COAL ASH CORROSION RESISTANT MATERIALS TESTING

Final Report

Including Topical Report: Removal of Section “B”

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Date published: December 2005

This report does not contain any Trade Secret/Proprietary Information.

The Quarterly Technical Report for report period January 1, 2006 through March 31, 2006 is incorporated herein.

This project was funded in part by the U. S. Department of Energy and the Ohio Coal Development Office, Ohio Air Quality Development Authority.

U.S. Department of Energy Contract:
Ohio Coal Development Office Grant Agreement:
McDermott Technology, Inc. Contract:

DE-FC26-99FT40525
CDO/D-97-02
CRD 1392

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ABSTRACT

In April 1999, three identical superheater test sections were installed into the Niles Unit #1 for the purpose of testing and ranking the coal ash corrosion resistance of candidate superheater alloys. The Niles boiler burns high sulfur coal (3% to 3.5%) that has a moderate alkali content (0.2% sodium equivalents), thus the constituents necessary for coal ash corrosion are present in the ash. The test sections were controlled to operate with an average surface metal temperature from approximately 1060°F to 1210°F which was within the temperature range over which coal ash corrosion occurs. Thus, this combination of aggressive environment and high temperature was appropriate for testing the performance of candidate corrosion-resistant tube materials. Analyses of the deposit and scale confirmed that aggressive alkali sulfate constituents were present at the metal surface and active in tube metal wastage. The test sections were constructed so that the response of twelve different candidate tube and/or coating materials could be studied. The plan was to remove and evaluate one of the three test sections at time intervals of 1 year, 3 years, and 5 years. This would permit an assessment of performance of the candidate materials as a function of time.

Test Section A was removed in November 2001 after about 24 months of service at the desired steam temperature set point, with about 15.5 months of exposure at full temperature. A progress report, issued in October 2002, was written to document the performance of the candidate alloys in that test section. The evaluation described the condition of each tube sample after exposure. It involved a determination of the rate of wall thickness loss for these samples. In cases where there was more than one sample of a candidate material in the test section, an assessment was made of the performance of the alloy as a function of temperature.

Test Sections B and C were examined during the November 2001 outage, and it was decided that, due to excessive wastage, certain tube samples needed to be removed and replaced in order to ensure that Test Sections B and C would have a chance of remaining in the boiler for their intended exposure period. These suspect tube samples were replaced and the two remaining test sections were put back into service. The tube samples that were removed from Test Sections B and C were set aside for later analysis at the end of the planned exposure period.

Test Sections B and C were again examined approximately six months later. At that time, measured wall thickness losses raised concerns about additional tube samples. These suspect samples were also removed, set aside for later analysis, and replaced. The test sections then went back into service until the end of the second exposure period, which was concluded in May 2003 when, due to evidence of excessive wastage, the valves were opened increasing cooling steam flow and thereby effectively stopping corrosion. In August 2003, Test Sections B and C were removed for closer examination. Section C had experienced about 42 months of service at the desired steam temperature set point with 28.5 months at temperature at full temperature. Additional suspect samples were removed from Test Section B, then, it was re-installed into the boiler (at the location originally occupied by Section C), where it remained in service until the end of the program. Due to this removal history, the samples from Test Section B had a total service duration that varied from a minimum of 15.5 months (for samples that performed poorly) to 37 months for samples that survived for the full intended service exposure for Section B. The figure below shows a schematic of Test Section B and indicates the length of service exposure for different locations.

The analysis of Test Section B followed much the same protocol that was employed in the assessment of the other two test sections. The focus was on determining and documenting the relative corrosion rates of the candidate materials; however, additional investigations were undertaken to better understand the wastage mechanism, and to characterize how selected candidate materials performed either well, or poorly, in the severe coal ash corrosion environment in the convection pass of Niles Unit #1. The detailed results of the investigation are included in this report as a series of twelve appendices. Each appendix is devoted to the performance of one of the candidate alloys. The table below summarizes metal loss rate for the worst case sample of each of the candidate materials in all three test sections. The body of this report compares these for all of the samples in the test section.

Review of this chart reveals that all twelve of the candidate materials performed similarly in all three test sections. Assessment of these maximum wastage rates reveals that eight of the twelve candidate material evidenced a wastage rate in excess of 100 mils per year. As such, it is questionable as to whether these materials could economically be used in a boiler having a severe coal ash corrosion environment.

Two materials experienced a maximum wastage rate in excess of 50 mils per year. Thermie was the monolithic tube alloy having the lowest maximum wastage rate (57 mils year). IN 52 Weld Overlay experienced a wastage rate of 59 mils per year; however, other issues arose with regard to this alloy. First, it should be noted that the weld overlay cladding was roughly 80 mils thick. So, at this rate the cladding thickness was breached long before completion of the full 37 month exposure period for Section B, and the calculated rate takes into account additional wastage on the underlying Incoloy 800HT tube substrate. The second issue with regard to the IN 52 Weld Overlay was the fact that cracks were found under the cladding within the heat affected zone of the Incoloy 800HT tube. The cause of this cracking was not resolved.

Lastly, it was noted that two of the twelve candidate materials evidenced a wastage rate in the range of 10 to 20 mils per year. Both of these materials involved a high chromium-nickel cladding: Incoloy 671 and IN 72 Weld Overlay, and these materials clearly performed well. The maximum wastage rate data for these materials is based on the measured wall thickness reduction for the low temperature sample, though the high-temperature sample was 3.2 feet (a quarter of the width of the connection pass) from the front wall so little wall effect would be expected.

Consideration was given as to why some of the candidate materials performed better than others, and the observation was made that, given a minimum level of chromium, wastage resistance appeared to be a function of total alloy content. This is depicted in the chart below which plots maximum wastage rate versus chromium plus nickel content. The more resistant alloys have high chromium and low iron concentrations.

An additional area of caution that should be considered is that, it was determined that the IN 72 Weld Overlay, while being relatively corrosion resistant, also had experienced a weld cracking phenomenon that may impact its service life. Investigations suggest that the as-produced cladding contained small, and difficult to detect, internal cracks prior to service exposure. The cause for this cracking is believed to be related to the cladding deposition procedure, however at this point, the issue has not yet been full resolved. So, for the sake of comparison, the data illustrated in the charts above only take corrosion wastage into account. If the wall thickness lost due to the observed cracking had been included in the wastage rate calculations, then the wastage rate would have increased by about 50%. However, if this additional 50% were taken into account, the total wall thickness lost for the IN 72 Weld Overlay still would be small relative to some of the other materials. Nonetheless, it must be remembered that the IN 72 Weld Overlay samples initially had only 80 mils of cladding to act as a corrosion barrier. Once the cladding is breached, as was noted for the IN 52 Weld Overlay, the wastage rate will be based on the resistance of the underlying Incoloy 800HT substrate.

Maximum Wastage Rate as a Function of Chromium Plus Nickel
(Note: for the purposes of this graph, the Thermie data point, includes the cobalt content.)

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INTRODUCTION

This Final Report represents the last in a series of three topical reports that document progress toward completion of the DOE-sponsored program to compare and rank the coal ash corrosion resistance of twelve candidate superheater tube materials (and/or coatings). (Contract No. DE-FC26-99FT40525).

The first topical report, issued on October 31, 2002, addressed the evaluation of Section A which was the first test section to be removed from the boiler. The Section A report provided the full details of the project background, material selection, fabrication of test materials and sections, description of the test system, and system installation and startup. The report also provided the operating history through 2001 along with the results of the evaluation of the candidate materials within the section. That information will not be repeated here. The reader is directed to “Topical Report: Removal of Section A” if this information is needed.

The second topical report, published in June 2003, addressed the evaluation of test Section C which was removed for evaluation in August 2003. Section C was the second test section to be removed from the boiler. The results of the evaluation of each candidate material in Section C were provided in the twelve separate appendices that accompanied the report. The main body integrates that information and drew preliminary observations and conclusions based on the results of Sections A and C.

On April 26, 2005, the final test section, Section B, was removed. This Final Report addresses the evaluation of test Section B, compares the results with those from Sections A and C, and draws observations and conclusions. Again, the results of the evaluation of each candidate material in Section B are contained in the twelve separate appendices that accompany this report. The main body integrates this information, makes comparisons with the results from the other sections and discusses observations and conclusions. Since the other two Topical Reports contain a time-line history of the program through 2003, Annex 1 documents the operating history of the test sections from the beginning of 2004 through 2005. Annex 1 can be found following the “Observations and Conclusions” section of this report.

1.0 EXECUTIVE SUMMARY

In April 1999, three identical superheater test sections were installed into the Niles Unit #1 for the purpose of testing and ranking the coal ash corrosion resistance of candidate superheater alloys. The Niles boiler burns high sulfur coal (3% to 3.5%) that has a moderate alkali content (0.2% sodium equivalents), thus the constituents necessary for coal ash corrosion are present in the ash. The test sections were controlled to operate with an average surface metal temperature from approximately 1060°F to 1210°F which was within the temperature range over which coal ash corrosion occurs. Thus, this combination of aggressive environment and high temperature was appropriate for testing the performance of candidate corrosion-resistant tube materials. Analyses of the deposit and scale confirmed that aggressive alkali sulfate constituents were present at the metal surface and active in tube metal wastage. The test sections were constructed so that the response of twelve different candidate tube and/or coating materials could be studied. The plan was to remove and evaluate one of the three test sections at time intervals of 1 year, 3 years, and 5 years. This would permit an assessment of performance of the candidate materials as a function of time.

Test Section A was removed in November 2001 after about 24 months of service at the desired steam temperature set point, with about 15.5 months of exposure at full temperature. A progress report, issued in October 2002, was written to document the performance of the candidate alloys in that test section. The evaluation described the condition of each tube sample after exposure. It involved a determination of the rate of wall thickness loss for these samples. In cases where there was more than one sample of a candidate material in the test section, an assessment was made of the performance of the alloy as a function of temperature.

Test Sections B and C were examined during the November 2001 outage, and it was decided that, due to excessive wastage, certain tube samples needed to be removed and replaced in order to ensure that Test Sections B and C would have a chance of remaining in the boiler for their intended exposure period. These suspect tube samples were replaced and the two remaining test sections were put back into service. The tube samples that were removed from Test Sections B and C were set aside for later analysis at the end of the planned exposure period.

Test Sections B and C were again examined approximately six months later. At that time, measured wall thickness losses raised concerns about additional tube samples. These suspect samples were also removed, set aside for later analysis, and replaced. The test sections then went back into service until the end of the second exposure period, which was concluded in May 2003 when, due to evidence of excessive wastage, the valves were opened increasing cooling steam flow and thereby effectively stopping corrosion. In August 2003, Test Sections B and C were removed for closer examination. Section C had experienced about 42 months of service at the desired steam temperature set point with 28.5 months at temperature at full temperature. Additional suspect samples were removed from Test Section B, then, it was re-installed into the boiler (at the location originally occupied by Section C), where it remained in service until the end of the program. Due to this removal history, the samples from Test Section B had a total service duration that varied from a minimum of 15.5 months (for samples that performed poorly) to 37 months for samples that survived for the full intended service exposure for Section B. The figure below shows a schematic of Test Section B and indicates the length of service exposure for different locations.

18.6 Months

22.5 Months

28.5 Months

37 Months

This report provides the results of the evaluation of Test Section B, including the samples that remained in the Test Section for the full exposure period as well as those that were removed early. This report also is intended to compare and summarize the results for all three test sections.

The analysis of Test Section B followed much the same protocol that was employed in the assessment of the other two test sections. The focus was on determining and documenting the relative corrosion rates of the candidate materials; however, additional investigations were undertaken to better understand the wastage mechanism, and to characterize how selected candidate materials performed either well, or poorly, in the severe coal ash corrosion environment in the convection pass of Niles Unit #1. The detailed results of the investigation are included in this report as a series of twelve appendices. Each appendix is devoted to the performance of one of the candidate alloys. The table below summarizes metal loss rate for the worst case sample of each of the candidate materials in all three test sections. The body of this report compares these for all of the samples in the test section.

Maximum Wastage Rate for Each Candidate Material In Test Sections A and C

Review of this chart reveals that all twelve of the candidate materials performed similarly in all three test sections. Assessment of these maximum wastage rates reveals that eight of the twelve candidate material evidenced a wastage rate in excess of 100 mils per year. As such, it is questionable as to whether these materials could economically be used in a boiler having a severe coal ash corrosion environment.

Two materials experienced a maximum wastage rate in excess of 50 mils per year. Thermie was the monolithic tube alloy having the lowest maximum wastage rate (57 mils year). IN 52 Weld Overlay experienced a wastage rate of 59 mils per year; however, other issues arose with regard to this alloy. First, it should be noted that the weld overlay cladding was roughly 80 mils thick. So, at this rate the cladding thickness was breached long before completion of the full 37 month exposure period for Section B, and the calculated rate takes into account additional wastage on the underlying Incoloy 800HT tube substrate. The second issue with regard to the IN 52 Weld Overlay was the fact that cracks were found under the cladding within the heat affected zone of the Incoloy 800HT tube. The cause of this cracking was not resolved.

Lastly, it was noted that two of the twelve candidate materials evidenced a wastage rate in the range of 10 to 20 mils per year. Both of these materials involved a high chromium-nickel cladding: Incoloy 671 and IN 72 Weld Overlay, and these materials clearly performed well. The maximum wastage rate for these materials on the low temperature sample, though the high-temperature sample, was 3.2 feet (a quarter of the width of the connection pass) from the front wall so little wall effect would be expected.

Consideration was given as to why some of the candidate materials performed better than others, and the observation was made that, given a minimum level of chromium, wastage resistance appeared to be a function of total alloy content. This is depicted in the chart below which plots maximum wastage rate versus chromium plus nickel content. The more resistant alloys have high chromium and low iron concentrations.

An additional area of caution that should be considered is that, it was determined that the IN 72 Weld Overlay, while being relatively corrosion resistant, also had experienced a weld cracking phenomenon that may impact its service life. Investigations suggest that the as-produced cladding contained small, and difficult to detect, internal cracks prior to service exposure. The cause for this cracking is believed to be related to the cladding deposition procedure, however at this point, the issue has not yet been full resolved. So, for the sake of comparison, the data illustrated in the charts above only take corrosion wastage into account. If the wall thickness lost due to the observed cracking had been included in the wastage rate calculations, then the wastage rate would have increased by about 50%. However, if this additional 50% were taken into account, the total wall thickness lost for the IN 72 Weld Overlay still would be small relative to some of the other materials. Nonetheless, it must be remembered that the IN 72 Weld Overlay samples initially had only 80 mils of cladding to act as a corrosion barrier. Once the cladding is breached, as was noted for the IN 52 Weld Overlay, the wastage rate will be based on the resistance of the underlying Incoloy 800HT substrate.

Maximum Wastage Rate as a Function of Chromium Plus Nickel

(Note: for the purposes of this graph, the Thermie data point, includes the cobalt content.)

2.0 EXPERIMENTAL

PROCEDURES & RESULTS

This section of the report documents the procedures and sequence of activities used to assess the condition of Test Section B after service. The primary focus is on determining the relative wastage resistance of the candidate superheater tube alloys. General results, taking into account all three test sections, also are offered in this section of the report. Detailed results are provided on a material-by-material basis in the attached appendices.

Overview:

At the beginning of the program, three identical test sections were installed side-by-side in the Niles Unit-1 boiler. These were identified as Test Sections A, B, and C. The intent was to remove and evaluate a section after each of three increasingly longer exposure increments. The purpose was to demonstrate how the candidate tube alloys performed relative to one another, and as a function of time. The original plan was to remove test Section A after one year. Section B was to be removed after three years of exposure, and Test Section C was to be removed at the end of the program, after approximately 5 years.

Due to various practical issues, and due to the fact that some of the candidate alloys corroded much more rapidly than expected, as the program progressed, it became necessary to deviate from the original plan. Test Section A was removed and analyzed first as planned. (The results of this analysis are provided in Reference 1). When it came time to remove and analyze the second test section, it was discovered that Section C was distorted (due to in situ maintenance), and that Section B was relatively unaffected.

Section B – As Removed

Section C – As Removed

Due to concerns about continued operation using the distorted section, and because the test sections were identical in design, it was decided to analyze samples from Section C (for the second test increment) and to reinstall Section B. The results of the analysis of Section C were presented in the previously issued report on this subject (Reference 2). The full Section B test exposure now has been completed and the test section was removed for analysis. This report provides the results of these analyses. It also summarizes the results of all three test sections, and attempts to draw conclusions.

Test Section Modification to Extend Service Life:

Test Section A was removed from Niles Unit-1 in November 2001, after 28.5 calendar months (approximately 21,200 hours) from start-up, 24 months with the desired steam temperature set point, and an equivalent of 11,288 hours (15.5 months) of exposure under conditions likely to cause coal ash corrosion (i.e. at a temperature above 1,000°F). At the time that Section A was removed for analysis, it became apparent that some of the tube samples in Sections B and C (particularly the Save 25 samples) would not survive the additional time required to reach the next planned exposure increment.

In an effort to ensure that Sections B and C would not fail prior to their scheduled removal time, questionable tube samples were removed from the test sections and replaced with “dutchmen” tube lengths. The dutchmen were intended to provide the corrosion allowance necessary to extend the life of the section. Six contiguous tubes (between welds G and M) were removed and replaced for both Sections B and C. The dutchman for Section B was made from a single length of Alloy 800H which was clad with IN 52 weld metal. The dutchman for Section C was made from two lengths of 310 HCbN that were joined together to cover the width of the gap.

Sections B and C then went back into service with the dutchmen in place. When they were examined about six months later, it was noted that a second round tube samples needed to be replaced due to excessive corrosion. Therefore, in June 2002, for both sections, three contiguous tube samples (between welds D and G) were removed and replaced with IN 52 clad dutchmen. When these repairs were made both sections went back into service until the outage in May 2003 when, due to evidence of excessive wastage, the valves were opened effectively stopping corrosion.

In August 2003, both sections were removed and visually evaluated. This examination revealed that Section C had become distorted due to field maintenance difficulties while Section B was relatively unaffected, (as discussed above). Based on this, it was decided that Section C would be removed and analyzed, and that Section B would be put back into service for the final testing increment.

Section B was visually and dimensionally inspected before it was put back into service. This inspection revealed additional evidence of tube wastage that suggested that a third round of tube samples would need to be replaced to ensure that the test section would survive to the completion of the program. All of the questionable samples from Section B were replaced, then the section was re-installed into the boiler at the position in the boiler that was previously occupied by Section C.

Section B Lay-Out

Figure 1 provides a schematic showing the position of the welds that join samples to one another to form Test Section B. Note that each weld has been given a letter designation. Using these, the tube sample positions are indicated by the weld letter designations at either end of the sample. As was mentioned earlier, the three test sections were identical, so, the same positions were occupied by the same candidate materials in all three test sections.

Figure 1 also shows the positions of the dutchmen in Section B at the time of its removal for analysis. As was mentioned above, the tube samples at these “Dutchmen” locations were removed early due to excessive corrosion, so they did not experience the full exposure interval for Section B. Nonetheless, the samples from these locations were set aside (at the time of their removal) and their assessment will be included in the analysis of Section B. The only sample that could not be fully analyzed was the HR 120 sample at location DD-EE. This was due to the fact that at some point, this sample was repaired with a weld pad, and put back into service. Otherwise the full sequence of tube samples is included in this analysis.

Table 1 provides the key to the sequence of candidate materials within the three test sections. In this table, the candidate alloys are listed in the sequence in which they are encountered in the test section as one progresses from the hottest location toward the coolest. This table includes the tube sample letter designations that are based on the weld lettering shown in Figure 1. Included in this table are calculated Test Section B average surface metal temperature at each location and the total exposure time for each sample.

Exposure Time

Initial exposure of the three test sections to flue gas occurred when Niles Unit-1 resumed operation in June of 1999, following a maintenance outage during which the sections were installed. Test Section B was removed from service on April 26, 2005, after a period of 63.4 calendar months in the boiler, and about 37 months at full temperature under conditions likely to cause coal ash corrosion. During this time the boiler shifted load and cycled on and off line in normal response to power demand and boiler maintenance requirements.

It is well understood that the rapid metal loss associated with coal ash corrosion of austenitic materials occurs over a temperature range between approximately 1000°F and 1300°F. The intent of this work was to control the test sample average surface metal temperatures to fall within this range over the full length of the test section. This required that the boiler be operated at sufficiently high load to assure reasonably constant gas temperatures. At low loads, reheat steam pressure and/or furnace exit gas temperature is 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 surface metal temperature at the hot end of the test section (Point-T at the “south” end of the section in Figure 1) was taken as the transition temperature above which the rate of coal ash corrosion is significant and below which it is negligible. For

Test Section B the accumulative time at full temperature under conditions likely to cause coal ash corrosion was approximately 26,640 hours.

Test Section Surface Metal Temperatures

As indicated above, desired test section temperatures are maintained by controlling the temperature of steam exiting the test section. It is constantly monitored by thermocouple measurement, and an arithmetic average outlet steam temperature is recorded at five minute intervals.

The external surface temperature of each alloy test segment is calculated at five minute intervals using the measured outlet steam temperatures, the average gas temperature, and B&W's heat transfer model for the test section. In the following appraisals of coal ash corrosion, an average surface metal temperature is determined for each test specimen. The indicated average surface metal temperatures are arithmetic averages of the calculated segment external surface metal temperatures for the time that the sample was exposed to the coal ash corrosion temperature range. Tube samples not removed early from Section B experienced the full 26,640 hours at full temperature. The average surface metal temperatures for samples that were removed early were calculated based on the exposure temperatures during their time in the boiler. For all of these samples, the indicated arithmetic average provides a reasonable and practical approximation of the "isothermal equivalent temperature", i.e. the isothermal temperature at which exposure over time would produce the observed extent of corrosion. The average surface metal temperature approximates the isothermal equivalent temperature to the extent that the corrosion rate is a linear function of temperature. This simplification is justified at this point due to the limited amount of available data, but the data seems to suggest that the corrosion rate may be departing from linearity for some of the materials under investigation. Table 1 shows the estimated average surface metal temperatures for test segments in Section B.

Temperatures were not constant. As gas, steam, and metal temperatures rose and fell at the beginning and end of each high-temperature boiler operating cycle, samples accumulated a few hours of coal ash corrosion below the target exposure surface metal temperature. Also, test section surface metal temperatures were low throughout an initial six month shakedown period. The full target section outlet steam temperature of 1075°F was only maintained after November of 1999. The temperature history of Section B, Segment "R-S" (Figure 2) illustrates the surface metal temperature variability. For this segment the average surface metal temperature over the duration of the test is 1195°F. As shown in Figure 2, surface metal temperatures are initially low. Then from July through December 1999, they climb to an average surface metal temperature appropriate for testing, and remain near this temperature whenever the section is operational until it is removed in from service May of 2003. Figure 2 also illustrates the daily surface metal temperature variability. The wide spread in values is generally caused by transients when the unit is taken off line. The estimated full load gas temperature at the test loop location was 2114°F.

Coal

The Niles cyclone boiler is fired with Ohio bituminous coal having a sulfur content of approximately 3% to 3.5%. The sulfur in this coal is pyretic and organic, with little sulfate.

Chlorine concentrations are typically less than 0.05%. Table 2 shows a representative coal analysis. This same coal has been used to date throughout the program.

Documentation:

Test Section Appearance Upon Receipt After Exposure: Figures 3 and 4 show the appearance of Test Section B when it was received at the Research Center. Two figures were needed to document the entire length of the test section; however, there is some overlap between them. The weld lettering designations are noted in these figures. The schematic provides a representation of how each tube sample was originally situated within the test section.

Tube Sample Surface Appearance: Close-up photographs were taken to document the condition of each tube sample. Figure 5 provides an example of this documentation for one tube sample. Three views were documented. The 12 o'clock position faced downward* into the oncoming gas flow. The 6 o'clock position was at the top of the tube on the side downstream of the gas flow direction. The 3 o'clock position was halfway between the two. These figures are intended to document the extent of deposit and scaling. In some cases where the deposit has fallen away, evidence also is seen of the chalky white deposit associated with alkali-iron-trisulfate hot corrosion. The rest of these are included in separate appendices to this report. Each appendix is devoted to a different candidate material.

- * By selecting the 12 o'clock orientation as the one facing directly into the gas flow direction, the resultant orientation yields an "upside-down" clock reference system relative to the physical position of the tube within the boiler, i.e. 12 o'clock faces downward.

Tube Sectioning:

Figure 6 provides a schematic that depicts how the tube sample was sectioned to extract specimens for evaluation. Figure 7 shows the sectioning plan for each tube sample. All cuts were made dry using a saw. As they were cut, samples were marked to maintain sample identity and tube orientation (i.e. 12 o'clock, 3 o'clock, and 6 o'clock).

Composition Verification:

For Test Section A, removed and analyzed earlier, a portion of the "extra material", identified as RS-4 in Figure 7, was sent to a third-party laboratory for confirmatory chemical analysis, primarily by optical emission spectrometry. The results of these analyses were compared with the reported heat analyses from the various providers of materials for test. They were also compared with material specifications if they were available. Otherwise, a "nominal" or "target" tube metal composition was used.

The results of these spectroscopic analyses for Test Section A, confirmed that the correct tube material had been used at each location in the test section, and that the tube material complied with its' intended chemical composition. The scanning electron microscope (SEM) also was used to perform a semi-quantitative chemical analysis (using the energy dispersive x-ray spectrometry (EDS)) for each of the twelve different material types in Test Section A. These results compared well with the somewhat more accurate optical emission spectrometry analyses as can be seen from reviewing the data in the appendices to the final report covering the Section A analysis, (see Reference 1).

With alloy identification confirmed for Test Section A, it was decided that only representative sampling would be used to verify that the correct materials were at their proper location within Test Sections B and C. It also was decided to use EDS as the analytical method, and that OES would be used as a fall-back if problems arose. To this end, twelve samples were chosen for analysis. Typically the sample selected represented the most aggressively attacked sample of each material type. The EDS analyses confirmed that all twelve samples were of the proper material type.

The results of these analyses are included in the appendices of this report which provide detail on a material-by-material basis. Figure 8 shows a typical example.

Surface Condition:

Dimension rings (identified as “RS-2” in Figure 7) were removed from the approximate centerline of each tube sample. These were grit blasted with aluminum oxide grit to remove deposit and scale. The surface condition of each ring was photographed, and is included in the appendices of this report. Figure 9 shows a typical example. These are intended to show and record the level and type of attack that was occurring at the external surface of these tubes (i.e. beneath the deposit/scale that are shown in Figure 5).

Figure 10 shows a typical example of a dimension ring cross section and associated measurements. Such figures provide, as a reference, the amount of wall thickness measured at the position indicated. Dimensioning is discussed in more detail below. In general, it was the side of the tube that faced the gas flow that experienced most of the metal loss. The maximum wall thinning was typically between the 12 o'clock and 9 o'clock (or 3 o'clock) positions.

It should be noted that the approach for weld clad overlays was somewhat different from that used for the other samples, in that, the “RS-2” ring was used to document the “surface condition” for these samples; however, these rings were not used for dimensioning. This decision was made at the beginning of the program due to concerns about potential dimensioning problems that might come about due to wall thickness variability related to the surface contour of the weld overlay. To address this, before the weld overlay samples were welded into the test section, approximately one inch of the O.D. surface at one end of each sample was surface ground to provide a consistent surface for subsequent measurements. Therefore, for the weld overlay specimens, the “before” and “after” wall thickness measurements were made at tube end rather than using the “RS-2” dimension ring.

Dimensioning:

The grit blasted rings were measured with certified micrometers that were accurate to ± 0.001 ". The measurements were taken at eight predetermined circumferential locations that were indicated by the “o'clock” positions: 12:00, 1:30, 3:00, 4:30, 6:00, 7:30, 9:00, and 10:30 o'clock. The “o'clock” positions were the same as those used above to express the orientation of the tube within the test section. Prior to service, measurements had been taken and recorded for each of these orientations for each of the tube samples. The measurements taken after service were compared with these and a “delta” calculated to express the wall thickness losses at each position. These are recorded for each candidate material in the appendices that follow.

Note that an attempt was made to determine the maximum wall thickness loss for each tube sample. In some cases, it was clear that the minimum wall thickness was not at one of the eight predetermined locations, so, there was no “before service” measurement for use as a reference. In these cases, the average “before service” wall thickness measurement was determined and used as the reference measurement for determining the wall thickness lost. The location and value of the maximum are also documented in the appendices in tables such as the one shown in Figure 10.

Note also that, with the exception of the weld overlay samples, it was not possible to take the “after service” measurements at the same axial position as the “before service” measurements, since these were taken at the tube ends, and the tube ends now were part of the welds that joined the tube samples to one another. Given the short lengths of the tube samples, and the overall consistency of the wall thickness measurements, it was judged that this 2 to 3-in. difference in axial location would have only a minor impact on the accuracy of the “delta” wall thickness calculations.

Metallography:

A full cross-section ring was polished and etched for one tube sample for each material type, (i.e. the ring identified as RS-1 in Figure 7). The same electrolytic etching procedure was used for each material. It involved using a 10% oxalic acid etchant with a 9 volt open circuit potential. These then were examined using the scanning electron microscope (SEM).

SEM/EDS:

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. Typically the examination was along the tube radius that extended through the thinnest wall for a given tube sample. Given the high level of resistance to steam-side oxidation for all of the candidate alloys, the focus of this analysis primarily was on the deposit/scale/metal interface at the external surface of the tubes. Nonetheless, the condition at the scale/metal interface also was documented for the internal surface of the tube. For both surfaces, photographs were taken to record the nature of the scale and the condition of the underlying metal. These are recorded in the appendices along with comments regarding distinctive and/or unique features.

While in the SEM, EDS(energy dispersive spectroscopy) analyses were made of selected regions of the deposit, scale, and underlying tube metal. For selected samples (e.g. Save 25), EDS elemental “dot maps” and “line scans” were used to gain a more detailed understanding of the deposit/scale/metal interfaces. These also are recorded in the appendices.

Weld Profile:

Welds that survived for the full 37 months exposure period of Section B were cross sectioned (as per sample RS-3 in Figure 7) and evaluated. The purpose of this was to investigate the condition of the welds and weld heat affected zones relative to the remainder of the tube. The weld cross sections were polished, etched and photographed to record their appearance. Typical results are shown in Figure 11.

Deposit Analysis:

Deposit was scraped and removed from the outside surface (of Inconel 671 Sample R-S) and submitted for elemental and compound identification by chemical analysis and x-ray diffraction respectively. The deposits were noted to be tight and adherent and lack a heavy loose outer deposit. Two layers of deposit were scraped from the outside surface for analysis. Deposits were subjected to inductively coupled plasma – optical emission spectrographic (ICP-OES) analysis. The results for all three test sections are provided in Tables 3 and 4.

