Coal Ash Corrosion Resistant Materials Testing Program
Evaluation of the First Section Removed in November 2001

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ABSTRACT

The "Coal Ash Corrosion Resistant Materials Testing Program" is being conducted by The Babcock & Wilcox Company (B&W), the U.S. Department of Energy (DOE) and the Ohio Coal Development Office (OCDO) at Reliant Energy's Niles plant in Niles, Ohio to provide full-scale, in-situ testing of recently developed boiler superheater materials. Fireside corrosion is a key issue for improving efficiency of new coal fired power plants and improving service life in existing plants.

In November 1998, B&W began development of a system to permit testing of advanced tube materials at metal temperatures typical of advanced supercritical steam temperatures (1100°F and higher) in a boiler exhibiting coal ash corrosive conditions. Several materials producers including Oak Ridge National Laboratory (ORNL) contributed advanced materials to the project.

In the spring of 1999 a system consisting of three identical sections, each containing multiple segments of twelve different materials, was installed. The sections are cooled by reheat steam, and are located just above the furnace entrance in Niles' Unit #1, a 110 MWe unit firing high sulfur Ohio coal. In November 2001 the first section was removed for thorough metallurgical evaluation after 33 months of operation. The second and third sections remain in service and the second is expected to be removed in the fall of 2003; the last is tentatively planned for the fall of 2004. This paper describes the program; its importance; the design, fabrication, installation and operation of the test system; materials utilized; experience to date; and results of the evaluation of the first section.

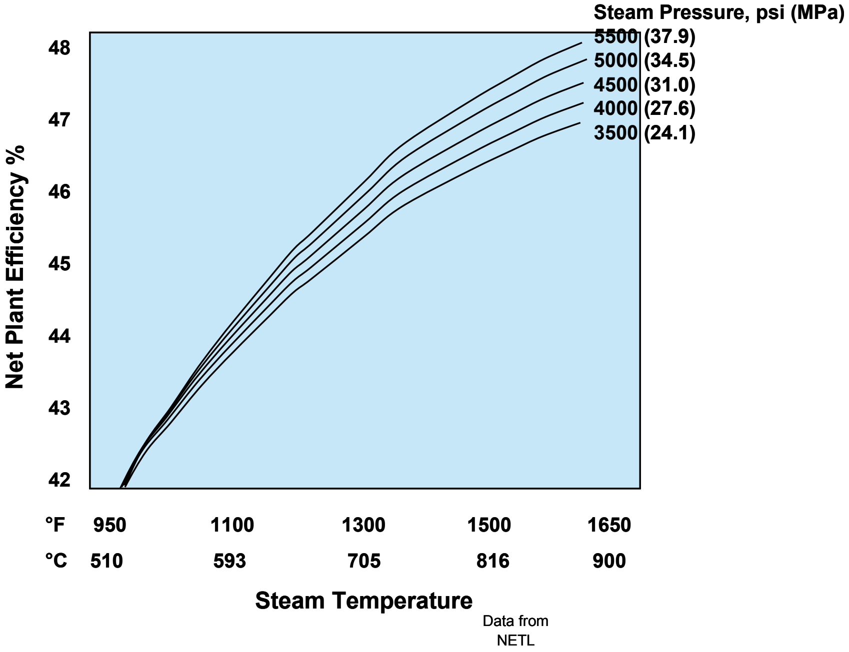
INTRODUCTION

The "Coal Ash Corrosion Resistant Materials Testing Program" is being conducted by Babcock & Wilcox (B&W) at Reliant Energy's Niles plant in Niles, Ohio. The total estimated cost of $1,864,603 is co-funded by DOE who is contributing 37.5%, OCDO is providing 33.3%. B&W is providing 17% with the remaining 12% being in-kind contributions by Reliant Energy and suppliers of tubing for the tests.

Materials development is important to the power industry and to the continued use of coal for power generation. At current or forecasted delivered costs of coal and natural gas and considering typical capacity factors for subcritical and supercritical coal fired plants versus natural gas combined cycle plants, subcritical coal-fired plants would dominate the market were it not for environmental concerns, especially CO_2. To minimize CO_2 generation as well as all other pollutants while using a fossil fuel, cycle efficiency must be improved.

Steam cycle efficiency is a function of the turbine cycle and boiler efficiencies and parasitic power requirements. Typically, about 11% of the cycle losses as a percentage of total heat input are from boiler efficiency, about 50% are from the condenser, and only about 2% are from parasitic power needs. This means that significant improvement will come primarily from the turbine cycle, and improving inlet steam conditions is the most effective approach.

As Figure 1 demonstrates, studies have shown that large increases in pressure have only a modest impact on efficiency, but the improvement is significant for just a 50°F increase in steam temperature. Increasing pressure also means that all pressure parts become proportionately thicker. This results in higher metal temperatures in the boiler requiring higher-grade alloys. Thus, significant environmental value would be needed to economically justify increasing cycle pressure to gain a small amount of efficiency.



