FOSTER WHEELER

FIRESIDE CORROSION TESTING OF CANDIDATE SUPERHEATER TUBE ALLOYS, COATINGS, AND CLADDINGS—

Phase II Field Testing

June 1998

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under
Subcontract 62X-SM-401C

for

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831

Managed by
LOCKHEED MARTIN ENERGY RESEARCH CORPORATION
for the
U. S. Department of Energy
under contract DE-AC05-96OR22464

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INTERIM REPORT
Project No.: 9-60550200

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CANDIDATE SUPERHEATER TUBE ALLOYS,
COATINGS, AND CLADDINGS—
Phase II Field Testing**

by
J. L. Blough, W. W. Seitz, and A. Girshik

June 1998

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ABSTRACT

In Phase I of this project, laboratory experiments were performed on a variety of developmental and commercial tubing alloys and claddings by exposing them to fireside corrosion tests which simulated a superheater or reheater in a coal-fired boiler. Phase II (in situ testing) has exposed samples of 347, RA85H, HR3C, RA253MA, $\text{Fe}_3\text{Al} + 5\text{Cr}$, Ta-modified 310, NF 709, 690 clad, 671 clad, and 800HT for up to approximately 16,000 hours to the actual operating conditions of a 250-MW, coal-fired boiler. The samples were installed on air-cooled, retractable corrosion probes, installed in the reheater cavity, and controlled to the operating metal temperatures of an existing and advanced-cycle, coal-fired boiler. Samples of each alloy were exposed for 4483, 11,348, and 15,883 hours of operation.

The present results are for the metallurgical examination of the corrosion probe samples after the full 15,883 hours of exposure. A previous topical report¹ has been issued for the 4483 hours of exposure.

SECTION I

INTRODUCTION

High-temperature fireside metal wastage in conventional coal-fired steam generators can be caused by gas-phase oxidation or liquid-phase coal-ash corrosion. Gas-phase oxidation is usually not a problem if tube and support materials are selected for their resistance to oxidation at the operating temperatures and for spalling, flaking, or other reactions to their environment. Coal-ash corrosion, on the other hand, usually results in accelerated attack and rapid metal wastage—even of stainless steels. The cause of this type of corrosion is usually the formation of alkali-iron-trisulfates on the tube surfaces. Some investigators have found that the presence of the low-melting-point alkali-aluminum sulfates also causes this type of corrosion. The corrosion occurs at the gas/ash interface where liquid sulfates actively corrode the surface of the metal beneath an overlying ash deposit.²⁻⁵

While substantial progress has been achieved through laboratory testing, actual utility service exposures are evidently necessary to verify any conclusions drawn from these tests. A number of important environmental parameters cannot be fully simulated in the laboratory.⁶⁻⁷

- The actual composition of the deposits formed on the tubes is more complex than the composition of the simulated ash.
- The SO_3 , formed by heterogeneous reaction on cooled surfaces, is variable.
- Very large temperature gradients occur within the ash deposits.
- The ash and fuel gas move past tubes at high velocity; the rate varies with design.
- The composition of the corrosive deposits changes with time.
- Metal and flue gas temperatures fluctuate.
- Fly-ash erosion removes the protective oxides, exposing a clean surface to fresh ash.

Foster Wheeler Development Corporation (FWDC) has performed a number of literature reviews and recent updates discussing the variables affecting the mechanism⁶⁻⁸ of coal-ash corrosion. Additionally, Foster Wheeler has conducted two sizable research projects—one a laboratory and in situ field testing at three utilities of commercially available alloys^{6,10,13-15} and this program (ORNL-FW2), combining laboratory and field testing to more completely cover the controlling variables for a longer duration.¹¹

SECTION II

PHASE I RESULTS

In Phase I of this ORNL program, "Fireside Corrosion Testing of Candidate Superheater Tube Alloys, Coatings, and Claddings," 20 commercial and developmental alloys listed in Table 1 were evaluated.¹⁰ The coupons of the metals were exposed to multiple types of synthetic coal ash and synthetic flue gases at 650 and 700°C (1202 and 1292°F) for up to 800 hours. The average thickness loss rate for 14- to 48-percent chromium-containing alloys and the intermetallic aluminides are shown in Figures 1 through 3.

Chromium content was found to be the largest factor in determining the resistance of an alloy to liquid coal-ash corrosion. For stainless steels and nickel alloys, additions of chromium up to 25 percent provided increased resistance to coal-ash attack; however, above the 25-percent chromium level, there appeared to be minimal benefit from more chromium, possibly because of the higher nickel content of those alloys. The exception is this is the good performance of the high chromium (approximately 50Cr-50Ni).

Molybdenum, on the other hand, may be detrimental to corrosion resistance. Silicon and aluminum were also beneficial, but to a lesser extent. The iron-aluminide intermetallics also showed a chromium dependence. Aluminides containing 5-percent chromium performed markedly better overall than those containing 2-percent chromium. The more resistant alloys showed lower corrosion rates at longer exposure times, indicating the formation of a passive layer; the less-resistant alloys exhibited increasing corrosion rates at longer exposures. Lower-chromium alloys generally suffered greater wastage rates at the higher testing temperature [700°C (1292°F)], while higher-chromium alloys suffered the same amount of wastage at 650 (1202) as at 700°C (1292°F).

Both the alkali content in the ash and SO₂ concentration in the flue gas affect the corrosivity of the alkali-iron-trisulfates in the ash layer. An increase in either resulted in a more corrosive environment and higher wastage rates.

SECTION III

PHASE II CORROSION PROBE TEST PLAN

In this project, the field tests comprised corrosion probe testing, coal characterization, and deposit/corrosion product analysis. The coals were analyzed to provide fuel characterization, a deposit analysis data bank, and possibly a corrosivity index for predicting corrosivity

Table 1. Composition of Alloys Examined

Alloy	Fe	Ni	Cr	Mo	C	Si	Mn	Al	N	S	P	Other
Fe ₃ Al-2Cr	81.86		2.19					15.93				B 0.01
Fe ₃ Al-5Cr	77.5		5.6					15.9				
(FeNi ₃)Al	11.7	70.1	7.2					11.0				
Modified 316 (LSS) [‡]	Bal	16.83	14.27	2.25	0.079	0.23	1.77	0.06	0.012	0.01	0.037	V 0.52, Nb 0.1, Ti 0.21
17-14 CuMo	Bal	14.08	16.37	1.95	0.078	0.72	0.88			0.005	0.023	Cu 3.34
Type 347 ^{††}	Bal	10.3	17.5		0.08	1.3	1.6			0.03	0.045	Nb 0.8
RA85H	Bal	15.26	18.50	0.06	0.24	3.90	0.50	0.70	0.10		0.015	Cu 0.39
Modified 800H	Bal	31.08	20.87	2.01	0.097		1.93	0.02	0.01	0.013	0.003	Nb 0.19, Ti 0.29, V 0.47
NF 709 ^{††}	Bal	24.3	21.5	1.0-2.0	<0.2	0.7	<1.5		0.05-0.02	<0.01	<0.03	Ta 0.68, Nb 0.07, W 2.45, B 0.01
Haynes 556	Bal	22.1	21.55	2.83	0.1	0.4	0.95	0.13	0.16	0.002	0.006	Nb 0.45
HR3C [†]	Bal	20.45	24.95		0.06	0.42	1.28		0.23	0.0001	0.013	
690/316	9.09	57.3	31.65	<0.05	0.048	0.26	0.17			0.002	<0.005	
690/800H	9.13	57.3	31.50	<0.05	0.049	0.26	0.17			0.002	<0.005	
690 [*]	9.5	Bal	30.0		0.03							
CR35A [†]	17.7	43.8	37.3				0.2					
72 Clad LSS [‡]	0.27	55.89	43.73		0.01	0.07	0.03			0.001		
72 Clad 800H	0.55	55.3	43.00	0.067	0.041	0.15	0.025			0.001	0.006	
671 Clad LSS [‡]		Bal	48.5	<0.05	0.057	0.11	<0.10	<0.05	0.0095	0.003	0.002	Ti 0.46, Nb <0.05, Cu <0.05
671 [*]		Bal	48.0		0.05							Ti 0.35
Sandvik 28 [†]	Bal	31.19	26.94	3.36	0.011	0.15	0.67		0.045	0.003	0.014	Cu 1.00
[*] Typical [†] Supplied by FWDC; all other supplied by ORNL [‡] Lean stainless steel ^{††} Modified Type 316												

under various combustion conditions. The equipment and the procedures for this phase have been previously used and perfected at three different utilities for over 3 years of in situ testing at each station.⁶

The utility that acts as host for test exposures should be burning an aggressive fuel to adequately evaluate the candidate alloys. The coals being burned at Tennessee Valley Authority's (TVA's) Gallatin Station had been previously analyzed,⁶ and numerous corrosion indices predicted high corrosivity in addition to the fact that installed T22 and Type 304SS tubing experienced about 7 years of life in the superheaters and reheaters of units 1 and 2.