Table 1: Tube Sample Designation, Average Surface Metal Temperature, and Exposure Time Based on Position in Test Section C

Sample Designation	Material	Average Surface Metal Temperature (F)	Exposure Time (hrs)
R-S	IN52 Weld Overlay	1195	26,640*
Q-R	IN72 Weld Overlay	1195	"
P-Q	Incoclad 671	1203	"
O-P	HR 120	1183	20,832
N-O	310 HCbN (HR3C)	1179	"
M-N	310 Ta	1178	"
L-M	Modified 800H	1172	13,590
K-L	Save 25	1168	"
J-K	NF 709	1165	"
I-J	347 HFG	1162	"
H-I	Thermie	1159	"
G-H	310 HCbN (HR3C)	1155	"
F-G	310 Ta	1153	15,807
E-F	Modified 800H	1149	"
D-E	Save 25	1145	"
C-D	NF 709	1141	20,832
B-C	Fe3Al	1138	"
A-B	347 HFG	1136	"
Return Bend	TP 310		
U-V	671 Clad	1121	26,640*
V-W	HR 120	1099	"
W-X	310 HCbN (HR3C)	1094	"
X-Y	310 Ta	1092	"
Y-Z	Modified 800H	1092	20,832
Z-AA	Save 25	1084	15,807
AA-BB	310 HCbN	1080	20,832
BB-CC	NF 709	1077	"
CC-DD	347 HFG	1075	"
DD-EE	HR 120	1077	26,640*
EE-FF	Incoclad 671	1074	"
FF-GG	IN72 Weld Overlay	1067	"
GG-HH	IN52 Weld Overlay	1062	"
HH-II	Thermie	1056	"
II-JJ	Save 25	1047	"

* Approximate time above 1000°F.

Table 2. Representative Analysis of Coal Burned in Niles Unit-1

Coal Analysis	
Moisture	5.0 %
Carbon	66.5 %
Hydrogen	4.9 %
Nitrogen	1.4 %
Sulfur	3.1 %
Alkali (as Na ₂ O)	0.2 %
Ash	12.3%
Ash Analysis	
SiO ₂	41.5 %
Al ₂ O ₃	19.5 %
TiO ₂	1.2 %
Fe ₂ O ₃	26.8 %
CaO	3.8 %
MgO	0.7 %
K ₂ O	1.6 %
Na ₂ O	0.5 %
SO ₃	3.3 %
P ₂ O ₅	0.6 %
BaO	0.1 %
Undetermined	0.3 %

Table 3: Deposit Analysis

Constituent*	Section A Outer Layers (wt%)	Section A Inner Layers (wt%)	Section C Outer Layers (wt%)	Section C Inner Layers (wt%)	Section B Outer Layers (wt%)	Section B Inner Layers (wt%)
Silicon, SiO ₂	31.84	28.64	23.39	20.51	24.70	28.24
Aluminum, Al ₂ O ₃	14.11	9.66	11.49	7.90	13.78	14.00
Iron, Fe ₂ O ₃	22.99	12.85	14.39	12.26	24.52	24.47
Titanium, TiO ₂	1.06	0.60	0.66	0.53	0.96	0.95
Calcium, CaO	3.60	4.06	4.26	7.61	3.71	3.35
Magnesium, MgO	0.35	0.17	0.84	0.76	0.52	0.41
Sodium, Na ₂ O	0.70	0.96	2.06	1.88	1.56	1.10
Potassium, K ₂ O	1.82	3.82	6.92	5.64	3.06	1.97
Phosphorous, P ₂ O ₅	0.88	0.91	1.02	0.89	0.75	0.75
Sulfur, SO ₃	11.64	20.00	--	--	--	--
Sulfur, SO ₄	--	--	34.79	41.84	11.59	9.09
Strontium, SrO	--	--	0.07	0.05	0.04	0.03
Manganese, MnO	--	--	0.06	0.06	0.05	0.04
Barium, BaO	--	--	0.06	0.07	0.05	0.04

Table 4: Deposit Analyses (X-Ray Diffraction Results)

Level		Scale Analysis	Approximate Percent (+/-5%)
Major	<ul style="list-style-type: none"> • Silicon 	<ul style="list-style-type: none"> • Cristobalite, (syn, SiO₂) • αQuartz, (SiO₂) 	<ul style="list-style-type: none"> • 29 • 37
Minor	<ul style="list-style-type: none"> • Iron • Chromium • Arsenic • Sulfur • Potassium • Calcium 	<ul style="list-style-type: none"> • Hematite (Fe₂O₃) • Eskolite (Cr₂O₃) • Gypsum (CaSO₄ (H₂O)₂) 	<ul style="list-style-type: none"> • 10 • 7 • 7
Trace	<ul style="list-style-type: none"> • Aluminum • Titanium • Nickel 		
		<ul style="list-style-type: none"> • Other 	<ul style="list-style-type: none"> • 10

Table 5: Carbon and Chlorine Analysis Results

Constituent	Outer Layers, (wt%)	Inner Layers, (wt%)
Carbon	0.19	0.10
Chlorine	0.006	0.0086

Figure 2: Daily Average Surface Metal Temperatures (F) for Tube Sample "R-S", Section B

Figure 3: Appearance of Test Section B After Removal From Service (Part 1)

- Note:
- 1) The regions highlighted in the schematic drawing of the test section are shown in the photographs below the schematic.
 - 2) The letters adjacent to the photograph indicate the positions of the various welds used to construct the test section. These letters also are used to identify the candidate metal samples that lie between them. For instance, Sample A-B lies between welds A and B. It was manufactured from 347 HFG. Sample B-C was manufactured from Fe₃ Al, etc.

Figure 4: Appearance of Test Section B After Removal From Service (Part 2)

Note: 1) The regions highlighted in the schematic drawing of the test section are shown in the photographs below the schematic.

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure 5: Typical Documentation of As-Received Appearance for Tube Sample L-M (Modified 800H)

Note: The chalky deposit/scale is highlighted in the box for the 6 o'clock orientation above.

Figure 6: Schematic Depicting Sectioning to Remove Tube Sample From the Test Section

Key	
Sample	Purpose
RS-1	Metallography ring
RS-2	Dimension ring
RS-3	Weld profile
RS-4, 5, 6	Extra material

Note:

- 1) Cut B - B' is at the approximate center of the tube sample
- 2) Specimens RS-1, RS-2, RS-3 are all about $\frac{1}{2}$ " thick

Figure 7: Schematic Depicting Sectioning of Tube Sample

Description: Nominal 22Cr/18Ni steel with Nb and N added to provide creep strength.
Source: Sumitomo Metal Industries (SMI)
Reference Composition: “Specified” chemistry – per SMI certificate.

Element	Reference Composition	Composition (a) Heat D621907	Tube Sample D-E	Tube Sample K-L	Tube Sample Z-AA	Tube Sample II-JJ
Ni	15.00 – 22.00	19.80	N/A	19.8	N/A	N/A
Cr	21.00 – 24.00	22.60	N/A	22.2	N/A	N/A
Fe	Balance	Balance	N/A	53.2	N/A	N/A
Mo	-	-	N/A	-	N/A	N/A
Co	-	-	N/A	-	N/A	N/A
C	0.05 – 0.12	0.07	N/A	-	N/A	N/A
N	0.15 – 0.30	0.22	N/A	-	N/A	N/A
B	-	-	N/A	-	N/A	N/A
Mn	2.0 max	0.64	N/A	0.45	N/A	N/A
Si	1.5 max	0.23	N/A	0.26	N/A	N/A
Al	-	-	N/A	-	N/A	N/A
Ti	-	-	N/A	-	N/A	N/A
Al+Ti	-	-	N/A	-	N/A	N/A
Nb	0.30 – 0.60	0.45	N/A	-	N/A	N/A
Ta	-	-	N/A	-	N/A	N/A
Nb+Ta	-	-	N/A	-	N/A	N/A
V	-	-	N/A	-	N/A	N/A
W	0.80 – 2.80	1.31	N/A	1.04	N/A	N/A
Cu	2.00 – 4.00	3.31	N/A	3.05	N/A	N/A
Sn	-	-	N/A	-	N/A	N/A
P	0.030 max	0.022	N/A	-	N/A	N/A
S	0.010 max	(c)	N/A	-	N/A	N/A
O2	-	-	N/A	-	N/A	N/A

a – Ladle analysis

b- By difference

c- Not detected

N/A = Sample not analyzed.

Figure 8: Typical Semi-Quantitative Composition Verification for Save 25

**(12 O'Clock
(324 mils lost)**

**3 O'Clock
(312 mils lost)**

**6 O'Clock
(15 mils lost)**

Figure 9: Typical Example of OD Surface Appearance After Grit Blast

Note: This particular example is for Save 25, Sample K-L.

Material:**SAVE 25****Sample Location:****K-L****Maximum Rate:****228 mils/yr****Maximum Loss Orientation:****Approx. 2:30 o'clock****Average Metal Temperature:****1168 F**

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.405	0.400	0.399	0.401	0.398	0.398	0.400	0.404	0.401	0.401
After	0.081	0.073	0.087	0.374	0.383	0.389	0.127	0.114		0.048
Delta	0.324	0.327	0.312	0.027	0.015	0.009	0.273	0.290		0.353

Figure 10: A Typical Silhouette with Wall Thickness Measurements Showing Metal Loss as a Function of Position

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

(a) Cross Section Through Weld "Q"

(b) Cross Section Through Weld "V"

Figure 11: Weld Profile Through Tube Samples

3.0 RESULTS AND DISCUSSION

It is understood that cycle efficiency can be improved by operating at increased superheater temperatures and pressures. This results in reduced fuel costs and proportionately reduced emissions. This approach was attempted in the early 1960's; however, it had to be discontinued primarily because the superheater tubing materials that were available at that time were not able to withstand the increasingly aggressive environment as temperature increased.

Coal ash corrosion is a barrier that must be overcome to make possible cost-effective boiler operations at higher temperatures with a wide range of coals. Coal ash corrosion leads to wastage of superheater tubing having a surface metal temperature in the range of roughly 1,000°F to 1,350°F. The aggressiveness of this mechanism is a function of the composition of the coal ash, with high sulfur coals being of particular concern. Studies have shown that this hot corrosion mechanism comes about when constituents in the coal ash deposit interact to form a molten (alkali iron tri-sulfate) salt. It has been theorized that, when this molten salt forms, it aggressively attacks and degrades the protective oxide scale that is relied upon to provide corrosion resistance for the tube material. With the protective oxide scale rendered ineffective, the underlying metal then becomes susceptible to rapid wastage and wall thinning.

Recently, there has been renewed interest in attempting once again to achieve the boiler efficiency improvements that are implied by boiler operations at increased temperatures. Advancements in alloy design since the 1960's may enable this transition. Over the years, new tubing and cladding materials have become available from a variety of sources, and many of these new materials have the potential to provide increased resistance to coal ash corrosion. In general, these newer alloys all have a chromium content in the range of 20 % to 25 %, along with other alloying element constituents designed to provide corrosion resistance, (and possibly strength), at temperature. If these can be demonstrated to be effective at resisting coal ash corrosion, then, a major barrier will be overcome toward achieving the desired boiler efficiency improvements.

Program Approach:

The primary goals of this program were to rank candidate improved tubes and coatings and to identify those candidates that are suitable for service in an aggressive high-sulfur coal ash environment. The candidate materials were identified by canvassing industry experts, along with end-user utilities, alloy developers, and material vendors. A total of twelve candidate alloys (and/or coatings) were selected for evaluation. The program approach was to evaluate the performance of these materials in situ in an operating utility boiler burning a relatively high-sulfur coal. To accomplish this, three identical test sections were fabricated using relatively short lengths of the candidate tube materials. If material was available, multiple tube samples were used for each candidate material. These were strategically positioned within the test section so that each candidate material was exposed at different positions within the test section. It should be understood that, during operation, the test section temperature varied from inlet to outlet over a range of roughly 1050°F to 1210°F. So, the positions of the test samples permitted an assessment of candidate material performance as a function of temperature.

The test sections used in this program were identified as Sections A, B and C. The intent was to remove and evaluate the Section A after roughly one year of exposure at temperature. Section B

was to be removed after roughly three years at temperature, and Section C would be removed after roughly five years. Given the fact that the sample placement within all three test sections was identical, then, taking this approach would permit an assessment of performance as a function of time and temperature.

Section A was removed from the boiler and evaluated in 2001 (after about 15.5 months of exposure at temperature). The results of this assessment are documented in Reference 1. Due to mitigating circumstances, the decision was made that Section C would be the second section to be evaluated. It was removed from the boiler and evaluated in 2003 (after about 28.5 months at temperature). The results of the assessment of Section C are documented in Reference 2. Section B was removed and evaluated in 2005 (after about 37 months of exposure). This report documents the results of the assessment of samples from Section B, and compares the results with data gathered in the previously reported assessments to draw inferences regarding the performance of a candidate material as a function of time.

As an aside, it needs to be recognized that not all of the candidate materials survived for the full 37 month exposure period for Section B. In fact, some materials performed so poorly that they did not survive for the full 28.5 month exposure period for Section C. In order to extend the life of the entire test section (and to gather additional data on the candidate materials that were performing well), it was decided that poorly performing materials would be monitored, and removed from the test section and replaced with “dutchmen” manufactured from a more corrosion resistant material. Consistent with this selected samples were removed from both Sections B and C after roughly 18.6 and 22.5 months of exposure. Additional samples were removed and replaced in Section B after 28.5 months (at the time that Section C was removed for assessment). All of the “removed early” samples were set aside for later analysis. The figure below provides a map of test Section B that shows the locations of the samples that were removed early.

Exposure Conditions:

Previous investigations have identified the following variables as contributing to the occurrence and severity of coal ash corrosion: flue gas temperature and composition, surface metal temperature, and coal ash and deposit composition. This investigation supports the case that coal ash conditions were present in the vicinity of the test sections within the Niles boiler.

Flue Gas Temperature: The flue gas temperature has a significant impact on the wastage rate for superheater tube materials in that it directly influences deposit chemistry. The flue gas temperature also affects the temperature gradient that is established across the deposit and scale that form on the tube. This gradient influences heat flux into the tube. The local temperature facilitates diffusion and provides the thermodynamic driving force for reactions that occur within the deposit and scale. The flue gas temperature in the region of interest in Niles Unit #1 was estimated to be 2114°F.

Surface Metal Temperature: For Section B, the average surface metal temperature, from the hot to the cooler end of the test section, was calculated to range from about 1195°F to 1047°F, see Table 1. It has previously been shown that the coal ash corrosion mechanism is active over this temperature range, and that, for austenitic alloys, the corrosion rate is generally expected to increase with increasing temperature. Recall that at about 1000°F, alkali-iron tri-sulfates in the coal ash become molten, and this molten constituent is very aggressive. The upper limit to this is about 1300°F where the stability of the complex sulfates decreases and the corrosion rate ebbs. The exact temperature range over which the sulfates are molten depends on the ash, gas and scale chemistries; however, at roughly 1200 - 1300°F, the wastage rate should be close to its maximum.

It should be understood that, for a given tube sample, the average surface metal temperature was not based on measurements taken at the tube sample. Rather, the average surface metal temperature for any given sample is a calculated value that is based on the outlet steam temperature for the section, the wall thickness for the sample, and the heat transfer characteristics of the material. It also needs to be understood that, depending on how the boiler is operated, the calculated surface metal temperature will vary as a function of time, see Figure 2. The decision was made that the calculated average would be based only upon time above a minimum value of 1000°F. That way the average temperature, and the total time at temperature, would reflect only those test conditions where coal ash corrosion might occur.

Coal Ash Composition: Coal and ash analyses were determined at the beginning of the program. The coal analysis in Table 2 shows that the Niles Unit #1 was burning a high sulfur coal (3.1%). The ash analysis in Table 2 also indicates the presence of sulfur (SO₃, 3.3%) along with alkali metals (K₂O, 1.6%) and (Na₂O, 0.5%). Thus, the constituents of the coal ash are conducive to the coal ash corrosion mechanism.

Deposit Composition: The composition of the inner and outer layers of the deposit was determined (via ICP optical emission spectroscopy for all three sections), see Table 3. Note that the Section A analysis was performed at a different lab than the one that performed the analyses for Section B and Section C. Nonetheless, the Section A analysis compared reasonably well with that of Section B, particularly with regard to the iron, sulfur, and potassium contents. On the other hand, the Section C analysis revealed higher sulfur and potassium, and a lower iron

content. It should be understood that the same coal was burned throughout this testing. The cause for this variability has not been determined; however, it may have been due to variability within the coal itself, or due to operating conditions.

X-ray diffraction analyses were performed for deposit/scale for all three sections. For Section C this analysis revealed the presence of an alkali iron trisulfate as a minor constituent, i.e. ferrinatriite ($\text{Na}_3\text{Fe}(\text{SO}_4)_3(\text{H}_2\text{O})_3$). This analysis also indicated potassium dihydrogen phosphate (KH_2PO_3) as a possible constituent of the ash. The analyses of the deposit/scale from the other two sections were less conclusive. For Section A, x-ray diffraction analysis of the inner layer identified the presence of potassium aluminum sulfate ($\text{KAl}(\text{SO}_4)_2$) as a medium constituent and hematite (Fe_2O_3) as a minor constituent. For Section B, gypsum ($\text{CaSO}_4 (\text{H}_2\text{O})_2$) and hematite (Fe_2O_3) were indicated (see Table 4, this report).

Lastly, it should be noted that carbon and chlorine contents were determined for all three test sections. The table below is a summary of the findings for the inner layer on a section by section basis.

Constituent	Section A (wt%)	Section C (wt%)	Section B (wt%)
Carbon	N/D	0.58	0.10
Chlorine	0.04	0.05	0.0086

N/D = Not Detected

The carbon content was determined due to concerns about the potential for carburization to degrade the corrosion resistance of the candidate materials. Neither this evidence nor the microstructural evidence support any role for carburization in this investigation. The chlorine content is sufficiently low that it is unlikely to have had a significant impact on the wastage during this program.

Wastage Rate Comparisons:

Based on the analyses above, (and taking into consideration the results of the dimensional and microstructural analyses that follow), it is judged that the service environment of all three test sections provided a suitable (and reasonably consistent) environment for ranking candidate superheater materials with respect to their resistance to coal ash corrosion. That the environment is aggressive is further confirmed by the fact that some of the candidate tube materials corroded at a very high rate, and that this resulted in the need to replace the majority of tube samples in Section B before the full exposure period was completed.

Candidate Alloy Rankings Based on Wastage Rate: Table 6 provides the wastage rate (mils of wall thickness lost per year) as a function of position within test Section B. Figure 12 presents this same information graphically. Table 7 provides the wastage rate with all of the samples of a given material grouped separately. Examination of these results allows one to determine the maximum wastage rate for each of the candidate materials. These maximum rates, shown in Table 8, are the limiting case for any of the candidate materials when exposed to the coal ash corrosion conditions for Section B.

Thus, these rates can be used to rank the performance of these materials relative to one another. From this it can be seen that Inconel 671 and IN 72 Weld Overlay exhibited the lowest maximum corrosion rates based on Section B exposure. These same materials also exhibited the

best corrosion resistance based on Section A and Section C exposure. It should also be noted that Save 25 exhibited the highest maximum corrosion rate for all three test sections. The other materials performed between these two extremes. However, eight of the twelve candidate materials exhibited a maximum corrosion rate in excess of 100 mils per year, and ten of the twelve exhibited a maximum corrosion rate in excess of 50 mils per year. Figure 13 provides a graphical comparison of these maximum wastage rates for all three test sections.

Wastage Rate as a Function of Temperature: Figure 14 shows a plot of wastage as a function of average service temperature for each of the twelve candidate materials in Section B. Interpretation of these data is complicated by the fact that, while some materials behaved as one would have expected, others did not. The data show that for some materials the wastage rate increased continuously with temperature, e.g. Save 25 and 800 Mod. Some materials exhibited an apparent decrease in wastage rate at intermediate temperatures, e.g. 347 HFG and HR 120. Other materials exhibited an apparent increase in wastage rate at an intermediate temperature, e.g. 310 HCbN and 310 Ta. Finally, the more resistant high-chromium, high-nickel alloys appeared to exhibit a decrease in rate as temperature increased, e.g. Inconel 671, IN 72 WO, and IN 52 WO. Review of the total program results revealed this sort of performance for all three sections. Figure 15 allows a comparison of the rates for Sections A and B. The data for Section C would plot similarly.

While it is not possible, at this point, to definitively state the cause(s) for the wastage rate versus temperature performance described above. It should be understood that the normal operating conditions within this region of the boiler are not as controllable as might attain during laboratory testing. Conditions may have been somewhat more corrosive toward the center of the test section (toward the center of the convection pass) than closer to the walls. Such variations can be caused by variations in gas velocity, ash loading, gas chemistry, gas and radiation temperature, and proximity to a central sootblower below the superheater bank in which the test sections were placed. Gas temperature probe traverses indicated that gas temperature was fairly uniform across the width of the boiler where samples were placed.

Wastage Rate as a Function of Time

One goal of this program was to characterize wastage as a function of time for each of the candidate materials. This information permits designers to balance tube life expectancy and initial cost. To facilitate this assessment, the three test sections were built to be identical in terms of the placement of the candidate alloy tube samples. Then, they were installed side-by-side within Niles Unit #1, on the assumption that, due to their close proximity to one another, all three sections would experience essentially the same exposure conditions. The tube samples in Test Section A were removed and examined after 15.5 months of exposure at full temperature. For Sections C and B, samples were removed early, after 18.6 and 21.6 months, due to concerns about excessive wastage. The full exposure period for Section C was 28.5 months (at temperature). For Section B, additional samples were removed early, after 28.5 months. The full exposure period for Section B was 37 months. This is illustrated in Table 9 which shows wastage rate data for all three sections.

The chart in Figure 16 was constructed by plotting the maximum wall thickness lost as a function of time for the materials from Section A and Section C. Then a straight-line was fit to the two data points for each material. As was indicated above, this is not to suggest that the corrosion rate was linear for these materials. Inspection of this chart, and given the fact that most of these materials started with an initial 400 mil wall thickness, the reason for the early removal of some of these materials becomes readily apparent.

Material Performance - Coated Specimen Considerations:

This program evaluated the performance of four different candidate coatings that were intended to provide wastage protection to an underlying substrate tube material. Two of the four coatings (IN 52 Weld Overlay and IN 72 Weld Overlay) involved high-nickel-chromium weld filler metals deposited using a gas metal arc welding process. One of the candidate coatings was a co-extruded high-nickel-chromium product (Inconclad 671). The final candidate coating involved electrospray discharge deposition of Fe_3Al onto the tube surface. An Incoloy 800HT tube provided the substrate for both of the weld overlay materials and for the co-extruded candidate material. Type 304H stainless steel provided the substrate for the Fe_3Al sample. Table 10 provides a basis of comparison of the composition and performance of these samples.

In general, it should be understood that the substrate tube material was selected for its ability to provide strength at temperature, creep strength, and resistance to steam side oxidation. This program focused primarily on the fire-side coal ash corrosion resistance of the candidate materials. Accordingly, while the condition of the internal surface of the tube was documented for each material type, the properties of the substrate were not addressed in detail. It should be pointed out however, that to some extent, the composition of the substrate affected the wastage resistance of the weld overlay coatings. This is due to the fact that the welding process melts and mixes filler metal along with some of the underlying substrate, thus changing the resultant coating composition in proportion to the amount of substrate consumed. It also should be pointed out that the wastage resistance of the substrate came into consideration for those coatings that did not survive for the full service exposure period. For instance, examination revealed that the Fe_3Al coated samples likely lost their coating very early in the program, and before the end of the 15.5 month exposure period for Section A. It also is likely that the protective coating on

some of the IN 52 Weld Overlay samples were breached before the end of the Section A exposure period.

The following sections provide a material by material overview of performance.

Overview: Fe₃Al-coated Type 304 H: All three test sections contained one Fe₃Al-coated specimen (Sample B-C). Sample B-C survived for the full exposure periods of Section A (15.5 months) and Section C (28.5 months); however, due to concerns about excessive wastage the Section B sample was removed at the same time as the Section C sample, i.e. after 28.5 months. So, to an extent the Section B and Section C samples would represent a duplicate test.

The figure below shows the appearance of a cross section through the middle of Sample B-C after exposure in Section B. This cross section has a wastage contour typically associated with coal ash corrosion.

Analysis of Section A showed that the original 2 mil thick Fe₃Al coating was breached and was separated from the tube early during the exposure period, and that corrosion was wasting away the underlying Type 304 H stainless steel substrate. The first figure below shows the original 2 mil Fe₃Al coating before service exposure. The second figure shows the condition of this interface after 15.5 months of exposure in Section A.

It should be emphasized that, during the Section A analysis, the Fe_3Al coating could not be found anywhere around the circumference of the sample, even in areas where there was no evidence of coal ash corrosion. This suggested that this material may have had adhesion problems, and likely did not survive the early heat-up/cool-down cycles. Examination of the Fe_3Al -coated samples in Sections B and C also revealed no evidence of the original Fe_3Al coating.

Based on this, it is deduced that shortly after these tubes went into service, the calculated wastage rate became heavily dependent on the wastage resistance of the Type 304 H substrate. Interestingly, while the data is limited for this material, (i.e. there was only one Fe_3Al -coated specimen in each test section), the results seem to show that the wastage rate was reasonably consistent as a function of time, (i.e. 145 mils/yr for Section A, 100 mils/yr for Section C, and 117 mils/yr for Section B). One might be tempted also to note that the Fe_3Al -coated specimen appears to have performed better than some other more highly alloyed materials, see Table 8. However, it should be stressed that the single Fe_3Al -coated specimen, Sample B-C, was located near the end of the test section where conditions may have been somewhat less corrosive than near the center of the test section, see the figure below. Thus, the comparison would be unfair relative to those candidate materials with samples in the higher wastage rate zone near mid-span of the test section.

Refer to Appendix E for additional details regarding the results of the analysis of this material.

Overview: IN 52 Weld Overlay (Incoloy 800HT substrate):

It should be understood that these samples went into service with a roughly 300 mil wall thickness. This roughly was comprised of a 80 mil thick IN 52 cladding on 220 mils of IN 800H. There were two IN 52 Weld Overlay samples in each test section. Sample GG-HH experienced a lower exposure temperature (for Section B, 1062 F); however, it was physically positioned at mid-span. Sample R-S experienced a higher exposure temperature however it was located closer to the front wall, see the figure below. Both samples survived for the full intended exposure period for all three test sections.

The analysis of Section A revealed that Sample GG-HH had a higher wastage rate (77 mils/yr) than that of Sample R-S (44 mils/yr). This also was true for the IN 52 weld overlay samples in Sections C and B. For Section B the wastage rates for Sample GG-HH and Sample R-S were 59 mils/yr and 31 mils/yr respectively. The chart below plots the wastage rates versus temperature for all three sections.

Recall that, for Section A, the Sample GG-HH exhibited a wastage rate of 77 mils/year. This resulted in a total wall reduction of 99 mils after 15.5 months of exposure. Thus, the 80 mil thick IN 52 cladding was totally breached prior to the end of the full exposure period for Section A, and the underlying Incoloy 800H was exposed to the environment and starting to corrode. It is assumed that, at about the same time, the IN 52 cladding was breached for Sample GG-HH in the other two test sections. Total wall losses for Sample GG-HH in Sections C and B were respectively 150 mils (after 28.5 months of exposure) and 181 mils (after 37 months of exposure).

If one assumes that, after 15.5 months, Sample GG-HH had experienced a total wall reduction of 99 mils for all three test sections, then, one can calculate the wastage rate for the underlying IN 800HT during this time period as 47 mils/year for Section C, and 46 mils/year for Section B. It is possible that the corrosion rate decreased as a function of time for a variety of reasons. However, it also is possible that the substrate had better wastage resistance than the protective cladding at this location (i.e. per this example, Sample GG-HH experienced a wastage rate of 77 mils/yr while the cladding was intact, and of roughly 46 mils/yr after the cladding was breached). In any case, the figure below shows the appearance of a cross section through Sample GG-HH after exposure in test Section B.

Lastly, while it has not been explored in detail, it was observed during the Section B analysis of these samples, Sample GG-HH exhibited what appeared to be welding-related intergranular cracking of the heat affected zone beneath the cladding in IN 800HT, see the figure below.

External Scale/Metal Interface for Section B, Sample GG-HH

It should be noted that this cracking was not observed in Sample GG-HH from Sections A or C, nor was it observed in Sample R-S from any of the three test sections. Lastly, this heat affected zone cracking was not observed in the tube-to-tube butt welds that joined the samples to one another to comprise the test section. The cause for this cracking has yet to be determined. It is recorded here only as an observation.

Refer to Appendix J for additional details regarding the results of this analysis.

Overview: IN 72 Weld Overlay (Incoloy 800HT substrate):

There were two IN 72 Weld Overlay samples in each test section. Sample FF-GG experienced a lower exposure temperature (for Section B, 1067 F) and sample Q-R experienced a higher exposure temperature (for Section B, 1195°F). The location of these samples is depicted in the figure below. Both samples survived for the full intended service life for all three test sections.

Review of the wastage rate data in Table 9 will show that IN 72 Weld Overlay performed similarly to the IN 52 Weld Overlay, in that, the lower temperature Sample FF-GG suffered wastage at a higher rate than did the higher temperature Sample Q-R. For Section B, the wastage rate for Sample FF-GG was 12 mils/year, and the rate for Sample Q-R was 1 mil/year.

For all three sections, the wastage rate as a function of temperature is shown in the chart that follows.

The IN 72 Weld Overlay also had an initial cladding thickness of approximately 80 mils. So, based on the rates shown above, (and discounting a cladding cracking phenomenon that will be described later), it can be seen that, at the end of the program, the IN 72 Weld Overlay cladding had not been breached and was providing continued protection the underlying Incoloy 800H substrate. Caution is urged in interpreting and extrapolating the wastage rate data. Had Sample Q-R, for example, been located near mid-span in the test section, it may have experienced a somewhat higher wastage rate. The figure below shows the appearance of a cross section through the middle of Sample FF-GG. As can be seen minimal wastage is in evidence.

For Section B, metallurgical analysis of the highest wastage rate region of Sample FF-GG revealed a continuous, but thin, chromium oxide scale at the scale/metal interface which may account for the wastage resistance demonstrated by this material. Review of the analyses documented in Appendix L will show that this sample demonstrated little or no chromium depletion associated with this interface. It seems likely that the initial high chromium content for the IN 72 Weld Overlay (nominally 44%) strongly influences its wastage resistance, as does its high nickel content (nominally 55%) and low iron content.

External Scale/Metal Interface for Section B, Sample FF-GG

For Section C, metallurgical analysis of the same Sample FF-GG revealed similar evidence; however, it was noted that the external corrosion in this case intersected with radial crack penetrations found within the cladding, see the figure below.

Further evaluations of the claddings on the Section C samples revealed evidence that these cracks originated within the cladding itself and were likely due to the cladding deposition process. The figure below shows the location and orientation of the cracks found in the Section C Sample FF-GG. Discussions with the cladding vendor revealed that a two-step welding process was employed to deposit the weld overlay cladding. In the first step, the full thickness of the IN 72 cladding was deposited using the gas metal arc process. In the second step, the vendor used a gas tungsten arc welding process to perform a “wash pass”. No filler metal was added during the “wash pass”. Instead its purpose was to re-melt the outer surface of the cladding to provide for a more regular surface contour. The molten fusion zone of the “wash pass” extended into the cladding roughly to mid-thickness. It was along this interface that the cracking was observed to have initiated (likely on-cooling). In follow-on work with the cladding vendor, it was demonstrated that no cracks were found in samples when the “wash pass” step was eliminated. However, the vendor indicated that the “wash pass” was originally employed to permit the clad tube to pass a bend test.