Data from NETL

Figure 1: Impact of Steam Pressure and Temperature on Efficiency

Materials with good creep strength at 1200°F and higher are available, and though fabricability is an issue, they could be used for components external to the boiler. But the high temperature leading rows of the superheater and reheater within the boiler operate 100°F to 150°F higher at their surface and are exposed to corrosive combustion gases. Long-term data on the corrosion resistance of these alloys is non-existent.

The Program

The objectives of the program are to 1) evaluate the corrosion performance of newer superheater/ reheater materials for coal-fired boilers at surface temperatures equivalent to 1100ºF (593ºC) steam, 2) select materials resistant to fireside corrosion, and 3) generate long-term corrosion field data.

The corrosion rate for most austenitic materials used for high temperature tubing increases exponentially with temperature to a peak around 1300°F, then decreases rapidly beyond the peak. To accelerate corrosion the system was designed to achieve high surface metal temperatures.

Design began in November 1998 and the sections were installed in April. The sections are cooled by 600°F, 315 psi reheat steam but are located within the superheater bank of the B&W 120 MWe cyclone-fired Niles boiler, a 1950s vintage subcritical unit burning a 3-3.5% sulfur Ohio coal. Figure 2 shows the location and Figure 3 shows the system arrangement.

Three identical four-row sections contain specimens of the twelve alloys tested; most are included three times within the top two rows to expose them to three temperature regimes. The only difference between sections is that the first section was scheduled for removal and evaluation after one year of operation, the second after three years and the third after five years.

Surface metal temperatures are continuously calculated by the data acquisition system and correlated to the internal steam temperature, measured by thermocouples at the inlet, intermediate bend and outlet, controlled by varying the steam flow by inlet valves.