Selection of Materials for Corrosion Probes

FWDC laboratory tested 20 different materials.¹¹ Because this quantity was impractical from both an economic and a probe-length standpoint, fewer materials (the ten listed in Table 2) were selected for the field tests. These materials provided a range of compositions and cost for both the commercially available and developmental alloys and claddings.

Table 2. Chemical Composition of Candidate Alloys (%)

Alloy	Cr	Ni	Others
85 H	18	15	Al = 1, Si = 3.9
Type 347	17-19	9-13	(Nb + Ta) = 10 × C (min.)
NF 709	20	25	Mo = 1.5, Mn = 1.0, Si = 0.6
253 MA	21	11	Si = 1.7
HR3C	25	20	Nb = 0.4
671 Clad/LSS*	48	52	
690 Clad/LSS*	30	58	
Fe ₃ Al + 5Cr	5	---	Al = 17
Ta-modified 310	25	20	Ta = 1.5
800HT	21	32	Al + Ti = 1
*Chemistry listed in Table 1.			

Field Corrosion Probe Design

The corrosion probes were designed to provide realistic exposures of metal samples to both actual boiler environments and also at the higher anticipated metal temperatures of an

advanced plant. The operation of the probes is independent from the main boiler, allowing removal without a boiler outage, and a fail-safe design that removes the probe from the boiler if there are any malfunctions. With these features, years of testing will not be compromised by a sudden overheating of the system.

The probes were exposed for 4483, 11,348, and 15,883 hours. This was accomplished by utilizing two probe test locations. At the upper test location, the probe was being exposed for 15,883 hours, while at the lower test location, the probe was removed after 4483 hours and a new probe inserted for the remaining 11,348 hours.

Each probe was a 2.56-m (8.4-ft)-long, 60.20-mm (2.37-in.)-OD tube that extends into the furnace for approximately 2.3 m (7.6 ft). Ring samples [38.1 mm (1.5 in.) wide] of the candidate alloys listed in Table 2 were installed at the end of the probe farthest from the furnace wall. The probe was cooled by air that flowed in the annular region between the probe tube ID and the tapered inner tube OD. The tapered inner tube was designed to obtain two bands of temperature on the outer surface of the samples. The alloy samples were duplicated in such a manner as to expose each alloy to a temperature in each of the temperature bands [621 to 677°C (1150 to 1250°F) and 677 to 727°C (1250 to 1340°F)].

Each probe had a retraction mechanism and three K-type thermocouples in duplicate to monitor the mean tube wall at the beginning and end of each test section group. A 19.95-mm (3/4-in.) OD × 6-ft-long thermowell with sheathed thermocouple was mounted between the upper and lower corrosion probes to measure flue gas temperature. Each probe has its own cooling-air control valve.

The control system monitored the selected control thermocouple and modulated the airflow to maintain an average surface metal temperature for each temperature band. The probes retracted automatically if failure of the cooling-air supply system or any other malfunction (instrument signal, power failure, or computer failure) caused the probe temperature to exceed the set limit of 746°C (1375°F) for 2 minutes. FWDC personnel accessed the field computer automatically for probe status and temperature data each morning or manually through its modem. A typical monthly plot of the thermocouples is shown in Figure 4. The number of hours in various temperature bands were counted as illustrated in Table 3, and the weighted average temperature over the complete test period was then obtained. Once the effective temperature was obtained for the ends of each test section, the effective temperature for each alloy sample can be calculated from the temperatures at the end points of the test section and the thermal properties of each alloy. The results are given in Table 4.

Table 3. Temperature Measurements*

Temperature Band	Upper (15,883 h)			Lower (11,348 h)			Flue Gas 1
	1/2	3/4	5/6	1/2	3/4	5/6	
1 - 900	2730	2766	2756	2782	2798	2799	1686
901 - 1000	28	1653	14	14	13	19	21
1001 - 1100	17	51	79	22	15	117	39
1101 - 1150	8	28	8487	29	26	5428	52
1151 - 1175	6	28	5513	26	9	8362	35
1176 - 1200	9	53	1559	28	17	1645	64
1201 - 1225	20	86	222	19	50	224	113
1226 - 1250	35	1534	39	34	2425	49	176
1251 - 1275	81	12059	2	89	12315	11	26
1276 - 1300	245	405	2	621	853	2	405
1301 - 1325	2297	8	0	6748	64	1	430
1326 - 1350	7900	1	1	7155	30	1	488
1351 - 1375	4983	1	1	961	26	0	787
1376 - 1400	301	0	1	98	15	0	787
1401 - 1500	13	0	0	32	4	0	4885
1501 - 1600	0	0	0	0	0	0	4669
1601 - 1700	0	0	0	0	0	0	929
1701 - 1800	0	0	0	0	0	0	6
1801 - 1900	0	0	0	0	0	0	0
1901 - 2000	0	0	0	0	0	0	0
2001 - 3000	0	0	0	0	0	0	0
1101 - 1400	15883	14203	15824	11348	11344	11345	13945
Wtd. Avg. T. [†]	1341	1260	1146	1325	1260	1153	1465
Total Hours	18672	18672	18673	18657	18657	18657	15690
*From 11/16/94 at 20:20:54 to 02/28/97 at 06:15:10. †Weighted average temperature (Wtd. Avg. T) is defined as the sum of the products of time and the average temperature in the band divided total time in the bands. For probes, the bands from 1100 to 1400 are used. For flue gas, the bands from 1100 to 3000 are used.							

Table 4. Estimated Average Midwall Specimen Temperatures

Sample	Material	T°F (4483 hours)	T°F (11,348 hours)	T°F (15,883 hours)
1	RA85H	1156	1163	1156
2	347	1166	1172	1167
3	NF 709	1175	1182	1177
4	RA253MA	1185	1192	1187
5	HR3C	1194	1202	1198
6	671	1204	1211	1208
7	690	1213	1221	1219
8	Fe ₃ Al	1223	1231	1229
9	310*	1232	1241	1239
10	800HT	1242	1250	1250
11	RA85H	1260	1266	1267
12	347	1267	1272	1275
13	NF 709	1275	1278	1282
14	RA253MA	1282	1284	1289
15	HR3C	1290	1290	1297
16	671	1294	1295	1304
17	690	1305	1301	1312
18	Fe ₃ Al	1312	1307	1319
19	310*	1320	1313	1326
20	800HT	1327	1319	1334
*Ta-modified 310.				

The locations in this plant (shown in Figure 5) were chosen because of cavity access and because they best represented the locations for the reheater or superheater outlet on the "Advanced Cycle" unit.⁶

In an ideal coal-ash corrosion probe exposure, only one coal would be burned at the plant. The practice of burning one coal is not common at many utilities since most have multiple long-term coal contracts; in fact, many are buying coal on the spot market. Gallatin burns a number of eastern high-sulfur coals, mainly Island Creek, Warrior, Dotiri, Pattiki, and

Constain, which are known to be corrosive and prone to alkali-iron-trisulfate formation. The coal analysis for the various coals burned as the primary fuel during these exposures is given in Table 5. The Borio Index¹⁶ for these coals typically ranges from 2.0 to 4.1, and the chloride level is 450 to 3000 ppm.

Coincidental with the installation of these corrosion probes was the installation of low NO_x burners. As reported later in the microscopic examination section, this low NO_x burner operation is believed to have changed the operating conditions and deposits from the previous EPRI study to produce a more carburizing environment.