External Scale/Metal interface for Section C, Sample FF-GG

Similar cracking was found in the Section B Sample FF-GG, see the figure below. One crack in this figure intersected the external surface. This crack contained a corrosion scale similar to that found in the crack shown in the figure above. The other crack was found to be entirely within the cladding, and at roughly its original mid-thickness. This internal crack contained no evidence of corrosion scale. The location of this crack and the lack of scale provide additional evidence that the cracking was generated during the cladding deposition process.

Cracks in Cladding for Section B, Sample FF-GG

Internal Crack in Cladding for Section B, Sample FF-GG

Additional investigations revealed that similar cracking was found in all IN 72 samples three test sections, and in archived material which had not seen service. However, it should be noted that the cracks found in the archived material were much smaller and very few in number, see the figure below.

Internal Crack in Cladding for Archive Material

These observations led to concerns that these welding-generated cracks might grow as a function of time in service. This issue remains open; however, it is important to note that, up to this point, no samples have been found where the crack extends completely through-thickness of the cladding.

Refer to Appendix L for additional details regarding the results of this analysis.

Overview: Incoclad 671 (Incoloy 800HT substrate):

The test sections contained Incoclad 671 tube samples at three sample positions, and all three Incoclad 671 samples survived for the full intended service period for all three test sections. As can be seen in the figure below, Sample EE-FF sat at mid-span at the lowest temperature position (for Section B, 1074 F). Sample U-V and Sample P-Q were at higher temperature locations (for Section B, 1109 F and 1191 F respectively).

Review of Table 9 will show that all of the Incoclad 671 samples exhibited excellent corrosion resistance. The chart below shows the wastage rate as a function of temperature for all three test sections.

While the occurrence of the maximum Incoclad corrosion rate at the minimum temperature may be attributed to its midspan location, some laboratory tests have shown a similar trend to this temperature range. The exceptional relative resistance of the Incoclad 671 is clearly illustrated by the much lower corrosion rate of the Incoclad as compared to the immediately adjacent HR120.

In any case, the initial cladding thickness for the Incoclad 671 was approximately 75 mils on a total wall thickness of approximately 260 mils. Based on the highest measured rate of 13 mils/year (for Sample EE-FF in Section A), after 37 months of exposure the cladding has not been breached, and would be expected to provide corrosion protection during continued service.

The figure below shows the appearance of a cross section through the middle of each of the Incoclad samples. As can be seen little, if any, wastage is in evidence for any of the three samples, including for Sample EE-FF which evidenced the highest wastage rate.

For Section B, metallurgical analysis of the highest wastage rate region of Sample EE-FF revealed a continuous, but thin, chromium oxide scale at the scale/metal interface which may account for the wastage resistance demonstrated by this material. The scale/metal interface for this sample is shown below. Similar microstructural evidence was found for Sample EE-FF in Section C. For Section A, Sample P-Q was evaluated (instead of Sample EE-FF). The Sample P-Q analysis revealed much less evidence of corrosion.

It seems likely that the initial high chromium content for the Inconel 671 (nominally 48%) strongly influences the wastage resistance of this material, as does its high nickel content (nominally 52%) and low iron content. The analysis reported in Appendix K, Figure K-16 revealed that the dark constituent in the reaction zone above is comprised of approximately 65% nickel, and 32% chromium, while the light colored constituent in the reaction zone is comprised of 59% chromium and 33% nickel. Evidence suggests that, as would be anticipated, the nickel-rich constituent is more susceptible to attack.

Refer to Appendix K for additional details regarding the results of this analysis.

Material Performance - Monolithic Specimen Considerations:

Recall that the candidate tube materials were selected based on their potential to perform well in a coal ash corrosion environment. This decision, primarily, was based on the conventional wisdom which correlates good coal ash corrosion resistance with the ability of an alloy to form and maintain a continuous (and sound) high-chromium oxide scale. Accordingly, the alloys (and coatings) that were chosen for evaluation all contained an equivalent or higher weight percent of chromium than is found in the conventional stainless steels that are commonly used in superheater tubing alloys.

Some of the candidate tube materials also contained additional alloying elements that were intended to provide an added measure of coal ash corrosion protection. Various mechanisms were proposed to account for their influence. These alloying elements might be postulated to influence, for instance: diffusion of chromium from the alloy to the scale/metal interface, slow the ingress of aggressive species across the scale/metal interface, and/or provide for a more coherent scale that remains in place during the normal thermal cycling anticipated for superheater tube service.

It should be understood that for the coating materials (whose performance was described in the previous section) alloy formulation was somewhat simplified in that the coating designer could focus solely on coal ash corrosion resistance and could rely on the underlying substrate to provide the other properties required to ensure for long service life. However, for the monolithic

tube materials, in addition to coal ash corrosion resistance, alloy selection also had to take into account the need for the tube to provide, as a minimum, strength at temperature, creep resistance, and internal steam-side oxidation resistance. Thus, it should be understood that the formulation of a monolithic tube alloy composition can be a complex proposition, and the testing described herein provides an important insight into comparative alloy performance when faced with the complex challenges presented by superheater service under coal ash corrosion conditions.

Table 10 provides a means for comparison of the twelve candidate alloys/coatings. The major alloying elements are listed and the alloy's performance is judged based on the maximum wastage rate determined for this alloy in Section B. This table will be discussed in more detail later in this report; however, review of the nominal compositions provided therein will provide some insight as to why these particular alloys were selected as candidates for evaluation. The monolithic tube alloys will be discussed below beginning with Thermie, the monolithic alloy that demonstrated the best wastage resistance, and ending with Save 25, the alloy that demonstrated the least wastage resistance.

Overview – Thermie Tubing:

Each of the test sections contained two Thermie tube samples at the positions indicated in the figure below. Sample H-I was located near the center of the mid-span section at the higher temperature position (for Section B, 1159 F). Sample HH-II was located at the edge of the mid-span section at the lower temperature position (for Section B, 1056 F). It should be pointed out that, while both Thermie samples evidenced good wastage resistance, only the Sample HH-II experienced the full 37 month exposure period for Section B. Sample H-I was removed from Sections B and C after 18.6 months of exposure due to practical considerations. Sample H-I was not removed from service due to wastage concerns.

The chart below plots wastage rate as a function of temperature for all three test sections. Review reveals that the rate was consistent from position to position and as a function of time.

The figure below shows the appearance of a cross section through the middle of both Thermie samples. As can be seen, Sample H-I, which had the greatest wastage rate, evidenced only minimal wastage compared to other monolithic alloys.

For Section B, metallurgical analysis of the highest wastage rate region of Sample H-I revealed the presence of a discontinuous scale. The figure below shows the appearance of the scale/metal interface in this region. A significant percentage of the Thermie tube surface lacked both deposit and scale. It cannot conclusively be determined for Sample H-I when or how often seals spalled from the sample, but presumably spalling occurred as the sample cooled to ambient temperatures. Such spalling of fireside and steam side scale is corrosive from austenitic stainless steel superheater tubing.

Discontinuous External Scale/Metal interface for Section B, Sample H-I

Alternative mechanisms were considered to account for the lack of scale and deposit on this sample. These include: spalling during service due to formation of a frangible scale, spalling due to thermal fluctuations, and spalling due to handling and transport after the test section had been removed for evaluation. It should be understood that great care was taken to preserve the condition of these samples prior to analysis, so, it seems likely that either, or both, of the other two mechanisms were active. In any case, Thermie appeared to perform well indicating the presence of a protective oxide scale through the periods of high temperature exposure.

Energy dispersive spectroscopy (EDS) was used to map the composition on either side of the scale/metal interface. These EDS dot maps showed that in addition to being chromium and oxygen-rich, the scale also contained a significant amount of sulfur, see the figure that follows.

Thermie 250x Maps

EDS Dot Map Showing the Sulfur Distribution Along the Scale/Metal Interface for Thermie Sample H-I

EDS semi-quantitative point analysis revealed a sulfur content of approximately 7.5% in the scale immediately adjacent to the interface, see the table in Appendix I, Figure I-14. Similar analyses showed no evidence of chromium depletion in the underlying tube metal.

Refer to Appendix I for additional details regarding the results of this analysis.

Overview – HR 120 Tubing:

There were three HR 120 tube samples in each of the three test sections. The figure below depicts the position of these samples within the section. The lowest temperature sample, Sample DD-EE (for Section B, 1077 F), was located in a mid-span position. The two higher temperature samples, Sample V-W (for Section B, 1099 F) and Sample O-P, for Section B, 1183 F), were located farther from the center of the sections. Sample V-W and Sample O-P both survived for the full intended exposure period for all three test sections. Sample DD-EE survived for the full intended exposure period for Sections A and C, however, Sample DD-EE in Section B was weld overlaid at some point in its service life; therefore no data was available for this sample.

The repair of Sample DD-EE was likely necessitated due to concerns about excessive wall thinning in the vicinity of weld EE where the HR 120 tube sample was joined to an Inconel 671 tube sample. To accomplish this joint during manufacture of the test section, it was necessary to reduce (in the vicinity of the weld) the initial 400 mil HR 120 wall thickness to match that of the adjacent Inconel 671, nominally 260 mils. For Section C, the calculated wastage rate for Sample DD-EE was only 79 mils/year. At this wastage rate, had the sample not been machined at its ends to form the necessary weld prep, the remaining wall thickness would have been adequate for this sample to survive for the full 37 month exposure period of Section B.

The chart below plots wastage rate as a function of temperature for all three test sections. Review reveals that the rate was consistent from position to position and as a function of time. For two of the three test sections, the sample with the highest calculated surface metal temperature, Sample O-P, exhibited the greatest wastage rate.

Note that for Section A, the low temperature sample, Sample DD-EE, which was situated near mid-span, exhibited a slightly higher wastage rate than either of the higher temperature samples located farther from the center of the boiler.

The figure below shows the appearance of a cross section through the middle each of the three HR 120 samples. Note that Sample O-P which had the greatest wastage rate for Section B showed evidence of a longitudinal weld bead (which suggests that this tube was manufactured using a roll-and-weld technique). The wastage contour in evidence on Sample O-P is consistent with a coal ash corrosion mechanism.

For Section B, metallurgical analysis of the highest wastage rate region of Sample O-P revealed the presence of a thin, but continuous, scale. EDS analysis showed that this high chromium (33.9%) scale also contained a significant level of both iron (31.0%), and nickel (11.8%). Analysis also identified a significant amount of sulfur in this scale, (3.32%). This evidence, taken together, may help account for the fact that this sample exhibited a relatively high wastage rate (100 mils/yr).

Continuous but Thin External Scale for Section B, Sample O-P

Refer to Appendix H for additional details regarding the results of this analysis.

Overview – 310 Ta Tubing:

There were three 310 Ta tube samples in each of the three test sections, see the figure below for their locations. Two of the samples were located near mid-span: Sample F-G (at 1153 F for Section B) and Sample M-N (at 1176 F for Section B). The other sample was located a little farther from the center of the test section: Sample X-Y (at 1092 F for Section B). Sample F-G exhibited a sufficiently high wastage rate that it had to be removed from Sections C and B after 21.5 months of exposure. Sample M-N survived for the full 28.5 month exposure period for Section C at which time it also was removed from Section B due to concerns about excessive corrosion. Only the lowest temperature sample, Sample X-Y survived for the full 37 month exposure period for Section B.

The chart below plots wastage rate as a function of temperature for 310 Ta in all three test sections. Review reveals that the rate was reasonably consistent as a function of time (with some explainable exceptions). For two of the three test sections, the highest temperature sample, Sample M-N, experienced the greatest wastage rate; however, for Section A, Sample F-G experienced a slightly higher rate. This variability may have been due to the normal data scatter

consistent with in situ testing. Such variability might also account for the variability shown in Sample X-Y where the Section A sample evidenced a much higher wastage rate.

The figure below shows the appearance of a cross section through the middle of the three 310 Ta samples. Note that while Sample M-N has a somewhat thinner wall than Sample F-G, this is understandable, in that, while Sample F-G had a higher wastage rate, it was in service for a shorter length of exposure (approximately 7 months less time at temperature). The contours of these tube cross sections are consistent with a coal ash corrosion mechanism.

Sample M-N	Sample F-G	Sample X-Y
1176 F	1153 F	1092 F
Service Life: 28.5 months	Service Life: 21.5 months	Service Life: 37 months

For Section B, metallurgical analysis of the highest wastage rate region of Sample M-N revealed the presence of a discontinuous external scale, see the figure below.

Discontinuous External Scale for Section B, Sample M-N

The figure below provides a higher magnification view of the scale shown above. The numbered locations show the positions of EDS analyses to characterize the scale and metal in the vicinity of the interface. The results of this analysis are included in Appendix F, Figure F-20 of this report. As will be clarified in the discussion below, the EDS reveal that the scale immediately adjacent to the interface has significantly more sulfur than in the bulk scale.

External Scale for Section B, Sample N-O

Per the EDS analyses reported in Appendix F, Figure F-20, the scale at location 2 above has a sulfur content of 2.41%, while at location 3 the sulfur content is 13.35%. It has been postulated, but not confirmed, that the high-sulfur region along the interface is frangible and facilitates separation of the scale from the surface. It should be noted that EDS analyses show that both locations 4 and 5 above have a composition similar to the tube at mid-wall, thus, no evidence of chromium depletion was found for this sample.

Refer to Appendix F for additional details regarding the results of this analysis.

Overview – 310 HCbN (HR3C) Tubing:

There were four 310 HCbN tube samples in each of the three test sections, see the figure below for their locations.

It should be noted that Sample G-H exhibited a sufficiently high wastage rate that it was required to be removed from test Sections B and C after 18.6 months of exposure.

Sample AA-BB and Sample N-O both survived for the full exposure period for Section C (28.5 months); however, concerns about excessive wall thinning caused them to be removed from Section B at that time. Only Sample W-X survived for the full intended exposure period for Section B.

The chart below plots wastage rate as a function of temperature for all three test sections. Review reveals that the rate was reasonably consistent from position to position and as a function of time. For all three test sections, Sample G-H had the highest wastage rate in spite of the fact that Sample N-O had a higher calculated surface metal temperature.

The figure below shows the appearance of cross sections through the middle of all four of the 310 HCbN samples. Note that while Sample N-O has a somewhat thinner wall than Sample G-H, Sample G-H experienced a higher wastage rate in that this sample experienced approximately 10 months less time at temperature. The contours of both cross sections are consistent with a coal ash corrosion mechanism.

Sample N-O	Sample G-H	Sample W-X	Sample AA-BB
1179 F	1155 F	1094 F	1080 F
Service Life: 28.5	Service Life: 18.6 months	Service Life: 37 months	Service Life: 28.5 months

For Section B, metallurgical analysis of the highest wastage rate region of Sample N-O revealed the presence of a discontinuous external scale, see the figure below.

Discontinuous External Scale for Section B, Sample N-O

The figure below provides a higher magnification view of the scale shown above. The numbered locations show the positions of EDS analyses to characterize the scale and metal in the vicinity of the interface. The results of this analysis reveal that the scale immediately adjacent to the interface has significantly more sulfur than in the bulk scale.

External Scale for Section B, Sample N-O

The scale at location 1 above has a sulfur content of 4.97%, while at location 2 the sulfur content is 7.41%. It has been postulated, but not confirmed, that the high-sulfur region along the interface is frangible and facilitates separation of the scale from the surface. It should be noted that EDS analyses show that both locations 3 and 4 above have a composition similar to the tube at mid-wall, thus, no evidence of chromium depletion was found for this sample.

Refer to Appendix G for additional details regarding the results of this analysis.

Overview – NF 709 Tubing:

There were three NF 709 tube samples in each of the three test sections, see the figure below for their locations. The highest temperature sample, Sample J-K, exhibited a sufficiently high wastage rate that it had to be removed from Sections C and B after 18.6 months of exposure. Sample C-D and Sample BB-CC survived for the full 28.5 month exposure period for Section C at which time they also were removed from Section B due to concerns about excessive corrosion. None of the NF 709 samples survived for the full 37 month exposure period for Section B.

The chart below plots wastage rate as a function of temperature for NF 709 in all three test sections. Review reveals that the rate was reasonably consistent as a function of time and temperature. For all three test sections, the highest temperature sample, Sample J-K, experienced the greatest wastage rate. In any case, all but one of the NF 709 samples demonstrated a high wastage rate in excess of 100 mils per year.

The figure below shows the appearance of a cross section through the middle of each of the three NF 709 samples. The contours of these tube cross sections are consistent with a coal ash corrosion mechanism.

For Section B, metallurgical analysis of the highest wastage rate region of Sample BB-CC revealed the presence of a discontinuous external scale, see the figure below.

Discontinuous External Scale for Section B, Sample BB-CC

The figure below provides a higher magnification view of the scale shown above. The numbered locations show the positions of EDS analyses to characterize the scale and metal in the vicinity of the interface. The results of this analysis are included in Appendix D, Figure D-18 of this report. As will be clarified in the discussion below, the EDS reveal that the scale immediately adjacent to the interface has significantly more sulfur than in the bulk scale.

External Scale for Section B, Sample BB-CC

Per the EDS analyses reported in Appendix D, Figure D-18, the scale at location 2 above has a sulfur content of 0.73%, while at location 3 the sulfur content is 4.29%. Similar to the other high

wastage rate samples, it has been postulated, but not confirmed, that the high-sulfur region along the interface is frangible and facilitates separation of the scale from the surface. It should be noted that EDS analyses show that the high chromium scale also contains a significant percentage of iron, and more iron was found at location 2 in the scale, than was found at location 3, (i.e. 36.1% versus 20.3%). These results suggest that iron is diffusing outward across the scale as sulfur is diffusing inward. It should be noted that EDS analyses of locations 4, 5 and 6 revealed little, if any, alloying element depletion in the metal adjacent to the interface (including chromium).

Refer to Appendix D for additional details regarding the results of this analysis.

Overview – 347 HFG Tubing:

There were three 347 HFG tube samples in each of the three test sections, see the figure below for their locations. Two of the samples were located near mid-span: Sample CC-DD (at 1075 for Section B) and Sample I-J (at 1162 F for Section B). The other sample (Sample A-B at 1136 F for Section B) was located closer to the convection pass wall where conditions may have been somewhat less aggressive. 347 HFG performed similarly to NF 709 in that the wastage rates were sufficiently high that none of the three samples survived for the full 37 month exposure period for Section B. The highest temperature sample, Sample I-J, exhibited a sufficiently high wastage rate that it had to be removed from Sections C and B after 18.6 months of exposure. Sample A-B and Sample CC-DD survived for the full 28.5 month exposure period for Section C at which time they also were removed from Section B due to concerns about excessive corrosion.

The chart below plots wastage rate as a function of temperature for 347 HFG in all three test sections. Review reveals that the rate was reasonably consistent as a function of time and temperature. For two of the three test sections, the highest temperature sample, Sample I-J, experienced the greatest wastage rate. The exception was for Section A where the low temperature sample, Sample CC-DD (at 1075°F for Section A) experienced a slightly higher wastage rate than the highest temperature sample, Sample I-J, (1164 F for Section A), i.e. 176 mils/year vs 174 mils/year. The intermediate temperature sample, Sample A-B that was located toward the end of the section had a lower corrosion rate than that for Sample CC-DD (i.e. 67 mils/year versus 176 mils/year), even though it was at a much higher temperature (1136°F vs 1075°F).

The figure below shows the appearance of a cross section through the middle of each of the three 347 HFG samples. The contours of these tube cross sections are consistent with a coal ash corrosion mechanism.

Sample I-J	Sample A-B	Sample CC-DD
1162 F	1136 F	1075 F
Service Life: 18.6 months	Service Life: 28.5 months	Service Life: 28.5 months

For Section B, metallurgical analysis of the highest wastage rate region of Sample CC-DD revealed the presence of a discontinuous external scale, see the figure below.

Discontinuous External Scale for Section B, Sample CC-DD

The figure below provides a higher magnification view of the scale shown above. The numbered locations show the positions of EDS analyses to characterize the scale and metal in the vicinity of the interface. The results of this analysis are included in Appendix C, Figure C-19 of this report. As will be clarified in the discussion below, the EDS reveal that the sulfur content of the scale increased from the outside surface inward, i.e. for locations 2, 3, and 4.

External Scale for Section B, Sample CC-DD

Per the EDS analyses reported in Appendix C, Figure C-19, the scale at location 2 above has a sulfur content of 2.11%. At location 3 the sulfur content increases somewhat to 3.79%, and at

location 5 it was measured to be 5.31%. Similar to the other high wastage rate samples, it has been postulated, but not confirmed, that the high-sulfur region along the interface is frangible and facilitates separation of the scale from the surface. It should be noted that EDS analyses show that the high chromium scale (roughly 48%) also contains a significant percentage of iron (roughly 26%). EDS analysis at locations 5 and 6 suggest the possibility of minimal chromium depletion adjacent to the interface. The chromium content at locations 5 and 6 measured 15.2% and 18.1% (versus 18.5% at mid-wall).

Refer to Appendix C for additional details regarding the results of this analysis.

Overview – Modified 800H Tubing:

There were three Modified 800H tube samples in each of the three test sections, see the figure below for their locations. All three of the samples were located near mid-span: Sample Y-Z (at 1088 for Section B) and Sample E-F (at 1149 F for Section B), and Sample L-M (at 1172 F for Section B). The highest temperature sample, Sample L-M, survived for 18.6 months in Sections B and C. The next highest temperature sample, Sample E-F, survived for 21.5 months in Sections B and C. The lowest temperature sample, Sample Y-Z survived for the full 28.5 month exposure period for Section C, but needed to be removed from Section B at the end of that period. So, none of the Modified 800H samples survived for the full 37 month exposure period of Section B.

The chart below plots wastage rate as a function of temperature for Modified 800H in all three test sections. Review reveals that the rate was reasonably consistent as a function of time and temperature, and that in general, the rate increased as a function of temperature. However, for two of the three test sections, the highest temperature sample, Sample J-K, experienced the greatest wastage rate. The exception was for Section A where the intermediate temperature sample, Sample E-F (at 1150°F for Section A) experienced a slightly higher wastage rate than the highest temperature sample, Sample L-M, (1174 F for Section A), i.e. 178 mils/year vs 169 mils/year. The reason for this has not been resolved; however, it is likely that these results fall within the normal scatter band for such data.

The figure below shows the appearance of a cross section through the middle of each of the three Modified 800H samples. The contours of these tube cross sections are consistent with a coal ash corrosion mechanism.

For Section B, metallurgical analysis of the highest wastage rate region of Sample Y-Z revealed the presence of a discontinuous external scale, see the figure below.

Discontinuous External Scale for Section B, Sample Y-Z

The figure below provides a higher magnification view of the scale and deposit found in another high wastage rate region on Sample Y-Z. The numbered locations show the positions of EDS analyses to characterize the scale and metal in the vicinity of the interface. The results of this analysis are included in Appendix B, Figure B-19 of this report. As will be clarified in the discussion below, EDS reveal that the scale immediately adjacent to the interface has significantly more sulfur than in the bulk scale.

External Scale for Section B, Sample CC-DD

Per the EDS analyses reported in Appendix B, Figure B-19, the scale at location 3 above has a sulfur content of 0.68%. At location 4 the sulfur content was measured to be 5.63%. Similar to the other high wastage rate samples, it has been postulated, but not confirmed, that the high-sulfur region along the interface is frangible and facilitates separation of the scale from the surface. It should be noted that EDS analyses show that the high chromium scale (roughly 49%) also contains a significant percentage of iron (roughly 25%). EDS analysis at locations 5 and 6 suggest the possibility of minimal chromium depletion adjacent to the interface. The chromium content at locations 5 and 6 measured 14.9% and 19.1% (versus 20.1% at mid-wall). Lastly, note that the 2.79% potassium was found in the outer deposit, i.e. at location 1 above. It was found to be lower in the deposit immediately adjacent to the scale, i.e. at location 2 the potassium content was measured at 0.31%.

Refer to Appendix B for additional details regarding the results of this analysis.

Overview – Save 25 Tubing:

There were four Save 25 tube samples in each of the three test sections, see the figure below for their locations.

The chart below plots wastage rate as a function of temperature for all three test sections. Review reveals that the rate was reasonably consistent from position to position and as a function of time. For all three test sections, the wastage rate increased as a function of temperature.

Sample K-L	Sample D-E	Sample Z-AA	Sample II-JJ
1168 F	1145 F	1084 F	1080 F
Service Life: 18.6	Service Life: 21.5 months	Service Life: 21.5 months	Service Life: 37 months

Metallurgical analysis, for Section B, focused on an evaluation of Sample K-L. The analysis focused on two areas of interest. The area marked as “2:30 o’clock” in the image above was orientation with the highest wastage rate. As such, it was one area of focus; however, analysis showed that this area lacked deposit and a consistent scale. So, the area marked as “10 o’clock” was evaluated because it had both.

The figure below shows the condition of the external scale/metal interface at the “2:30 o’clock” orientation for Sample K-L. Note that, in this image, the presumably protective scale can be seen to be separating from the underlying substrate.

External Scale at 2:30 O’Clock for Section B, Sample K-L

The cause, and timing, for this separation has not been established; however, a closer examination of the region highlighted in the box above is provided in the higher magnification image in the figure below. The numbered locations show the positions of

External Scale at 2:30 O'Clock for Section B, Sample K-L

EDS analyses to characterize this interface, reported in Appendix A, Figure A-26. EDS analysis indicates the presence of a two-layer scale. The outer analysis at location 1 shows that the scale is high in iron (55.2%), chromium (22.4%), and nickel (4.02%). The inner analysis at location 2 shows the scale in this region along the interface has a somewhat lower iron content (38.6%), but both the chromium content (27.4%) and the nickel content (20.5%), are increased. Also, copper was found in the scale along the interface while it was not found in the bulk scale (i.e. at location 1). These results seem to indicate that iron is diffusing from the metal across the interface and scale. In any case, of all of the candidate materials, Save 25 is the only material whose scale showed a higher iron than chromium content. This of course raises the question as to whether the scale was truly protective.

Also of interest in the analysis of locations 1 and 2 above is the fact that the sulfur content was somewhat higher at location 2 (3.01%) than it was at location 1 (2.00%). This is consistent with the evidence found for other materials which suffered a high wastage rate, in that, the scale/metal interface was found to be enriched in sulfur, and in this case, it clearly can be seen that the scale is separating from the surface along this boundary.

The figure below shows the appearance of a cross section through the external surface at the 10:00 orientation for Sample K-L. As can be seen, the sample at this location had retained a significant amount of both deposit and scale.

Tube Cross Section Showing Deposit and Scale at 10:00 O'Clock for Section B, Sample K-L

The figure below is a somewhat higher magnification view of the deposit/scale/metal interface depicted above. Note that the outer layers of the deposit have a coarse granular appearance typical of furnace deposits (locations 3 and 4 are typical). However, the deposit and scale that are positioned closer to the metal surface have a stratified appearance. EDS analysis and dot maps later will show that the light appearing layers are iron-rich, and that the darker layers have a composition more typical of furnace deposits.

Stratified Layers of
Deposit and Scale

Tube Cross Section Showing Deposit and Scale at 10:00 O'Clock for Section B, Sample K-L

Tube Cross Section Showing Deposit and Scale at 10:00 O'Clock for Section B, Sample K-L

The figure above shows a higher magnification view of the external deposit/scale/metal interface at the 10:00 o'clock orientation for Sample K-L. EDS analyses at the numbered locations are documented in Appendix A, Figure A-20. The scale at location 8 is shown to be chromium-rich (52.2%), with significant amounts of iron (18.3%) and nickel (8.84%). The scale at location 7 has significantly more iron (55.2%) and nickel (22.9%), and much less chromium (8.68%). Copper was not in evidence in the scale. Once again, the sulfur content of the inner scale was found to be enriched relative to the outer scale (3.74% versus 0.53%). No significant chromium depletion was noted in the metal along the interface, in fact, comparison of the analyses at locations 9 and 11 seems to indicate slight chromium enrichment (28.6% versus 22.6%), and slight iron depletion (48.2% versus 53.2%) at the interface. It could be argued that this evidence is consistent with iron diffusion outward across the scale and sulfur diffusion inward toward the scale/metal interface. This evidence also is consistent with the layers of iron-rich scale noted stratified within the deposit.

The figures below are a series of EDS dot maps that show the distribution of selected elements of interest.

Save 25 cross section 1000x maps

Iron Distribution at Scale Metal Interface

Chromium Distribution at Scale Metal Interface

Note from the above that the scale at this location is primarily chromium-rich, but that an iron-rich layer is immediately above the adherent oxide.

In summary for Save 25, deposit and scale at the two positions investigated for Sample K-L revealed the following. For the highest wastage rate location (10:30 o'clock), only minimal deposit was in evidence and a thin iron-rich scale was found to be separating from the tube surface. For the lower rate location (2:00 o'clock), a significant amount of deposit and scale were present. It appeared that iron was diffusing across the scale ultimately separating from the surface and forming strata of iron-rich layers above the interface. In both cases, Save 25 was different from the other high wastage rate materials relative to the role that iron played in scale formation. No evidence was found to indicate the role that might have been played by copper in the performance of this alloy; however, its relatively high copper content is another obvious distinguishing factor.

Refer to Appendix A for additional details regarding the results of this analysis.

Material Performance – Summarizing Statements:

The following summary statements are offered with regard to the results reported above. In considering the implications of this work it's important to keep in mind that the major objective of this work was to:

- Rank the relative performance of candidate materials within a boiler convection pass operating in a highly aggressive coal ash corrosion environment.

It can be stated without qualification, that this objective was successfully accomplished.

Secondary, but important, objectives were to:

- Determine wastage rate data that could be used to guide future boiler design decisions.

- Gain a better understanding as to why the selected candidate materials perform well, or poorly, in such an environment.

Progress was made toward these secondary objectives; however, more work would be required if definitive answers are needed. The reasons for this are offered below.

It should be understood that in situ testing, such as that reported herein, has inherent strengths and weakness. The most obvious strength is the relevance of the results to an understanding of material performance under the “real world” conditions that exist within a boiler. An alternative approach toward more realistic testing would be to evaluate the performance of an entire test section constructed using each candidate material, then to evaluate its condition after service in an operating boiler. Obviously, if one were to try to rank materials using such an approach, it would be cost-prohibitive, time-consuming, and the results would remain subject to questioning (regarding the consistency of boiler operations) when attempting to compare the performance of one material with that of another. The work reported herein is considered a cost-effective means to achieving the major objective of this effort, in that, the performance of a multiplicity of candidate materials can be evaluated, as a function of time, under typical boiler operating conditions.

