculations also suggest that chlorides and hydroxides are the primary vapor carrier species in the reducing gasification fuel gas.^{3,5,19} Because sulfur is essentially present as H₂S in the gasification fuel gas, alkali sulfates are not formed in this environment.

Quantification of the alkali vapor in PFBC effluent is a critical issue that has been addressed by many institutions.¹⁹⁻³¹ An Ames on-line, real-time alkali analyzer^{32,33} has been extensively tested at Argonne National Laboratory to measure the alkali (Na and K) vapor concentration in PFBC effluent. In these measurements, 0.64-cm-dia. (1/4-in.) Type 304 stainless steel tubing was used as a sampling line to extract PFBC effluent for alkali-vapor analysis. In the early phase of calibrating and testing the Ames alkali analyzer with NaCl vapor, a loss of some of the vapor in the heated (>700°C) stainless steel sampling line was observed.²⁰ To further study this phenomenon, a series of laboratory tests was conducted to expose heated (840-950°C) Type 304 stainless steel tubing to simulated, high-pressure (9.2 atm absolute) PFBC effluent (average composition 3.3% O₂, 0.14% H₂O vapor, 540 ppmV SO₂, alkali vapors, and the balance N₂) and to examine its high-temperature behavior toward both NaCl and KCl vapors.²¹ Figure 5 shows schematically the experimental setup. Typical results from this series of tests are shown in Fig. 6.

Figure 6 clearly shows that, after exposure for 3 h to a nitrogen gas stream that contained 0.4-2.2 ppmW sodium (as NaCl vapor) and 0.4-1.5 ppmW potassium (as KCl vapor), the heated stainless steel gas transport line continuously released both Na and K into the alkali-vapor-free

Fig. 5. Schematic of Pressurized NaCl-KCl-Vapor Generation Unit Integrated with Ames On-Line, Real-Time Alkali Analyzer²¹

Fig. 6. Measured Sodium and Potassium Concentrations in the Gas Stream for Test of Type 304 Stainless Steel Sampling Line at 840-950°C and 9.2 atm Absolute²¹

N₂ gas stream. Initial releases ranged from 45-50 ppbW of Na and 25-30 ppbW of K, and rapidly increased to 220-280 ppbW of Na and 180-240 ppbW of K when the alkali-vapor-free simulated off-gas flowed through the line. Similar phenomena were observed when the line was exposed to a simulated PFBC off-gas containing NaCl-KCl vapor. The results of this series of tests verify the previous observation²⁰ that heated stainless steel captures NaCl and KCl vapors when exposed to a NaCl-KCl-vapor-bearing gas stream. Also, the captured alkalis are reversibly released to an alkali-vapor-free gas stream. Mechanisms of the alkali vapor capture by and alkali release from the heated Type 304 stainless steel tubing are not known.

This study, conducted under the auspices of the U.S. Department of Energy, used thermogravimetric analysis (TGA) to experimentally evaluate several candidate materials (iron-, nickel-, and cobalt-based alloys, as well as noble-metal-coated and ceramic-lined alloys) for their capture of alkali vapor under both simulated PFBC (oxidizing) and coal gasification (reducing) environments. The treated materials were analyzed by using various techniques to characterize their alkali adsorption behavior. The objective of this study was to identify non-alkali-adsorbing material(s), if any, that might be suitable for use as process component materials in advanced coal-utilization systems. One specific use would be in the gaseous sampling line for an on-line alkali analyzer. An inert sampling line is needed to ensure the analytical accuracy of the analyzer.

2.0 EXPERIMENTAL PROCEDURES

2.1 Candidate Materials and Their Preparation

2.1.1 Candidate Materials

Table 1 lists the chemical compositions of the nine candidate materials that were tested for their capture of NaCl vapor in a simulated PFBC off-gas. The 304 SS was included as a base material for comparison. In the second phase of this work, Haynes No. 188 and aluminized 304 SS were also tested for their NaCl-vapor capture in a simulated gasification fuel gas.

Table 1. Chemical Compositions of Candidate Materials, wt%

Material	C	Cr	Ni	Mn	Si	Mo	W	Fe	Other
304 SS	0.08	18.3	8.10	1.5	0.27	0.27	-	Bal. ^a	-
Hastelloy X	0.10	22.0	Bal.	0.5	0.5	9.0	0.6	18.5	Co 1.5
Hastelloy C-276	-	15.5	Bal.	1.0	-	16.0	3.8	5.5	Co 2.5, V 0.35
Haynes No. 188	0.08	23.4	23.3	0.7	0.40	0.60	14.6	1.40	Co 35.7
Pt-Coated 304 SS	0.08	18.3	8.10	1.5	0.27	0.27	-	Bal.	Pt coating
Au-Coated 304 SS	0.08	18.3	8.10	1.5	0.27	0.27	-	Bal.	Au coating
Ag-Coated 304 SS	0.08	18.3	8.10	1.5	0.27	0.27	-	Bal.	Ag coating
Aluminized 304 SS	0.08	18.3	8.10	1.5	0.27	0.27	-	Bal.	Al diffusion coating
ZrO ₂ -Coated 304 SS	0.08	18.3	8.10	1.5	0.27	0.27	-	Bal.	ZrO ₂ coat- ing

^a Bal. = balance

2.1.2 Preparation of Specimen Coupons

Two sets of specimen coupons of each of the candidate materials were prepared. One set was tested in a baseline (containing no NaCl vapor) simulated PFBC off-gas and coal gasification fuel gas. The second set was tested in the same simulated gas stream containing about 80 ppmW NaCl vapor.

Coupons [1.27 cm (1/2 in.) wide, 2.54 cm (1 in.) long, and 0.127 cm (0.05 in.) thick] were prepared from 304 SS, and from the Hastelloy C-276, Hastelloy X, and Haynes No. 188 alloys. The specimens were finished by polishing with 4000-grit SiC paper, cleaned in an ultrasonic water bath, and finally rinsed with alcohol. For preparation of the noble-metal-coated specimens, finished 304 SS coupons (1.27 x 1.27 x 0.127 cm) were sputter-deposited with the appropriate metal. The deposited layers were approximately 1 μm thick. The sputter-deposited specimens were analyzed using Auger electron spectroscopy (AES). Figure 7 shows the AES spectra and depth profile data for the Pt-deposited specimen, verifying the presence of the Pt layer.

The addition of aluminum to all grades of steel and stainless steel is known to improve their resistance to high-temperature sulfidation, oxidation, and carburization. A commonly known method to achieve this aluminizing is a technique whereby the steel (or stainless steel) material is enclosed in a pack that contains Fe-Al powder, inert refractory powder, and a halide activator. The packed material is heated (950-1000°C) for a sufficient time to allow the elemental aluminum to diffuse into the surface of the steel substrate (average depth of diffusion zone is 150-200 μm). An aluminum-rich alloy (not an aluminum coating) is formed on the surface. Upon further exposure to high temperature in an oxidizing environment, this alloy develops a slow-growing alumina scale that can protect the underlying substrate steel and reduce corrosion.