Table 5. Coal Analysis—Gallatin

Description	Island Creek	Warrior	Dotiri	Pattiki	Lodestar	Lodestar Blend	Constain
Coal Basis, %							
Fe ₂ O ₃	1.50	2.70	1.71	1.71	1.92	1.63	1.60
CaO	0.18	0.47	0.42	0.33	0.26	0.14	0.13
MgO	0.06	0.11	0.06	0.04	0.07	0.97	0.07
CaO + MgO (Eq.)	0.26	0.63	0.50	0.39	---	0.23	0.23
Acid Soluble, ppm(w)							
Na ₂ O	161	81	325	559	410	313	422
K ₂ O	1085	1310	1164	921	390	325	392
K ₂ O (as Na ₂ O Eq.)	705	916	757	598	250	212	255
MgO	348	829	462	398	340	203	336
CaO	1203	3498	4305	2646	600	432	604
Chloride	1490	452	2100	1900	2900	---	2750
Indices							
Borio Index	2.0	2.6	2.3	4.1	---	---	3.0
Proximate, wt%							
Fixed Carbon	53	52	52	56	52	56	56
Volatile Matter	39	37	39	37	39	35	35
Ash	8	11	9	7	9	9	9

Table 5. Coal Analysis—Gallatin (cont)

Description	Island Creek	Warrior	Dotiri	Pattiki	Lodestar	Lodestar Blend	Constain
Ultimate, wt%							
Carbon	74	71	74	73	77	76	76
Hydrogen	5	5	5	5	5	5	5
Oxygen	8	8	6	9	4	6	6
Nitrogen	2	2	2	2	2	2	2
Sulfur	3	3	3	3	3	2	2
Ash	8	11	9	8	9	9	9
HHV, Btu/lb	13,598	12,926	13,429	13,252	13,809	13,517	13,517
Sulfur, %							
Sulfatic	0	0	0	0	0	0	---
Pyritic	1.09	1.66	0.83	0.88	1.21	1.2	1.2
Organic	1.99	1.46	2.55	2.46	1.99	0.53	0.53
Total	3.08	3.12	3.38	3.34	3.20	1.73	1.73

SECTION IV

POST-EXPOSURE ANALYSIS

Quarterly Examinations

During the quarterly inspections, FWDC personnel at the site manually retracted the probes, selectively removed deposits, and made ultrasonic wall thickness measurements on the 4483- and 11,348-hour probe samples of the probe set. The 15,883-hour probe was left untouched during these visits. Figure 6 (top) shows the two probes in the retracted position. The nearby soot blower can be seen to the right of the corrosion probes. This soot blower operated once during each 8-hour shift. The 4483- and 11,348-hour probes were carefully cleaned [as shown in Figure 6 (bottom)] with a wire wheel and/or sanding disk to remove the deposit and scale without removing any metal. Thickness losses were calculated, but they could be taken as only relative values because they do not include any internal penetration measurements and are not as accurate as micrometer and microscopic examination. The quarterly inspections provided preliminary nondestructive corrosion data before the three

destructive examinations. With these data, corrosion can be tracked and any complete wall penetration determined. The complete wall penetration would be harmful in two ways. Its occurrence and when it happened is needed for a corrosion rate calculation; but more importantly, cooling air leakage from a penetration could change the local exposure conditions of neighboring samples.

The laboratory analysis of the removed deposits characterized the composition and determined whether alkali sulfates were present and aided in interpreting the effects of fuel changes on coal-ash corrosion. An example of the chemical analysis for the coal ash collected on the corrosion probe is given in Table 6.

Table 6. Deposit Analysis

Element	As Oxide, %	Element	As Oxide, %
Silicon Dioxide	46.7	Sodium Oxide	<0.1
Aluminum Oxide	24.5	Potassium Oxide	3.1
Titanium Dioxide	1.6	Sulfur Trioxide	0.7
Ferric Oxide	18.5	Phosphorus. Pentoxide	0.3
Calcium Oxide	2.0	Loss on Ignition	1.84
Magnesium Oxide	0.7		

Previous x-ray diffraction analysis of deposits from the reheater tubes disclosed the presence of potassium iron trisulfide.¹³

Destructive Testing

At the end of each test period, the designated probe was removed, and post-exposure metallurgical evaluation was performed including:

- Visual examination and selective photographic documentation
- Selective removal of deposits
- Disassembly of probes
- Cutting of two transverse sections through the center of the ring sample
- Light grit blasting of one transverse ring section of each sample
- Visual examination of the cleaned samples

- Wall thickness measurements at 45-deg points or maximum loss areas on the leading 180-deg side of cleaned transverse ring from each alloy
- Mounting of the uncleaned ring samples to analyze the scale/deposit
- Microscopic measurement of the penetration and calculation of total metal loss
- Selective scanning electron microscopy/energy-dispersive x-ray (SEM/EDX) examination to analyze corrosion mechanism.

These same steps were performed on the two probes, 11,348- and 15,883-hour exposure, which were extracted from the boiler after this past outage. The results of the 4483-hour probe were previously reported.¹

MACROSCOPIC EXAMINATION

Both the 11,348- (lower) and 15,883- (upper) hour probes were received with a tan deposit on their outer surfaces. The deposits were removed and stored separately for later examination. After the probes were cleaned, they were both cut in half at the second thermocouple location as shown in Figure 7. [Note: The top 20 samples belong to the 11,348-hour probe and the bottom 20 samples belong to the 15,883-hour probe.] As illustrated, the probes are orientated with the 90-deg location (on-coming flue gas) facing out of the photo-macrograph. Two 1/4-in.-long transverse ring sections were removed from each sample on both probes. One of the ring sections was lightly grit blasted and used for thickness measurements while the other was mounted for microscopic and SEM/EDX analysis.

The appearance of the cleaned transverse cross sections used for wall thickness measurements is shown in Figures 8 and 9. As illustrated, the middle of the ring sections is approximately the 135-degree location. Shallow pitting and some surface roughening are evident in some of the samples. The more prominent surface roughness or pitting was noted on samples 1 (RA85H), 2 (347), 3 (NF 709), 11 (RA85H), and 12 (347) from the 11,348-hour (Figure 8) probe, and 1 (RA85H), 2 (347), 4 (253MA), 11 (RA85H) and 12 (347) in the 15,883-hour probe. Post-exposure wall thickness readings were performed at the 45-, 135-, and 270-degree locations, and calculated wall loss at the three locations is presented in Table 7. [Note: Further microexamination revealed that some of the wall loss in composite tube samples 6, 7, 16, and 17 resulted from the oxidation of the lower alloy LSS inside surface and not from corrosion of the higher alloy outside surface. One half of the scale thickness (microscopic evaluation, page 17) was calculated to be metal loss and was therefore added back into the wall thickness measurements to determine the loss from the OD only. Also, because of the swelling of the Fe₃Al samples, possibly because of a phase change, wall

thickness losses were negative and could not be used to indicate wall loss as a result of corrosion. Since the corrosion was minimal and the original OD surface could be determined, the wall thickness loss from the OD was measured microscopically.]

Table 7. Wall Loss at Measured Locations

Sample	Material	Wall Loss* (mils)					
		Lower Probe (11,348 h)			Upper Probe (15,883 h)		
		45°	135°	270°	45°	135°	270°
1	RA85H	1.4	6.6	0.4	2.2	-0.9	0.5
2	347	1.2	3.9	-4.8	6.4	7.0	0.4
3	NF 709	0.8	4.8	-0.2	6.1	3.6	1.8
4	RA253MA	0.2	1.1	0.6	7	2.6	0.8
5	HR3C	0.9	5.5	0.1	0.3	3.6	0.0
6	671	16.7	13.5	4.0	14.1	23.7	8.2
7	690	2.6	4.5	0.4	3	6.5	0.9
8*	Fe ₃ Al	-4.5	-5.5	-2.0	-3.0	-5.0	-2.0
9	310 [†]	1.7	1.2	-0.2	0.5	2.8	0.9
10	800	0.0	0.0	-0.1	0.3	1.7	0.7
11	RA85H	-0.2	-0.4	-0.1	9.8	3.0	1.6
12	347	-0.4	4.2	2.6	-0.6	15.2	0.6
13	NF 709	1.0	0.2	-0.2	10.2	4.4	0.5
14	RA253MA	0.9	0.7	0.3	0.1	2.6	0.7
15	HR3C	2.0	1.9	-0.2	0.4	-5.9	0.8
16	671	18.8	17.6	5.9	21.6	33.1	14.0
17	690	15.8	10.2	5.2	-1.3	22.0	5.4
18*	Fe ₃ Al	-10	-5.5	-4	-6.5	-4	-3.0
19	310 [†]	2.3	0.8	0.5	0.0	3.5	0.6
20	800	0.6	0.1	-0.1	0.4	2.1	0.9
*These negative numbers represent the swelling of the material which is not indicative of the actual wall thickness loss. †Ta-modified 310.							