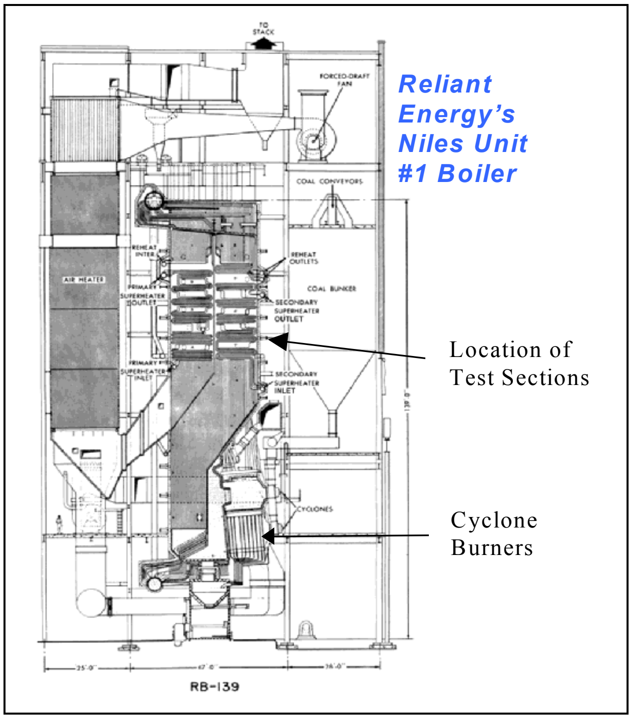


Figure 2: Niles Boiler

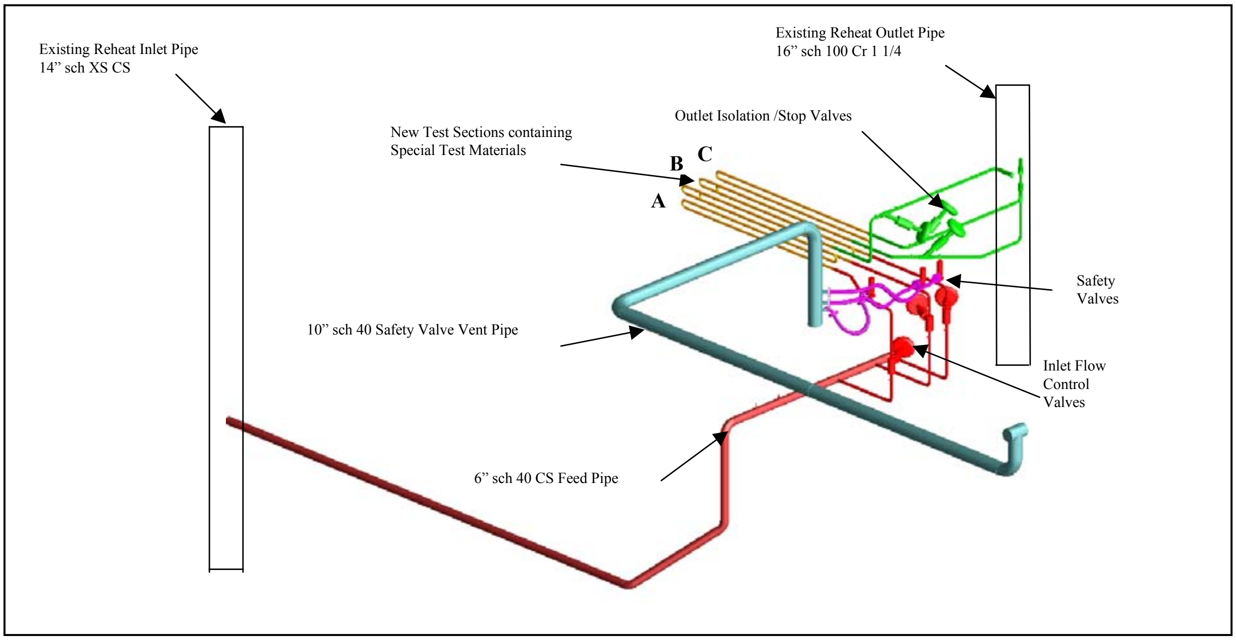


Figure 3: System Arrangement

Each of the three (3) identical test sections contain ten (10) primary and two (2) secondary advanced material samples. The primary samples are placed in three different locations within the section (see Figure 4 and Table 1). The three sections extend through the furnace front wall for the full depth of the furnace up-pass. The sections are supported from the baffle wall at their rear and the furnace front wall at their front; the wall penetration is sealed with an insulated casing box.

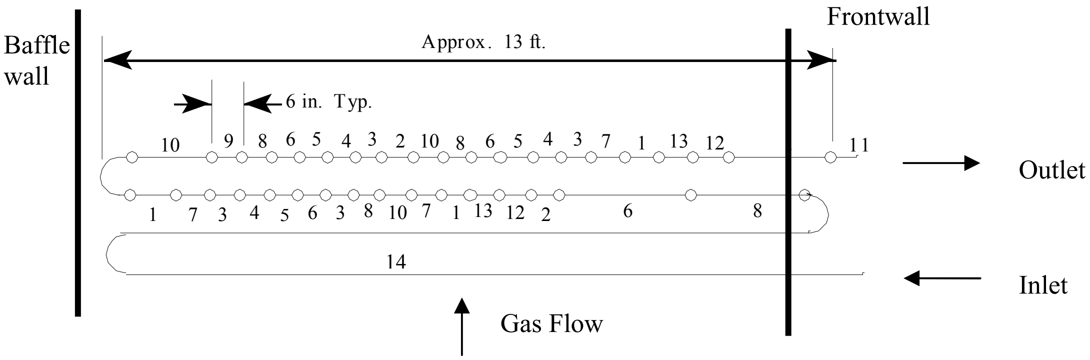


Figure 4: Location of Specimens within the Section

Table 1: Advanced Materials				
#	MATERIAL	SUPPLIER	ASME RECOGNIZED	SIMILAR MATERIAL
1	Incoclad – Core is Incoloy 800H	INCO	Yes - Code Case 1325	SB407-UNS N08800
2	Thermie	ORNL	No	Inconel 617
3	HR3C – SA213TP310HCbN	Sumitomo	Yes	
4	Ta Modified 310	ORNL	No	SA213TP310H or SA213TP310HCbN
5	800 Modified	ORNL	No	Incoloy 800H
6	Save25	Sumitomo	No	SA213TP310H or SA213TP310HCbN
7	HR120	Haynes	No	SA213TP310H
8	NF709	Nippon Steel	No	SA213TP310H or SA213TP310HCbN
9	Fe3Al-2Cr/304H	ORNL	Yes	Core is SA213TP304H
10	TP347HFG – SA213TP347HFG	Sumitomo	Yes	
11	Transition Piece	SA312TP304H	Yes	
12	690 clad 800HT weld metal INCO 52	INCO	Yes	Incoloy 800H
13	671 clad 800HT weld metal INCO 72	INCO	Yes	Incoloy 800H
14	SA213TP310H	NA	Yes	

The Sections were fabricated at McDermott Technologies Inc., B&W's research facility in Alliance, Ohio. All but one of the 6 in. long specimens are 2.5 in. diameter by 0.400 wall. They were joined using alloy 625 filler metal by rotating the tube in a tungsten-arc orbital welder; every one of the 116 welds was x-ray clear.

Installation was completed in May 1999, followed by shakedown and controls tuning (see Figures 5 & 6). During this period the steam temperature was controlled first to 1000°F and then to 1050°F before being raised to the current temperature of 1075°F, which produced surface metal temperatures in the top row that would accelerate corrosion.

The system was plagued from startup with valve controller overheat failures as a result of unexpectedly high ambient temperatures that caused the inlet valve to open, cooling the section to around 800°F at the outlet. This condition has seldom lasted more than a day or two, thanks to the rapid response of the operators at the Niles plant. To eliminate this problem, a cooling fan and ductwork were installed to blow cool air across each of the valves. This resulted in significant improvement but occasional problems continued. The electronic controllers were eventually replaced with mechanical devices.