For this study, a finished 304 SS coupon (1.27 x 1.27 x 0.127 cm) was aluminized by a commercial vendor (Alon Processing, Inc., PA). To monitor the rate of development of alumina scale, the aluminized specimen was pre-oxidized in a muffle furnace at 1000°C for 2 and 50 h. Figure 8 shows SEM micrographs of the aluminized 304 SS sample in the as-aluminized condition (a), and after exposure to air at 1000°C for 2 and 50 h (b and c). The figure shows that the specimen develops a continuous Al_2O_3 scale after exposure to air at 1000°C for 50 h.

The specimens were subsequently analyzed to establish elemental concentrations in the coating-affected regions near the surface. Figure 9 shows the elemental concentration profiles for Al, Fe, Cr, Ni, and O for aluminized samples in the as-aluminized condition and after exposure to air. The data indicate that the iron concentration varied from 10-40 wt% in the coated region of the as-aluminized specimen. The effect of pretreatment in air at 1000°C was to enhance the formation of alumina scale. The iron concentration was 8-10 wt% in the 2-h-exposed sample and close to zero in the 50-h-exposed specimen. The alumina scale thickness was >50 μm after 50 h exposure at 1000°C in air. Based on these results, all aluminized 304 SS coupon specimens were pre-oxidized at 1000°C in air for 50 h before they were subjected to further testing.

Fig. 7. Auger Electron Spectroscopy (Top) and Depth Profile Analysis (Bottom) for Pt-Coated 304 SS Specimen

The ZrO_2 -coated 304 SS coupon specimen ($1.27 \times 1.27 \times 0.127$ cm) was prepared by depositing (1) a layer of bond coat of (Ni, Co) Cr Al Y and (2) an external ceramic coating of ZrO_2 by use of a thermal spray process. Due to the nature of the coating process, only one side of the coupon was coated with ZrO_2 . The bond layer and the ZrO_2 coating were ~ 100 and ~ 500 μm thick, respectively.

2.2 Test Equipment and Procedures

Figure 10 shows schematically the thermogravimetric analyzer (TGA) setup for experimental testing of the candidate materials (Table 1) in a simulated PFBC off-gas. A coupon was suspended in the TGA and heated to a controlled temperature by a 3-zone tubular furnace. The

Fig. 8. SEM Micrographs of Cross Sections of Aluminized 304 SS in the (a) as-Aluminized Condition, and after Exposure to Air at 1000°C for (b) 2 and (c) 50 h

NaCl vapor generated from a NaCl bed was carried upward to the coupon by preheated simulated PFBC off-gas that was introduced into the TGA from the bottom of the Al_2O_3 reactor tube (2.54-cm ID). A packed bed of Al_2O_3 chips served as a heat-transfer medium. To prevent vapor condensation on the platinum wire on which the coupon specimen was suspended, a downflow of nitrogen purge gas was introduced into the TGA, as shown in Fig. 10. Temperatures of both the specimen and the NaCl bed were monitored by thermocouples. Table 2 shows the test conditions. The coupons were exposed to the simulated PFBC off-gas at 870-875°C and atmospheric pressure for 100 h. The weight change of the sample was continuously recorded for the duration of the test.

Baseline testing was conducted in the TGA in the absence of an NaCl bed. All baseline tests were completed first to prevent contamination of the setup by NaCl vapor. For tests with NaCl vapor, the coupon was maintained at a much higher temperature (870-875°C) than the NaCl bed (715°C) to prevent NaCl vapor from condensing on the specimen. In the initial tests

Fig. 9.

Elemental Concentration Profiles for Al, Cr, Fe, Ni, and O in the Near-Surface Regions of Aluminized 304 SS:

(Top) as-Aluminized Condition, (Middle) after Exposure in Air at 1000°C for 2 h, (Bottom) after Exposure for 50 h

Fig. 10.

TGA Setup for Studying Alkali-Vapor Capture by Metallic Materials

Table 2. Experimental Conditions for Atmospheric TGA Tests of Candidate Materials in Simulated PFBC Environment

Coupon Temperature	870-875° C	
Total Flow Rate to Reactor	500 mL/min	
Test Duration	100 h	
Simulated PFBC Off-Gas Compositions	Component	Concentration
	O ₂	3.1 vol%
	CO ₂	14.7 vol%
	H ₂ O Vapor	2.0 vol%
	SO ₂	880 ppmV
	NaCl Vapor	0 and 80 ppmW
	N ₂	Balance

with NaCl vapor, the coupon and the NaCl bed were cooled simultaneously (by shutting off the power to the tubular furnace), which is referred to as "initial test-end cooling." There was a concern that, during the cooling period, the residual NaCl vapor in the reactor tube might either condense on the specimen or react with SO₂ to form Na₂SO₄, which might subsequently condense on the specimen. Thus, the test-end cooling procedure was modified as follows: the specimen was kept at the test temperature while the NaCl bed was cooling and the simulated

PFBC off-gas was shut off; after the NaCl bed had cooled to $<400^{\circ}\text{C}$, the coupon itself was cooled. This modified procedure is referred to as "modified test-end cooling."

For tests in the simulated coal gasification fuel gas, the TGA setup was slightly modified to accept the simulated fuel gas (i.e., 20% H_2 , 19% CO , 5% CH_4 , 0.2% H_2S , 12% CO_2 , 2% H_2O vapor, 0 and 80 ppmW NaCl vapor, and the balance N_2). The combustible gas stream (a mixture of H_2 , CO , CH_4 , H_2S , and N_2) was introduced into the reactor through the central Al_2O_3 tubing. Because of the presence of combustible gases in the simulated fuel gas stream, a comprehensive safety review of the setup and test procedures was conducted to ensure the safe operation of the system.

At the end of each test, the after-test coupon specimen was analyzed by SEM/EDX. Near-surface regions of selected coupons were further analyzed by AES, a technique that can be used to determine the elemental composition of the outer monolayer of an electrically conductive solid without the use of standards. The average detectability limit is ~ 0.1 at.%. The technique involves striking the sample with an electron beam and measuring the energy of the Auger electrons that the sample emits. These Auger electrons have an escape depth of 5-50 Å. Analysis of coupons was also conducted in a AES system equipped with an ion gun that was used to fire high voltage argon ions into the sample. In time these ions erode the sample. By monitoring the signal from the Auger electrons with respect to sputtering time it is possible to generate a "sputter depth profile" which determines the concentration of the elements as a function of sample depth.

3.0 RESULTS AND DISCUSSION

3.1 Tests in Baseline Simulated PFBC Off-Gas

Table 3 shows the total weight change of test specimens after exposure to the baseline simulated PFBC off-gas (Table 2) at $870\text{-}875^{\circ}\text{C}$ for 100 h. Figure 11 shows SEM micrographs of the test specimens. Prior to testing, the finished coupons of 304 SS, Hastelloy X, Hastelloy C-276, Haynes No. 188, Pt-coated 304 SS, Au-coated 304 SS, and Ag-coated 304 SS were shiny; however, during the exposure they all formed black scales. These scales were basically oxides of Cr, Fe, and/or Ni, which caused the weight gain of the tested coupon specimens, as shown in Table 3. The weight loss of the Ag-coated 304 SS was probably due to the spalling off of the scale during the test.