MICROSCOPIC EXAMINATION and EDX ANALYSIS

All the specimens from each probe were mounted and microscopically examined to determine the subsurface penetration. For reporting purposes, after the macroscopic examination of both the 11,348- and the 15,883-hour probes, it was determined that the 15,883-hour probe would be the basis for our microscopic evaluation. This decision was reached using the following thought process: Photomicrographs of all the specimens would be quite voluminous and difficult to read; therefore, effort was concentrated on the longer-exposed samples. The 15,883-hour probe was left untouched (not prepared for UT measurements) in the boiler environment. That amount of time was enough for the materials to generate the protective barriers required to resist coal-ash corrosion or for the corrosion mechanisms to become noticeably active. Therefore, the photomicrographs displayed in the report are from the 15,883-hour probe.

Short sections from the 45-, 135-, and 270-degree locations of the samples were prepared for microscopic examination. Photomicrographs depicting various surface conditions in the samples are presented in Figures 10 through 29. A summary of the examination follows.

RA85H (Figures 10 and 11) — The representative microscopic appearance of the RA-85H alloy is shown in Figure 10. The samples from both probes were very similar in terms of their intergranular penetration and general internal attack on the outside surface to a depth of approximately 1.5 to 2.0 mils. The worst attack was noted at the 135-degree location of sample 11, which operated at a higher temperature than sample 1. Along the surface, the sample exhibited a two-part scale which consisted of a lighter scale on top of a darker scale; subsurface the material had numerous phases which warranted an EDX investigation. The lighter layer (location 1) was mainly an iron-oxide scale with trace amounts of aluminum, silicon, calcium, and chromium. The darker layer (location 2) was more of a chromium-rich oxide with nickel present and trace amounts of iron, aluminum, and silicon. Subsurface, the sample exhibited needle-like phases (location 3) which consisted mainly of aluminum and iron along with trace amounts of oxygen, silicon, chromium, and nickel. The gray phase noted at the leading edge of intergranular penetration (location 4) was comprised of chromium, aluminum, and oxygen with small amounts of silicon, molybdenum, sulfur, titanium, vanadium, iron, and nickel. Also, the alloy displayed a very light gray, spherical phase (location 5) which resembled a sulfide. However, the EDX analysis revealed it was most likely a chromium carbide with a minute amount of silicon, sulfur, vanadium, iron, and nickel. The resultant EDX spectra are shown in Figure 11.

Etching the samples revealed that each sample had a decarburized layer that was approximately 1 to 2 mils thick along the outside surface. Under the decarburized zone, the samples exhibited a microstructure loaded with carbide formations throughout. In addition, the IDs of samples 1 and 11 were found to have suffered penetration to depths of 2.8 and 3.3 mils (15,883-hour probe) and 2.3 and 3.0 mils (11,348-hour probe), respectively.

347 (Figures 12 and 13) — The representative appearance of the worst area of attack displayed by alloy 347 after 15,883 hours is shown in Figure 12. Both the 11,348- and 15,883-hour sets of samples exhibited a heavy scale layer which was basically chromium oxide with trace amounts of silicon, niobium, sulfur, calcium, iron, and nickel (location 6). The gray, nonmetallic phase (location 7) which penetrated into the material was found to be similar to the outer scale layer in terms of its chemical composition. The materials from both probes also exhibited heavy sulfide penetration. EDX analyses revealed that the sulfides (location 8) contained iron, nickel, manganese, chromium, and oxygen. The samples suffered approximately 1.5 and 3.5 mils of penetration (11,348- and 15,883-hour samples, respectively). The resultant EDX spectra are shown in Figure 13. After etching the samples, it was noted that the 347 material exhibited a microstructure with large carbide formations along the grain boundaries. The carbide formations were more prevalent and larger in size on the hotter samples than on the cooler ones. In addition, the samples on the upper 15,883-hour probe (samples 6 and 12) suffered 2.3 and 4.0 mils, respectively, of oxygen penetration along the ID surface.

NF 709 (Figure 14 and 15) — The representative appearance of alloy NF 709 is shown in Figure 14. All of the samples exhibited a thin scale layer along the outside surface. The photomicrograph illustrates the worst area of attack exhibited by the alloy (cooler specimen on 15,883-hour probe; however, the other hotter sample displayed subsurface penetration and attack that was very similar but to a lesser degree. The area that is depicted represents the shallow pitting which was noted during the macroscopic evaluation. The scale was comprised of light and dark gray layers which gave the scale a striated appearance. The dark gray layers (location 9) were chromium oxide with trace amounts of aluminum, silicon, sulfur, iron, and nickel. The light gray layers (location 10) were comprised mainly of iron oxide along with traces of aluminum, sulfur, chromium, and nickel. The alloy also displayed nonmetallic phases which were in two basic shapes; irregular and spherical. The irregularly shaped ones (location 11) consisted of chromium, oxygen, iron, nickel, aluminum, silicon, and sulfur. The spherically shaped phases (location 12) were revealed as sulfides which contained oxygen, chromium, manganese, iron, and nickel. The spectra coinciding with the indicated locations

are shown in Figure 15. A layer of carburization approximately 3 to 4 mils deep was noted after the samples were etched.

RA253MA (Figures 16 and 17) — The representative microscopic appearance of the RA253MA sample is shown in Figure 16 (top photomicrograph). The RA253MA sample that was in the hotter section of the 15,883-hour probe revealed a more roughened and irregular surface than its cooler counterpart. Both exhibited a two-layered scale along their outside surfaces; however, the hotter sample had the thicker layers. The outer layer of scale consisted mainly of iron oxide with small amounts of aluminum, silicon, sulfur, calcium, chromium, and nickel (location 13). The inner layer of scale was revealed to be chromium oxide with small amounts of iron, nickel, silicon, and sulfur (location 14). Beneath the scale, the sample displayed sulfide penetration to a depth of approximately 4.5 mils. EDX analyses of the sulfides revealed them to be comprised of chromium, nickel, iron, and manganese (location 15). The resultant EDX spectra are given in Figure 17. Etching the sample revealed the carbide formations strewn throughout the microstructure (middle photomicrograph).

HR3C (Figures 18 and 19) — The representative appearance of the HR3C alloy is displayed in Figure 18 (top photomicrograph). The section illustrated is from sample 5 of the 15,883-hour probe, which was the cooler sample. The sample displayed a thin scale layer along the surface which was comprised of fused fly-ash particles and remnant sample material. The bottom photomicrograph displays the areas used for EDX analyses of the miscellaneous phases noted in the material. The material inside the scale layer was found to be comprised of high amounts of oxygen, nickel, sulfur, iron, chromium, and manganese (location 16). The inner portion of the scale was basically a chromium oxide with trace amounts of various other elements (location 17). The sample also displayed some areas of localized attack with subjacent internal oxidation and heavy sulfur penetration. The sulfide islands noted subsurface of the scale were comprised of iron, chromium, nickel, and manganese (location 18). The subsurface oxidation was basically chromium oxide with notable additions of aluminum, silicon, sulfur, iron, nickel, and manganese (location 19). The correlating EDX spectra are given in Figure 19. The depth of penetration was approximately 4 and 0.5 mils for the low- and high-temperature samples, respectively. Etching the alloy revealed that the samples had a 1- to 2-mil decarburized layer directly below the outside surface. Below the decarburized layer the material exhibited heavy carburization.

671 (Figures 20 and 21)— The representative appearance of the 671 alloy is shown in Figure 20. Both samples from both probes displayed a broken, irregular scale along their outside surfaces. In addition, the samples exhibited some shallow pitting and localized areas of

subsurface attack. The scale along the outside surface was comprised of two distinct layers, a dark gray and a light gray one (location 20 and 21, respectively). The dark gray layer was an iron oxide with traces of aluminum, silicon, chromium, and nickel. The light gray layer was a chromium oxide with some small quantities of sulfur, iron, and nickel in it. The iron is believed to be from the coal since there is no iron in the alloy. The areas of localized attack had two distinguishable phases within their boundaries. The first was identified as a chromium-oxide phase which contained additional components such as aluminum, titanium, iron, and nickel (location 22). The other phase resembled a sulfide island; however, it was not a sulfur species at all. Rather, it was a titanium-oxide phase with trace amounts of iron, nickel, and chromium (location 23). The EDX spectra generated from the above-mentioned locations are shown in Figure 21. These internal corrodants penetrated to a depth of approximately 5 and 3 mils for the high- and low-temperature samples, respectively. In addition, both samples on both probes exhibited a scale along their inside surfaces. [Note: In these tests, 671 was a coextruded cladding on a LSS stainless steel tube.] The hotter sample (sample 16) in the 15,883-hour probe contained a 1.8-mil thick ID scale while the cooler sample (sample 6) exhibited a 3-mil ID scale. In the 11,348-hour probe, the hotter sample (sample 16) contained a 5.8-mil ID scale, and the cooler sample (sample 6) had a 4.2-mil thick ID scale. Etching the samples revealed a decarburized zone along the outside surface of the material as well as large carbide formations which made up the rest of the microstructure, shown in the middle photomicrograph.