Nonetheless, the approach adopted in this program also has an obvious weakness. The weakness is based on the fact that the “real world” conditions within an operating boiler are not as controllable as one might desire and be able to achieve in laboratory testing. This potential for variability makes it impractical to define and control all of the factors that affect material corrosion and degradation. The wastage rates calculated in this test program are certain to have been influenced by several factors that affects rates of the coal ash corrosion.

It should be pointed out at this point that many of the wastage rate results obtained, and reported, in this program were, to some extent, unexpected. When early results were reported, a few knowledgeable individuals took issue with some of the relative wastage resistance rankings obtained in this work. For instance, conventional wisdom, based earlier laboratory work, suggested that Save 25 would perform much better than was shown in this program*. Also, earlier laboratory work suggested that the high-chromium-nickel coatings would have performed somewhat more poorly.

* It should be noted that more recent, reported by Natesan, (Ref. 3) would seem to verify the poor performance of Save 25 in a high sulfur coal ash environment).

Considering all this the following summarizing statements are offered.

1. Candidate materials in this program were exposed to the coal ash constituents known to cause severe coal ash corrosion. Over the duration of this program, Niles Unit #1 burned coal from only one source, and the coal ash derived from that coal contained the elemental constituents necessary for coal ash corrosion, (including a high sulfur content), see Tables 2, 3, 4, and 5. The “chalky white” deposit observed on tube surfaces is considered further objective evidence that the coal ash constituents combined to yield the alkali iron tri-sulfate known to be the causative agent, (see Figure 5 as an example). Furthermore, EDS analyses (reported in the various appendices) demonstrated the presence of the necessary elemental constituents within the deposit (e.g. potassium, sulfur, and iron oxide).
2. Candidate materials were exposed to a temperature range over which the coal ash corrosion mechanism is known to be active. As a rule of thumb, for austenitic materials, the coal ash corrosion mechanism is known to have an influence over the temperature range of roughly 1000°F to 1300°F. For this program, the test sample surface metal temperature was calculated based on steam temperature measurements as it exited the test section. For this program, the calculated test specimen surface metal temperatures were controlled to be within a temperature nominally 1050°F to 1200°F. The 1200°F peak temperature corresponds roughly to the temperature at which the coal ash corrosion would be at a maximum. Based on this, it was anticipated that the wastage rate, for a given candidate material, would continue to increase from one end of the test section to the other. However, it should be understood that the actual coal ash corrosion temperature range, and peak temperature, is a function of the local composition of the deposit, and to some extent the composition of the underlying tube metal

It should also be understood that, due to normal boiler operations, the temperature of the test section fluctuated as this program progressed, see Figure 2. This was taken into consideration in calculating the wastage rate (and the average surface metal temperature), in that only time above 1000°F was counted as exposure time.

3. Candidate materials in this program exhibited a higher wastage rate than originally anticipated when the test section was designed. Eight of the twelve candidate materials demonstrated a maximum wastage rate that was equal to, or greater than, 100 mils per year, see Table 10. Most of these materials had a relatively thick, 400 mil wall thickness which was intended to provide a corrosion allowance that would increase the probability that the samples would remain in service until the final test section was removed from service. In reality, many candidate material tube samples had to be removed and replaced over the course of this testing in order to achieve the desired service exposure durations. The reason for these higher than anticipated wastage rates has not been conclusively determined; however, the wastage rates that were experienced in this testing are much higher than those reported based on laboratory work. It should be pointed out that high wastage rates, such as those determined in this testing, would disqualify most of these materials as a candidate for service (if service conditions match those experienced in this program).

4. Wastage rates appear to have been influenced by the physical location of the sample within the test section. Results indicated that samples located near “mid-span” in the test section demonstrated higher wastage rates than those located at either end of the test section. When this was first noted, it was postulated that the boiler walls effectively cooled the local environment resulting in gas and metal temperatures somewhat lower than estimated. Another alternative postulated as a “wall effect” was the possibility that the upward flow of combustion gases was different in the vicinity of the wall, and that this influenced the wastage rate. Either of these wall-proximity influences may have had an influence on the local environment.
5. At the time of the analysis, some, but not all, of the materials that demonstrated high wastage resistance had in place a continuous high-chromium scale. Examination of the scale/metal interface for materials such as Inconel 671 and IN 72 weld overlay revealed a continuous high chromium scale. IN 52 also appears to have been able to maintain a continuous high chromium scale; however, this cladding material appears to have been less resistant to wastage, and by the completion of this program, the IN 52 weld overlay had been completely breached and the underlying 800H substrate was exposed to corrosive conditions.

It should be noted that the metallurgical examination of Thermie did not reveal the presence of a continuous scale (since Thermie performed well relative to the other monolithic tubing materials) and high chromium scale appears to be vital in maintaining wastage resistance, the lack of such a scale on Thermie raises the question as to at what point the scale separates from the surface. Potential mechanisms for scale separation include:

- Formation of a frangible scale that easily separates from the surface with continued time at exposure temperatures as thickness increases and internal stresses build.
- Scale separation (frangible or otherwise) during thermal fluctuations due primarily to differences in thermal expansion between the scale and underlying metal.
- Scale separation (frangible or otherwise) due to physical handling in spite of care taken during extraction and transport of the test section.

Initial assessments (based on coloration) suggest that physical handling was not the cause of the observed scale separation for most of the tube samples in this program. Since Thermie was highly resistant in service, the protective scale is presumed to have spalled as the tubing cooled to room temperature, as it commonly does from austenitic stainless steels.

6. At the time of the analysis, the materials that demonstrated low wastage resistance lacked a continuous high-chromium scale. The survey of materials presented in the previous section of this report showed that, in general, the materials with low wastage resistance (>100mils/year) lacked a continuous protective scale (at the location of greatest metal loss). For most of these materials, remnants of a presumably protective high chromium scale were present; however, at the time of the examination bare metal was exposed to the environment over a significant percentage of the surface area. Examination revealed

that these scales tend to become enriched in sulfur along the scale/metal interface, and this plane appears to be the plane along which the scale tends to separate from the tube surface. This effect may further accelerate corrosion of materials such as HR 120, 310 Ta, 310 HCBN, Modified 800H, NF 709 and 347 HFG.

Analysis of Save 25 revealed a complex response to the coal ash corrosion conditions developed in this test program. In its region of greatest metal loss, Save 25 performed somewhat differently than the other high wastage rate materials, in that, the scale was found to be iron rich (instead of chromium rich). This suggests the possibility that Save 25 performed poorly at this location because it was unable to generate and maintain a protective high chromium scale. Examination of the deposit/scale/metal interface at another location about the circumference of the same tube sample suggested that, while the scale at that location was higher in chromium, iron was diffusing faster across the scale and ultimately separating from the surface to form stratified layers in the deposit.

7. In general, higher chromium content results in increased wastage resistance. Furthermore, given an adequate level of chromium, wastage resistance increases as iron is replaced by nickel (and perhaps cobalt). Table 10 provides a summary of the major alloying elements in each candidate material along with its maximum wastage rate (as measured for Section B). Figure 17 provides a plot of maximum wastage rate versus chromium content for all three test sections. Figure 18 provides a plot of wastage rate versus chromium plus nickel (and cobalt). As can be seen from inspection, and in spite of the caveats mentioned in the sections leading to this point, the data seem to conform well to a linear regression fit.
8. Other issues worthy of consideration:
 - Steam-Side Oxidation – The attached appendices document the condition of the internal surface for each of the candidate materials. It should be noted that, for all of the monolithic tube materials, the internal surface of the tube was unaffected due to steam-side exposure in Section B, see Figure 19a for an example. Steam-side oxidation was found for the Incoloy 800HT substrate used to evaluate the performance of the weld overlay and Inconel material. Figure 19b shows a case where the oxide was found in place. Figure 19c shows a case where the oxide had exfoliated. In any case, it needs to be understood that this test was not designed to evaluate steam-side oxidation resistance, and as such, this documentation is provided for information purpose only.
 - IN 72 Weld Overlay Cracking – While this cladding material demonstrated excellent wastage resistance, metallurgical examination of samples from all three test sections revealed the presence of radial cracks at roughly the centerline of this 80 mil thick cladding. Analysis suggests that this cracking is related to the cladding deposition procedure, in that, it appears to occur at the root of a gas tungsten arc “wash pass”. A small number of similar (but much smaller) cracks were found in archive material that hadn’t seen service. The cladding provider has demonstrated the ability to eliminate these cracks by eliminating the wash pass; however, he indicated that the wash pass was needed to ensure that these samples pass bend tests during procedure qualification trials. This issue has been left unresolved; however, it would be important to: 1) demonstrate conclusively that the cracking can be eliminated by discontinuing the use of a wash pass, 2)

demonstrate that the resultant clad tubes are able to pass all of the required procedure qualification tests, and 3) verify that IN 72 is not sensitive to time dependent cracking in these same locations.

- IN 52 Weld Overlay / Incoloy 800H Heat Affected Zone Cracking – This evidence was only found in one of the three test sections (Section B). Nonetheless, if Incoloy 800H is to be used in the future, it would be appropriate to perform additional tests to better understand the cause for, and eliminate, the observed cracking. The heat affected zones for the tube to tube butt welds would also merit additional assessment.
- IN 625 Weld Filler Metal – While it hasn't been emphasized, the point should be made that the test sections were fabricated by using Inconel 625 filler metal to join the candidate tube metal samples to one another, and that weld cross sections revealed that the Inconel 625 filler metal performed as well, if not better than many of the candidate alloys. For example, this cross section shows that Inconel 625 performed better than IN 52 at this location, but not quite as well as IN 72. Similar cross sections can be found in the appendices.

Table 6: Maximum Wastage Rate as a Function of Position in Test Section B

Material	Tube Sample	Rate Metal Lost* (mils/yr)	Average Surface Metal Temperature, (F)
52 Weld Overlay	R-S	31	1195
72 Weld Overlay	Q-R	1	1195
Inconel 671	P-Q	1	1191
HR 120	O-P	100	1183
310 HCBN	N-O	111	1179
310 Ta	M-N	110	1176
800 Mod	L-M	161	1172
Save 25	K-L	228	1168
NF 709	J-K	164	1165
347 HFG	I-J	175	1162
Thermie	H-I	57	1159
310 HCBN	G-H	121	1155
310 Ta	F-G	106	1153
800 Mod	E-F	140	1149
Save 25	D-E	169	1145
NF 709	C-D	92	1141
Fe3Al	B-C	117	1138
347 HFG	A-B	67	1136
Inconel 671	U-V	1	1109
HR 120	V-W	42	1099
310 HCBN	W-X	57	1094
310 Ta	X-Y	70	1092
800 Mod	Y-Z	109	1088
Save 25	Z-AA	168	1084
310 HCBN	AA-BB	101	1080
NF 709	BB-CC	119	1077
347 HFG	CC-DD	139	1075
HR 120	DD-EE	**	1077
Inconel 671	EE-FF	11	1074
72 Weld Overlay	FF-GG	16***	1067
52 Weld Overlay	GG-HH	59	1062
Thermie	HH-II	27	1056
Save 25	II-JJ	50	1047

* Metal loss rate is based on time at temperature, not total time within the boiler.

** N/A = Sample overlain with weld metal, thus no data available.

*** The calculated rate is based solely on wall thickness measurements and does not take into account that corrosion had removed sufficient material to connect an underlying weld crack with the surface.

Key: Sample removed from service November 2001 -----
Sample removed from service June 2002 -----
Sample removed from service in September 2003 -----
Sample remained in service until the end of Section B exposure in May 2003 -----

Table 7: Rankings Per Material Based on Rate of Metal Loss in Test Section B

Material	Tube Sample	Maximum Rate Metal Lost* (mils/yr)	Average Surface Metal Temperature, (F)
Save 25	K-L	228	1168
Save 25	D-E	169	1145
Save 25	Z-AA	168	1084
Save 25	II-JJ	50	1047
800 Mod	L-M	161	1172
800 Mod	E-F	140	1149
800 Mod	Y-Z	109	1088
347 HFG	I-J	175	1162
347 HFG	CC-DD	139	1075
347 HFG	A-B	67	1136
NF 709	J-K	164	1165
NF 709	C-D	92	1141
NF 709	BB-CC	119	1077
Fe3Al	B-C	117	1138
310 Ta	M-N	110	1176
310 Ta	F-G	106	1153
310 Ta	X-Y	70	1092
310 HCbN	G-H	121	1155
310 HCbN	N-O	111	1179
310 HCbN	AA-BB	101	1080
310 HCbN	W-X	57	1094
HR 120	O-P	100	1183
HR 120	DD-EE	**	1077
HR 120	V-W	42	1099
Thermie	H-I	57	1159
Thermie	HH-II	27	1056
52 WO	GG-HH	59	1062
52 WO	R-S	31	1195
72 WO	FF-GG	16***	1067
72 WO	Q-R	1	1195
671 Clad	EE-FF	11	1074
671 Clad	P-Q	1	1191
671 Clad	U-V	1	1109

* Metal loss rate is based on time at temperature, not total time within the boiler.

** N/A = Sample overlain with weld metal, thus no data available.

*** The calculated rate is based solely on wall thickness measurements and does not take into account that corrosion had removed sufficient material to connect an underlying weld crack with the surface.

Key: Sample removed from service November 2001 -----
Sample removed from service June 2002 -----
Sample removed from service in September 2003 -----
Sample remained in service until the end of Section B exposure in May 2003 -----

Table 8: Maximum Rate of Metal Loss for Each Candidate Material

Material	Tube Sample	Section B Maximum Rate of Metal Loss (mils/yr)	Surface Metal Temperature (F)
Save 25	K-L	228	1168
347 HFG	I-J	175	1162
NF 709	J-K	164	1165
800 Mod	L-M	161	1172
310 HCBN	G-H	121	1155
Fe3Al	B-C	117	1138
310 Ta	M-N	110	1176
HR 120	O-P	100	1183
IN 52 WO	GG-HH	59	1062
Thermie	H-I	57	1159
IN 72 WO	FF-GG	16	1067
671 Clad	EE-FF	11	1074

* Note: this rate does not take wall loss due to internal cracking in this weld overlay material.

Key: Sample removed from service November 2001 -----
 Sample removed from service June 2002 -----
 Sample removed from service in September 2003 -----
 Sample remained in service until the end of Section B exposure in May 2003 -----

Table 9: Maximum Wastage Rate as a Function of Time and Position

Material	Tube Sample	SECTION A		SECTION C		SECTION B	
		Rate Metal Lost* (mils/yr)	Exposure Temp. (F)	Rate Metal Lost* (mils/yr)	Exposure Temp. (F)	Rate Metal Lost* (mils/yr)	Exposure Temp. (F)
52 Overlay	R-S	44	1198	48	1208	31	1195
72 Overlay	Q-R	10 ***	1198	6 ***	1208	1 ***	1195
Incoclad 671	P-Q	4	1193	2	1203	0	1191
HR 120	O-P	102	1184	124	1194	100	1183
310 HCbN	N-O	108	1180	133	1190	111	1179
310 Ta	M-N	123	1178	131	1188	110	1176
800 Mod	L-M	169	1174	183	1185	161	1172
Save 25	K-L	259	1170	>259	1180	228	1168
NF 709	J-K	170	1167	181	1178	164	1165
347 HFG	I-J	174	1164	204	1174	175	1162
Thermie	H-I	53	1160	77	1171	57	1159
310 HCbN	G-H	133	1157	141	1167	121	1155
310 Ta	F-G	136	1154	127	1166	106	1153
800 Mod	E-F	178	1150	176	1162	140	1149
Save 25	D-E	224	1146	N/A**	1158	169	1145
NF 709	C-D	136	1142	114	1153	92	1141
Fe3Al	B-C	145	1139	100	1149	117	1138
347 HFG	A-B	83	1137	76	1147	67	1136
Incoclad 671	U-V	2	1110	1	1121	1	1109
HR 120	V-W	61	1100	46	1110	42	1099
310 HCbN	W-X	98	1095	52	1106	57	1094
310 Ta	X-Y	120	1092	64	1103	70	1092
800 Mod	Y-Z	154	1088	79	1099	109	1088
Save 25	Z-AA	208	1084	148	1096	168	1084
310 HCbN	AA-BB	129	1081	79	1092	101	1080
NF 709	BB-CC	145	1077	100	1088	119	1077
347 HFG	CC-DD	176	1075	120	1086	139	1075
HR 120	DD-EE	109	1077	79	1088	N/A	1077
Incoclad 671	EE-FF	13	1075	10	1086	11	1074
72 Weld Overlay	FF-GG	21 ***	1068	14***	1079	12 ***	1067
52 Weld Overlay	GG-HH	77	1062	63	1073	59	1062
Thermie	HH-II	31	1056	34	1067	27	1056
Save 25	II-JJ	67	1047	56	1058	50	1043

* - Metal loss rate based on time at temperature, not total time within the boiler.

** - N/A = Sample overlain with weld metal, thus no data available

*** - Calculated rate based solely on wall thickness measurements and does not take into account underlying cracking due to weld procedure.

Key: Sample removed from service November 2001 -----
 Sample removed from service June 2002 -----
 Sample removed from service in September 2003 -----
 Sample remained in service until the end of Section B exposure in May 2003 -----

Table 10: Maximum Wastage Rate (for Section B Samples) and Nominal Composition for Each Candidate Material

		Composition, (wt%)									
Candidate Material	Maximum Wastage Rate in Section B (mils/yr)	Cr	Ni	Fe	Co	Mo	Nb	Cu	Mn	Other	Comments
Coating:											
Incoclad 671	11	48	51.5	--	--	--	--	--	--	--	
IN 72 Weld Overlay	16*	44	55	--	--	--	--	--	0.1	--	
IN 52 Weld Overlay	59*	30	51	9	--	--	--	--	1 max	--	
Fe ₃ Al	117**	--	2	82	--	--	--	--	--	Al: 16%	
Monolithic Tube:											
Thermie	57	24	48	2	19.8	0.5	2	--	0.8	Ti: 2%	Wastage rate based on highest temperature sample at mid-span.
HR 120	100	25	37	30	3	2.5	0.7	--	0.7	W: 2.5%	
310 Ta	110	24.5	21	51	--	--	--	--	2	Ta: 1.75%	Wastage rate based on highest temperature sample at mid-span.
310 HCBN	121	25	20	52	--	--	0.6	--	2 max	--	
Modified 800H	161	20	31	45	--	1.5	0.25	--	2	V: 0.4% Ti: 0.25%	Wastage rate based on highest temperature sample at mid-span.
NF 709	164	21	25	50	--	1.5	0.25	--	1.5 max	--	Wastage rate based on highest temperature sample at mid-span.
347 HFG	175	18.5	11	67	--	--	1 max	--	2 max	--	Wastage rate based on highest temperature sample at mid-span.
Save 25	228	22.5	18.5	52	--	--	0.45	3	2 max	W: 1.8%	Wastage rate based on highest temperature sample at mid-span.

* Note: this rate does not take wall loss due to internal cracking in this weld overlaid material.

** To a great extent, this rate reflects the wastage rate for the Type 304H substrate.

Figure 12: Maximum Wastage Rate as a Function of Position within Section B

Note:

1. The materials are listed in sequence according to their position within the test section, with the hottest end of the test section to the left, and the coolest end of the test section to the right.
2. No data provided for HR 120 tube Sample D-E because it had been overlain with weld metal

Figure 13: Maximum Wastage Rate for Each Candidate Material in All Three Sections

Figure 14: Wastage as a Function of Average Surface Metal Temperature for the Twelve Candidate Alloys in Test Section B

Section A: Wastage Rate vs Temperature

Section B: Wastage Rate vs Temperature

Figure 15: Wastage as a Function of Average Surface Metal Temperature for the Twelve Candidate Alloys in Test Sections A and B

Figure 16: Maximum Wastage as a Function of Time for the Candidate Materials

Figure 17: Chromium Content Versus Wastage Rate for Both Sections A and C With Logarithmic Trend Line

Figure 18: Chromium Plus Nickel Content Versus Wastage Rate With Linear Regression Fit Trend Line

(Note: for the purposes of this graph, the Thermie data point, includes the cobalt content.)

a) Internal Scale/Metal Interface for Save 25

b) Internal Scale/Metal Interface for Incoloy 800 HT – Oxide in Place

c) Internal Scale/Metal Interface for Incoloy 800 HT – Oxide Exfoliated

Figure 19 Typical Examples of the Condition of the Internal Scale/Metal Interface after Service

4.0 CONCLUSIONS

Evaluation of tubes removed from Section B suggests the observation that the candidate materials performed very similarly for all three sections.

- The relative rankings of the candidate materials (based on wastage rate) are summarized as follows.

- These data reveal that eight of the twelve candidate materials had a maximum wastage rate that exceeded 100 mils per year. Such a high wastage rate likely would make the use of such materials uneconomical for this application.
- Two materials exhibited a maximum wastage rate that consistently exceeded 50 mils per year for the duration of this testing: Thermie and IN 52 Weld Overlay. It should be noted that the 80 mil thick IN 52 cladding was breached before the end of the full 37 month exposure period for Section B.
- Two materials exhibited a relatively low maximum wastage rate (i.e. between 10 and 20 mils per year): IN 72 Weld Overlay and Incoclad 671.
- In addition to coal ash corrosion, IN 72 suffered from a deposition process-related cracking problem that needs to be fully resolved.
- In addition to coal ash corrosion, the deposition process for IN 52 led to cracking in the heat affected zone of the underlying Incoloy 800HT. This problem should be further investigated.

5.0 REFERENCES

1. "Coal Ash Corrosion Resistant Materials Testing, Topical Report: Removal of Section A", McDonald, D.K., Daniel, P.L., DeVault, D.J. Robitz, E.S., October 2002.
2. "Coal Ash Corrosion Resistant Materials Testing, Topical Report: Removal of Section C", McDonald, D.K., Daniel, P.L., DeVault, D.J., Robitz, E.S., June 2004.

ACRONYMS & ABBREVIATIONS

A	AFUDC	Allowance for Funds Used During Construction
B	B&W	Babcock & Wilcox
	BWRC	Babcock & Wilcox Research Center
C	CRD	Contract Research Division
	COE	Cost of Energy
	C2000	Combustion 2000
D	DOE	Department of Energy
E	EDS	Energy Dispersive Spectrometry
	ERPI	Electric Power Research Institute
F	FERC	Federal Energy Regulatory Commission
I	ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrographic
	IN	Inconel
K	kw	Kilowatt
	kWh	Kilowatt Hour
L	LEBS	Low Emission Boiler System
M	MBtu	Million British Thermal Units
	Mod	Modified
O	OCDO	Ohio Coal Development Office
	ODOD	Ohio Department of Development
	OD	Outside Diameter
	O&M	Operate and Maintain

S	SEM	Scanning Electron Microscope
T	TPC	Total Plant Cost
	TPI	Total Plant Investment
W	WO	Weld Overlay
Y	Yr	Year

ANNEX 1 - PROGRAM TIMELINE: 2003 – 2005

In October 2002 a “Topical Report: Removal of Section A” providing the full details of the project background, material selection, fabrication of the test materials and sections, description of the test system, and system installation, start-up and operating history through 2001 was provided along with the results of evaluation of Section A removed in November of 2001. That information will not be repeated herein and the reader is referred to “Topical Report: Removal of Section A” attached to this report for that information.

In June of 2004 a “Topical Report: Removal of Section C” providing the operating history of the remaining sections beginning where the Section A report left off through the end of 2003. The following provides the operating history of the sections beginning where the Section C report left off through the end of 2005. It is followed by the results of evaluation of the third section, Section B, removed in April of 2005.

2004

A paper for the Clearwater Conference describing the results of evaluation of Section C was written in January and submitted in February for presentation in April.

After startup of Section B (in the C location) in late December, checkout began in January and it was discovered that the position transmitter for the flow control valve was malfunctioning so a new one was ordered. Without a proper valve position reading it was possible for the valves to completely close and damage the sections if it occurred for any significant length of time. This was discovered when it very briefly occurred during checkout (no damage resulted). The inlet valve was locked open until the transmitter arrived and reinstalled (required a brief outage due to the temperature in the equipment location).

Metallurgical analysis of all twelve candidate alloys in Section C was completed including a characterization of the external scale/metal interface and chemical analysis of selected regions. Analysis and characterization of the coal ash deposit on the surface of the tubes and assessment of metal loss across weld regions were also completed. Of particular concern was that the heat affected zone of the tube-to-tube welds might be less resistant to corrosion which proved not to be the case.

A first draft of the appendices for the Section C report was completed with one appendix dedicated to each of the twelve candidate materials. This format is the same as that of the report for Section A. It was noted that although the IN72 samples appear very resistant to hot corrosion, they seem to have experienced a grain boundary cracking that increased as a function of time. This was further investigated. The first draft of the Section C report was released for internal review in early March but due to resource availability, the external release was expected to be in late May.

Though there was a brief outage on February 22, the new position transmitter for the flow control valve arrived on site a couple days later so installation was postponed until the next opportunity. Meanwhile the inlet valves remained locked open and Section B operated at reduced temperature. Unfortunately, there were no brief outages in March.

In April, all comments on the draft Section C report were returned to the author. The Introduction and operating history for 2002 and 2003 were written and sent to the writer as well. Incorporation of this section and the comments was underway and release to DOE and OCDO for review was expected in May. In May and June incorporation of all internal comments was completed and some additional investigation of results was completed in response to internal questions. The draft Topical Report was sent for release to OCDO and DOE in late June.

The unit came down on May 19 for a tube failure and the failed transmitter was replaced. The unit was restarted but had to shut down again on May 25 so controls tuning did not take place. On June 2 the unit restarted and shortly thereafter the section controls were released and the section began operating at intended temperature.

The paper for the Clearwater Conference describing the results of evaluation of Section C was presented at the conference held April 19-22, 2004. In May a paper on the evaluation of Section C for EPRI's "4th International Conference on Advances in Materials Technology for Fossil Power Plants" was accepted for presentation at the conference October 25-26, 2004. In June a poster was prepared for and presented at DOE's Fossil Energy Materials Conference in Knoxville Tenn. June 2-4.

Comments from OCDO and DOE on the draft Topical Report on the Section C were received in August. The report was revised to address the comments and was resent to DOE for approval on September 3.

In July and August, the last Section continued to operate at intended temperature and data collection continued. It continued to operate at intended temperature until the boiler shut down on September 28 for a two-week outage (unrelated to the project).

The Section was originally labeled "B" but in December 2003, it was refurbished and re-installed in the original "C" location. During this outage, it was inspected as shown in Photo 7. Figure 5 shows OD measurements taken with calipers during the inspection. The measurements greater than 2.5 in. indicate ash deposition on the top of the tube, while those less than 2.5 in. indicate wastage (perhaps with some ash deposition masking the wastage magnitude). Although some wastage was indicated (oblique flats on some tube sections), most of it was believed to have been present at reinstallation. In addition, the lower bend support lug had detached, allowing some lateral movement. The upper support lug remained intact. Overall, the Section appeared to be in good condition.

PHOTO 7: SECTION B – IN ORIGINAL ‘C’ LOCATION, AT INSPECTION 9/28/04

FIGURE 5: OD MEASUREMENTS SECTION B (in C Location) 9/28/04 - Original OD = 2.5 in

In July the paper on the evaluation of Section C for EPRI’s “4th International Conference on Advances in Materials Technology for Fossil Power Plants” was completed and released internally for review and approvals and in August it was released to EPRI.

A paper on the evaluation of Section C for EPRI’s “4th International Conference on Advances in Materials Technology for Fossil Power Plants” was presented at the conference October 25-26, 2004.

The last section (Section B in the C location) continued to operate at intended temperature through the end of the year.

2005

The last section continued to operate at intended temperature from January until it was removed during a scheduled outage on April 26 and shipped to the B&W Research Center where evaluation was initiated. All time and temperature data was reduced in May and provided to BWRC for use in evaluation of the specimens. The section was cut into dimensioning rings and measurements were completed in June and final report writing was being initiated. Nearly all of the analytical work was completed in July. Evaluation of the final section and writing of the final report began in August and September. Work on the Impact on Cost of Electricity (COE) began in September. A draft of the final report (not including the section on COE) was completed for internal review in October and released to the DOE and OCDO in December.

ANNEX 2 - IMPACT ON DESIGN AND COST OF ELECTRICITY

According to Task 7.0 of the Statement of Work, “the materials selected as a result of this program will be incorporated into the Combustion 2000 (C2000) Low Emission Boiler System (LEBS) boiler design, the costs will be appropriately adjusted and the impact on boiler and plant cost of electricity will be determined and reported using the Combustion 2000 cost analysis basis”.

The purpose of the LEBS design was to integrate the selected technologies into a “new” plant design that would accomplish the emission and performance targets for the LEBS program. The results can be found in the documents associated with DOE Contract number DE-AC22-92PC92160. Information on the boiler design, performance and costs, and an assessment of the impact on the economic analysis performed for LEBS are provided in this section as well as comments on that design and performance relevant to the current state-of-the-art to take into account developments since the C2000 work was concluded in May of 1997.

Boiler

The boiler for the Combustion 2000 program, completed in 1997, was a once-through, variable pressure, double reheat design at 4500 psi throttle pressure and 1100F for main steam and reheat temperatures. Current technology continues to be a supercritical, once-through variable pressure design with some differences.

Since that work 1100°F main steam and reheat temperatures have become common in specifications for new plant design and several units have been built, albeit for low sulfur PRB coals. In fact, current specifications request 1110°F /1148°F (600°C/620°C). However, it has been realized that the high pressure of 4500 psi used for LEBS is not necessary to achieve high efficiency since increasing pressure has a small impact on heat rate compared with increasing temperature. Increasing the pressure proportionately increases the thickness of all pressure parts from the feedwater pump discharge to the steam turbine, including the High Pressure turbine casing. This added thickness not only directly increases material cost for the pressure parts and requires additional building steel and foundation costs to support the additional weight, it also causes the surface metal temperatures of the boiler and superheater tubes to increase requiring more costly alloy materials. For these reasons it has been determined that steam pressure should not be increased beyond the critical pressure any more than required by the thermodynamic expansion characteristic of the steam turbine given the inlet temperature/flow conditions.

In the past few years, consideration of arrangement and design of the convection pass for high sulfur coals and high steam temperatures has progressed. Surface arrangements to shield the highest temperature rows, most susceptible to corrosion, can be made which reduce the surface metal temperatures. These require additional surface but can lower overall cost since corrosion resistant material requirements are not as severe. Another approach is to arrange the rows most sensitive to corrosion to minimize time and cost of removal and replacement and use materials designed to provide a corrosion life comparable to a turbine outage cycle (or two). This approach is being examined to determine whether periodic replacement (10-15 years) is more economical than designing for a 30 year life using very expensive clad materials.

Another difference between current technology and the LEBS design is double reheat. Although double reheat has been applied in years past and it does decrease heat rate, the reduction in heat rate seldom justifies the added cost. The 431 MWe gross output of the plant is too small to make a second reheater economical.

Environmental equipment has also progressed significantly since the C2000 work is in sulfur removal. Since 1997 the performance of a wet scrubber with auxiliaries has greatly improved along with major reductions in cost and the production of a salable gypsum byproduct. As a result, the E-LIDS system included in the C2000 capital cost and COE would not be selected today. The monetary impact of improved environmental performance has not been addressed in this assessment. Table 11 compares conventional 1997 technology, the LEBS design, and current technology emissions and efficiency.