The scale thicknesses for the 304 SS, Hastelloy X, and Haynes No. 188 were fairly uniform, in the range of 2-3 μm . The scale on the Hastelloy C-276 was 8-10 μm thick and exhibited a ragged surface morphology with a number of cracks and voids. Results of the EDX elemental analyses of the base metal and scale of the exposed specimens are shown in Figs. 12 and 13. The scale was predominantly Cr_2O_3 for 304 SS, Hastelloy X, and Haynes No. 188 whereas the oxide scale on Hastelloy C-276 contained Cr, Fe, and Ni. The lower concentration of chromium (15.5 wt%) in Hastelloy C-276 is not sufficient to form pure chromia scale at the temperature range of $870\text{-}875^{\circ}\text{C}$. No sulfur was detected in the scale on the alloy substrate.

Table 3. Total Weight Change of Candidate Materials Tested in Baseline Simulated PFBC Off-Gas (No NaCl Vapor)

Material	Specimen Dimensions, ^a cm	Initial Specimen Wt, g	Total Wt Change, ^b mg/cm ²
304 SS	2.54 x 1.27 x 0.127	2.9936	+0.43
Hastelloy X	2.54 x 1.27 x 0.127	2.7802	+0.42
Hastelloy C-276	2.54 x 1.27 x 0.127	3.5294	+0.36
Haynes No. 188	2.54 x 1.27 x 0.127	3.1149	+0.19
Pt-coated 304 SS	1.27 x 1.27 x 0.127	1.5963	+0.44
Au-coated 304 SS	1.27 x 1.27 x 0.127	1.5503	+0.44
Ag-coated 304 SS	1.27 x 1.27 x 0.127	1.5513	-1.42
Aluminized 304 SS ^c	1.27 x 1.27 x 0.127	1.8702	+1.40

^aL x W x T.

^bWeight change after 100-h exposure.

^cThe specimen had been preheated in air at 1000°C for 50 h.

For Pt-, Au-, and Ag-coated 304 SS, the sputter deposit of the noble metals did not prevent outward diffusion of substrate elements (Cr and/or Fe) and subsequent oxidation of these elements, but the oxide morphology was very different from that obtained without the coating. The oxide thicknesses were in the same range (2-3 μm), however, the oxides on the uncoated sample exhibited ragged morphology while those on the coated specimens were smooth. As shown in Fig. 13, the oxide composition in the Pt-coated 304 SS coupon specimen was almost pure Cr_2O_3 , that in the Au-coated sample was (Cr, Fe) oxide, and that in the Ag-coated sample was iron oxide. Some of this iron oxide probably spalled off during the test, resulting in the weight loss shown in Table 3. No sulfur was detected in any of the samples after exposure to the SO_2 -containing PFBC off-gas.

As a result of the aluminizing process, the pretreated aluminized 304 SS coupon exhibited a rough and light-brownish surface. As shown in Table 3, this specimen also gained weight after exposure to the baseline simulated PFBC off-gas, suggesting the continuing growth of Al_2O_3 scale during the exposure (100 h). The SEM micrographs for the cross-section of the exposed specimen (Figure 11) show that the alumina scale (developed during the pretreatment in air at 1000°C for 50 h) was continuous and intact after exposure. No sulfur was detected in the scale or the alloy substrate. Figure 14 shows the elemental concentration profiles across the scale and substrate alloy (top figure) and in the near surface regions (bottom figure) of the exposed specimen. It is evident that the alumina scale remained intact to a depth of 40 μm during the 100-h exposure.

Fig. 11. SEM Micrographs of Cross Sections of Test Specimens after Exposure to Baseline Simulated PFBC Off-Gas (No NaCl Vapor): (a) 304 SS, (b) Hastelloy X, (c) Hastelloy C-276, (d) Haynes No. 188, (e) Pt-Coated 304 SS, (f) Au-Coated 304 SS, (g) Ag-Coated 304 SS, and (h) Pretreated (1000°C for 50 h in air) Aluminized 304 SS

Fig. 12. EDX Analysis of (a) Hastelloy X, (b) Hastelloy C-276, and (c) Haynes No. 188 after Exposure to Baseline Simulated PFBC Off-Gas (No NaCl Vapor): (Top) Base Metal and (Bottom) Scale

Fig. 13. EDX Analysis of Scales of (a) Pt-Coated 304 SS, (b) Au-Coated 304 SS, and (c) Ag-Coated 304 SS after Exposure to Baseline Simulated PFBC Off-Gas (No NaCl Vapor)

Fig. 14. Elemental Concentration Profiles for Al, Cr, Fe, Ni, and O in the Pretreated Aluminized 304 SS after Exposure to Baseline Simulated PFBC Off-Gas (No NaCl Vapor): (Top) Across the Scale and Substrate Alloy and (Bottom) Near-Surface Regions

3.2 Tests in Simulated PFBC Off-Gas Containing NaCl Vapor

Table 4 summarizes the total weight gain of all the coupons after exposure to the simulated PFBC off-gas (Table 2) containing ~80 ppmW NaCl vapor. As in the baseline tests, the coupons of 304 SS, Hastelloy X, Hastelloy C-276, Haynes No. 188, Pt-coated 304 SS, Au-coated 304 SS, and Ag-coated 304 SS were initially shiny, but became black during exposure, suggesting the formation of oxide scales that resulted in the weight gain. The weight gains were significantly greater than those observed in the baseline tests (Table 3). The black scales of the 304 SS, Hastelloy X, Haynes No. 188, Pt-coated 304 SS, and Au-coated 304 SS

Table 4. Total Weight Change of Candidate Materials Tested in Simulated PFBC Off-Gas Containing NaCl Vapor

Material	Specimen Dimensions, ^a cm	Total Wt Change, ^b mg/cm ²
304 SS	2.54 x 1.27 x 0.127	+1.31
Hastelloy X	2.54 x 1.27 x 0.127	+1.68
Hastelloy C-276	2.54 x 1.27 x 0.127	>+8.69 ^c
Haynes No. 188	2.54 x 1.27 x 0.127	+1.70
Pt-Coated 304 SS	1.27 x 1.27 x 0.127	+2.97
Au-Coated 304 SS	1.27 x 1.27 x 0.127	+1.27
Ag-Coated 304 SS	1.27 x 1.27 x 0.127	>+3.72 ^c
Aluminized 304 SS ^d	1.27 x 1.27 x 0.127	+3.36
ZrO ₂ -Coated 304 SS	1.27 x 1.27 x 0.127	N.D. ^e

^a L x W x T.

^b Weight change after 100-h exposure.

^c The after-test specimen was badly corroded. Some scales may have peeled off.

^d The specimen had been preheated in air at 1000°C for 50 h.

^e Not determined.

specimens appeared visually firm and smooth. By contrast, the Hastelloy C-276 and Ag-coated 304 SS specimens became severely corroded with the black scales peeling off the specimens. Their abnormal weight gain shown in Table 4 reflects this observation. A repeat test with the Hastelloy C-276 coupon under the same experimental conditions for 25 h showed similar results. The rough, light-brownish surface of the pre-oxidized aluminized 304 SS coupon specimen, which is a result of the aluminizing process, appeared intact (no color change) after the test. However, the weight gain of this aluminized 304 SS was also significantly greater than that obtained in the baseline condition (no NaCl vapor). Due to the nature of the coating process, the ZrO₂-coated 304 SS coupon specimen was coated only on one side; therefore, a meaningful weight gain could not be obtained.

The exposed coupons were analyzed by both SEM and AES. Figures 15, 16, 17, and 18 show the SEM micrographs and Tables 5 and 6 summarize the AES data for all tested specimens.