Figure 5: Tungsten-arc Orbital Welder

Figure 6: Installation into Niles Boiler

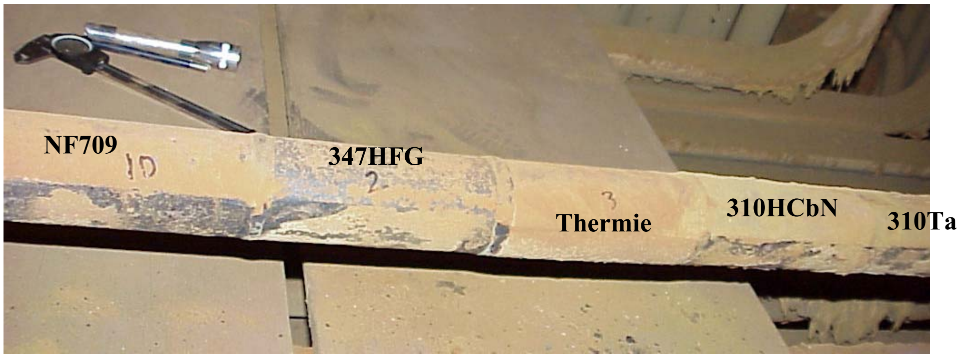


Figure 7: March 12, 2001 In-situ Inspection

Between startup and removal, inspections have been made on about 6-month intervals to monitor the extent of corrosion to avoid a failure. Figure 7 shows the in-situ condition in March 2001.

As Figure 8 shows, varying corrosion was exhibited among the specimens with extreme corrosion experienced in the SAVE25 piece. After 22 months of operation, the SAVE25 specimen actually developed a pinhole leak just prior to removal. As a result, when the first Section was removed in November 2001, a short piece of the top row, which included the SAVE 25 specimens, was removed from the two remaining sections and replaced with Incoclad tubing.

Section A Results

Test Section A was removed from Niles Unit 1 after 29 months (approximately 21,200 hours) of operation. Due to dispatch and outages, the sections actually experienced 15 months or 11,288 hours (1.29 years) of exposure at full temperature under conditions likely to cause coal ash corrosion. This first increment of exposure was slightly longer than the original proposed time span of one year for Test Section A.

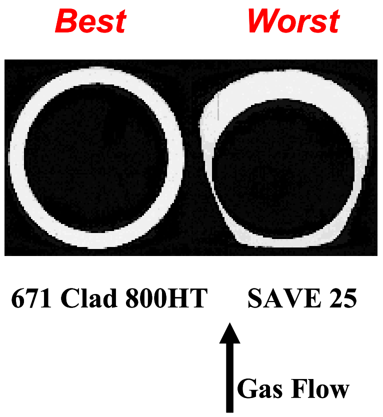


Figure 8: Best and Worst Specimens from First Section

Test section surface metal temperatures were controlled so coal ash corrosion could only occur when the boiler operated at sufficiently high load to assure reasonably constant gas temperatures and assure that tube metal temperatures could be controlled within the desired range. At low loads, reheat steam pressure was too low for good temperature control. Through the initial phase of each startup, final stage of shutdowns, and other times when the unit load was low, steam flow through the sections was maximized to keep surface metal temperatures below 1000°F. In this way, coal ash corrosion was retarded during these periods when test conditions could not be controlled. For the purpose of this test, 1000°F predicted surface metal temperature at the outlet of the test section was taken as the transition temperature above which the rate of coal ash corrosion is significant and below which it is negligible.

Following removal, each material sample was evaluated including a description of its condition after exposure, and determination of the rate of wall thickness loss. In addition, the microstructure of the scale/metal interface was examined to describe and record the characteristics of the attack and, in cases where there was more than one sample of the same material, an assessment was made of the performance of the alloy as a function of temperature. Though both the internal and external surfaces were examined, the focus was on the external surface.

Figure 4 provides the location of the materials within the section and Figure 9 provides a means of identifying each sample labeled from coolest to hottest.

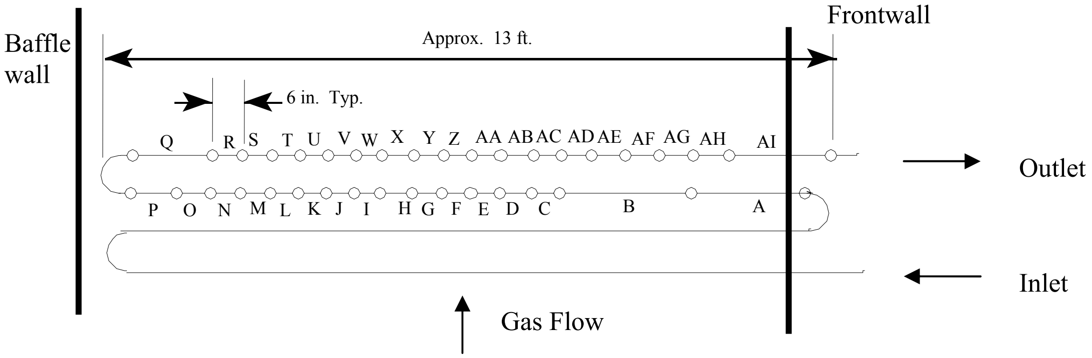


Figure 9: Numbering of Specimens within the Section

Surface Metal Temperatures – The desired test section temperatures were maintained by controlling the test section **outlet steam temperature** which is the temperature of steam exiting the test section. This temperature was constantly monitored by thermocouples and an arithmetic average outlet steam temperature was recorded at five minute intervals. The surface (external) metal temperature of each segment was also calculated at five minute intervals using the measured outlet steam temperatures, the average gas temperature, and a heat transfer model. In the evaluation of coal ash corrosion, an **average surface metal temperature**, defined as the arithmetic average of the calculated surface metal temperatures over the 11,288 hours of time at corrosive conditions, was used to provide a reasonable and practical approximation of the "isothermal equivalent temperature," the temperature which would produce the observed extent of corrosion based on a corrosion rate that is linear with temperature.