Table 11: Comparison of Current Environmental Technology with the LEBS System

Phase	NO _x Lb/MBtu	SO ₂ Lb/MBtu	Particulate Lb/MBtu	Net % Efficiency
Conventional 1997	0.46	0.6	0.03	37.5 ³
LEBS Boiler Goals	0.1	0.1	0.005	42.27 ²
Current Conventional ¹	0.05	0.07	0.018	39.5 ³

¹ Current Conventional is 3600psi/1100F/1100F with SCR, baghouse, and WFGD

² Condenser pressure 1 in Hg

³ Condenser pressure 2.0 in Hg

Cost Impact

It should also be noted that some of the assumptions made for the C2000 cost analysis would differ were it done today, several of which would produce a more favorable outcome. On the other hand, modernization of third world countries, especially China, has resulted in major increases in material costs, especially alloys, in the past two years. These factors imply that the quantitative capital costs and COE do not reflect the current cost of a state-of-the-art plant. However, the difference in capital cost for the boiler and the impact of the boiler on the COE are qualitatively relevant.

To determine the cost impact and maintain a common basis, the LEBS design was revisited and all materials operating above an acceptable predicted corrosion rate were changed to use to be INCO 671 clad tubes. For the reasons discussed above, this is believed to be a conservative approach. The incremental costs for the superheater and reheaters was then determined using tubing costs obtained in the 1997 timeframe (to avoid skewing by recent material cost increases). Since these changes only impact the higher temperature portions of the superheater and reheaters, they are reflected only in the increase in FERC Account 312 for the steam generator as shown in Table 12.

Table 13 shows the economic factors used in the LEBS analysis in 1997. In order to maintain a common basis, they are used again here, although some would be different if a current analysis were to be done. The discussion on Capital Cost, Total Plant Cost, and Total Investment are excerpted from the cost analysis section of LEBS Phase 2 Final Report and modified for accordingly for this discussion. The net output in all cases is assumed to be 406.4 MWe.

Capital Cost

As per DOE direction¹, the procedure for calculating the cost of electricity is to be consistent with the methodology used by the Electric Power Research Institute (EPRI). The definitions of capital cost follow EPRI's definitions for the "total plant cost" (TPC) and the "total plant investment" (TPI). The total plant cost represents a capital cost for "instantaneous construction" while the total plant investment includes the effects of escalation and interest for the construction cash flows. The total plant cost is summarized next and followed by a summary of the total plant investment.

Total Plant Cost (TPC)

The total plant cost (TPC) represents the cost for engineering, procurement and construction² at the commercial operation date of January 1, 1997. The TPC essentially represents the cost as if the plant could be constructed instantaneously at that date. Therefore, the effects of escalation and interest during construction (also called "allowance for funds used during construction") are not included.

The development of the TPC is described in the estimate basis which is provided as an attachment to the report. The TPC estimate basis is summarized below.

- Construction approach: 100% subcontracted union-shop labor force. A construction management staff was included to oversee performance of the subcontractors.
- Estimating method: quantity basis including earthwork, concrete, structural steel, equipment, piping, electrical, instrumentation & controls, painting, insulation, buildings and architectural, and demolition.
- Pricing basis: B&W pricing, other manufacturer pricing, Raytheon actual project experience.
- Cost date: January 1, 1997 assumed for commercial operation date.
- Schedule for engineering, procurement and construction: 3 years. The effects of escalation and AFUDC are included in the total plant investment (not the total plant cost).
- Contingency: 10% as per DOE guidelines.
- Exclusions:
 - ◆ Land, and rights-of-way
 - ◆ Licensing, permits
 - ◆ Preproduction costs
 - ◆ Working capital
 - ◆ Legal fees
 - ◆ Owner's costs (engineering, studies, development costs)
 - ◆ Others as described in the detailed estimate basis.
 - ◆ Electrical switchyard
 - ◆ Inventory costs for startup
 - ◆ Spare parts
 - ◆ Financing fees

¹ As defined in DOE's "Unified Basis for Estimating the Capital Costs and Cost of Electricity for the Low Emission Boiler Systems", originally dated January 18, 1994, revised January 31, 1997.

² According to the FERC Code of Accounts, the TPC represents the "base construction cost" plus contingency. According to the EPRI guidelines, the TPC includes "process facilities capital, general facilities capital, engineering and home office overhead, contingencies, land (\$0 for this analysis), and miscellaneous expenses.

Table 12: Capital Cost Summary (\$ million)

FERC Account	Account Description	Conventional	LEBS	UPDATED LEBS
311	General Facilities Improvements Main Power Station Bldg Misc Structures Coal & Ash Storage	62.9	62.5	
312	Steam Generator Draft System Feedwater & Supply System Fuel System Ash Handling System Boiler Plant Instruments & Controls Piping-Boiler Island FGD System Pulverizers Water Supply & Purification Boiler Plant Miscellaneous Items	217.9	233.3	239.3
314	Turbine Generator & Accessories Condensing System Circulating Water & Cooling System Central Lubrication Automatic Steam bypass Turbine Plant Instrumentation & Controls Piping-Turbine Island	59.1	69.1	
315	Switchgear Station Service Equipment Switchboards Protective Equipment Electrical Wiring Duct & Conduit Power & Control Wiring Other Electrical Work Electrical Equipment FGD System Electrical Heating Miscellaneous Electrical	32.5	33.2	
316	Cranes & Hoisting Equipment Air Compressors & Receivers Fire Protection Equipment Hydrogen, Nitrogen & CO ₂ Storage Transportation Equipment Vacuum Cleaning Equipment Station Maintenance Equipment Miscellaneous Spare Parts	2.7	2.6	
352.1 353.1	Electrical Equipment Foundations Main Power Transformer	4.1	4.8	
	Total Direct Field Cost Distributable Construction Costs Engineering/Procurement/Construction Management Contingency	115.4	125.4	
	Total Plant Cost (TPC) (instantaneous construction at 01-Jan-97)	494.6	530.9	536.9

Table 13: Economic Factors used for LEBS

Description	Units	Parameter
<u>Time Frames</u>		
Construction period	years	3
Economic service life	years	30
Cost Date		01-Jan-97
Beginning of service life		01-Jan-97
<u>Economic Factors</u>		
Discount rate (constant \$)	%/year	4.3%
Levelized fixed charge rate (constant \$)	%/year	9.2%
AFUDC rate (current \$)	%/year	7.4%
Capital escalation rate prior to startup (for AFUDC calculations)	%/year	1.1%
Inflation rate during service life	%/year	3.0%

The TPC values and summary definitions of the FERC code of accounts are described in Table 12. The LEBS plant has a greater initial capital cost for most of the plant systems because of the more expensive materials of construction and the advanced design considerations to improve efficiency. The Updated LEBS Cost includes the impact of enhanced corrosion protection.

Total Plant Investment (TPI)

The total plant investment (TPI) includes the effects of escalation and interest during construction as follows:

- Total cash expended (TCE) represents the cost of engineering, procurement and construction on an as-built basis³. Since the plant is assumed to be in commercial operation at January 1, 1997, construction would need to begin several years earlier. The methodology is based on de-escalating the TPC (assuming constant dollar annual expenditures of “TPC/3”) over the three-year construction period to estimate the total cash expended (TCE). The escalation rate is assumed to be 1.1% per year⁴.
- Allowance for funds used during construction (AFUDC) which represents the cost of interest during construction assuming a 7.4% interest rate. The AFUDC rate is applied to the estimates of total cash expended at the end of each of the three years of construction to calculate the total AFUDC.

³ Since the plant is assumed to be in commercial operation at January 1, 1997, construction would need to begin several years earlier.

⁴ As defined in DOE’s “Unified Basis for Estimating the Capital Costs and Cost of Electricity for the Low Emission Boiler Systems”, originally dated January 18, 1994, revised January 31, 1997.

The total plant investment (TPI) is compared for 1997 conventional, LEBS and Updated LEBS plants in Table 14. This table includes TPI in terms of either the costs in millions of dollars or \$/kW. The TPI is based on the sum of the total cash expended (TCE) and the allowance for funds used during construction “AFUDC” (interest during construction).

In accordance with the guidelines established by DOE, owner’s costs such as preproduction costs, legal fees, owner’s engineering, permits, inventory, financing costs, working capital and other development costs are not included since these can be highly variable for site specific projects.

Table 14: Total Plant Investment

	Conventional 1997		LEBS		Updated LEBS	
	1997 dollars	1997 \$/kW	1997 dollars	1997 \$/kW	1997 dollars	1997 \$/kW
Total Cash Expended	489.2	1204	525.1	1292	531.0	1307
AFUDC	36.8	91	39.5	97	40.0	98
Total Plant Investment	526	1294	564.7	1389	571.0	1405

The relative difference between the three plants is important to the analysis and has a greater level of accuracy than the magnitudes of the estimates. The estimate basis defines the scope and level of effort in estimating. Care should be taken when comparing the magnitude of these capital costs with other industry data because of the wide variation that can occur from factors such as:

- Regional cost escalation
- Construction labor and productivity
- Scope
 - ◆ Boiler and turbine type (conventional versus advanced)
 - ◆ Flue gas desulfurization type
 - ◆ Particulate control type
 - ◆ Type of cycle cooling,
 - ◆ Coal handling system (rail versus truck delivery of coal)
 - ◆ Other scope differences (e.g. rail spur or transmission line)
 - ◆ Degree and type of “soft” costs included (such as working capital, financing fees, permitting, legal expenses, extent of environmental studies)
- Coal quality
- Number of units (standalone greenfield versus add-on unit with shared systems)
- Degree of equipment sparing
- Degree of over-design in major systems to handle a variety of coals
- Equipment redundancy
- Type of soil (foundations) or site preparation
- Indoor or outdoor design
- Use of standard or reference plant design
- Number of contract packages and method of equipment contracting

- Type of construction management
- Extent of utility overhead costs
- Method of bidding (e.g. cost plus, firm-price)
- Schedule delays

Levelized Busbar Costs

The sensitivity of the levelized busbar cost to key cost drivers was evaluated for the LEBS plant as part of the Combustion 2000 program. Subsequently, the sensitivity of the busbar cost comparison with the conventional plant was evaluated for the two effects that reflect key differences between the two options - plant efficiency and coal price.

The sensitivity of the levelized busbar cost for the LEBS Plant to variations in key parameters is provided in Table 15. The sensitivity analyses are grouped into three main categories: capital cost and financing, plant performance, and fuel and O&M costs. The table permits correction for the key parameters allowing adjustment of the TPI and busbar cost for a wide range of variations.

Table 15: Sensitivity Analysis for LEBS Plant Capital and Busbar Costs

Parameter Description	Input Data	Parameter		Case	Total		Levelized Busbar Cost	
	Difference From Base	Value	Units		Plant Investment		Difference From Base	
					\$million	\$/kW net		(cents/kWh)
Capital Cost and Financing								
Total Plant Cost	-15%	1,110	\$/kW	3	479,956	1,181	3.34	-9.3%
AFUDC Rate	-10%	1,176	\$/kW	4	508,189	1,251	3.45	-6.2%
	Base	1,306	\$/kW	2	564,654	1,389	3.68	0.0%
	10%	1,437	\$/kW	5	621,119	1,528	3.90	6.2%
		8.4%		6	570,141	1,403	3.70	0.5%
	Base	7.4%		2	564,654	1,389	3.68	0.0%
		6.4%		7	559,202	1,376	3.66	-0.5%
Performance								
Turbine Cycle Heat I	-5%	6,470	Btu/kWh	8	564,654	1,389	3.63	-1.4%
	Base	6,811	Btu/kWh	2	564,654	1,389	3.68	0.0%
	5%	7,152	Btu/kWh	9	564,654	1,389	3.73	1.4%
Auxiliary Power								
	-10%	22.2	MW	10	564,654	1,389	3.67	-0.2%
	Base	24.6	MW	2	564,654	1,389	3.68	0.0%
	10%	27.1	MW	11	564,654	1,389	3.68	0.2%
Capacity Factor								
		85%		12	564,654	1,389	3.39	-7.8%
	Base	75%		2	564,654	1,389	3.68	0.0%
		65%		13	564,654	1,389	4.05	10.1%
Fuel and O&M Costs (July 96)								
Fuel Price	-10%	1.19	\$/MBtu	14	564,654	1,389	3.58	-2.6%
	Base	1.32	\$/MBtu	2	564,654	1,389	3.68	0.0%
	10%	1.45	\$/MBtu	15	564,654	1,389	3.77	2.6%
Total O&M Cost								
	-10%			16	564,654	1,389	3.60	-2.1%
	Base			2	564,654	1,389	3.68	0.0%
	10%			17	564,654	1,389	3.75	2.1%
Optimistic Case ¹								
				18	475,322	1,170	2.87	-22.0%
	Base			2	564,654	1,389	3.68	0.0%

Notes: 1 Optimistic case assumes 85% capacity factor, 15% reduction in TPC, 10% reduction in coal price, 10% reduction in O&M costs, 5% reduction in TCHR, 1% reduction in the AFUDC rate.

(constant \$, Jan-97)

The most significant effects on busbar cost are caused by variations in the total plant cost, the capacity factor, the fuel price, and the total O&M costs. The effect of a plus or minus 10% reduction in the total plant cost (TPC) can vary the levelized busbar cost by approximately 6%. An increase in the capacity factor to 85% would decrease the levelized busbar cost by nearly 8%. A 10% reduction in the coal price would decrease the busbar cost by approximately 2.6%. A 10% reduction in the total O&M costs would decrease the busbar cost by approximately 2.1%.

An optimistic case was developed to assess the “downside” limits of the levelized busbar cost. These limits include reductions from the base case for parameters that have a significant effect on levelized busbar cost (such as capital, turbine cycle heat rate, coal price, O&M cost). This optimistic case is projected to incur a busbar cost of just less than 3 cents/kWh.

Conclusion

Utilizing the results of this sensitivity analysis and the Total Plant Cost for the Updated LEBS plant of \$536.9 million dollars, the levelized busbar cost is interpolated to be 3.71 cents/kWh versus 3.68 for the base LEBS design. Table 16 compares the capital, levelized busbar, and coal costs for the three plants showing that the cost impact of even a conservative approach to providing corrosion resistance is a 1.1% increase in TPI and less than 1% in busbar cost indicating minimal, perhaps negligible impact in whatever the current cost context becomes.

Table 16: Comparison of Costs

Phase	Capital Cost ¹ \$/kW	Busbar Cost ¢/kW	Coal Price \$/MBtu
Conventional 1997	\$1,217	3.7	1.32
LEBS Boiler Goals	\$1,306	3.68	1.32
Updated LEBS	\$1,321	3.71	1.32

¹ Capital cost is without AFUDC

COAL ASH CORROSION RESISTANT MATERIALS TESTING
Final Report
Including Topical Report: Removal of Section “B”

APPENDICES

U.S. Department of Energy Contract:
Ohio Coal Development Office Grant Agreement:
McDermott Technology, Inc. Contract:

DE-FC26-99FT40525
CDO/D-97-02
CRD 1392

INDEX TO APPENDICES

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Appendix A
Analysis of Performance
Section B
Save 25

Overview of Results: Save 25

Four Save 25 samples were installed into four different locations each of the three test sections. The samples were located at positions that resulted in a progressively higher exposure temperature. All four of the Save 25 samples survived for the full intended exposure period for test Section A (i.e. 15.5 months). However, Save 25 exhibited an excessive wastage rate at higher temperature, and none of the Save 25 samples located in these positions in test Sections B and C survived for their full intended exposure period. This is summarized in the paragraphs that follow and in the table below.

The analysis of Section A revealed that, after approximately 15.5 months of exposure, the Save 25 Sample K-L had lost 334 mils of its original 400 mil wall thickness. Shortly thereafter, the Save 25 Sample K-L in Section C was found to be completely perforated after 18.6 months. Due to this event, and based on in situ measurements within the Niles boiler, the Save 25 Sample K-L was also removed from Section B after 18.6 months and replaced with a more corrosion resistant material.

The high corrosion rate of the K-L samples raised concerns about the potential for early failure of the Save 25 samples that were continuing in service at other locations in Sections B and C. Monitoring revealed that, after about 21.5 months of service, the Save 25 samples at locations, D-E and Z-AA had suffered severe wastage. When this excessive wastage was discovered, Sample D-E in Section C was weld overlay repaired and put back into service. For Section B, Sample D-E was removed from service and replaced with a more corrosion resistant material. Similarly, Sample Z-AA was removed and replaced in Sections B and C after 21.5 months of service.

It should also be noted that the Save 25 sample with the lowest temperature exposure (Sample II-JJ) survived for the full intended exposure period for all three sections. See the summary table below.

		Section A	Section C	Section B
	Full Exposure Period:	15.5 months	28.5 months	37 months
Sample	Nominal Temperature	Removed	Removed	Removed
K-L	1168 – 1180 F	15.5 months	18.6 months	18.6 months
D-E	1145 – 1158 F	15.5 months	18.6 months *	21.5 months
Z-AA	1084 – 1096 F	15.5 months	18.6 months	21.5 months
II-JJ	1043 – 1058 F	15.5 months	28.5 months	37 months

* - This sample was not removed from service. Instead it was weld overlay repaired, and as such, continued in service. The weld overlay made this sample useless for further analysis.

The dimensional analyses of all four of the Save 25 tube samples from Section B are included in this report. However, the metallurgical analysis focused on Sample K-L which had the highest wastage rate of any of the Save 25 samples in the test section. The “gray” colored boxes above show which sample was subjected to metallurgical analysis for each test section.

Review of the data revealed that, with the exception of the low exposure temperature Sample II-JJ, the remaining three Save 25 samples all experienced especially high wastage rates (ranging from 168 mils/year to 228 mils/year). The wastage rate generally increased as a function of

temperature, see Figure A-16. The figure below provides the positions within Section B for each of the four Save 25 samples.

Evaluation of the metallographic cross section for Sample K-L (1168 F) from Section B revealed that, for the highest wastage rate 2:30 o'clock orientation, the external surface evidenced a reasonably continuous two-layer scale. The inner layer, adjacent to the scale/metal interface, was high in chromium and sulfur, (see Figure A-26 for the results of analyses, and Figure A-25b for locations). This inner layer appeared to be frangible facilitating separation of the scale from the metal along the interface, see Figure A-25a. The outer layer of the scale was enriched in iron and depleted in nickel. It also was coated with a very thin deposit/scale conglomerate which evidenced some small amount of potassium (0.36%).

A second high wastage rate region also was examined for Sample K-L. The 9:30 o'clock orientation was noted to have a significant amount of scale and deposit intact and in place. The analysis at this orientation focused on characterizing the nature of the deposit and scale. It also attempted to characterize any diffusion gradients observed in the metal along the interface. The intent was to gain a better understanding regarding the corrosion mechanism, and to better understand why Save 25 corroded more rapidly than other alloys of similar chromium content.

An SEM/EDS evaluation of Sample K-L in the 9:30 o'clock orientation revealed that the deposit was comprised of two layers, see Figure A-18. Figure A-19a reveals that the outer layer had a fine granular appearance. Analysis revealed this layer to have iron, silicon, and aluminum, and oxygen constituents consistent with fly ash, see the table in Figure A-20. This region also was rich in sulfur (7.36%), phosphorous (2.57%) and potassium (6.64%). Thus, the deposit contained the elemental constituents needed to support a coal ash corrosion mechanism.

Figure A-19b shows that the inner layer of the deposit was "stratified", having alternate layers of deposit and iron-rich corrosion product. Per the table in Figure A-20 this layer contained reduced concentrations of sulfur (1.23%) and potassium (0.59%). The stratified characteristic of the deposit in this layer suggests that the underlying tube metal was the source for the iron-rich corrosion product (rather than it being carried to this location and deposited). This is consistent with the iron-rich (55.2%) characteristics of the outer layer of the scale that coats the scale/metal interface. It is, however, interesting to note that the corrosion scale strata contain little if any of the other metallic constituents of the underlying tube. Only minimal chromium (0.50%) was found in the scale, and no nickel, copper, or tungsten.

Per the table in Figure A-20, and as was suggested above, the outer layer of the scale is iron-rich (55.2%). It also has a significant amount of nickel (22.9%), and a smaller amount of chromium (8.68%). The oxygen content is 11.5%. Sulfur is present at a reduced level relative to the deposit (0.53% vs 1.23%), and no potassium was found in this layer.

The EDS analysis (in Figure A-20) reveals that the inner layer of the scale (shown in Figure A-19b) had a reduced content of iron (18.3%) and nickel (8.84%), but it was significantly enriched in chromium (52.2%) and sulfur (3.74%). It should be noted that sulfur enrichment also was noted in the scale immediately adjacent to the scale/metal interface at the 2:30 orientation of this sample. The combined evidence suggests that a chromium rich scale was established with iron and nickel diffusing outward to the scale/deposit interface, and sulfur diffusing inward.

Closer examination of the scale/deposit interface revealed evidence of a layer that can be described as a “fused conglomerate”, see Figure A-21. Coal ash corrosion involves dissolution of a protective oxide scale by a molten alkali-metal-sulfate, and the “fused conglomerate” might well have been molten at service temperatures. EDS analyses show that the light colored matrix of this conglomerate is primarily an iron-rich oxide, (see the analysis in Figure A-24b), and the spherical particles are comprised of iron, silicon, aluminum, oxygen and potassium, (see the analysis in Figure A-24a). EDS “dot maps” (Figure A-22) and “line scans” (Figure A-23) were performed, but provided no further clarification.

EDS analysis of the tube metal adjacent to the scale/metal interface (see the table in Figure A-20) reveals that this region is somewhat enriched in chromium (28.6% vs 22.2% in the bulk), and slightly depleted in iron (48.2%) and nickel (18.8%). This is consistent with the evidence above where it was noted that these two constituents were diffusing outward across the scale, and suggests that this is taking place more rapidly than chromium is being taken up into the scale. Copper is somewhat depleted along the scale/metal interface (2.75% vs 3.05% in the bulk). As was pointed out above, copper was not found present in either the inner or outer scale layer.

It should be noted, that while it was not the focus of this investigation, no evidence of metal loss could be found at the I.D. surface of Sample K-L, see Figure A-28. A cross section through the tube-to-tube weld adjacent to Sample II-JJ revealed only that the Inconel 625 weld metal appears to be more resistant to corrosion than adjacent Save 25 tube metal, see Figure A-29.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: Save 25

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• In assessing the data for Section B, it is important to understand that, due to excessive thinning, three of the four Save 25 tube samples did not survive for the full 37 month exposure period for Section B.• Figure A-1 shows the positions of all four Save 25 samples within Section B when it was initially installed. Sample K-L (1168 F) was removed after 18.6 months of service. Sample D-E (1145 F) and Sample Z-AA) were removed after 21.6 months of service. The lowest temperature sample, Sample II-JJ (1043 F), survived for the 37 month exposure period of Section B.• The samples that were removed early were set aside for later analysis, and have been included in the current evaluation along with the other tube samples that made up Section B.
Composition Verification.	<ul style="list-style-type: none">• The Save 25 tube samples for this program were manufactured from one heat of material (Heat D621907) by Sumitomo Metals Industries (SMI). The table in Figure A-2 provides a “specified” composition and ladle analysis per the SMI-provided materials certificates.• Previous analysis of the Save 25 samples from Section A showed that for three of the four tube samples, the actual tube copper concentration was slightly high relative to the specified maximum of 4 wt%.• For Section B, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube Sample K-L confirmed that the correct material was used at this location.

Material: Save 25

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance	<ul style="list-style-type: none">• Figure A-3 shows the appearance of the Save 25 tube before exposure.• Figures A-4 through A-7 document the as-received appearance of the Save 25 tube samples after service. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the back-side of the tube relative to the gas flow direction).• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the "o'clock" conventions described above, (with the 12 o'clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o'clock side of the tube faces downward, and the 6 o'clock orientation faces upward within the boiler.• For Figure A-4, the 12 o'clock and 3 o'clock provide evidence of extensive wastage on Sample K-L. At the 6 o'clock position, Sample K-L shows a relatively thick deposit and scale, and evidence of the "white layer" typically associated with coal ash corrosion attack.• Figures A-5 and A-6 show that Sample D-E and Sample Z-AA had little or no deposit on their surface. Sample D-E appeared to have an intermittent scale in the 3 o'clock view as did Sample Z-AA.• Sample II-JJ shows evidence of the gray/white scale associated with molten alkali-iron sulfate attack.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures A-8 through A-11 show the appearance of the external surface of the Save 25 tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for all four samples show the appearance of general wastage due to fireside corrosion.• All four of the Save 25 samples showed evidence of pitting at the 6 o'clock position.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures A-12 through A-15.• The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost.• In some cases, the minimum wall thickness in the cross section was not at one of the eight predetermined locations, (Samples K-L and II-JJ are examples). In these cases, there was no "before" measurement for comparison. So, the average "before" wall thickness was used to calculate the wall thickness lost at these off locations.• For Sample K-L, the wall was completely perforated, so, it was not possible to determine an accurate maximum rate of metal loss.

Material: Save 25

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure A-16 plots the maximum wastage rate against the calculated average surface metal temperature for each of the four Save 25 samples.• As a general trend, it is apparent that the rate of attack increases continuously as the temperature is raised over the interval of roughly 1040 F to 1180 F.• It also was noted that Save 25 suffers minimal wall reduction at 1040 F, but that the rate of metal loss increases dramatically when the temperature is raised to 1080 F.• The observed high rate of metal loss provides the reason that all of the Save 25 samples that saw an exposure of 1080 F and above were removed early from service. Only Sample II-JJ (1040 F) survived for the full 37 month exposure period for Section B.
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure A-17 plots metal loss as a function of time for Save 25 in all three test sections. Note: for Section C, Sample D-E data was not plotted because this sample had been overlain with weld metal, so, no data was available.• The (401 mils) data point for Sample K-L represents complete penetration of the wall (after 18.6 months).• While the data is very limited, data for Sample Z-AA suggest that the corrosion rate slowed with time after an initial rapid loss of wall thickness.• For Sample II-JJ metal loss versus time appears to be linear over the 37 month exposure period.
Metallurgical Analysis – SEM (Sample K-L, 9:30 o'clock)	<ul style="list-style-type: none">• Sample K-L was selected for a detailed SEM/EDS assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected because it had lost the most total wall thickness (and had the highest wastage rate).• Figures A-18 shows the appearance of Sample K-L at the 9:30 o'clock orientation. This orientation was selected for examination due to the fact that a significant amount of deposit and scale remained intact. (The appearance of the scale/metal interface at the highest wastage rate orientation (2:30 o'clock) are discussed later in this appendix).• Figure A-19 shows higher magnification views of the scale/metal interface for the 9:30 o'clock orientation. Figure A-19a shows a relatively thick deposit atop a stratified scale. Figure A-19b shows a higher magnification view of the scale/metal interface.• The numbers on Figures A-19a and A-19b provide the locations for the EDS analyses reported in Figure A-20.

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued. (Sample K-L, 9:30 o'clock)	<ul style="list-style-type: none"> Per Figure A-19a and A-19b, six distinct microstructural regions are in evidence at the scale/metal interface for Sample K-L, (9:30 o'clock). These regions are, starting within the metal and working out: <ul style="list-style-type: none"> <u>Base metal</u> – etch shows grain boundaries and carbides. <u>Diffusion zone – deep etching</u> - This region is obvious as a dark-appearing band that is parallel to, and approximately one grain diameter removed from the metal surface. <u>Diffusion zone – shallow etching</u> – This constitutes the leading edge of the grains as they interface with the scale. <u>Tightly adhering scale</u> – this is seen continuous along the scale/metal interface in this view. <u>Stratified scale (and deposit)</u> – This region lies above and is separated from the adherent scale along the interface. <u>Bulk deposit</u> – A relatively thick layer of deposit is seen in this view.
EDS Analysis Results (Sample K-L, 9:30 o'clock)	<ul style="list-style-type: none"> The table in Figure A-20 provides a summary of the EDS analyses of the locations numbered in Figure A-19a and A-19b. Also shown in this table is a summary of the spectrographic analysis, see Figure A-2. Review of this table suggests the following: <ul style="list-style-type: none"> <u>Area 1: Deposit analysis – light vein in outer layer</u> – The iron content if this region of the deposit is (74.7%), the oxygen content is (17.0%), with silicon (3.09%), aluminum (2.03%), and arsenic (1.71%) comprising the bulk of the remainder. (Based on its location it is assumed that the iron in this region was deposited rather than from the underlying tube metal). <u>Area 2: Deposit analysis – dark fine textured deposit</u> – This bulk deposit is rich in the oxides of silicon (22.2%), iron (19.8%), and aluminum (11.4%). Significantly it is also rich in potassium (6.64%), sulfur (7.36%), and phosphorous (2.57%). <u>Area 3: Deposit analysis – dark fine textured deposit</u> - This area was similar to Area 2 except that the sulfur content was somewhat reduced (1.04%). <u>Area 4: Deposit analysis – light vein in stratified inner layer</u> – This layer is iron (47.0%) and aluminum (37.9%) rich and low in silicon 0.87%). No sulfur was found at this location. <u>Area 5: Deposit analysis – dark vein in stratified inner layer</u> – This layer is comprised almost entirely of iron (83.1%) and oxygen (13.05). Some sulfur (1.23%) also is present. <u>Area 6: Deposit analysis – very dark vein in stratified inner layer</u> – This analysis is suggestive of the analysis for Area 2 (from the outer layer); however, it has lower potassium (2.89%) and sulfur (1.13%). These are offset by a significant increase in the arsenic (18.2%) content in this region.

Material: **Save 25**

Summary of Findings, (continued)

Issue	Discussion
EDS Analysis Results (Sample K-L, 9:30 o'clock)	<ul style="list-style-type: none">• <u>Area 7: Outer scale</u> – This region of the scale is primarily comprised of the oxides of the underlying tube metal (with the exception of copper). However, relative to the tube metal composition, this scale is enriched in iron (55.2%), and to some extent nickel (22.9%). The outer scale contains somewhat less chromium (8.68%) than the underlying tube metal.• <u>Area 8: Inner scale</u> – Relative to the outer scale (Area 7), this region of the scale along the scale/metal interface is enriched in chromium (52.2%), and depleted in iron (18.3%) and nickel (8.84%). Significantly this region shows an increase in sulfur relative to the outer scale (3.74% vs 0.53%). It also was noted that the scale has picked up tungsten from the underlying tube metal (2.69%), however, no copper was in evidence.• <u>Area 9: Tube metal - light-etching band adjacent to scale/metal interface</u> – The layer of metal adjacent to the scale/metal interface appears to be enriched in chromium relative to the bulk tube composition (28.6% vs 22.2%) and somewhat depleted in iron (48.2% vs 53.1%), and copper (2.75% vs 3.05%)• <u>Area 10: Tube metal - dark-etching band near scale/metal interface</u> – This band is similar to that adjacent to the scale metal/interface except that now it is only slightly enriched in chromium (25.7% vs 22.2%), and only slightly depleted in iron (51.0% vs 53.1%). In contrast, however, it was noted that this band is somewhat enriched in copper (3.56% vs 3.05%).• <u>Area 11: Tube metal – two grain diameters distant from the scale/metal interface.</u> This area is essentially identical to the bulk tube analysis except that the copper content is somewhat elevated (3.24% vs 3.05%)
EDS Analysis Results – “Dot Maps” (Sample K-L, 9:30 oclock)	<ul style="list-style-type: none">• Figure A-21 shows increasingly higher magnifications of the scale/metal interface shown in Figure A-19, and analyzed point-by-point above. The scale in this region was of particular interest. Note that it is continuous along the interface. Also note, along the outer surface of the scale is what appears to be a fused conglomerate of spherical deposit particles embedded in a matrix. This region was subjected to an EDS “elemental dot mapping”, and an EDS “elemental line scan” to better understand the corrosion mechanism.• Figure A-22 provides elemental dot maps for: chromium, sulfur, oxygen, potassium, copper, nickel, iron, silicon, and sodium. The following observations are offered:• The adherent scale adjacent to the scale/metal interface is enriched in chromium, sulfur, and oxygen. The conglomerate atop the adherent scale is enriched in nickel, iron, and silicon. No evidence was found of potassium or sodium in this region. Nor was copper found in the scale.