3.2.1 304 SS

Earlier laboratory studies^{20,21} indicated that the heated Type 304 stainless steel tube (used as a sampling line in the on-line Ames alkali analyzer) captures NaCl and KCl vapors when exposed to NaCl-KCl-vapor-bearing simulated PFBC off-gas. The 304 SS was included in this study as a base material for comparison. Figure 15 shows SEM micrographs of surfaces and cross-sections of two 304 SS coupons (Specimen 304 SS-1 and Specimen 304 SS-2). Specimen 304 SS-1 (Figs. 15a and 15b) underwent a 100-h test completed by initial test-end cooling; and Specimen 304 SS-2 (Figs. 15c and 15d) underwent a duplicate 90-h test with the modified test-end cooling procedure.

Fig. 15. SEM Micrographs of Surfaces (Left Column) and Cross Sections (Right Column) of 304 SS (a, b, c, and d) and Hastelloy X (e, f, g, and h) after Exposure to Simulated PFBC Off-Gas Containing NaCl Vapor
 (a), (b), (e), and (f): 100-h Test w/ Initial Test-End Cooling
 (c) and (d): 90-h Test w/ Modified Test-End Cooling
 (g) and (h): 100-h Test w/ Modified Test-End Cooling

Fig. 16. SEM Micrographs of Surfaces (Left Column) and Cross Sections (Right Column) of Hastelloy C-276 (a, b, and c) and Haynes No. 188 (d, e, f, and g) after Exposure to Simulated PFBC Off-Gas Containing NaCl Vapor (a), (b), (d), and (e): 100-h Test w/ Initial Test-End Cooling (c): 25-h Test w/ Initial Test-End Cooling (f) and (g): 100-h Test w/ Modified Test-End Cooling

Fig. 17. SEM Micrographs of Surfaces (Left Column) and Cross Sections (Right Column) of Pt-Coated (a and b), Au-Coated (c and d), and Ag-Coated (e and f) 304 SS after Exposure to Simulated PFBC Off-Gas Containing NaCl Vapor
(a), (b), (c), and (d): 100-h Test w/ Initial Test-End Cooling
(e) and (f): 100-h Test w/ Modified Test-End Cooling

Figure 15a shows that the light area in the photograph was composed of 53.1 wt% Cr, 34.1 wt% O₂, and 10.2 wt% Mn, while the dark area was composed of 33.0 wt% Na, 38.4 wt% S, 21.3 wt% O₂, and 5.6 wt% Mn. These data suggest that a layer of Na₂SO₄ was distributed on a thin oxide scale, shown in Fig. 15b. The AES data in Tables 5 and 6 show that sodium concentration in Specimen 304 SS-1 was high both on the surface (26.7 at.%) and at a depth of 2700 Å (21.1 at.%), which confirms the SEM analyses. The SEM micrographs of

Specimen 304 SS-2 (Figs. 15c and 15d) show no Na_2SO_4 layer, and the scale was predominantly (Cr, Fe) oxide. However, the AES also detected a relatively high sodium concentration on the surface (11.8 at.%) and at a depth of 2700 Å (4.2 at.%). These sodium concentrations are lower than those measured on the surface of Specimen 304 SS-1, which is probably due to the shorter test duration and the different test-end cooling procedure.

Fig. 18. SEM Micrographs of Surfaces (Left Column) and Cross Sections (Right Column) of Aluminized 304 SS (a, b, c, and d) and ZrO_2 -Coated 304 SS (e and f) after Exposure to Simulated PFBC Off-Gas Containing NaCl Vapor (a) and (b): 100-h Test w/ Initial Test-End Cooling (c) and (d): 150-h Test w/ Modified Test-End Cooling (e) and (f): 120-h Test w/ Modified Test-End Cooling

Table 5. AES Surface Concentrations in Coupon Specimens Exposed to Simulated PFBC Off-Gas Containing NaCl Vapor

Specimen	Elemental Analysis, at. %							
	O	Cr	S	Na	Fe	Mn	Al	Other
304 SS-1 ^a	35.6	9.1	4.4	26.7	7.5	11.6	--	P 5.0
304 SS-2 ^b	55.5	6.1	2.5	11.8	20.9	--	--	Cl 2.8
Hastelloy X ^c	38.2	2.3	4.8	28.6	4.8	5.5	--	P 4.6, Cl 2.2, Co 4.1, Ni 3.4
Hastelloy C-276 ^d	NA							
Haynes No. 188 ^e	42.1	7.9	4.0	19.0	5.0	--	--	P 3.4, Cl 0.8, Co 10.9, Ni 6.9
Pt/304 SS ^f	49.9	7.9	3.0	20.2	6.3	10.1	--	--
Au/304 SS ^g	49.3	6.4	3.7	16.1	24.2	--	--	--
Ag/304 SS ^h	45.1	11.7	2.2	15.3	22.0	--	--	Ni 2.5
Al/304 SS-1 ⁱ	7.4	--	0.9	6.1	--	--	85.6	--
Al/304 SS-2 ^j	57.9	--	1.2	8.5	10.9	--	21.3	--
ZrO ₂ /304 SS ^k	28.8	--	7.8	26.7	--	--	--	Zr 28.3, P 7.4

^a The specimen and the NaCl bed were cooled simultaneously at the end of the test (referred to as initial test-end cooling).

^b A duplicate test for 90 h. The NaCl bed was first cooled to <400°C and then the specimen was cooled (referred to as modified test-end cooling).

^c Initial test-end cooling.

^d Not analyzed due to severe corrosion of the tested specimen.

^e Initial test-end cooling.

^f Pt-Coated 304 SS, initial test-end cooling.

^g Au-Coated 304 SS, initial test-end cooling.

^h Ag-Coated 304 SS, modified test-end cooling.

ⁱ Pretreated (at 1000°C for 50 h in air) aluminized 304 SS, initial test-end cooling.

^j A duplicate test for 150 h with modified test-end cooling.

^k ZrO₂-coated 304 SS, modified test-end cooling.

The presence of Mn, Fe, and Cr, and the substantial amount of oxygen on the surface of the 304 SS specimens (Tables 5 and 6) indicate that the captured sodium could be reacting with the base metal elements to form complex (Na, Cr, Mn, Fe) oxides as reaction products. The analysis shows that the relative ratios of Na:M:O at the surface and at a depth of 2700 Å of Specimen 304 SS-1 are ~3:3:4 and ~2:3:4, respectively, where M represents the total concentrations of Fe, Cr, and Mn. The corresponding ratios for Specimen 304 SS-2 are ~1.5:3:6 and ~0.5:4:6. These results indicate that in both specimens the sodium concentration was much greater at the surface than at 2700 Å.