690 (Figures 22 and 23) — The representative microscopic appearance of the 690 alloy is shown in Figure 22. Similar to the 671 samples, all of the 690 samples displayed a very thin, chromium-rich oxide layer on the outside surface. Internal oxidation was noted and was revealed to be mostly chromium oxide with traces of aluminum, titanium, iron, and nickel (location 24). The sulfides (location 25) were characterized as chromium sulfides along with ox-ygen, titanium, iron, and nickel. The resultant EDX spectra are shown in Figure 23. The subsurface oxidation and sulfidation were evident in all the samples; however, the hotter samples exhibited a deeper penetration of the attack (approximately 6 mils compared to 2 to 3 mils in the cooler sections). The inside surface of this coextruded clad tube (which also consisted of LSS stainless steel) contained a 2.2-mil thick ID scale in the hotter section (sample 17) and a 3.3-mil thick ID scale in the cooler section (sample 7). The samples in the 11,348-hour probe exhibited the same inside surface scale formation; sample 17 (hotter) had a 2-mil thick scale and sample 7 (cooler) had a 1-mil thick scale. The material also exhibited a decarburized layer along the outside surface as in the 671 sample. However, the general mi-

microstructure did not contain the larger carbide formations that were observed in the 671 samples.

Fe₃Al + 5Cr (Figures 24 and 25) — The representative appearance of the Fe₃Al + 5Cr alloy is shown in Figure 24 (top photomicrograph). The outside surface of the samples exhibited a dark gray scale with intermittent layers of a light gray scale. The dark gray scale (location 26) was an aluminum-rich oxide with small amounts of chromium, iron, and sulfur. The lighter gray scale (location 27) was revealed to be a chromium-rich oxide which had a substantial amount of iron mixed in as well as traces of calcium, potassium, silicon, and aluminum. Beneath the scale layer, the surface of the metal was roughened and irregular with some definite evidence of shallow pitting and sulfur penetration. The depth of penetration exhibited by the 15,883-hour samples was approximately 4 mils for the cooler sample (sample 8) and 1 mil for the hotter sample (sample 18). The penetration of the sulfides in the 11,348-hour samples was noted at depths of approximately 0.5 mil in the cooler sample (sample 8) and 2 mils in the hotter sample (sample 18). In addition, a needle-like phase (location 28) was noted throughout the entire thickness of all the samples. These phases were revealed to be high in iron, niobium, oxygen, and aluminum, with a small amount of chromium. The spectra generated from the above-mentioned locations are given in Figure 25.

Ta-Modified 310 (Figures 26 and 27) — The representative microscopic appearance of the Ta-modified 310 samples is shown in Figure 26 (top photomicrograph). The Ta-modified 310 alloy in both probes contained a dark-colored scale (location 29) which had embedded fly-ash particles in it. The resultant spectrum revealed that the dark scale was mainly an iron oxide with small amounts of elements typically found in fly ash: aluminum, silicon, chromium, sulfur, potassium, and calcium. Beneath the scale, the material exhibited internal oxidation and sulfidation which, on the lower-temperature samples, was more pronounced. The sulfides (location 30) consisted of manganese, oxygen, chromium, iron, and nickel. The relevant spectra are shown in Figure 27. The depth of penetration for the 15,883-hour probe was approximately 1.5 to 2 mils for the cooler sample (sample 9) and 2.5 mils for the hotter sample (sample 19). In the 11,348-hour probe, the numbers were almost the same—2 mils for the cooler (sample 9) and 2.2 mils for the hotter (sample 19). Etching the sample (depicted in the middle photomicrograph) illustrated the thin, decarburized layer along the outside surface and the sigmatization of the rest of the microstructure.

800HT (Figures 28 and 29) — The representative appearance of the 800HT alloy is shown in Figure 28 (top photomicrograph). All of the 800HT samples exhibited a two-layer scale/deposit along the outside surface with some minor internal oxidation and sulfidation.

The outer layer was comprised of embedded fly-ash particles while the inner layer was predominantly chromium oxide (location 31). Beneath the ash, the material exhibited evidence of intergranular attack. The corrosion product (location 32) that was noted at the intergranular attack sites was comprised of iron, nickel, chromium, and oxygen. The sulfides (location 33) contained manganese, chromium, iron, and nickel. The correlating EDX spectra are shown in Figure 29. The depth of the internal penetration was noted as being deeper in the hotter sections of the 15,883- and 11,348-hour probes (5.5 and 5.3 mils, respectively). The cooler samples displayed penetration depths of 2 and 3 mils for 15,883- and 11,348-hour probes, respectively.

DISCUSSION OF RESULTS

The results of the numerical evaluations performed on the 4483-, 11,348-, and 15,883-hour test probes are given in Table 8 along with the materials' corresponding temperature data. The total wastage was defined as the maximum wall loss (Table 7) plus the penetration measured from the microscopic examination of the cross sections. The corrosion rates were calculated using the total wastage values multiplied by a time correction factor to make the end result mils/yr. These data are presented graphically in Figures 30 through 33.

EFFECT OF ALLOY ELEMENT ON CORROSION RESISTANCE

From past work done in laboratories and in the field, it was recognized that the materials with the higher chromium content would be the ones exhibiting the higher corrosion resistance. This experiment did not show much, if any, deviation from those past findings. The wastage and corrosion rates of the 15,883-hour samples were plotted against the increasing percent-chromium content, producing Figures 30 through 32 and Figure 33, respectively. These were compared with those graphs produced by the 11,348-hour data, and it was found that they were very similar; therefore, only the longer-term 15,883-hour data are presented here. The graphs show that, for the most part, the materials which contained at least 25-percent chromium exhibited better corrosion resistance than those with lower amounts. The exception is the $\text{Fe}_3\text{Al} + 5\text{Cr}$ and 85H at the lower temperature.

In previous work, the effect of nickel was found to be marginal and possibly detrimental at levels above 30 percent. If the chromium levels are increased, the nickel detriment is overcome. This appeared to be true with the materials in this experiment. The wastage displayed by the 671, and 690 alloys (52- and 58-percent nickel, respectively) was similar in

Table 8. Results of Numerical Evaluation

Sample	Cr (%)	Ni (%)	Total Metal Wastage (mils)			Corrosion Rate (mils/yr)			Temperature (°F)		
			4483 (hr)	11,348 (hr)	15,883 (hr)	4483 (hr)	11,348 (hr)	15,883 (hr)	4483 (hr)	11,348 (hr)	15,883 (hr)
Fe ₃ Al	5	0	0.0	4.0	5.0	0.0	3.1	2.8	1313	1307	1319
Fe ₃ Al	5	0	0.0	5.5	6.5	0.0	4.2	3.6	1223	1231	1229
RA85H	18	12	2.5	5.0	12.5	4.9	3.9	6.9	1260	1266	1267
RA85H	18	12	3.0	9.6	4.2	5.9	7.4	2.3	1157	1163	1156
347	18	15	2.7	5.7	21.6	5.3	4.4	11.9	1267	1272	1275
347	18	15	2.0	5.4	10.3	3.9	4.2	5.7	1166	1172	1167
NF 709†	20	25	0.5	2.5	10.7	1.0	1.9	5.9	1275	1278	1282
NF 709†	20	25	1.6	8.3	9.6	3.1	6.4	5.3	1176	1182	1177
RA253MA	21	11	2.4	2.4	5.6	4.7	1.9	3.1	1283	1284	1289
RA253MA	21	11	1.4	2.7	11.5	2.7	2.1	6.3	1185	1192	1187
800HT	21	32	1.5	3.1	7.6	2.9	2.4	4.2	1328	1319	1334
800HT	21	32	1.5	4.3	8.5	2.9	3.3	4.7	1242	1250	1250
Ta Mod 310	25	20	0.0	4.1	7.2	0.0	3.2	4.0	1321	1313	1326
Ta Mod 310	25	20	0.1	3.2	4.3	0.2	2.5	2.4	1233	1241	1239
HR3C†	25	20	0.3	3.5	0.9	0.6	2.7	0.5	1290	1290	1297
HR3C†	25	20	0.8	6.0	6.6	1.6	5.0	3.6	1195	1202	1198
690	30	58	0.5	3.0	7.9	1.0	2.3	4.4	1305	1301	1312
690	30	58	0.5	4.0	7.0	1.0	3.1	3.9	1214	1221	1219
671	48	52	0.5	3.5	5.0	1.0	2.7	2.8	1298	1295	1304
671	48	52	0.5	2.5	5.3	1.0	1.9	2.9	1204	1211	1208

*For each alloy: Top sample is hot, bottom sample is cold.