However, temperatures were not isothermal. As gas, steam, and metal temperatures rose and fell at the beginning and end of each boiler operating cycle, samples accumulated a few hours of coal ash corrosion below the targeted surface metal temperature. Also, test section surface metal temperatures were low through the initial six month startup period. The target section outlet steam temperature of 1075°F was maintained after November 1999. The temperature history of Section-A Segment AH (Figure 10) illustrates the surface metal temperature variability. For this segment, the average surface metal temperature over the duration of the test was 1198°F.

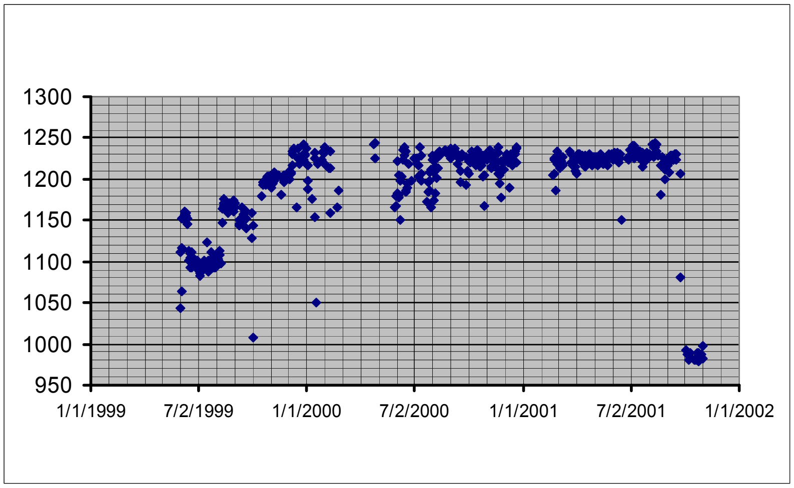


Figure 10: Daily Average Surface Metal Temperatures (°F) for Tube Segment AH

As shown in Figure 10, surface metal temperatures are initially lower, averaging 1097°F in July of 1999. From July through December 1999, they climbed to an average daily temperature of 1221°F in December, and they remained near that temperature whenever the section was operational until it was removed in November of 2001.

Evaluation – The section appearance was photographically documented and close-up photographs were taken to document the condition of each tube sample from three views: top down, bottom up and from the side (gas flows upward impacting the bottom of the tube). The tube was sectioned using a saw to extract specimens for evaluation. A portion of the material was sent to a third-party laboratory for confirmatory chemical analysis and the results were compared with the reported heat analyses from the various providers of the materials, material specifications if available, or "nominal" tube metal composition. No significant deviations were found.

Dimension rings were removed from the middle of each tube sample, grit blasted to remove deposit and scale, and the external surface condition of each ring was photographed to show the extent and type of attack occurring below the deposit/scale. As expected, the side of the tube that faced the gas flow experienced most of the metal loss. The maximum wall thinning was typically between the 6 o'clock and 3 o'clock or 9 o'clock positions (12 o'clock at the top of the tube on the downstream side relative to gas flow). The rings were also dimensioned and compared at eight predetermined circumferential locations, with dimensions taken before the sections went into service, to quantify the wall thickness losses at each position.

A full cross-section ring was polished and etched for each tube sample. These were then examined using the scanning electron microscope (SEM), and optical microscopy. One tube sample from each candidate material was selected for a detailed assessment of the microstructures of both the external and internal interfaces. Typically, the sample selected was the one that experienced the greatest amount of metal loss and the examination was along the tube radius that extended through the thinnest wall for a given tube sample.

Summary of Results - The goal was to assess the relative performance of candidate superheater tube alloys for application in boilers fired with corrosive high-sulfur coals. The operational history of Niles Unit #1 demonstrates that the service conditions for Test Section A provided an appropriately corrosive environment.

At about 1000°F, the coal ash becomes molten, and in its molten form is much more aggressive. At about 1300°F the stability of the complex sulfates generally begins to decrease and the corrosion rate ebbs. The average surface metal temperature, from the hot to the cooler end of the test section, ranged from 1198°F to 1047°F. Over this temperature range, all things being equal, the corrosion rate for these austenitic alloys would be expected to increase with increasing temperature.

In addition to influencing tube metal temperature, flue gas temperature also affects the deposition and diffusion processes forming the inner layer of corrosive alkali sulfate which significantly increases corrosion rate. The flue gas temperature in the region of interest in Niles Unit #1 was estimated to be over 2100°F.

The internal pressure for the test section was low, at approximately 300 psig, which has the benefit of making almost the full wall thickness of the tube available as a "corrosion allowance." Though the imposed pressure stresses are atypical of a supercritical boiler, the reliability benefit outweighed the importance of these stresses in the corrosion process.