Table 6. AES Surface Concentrations at a Depth of 2700 Å in Coupon Specimens
Exposed to Simulated PFBC Off-Gas Containing NaCl Vapor

Specimen ^a	Elemental Analysis, at.%							
	O	Cr	S	Na	Fe	Mn	Al	Other
304 SS-1	40.3	15.6	4.5	21.1	3.3	11.0	--	P 3.3
304 SS-2	54.9	10.1	0.6	4.2	25.8	--	--	Ni 4.4
Hastelloy X	37.8	4.1	8.0	20.3	5.6	5.1	--	P 8.3
Hastelloy C-276	NA	--	--	--	--	--	--	--
Haynes No. 188	43.4	8.1	4.7	11.6	2.3	--	--	P 2.3, Ni 6.7 Co 15.7
Pt/304 SS	53.7	16.4	4.4	10.6	4.6	10.3	--	P 4.6
Au/304 SS	54.3	5.1	2.0	7.8	31.0	--	--	--
Ag/304 SS	45.9	8.8	3.2	7.7	28.6	--	--	Ni 5.1, Ag 0.7
Al/304 SS-1	33.6	8.1	6.6	14.3	9.4	--	28.1	--
Al/304 SS-2	35.2	5.6	1.6	10.0	7.7	--	39.9	--
ZrO ₂ /304 SS	32.5	--	7.7	24.0	--	--	--	Zr 28.3, P 7.4

^a Sample identification is given in Table 5.

Some chlorine (2.8 at.%) was detected on the surface of Specimen 304 SS-2 (Table 5), indicating the adsorption of NaCl vapor on the Cr₂O₃ scale. This observation may suggest that NaCl vapor was initially adsorbed on the surface and then gradually reacted with adsorbed SO₂, O₂, and H₂O vapor to form the Na₂SO₄ layer (as observed by SEM) according to the following reaction:

Results of this test are in agreement with earlier observations that the heated (840-950°C) 304 SS sampling line used in the on-line alkali analyzer captures NaCl and KCl vapors when exposed to NaCl-KCl-vapor-bearing simulated PFBC off-gas.^{20,21}

3.2.2 Hastelloy X

The first test of Hastelloy X was completed by using initial test-end cooling. The SEM micrographs of the after-test specimen are shown in Figs. 15e (surface) and 15f (cross-section). The specimen developed a (Cr, Fe) oxide scale, ~5 µm thick, in contrast to the pure Cr₂O₃ scale, 2-3 µm thick, that formed on the specimen exposed to the baseline PFBC off-gas. The EDX analysis showed the dark regions in Fig. 15e to be predominantly Na, S, and O, suggesting that a Na₂SO₄ layer deposited on the oxide scale, as shown in Fig. 15f. The light areas of Fig. 15e were chromium-rich oxide with very little sulfur. The boundary between the dark

and light areas contained Ni, Cr, O, and S. No Na or Cl was detected. The AES analyses of the specimen showed similarly high sodium concentrations as measured for Specimen 304 SS-1 both on the surface (28.6 at.%) and at a depth of 2700 Å (20.3 at.%). These results confirm the SEM observations. The AES analysis also detected a small amount (2.2 at.%) of chlorine on the surface of the specimen.

A duplicate test was conducted using the modified test-end cooling procedure; Figs. 15g and 15h show the SEM micrographs. A Na_2SO_4 deposit layer was also observed on this specimen and the scaling characteristics with regard to morphology and composition were similar to those observed in the first test.

3.2.3 Hastelloy C-276

As shown in SEM micrographs (Figs. 16a and 16b), the Hastelloy C-276 sustained severe corrosive attack and substantial internal sulfidation in the PFBC test. Corrosion was equally severe after only 25 h exposure (Fig. 16c). It is evident that the oxide scale in this alloy did not protect against NaCl vapor attack. On the other hand, Hastelloy X exhibited virtually no signs of corrosive attack under the same test conditions. The enhanced attack on Hastelloy C-276 can be attributed to the lower chromium content of the alloy (15.5 wt%) compared with the Hastelloy X (22 wt%).

The EDX analysis (Fig. 12) of the after-test specimen showed that the thick outermost layer consisted of NiO and chromium sulfides. The inner layer contained Ni, Cr, Fe, and O. The interior of the specimen had significant precipitates of sulfides in the grain boundary regions. The extent of corrosion was very severe and the corrosion product layers were much more complex than in other alloys tested; as a result, EDX analysis could not detect the presence of Na or Cl.

3.2.4 Haynes No. 188

Figures 16d and 16e are SEM micrographs of the exposed coupon (initial test-end cooling procedure). The EDX analysis showed that the fine-grained area in Fig. 16d consisted of chromium-rich oxide, the dark areas were rich in sodium, and the larger particles were cobalt oxide. The cross section of the specimen (Fig. 16e) showed the outmost layer to be rich in sodium salt while the internal continuous layer was oxide scale. The interior of the specimen contained chromium-rich sulfides and tungsten-containing oxides. The AES analysis (Tables 5 and 6) of the specimen showed significant sodium concentrations on the surface (19.0 at.%) and at 2700 Å (11.6 at.%). These data are in agreement with the EDX analysis. A small amount (0.8 at.%) of chlorine was also detected by AES on the surface of the specimen. A duplicate test completed with the modified test-end cooling procedure also revealed sodium salt on the exposed after-test specimen, as shown in Fig. 16f.

3.2.5 Noble-Metal-Coated 304 SS

Figure 17 shows SEM micrographs for surfaces and cross sections of Pt-, Au-, and Ag-coated 304 SS coupons. Testing of the first two coupons was completed by using the

initial test-end cooling procedure, while the Ag-coated specimen was cooled with the modified test-end procedure. The EDX analyses of after-test specimens showed that the Pt-coated specimen developed a thin scale, predominantly chromium oxide. The morphology of the Pt-enriched near-surface indicates that strong Fe-Pt interactions prevent iron transport while enabling transport of chromium outwards from the bulk alloy. By contrast, the Au- and Ag-coated specimens developed a predominantly iron oxide scale, which was much thinner in the Au-coated than in the Ag-coated specimen. Substantial segregation of Au and Ag was observed at the scale/alloy interface, indicating that a Au or Ag coating does not act as a barrier against outward diffusion and subsequent oxidation of iron from the bulk alloy. Some sulfides were observed in the interior of the specimens.

Some sodium was observed in the EDX analyses of the surfaces of these specimens but it was intermixed with the alloy/coating constituents, indicating that sodium capture is confined to a very thin layer on the surface. The AES analyses gave concentrations of 20.2, 16.1, and 15.3 at.% on surfaces of Pt-, Au-, and Ag-coated specimens, respectively, as shown in Table 5. Sodium concentrations decreased to 10.6, 7.8, and 7.7 at.% at a depth of 2700 Å, as shown in Table 6. The test-end cooling procedure used in carrying out the shut-down of the test did not appear to have any significant effect on the sodium concentration.

3.2.6 Aluminized 304 SS

Figures 18a and 18b show SEM micrographs for the surface and the cross section, respectively, of the exposed aluminized 304 SS specimen. Cooling was according to the initial test-end procedure. The SEM micrographs from a duplicate test (150-h exposure, cooling by the modified test-end cooling procedure) are shown in Figs. 18c and 18d. These figures show that the continuous Al_2O_3 scale developed during the pretreatment remained intact after exposure (as in the baseline test), and no sulfur was detected in the scale or the alloy substrate.

The AES analyses (Tables 5 and 6) of these two specimens showed the presence of sodium on the surface (6.1 and 8.5 at.% for 100-h and 150-h tests, respectively) and at 2700 Å (14.3 and 10.0 at.%). The surface sodium concentration of this aluminized 304 SS was the lowest of all the specimens tested, as shown in Table 5.