Material: **Save 25**

Summary of Findings, (continued)

Issue	Discussion
EDS Analysis Results – “Line Scans” (Sample K-L, 9:30 oclock)	<ul style="list-style-type: none">• Figure A-23 shows elemental line scans across the scale/metal interface analyzed above. The same trends are indicated as were found in the dot maps with the exception that copper appeared to be somewhat enriched in the outer scale conglomerate.
EDS Analysis Results – Point Analysis of Outer Scale Conglomerate (Sample K-L, 9:30 oclock)	<ul style="list-style-type: none">• Figure A-24a shows the results of a point to point analysis of the spherical particles in the outer scale conglomerate. These particles contain significant amounts of iron (33.8%), silicon (23.1%), aluminum (18.1%), and oxygen (16.0%). A significant amount of potassium (4.58%) also was found.• Figure 24b shows the results of a point to point analysis of the matrix of the outer scale conglomerate. The matrix was predominantly iron (81.1%) and oxygen (11.8%), with lesser amounts of silicon (2.27%), and aluminum (1.06%), and much less potassium (0.37%).
Metallurgical Analysis – SEM, Continued. (Sample K-L, 2:30 o'clock)	<ul style="list-style-type: none">• Figure A-25 shows the scale metal interface at the highest wastage rate orientation.• The deposit in this orientation is very thin and appears as a component in the outer scale conglomerate (as described above).• The higher magnification view in Figure A-25b shows that the inner scale is comprised of two layers, a light colored layer (Point “1”) and a dark colored layer adjacent to the scale/metal interface (Point 2).• Figure A-25a shows that the relatively thin deposit and scale have separated from the interface along the line suggested by the dark colored band mentioned above, i.e. the band indicated by Point 2.
EDS Analysis Results – (Sample K-L, 2:30 oclock)	<ul style="list-style-type: none">• The EDS analysis results provided in Figure A-26 show that:<ul style="list-style-type: none">• <u>Area 1: Outer scale</u> - Relative to the underlying tube metal, the outer scale is somewhat enriched in iron (55.2% vs 51.2%) and depleted in nickel (4.02%). The oxygen content is 12.6%). Significant sulfur (2.00%) was present. Potassium (0.36%) was present in a small amount. No copper could be found.• <u>Area 2: Inner Scale</u> - The inner scale differed from the outer scale in that the nickel content was approximately the same as that of the underlying tube metal, i.e. (20.5% vs 19.8%). However, the chromium content was enriched (27.4% vs 22.2%) and the iron content was reduced (38.6% vs 53.1%). Copper was present in the inner scale (1.93%) as was potassium (1.53%). Sulfur (3.01%) was higher than in the outer scale.• <u>Area 3: Light-etching band along scale/metal interface</u> - Slight chromium enrichment was indicated relative to the tube metal composition (25.9% vs 22.2%). Nickel and copper were present at levels reduced relative to the bulk tube metal, (18.5% vs 19.8%) and (2.41% vs 3.05%) respectively.

Material: **Save 25**

Summary of Findings, (continued)

Issue	Discussion
EDS Analysis Results – (Sample K-L, 2:30 oclock)	<ul style="list-style-type: none">• <u>Area 4: Dark etching band near scale/metal interface</u> - The composition here is similar to that of Area 3 with the exception that the chromium content (22.0%) is reduced to that of the bulk tube. However, the copper content is further reduced (1.86%).• <u>Area 5: Near lenticular precipitate</u> – This analysis was not adequate to identify the precipitate.
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">• Figure A-26 shows the duplex nature of the grain size at mid-wall in Sample K-L)• Figure A-27 shows the appearance of the internal surface for Sample K-L. Little evidence of an oxide scale was found.• Figure A-29 shows the appearance of a cross section through Sample II-JJ adjacent to weld “II”

Figure A-1: Schematic Drawing Showing Position of Save 25 Tube Samples Within Section B

1. Drawing shown in same relative orientation as per the actual installation.
2. This group of tube samples was removed from service in November 2001 - highlighted in red.
3. This group of tube samples was removed from service in June 2002 - highlighted in yellow.
4. This group of tube samples was removed from service in September 2003 - highlighted in blue.

Description: Nominal 22Cr/18Ni steel with Nb and N added to provide creep strength.
Source: Sumitomo Metal Industries (SMI)
Reference Composition: “Specified” chemistry – per SMI certificate.

Element	Reference Composition	Composition (a) Heat D621907	Tube Sample D-E	Tube Sample K-L	Tube Sample Z-AA	Tube Sample H-JJ
Ni	15.00 – 22.00	19.80	N/A	19.8	N/A	N/A
Cr	21.00 – 24.00	22.60	N/A	22.2	N/A	N/A
Fe	Balance	Balance	N/A	53.2	N/A	N/A
Mo	-	-	N/A	-	N/A	N/A
Co	-	-	N/A	-	N/A	N/A
C	0.05 – 0.12	0.07	N/A	-	N/A	N/A
N	0.15 – 0.30	0.22	N/A	-	N/A	N/A
B	-	-	N/A	-	N/A	N/A
Mn	2.0 max	0.64	N/A	0.45	N/A	N/A
Si	1.5 max	0.23	N/A	0.26	N/A	N/A
Al	-	-	N/A	-	N/A	N/A
Ti	-	-	N/A	-	N/A	N/A
Al+Ti	-	-	N/A	-	N/A	N/A
Nb	0.30 – 0.60	0.45	N/A	-	N/A	N/A
Ta	-	-	N/A	-	N/A	N/A
Nb+Ta	-	-	N/A	-	N/A	N/A
V	-	-	N/A	-	N/A	N/A
W	0.80 – 2.80	1.31	N/A	1.04	N/A	N/A
Cu	2.00 – 4.00	3.31	N/A	3.05	N/A	N/A
Sn	-	-	N/A	-	N/A	N/A
P	0.030 max	0.022	N/A	-	N/A	N/A
S	0.010 max	(c)	N/A	-	N/A	N/A
O2	-	-	N/A	-	N/A	N/A

a – Ladle analysis
b- By difference
c- Not detected

N/A = Sample not analyzed.

Figure A-2 Semi-Quantitative Composition Verification for Save 25

Figure A-3: Appearance of Save 25 Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure A-4: As-Received Appearance of Sample K-L (Save 25)

(Average metal temperature: 1168 F)

Note: this tube sample was removed from service in November 2001

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure A-5: As-Received Appearance of Sample D-E (Save 25)
(Average metal temperature: 1145 F)

This tube sample was removed from service in June 2002

12 O'Clock – Facing Gas Flow
 (Note: 3 o'clock is up in this image)

3 O'Clock
 (Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure A-6: As-Received Appearance of Sample Z-AA (Save 25)

(Average metal temperature: 1084 F)

Note: this sample was removed from service prematurely in June 2002

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure A-7: As-Received Appearance of Sample II-JJ (Save 25)

(Average metal temperature: 1043 F)

Note: this sample survived for the full 37 month exposure period for Section B.

12 O'Clock
(324 mils lost)

3 O'Clock
(312 mils lost)

6 O'Clock
(15 mils lost)

Figure A-8: OD Surface Appearance After Grit Blast

Material: Save 25
Sample: K-L

12 O'Clock
(288 mils lost)

3 O'Clock
(268 mils lost)

6 O'Clock
(4 mils lost)

Figure A-9: OD Surface Appearance After Grit Blast

Material: Save 25
Sample: D-E

12 O'Clock
(253 mils lost)

3 O'Clock
(59 mils lost)

6 O'Clock
(2 mils lost)

Figure A-10: OD Surface Appearance After Grit Blast

Material: Save 25
Sample: Z-AA

12 O’Clock
(112 mils lost)

3 O’Clock
(47 mils lost)

6 O’Clock
(4 mils lost)

Figure A-11: OD Surface Appearance After Grit Blast

Material: Save 25
Sample: II-JJ

Material: SAVE 25

Sample Location: K-L

Maximum Rate: 228 mils/yr
Maximum Loss Orientation: Approx. 2:30 o'clock
Average Metal Temperature: 1168 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.405	0.400	0.399	0.401	0.398	0.398	0.400	0.404	0.401	0.401
After	0.081	0.073	0.087	0.374	0.383	0.389	0.127	0.114		0.048
Delta	0.324	0.327	0.312	0.027	0.015	0.009	0.273	0.290		0.353

Figure A-12: Silhouette and Wall Thickness Measurements for Sample K-L

Note: this tube sample was removed from service in November 2001.

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Material: SAVE 25

Sample Location: D-E

Maximum Rate: 169 mils/yr
Maximum Loss Orientation: 9:30
Average metal Temperature: 1145 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.400	0.399	0.402	0.400	0.401	0.405	0.401	0.400	0.401	0.401
After	0.112	0.160	0.134	0.396	0.397	0.394	0.168	0.148		0.099
Delta	0.288	0.239	0.268	0.004	0.004	0.011	0.233	0.252		0.302

Figure A-13: Silhouette and Wall Thickness Measurements for Sample D-E

Note: this tube sample was removed from service in June 2002.

Material: SAVE 25

Sample Location: Z-AA
Maximum Rate: 168 mils/yr

Maximum Loss Orientation: **Approx. 9:30 o'clock**
Average metal Temperature: **1084 F**

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.395	0.394	0.398	0.397	0.395	0.395	0.396	0.399	0.396	0.396
After	0.142	0.250	0.339	0.397	0.393	0.388	0.126	0.123		0.095
Delta	0.253	0.144	0.059	0.000	0.002	0.007	0.270	0.276		0.301

Figure A-14: Silhouette and Wall Thickness Measurements for Sample Z-AA

Note: this tube sample was removed from service in June 2002.

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Material: **SAVE 25**

Sample Location: **II-JJ**
Maximum Rate: **50 mils/yr**

Maximum Loss Orientation: **Approx. 9:30 o'clock**
Average metal Temperature: **1047 F**

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.421	0.420	0.423	0.423	0.426	0.428	0.431	0.424	0.425	0.425
After	0.309	0.361	0.376	0.413	0.422	0.424	0.334	0.273		0.270
Delta	0.112	0.059	0.047	0.010	0.004	0.004	0.097	0.151		0.155

Figure A-15: Silhouette and Wall Thickness Measurements for Sample II-JJ

Note: this sample survived for the full 37 month exposure period for Section B.

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Figure A-16: Metal Loss Rate as a Function of Temperature

Material: Save 25

Note: In analyzing these data it is important to keep in mind that, due to excessive corrosion losses, certain samples from Sections B and C were removed early. For example, Sample K-L from Sections B and C (1168 F and 1180 F respectively) were removed in November 2001, shortly after Section A was removed for analysis. Sample D-E from Section C (1158 F) had its' wall thickness built-up using a weld overlay. It then was removed from service at the same time as the Sample Z-AA, i.e. in June 2002. The weld overlay destroyed wall thickness data for Sample D-E in Section C, and accounts for the fact that no data is plotted for this sample. Sample D-E from Section B was not weld overlaid; however it also was removed from service in June 2002.

* - The wall thickness for this sample was completely penetrated; therefore, this data point represents a minimum rate of loss.

Figure A-17: Metal Loss as a Function of Time

Material: Save 25

Note: From the plot above it can be seen that Sample K-L from Section C, which was completely perforated, had somewhat more exposure than the Section A or the Section B samples, even though it was removed at roughly the same time, i.e. November 2001. There was no data for the D-E sample from Section C due to the fact that it was overlain with weld metal. The Z-AA samples from Sections B and C were removed in June 2002. Sample II-JJ experienced the full exposure life for all three sections.

Figure A-18: Low Magnification View of Cross Section in Thinned Region at about 9:30 O'Clock for Tube Sample K-L

(a) External Scale/Metal Interface (BEI - Intermediate Magnification)

(a) External Scale/Metal Interface (BEI - Higher Magnification)

Figure A-19: OD Scale/Metal Interface with Locations of EDS Analyses (9:30 o'clock, Sample K-L)

Figure A-20: EDS Analysis of Deposit/Scale/Metal Interface for Save 25 (Sample K-L)

Area	Description	Ni	Cr	Fe	Cu	Mn	W	Ti	Al	Si	C	O	Ca	K	Na	Mg	As	P	S
1	Light vein in outer deposit	--	--	74.7	--	--	--	0.37	2.03	3.09	--	17.0	--	0.42	--	--	1.71	0.20	0.48
2	Dark fine-textured deposit	--	--	19.8	--	--	--	0.94	11.4	22.2	--	25.2	2.07	6.64	0.92	--	0.845	2.57	7.36
3	Dark fine-textured deposit	--	--	15.6	--	--	--	1.14	17.0	32.9	--	23.3	--	6.16	1.05	0.52	1.04	0.35	1.04
4	Light vein in inner layer of deposit	--	--	47.0	--	--	--	--	37.9	0.87	--	13.8	0.18	0.30	--	--	--	--	--
5	Dark vein in inner deposit	--	--	83.1	--	--	--	0.25	0.46	0.29	--	13.0	--	0.59	0.42	--	0.68	--	1.23
6	Very dark vein in inner deposit	--	0.50	24.9	--	--	--	--	9.67	21.9	--	15.6	--	2.89	--	--	18.2	3.26	1.13
7	Outer scale	22.9	8.68	55.2	--	--	--	--	0.18	0.21	--	11.5	--	--	--	--	0.71	--	0.53
8	Inner scale	8.84	52.2	18.3	--	--	2.69	--	--	--	--	14.2	--	--	--	--	--	--	3.74
9	Light etching band of metal at interface	18.8	28.6	48.2	2.75	0.62	1.06	--	--	--	--	--	--	--	--	--	--	--	--
10	Dark etching band	18.2	25.7	51.0	3.56	0.52	1.00	--	--	--	--	--	--	--	--	--	--	--	--
11	Two grains away from interface	19.7	22.6	53.2	3.24	0.48	0.76	--	--	--	--	--	--	--	--	--	--	--	--
	Midwall	19.8	22.2	53.1	3.05	0.46	1.04	---	--	0.26		--	--	--	--	--	--	--	--
	Reference bulk composition	19.2	21.8	51.2	4.1	0.66	1.35	0.008	0.016	0.24	0.07	--	--	--	--			0.018	0.001

External Scale/Metal Interface (BEI - High Magnification)

(b) External Scale/Metal Interface (BEI - High Magnification)

**Figure A-21: Higher Magnification Views of OD Scale/Metal Interface
(9:30 o'clock, Sample K-L)**

Save 25 cross section 1000x maps

(a) EDS Dot Map for Chromium

Save 25 cross section 1000x maps

(b) EDS Dot Map for Sulfur

Figure A-22: Higher Magnification EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution

Save 25 cross section 1000x maps

(c) EDS Dot Map for Oxygen

Save 25 cross section 1000x maps

(d) EDS Dot Map for Potassium

Figure A-22, Cont. : EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution

Save 25 cross section 1000x maps

(e) EDS Dot Map for Copper

Save 25 cross section 1000x maps

(f) EDS Dot Map for Nickel

Figure A-22, Cont. : EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution

Save 25 cross section 1000x maps

(g) EDS Dot Map for Iron

Save 25 cross section 1000x maps

(h) EDS Dot Map for Silicon

Figure A-22, Cont. : EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution

Save 25 cross section 1000x maps

(i) EDS Dot Map for Sodium

Figure A-22, Cont. : EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution

(a) Chromium Distribution

(b) Sulfur Distribution

Figure A-23: EDS Line Scans of OD Scale/Metal Interface Showing Elemental Distribution

(c) Oxygen Distribution

(d) Nickel Distribution

Figure A-23, Cont. : EDS Line Scans of OD Scale/Metal Interface Showing Elemental Distribution

(e) Copper Distribution

(f) Iron Distribution

Figure A-23, Cont. : EDS Line Scans of OD Scale/Metal Interface Showing Elemental Distribution

(g) Sodium Distribution

(h) Sodium Distribution

Figure A-23, Cont. : EDS Line Scans of OD Scale/Metal Interface Showing Elemental Distribution

Figure A-24a: EDS Analysis of Spherical Particle in Outer Scale Conglomerate

Elt.	Line	Conc	Units	
O	Ka	16.017	wt.%	
Na	Ka	0.567	wt.%	
Mg	Ka	0.421	wt.%	
Al	Ka	18.102	wt.%	
Si	Ka	23.118	wt.%	
S	Ka	0.311	wt.%	
K	Ka	4.577	wt.%	
Ca	Ka	0.678	wt.%	
Ti	Ka	0.774	wt.%	
Cr	Ka	0.625	wt.%	
Fe	Ka	33.815	wt.%	
Ni	Ka	0.994	wt.%	
		100.000	wt.%	Total

Figure A-24b: EDS Analysis of Matrix of Outer Scale Conglomerate

Elt.	Line	Conc	Units	
O	Ka	11.804	wt.%	
Al	Ka	1.057	wt.%	
Si	Ka	2.266	wt.%	
P	Ka	0.252	wt.%	
S	Ka	0.607	wt.%	
K	Ka	0.371	wt.%	
Ti	Ka	0.193	wt.%	
Cr	Ka	0.930	wt.%	
Mn	Ka	0.130	wt.%	
Fe	Ka	81.072	wt.%	
Ni	Ka	1.318	wt.%	
		100.000	wt.%	Total

(a) External Scale/Metal Interface (BEI - Intermediate Magnification)

(b) External Scale/Metal Interface (BEI - High Magnification)

**Figure A-25: OD Scale/Metal Interface with Locations of EDS Analyses
(2:30 o'clock, Sample K-L)**

Figure A-26: EDS Analysis of Deposit/Scale/Metal Interface for Save 25 (Sample K-L)

Area	Description	Ni	Cr	Fe	Cu	Mn	W	Ti	Al	Si	C	O	Ca	K	Na	Mg	As	P	S
1	Outer scale	4.02	22.4	55.2	--	--	--	--	0.24	2.24	--	12.6	--	0.36	--	--	0.88	--	2.00
2	Inner scale	20.5	27.4	38.6	1.93	--	--	--	--	0.81	--	6.18	--	1.53	--	--	--	--	3.01
3	Light etching band of metal at interface	18.5	25.9	52.3	2.41	--	0.49	--	--	0.32	--	--	--	--	--	--	--	--	--
4	Dark etching band	18.5	22.0	51.8	1.86	--	0.34	--	--	--	--	4.87	--	0.66	--	--	--	--	--
5	Near lenticular precipitate	18.6	22.5	46.1	1.69		0.73				4.94	4.79		0.62					
	Midwall	19.8	22.2	53.1	3.05	0.46	1.04	---	--	0.26		--	--	--	--	--	--	--	--
	Reference bulk composition	19.2	21.8	51.2	4.1	0.66	1.35	0.008	0.016	0.24	0.07	--	--	--	--			0.018	0.001

Figure A-27: SEM Mid-Wall Microstructure: Save 25 (Sample K-L)
Note: Electrolytic 10% oxalic acid etch, 9V OCP

Figure A-28: SEM ID Microstructure: Save 25 (Sample K-L)

Figure A-29: Longitudinal Cross-Section: Save 25 Adjacent to Weld “II”

Appendix B
Analysis of Performance
Section B
Modified 800H

Overview of Results: Modified 800H

During the analysis of Section A, in 2002, dimensional measurements showed that, after approximately 15.5 months of exposure, the Modified 800H Sample L-M had lost 230 mils of its original 400 mil wall thickness. It thus had sustained a rate of wall thickness loss of 178 mils per year*. This high wastage rate raised concerns about the potential longevity of the Modified 800H samples at the L-M positions in Sections B and C. So, the L-M samples were removed, after about 18.6 months of exposure, and replaced with a more corrosion resistant material. The intent was to ensure that neither Section C nor Section B would need to come out early.

The performance of the L-M samples raised concerns about the potential for early failure of Modified 800H samples at other locations. So, the Modified 800H samples at locations, E-F and Y-Z were monitored closely during subsequent outages. This led to the Sample E-F being removed and replaced in Sections B and C after about three additional months at temperature.

Lastly, due to similar concerns about excessive metal loss, the tube sample at location Y-Z was removed from Section B at the same time that the Section C sample was removed for evaluation. Thus, all of the Modified 800H samples survived for the full exposure period for Section A, One of the samples survived for the full exposure period for Section C, and none of the samples survived for the full intended 37 months of exposure for Section B. This history is summarized in the table below:

		Section A	Section C	Section B
	Full Exposure Period:	15.5 months	28.5 months	37 months
Sample	Nominal Temperature	Removed	Removed	Removed
L-M	1172 – 1185 F	15.5 months	18.6 months	18.6 months
E-F	1149 – 1162 F	15.5 months	21.5 months	21.5 months
Y-Z	1088 – 1099 F	15.5 months	28.5 months	28.5 months

The dimensional analysis of all three of the Section B tube samples (i.e. Sample L-M, Sample E-F, and Sample Y-Z) is included in this report. However, the metallurgical analysis focused on Sample Y-Z which had the longest test exposure for any of the Section B samples (i.e. 28.5 months), and the lowest exposure temperature (i.e. 1092 F). At the time of its removal, Sample Y-Z had lost a slightly greater percentage of its wall thickness than for the other two samples (which albeit had been removed earlier). The “gray” colored boxes above show which sample was subjected to metallurgical analysis for each test section.

Review of the data revealed that the metal loss rate for the Modified 800H samples was generally high and generally increased as a function of temperature, see Figure B-13. The Section A data presented the only instance where there was a slight decrease in rate at the highest exposure temperature. It was also noted that there was considerable spread in the data at the lowest exposure temperatures (i.e. for Sample Y-Z). The figure below provides the locations for these samples.

Material: Modified 800H

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• In assessing the data for Section C, it is important to understand that some tube samples had to be removed from the section early due to excessive thinning. The schematic in Figure B-1 shows the relative positions of the Modified 800H samples in all three sections. Also, shown are the positions of all of the excessively thinned tubes that were removed and replaced in order to extend the life of Section B.• All three of the modified 800H samples were removed early. Sample L-M was removed in November 2001. Sample E-F was removed in June 2002. Sample Y-Z was removed in September 2003.• The samples that were removed early were set aside for analysis, the results of which have been included in the current evaluation.• Also shown in this figure is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• The table in Figure B-1 provides a reference composition from Oak Ridge National Laboratory (ORNL) literature for this alloy.• ORNL provided material from three different heats of Modified 800H for assessment in this program. The composition for each of the three heats also is reported.• During the Section A evaluation, detailed composition verification was undertaken for each tube sample that was removed from service. This served, in part, to verify that each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample Y-Z confirmed that the correct material was used at this location.

Material: Modified 800H

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance	<ul style="list-style-type: none">• Figure B-3 documents the typical appearance of this material when it was received from ORNL.• Figures B-4 through B-6 document the as-received appearance of the external surface of the tube samples after service exposure. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the "o'clock" conventions described above, (with the 12 o'clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o'clock side of the tube faces downward, and the 6 o'clock orientation faces upward within the boiler.• External tube wastage is visible for all three samples; however, this is more clearly shown in the tube silhouette images that follow.• A relatively thick deposit and scale is seen on Sample L-M (removed November 2001). This deposit was thickest on the 6 o'clock (upward) side of the tube. A thick build up is not in evidence on Sample E-F (removed June 2002) or Sample Y-Z (removed September 2003).• The gray/white deposit/scale (and underlying shiny black scale) associated with molten alkali-iron sulfate attack is clearly shown at the 6 o'clock position for Sample L-M. The 3 o'clock (high metal loss position) is relatively bare of deposit.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures B-7 through B-9 show the appearance of the external surface of the Modified 800H tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for all three samples show the appearance of general wastage. For all three samples, the 6 o'clock position shows evidence of shallow pitting.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures B-10 through B-12.• The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost.• For all three tube samples, the minimum wall thickness in the cross section was not at one of the eight predetermined locations. In these cases, there was no "before" measurement for comparison. So, the average "before" wall thickness was used to calculate the wall thickness lost at these off locations.

Material: Modified 800H

Summary of Findings, (continued)

Issue	Discussion
Rate of Wall Thickness Loss Versus Average Surface Metal Temperature	<ul style="list-style-type: none">• The chart in Figure B-13 plots the maximum rate of wall thickness lost against the calculated average surface metal temperature for the three Modified 800H samples in Section B. Similar data from Sections A and C also are provided on this chart.• Review of these data reveals a relatively high rate of metal loss for all locations.• For Sections B and C, the rate of metal loss increased with temperature. These are similar to the results for Section A with the exception that, for Section A, the rate at 1150 F was somewhat higher than that at 1174 F.• It also was noted that Sample Y-Z experienced a much higher rate of metal loss in Section A than it did in Sections B or C.• These inconsistencies are noted, however, they are not surprising given the relatively limited sampling of this program..
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure B-14 plots metal loss as a function of time for each sample locations for all three sections.• Shortly after Section A was removed for analysis, the tube Sample L-M was also removed and replaced in Sections B and C due to excessive metal loss.• Metal losses in Sample E-F as a function of time provide the reason that it was removed early from Sections B and C.• In Section C, Sample Y-Z lost less wall thickness in 28.5 months of exposure, than it did in Section A in 18.6 months.• The variability noted here for all three samples is taken as an indication of the data spread that can be anticipated for this sort of in situ testing.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample Y-Z was selected for metallographic (and SEM) evaluation because it was the only Modified 800H samples to survive for the full 37 month exposure period of Section B.• It should be noted that this sample selection focused the metallurgical analysis on the lowest temperature location (1099 F) rather than on one of the higher temperature / higher rate specimens.• An SEM/EDS assessment was performed to characterize the constituents and structure at the external and internal surfaces.• The SEM evaluation focused on the region of the tube where the maximum amount of material was lost.

Material: Modified 800H

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">• Figure B-15a shows a back scattered electron image of Sample Y-Z at the thinnest location. No external deposit is in evidence at this location, and the external scale is not continuous. This is further emphasized in Figure 15b which shows a higher magnification view of the external scale/metal interface.• Figure 16 shows the scale metal interface at a location where some small amount of external deposit remained.• Figure 16 (and Figure 15b) shows regions of interest starting within the metal and working out:<ul style="list-style-type: none">○ <u>Base metal</u> – oxalic acid etch delineates grain boundaries and carbides.○ <u>Deeply etching base metal</u> – this region is obvious as a dark-appearing band that is parallel to the metal surface, (see Area 6, Figure B-16). This deeper etch likely reflects composition differences due to diffusion in this region.○ <u>Light etching base metal</u> – this region is comprised of the grains along the scale/metal interface. It will later be shown to be somewhat depleted in chromium.○ <u>Thin adhering scale</u> – this is seen continuous along the surface. EDS analysis will later show that this is predominantly a sulfur-bearing chromium-oxide.• Figure B-17 shows the duplex grain size microstructure at mid-wall in Sample Y-Z. A blocky intragranular precipitate was in evidence along with fine precipitates throughout.• Figure B-17 shows the appearance of the internal metal surface for Sample Y-Z. This region seems relatively unaffected due to service exposure.
EDS Analysis Results	<ul style="list-style-type: none">• The table in Figure B-19 provides a summary of the EDS analyses of the locations numbered in Figure B-16. Review suggests:<ul style="list-style-type: none">• <u>Area 1: The outer deposit layer (See Figure B-16)</u> – The deposit is primarily comprised of the oxides of iron, nickel, silicon and aluminum. A significant amount of potassium was noted (2.79%). Sulfur was on the order of 0.36%.• <u>Area 2: Fused inner deposit</u> – This region had significantly more iron and nickel, and much less silicon, aluminum, potassium, and sulfur.• <u>Area 3: Light colored outer scale</u> - This zone was predominantly comprised of oxides of chromium (48.8%), iron (25.4%), and nickel (10.5%). Potassium was significantly decreased relative to its content in the outer deposit (0.18%). Sulfur was increased relative to its content in the outer deposit (0.68%).

Material: Modified 800H

Summary of Findings, (continued)

Issue	Discussion
EDS Analysis Results, continued.	<ul style="list-style-type: none"><li data-bbox="548 384 1365 541">• <u>Area 4: Dark colored inner scale</u> – The chromium content of this zone is somewhat increased while the contents of iron and nickel are somewhat decreased. The most important issue identified was that the sulfur increased significantly (5.63%) along the scale/metal interface.<li data-bbox="548 552 1365 716">• <u>Area 5: Light etching metal along scale/metal interface</u> – This zone appears to be depleted in chromium relative to the bulk (14.9% vs 20.4%). It thus also is somewhat enriched in iron and nickel. Some small amount of sulfur is present (0.36%) which is over and above that of the bulk chemistry.<li data-bbox="548 726 1365 850">• <u>Area 6: Dark etching metal adjacent to Area 5:</u> - Chromium content is the same as the bulk at this location, as are the concentrations of iron and nickel.. This area also is somewhat enriched in sulfur (0.50%).

Figure B-1: Schematic Drawing Showing Position of Modified 800H Tube Samples Within Section B

1. Drawing shown in same relative orientation as per the actual installation.
2. This group of tube samples was removed from service in November 2001 - highlighted in red.
3. This group of tube samples was removed from service in June 2002 - highlighted in yellow.
4. This group of tube samples was removed from service in September 2003 - highlighted in blue.

Figure B-2 Semi-Quantitative Composition Verification for Modified 800H

Description: Nominal 20Cr/30Ni steel with improved creep strength due to addition of V, Nb, Ti, and B
Source: Oak Ridge National Laboratory (ORNL)
Reference Composition: “Target” Chemistry per ORNL (Reference 1).