Based on these factors and considering the operational environment, it is believed that the observed corrosion was suitable for discriminating between candidate superheater materials with respect to their resistance to coal ash corrosion. Due to differences in average surface metal temperature along the test section, and due to the locations selected for the placement of tube samples within the test section, some materials experienced a somewhat more aggressive environment than others. Hence, alloy performance must be compared by looking at their relative performance on graphs of corrosion rate versus temperature. Figure 11 provides the wastage rate (mils of wall thickness lost per year, mpy) as a function of position within the Test Section A. Table 2 provides the wastage rate with all of the samples of a given material grouped separately.

Interpretation of this is complicated by the fact that, while some materials behaved classically (e.g. for Save 25 wastage increased with increasing temperature), others did not. Figure 12 shows a plot of wastage as a function of average surface metal temperature for each of the twelve candidate materials. It can be seen from these data that some materials showed an increase in wastage rate at intermediate temperatures (e.g. modified 800H, and 310 Ta,). Other materials experienced an apparent decrease in wastage rate at intermediate temperatures (e.g. 347 HFG, and HR 120). Furthermore, the wastage rate appeared to <u>decrease</u> with increasing temperature for the nickel-base alloys (IN 52, IN72, and Incoclad 671). Finally, for 310 HCbN which had four tube samples in the test section, one of the intermediate temperatures showed a decrease in wastage rate, while the other showed an increase. This all points to the fact that one must proceed with caution in interpreting the significance of these wastage rate results. This is particularly true regarding correlations between wastage rates and exposure temperatures. Nonetheless, the results clearly define the relative resistance of the alloys and identify alloys that are adequately resistant over the temperature range of interest.