3.2.7 ZrO₂-Coated 304 SS

The ZrO₂-coated 304 SS coupon was exposed for 120 h, and cooled with the modified test-end cooling procedure. The EDX analysis of the surface of the exposed specimen showed predominantly Na, S, O, and Zr, and virtually no Cl. Figures 18e and 18f show SEM micrographs of the surface and the cross section, respectively, of the exposed specimen. The specimen had a fairly uniform deposit layer of Na₂SO₄ with a 30-μm diameter globular shape, as shown in Fig. 18e. The deposit exhibited some porosity, accompanied by chipping and cracking of the coating in a few areas.

The photomicrograph of the cross section of the exposed specimen (Fig. 18f) showed that the bond layer and the ZrO₂ coating were approximately 100 and 500 μm thick,

respectively. The sodium-rich area was confined to the surface region ($\sim 1 \mu\text{m}$ thick) of the ZrO_2 coating. This is in agreement with the AES spectra shown in Tables 5 and 6, which indicate sodium concentrations of 26.7 at.% on the surface and 24.0 at.% at a depth of 2700 Å. The EDX analysis of the cross sections of the exposed specimens showed that the bond coat developed alumina at the grain boundary/crack regions of the bond coat, indicating that the ZrO_2 coating was not impervious to gaseous diffusion.

3.3 Tests in Baseline Simulated Gasification Fuel Gas

The simulated gasification fuel gas (Section 2.2) consisted predominantly of CO and H_2 , which resulted in an extremely low partial pressure of oxygen in the exposure environment. The sulfur was present as H_2S , not SO_2 as in the simulated PFBC environment. The gas for the baseline test did not contain any NaCl. Two materials, namely, aluminized 304 SS and Haynes No. 188 alloy were exposed to fuel gas for 90 and 100 h, respectively, at 870-875°C. Since no alkali chloride was present in the baseline test, the scaling of the alloys was influenced by the oxidation and sulfidation reactions that can occur between the substrate constituents and the oxygen and sulfur reactants in the gas phase.

At the end of the test, both aluminized 304 SS and Haynes No. 188 specimens had become black. Table 7 shows the total weight gain of the specimens. Both specimens, especially the aluminized 304 SS, gained significantly more weight than in the simulated PFBC off-gas exposure (Table 3).

Table 7. Total Weight Gain of Aluminized 304 SS and Haynes No. 188 under Baseline Simulated Gasification Fuel Gas (No NaCl Vapor)

Material	Specimen Dimensions, ^a cm	Initial Wt, g	Total Wt Change, ^b mg/cm ²
Aluminized 304 SS ^c	1.27 x 1.27 x 0.127	1.8210	+ 27.64
Haynes No. 188	2.06 x 1.43 x 0.127	2.9984	+ 0.55

^aL x W x T.

^bWeight change after 90- and 100-h exposure for aluminized 304 SS and Haynes No. 188, respectively.

^cThe specimen had been preheated in air at 1000°C for 50 h.

Figure 19 shows SEM micrographs of the surface and cross section of the aluminized 304 SS specimen, and Fig. 20 shows EDX spectra for the specimen surface and at several locations identified as A, B, C, D, and E in Fig. 19. As indicated earlier (Fig. 8c), a continuous Al_2O_3 scale was originally developed during a 1000°C pretreatment of the specimen. After exposure for 100 h to the simulated PFBC off-gas (oxidizing), this Al_2O_3 scale remained intact (Fig. 11h), and no sulfur was detected in the scale and the alloy substrate. By contrast, exposure to the simulated gasification fuel gas (reducing) subjected the Al_2O_3 scale to attack by H_2S in isolated regions, as shown by the dark locations, B, D, and E, in Fig. 19.

Fig. 19. SEM Micrographs of Surface (Left) and Cross Section (Right) of Aluminized 304 SS after Exposure to Baseline Simulated Gasification Fuel Gas (No NaCl Vapor). Results of EDX analysis for locations A, B, C, D, and E are shown in Fig. 20.

The formation of (Cr, Mn, Fe) sulfides in these regions is seen in the EDX analysis in Fig. 20. Apparently, this sulfide formation resulted in the substantial weight gain shown in Table 7. The lighter regions, A and C, in Fig. 19 are basically the intact Al_2O_3 scale, as indicated in the EDX analyses in Fig. 20.

Figure 21 shows SEM micrographs for the surface and cross section and EDX spectra for locations A and B on the surface of the Haynes No. 188 specimen after baseline exposure. The specimen formed a continuous, uniform black scale on the surface. The EDX analysis showed that the scale consists of chromium-rich (Cr, Mn, Fe) oxides, and a trace amount of sulfur was detected on the surface of the specimen. In the simulated PFBC off-gas (Fig. 12c) by contrast, only Cr_2O_3 scale was formed and no sulfur was detected in the scale and the alloy substrate.

3.4 Test in Simulated Gasification Fuel Gas Containing NaCl Vapor

For this test, the aluminized 304 SS and Haynes No. 188 coupons were hung together in the TGA setup (Fig. 10) and exposed simultaneously to the simulated gasification fuel gas containing 80 ppmW NaCl vapor at 870-875°C for 70 h. Table 8 summarizes the total weight gain of the two specimens. The aluminized 304 SS was found to be badly corroded, resulting in the unusually large weight gain shown in Table 8. Some black scale peeled off easily during handling of the tested specimen. As in earlier tests, the initially shiny Haynes No. 188 specimen became black after testing.

Fig. 20. EDX Spectra of the Surface of Aluminized 304 SS after Exposure to Baseline Simulated Gasification Fuel Gas (No NaCl vapor). Locations A, B, C, D, and E are identified in Fig. 19.

3.4.1 Aluminized 304 SS

Figure 22 shows SEM micrographs for the surface and cross section and EDX spectra at several locations identified as A, B, and C of the surface of the aluminized 304 SS

specimen. The EDX analyses clearly showed the formation of (Cr, Mn, Fe) oxides and sulfides in the isolated areas of the surface, such as locations A and C. Apparently, the formation of these corrosion products undermined the Al_2O_3 layer originally developed on the surface of the

Fig. 21. SEM Micrographs (Top) of Surface (Left) and Cross Section (Right) and EDX Spectra (Bottom) for Locations A and B on the Surface of Haynes No. 188 after Exposure to Baseline Simulated Gasification Fuel Gas (No NaCl Vapor)

Table 8. Total Weight Gain of Aluminized 304 SS and Haynes No. 188 under Simulated Gasification Fuel Gas Containing NaCl Vapor

Material	Specimen Dimensions, ^a cm	Initial Wt, g	Total Wt Change, ^b mg/cm ²
Aluminized 304 SS ^c	1.27 x 1.27 x 0.127	1.8155	+ 41.82
Haynes No. 188	1.27 x 0.635 x 0.127	0.8460	+ 0.81

^aL x W x T.

^bWeight change after 70-h exposure.

^cThe specimen had been preheated in air at 1000°C for 50 h.

specimen during pretreatment and caused the Al₂O₃ scale to spall off the surface. This is shown in the cross-section SEM micrograph, in which the originally developed continuous Al₂O₃ scale disappeared from the tested specimen.

The EDX analyses also showed the presence of sodium along with sulfur on the surface of the Al₂O₃ scale (EDX spectra for surface and location B), but not in the corroded locations (A and C). This suggests the affinity of the Al₂O₃ scale for sodium adsorption. Detailed analysis of the specimen cross section showed that the sodium adsorbed layer was confined to a layer ~1 μm thick at the surface of the aluminized region.