†Carburized.

terms of the amount of penetration and thickness loss exhibited by each material even though the chromium was much higher (48 and 30, respectively).

The work done by Rehn^{8,12} indicated that aluminum, in small amounts, was beneficial for scale stabilization, but in higher-nickel alloys there seems to be no additional benefit. This was observed somewhat for the 800HT and the RA85H which contain ≤ 1 -percent aluminum but may be overshadowed by the silicon in 85H. The greatest benefit of aluminum occurs in the Fe₃Al material (17-percent Al and only 5-percent Cr) which exhibited one of the best overall performances in terms of total wastage and corrosion rate. The aluminum was present not only in the scale (as shown in the microscopic examination) but also in needle-like phases throughout the material.

The advantage, if any, from the addition of silicon was difficult to evaluate. The three silicon-containing alloys (NF 709: 0.6 percent; RA253MA: 1.7 percent; RA85H: 3.9 percent) exhibited different levels of corrosion at the two temperature ranges. At the cooler temperatures, the RA85H displayed better resistance than the RA253MA (which has the higher chromium content), while at the hotter temperatures the roles were reversed.

EFFECT OF TEMPERATURE

The relationship between corrosion and temperature for molten salt corrosion is usually linearly defined with corrosion increasing as temperature increases. However, with coal-ash corrosion, the relationship is defined by more of a bell-shaped curve due to the thermodynamic stability of the alkali-iron-trisulfate. It has been determined that the wastage increases as the temperature rises in the stable temperature range of the molten alkali-iron-trisulfate (1112 to 1292°F). The wastage decreases in the higher temperature range, since the molten alkali-iron-trisulfate disassociates. The peak temperature for wastage is different for each material since the temperature range in which the molten salt is stable depends on the surface corrosion of the material. Corrosion products generated by the test materials can also have an effect on the melting temperature of the salt.^{8,12} The corrosion rates of the 11,348- and 15,883-hour samples were plotted against their respective temperature ranges in an effort to examine whether there was any temperature dependency displayed by the materials (shown in Figures 34A and 34B). The examination revealed little, if any, consistent temperature dependency between the 11,348- and 15,883-hour samples as is illustrated in the graphs. Examining the data from a different angle by plotting the two temperature ranges separately against the three exposure times revealed that, for the most part, the 15,883-hour

samples exhibited a higher corrosion rate than their 11,348-hour counterparts (Figure 35A and 35B).

DISCUSSION

The examination revealed that, for the most part, the 15,883-hour probe samples exhibited the most attack with respect to the microscopic appearance and total metal wastage of the samples. In terms of the corrosion rate, if the short-term probe is discounted, then for the most part, the 15,883-hour probe has a higher rate when extrapolated linearly. None of the samples were immune to the environment; all exhibited varying degrees of internal oxidation, while most displayed evidence of carburization and sulfidation. The pitting morphology and surface irregularity along with the potassium and sulfur ratios in the corrosion products indicate the active corrosion from coal-ash corrosion, probably from potassium-iron-trisulfate. The total metal wastage and corrosion rate values are given in Table 8.

The relationship between the corrosion resistance and material chemistry appears to follow trends established in earlier work. Chromium content was found to be the largest factor in determining the resistance of an alloy to liquid coal-ash corrosion. For stainless steels and nickel alloys, additions of 25-percent chromium provide increased resistance to coal-ash attack; however, above the 25-percent chromium level, there appears to be minimal additional benefit from more chromium, possibly because of the higher nickel content of those higher-chromium-containing alloys. This was confirmed based on the collected data which clearly illustrate the corrosion resistance improving when the chromium content exceeds the 25-percent mark. Consequently, with the exception of the iron-aluminide alloy, the higher-chromium-containing alloys displayed very promising corrosion rates (≤ 10 mils/yr).

It was determined that the benefits of nickel addition reached their limit at about 35 percent by comparing 800H to 690. Above this amount, an increase in nickel seemed not to produce any additional benefits except if about 50-percent chromium was added (671). Silicon and aluminum were also beneficial, but to a lesser extent. Molybdenum, on the other hand, has been found to be detrimental to corrosion resistance in high-molybdenum-containing alloys (as shown by Rehn^{8,12} and Kihara^{7,10}), but the alloys used in this experiment could not be used to check this effect since the highest molybdenum content was limited to 1.5 percent (NF 709). The iron-aluminide intermetallics also showed a chromium dependence in the phase 1 testing.¹¹ Aluminides containing 5-percent chromium performed markedly better overall than those containing 2-percent chromium. In the phase 2 field test, only the 5-percent chromium aluminide was used.

Closer examination of the other elements employed as alloying additions revealed some interesting results. The materials which contained aluminum gave results at each position of the performance scale. The Fe₃Al contained 17-percent aluminum and only 5-percent chromium; however, it exhibited a low-end total metal wastage and corrosion rate at both hot and cool temperature locations, in both the 11,348- and 15,883-hour probes. The noticeable trait that separated it from the other alloys was that it had an aluminum-rich scale as well as an aluminum-rich phase throughout its matrix. In this case, the aluminum scale seemed to be inert and sufficiently stable to prevent the ingress of any aggressive species. The RA85H and the 800HT materials also contained aluminum in the 1-percent range. The difference between the two was that the RA85H contained silicon (3.9 percent) while the 800HT contained titanium (<1 percent). The 800HT gave very consistent performance (about 3 to 4 mils/yr) and was ranked in the middle of the group (around fourth or fifth best). On the other hand, the corrosion behavior of RA85H was very erratic, exhibiting higher wastage values in the 11,348-hour samples and the hotter 15,883-hour sample but low values in the cooler 15,883-hour sample. The results suggest that the aluminum in higher concentrations seemed to have a more profound effect on imparting resistance to corrosion, which agrees with the results achieved by Rehn.^{8,12}

The benefits of silicon as an alloying addition were also examined because of the potential for forming a protective subscale of silica. Of the three silicon-containing materials, RA253MA (1.7 percent) exhibited the best corrosion resistance in the higher temperature ranges followed by NF 709 (0.6 percent) and RA85H (3.9 percent). In the cooler temperature range on the 11,348-hour probe, the RA85H material exhibited the best resistance, while the RA253MA displayed the worst. The results are not conclusive concerning any beneficial effects of silicon additions because the results were different in the two different temperature ranges. However, one could postulate that in the lower temperature range, both the silicon and aluminum content helped to stabilize the protective scale on RA85H, while in the higher temperature range, the higher chromium content in the RA253MA, along with the addition of the silicon, provided a more protective scale.

The more resistant alloys showed lower corrosion rates at longer exposure times, indicating the formation of a protective layer; the less-resistant alloys exhibited increasing corrosion rates at longer exposures. Also, the lower-chromium alloys generally suffered greater wastage rates at the higher testing temperature [700°C (1292°F)], whereas higher-chromium alloys suffered similar levels of wastage at 650 (1202) as at 700°C (1292°F).

The temperature-dependence relationship of coal-ash corrosion is defined by a bell-shaped curve due to the thermodynamic stability of the alkali-iron-trisulfate.^{2-5,12} Typically, it has been observed that the wastage increases as the temperature rises in the temperature range where the molten alkali-iron-trisulfate (1112 to 1292°F) is stable. The decrease in wastage in the higher temperature range is due to the fact that the molten alkali-iron-trisulfate disassociates. The peak temperature for wastage is somewhat different for each alloy, since the temperature range in which the molten salt is stable depends on the interaction of the molten salt with the surface of the alloy. Corrosion products generated by the test materials can also have an effect on the melting temperature of the salt. The corrosion rates of the 11,348- and 15,883-hour samples were plotted against their respective temperature ranges to examine the temperature dependency displayed by the materials (shown in Figure 34). Even though the examination revealed no clear temperature dependency with 15,883-hour samples, most of the materials in the 11,348-hour group exhibited a trend to decreased corrosion rate with increased temperature. Plotting the two temperature ranges separately against the three exposure times revealed a general trend for the corrosion rate to be essentially constant or to slightly increase with time, with some exceptions. For the most part, the 15,883-hour samples exhibited a higher corrosion rate than their 4483- or 11,348-hour counterparts (Figure 35).