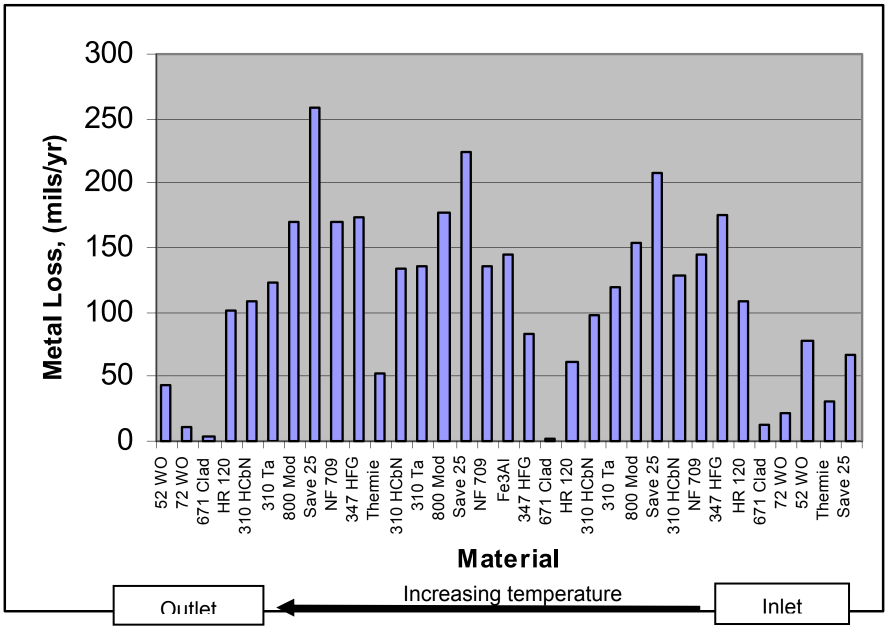


Figure 11: Wastage Rate as a Function of Position in Test Section A

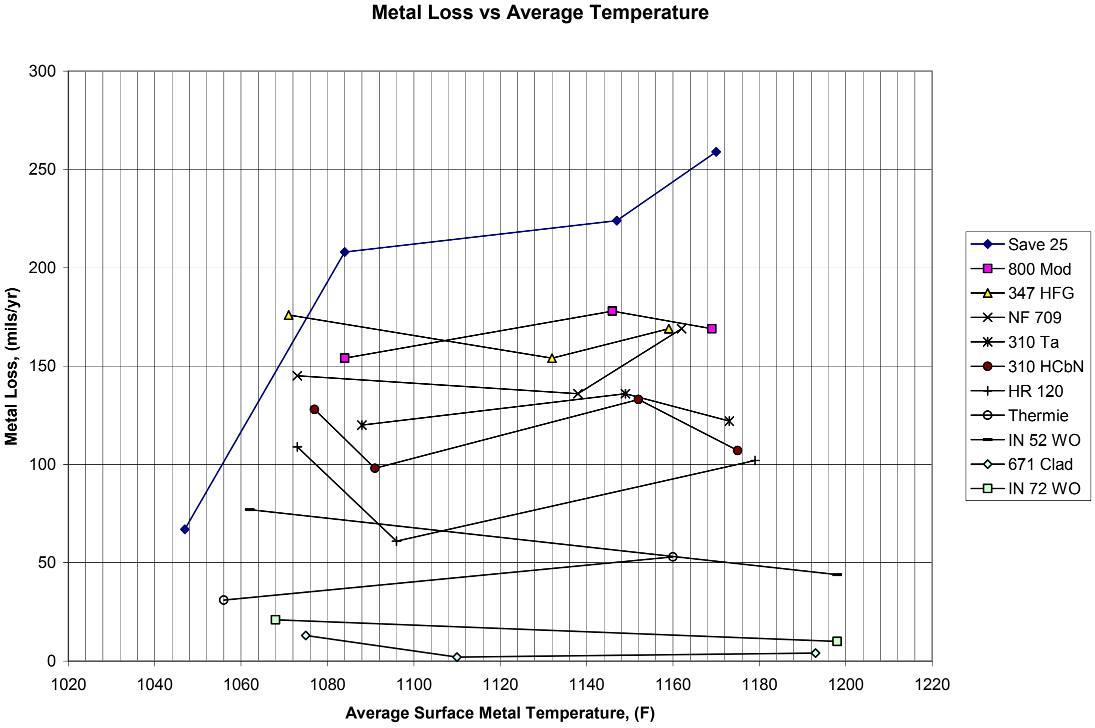


Figure 12: Wastage as a Function of Average Surface Metal Temperature

The reasons for the differences between alloy performance, though not the thrust of this program and not studied in depth, indicated some general trends. First, the chromium content was assumed to be a strong indicator of life expectancy. This is technically substantiated by the chromium-rich protective scale that formed on the surface of these high-chromium alloys. This assumption was generally substantiated by the results as shown in Figure 13.

Though corrosion rate correlates reasonably well to chromium content, it was observed that the rate appeared to be inversely related to the total alloy content, particularly the sum of the nickel and chromium. Figure 14 shows a plot of this sum versus maximum wastage rate. The data suggests that the corrosion rate is inversely proportional to the chromium plus nickel content, or roughly proportional to the iron content.

Scale/Metal Interface - Both the internal and external scale/metal interfaces were examined for every tube sample to verify that the tube thickness was not further reduced by grain boundary and/or other local penetrations, and to select one for a more detailed study. Examination of the microstructure revealed that wastage-sensitive materials seemed to have some common characteristics at the external scale/metal interface as shown in Figure 15.

Region A: Oxides of silicon, aluminum, and iron predominate but significant amounts of the alkali metals and sulfur were present. Arsenic was also found, but is believed to have little or no impact on the wastage rate. Chlorine was only found in small amounts in one of the eleven (11) samples analyzed.

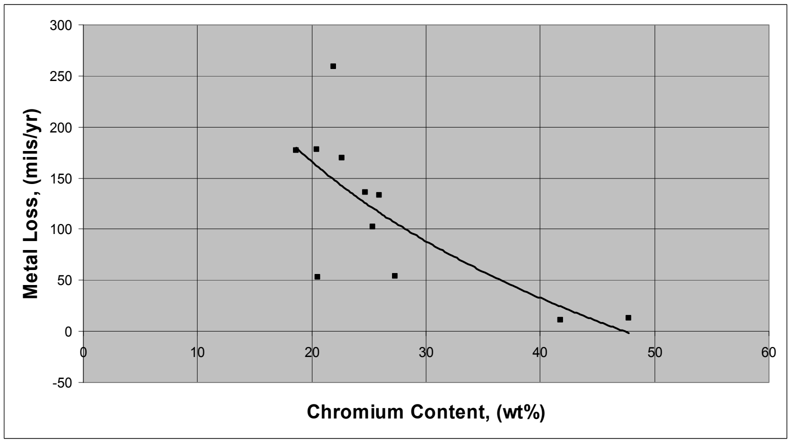


Figure 13: Chromium Content vs. Wastage Rate
(Logarithmic fit)

Region B: In almost every case there was a line of separation between this scale and a tightly adhering scale that lies beneath it. The analysis of this region reflected the combined composition of the commingled deposit and scale but depending upon the region scanned, the analysis could bias toward one or the other.

Region C: There was typically a chromium-rich oxide that contains significant levels of both nickel- and iron- oxides, presumably a function of the composition of the underlying metal, but may also reflect diffusion kinetics at or near to the surface. It also often contained a significant amount of sulfur but none of the alkali metals were found.

Region D: Typically alloy depleted in chromium and enriched in carbon relative to the bulk tube metal, the significance of the high carbon content in this region is not clear.

Region E: Typically at most a grain diameter in width, this layer may be interpreted as an etching "edge effect" in some cases. However, in most cases analysis suggested chromium depletion in this region.