3.4.2 Haynes No. 188

Figure 23 shows SEM micrographs for the surface and cross section and EDX spectra of the surface of the exposed Haynes No. 188 specimen. As in the baseline exposure, the specimen developed a continuous, uniform, black oxide scale on the surface, more noticeably in isolated locations. However, virtually no sodium was detected in this Haynes No. 188 specimen, indicating that the scale lacks sorption affinity for NaCl vapor. This is in contrast to the Cr₂O₃ scale developed in the oxidizing PFBC off-gas environment, on which NaCl vapor was shown to be adsorbed and gradually converted into Na₂SO₄.

4.0 CONCLUSIONS AND RECOMMENDATIONS

All nine candidate materials, 304 SS, Hastelloy C-276, Hastelloy X, Haynes No. 188, Pt-coated 304 SS, Au-coated 304 SS, Ag-coated 304 SS, aluminized 304 SS and ZrO₂-coated 304 SS, showed various degrees of NaCl-vapor adsorption after exposure at 870-875°C to the simulated PFBC off-gas (oxidizing) containing 80 ppmW NaCl vapor. The aluminized 304 SS exhibited the least tendency to adsorb NaCl vapor, as well as an excellent resistance to corrosion as a result of the formation of the protecting Al₂O₃ layer on the surface. In the simulated gasification fuel gas (reducing) containing 80 ppmW NaCl vapor, however, the aluminized 304 SS was badly corroded by H₂S attack, whereas the Haynes No. 188 showed virtually no NaCl-vapor adsorption and only limited H₂S attack.

Fig. 22. SEM Micrographs (Top) of Surface (Left) and Cross Section (Right) and EDX Spectra (Bottom) for Locations A, B, and C on the Surface of Aluminized 304 SS after Exposure to Simulated Gasification Fuel Gas Containing NaCl Vapor

This work was designed to be a preliminary screening study to identify material(s) that possesses little or no affinity for alkali vapor. Based on results of this study, we recommend performance of long-term parametric studies on alkali-vapor adsorption by (1) the aluminized

Fig. 23. SEM Micrographs (Top) of Surface (Left) and Cross Section (Right) and EDX Spectra (Bottom) for Locations A and B on the Surface of Haynes No. 188 after Exposure to Simulated Gasification Fuel Gas Containing NaCl Vapor

304 SS in the PFBC off-gas environment and (2) the Haynes No. 188 in the gasification fuel gas environment. It will be valuable to obtain quantitative estimates of alkali-vapor adsorption by these materials as a function of operating variables, for example, temperature, pressure, exposure duration, and the level of alkali-vapor concentration in the gas stream. The control of alkali vapor to a few parts per million is recommended.

5.0 ACKNOWLEDGMENTS

The authors are pleased to acknowledge D. L. Rink of Energy Technology Division for his assistance in performing SEM/EDX analyses of coupon specimens for this work. Valuable assistance has also been given by V. P. Kothari, N. T. Holcombe, and K. Das, Program Managers for this project at the U.S. DOE/Morgantown Energy Technology Center.

6.0 REFERENCES

1. H. S. Spacil, and K. L. Luthra, "Volatilization/Condensation of Alkali Salts in a Pressurized Fluidized Bed Coal Combustor/Gas Turbine Combined Cycle," J. Electrochem. Soc. 129, 2119-2126 (1982).
2. L. A. Scandrett, and R. Clift, "The Thermodynamics of Alkali Removal from Coal-Derived Gases," J. Inst. Energy 57, 391-397 (1984).
3. W. Mojtahedi, and R. Backman, "The Fate of Sodium and Potassium in the Pressurized Fluidized-Bed Combustion and Gasification of Peat," J. Inst. Energy 62, 189-196 (1989).
4. W. T. Reid, Ed., *External Corrosion Deposits—Boilers and Gas Turbines*, 1st Ed., American Elsevier Publishing Co., New York (1971).
5. H. H. Lunt, "Hot Corrosion in Gas Turbines," ASME Paper No. 77-WA/Fu-3 (1977).
6. S. H. D. Lee, and I. Johnson, "Removal of Gaseous Alkali Metal Compounds from Hot Flue Gas by Particulate Sorbents," J. Eng. Power, ASME Trans. 102, 397-402 (1980).
7. S. H. D. Lee, and K. M. Myles, "Alkali Measurement in PFBC and its Control by Granular Bed of Activated Bauxite," Proc. Int. Conf. on Fluidized-Bed Combustion, Boston, MA, May 3-7, 1987, Vol. II, pp. 793-801 (1987).
8. D. M. Bachovchin, M. A. Alvin, E. A. Dezubay, and P. R. Mulik, *A Study of High Temperature Removal of Alkali in a Pressurized Gasification System*, Report No. DOE-MC-20050-2226, Westinghouse Res. Dev. Center, Pittsburgh, PA (1986).
9. M. Uberoi, W. A. Punjak, and F. Shadman, "The Kinetics and Mechanism of Alkali Removal from Flue Gases by Solid Sorbents," Prog. Energy Combust. Sci. 16, 205-211 (1990).
10. K. Natesan, "Role of FBC Deposits in the Corrosion of Heat Exchanger Materials," High Temperature Technology 4, 193 (1986).
11. K. Natesan, *Laboratory Studies on Corrosion of Material for Fluidized Bed Combustion Applications*, Argonne National Laboratory Report, ANL/FE-90/1 (Oct. 1990).

12. J. Stringer, "Hot Corrosion of High Temperature Alloys," *Ann. Rev. Mater. Sci.* 7, 477 (1977).
13. J. A. Goebel, F. S. Pettit, and G. W. Goward, "Mechanisms for the Hot Corrosion of Nickel-Base Alloys," *Met. Trans.* 4, 261 (1973).
14. K. L. Luthra, and D. A. Shores, "Mechanism of Na_2SO_4 Induced Corrosion at 600-900°C," *J. Electrochem. Soc.* 127, 2202 (1980).
15. S. Kihara, and K. Nakagawa, *Laboratory Coal Ash Corrosion Tests*, Electric Power Research Institute Report, 77 EPRI GS-6449 (July 1989).
16. *An Investigation of Hot Corrosion and Erosion Occurring in a Fluid Bed Combustion--Gas Turbine Cycle Using Coal as Fuel*, U.S. Energy Research and Development Administration, FE/1536-2 (May, 1977).
17. C. C. Hsu, I. Johnson, and M. Blander, *Chemical Activities of Alkali Sulfates in Hot Corrosion*, Argonne National Laboratory Report, ANL-77-84 (1978).
18. M. A. Alvin, E. P. O'Neill, and D. L. Kearns, "Thermodynamic Projections of Trace Element Release in Fluidized-Bed Combustion Systems," *Proc. 5th Int. Conf. on Fluidized Bed Combustion*, December 12-14, 1977, Washington, DC, Vol. II, pp. 526-541 (1978).
19. P. R. Mulik, M. A. Alvin, and D. M. Bachovchin, *Simultaneous High-Temperature Removal of Alkali and Particulates in a Pressurized Gasification System*, Final Technical Progress Report for April 1981 to July 1983, Westinghouse Electric Corporation, DOE/MC/16372-1548 (DE84005777), pp. 3-39 (September 1983).
20. S. H. D. Lee, R. F. Henry, S. D. Smith, W. I. Wilson, and K. M. Myles, *Alkali Metal Vapor Removal from Pressurized Fluidized-Bed Combustor Flue Gas*, Annual Report for October 1984-September 1985, Argonne National Laboratory Report, ANL/FE-86-7 (Nov. 1986).
21. S. H. D. Lee, and E. L. Carls, *Measurement of Alkali Metal Vapors and Their Removal from a Pressurized Fluidized-Bed Combustor Process Stream*, Annual Report for October 1986-September 1987, Argonne National Laboratory Report, ANL/FE-88-4 (March 1989).
22. R. L. McCarron, A. M. Beltran, H. S. Spacil, and K. L. Luthra, "Turbine Materials Corrosion in the Coal-Fired Combined Cycle," *Proc. 5th Int. Conf. on Fluidized-Bed Combustion*, Washington, DC, December 12-14, 1977, Vol. III, pp. 714-736 (1977).
23. *Pressurized Fluidized-Bed Combustion*, R&D Report No. 85, Interim No. 1, prepared by National Research Development Corporation, London, England, for Office of Coal