Element	Reference Composition	Composition Heat 17423	Composition Heat 17424	Composition Heat 17433	Tube Sample E-F	Tube Sample L-M	Tube Sample Y-Z
Ni	31.0	30.74	31.04	31.10	N/A	N/A	31.4
Cr	20.0	19.89	19.98	19.91	N/A	N/A	20.1
Fe	Balance	-	-	-	N/A	N/A	45.4
Mo	1.5	1.50	1.52	1.51	N/A	N/A	0.90
Co	-	0.03	<0.01	<0.01	N/A	N/A	--
C	0.09	0.10	0.10	0.10	N/A	N/A	--
N	-	0.026	0.029	0.018	N/A	N/A	--
B	0.005	-	-	-	N/A	N/A	--
Mn	2.00	1.93	1.94	1.93	N/A	N/A	1.77
Si	0.25	0.24	0.24	0.26	N/A	N/A	0.42
Al	-	<0.01	<0.01	<0.01	N/A	N/A	--
Ti	0.25	0.11	0.15	0.03	N/A	N/A	--
Nb	0.25	0.26	0.26	0.25	N/A	N/A	--
Ta	-	<0.01	(a)	(a)	N/A	N/A	--
Nb+Ta	-	-	-	-	N/A	N/A	--
V	0.4	0.38	0.23	0.37	N/A	N/A	--
Cu	-	<0.01	<0.01	<0.01	N/A	N/A	--
Sn	-	-	-	-	N/A	N/A	--
P	-	0.009	(a)	0.002	N/A	N/A	--
S	-	0.003	0.002	0.005	N/A	N/A	--
O2	-	0.004	0.008	0.015	N/A	N/A	--

- a- Not analyzed.
b- By difference.

Reference 1: “Fabrication of Test Tubes for Coal Ash Corrosion Testing”, Sikka, V.K., Swindeman, R.W., Wright, I.G., Judkins, R.R., Johnson, R., Proc, 13th Annual Conf. on Fossil Energy Mat’ls, May 1999.

Note: Sample E-F was from Heat 17433
Sample L-M was from Heat 17423
Sample Y-Z was from Heat 17424
N/A = Tube sample not analyzed.

Figure B-3: Appearance of Modified 800H Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
 (Note: 3 o'clock is up in this image)

3 O'Clock
 (Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow
 (Note: box shows location of deposit and scale associated with coal ash corrosion)

Figure B-4 As-Received Appearance of Sample L-M (Modified 800H)
 (Average surface metal temperature: 1172 °F)

Note: this tube sample was removed from service on November 2001

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure B-5 As-Received Appearance of Sample E-F (Modified 800H)
(Average surface metal temperature: 1149 °F)

Note: this tube sample was removed from service in June 2002

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure B-6 As-Received Appearance of Sample Y-Z (Modified 800H)

(Average surface metal temperature: 1088 °F)

Note: this tube sample was removed from service in September 2003

12 O'Clock
(191 mils lost)

3 O'Clock
(239 mils lost)

6 O'Clock
(4 mils lost)

Figure B-8 OD Surface Appearance After Grit Blast

Material: Modified 800H
Sample: L-M

12 O'Clock
(212 mils lost)

3 O'Clock
(204 mils lost)

6 O'Clock
(7 mils lost)

Figure B-8 OD Surface Appearance After Grit Blast

Material: Modified 800H
Sample: E-F

12 O'Clock
(158 mils lost)

3 O'Clock
(78 mils lost)

6 O'Clock
(2 mils lost)

Figure B-9 OD Surface Appearance After Grit Blast

Material: Modified 800H

Sample: Y-Z

Material:

Modified 800H

Sample Location:

L-M

Maximum Rate:

161 mils/yr

Maximum Loss Orientation:

Approx. 2:00 o'clock

Average Metal Temperature:

1172 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.402	0.401	0.400	0.400	0.398	0.398	0.399	0.400	0.400	0.399
After	0.211	0.228	0.161	0.388	0.394	0.387	0.237	0.227		0.150
Delta	0.191	0.173	0.239	0.012	0.004	0.011	0.162	0.173		0.249

Figure B-10: Silhouette and Wall Thickness Measurements for Sample L-M

Note: this tube sample was removed from service on November 2001.

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Material:

Modified 800H

Sample Location:

E-F

Maximum Rate:

140 mils/yr

Maximum Loss Orientation:

Approx. 2:00 o'clock

Average Metal Temperature:

1149 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.399	0.399	0.399	0.399	0.398	0.399	0.400	0.400	0.399	0.399
After	0.187	0.209	0.195	0.391	0.391	0.389	0.220	0.226		0.152
Delta	0.212	0.190	0.204	0.008	0.007	0.010	0.180	0.174		0.247

Figure B-11: Silhouette and Wall Thickness Measurements for Sample E-F

Note: this tube sample was removed from service in June 2002.

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Material:	Modified 800H
Sample Location:	Y-Z
Maximum Rate:	109 mils/yr
Maximum Loss Orientation:	Approx. 9:30 o'clock
Average Metal Temperature:	1088 °F

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.400	0.400	0.400	0.400	0.400	0.399	0.400	0.399	0.400	0.400
After	0.242	0.311	0.322	0.394	0.398	0.395	0.224	0.154		0.141
Delta	0.158	0.089	0.078	0.006	0.002	0.004	0.176	0.245		0.259

Figure B-12: Silhouette and Wall Thickness Measurements for Sample Y-Z

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Note: this tube sample was removed from service in September 2003.

Figure B-13: Metal Loss Rate as a Function of Temperature

Material: Modified 800H

Note: In analyzing these data it is important to understand that the three Section C samples were removed at different times, and so they experienced different lengths of exposure. Sample L-M (1185 F) was removed November 2001, shortly after the Section A samples. Sample E-F (1162 F) was removed in June 2002. Sample Y-Z (1099 F) was removed in September 2003.

Figure B-14: Metal Loss as a Function of Time

Material: Modified 800H

Note: Due to concerns about excess wall thinning:

- Sample L-M was removed early from Sections B and C (in November 2001) shortly after the Section A samples were removed.
- Sample E-F was removed early from Sections B and C (in June 2002)
- Sample Y-Z was removed early from Section B at the same time as the Section C samples were removed (in August 2003).

(a) Thinned Region of Tube (Low Magnification)
Note: Box shows position of enlarged area below.

(b) External Scale/Metal Interface (Intermediate Magnification)
Note: that the adherent scale was not continuous along the external surface.

Figure B-15: Microstructure: Modified 800H (Sample Y-Z)

Microstructure at external scale/metal interface.

Figure B-16: Microstructure: Modified 800H (Sample Y-Z)

Note: Numbers indicate the locations of EDS analyses reported later in this appendix.

Note: Photomicrograph at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Figure B-17: Midwall Microstructure: Modified 800H (Sample Y-Z)

Internal Surface Appearance

Figure B-18: ID Microstructure: Modified 800H (Sample Y-Z)

Figure B-19: EDS Analysis of Deposit/Scale/Metal Interface for Modified 800H (Sample Y-Z)

Area	Description	Ni	Cr	Fe	Mo	Mn	V	Ti	Al	Si	C	O	Ca	K	Na	Mg	As	P	S
1	Outer deposit	10.3	0.32	41.5	--	--	0.24	0.42	8.00	13.9	--	15.7	--	2.79	--	--	4.83	1.53	0.36
2	Fused inner deposit	16.2	0.34	64.4	--	--	0.19	0.23	1.38	2.16	--	12.8	--	0.31	--	--	1.28	0.60	0.16
3	Light colored outer scale	10.5	48.8	25.4	--	--	0.38	0.28	--	0.49	--	13.2	--	0.18	--	--	--	--	0.68
4	Dark inner scale	7.80	52.0	20.0	--	--	0.43	0.21	--	0.85	--	13.0	--	--	--	--	--	--	5.63
5	Light etching metal adjacent to scal	35.2	14.9	47.1	--	1.78	--	0.38	--	0.24	--	--	--	--	--	--	--	--	0.36
6	Dark etching band	31.8	19.1	46.3	--	1.74	0.23	--	--	0.33	--	--	--	--	--	--	--	--	0.50
7	Two grains away from interface	31.4	19.9	45.3	1.26	1.60	0.29	--	--	0.23	--	--	--	--	--	--	--	--	--
	Midwall	31.4	20.1	45.4	0.90	1.77	--	--	--	0.42	--	--	--	--	--	--	--	--	--
	Reference composition	30.6	20.4	44.4	1.33	2.13	0.36	--	0.02	0.28	--	--	--	--	--	--	--	--	--

Appendix C
Analysis of Performance
Section B
347 HFG

Overview of Results: 347 HFG

The maximum rate of metal loss for Sample I-J and Sample CC-DD were 175 mils/year and 139 mils/year respectively. Given the fact that these samples had an initial wall thickness of 400 mils, it was anticipated that they would not survive for the full intended 37 month exposure period for test Section B. Accordingly, Sample I-J was removed from Section B after about 18.6 months of exposure, and Sample CC-DD was removed after about 28.5 months in service. Subsequent measurements showed that Sample A-B exhibited a lower wastage rate (67 mils/year) which would have predicted that this sample might have survived for the full 37 month exposure period. However, based on visual inspection, in situ measurements, and judgment at the time, this sample also was removed from service after 28.5 months. Thus, none of the 347 HFG samples were in place in Section B when it was removed after 37 months. The table below provides a summary.

		Section A	Section C	Section B
	Full Exposure Period:	15.5 months	28.5 months	37 months
Sample	Nominal Temperature	Removed	Removed	Removed
I-J	1162 – 1174 F	15.5 months	18.6 months	18.6 months
A-B	1136 – 1147 F	15.5 months	28.5 months	28.5 months
CC-DD	1075 – 1086 F	15.5 months	28.5 months	28.5 months

Comparison of the metal loss rate versus temperature results for Sections A, B and C (see Figure C-13) revealed that, for all three test sections, the sample which saw an intermediate temperature exposure (Sample A-B, at 1136 F in Section B) experienced a lower rate of metal loss than the samples that were at a higher temperature (Sample I-J at 1162 F) and at a lower temperature (Sample CC-DD at 1075 F). It was noted that the sample that experienced the lowest corrosion rate (Sample A-B) was located closer to a boiler wall than the other two samples which were located closer to mid-span. The figure below attempts to make this clearer. The locations of the 347 HFG samples are highlighted in orange.

The tube samples that were subjected to a full metallurgical analysis are highlighted in “gray” in the table above. For each test section, it was originally intended that a full metallurgical analysis would be performed on the sample that experienced the highest rate of metal loss. For example, for Section A, Sample I-J (1164 F) experienced the highest rate of metal loss, so, the results of its analysis are included in the Section A report. Likewise, for Section C, Sample CC-DD (1086 F) experienced the greatest rate of metal loss, and its analytical results are provided in the Section C report. For Section B, Sample I-J (1162 F) had the highest wastage rate; however, Sample CC-

DD (1075 F) was selected for analysis. This decision was based on the fact that Sample CC-DD had a relatively high wastage rate relative to Sample I-J (139 mils/year vs 175 mils/year), and Sample CC-DD had a significantly longer exposure period, (28.5 months vs 15.5 months).

Evaluation of the metallographic cross section for Sample CC-DD revealed that, for the region where the corrosion rate was highest, the sample was almost completely bare of deposit and that the surface scale was discontinuous, see Figure C-15.

The photograph of the scale/metal interface shown in Figure C-16 provides a map for EDS analyses to characterize the nature of scale and deposit on either side of the interface. The following observations are offered relative to the scale:

- A minimal amount of deposit, if any, remains intact on the surface of the scale. Calcium and a small amount of silicon were indicated; however, aluminum, arsenic, potassium and sodium were not.
- The scale contains oxides of the three major alloying elements that comprise 347 HFG, roughly in the proportion, chromium (50%), iron (25%), and nickel (5%). The chromium and nickel content of the scale increased as one progresses from the scale/metal interface outward. The iron content decreased.
- The scale adjacent to the surface had a high sulfur content (5.31%). Progressing outward from the interface, the scale had a band that contained little or no sulfur, and beyond that, the sulfur content rose again but not to the extent encountered at the interface (to approximately 2 to 3%).

The following observations are offered relative to the 347 HFG adjacent to the scale metal interface.

- Chromium depletion was encountered within one or two grain diameters of the interface otherwise the material was unaffected. The chromium depletion was offset by a concomitant increase in iron content in this region. The nickel content remained roughly unchanged.
- There was no evidence of grain boundary penetration. Neither was there evidence of internal sulfidation or oxidation.

In summary, it would appear that sulfur had a strong influence on both the formation and character of the surface scale.

Lastly, it should be noted, that while it was not the focus of this investigation, no evidence of metal loss could be found at the I.D. surface of Sample CC-DD. Also, no weld cross sections are provided in this evaluation because none of the 347 HFG samples survived for the full exposure period, and weld cross sections previously have been provided to characterize performance in the vicinity of welds at shorter exposure periods.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: 347 HFG

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• In assessing the data for Section B, it is important to understand that some tube samples had to be removed from the section early due to excessive thinning. The schematic in Figure C-1 shows the relative positions of the 347 HFG samples in all three sections. Also, shown are the positions of the excessively thinned tubes that were removed and replaced in order to extend the life of Section B.• All three of the 347 HFG sample were removed early. Sample I-J was removed in November 2001, (i.e. about the same time that Section A was removed from service for evaluation). The other two 347 HFG samples were removed when Section C was removed for evaluation (in 2003).• The samples that were removed early were set aside for later analysis, and have been included in the current evaluation.• Also shown in this figure is the calculated average surface metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• The table in Figure C-2 provides the specified composition from ASTM A213 (TP347 HFG).• All of the 347 HFG tubing used in this program came from one heat of material. The table in Figure C-2 provides the heat analysis reported by Sumitomo. The analysis compares well with the specification.• During the Section A evaluation, detailed composition verification was undertaken for every tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample CC-DD confirmed that the correct material was used at this location.

Material: 347 HFG

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance	<ul style="list-style-type: none">• Figure C-3 shows the typical appearance of the 347 HFG material prior to service.• Figures C-4 through C-6 document the as-received appearance of the external surface of the 347 HFG tube samples after they had been removed from service. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the "o'clock" conventions described above, (with the 12 o'clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o'clock side of the tube faces downward, and the 6 o'clock orientation faces upward within the boiler.• Wastage is visible for all three samples in all three orientations.• A rust-red back-side deposit/scale build-up is seen at the 6 o'clock position on all three samples.• A relatively thin red-brown deposit/scale is seen on other surfaces. A dark gray scale appears to underlie the red-brown deposit/scale.• There is no clear evidence in these figures of the gray/white scale associated with molten alkali-iron sulfate attack.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures C-7 through C-9 show the appearance of the external surface of the 347 HFG tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for all three samples show the appearance of general wastage due to fireside corrosion.• No significant pitting was found on the back-side of these samples.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures C-10 through C-12.• The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost.• For all three samples, the minimum wall thickness in the cross section was not at one of the eight predetermined locations. In these cases, there was no "before" measurement for comparison. So, the average "before" wall thickness was used to calculate the wall thickness lost at these off-locations.

Material: 347 HFG

Summary of Findings, (continued)

Issue	Discussion
Rate of Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure C-13 plots the maximum wall thickness lost against the calculated average surface metal temperature for each of the three 347 HFG samples in Section B. Similar data for Sections A and C also are plotted on this chart.• It was noted that, for all three sections, the maximum rate of metal loss was greater at the low and high temperatures, and dipped significantly at an intermediate temperature, i.e. for Sample A-B. The reason for this has not been conclusively determined; however, it has been speculated that the lower corrosion rate for Sample A-B may have been due to the fact that this sample was positioned close to the end of the test section and adjacent to the wall, while the other two specimens were located mid-span in the test section.• It should be noted that all of the 347 HFG samples had an initial wall thickness of 400 mils, and that Sample I-J and Sample CC-DD had a calculated metal loss rate of 175 mils/year and 139 mils/year respectively. If these rates were to continue, these sample would not survive the full 37 months exposure period for Section B. This provides further justification as to why these samples were removed early from all three sections.• The Sample A-B was removed early based on measurements and a judgment call; however, with a metal loss rate of 67 mils/year, it may well have survived for the full 37 month exposure period.
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure C-14 plots metal loss as a function of time for each sample location for all three test sections.• As was previously mentioned, the Sample I-J specimens were removed from Sections B and C after about 18.6 months of exposure. Thus, the reader will find two data points at the end of this time period. The same is true at the 28.5 month exposure durations for Sample A-B and Sample CC-DD.

Material: 347 HFG

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample CC-DD was selected for a detailed SEM/EDS assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that, between the two samples that survived the full Section C exposure period, Sample CC-DD had lost material at the maximum rate. The focus of this investigation was in the region of the tube where the maximum amount of material was lost, i.e. in the thinnest section.• Figure C-15a shows the full cross section in the thinnest region. Little or no deposit can be seen on the external surface of the tube at this location.• Figure C-15b is higher magnification view of the surface at the location indicated by the box in Figure C-15a. This photograph shows that the corrosion scale is not continuous along the surface.• Figure C-16 provides a view of the external scale/metal interface, and documents the numbered positions for EDS analyses that are reported later in this appendix.• A description of the regions is provided below, starting within the metal and working out:<ul style="list-style-type: none">○ <u>Base metal</u> – oxalic acid etch delineates grain boundaries and carbides. It was noted that the grain size was relatively small. Blocky precipitates were noted primarily along grain boundaries. Fine precipitates intra- and intergranular precipitates also were noted.○ <u>Deep etching base metal</u> – It can be seen as the relatively dark-appearing band that is parallel to, and approximately two grain diameters removed from the metal surface.○ <u>Light etching base metal</u> – This region is contiguous with the scale/metal interface (2 to 3 grains wide). Later EDS analysis will show evidence of chromium depletion in this region.○ <u>Corrosion scale</u> – in Figure C-16 this scale continuous along the interface with the underlying metal. EDS analysis will show that this is a chromium-rich oxide. A layered effect is noted that appears to be related to the sulfur content of various regions.○ <u>Thin deposit layer</u> – Figure C-16 seems to show evidence of a thin deposit layer on the outer edges of the scale.• Figure C-17 documents the relatively fine-grain appearance of the mid-wall microstructure for Sample CC-DD.• Figure C-18 shows a cross section along the internal surface of Sample CC-DD. Little or no scale or metal loss was in evidence, however, some etch pits (anomalies of sample preparation technique) are observed.

Material: 347 HFG

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none">• No weld cross sections were taken due to the fact that none of the 347 HFG samples survived for the full 37 month exposure period of Section B.
EDS Analysis Results	<ul style="list-style-type: none">• The table in Figure C-19 provides a summary of the EDS analyses of the locations numbered in Figure C-16. The “areas” below correspond to the numbered locations indicated in that figure.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Area 1: Outermost scale</u> – the visual appearance (in Figure C-16) suggested the possibility of some minimal deposit/scale interface at this location. The EDS analysis shows little evidence of deposit, with the possible exception that some small amount of calcium was found. Sulfur was present in a significant amount (2.11%), however, no evidence was found of potassium• <u>Area 2: Bulk scale</u> – this region appears to be primarily a chromium rich (48.2%) oxide with a significant amount of iron (26.1%) and nickel (6.30%). Sulfur is present at a somewhat increased level (3.79%). No evidence was found of any of the alkali metals.• <u>Area 3: Dark band in scale</u> – the composition of the scale in this region is similar to that of Area 2 with the exception that manganese is increased (3.05% vs 1.39%) and perhaps more significantly sulfur was not detected.• <u>Area 4: – Scale adjacent to scale/metal interface</u> – This scale is similar to the composition of the dark band with the exception that nickel is slightly decreased, and a significant amount of sulfur was found (5.31%)• <u>Area 5: - Metal adjacent to scale/metal interface</u> – This region is somewhat depleted in chromium versus the bulk composition (15.2% vs 18.6%).• <u>Area 6: - Metal approximately five grain diameters from surface</u> – At this point the composition is essentially the same as that at mid-wall.

Figure C-1: Schematic Drawing Showing Position of 347 HFG Tube Samples Within Section B

1. Drawing shown in same relative orientation as per the actual installation.
2. This group of tube samples was removed from service in November 2001 - highlighted in red.
3. This group of tube samples was removed from service in June 2002 - highlighted in yellow.
4. This group of tube samples was removed from service in September 2003 - highlighted in blue.

Figure C-2 Semi-Quantitative Composition Verification for 347 HFG

Description: Nominal 18Cr/11Ni steel with Nb and Ta added to provide creep strength.
Source: Sumitomo Metal Industries (SMI)
Reference Composition: “Specified” chemistry – per ASTM A213 (TP347 HFG).

Element	Reference Composition	Composition (a) Heat D892703	Tube Sample A-B	Tube Sample I-J	Tube Sample CC-DD
Ni	9.00 – 13.0	11.98	N/A	N/A	11.6
Cr	17.0 – 20.0	18.4	N/A	N/A	18.5
Fe	Balance	Balance	N/A	N/A	68.5
Mo	-	-	N/A	N/A	--
Co	-	-	N/A	N/A	--
C	0.06 – 0.10	0.09	N/A	N/A	--
N	-	-	N/A	N/A	--
B	-	-	N/A	N/A	--
Mn	2.00 max	1.46	N/A	N/A	1.12
Si	0.75 max	0.41	N/A	N/A	0.35
Al	-	-	N/A	N/A	--
Ti	-	-	N/A	N/A	--
Al+Ti	-	-	N/A	N/A	--
Nb	-	-	N/A	N/A	--
Ta	-	-	N/A	N/A	--
Nb+Ta	(8 x C) min- 1.0 max	0.9	N/A	N/A	N/D
V	-	-	N/A	N/A	--
W	-	-	N/A	N/A	--
Cu	-	-	N/A	N/A	--
Sn	-	-	N/A	N/A	--
P	0.040 max	0.027	N/A	N/A	--
S	0.030 max	0.001	N/A	N/A	--
O2	-	-	N/A	N/A	--

N/D = EDS technique (gold coating) precluded an accurate niobium determination.

N/A = Tube sample not analyzed.

Figure C-3: Appearance of 347 HFG Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure C-4 As-Received Appearance of Sample I-J (347 HFG)

(Average metal temperature: 1162 F)

Note: this tube sample was removed from service in November 2001.

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure C-5 As-Received Appearance of Sample A-B (347 HFG)

(Average metal temperature: 1136 F)

Note: this tube sample was removed from service in September 2003.

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure C-6 As-Received Appearance of Sample CC-DD (347 HFG)

(Average metal temperature: 1075 F)

Note: this tube sample was removed from service in September 2003.

12 O'Clock
(195 mils lost)

3 O'Clock
(251 mils lost)

6 O'Clock
(7 mil lost)

Figure C-7: OD Surface Appearance After Grit Blast

Material: 347 HFG
Sample: I-J

12 O'Clock
(118 mils lost)

3 O'Clock
(63 mils lost)

6 O'Clock
(12 mil lost)

Figure C-8: OD Surface Appearance After Grit Blast

Material: 347 HFG
Sample: A-B

12 O'Clock
(222 mils lost)

3 O'Clock
(110 mils lost)

6 O'Clock
(8 mils lost)

Figure C-9: OD Surface Appearance After Grit Blast

Material: 347 HFG
Sample: CC-DD

Material: 347 HFG
Sample Location: I-J
Maximum Rate: 175 mils/yr
Maximum Loss Orientation: Approx. 2:30 o'clock
Average metal Temperature: 1162 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.395	0.396	0.399	0.396	0.397	0.402	0.400	0.396	0.398	0.398
After	0.200	0.211	0.148	0.375	0.390	0.382	0.215	0.221		0.126
Delta	0.195	0.185	0.251	0.021	0.007	0.020	0.185	0.175		0.272

Figure C-10: Silhouette and Wall Thickness Measurements for Sample I-J

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Note: this tube sample was removed from service in November 2001.

Material: 347 HFG
Sample Location: A-B
Maximum Rate: 67 mils/yr
Maximum Loss Orientation: Approx. 9:30 o'clock
Average metal Temperature: 1136 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.435	0.439	0.444	0.446	0.444	0.439	0.433	0.431	0.439	0.439
After	0.317	0.373	0.381	0.426	0.432	0.432	0.326	0.330		0.280
Delta	0.118	0.066	0.063	0.020	0.012	0.007	0.107	0.101		0.159

Figure C-11: Silhouette and Wall Thickness Measurements for Sample A-B

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Note: this tube sample was removed from service in September 2003.

Material: 347 HFG
Sample Location: CC-DD
Maximum Rate: 139 mils/yr
Maximum Loss Orientation: Approx. 9:30 o'clock
Average metal Temperature: 1075 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.397	0.400	0.402	0.403	0.402	0.399	0.396	0.397	0.400	0.400
After	0.175	0.274	0.292	0.387	0.394	0.383	0.123	0.124		0.069
Delta	0.222	0.126	0.110	0.016	0.008	0.016	0.273	0.273		0.331

Figure C-12: Silhouette and Wall Thickness Measurements for Sample CC-DD

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Note: this tube sample was removed from service in September 2003.

Figure C-13: Metal Loss Rate as a Function of Temperature

Material: 347 HFG

Note: In analyzing these data it is important to understand that one of the three Section B samples was removed at an earlier date than the other two., and that none of them experienced the full Section B exposure period of 37 months. Sample I-J (1162 F) was removed in November 2001, at about the same time as the Section A samples. Sample A-B (1136 F) and Sample CC-DD (1075 F) were removed in September 2003.

Figure C-14: Metal Loss as a Function of Time

Note: From the plot above it can be seen that, for Section B, Sample I-J was removed from service due to excessive metal losses shortly after Section A was removed for evaluation, i.e. after about 18.6 months of service. Samples CC-DD and A-B both were removed after 28.5 months at about the same time as Section C was removed from service. None of the samples experienced the full 37 month life intended for the samples in Section B.

(a) Thinnest Tube Cross Section (BEI - Low Magnification)

**(b) External Scale/Metal Interface at Area Indicated Above
(BEI - Intermediate Magnification)**

Figure C-15: Microstructure: 347 HFG (Sample CC-DD)

**External Scale/Metal Interface
(BEI - Intermediate Magnification)**

Figure C-16: Microstructure: 347 HFG (Sample CC-DD)

(BEI - Intermediate Magnification)

C-17: Mid-Wall Microstructure: 347 HFG (Sample CC-DD)

Note: Etchant - Electrolytic 10% oxalic acid etch, 9V OCP

BEI - Internal Surface Appearance

Figure C-18: Microstructure: 347 HFG (Sample CC-DD)

Note: Etch pits noted along ID surface.

Figure C-19: EDS Analysis of Deposit/Scale/Metal Interface for 347 HFG (Sample CC-DD)

Area	Description	Ni	Cr	Fe	Cu	Mn	Nb	Mo	Al	Si	C	O	Ca	K	Zn	As	P	S
1	Outermost scale	7.32	57.4	17.5	--	--	--	--	--	1.11	--	14.2	0.30	--	--	--	--	2.11
2	Bulk scale	6.30	48.2	26.1	--	1.39	--	--	--	1.25	--	13.0	--	--	--	--	--	3.79
3	Dark band in scale.	4.82	47.0	24.5	--	3.05	--	--	--	1.62	--	12.1	--	--	--	--	--	--
4	Scale adjacent to metal interface	2.57	48.5	26.3	--	3.07	--	--	--	1.35	--	12.9	--	--	--	--	--	5.31
5	Metal adjacent to interface.	12.2	15.2	70.9	--	1.22	--	--	--	0.51	--	--	--	--	--	--	--	--
6	Metal approx. 5 grains from surface	11.8	18.1	68.5	--	1.13	--	--	--	0.42	--	--	--	--	--	--	--	--
	Midwall analysis	11.6	18.5	68.5	--	1.12	--	--	--	0.35	--	--	--	--	--	--	--	--
	Reference bulk composition	11.9	18.6	64.8	0.20	1.48	0.91	0.24	0.014	0.39	0.10	--	--	--	--	--	--	--

Appendix D
Analysis of Performance
Section B
NF 709

Overview of Results: NF 709

The maximum rate of metal loss for Sample J-K, in Section B, was 164 mils/year. Given the fact that this sample had an initial wall thickness of 400 mils, it was anticipated that this sample would not survive for the full intended 37 month exposure period for test Section B, and it was removed from Section B after about 18.6 months of exposure. Samples C-D and Sample BB-CC experienced a maximum metal loss rate of 92 mils/year and 119 mils/year respectively. These samples were removed from Section B after 28.5 months at temperature due to concerns about the remaining wall thickness. Thus, all of the NF 709 test samples had been replaced before Section B was removed for evaluation after 37 months. The table below provides a summary.

		Section A	Section C	Section B
	Full Exposure Period:	15.5 months	28.5 months	37 months
Sample	Nominal Temperature	Removed	Removed	Removed
J-K	1165 – 1178 F	15.5 months	18.6 months	18.6 months
C-D	1141 – 1153 F	15.5 months	28.5 months	28.5 months
BB-CC	1077 – 1088 F	15.5 months	28.5 months	28.5 months

Comparison of the metal loss rate versus temperature results for Sections A, B and C (see Figure D-13) revealed that, for two of the three test sections, the sample which saw an intermediate temperature exposure (Sample C-D, at 1141 F in Section B) experienced a lower rate of metal loss than the samples that were at a higher temperature (Sample J-K at 1165 F) and at a lower temperature (Sample BB-CC at 1077 F).

The intermediate test sample for test Section C deviated somewhat from the trend noted above in that the metal loss rate for the intermediate temperature sample was between that of the lower and higher temperature samples. Nonetheless, the metal loss rate for the intermediate sample was very close to that of the low temperature sample and these two measurements are judged to be within experimental error, i.e. 100 mils/year for Sample BB-CC (1088 F), and 114 mils/year for Sample C-D (1153 F).

The sample that experienced the lowest corrosion rate for Sections A and B (Sample C-D) was located somewhat closer to a boiler wall than the other two samples which were located closer to mid-span. The figure below shows the sample locations within the test section.

For each test section, the tube samples that were subjected to a full metallurgical analysis are highlighted in "gray" in the table above. It was originally intended that, for any given test section, a full metallurgical analysis would be performed only on the sample that experienced the highest rate of metal loss. For example, for Section A, Sample J-K (1167 F) experienced the highest rate of metal loss, so, the results of its analysis are included in the Section A report. However, for Section C and for Section B, the sample selected for analysis was the sample which had the highest rate of metal loss over the longest exposure period. Thus, for Section C, Sample C-D

(1153 F) was selected for analysis, and its analytical results are provided in the Section C report. For Section B, Sample BB-CC (1077 F) had the higher wastage rate of the two samples that had seen 28.5 months of exposure, thus, it was selected for analysis.

Evaluation of the metallographic cross section for Sample BB-CC revealed that, for the region where the corrosion rate was highest, the sample was almost completely bare of deposit and that the surface scale was discontinuous, see Figure D-15.