The performance of the test alloys with respect to the three exposure periods is summarized in the following comments:

- **RA85H** — The samples from both the 11,348- and 15,883-hour probes exhibited similar intergranular oxidation along with sulfur penetration and a heavy density of carbide formation throughout the thickness. The samples also displayed intergranular penetration of the ID surface to an average depth of approximately 3 mils. A trend was noted in which the 15,883-hour samples exhibited the most total wastage with respect to the hotter samples of the three probes. Among the cooler samples, this trend was not apparent because the 11,348-hour samples had a higher total wastage value than the 15,883-hour samples.
- **347** — The 347 samples from both probes displayed similar OD scale growth, sulfur penetration, and carbide formation, although the hotter samples exhibited a higher carbide density than the cooler ones. In addition, the 15,883-hour samples displayed sulfur penetration along the ID. In the 15,883-hour test samples of all the alloys, the total metal wastage and corrosion rate of 347 was as expected at the high side of the data set for all the alloys.

- **NF 709** — In both the 11,348- and 15,883-hour test, NF 709 samples exhibited a striated scale as well as some superficial pitting. Also, beneath the surface two different, nonmetallic phases were observed, one irregular and one spherical. The irregular phase was essentially chromium-aluminum, while the spherical phase was a sulfide penetrant. The total metal wastage for the material increased from the 4483- to the 11,348- to the 15,883-hour probe, for both the hotter and cooler samples. On the other hand, the wastage rates followed this pattern in terms of the hotter set of samples but strayed from it with the cooler set, in which the 11,348-hour sample had a slightly higher rate than the 15,883-hour sample.
- **RA253MA** — The scale formed on the OD surface of the RA253MA samples typically was found to consist of iron and chromium oxides. Beneath the scale, the microstructure of both the 11,348- and 15,883-hour samples exhibited a heavy density of carbide and sulfide islands. The 15,883-hour samples experienced the higher amount of total metal wastage when compared to the shorter time exposures. However, there was no obvious trend in the corrosion rates, since the rates of the hotter 4483-hour sample were higher than for the 15,883-hour sample. The situation was reversed in the cooler samples, with the 15,883-hour sample having a higher rate than the 4483-hour one. In both instances, the 11,348-hour samples had the lowest rate.
- **HR3C** — The HR3C samples exhibited areas of localized attack in the form of small pits which exhibited subjacent internal oxidation, sulfur penetration, and carburization. In terms of the total metal wastage and corrosion rate values, there was no obvious trend with time or temperature. The cooler 15,883-hour sample exhibited the highest total metal wastage, whereas the cooler 11,348-hour sample exhibited the highest corrosion rate.
- **671** — The 671 samples displayed a broken scale along the OD surface accompanied by some shallow pitting and localized areas of subsurface attack. The subsurface attack was composed of a titanium phase which had oxidized. The samples also displayed scale growth along their ID surfaces. The microstructures of both the 11,348- and 15,883-hour samples exhibited large carbide formations. The total metal wastage and corrosion rates were highest for the 15,883-hour samples, followed by the 11,348- and then the 4483-hour samples.
- **690** — The 690 samples exhibited a roughened surface with a thin, chromium-oxide outer scale layer upon it. Beneath the scale layer, the samples displayed a thin, decarburized band which contained sulfide islands (some of which were oxidized). Underneath the

decarburized band there was a carbide formation along grain boundaries as well as in the general matrix of the grains. In addition, the 15,883-hour samples exhibited the highest total metal wastage and the highest corrosion rates, followed by the 11,348- and 4483-hour samples.

- **Fe₃Al** — The OD surface of the Fe₃Al samples exhibited a two-colored scale which was dark gray with a light gray band running through it. The dark part of the scale was aluminum oxide with traces of iron, sulfur and chromium, while the light gray band was mainly chromium oxide with noticeable amounts of iron, calcium, potassium, silicon, and aluminum. The surface underneath the scale was found to be slightly irregular. In addition, the samples also exhibited a needle-like phase throughout their entire thicknesses. This phase consisted of iron, niobium, aluminum, and chromium, and did not seem to be detrimental to the sample since no subsurface corrosion activity was noted in or around it. The highest total metal wastage and the highest corrosion rates were exhibited by the 15,883-hour samples, followed by the 11,348- and 4483-hour samples.
- **Ta-modified 310** — The Ta-modified 310 samples displayed a thin, iron-oxide scale layer which was found to contain fly-ash particles. Under this layer, the surface was slightly irregular with some intergranular oxidation and sulfur penetration. The entire sample was sigmatized. For the most part, the 15,883-hour samples exhibited the highest total metal wastage and corrosion-rate values, followed by the 11,348- and 4483-hour samples.
- **800HT** — The 800HT samples exhibited a two-layered scale/deposit with some internal oxidation and sulfur penetration beneath it. The deposit consisted of fly-ash particles, while the scale was mainly of chromium oxide. The 15,883-hour samples exhibited the highest total metal wastage and the highest corrosion rates.

CONCLUSIONS

Based on the examination of the samples reported above, the following conclusions can be drawn:

- Chromium levels of 25 percent were found to be necessary for improved corrosion resistance with little further improvement at higher levels, except for levels of 50 percent.
- Nickel was observed to have a beneficial effect up to about 35 percent, but higher levels did not reduce the corrosion and were sometimes detrimental, except if very high levels (50 percent) of chromium were added.

- The effect of aluminum was not clearly defined. At the lower percentages (≤ 1 percent), there was little observable effect on the ability to resist the molten trisulfate attack, but at higher concentrations, as in the Fe₃Al alloy (17-percent Al), where an alumina scale was formed, protective behavior was promoted.
- The effect of silicon on the corrosion resistance of the test materials could not be clearly determined because of the inconsistent results from the high- and low-temperature ranges of the 11,348- and 15,883-hour probes.
- The ranking of the alloys based on the longest exposure was as follows:

1146-1249°F		1267-1341°F	
Material	Mils/yr	Material	Mils/yr
85H	2.3	HR3C	0.5
Ta-modified 310	2.4	671	2.8
671	2.9	Fe ₃ Al	2.8
Fe ₃ Al	3.6	253MA	3.1
HR3C	3.6	Ta-modified 310	4.0
690	3.9	800HT	4.2
800HT	4.7	690	4.4
NF 709	5.3	NF 709	5.9
347	5.7	85H	6.9
253MA	6.3	347	11.9

- If the advanced-cycle plant is going to have a superheater or reheater at an OD skin temperature of 1350°F, then the complete component will have both temperature conditions and therefore will have the following rankings:

Alloy	Mils/Yr	Alloy	Mils/Yr
671	2.9	800HT	4.7
Fe ₃ Al	3.6	NF 709	5.9
HR3C	3.6	85H	6.9
Ta-modified 310	4.0	253MA	6.3
690	4.4	347	11.9

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Fig. 1. Average thickness loss rate of alloys containing 14- to 30-percent chromium. (Alloys marked with an asterisk contain between 1- and 4-percent molybdenum.)

Fig. 2. Average thickness loss rates of various monolithic alloys and claddings coated with ash containing 10 wt% alkali sulfates and exposed for 800 hours

Fig. 3. Average thickness loss rates of three intermetallic aluminides and two stainless steels exposed to a variety of environments. (* = low sulfate ash, ** = high sulfate ash)

12/01/95 1 Upper T/C 1: 2 Upper T/C 4: 3 Upper T/C 5: 4 Lower T/C 1
 00:10:06 5 Lower T/C 3: 6 Lower T/C 5: 7 Furnace T/C

Fig. 4. Typical monthly temperature plot

Fig. 5. Side elevation of reheater at TVA Gallatin unit 2

Fig. 6. The two retracted probes on the left and the soot blower on the right are shown in the top photograph. The bottom photograph shows the cleaned probe for ultrasonic thickness measurements.

Fig. 7. The 11,348- and 15,883-hour probes are shown (top and bottom, respectively) after being cut in half at the second thermocouple location. As illustrated, the probes are orientated with the 90-deg (direction of oncoming 'flue gas') location facing out of the photomacrograph.