- Research, Department of Interior, Washington, DC 20240. Contract No. 14-32-0001-1511 (1975).
24. *Energy Conversion From Coal Utilizing CPU-400 Technology*, Final Report, Vol. I., FE/1536-1, Combustion Power Co., Inc. (March 1977).
 25. A. G. Roberts, S. N. Barber, R. N. Phillips, K. K. Pillai, P. Raven, and P. Wood, *Fluidized Bed Combustion--1000 Hour Test Program, Vol. III--Combustion Emission and Hot Gas Cleanup*, NCB/Coal Utilization Research Laboratory, Report No. DOE/EF/10423-1103 (September 1981).
 26. A. G. Roberts, K. K. Pillai, and P. Raven, *Pressurized Fluidized Bed Combustion--Part Load Behavior, Vol I--Summary Report*, NCB/Coal Utilization Research Laboratory, Report No. DOE/MC/14129-171 (or FE-14129-6) (September 1981).
 27. *Fluidized Bed Combustor--Initial Results Obtained in a 1 Ft by 1 Ft Fluidized-Bed Combustor Operating at Pressures up to 20 Atm*, NCB/Coal Utilization Research Laboratory, Report No. DOE/MC/14129-1309 (September 1982).
 28. V. Zakkay, J. D. McClung, P. Radhakrishnan, S. Panunzio, K. Sellakumar, A. Ganesh, "Gas and Alkali Emission from Pressurized Fluidized-Bed Combustion of Lignite," Proc. of 8th Int. Conf. on Fluidized-Bed Combustion, Vol. III, pp. 1186-1196 (July 1985).
 29. W. J. Haas, Jr., and D. E. Eckels, *Real Time Monitoring of Sodium and Potassium Concentrations in Flue Gas Produced During July and August 1987 Coal Combustion/Hot Gas Cleanup Studies at the Grimethorpe (England) PFBC Establishment*, Ames Laboratory Report No. IS-4956 (July 1988).
 30. S. H. D. Lee, and E. L. Carls, "Measurement of Sodium and Potassium Vapours in Pressurized Fluidized-Bed Combustion of Beulah Lignite," J. Inst. Energy 63, 203-210 (1990).
 31. S. H. D. Lee, F. G. Teats, W. M. Swift, and D. D. Banerjee, "Alkali-Vapor Emission from PFBC of Illinois Coals," Combust. Sci. and Tech. 86, 327-336 (1992).
 32. W. J. Haas, Jr., D. E. Eckels, R. N. Kniseley, and V. A. Fassel, "Development of Alkali and Trace Heavy Metal Monitors," Proc. of DOE Contractors' Meeting on High Temperature, High Pressure Particulate and Alkali Control in Coal Combustion Process Streams, February 3-5, 1981, Morgantown, WV, pp. 599-620 (1981).
 33. W. J. Haas, Jr., D. E. Eckels, S. H. D. Lee, and R. F. Henry, "Recent Developments and Observations Pertinent to Real-Time Monitoring of Alkali Concentrations in Hot Gas Streams from Fluidized-Bed Combustion of Coal," Proc. DOE Fifth Annual Contractors' Meeting on Contaminant Control in Hot Coal-Derived Gas Streams, May 7-9, 1985, Morgantown, WV, pp. 493-512 (January 1986).

Distribution for ANL-FE-95-01Internal:

J. E. Harmon	K. M. Myles	W. J. Shack
T. F. Kassner	K. Natesan (5)	W. M. Swift
J. J. Laidler	R. B. Poeppel	R. W. Weeks
S. H. D. Lee (10)	D. K. Schmalzer	TIS Files
S. A. Miller		

External:

DOE-OSTI, for distribution per UC-103 (40)

ANL-E Library (2)

ANL-W Library

Manager, Chicago Operations Office, DOE

D. L. Bray, DOE-CH

Chemical Technology Division Review Committee Members:

E. R. Beaver, Monsanto Company, St. Louis, MO

D. L. Douglas, Consultant, Bloomington, MN

R. K. Genung, Oak Ridge National Laboratory, Oak Ridge, TN

J. G. Kay, Drexel University, Philadelphia, PA

G. R. St. Pierre, Ohio State University, Columbus, OH

J. Stringer, Electric Power Research Institute, Palo Alto, CA

J. B. Wagner, Arizona State University, Tempe, AZ

R. C. Bedick, USDOE, Morgantown Energy Technology Center, Morgantown, WV

D. J. Beecy, USDOE, Office of Fossil Energy, Germantown, MD

H. Birnbaum, University of Illinois, Urbana, IL

D. Bonk, USDOE, Morgantown Energy Technology Center, Morgantown, WV

R. C. Buchanan, University of Cincinnati, Cincinnati, OH

J. P. Carr, USDOE, Office of Fossil Energy, Germantown, MD

D. C. Cicero, USDOE, Morgantown Energy Technology Center, Morgantown, WV

K. Das, USDOE, Morgantown Energy Technology Center, Morgantown, WV

M. S. Dresselhaus, Massachusetts Institute of Technology, Cambridge, MA

D. E. Eckels, Ames Laboratory, Iowa State University, Ames, IA

M. R. Ghate, USDOE, Morgantown Energy Technology Center, Morgantown, WV

N. Holcombe, USDOE, Morgantown Energy Technology Center, Morgantown, WV

Illinois Institute of Natural Resources, Champaign, IL

B. G. Jones, University of Illinois, Urbana, IL

R. R. Judkins, Oak Ridge National Laboratory, Oak Ridge, TN

V. P. Kothari, USDOE, Morgantown Energy Technology Center, Morgantown, WV

C.-Y. Li, Cornell University, Ithaca, NY

S.-N. Liu, Freemont, CA

K. E. Markel, USDOE, Morgantown Energy Technology Center, Morgantown, WV

M. W. Pitt, USDOE, Office of Fossil Energy, Germantown, MD

J. Shang, USDOE, Office of Fossil Energy, Washington, DC

R. E. Smith, Altran Corporation, Huntersville, NC

M. Williams, USDOE, Morgantown Energy Technology Center, Morgantown, WV

J. F. Zievers, Industrial Filter & Pump Manufacturing Co., Cicero, IL