Table 2: Rankings Per Material Based on Rate of Metal Loss			
Material	**Tube Sample Label**	**Rate Metal Lost* (mils/yr)**	**Average Surface Metal Temperature, (F)**
Save 25	AA	259	1170
Save 25	T	224	1146
Save 25	K	209	1084
Save 25	B	67	1047
800 Mod	U	178	1150
800 Mod	AB	169	1174
800 Mod	L	154	1092
347 HFG	H	176	1075
347 HFG	Y	174	1164
347 HFG	Q	83	1137
NF 709	Z	170	1167
NF 709	I	145	1077
NF 709	S	136	1142
Fe3Al	R	145	1139
310 Ta	V	136	1154
310 Ta	AC	123	1178
310 Ta	M	120	1092
310 HCbN	W	133	1157
310 HCbN	J	129	1081
310 HCbN	AD	108	1180
310 HCbN	N	98	1095
HR 120	G	109	1077
HR 120	AE	102	1184
HR 120	O	61	1100
Thermie	X	53	1160
Thermie	C	31	1056
52 WO	D	77	1062
52 WO	AH	44	1198
72 WO	E	21	1068
72 WO	AG	10	1198
671 Clad	F	13	1075
671 Clad	AF	4	1193
671 Clad	P	2	1110

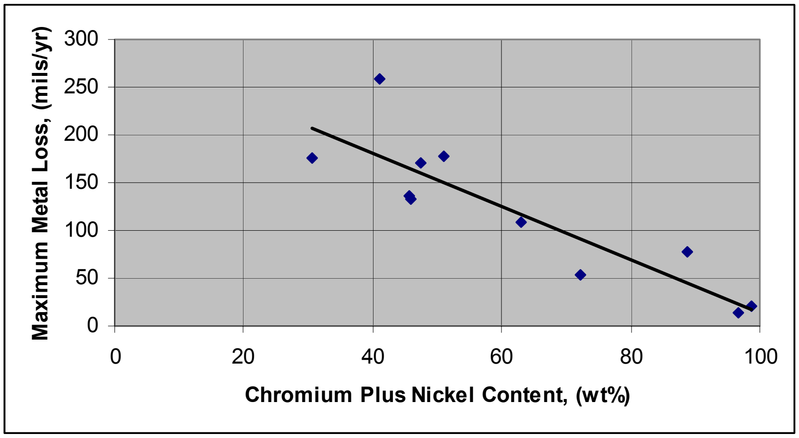


Figure 14: Chromium + Nickel Content vs. Wastage Rate
(Linear Regression Fit)

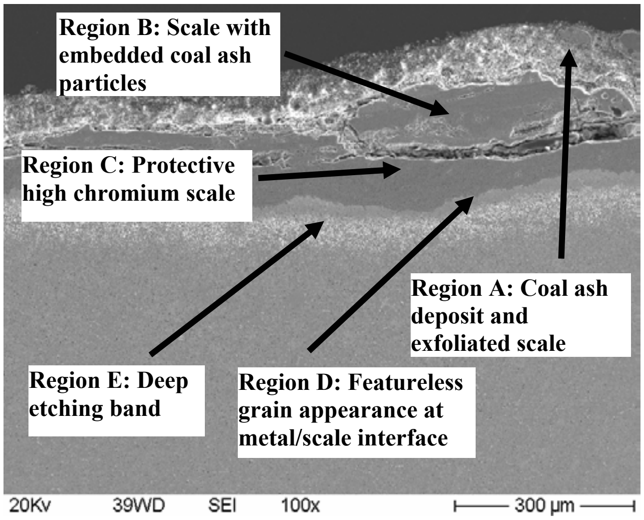


Figure 15: Characteristics at Scale/Metal Interface

Conclusions - As hoped, the test conditions were severe and corrosion was accelerated, reducing the time to observe significant results. Corrosion rates for the Type 347 stainless steel and the Incoloy tubing are much higher than the fastest corrosion rates for these alloys in superheaters and reheaters of existing boilers. Factors contributing to the severity of the conditions are the high sulfur content of the coal, cyclone combustion, proximity of test sections to the furnace outlet, and high surface metal temperatures. Over the test range of surface metal temperatures, corrosion rates were relatively constant so they were generally less affected by temperature than by alloy, which simplifies alloy comparison.

- Several of the materials tested are more resistant than the Type 304, 347, 321, and 316 stainless steels currently used in superheaters and reheaters.

- Of the alloys tested, the most resistant is Incoclad (approximately 48%Cr and 52%Ni), for which the maximum corrosion rate for the test period and temperature range was 13 mpy. The next most resistant materials is Inconel 72 weld clad, for which the maximum corrosion rate was about 21 mpy. Of the materials tested, only these appear to have potential for the most severe applications. Ongoing longer duration tests will better define the corrosion behavior of these more resistant alloys, and future tests under the DOE/OCDO Ultra Supercritical Advanced Materials Project are to determine their performance at still higher temperatures.

- Of the two weld overlay alloys tested, the Inconel 72 is significantly more resistant than Inconel 52, which corroded at a maximum rate of 77 mpy.

- Of the monolithic tube materials, Thermie (now designated Inconel 740) is the most resistant, with a maximum corrosion rate of 53 mpy. The next most resistant of the monolithic tube alloys is HR120 with a maximum corrosion rate of 109 mpy. Corrosion rates for modified 310 stainless steel alloys with 24-26% chromium were higher and those for the lower chromium alloys (NF709, modified 800, and Save 25) were higher yet.

- Like the Inconel 72 weld clad tube segments, Inconel 72 clad butt welds are highly resistant to corrosion. Also, Alloy 625 (SFA 5.14, ERNiCrMo-3) welds between alloy test segments are more resistant than most of the monolithic tube alloys. Nonetheless, evidence of "notching" at the toe of the weld joining the weld clad tubes deserves further evaluation in upcoming work.

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