Fig. 8. The transverse cross sections removed from the cooler and hotter 11,348-hour probe samples are shown (top and bottom, respectively). The sections are oriented with the 135-deg location facing out of the photomicrograph.

Fig. 9. The transverse cross sections removed from the cooler and hotter 15,883-hour probe samples are shown (top and bottom, respectively).

4 mils

4 mils

1 mil

Fig. 10. The representative microscopic appearance of the RA85H alloy is shown in the un-etched and etched condition (top and middle, respectively). The samples exhibited a two-part scale, a decarburized layer (approximately 1 to 2 mils thick), and intergranular oxidation/sulfidation.

25-APR-97 10:36:04 EDAX READY
 RATE= 0CPS TIME= 100LSEC
 FB= 6960CNT PRST= OFF
 A = 11-135 85H

1

25-APR-97 10:43:16 EDAX READY
 RATE= 0CPS TIME= 101LSEC
 FB= 3750CNT PRST= OFF
 A = 11-135 85H

2

25-APR-97 10:52:49 EDAX READY
 RATE= 4057CPS TIME= 102LSEC
 FB= 6967CNT PRST= OFF
 A = 11-135 85H

3

25-APR-97 11:05:29 EDAX READY
 RATE= 2CPS TIME= 102LSEC
 FB= 5110CNT PRST= OFF
 A = 11-135 85H

4

25-APR-97 11:26:50 EDAX READY
 RATE= 0CPS TIME= 116LSEC
 FB= 7721CNT PRST= OFF
 A = 11-135 85H

5

Fig. 11. The EDX spectra generated from the locations noted in the RA85H sample (Figure 10) are shown.

Fig. 12. The representative unetched and etched appearance of the 347 alloy is shown (top and middle, respectively). The material exhibited a scale layer along the OD surface and evidence of internal oxidation/sulfidation.

25-APR-97 13:27:52 EDAX READY
 RATE= 0CPS TIME= 126LSEC
 FS= 7468CNT PRST= OFF
 A =12-135 347

6

25-APR-97 13:34:40 EDAX READY
 RATE= 0CPS TIME= 115LSEC
 FS= 8719CNT PRST= OFF
 A =12-135 347

7

25-APR-97 13:41:11 EDAX READY
 RATE= 0CPS TIME= 100LSEC
 FS= 5961CNT PRST= OFF
 A =12-135 347

8

Fig. 13. The EDX spectra generated from the locations noted in the 347 sample (Figure 12) are shown.

Fig. 14. The representative appearance of alloy NF 709 in the unetched and etched condition is shown (top and middle, respectively). The samples exhibited a multilayered scale along the OD surface and a layer of subsurface carburization approximately 3 to 4 mils deep.

25-APR-97 14:18:43 EDAX READY
 RATE- 8CPS TIME- 121LSEC
 FS- 5811CNT PRST- OFF
 A -3-45 NF709

9

25-APR-97 14:25:07 EDAX READY
 RATE- 8CPS TIME- 112LSEC
 FS- 4361CNT PRST- OFF
 A -3-45 NF709

10

25-APR-97 14:36:03 EDAX READY
 RATE- 8CPS TIME- 100LSEC
 FS- 5192CNT PRST- OFF
 A -3-45 NF709

11

25-APR-97 14:52:39 EDAX READY
 RATE- 8CPS TIME- 100LSEC
 FS- 4798CNT PRST- OFF
 A -3-45 NF709

12

Fig. 15. The EDX spectra generated from the locations noted in the NF 709 sample (Figure 14) are shown.

Fig. 16. The representative microscopic appearance of the RA253MA sample is shown in the unetched and etched condition (top and middle, respectively). The samples exhibited a two-layer scale along their OD surfaces and sulfide penetration to an approximate depth of 2 to 4.5 mils (hotter and cooler samples, respectively).

13

14

15

Fig. 17. The EDX spectra generated from the locations noted in the 253MA sample (Figure 16) are shown.

4 mils

4 mils

1 mil

Fig. 18. The representative appearance of the unetched and etched HR3C alloy is shown (top and middle, respectively). The sample displayed a thin surface scale and areas of localized attack and subjacent internal oxidation/sulfidation.

16

17

18

19

Fig. 19. The EDX spectra generated from the locations noted in the HR3C sample (Figure 18) are shown.

Fig. 20. The representative appearance of the 671 alloy is shown in the unetched and etched condition. The samples displayed a broken, irregular scale in addition to some shallow pitting and localized areas of subsurface attack.

28-APR-97 10:47:19 EDAX READY
 RATE- 8CPS TIME- 101LSEC
 FB- 5992CNT PRST- OFF
 A -6-135 671

20

28-APR-97 10:41:48 EDAX READY
 RATE- 2CPS TIME- 104LSEC
 FB- 8513CNT PRST- OFF
 A -6-135 671

21

28-APR-97 10:53:58 EDAX READY
 RATE- 8CPS TIME- 105LSEC
 FB- 5941CNT PRST- OFF
 A -6-135 671

22

28-APR-97 11:00:59 EDAX READY
 RATE- 8CPS TIME- 108LSEC
 FB- 8564CNT PRST- OFF
 A -6-135 671

23

Fig. 21. The EDX spectra generated from the locations noted in the 671 sample (Figure 20) are shown.

Fig. 22. The representative microscopic appearance of the unetched and etched condition of the 690 alloy is shown (top and middle, respectively). The samples displayed a very thin scale with subsurface oxidation/sulfidation.

24

25

Fig. 23. The EDX spectra generated from the locations noted in the 690 sample (Figure 22) are shown.

Fig. 24. The representative appearance of the Fe₃Al alloy is shown. The outside surface of the samples was irregular and exhibited a predominantly dark gray scale with veins of a lighter gray phase inside it.

30-APR-97 07:28:47 EDAX READY
 RATE- 0CPS TIME- 101LSEC
 FS- 11142CNT PRST- OFF
 A -18-45 Fe3AL

26

30-APR-97 07:22:29 EDAX READY
 RATE- 0CPS TIME- 109LSEC
 FS- 4432CNT PRST- OFF
 A -18-45 Fe3AL

27

30-APR-97 07:38:09 EDAX READY
 RATE- 0CPS TIME- 115LSEC
 FS- 5907CNT PRST- OFF
 A -18-45 Fe3AL

28

Fig. 25. The EDX spectra generated from the locations noted in the Fe₃Al sample (Figure 24) are shown.

Fig. 26. The representative microscopic appearance of the Ta-modified 310 alloy in the un-etched and etched condition is shown (top and middle, respectively). The surface of all the samples displayed a dark-colored scale with embedded fly-ash particles, subsurface oxidation/sulfidation, and sigmatization.

Fig. 28. The representative appearance of the 800HT alloy is shown. All of the 800HT samples exhibited a two-layer scale/deposit and subsurface oxidation/sulfidation.

30-APR-97 09:28:12 EDAX READY
 RATE= 0CPS TIME= 100LSEC
 FS= 8757CNT PRST= OFF
 A =20-135 800H

31

30-APR-97 09:35:38 EDAX READY
 RATE= 0CPS TIME= 101LSEC
 FS= 3701CNT PRST= OFF
 A =20-135 800H

32

30-APR-97 09:43:27 EDAX READY
 RATE= 0CPS TIME= 103LSEC
 FS= 7267CNT PRST= OFF
 A =20-135 800H

33

Fig. 29. The EDX spectra generated from the locations noted in the 800HT sample (Figure.28) are shown.

Fig. 30. Graphical representation of the total wastage vs. increasing percent chromium for the 15,883-hour samples is shown.

Fig. 31. Graphical representation of the total wastage vs. increasing percent chromium for the 15,883-hour samples is shown.

Fig. 32. Graphical representation of the total wastage vs. increasing percent chromium for the 15,883-hour samples is shown.

Fig. 33. Graphical representation of the corrosion rate vs. the increasing percent chromium for the 15,883-hour samples is shown.

11,348 Hour Probe

Fig. 34A. Graphical representation of corrosion rate vs. temperature for the 11,348-hour samples is shown.

Fig. 34B. Graphical representation of corrosion rate vs. temperature for the 15,883-hour samples is shown.

Fig. 35A. Graphical representation of corrosion rate vs. time for all three probes is shown.

Fig. 35B. Graphical representation of corrosion rate vs. time for all three probes is shown.

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