The photograph of the scale/metal interface shown in Figure D-15b provides a map for EDS analyses to characterize the nature of scale and deposit on either side of the interface. The following observations are offered relative to the scale:

- A minimal amount of deposit, if any, remains intact on the surface of the scale. This is supported by the amounts of iron (36.3%), silicon (23.4%), aluminum (6.60%), and oxygen (16.2%) that were found. A significant amount of potassium (3.50%) and sulfur (1.38%) were noted, as was a significant amount of arsenic (4.87%) and phosphorous (3.22%).
- The scale contains oxides of the three major alloying elements that comprise NF 709. The chromium content is very high (57.7%) adjacent to the scale/metal interface. The chromium content drops off at the outer edge of the scale (44.3%). While the amounts of iron and nickel increase at the outer edge i.e. from 20.3% to 36.1% for iron, and from 1.59% to 3.35% for nickel.
- The scale adjacent to the surface had a high sulfur content (4.29%). Near to the scale/deposit interface the sulfur content dropped off to (0.73%).

The following observations are offered relative to the NF 709 adjacent to the scale metal interface.

- No evidence of chromium depletion could be found for Sample BB-CC (1077 F), for Section B. Within the limits of the EDS, the composition of the metal was essentially the same (roughly 23% chromium) regardless of position. It should be noted that significant chromium depletion (12.2% chromium) was found during the analysis of Sample C-D (1153 F), for Section C, and that somewhat lesser depletion (19.4% chromium) was found during the analysis of Sample J-K (1167 F), for Section A.
- The variability in chromium depletion between Sections A, B, and C could not be correlated with: temperature, time at temperature, or metal loss rate.
- There was no evidence of grain boundary penetration. Neither was there evidence of internal sulfidation or oxidation.

In summary, it would appear that sulfur had a strong influence on both the formation and character of the surface scale. The high sulfur content at the scale/metal interface would seem to be particularly relevant.

Lastly, it should be noted, that while it was not the focus of this investigation, no evidence of metal loss could be found at the I.D. surface of Sample BB-Cc. Also, no weld cross sections are provided in this evaluation because none of the NF 709 samples survived for the full exposure period, and weld cross sections previously have been provided to characterize performance in the vicinity of welds at shorter exposure periods.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: NF 709

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• In assessing the data for Section B, it is important to understand that some tube samples had to be removed from the section early due to excessive thinning. The schematic in Figure D-1 shows the relative positions of the NF 709 samples in all three sections. Also, shown are the positions of all of the excessively thinned tubes that were removed and replaced in order to extend the life of Section B.• All three NF 709 samples in Section B were removed early. Sample J-K was removed in November 2001, after about 18.6 months in service. The other two NF 709 samples were removed after about 28.5 months in service.• The samples that were removed early were set aside for later analysis, and have been included in the current evaluation along with the other tube samples that made up Section B.• Also shown in this figure is the calculated average surface metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• Tubes from one heat of NF 709 (Heat 58733) were provided by Nippon Steel Corporation (NSC) for testing in this program. NSC also provided the composition for Heat 58733, and a reference target composition that provided the tolerances for the alloying elements in this material. These are shown in the table in Figure D-2 along with the results of a semi-quantitative analysis that was used to verify the composition of one of the NF 709 tubes in Section B.• During the evaluation of Section A, detailed composition verification was undertaken for every tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample BB-CC confirmed that the correct material was used at this location.

Material: NF 709

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance	<ul style="list-style-type: none">• Figure D-3 shows the typical appearance of this tube material as it came from NSC.• Figure D-4 through D-6 document the as-received appearance of the external surface after service in Section B. Three views are provided for each of the three tube samples: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the "o'clock" conventions described above, (with the 12 o'clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o'clock side of the tube faces downward, and the 6 o'clock orientation faces upward within the boiler.• Wastage is most clearly visible at the 3 and 12 o'clock orientations for all three samples. The raised surface of the adjoining Inconel 625 weld metal provides a good reference for this.• No evidence was found of the gray/white scale associated with molten alkali attack.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures D-7 through D-9 show the appearance of the external surface of the NF 709 tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for all three samples show the appearance of general wastage due to fireside corrosion.• The 6 o'clock position for Samples J-K and C-D show the pitting that occurred on the back-side of these samples. Only minimal pitting was noted at the 6 o'clock position for Sample BB-CC.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures D-10 through D-12.• The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost.• For all three samples, the minimum wall thickness in the cross section was not at one of the eight predetermined locations. In these cases, there were no "before" measurement for comparison to determine the "delta". So, the average "before" wall thickness was used to calculate the wall thickness lost at these off-locations.

Material: NF 709

Summary of Findings, (continued)

Issue	Discussion
Rate of Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure D-13 plots the maximum wall thickness lost against the calculated average metal temperature for the three NF 709 samples. Similar data for Sections A and C also are plotted on this chart.• For all three sections, it was noted that there appears to be a “knee” in the plotted curve that comes about due to a decrease in metal loss rate at the intermediate exposure temperature, i.e. Sample C-D (at 1141 F for Section B).
Metal Loss as a Function of Time at Each Location	<ul style="list-style-type: none">• The chart in Figure D-14 plots metal loss as a function of time for each sample location for all three test sections.• Note that the samples from Section B experienced generally longer exposure times; however, all of the Section B samples were removed before the full 37 month exposure period was completed.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample BB-CC was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it had lost the most wall thickness of the two samples that survived for 28.5 months.. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.• Figures D-15a shows a low magnification view of the external scale/metal interface for the thinnest region of Sample BB-CC. Note that there is minimal, if any, deposit remaining at this location, and that the external scale is not continuous.• Figure D-15b shows a higher magnification view of the surface shown in D-15a. The numerical annotation on this image shows the locations of EDS analyses that will be discussed later in this appendix.• Examination of the microstructure at the scale/metal interface reveals the following distinct regions.:<ul style="list-style-type: none">○ <u>Base metal</u> – oxalic acid etch delineates grain boundaries and carbides.○ <u>Dark etching base metal</u> – this region is obvious as a dark-appearing band that is parallel to the metal surface, perhaps see most clearly in Figure D-15b, (location 5). This figure shows that this band runs parallel to the scale/metal interface, and is about two grains wide. While the appearance of the microstructure in this region this is not believed to be an edge effect artifact, the composition was not significantly different from the bulk analysis.○ <u>Light etching diffusion zone</u> – This region constitutes the leading edge of the grains as they interface with the scale, see Figure D-25b, (location 4). A slightly increased sulfur content was the only compositional difference between this location and the bulk.

Material: NF 709

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">○ <u>Tightly adhering scale</u> – This scale is not continuous along the scale/metal interface, see Figure D-15a, and note Figure D-15b, (location 3). EDS analysis shows the scale to be a chromium-rich oxide, and that it contains a significant amount of sulfur.○ <u>Thick and porous deposit/scale conglomerate</u> – see the deposit/scale flake that has separated from the bulk of the scale, locations 1 and 2 in Figure D-15b. EDS analysis shows both potassium and sulfur.• Figure D-16 shows the appearance of the mid-wall microstructure.• Figure D-17 shows the appearance of the internal metal surface for Sample BB-CC. While there was a band of etch pits along the edge of the specimen, no evidence was found of internal metal loss or of an internal oxide scale.
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none">• No weld cross sections were taken due to the fact that none of the NF 709 samples survived for the full 37 month exposure period of Section B.
EDS Analysis Results	<ul style="list-style-type: none">• The table in Figure D-18 provides a summary of the EDS analyses of the locations numbered in Figure D-15b. Also shown for reference in this table are the results the spectrographic analysis that was performed during the assessment of Section A.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Area 1: Deposit attached to outer scale</u> – While the deposit layer is thin, this layer is comprised primarily of the oxides of iron, silicon, and aluminum. Nickel and chromium also were found, presumably as a component of the adjacent scale which had detached from the surface. Alkali metals are present, in particular, potassium at (3.50%). Phosphorous (3.22%) and sulfur (1.38%) are present in significant amounts, as is arsenic (4.87%).• <u>Area 2: Detached scale near interface with deposit</u> – This layer is comprised primarily of a chromium-rich (44.2%) and iron-rich (36.1%) oxide, although there is some small amount of nickel (3.35%). The potassium level is significantly decreased (0.32% vs 3.50%), and only a small amount of silicon, aluminum, and calcium remain. The arsenic and phosphorous are completely missing and the sulfur level has decreased to 0.73%.• <u>Area 3: Adherent scale</u> – the scale adjacent to the scale/metal interface has a significantly increased chromium (57.7%) and sulfur (4.29%) content. The increase in chromium is offset to a great extent by decreases in the iron and nickel contents. Manganese (1.51%) is also present in the scale at a level slightly increased over that of the bulk metal (0.97%)

Material: NF 709

Summary of Findings, (continued)

Issue	Discussion
EDS Analysis Results	<ul style="list-style-type: none">• <u>Area 4: Light etching grains along scale/metal interface</u> – with the exception of a somewhat increased sulfur content the composition of this band is very similar to that of the bulk.• <u>Area 5: Dark etching band</u> – similar in composition to that of the bulk.• <u>Area 6: Bulk composition</u> - compares well with optical spectrograph results.

Figure D-1: Schematic Drawing Showing Position of NF 709 Tube Samples Within Section B

1. Drawing shown in same relative orientation as per the actual installation.
2. This group of tube samples was removed from service in November 2001 - highlighted in red.
3. This group of tube samples was removed from service in June 2002 - highlighted in yellow.
4. This group of tube samples was removed from service in September 2003 - highlighted in blue.

Figure D-2 Semi_Quantitative Composition Verification for NF709

Description: Nominal 20Cr/25Ni steel with Nb and Ti added to provide creep strength.
Source: Nippon Steel Corporation (NSC)
Reference Composition: “Specified” chemistry – per NSC inspection certificate for heat delivered.

Element	Reference Composition	Composition Heat E58733	Tube Sample C-D	Tube Sample J-K	Tube Sample BB-CC
Ni	22.00 - 28.00	24.87	N/A	N/A	24.9
Cr	19.00 - 23.00	22.29	N/A	N/A	22.4
Fe	-	-	N/A	N/A	50.8
Mo	1.00 - 2.00	1.42	N/A	N/A	-
Co	-	-	N/A	N/A	-
C	0.1 max	0.02	N/A	N/A	-
N	0.100 - 0.250	0.176	N/A	N/A	-
B	0.0020 - 0.0100	0.0044	N/A	N/A	-
Mn	1.50 max	0.97	N/A	N/A	0.74
Si	1.00 max	0.40	N/A	N/A	0.54
Al	-	-	N/A	N/A	-
Ti	0.02 - 0.20	0.05	N/A	N/A	-
Al+Ti	-	-	N/A	N/A	-
Nb	0.10 - 0.40	0.23	N/A	N/A	-
Ta	-	-	N/A	N/A	-
Nb+Ta	-	-	N/A	N/A	-
V	-	-	N/A	N/A	-
W	-	-	N/A	N/A	-
Cu	-	-	N/A	N/A	-
Sn	-	-	N/A	N/A	-
P	0.030 max	0.010	N/A	N/A	-
S	0.010 max	0.001	N/A	N/A	0.62
O2	-	-	N/A	N/A	-

N/D = EDS technique (gold coating) precluded an accurate niobium determination.

N/A = Tube sample not analyzed.

Figure D-3: Appearance of NF 709 Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure D-4 As-Received Appearance of Sample J-K (NF 709)

(Average metal temperature: 1165 F)

Note: this tube was removed from service in November 2001

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure D-5 As-Received Appearance of Sample C-D (NF 709)

(Average metal temperature: 1141 F)

Note: this tube was removed from service in September 2003

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure D-6 As-Received Appearance of Sample BB-CC (NF 709)

(Average metal temperature: 1077 F)

Note: this tube was removed from service in September 2003

12 O'Clock
(192 mils lost)

3 O'Clock
(232 mils lost)

6 O'Clock
(5 mil lost)

Figure D-7: OD Surface Appearance After Grit Blast

Material: NF 709
Sample: J-K

Note: this tube was removed from service in November 2001

12 O'Clock
(196 mils lost)

3 O'Clock
(141 mils lost)

6 O'Clock
(8 mils lost)

Figure D-8: OD Surface Appearance After Grit Blast

Material: NF 709
Sample: C-D

Note: this tube was removed from service in September 2003

12 O'Clock
(204 mils lost)

3 O'Clock
(119 mils lost)

6 O'Clock
(0 mils lost)

Figure D-9: OD Surface Appearance After Grit Blast

Material: NF 709
Sample: BB-CC

Note: this tube was removed from service in September 2003

Material: NF 709
Sample Location: J-K
Maximum Rate: 164 mils/yr
Maximum Loss Orientation: Approx. 2:00 o'clock
Average metal Temperature: 1165 F

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.403	0.403	0.403	0.402	0.402	0.400	0.400	0.400	0.402	0.402
After	0.211	0.203	0.171	0.381	0.397	0.388	0.237	0.212		0.148
Delta	0.192	0.200	0.232	0.021	0.005	0.012	0.163	0.188		0.254

Figure D-10: Silhouette and Wall Thickness Measurements for Sample J-K

Note: this tube was removed from service in November 2001.

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Material: NF 709
Sample Location: C-D
Maximum Rate: 92 mils/yr
Maximum Loss Orientation: Approx. 9:30 o'clock
Average metal Temperature: 1141 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.400	0.401	0.401	0.401	0.400	0.398	0.398	0.401	0.400	0.400
After	0.204	0.231	0.260	0.392	0.392	0.389	0.215	0.208		0.182
Delta	0.196	0.170	0.141	0.009	0.008	0.009	0.183	0.193		0.218

Figure D-11: Silhouette and Wall Thickness Measurements for Sample C-D

Note: this tube was removed from service in September 2003.

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Material: NF 709
Sample Location: BB-CC
Maximum Rate: 119 mils/yr
Maximum Loss Orientation: Approx. 9:30 o'clock
Average metal Temperature: 1077 F

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.403	0.401	0.403	0.400	0.398	0.400	0.402	0.402	0.401	0.401
After	0.199	0.287	0.284	0.394	0.398	0.388	0.127	0.220		0.118
Delta	0.204	0.114	0.119	0.006	0.000	0.012	0.275	0.182		0.283

Figure D-12: Silhouette and Wall Thickness Measurements for Sample BB-CC

Note: this tube was removed from service in September 2003.

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Figure D-13: Metal Loss Rate as a Function of Temperature

Material: NF 709

Note: In analyzing these data it is important to understand that all three of the three Section B samples was removed early due to excessive corrosion losses. Sample J-K (1165 F) was removed in November 2001, shortly after Section A was removed for analysis. Sample C-D (1141 F) and Sample BB-CC (1077 F) were removed in September 2003.

Figure B-14: Metal Loss as a Function of Time

Material: Modified NF 709

Note: From the plot above, due to excessive metal losses, Section B Sample J-K was removed early for evaluation in November 2001. Samples C-D and BB-CC were also removed early and at the same time in September 2003..

(a) External Scale/Metal Interface (BEI - Low Magnification)

(b) External Scale/Metal Interface (SEI - Intermediate Magnification)

Figure D-15: Microstructure: NF 709 (Sample BB-CC)

Note: Numbers on photos indicate distinct areas characterized by the visual assessment and EDAX analyses that follow.

Mid-Wall Microstructure (BEI - Low Magnification)

Figure D-16: Microstructure: NF 709 (Sample BB-CC)

Note: Photomicrograph at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Internal Surface Appearance

Figure D-17: ID Microstructure: NF 709 (Sample BB-CC)

Figure D-18: EDS Analysis of Deposit/Scale/Metal Interface for NF 709 (Sample BB-CC)

Area	Description	Ni	Cr	Fe	Mo	Mn	Nb	Ti	Al	Si	C	O	Ca	K	Na	Mg	As	P	S
1	Deposit attached to outer scale	1.22	2.02	36.3	--	--	--	0.57	6.60	23.4	--	16.2	0.22	3.50	0.43	--	4.87	3.22	1.38
2	Scale near scale/deposit interface	3.35	44.3	36.1	--	--	--	--	0.18	1.09	--	13.9	0.07	0.32	--	--	--	--	0.73
3	Adherent inner scale	1.59	57.7	20.3	--	1.51	--	--	--	1.26	--	13.3	--	--	--	--	--	--	4.29
4	Light etching band of metal at interface	24.7	23.6	49.0	--	1.03	--	--	--	0.59	--	--	--	--	--	--	--	--	1.08
5	Dark etching band	25.4	23.1	49.4	--	0.88	--	--	--	0.42	--	--	--	--	--	--	--	--	0.79
6	4-5 grains away from interface	25.1	25.6	50.3	--	0.94	--	--	--	0.48	--	--	--	--	--	--	--	--	0.65
	Midwall	24.9	22.4	50.8	--	0.74	--	--	--	0.54	--	--	--	--	--	--	--	--	0.62
	Reference bulk composition	24.9	22.3	Bal.	1.42	0.97	0.23	0.05	--	0.40	0.02	--	--	--	--	--	--	0.010	0.001

Appendix E
Analysis of Performance
Section B
Fe₃Al / TP 304H

Overview of Results: Fe₃Al / TP 304H

The Fe₃Al / TP 304H tube Sample B-C was removed from Section B and Section C after the same 28.5 month exposure period. These samples exhibited similar metal loss rates of 117 mils/year and 100 mils/year respectively. Both samples experienced a lower rate of metal loss than that of the Fe₃Al / TP 304H sample that was removed from Section A. The Section A sample had a loss rate of 145 mils/year after 15.5 months of exposure. The reason for these differences in wastage rate is not clear. However, it should be noted that, for all three samples, the protective Fe₃Al coating was not in evidence anywhere on the tube surface at the time of the analysis, and based on performance in Section A, it likely disappeared early during the life of the tube sample, (i.e. in less than 15.5 months). In any case, the limited number of Fe₃Al / TP 304H samples in this program, makes it difficult to draw substantive conclusions. The position of Sample B-C is indicated in orange in the following figure.

* **Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: Fe₃Al / TP 304H

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">The schematic in Figure E-1 shows the position of the one Fe₃Al / TP 304H sample in Section B. Also, shown is the calculated average metal temperature at this location.
Composition Verification.	<ul style="list-style-type: none">The table in Figure E-2 provides the composition of tube Sample B-C after exposure. An attempt was made to find and analyze the composition of the iron-aluminide coating on the “after service” samples, but none could be found. It is assumed that the coating either spalled or was corroded away from the surface at some point during the 28.5 months of exposure in Section B. This is consistent with similar results for Sections A and C.The table in Figure E-2 provides EDS analyses of the Fe₃Al coating prior to service. Numerous samplings were made and found to be highly variable. The reported results are for material at the extreme outer surface. A bulk analysis was also attempted and reported. The significance of deviations from the target chemistry is unclear.EDS semi-quantitative analysis at mid-wall for Sample B-C confirms that this material is consistent with TP 304H, thus it verifies that the correct sample was located at position B-C.
As-Received Appearance	<ul style="list-style-type: none">Figure E-3 shows the appearance of the surface of the Fe₃Al coated tube prior to service.Figure E-4 documents the appearance of the external surface of Sample B-C after service. Three views are provided for this tube: 12 o’clock (the view that faces on-coming gas flow), 3 o’clock (the view where the gas flow is tangent to the surface), and 6 o’clock (the view that shows the back-side of the tube relative to the gas flow direction).The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the “o’clock” conventions described above, (with the 12 o’clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o’clock side of the tube faces downward, and the 6 o’clock orientation faces upward within the boiler.Figure E-4 reveals that almost no deposit remained at the 12 o’clock through 3 o’clock positions. A rust-red scale was visible on the 6 o’clock side of the tube. A brown-to-black scale was visible elsewhere.There was no evidence on this tube sample of the gray/white scale associated with molten alkali-iron sulfate attack.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">Figure E-5 shows the appearance of the external surface of the Fe₃Al / TP 304H tube samples after grit-blasting to remove deposit and scale. General wastage is most clearly shown at the 12 o’clock orientation.The 6 o’clock position shows very little evidence of attack.

Material: Fe₃Al / TP 304H

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss Determined	<ul style="list-style-type: none">• A tube cross-section was prepared to allow for measurement of wall thickness to determine metal loss due to exposure. This is shown in silhouette in Figure E-6.• The same relative “o’clock” positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost.• For the sample in question, the minimum wall thickness in the cross section was not at one of the eight predetermined locations. So, there were no “before” measurement for comparison to determine the “delta”. To address this, the average “before” wall thickness was used to calculate the wall thickness lost at this off-location.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure E-7 plots the maximum wall thickness lost against the calculated average metal temperature for Sample B-C in all three test sections.• The rate metal loss was somewhat greater for Section A than for Sections B and C. It’s difficult to draw conclusions from this particularly given the fact that the iron-aluminide coating was likely gone from all of these samples very early in their life.
Metal Loss as a Function of Time	<ul style="list-style-type: none">• The chart in Figure E-8 plots metal loss as a function of time.• Note that the Sample B-C was removed from test Sections B and C after the same total 28.5 months of exposure. The Section C sample (1149 F) experienced a maximum total wall thickness loss of 239 mils in this time period. The Section B sample (1138 F) experienced a maximum total wall thickness loss of 279 mils.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample B-C was subjected to a detailed SEM/EDS assessment of the constituents and structure in the vicinity of the external and internal surfaces. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.• Figures E-9a and b show backscattered electron images (BEI) of the external surface. No deposit was visible in this view. A discontinuous scale was observed at the interface.• The numbered locations in Figure E-9b show the locations of EDS analyses that follow. Location 1 was taken to characterize the composition of the scale. Location 2 characterized the composition of the bulk metal. No microstructural evidence was present to indicate the presence of a diffusion zone adjacent to the scale/metal interface.• Figure E-10 represents the microstructure at mid-wall in the tube.• Figure E-11 shows the appearance of the internal metal surface for Sample B-C. A continuous scale is observed along with local penetrations into the surface.

Material: Fe₃Al / TP 304H

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none">• No weld cross sections were taken due to the fact that none of the Fe₃Al samples survived for the full 37 month exposure period of Section B.
EDS Analysis Results	<ul style="list-style-type: none">• The table in Figure E-12 provides a summary of the EDS analyses of the locations numbered in Figures E-9. Also shown in this table is a summary of the spectrographic analysis reported earlier.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Area 1: Scale at scale/metal interface</u> – The scale primarily is comprised of the oxides of the three major alloying elements in TP 304H, i.e. iron, chromium, and nickel. Relative to the underlying base metal, the scale is enriched in chromium (53.6% vs 18.8%) and depleted in iron (21.9% vs 69.4%) and nickel (1.99% vs 8.51%). It is also important to note that the scale was rich in sulfur (5.02%), and there was no evidence of alkali metals such as potassium, sodium, etc.• <u>Area 2: Base metal (approximately 5 grain diameters away from scale/metal interface)</u> – Within the limits of EDS, the results of this analysis are virtually identical to those for the base metal at mid-wall.

Figure E-1: Schematic Drawing Showing Position of Fe₃Al / TP 304H Tube Sample Within Section B

1. Drawing shown in same relative orientation as per the actual installation.
2. This group of tube samples was removed from service in November 2001 - highlighted in red.
3. This group of tube samples was removed from service in June 2002 - highlighted in yellow.
4. This group of tube samples was removed from service in September 2003 - highlighted in blue.

Figure E-2 Semi-Quantitative Composition Verification for Fe₃Al / TP 304H

Description: Commercially available iron Aluminide alloy (FAS) electrospark discharge coated onto Type 304H stainless steel (roughly 30 to 60 mils thick)..

Source: FAS developed by Oak Ridge National Laboratory (ORNL), applied by Pacific Northwest National Laboratory (PNNL)

Reference Composition: “Target” chemistry for coating – per Reference 1.

Element	Reference Composition of Coating	Composition (a) Heat 17433	EDS of Coating at Outer Surface	EDS of Bulk Coating		Element	Reference Composition SA 213 TP 304H	Tube Sample B-C
Ni	-	<0.01	1.22	3.99		Ni	8.00-11.0	8.54
Cr	2.19	1.59	3.92	10.8		Cr	18.0-20.0	18.4
Fe	Balance	-	79.5	67.8		Fe	Balance	71.0
Mo	-	0.01	-	-		Mo	-	-
Co	-	<0.01	-	-		Co	-	-
C	-	0.008	-	-		C	0.04-0.10	-
N ₂	-	0.001	-	-		N ₂	-	-
B	0.011	0.010	-	-		B	-	-
Mn	-	<0.01	-	1.34		Mn	2.00 max	1.60
Si	-	<0.01	-	-		Si	0.75 max	0.51
Al	15.93	15.79	11.7	5.22		Al	-	-
Ti	-	-	-	-		Ti	-	-
Al+Ti	-	-	-	-		Al+Ti	-	-
Nb	-	<0.01	3.65	10.8		Nb	-	-
Ta	-	-	-	-		Ta	-	-
Mo	-	-	-	-		Nb+Ta	-	-
V	-	<0.01	-	-		V	-	-
W	-	-	-	-		W	-	-
Cu	-	-	-	-		Cu	-	-
Sn	-	-	-	-		Sn	-	-
P	-	-	-	-		P	0.040 max	-
S	-	0.002	-	-		S	0.030 max	-

a – Reported analysis of wire used in deposition process by PNNL.

b – By difference.

Figure E-3: Appearance of Fe₃Al Coated TP 304H Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure E-4 As-Received Appearance of Sample B-C (Fe_3Al / TP 304H)

(Average metal temperature: 1138 F)

Note: this tube was removed from service in September 2003

12 O'Clock
(238 mils lost)

3 O'Clock
(125 mils lost)

6 O'Clock
(21 mils lost)

Figure E-5: OD Surface Appearance After Grit Blast

Material: Fe₃Al / TP 304H
Sample: B-C

Note: this tube was removed from service in September 2003

Material: Fe_3Al / TP 304H
Sample Location: B-C
Maximum Rate: 117 mils/yr
Maximum Loss Orientation: Approx. 10:00 o'clock
Average metal Temperature: 1138 F

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.394	0.394	0.396	0.395	0.397	0.394	0.394	0.393	0.395	0.395
After	0.156	0.250	0.271	0.379	0.376	0.376	0.174	0.146		0.116
Delta	0.238	0.144	0.125	0.016	0.021	0.018	0.220	0.247		0.279

Figure E-6: Silhouette and Wall Thickness Measurements for Sample B-C

Note: this tube was removed from service in September 2003

Figure E-7: Metal Loss Rate as a Function of Temperature

Material: Fe₃Al / TP 304H

Note: In analyzing these data, it is important to understand that the Section A sample was removed as per the original schedule, but the Section B and Section C samples were removed early in September 2003.

Figure E-7: Metal Loss as a Function of Time

Material: Fe₃Al / TP 304

Note: In analyzing these data, it is important to understand that the Section A sample was removed as per the original schedule (after 15.5 months), but the Section B and Section C samples were removed early in September 2003 (after 28.5 months).

(a) External Scale/Metal Interface (SEI - Low Magnification)

(b) External Scale/Metal Interface (SEI - Intermediate Magnification)

Note: Numbers indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

Figure E-9: Microstructure: Fe_3Al / TP 304H

(BEI - Low Magnification)

Figure E-10: Mid-wall Microstructure: Fe₃Al / TP 304H

Note: Photomicrograph at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

(BEI - Intermediate Magnification)

Figure E-11: Microstructure: Internal Scale/Metal Interface : Fe_3Al / TP 304H

Figure E-12: EDS Analysis of Deposit/Scale/Metal Interface for Fe₃Al /TP304H (Sample B-C)

Area	Description	Ni	Cr	Fe	Cu	Mn	W	Ti	Al	Si	C	O	Ca	K	Na	Mg	As	P	S
1	Scale / metal interface	1.99	53.6	21.9	--	--	--	--	--	1.07	--	11.4	--	--	--	--	--	--	5.02
2	Metal 4-5 grains from interface	8.11	19.0	70.7	--	1.65	--	--	--	0.57	--	--	--	--	--	--	--	--	--
	Midwall	8.54	18.4	71.0	--	1.60	--	--	--	0.51	--	--	--	--	--	--	--	--	--
	Reference bulk composition (substrate)	8.51	18.8	69.4	0.17	1.77	0.028	0.002	0.007	0.37	0.05	--	--	--	--			0.029	0.001

Appendix F
Analysis of Performance
Section B
310 Ta

Overview of Results: 310 Ta

Type 310 Ta experienced a high rate of metal loss at two of the three locations in Section B. The metal loss rates for Samples F-G and M-N were 106 and 110 mils per year* respectively. These rates were very similar to those determined for these same sample locations in Sections A and C. Due to these high wastage rates, Sample F-G and Sample M-N had to be removed early (i.e. after 21.5 and 28.5 months respectively) and thus did not survive for the full 37 month exposure period for Section B. The table below provides tube sample service life versus intended service exposure time for each of the three test sections.

		Section A	Section C	Section B
	Full Exposure Period:	15.5 months	28.5 months	37 months
Sample	Nominal Temperature	Removed	Removed	Removed
M-N	1176 – 1188 F	15.5 months	28.5 months	28.5 months
F-G	1153 – 1166 F	15.5 months	21.5 months	21.5 months
X-Y	1092 – 1103 F	15.5 months	28.5 months	37 months

For Section A, the sample at the lowest temperature location, Sample X-Y, had a relatively high metal loss rate of 120 mils per year. The wastage rate for Sample X-Y was significantly lower for Section C (64 mils/year) and for Section B (70 mils/year). The figure below provides the locations for these samples.

For each test section, the tube samples that were subjected to a full metallurgical analysis are highlighted in “gray” in the table above. It was originally intended that, for any given test section, a full metallurgical analysis would be performed only on the sample that experienced the highest rate of metal loss. For example, for Section A, Sample F-G (1167 F) experienced the highest rate of metal loss, so, the results of its analysis are included in the Section A report. However, for Section C and for Section B, the sample selected for analysis was the sample which had lost the most wall thickness. Thus, Sample M-N was selected for analysis for both Section B and C.

Evaluation of the metallographic cross section for Sample M-N revealed that, for the region where the corrosion rate was highest, the sample was almost completely bare of deposit and that the surface scale was discontinuous, see Figure F-14.

The photograph of the scale/metal interface shown in Figure F-15 provides a map for EDS analyses to characterize the nature of scale and deposit on either side of the interface. The following observations are offered relative to the scale:

- A significant amount of deposit was found at this location on the tube external surface. This is supported by the amounts of iron (60.2%), silicon (9.91%), nickel (5.08%), aluminum (4.04%), and oxygen (14.8%) that were found. Potassium (0.96%) and sulfur (0.27%) were noted, as was a significant amount of arsenic (2.91%) and phosphorous (1.06%)
- The scale contains oxides of the three major alloying elements that comprise 310 Ta. The chromium content is very high (59.7%) adjacent to the scale/metal interface. The chromium content drops off somewhat in the bulk of the scale (50.5%). The amounts of iron and nickel increase in the bulk (relative to the inner scale) i.e. from 9.78% to 26.8% for iron, and from 1.92% to 2.13% for nickel.
- The scale adjacent to the surface had a very high sulfur content (13.4%). In the bulk, the sulfur content dropped off to (2.41%)

The following observations are offered relative to the NF 709 adjacent to the scale metal interface.

- No evidence of chromium depletion could be found for Sample M-N (1176 F), for Section B. Within the limits of the EDS, the composition of the metal was essentially the same (roughly 24% chromium) regardless of position. It should be noted that significant chromium depletion (12.2% chromium) was found during the analysis of Sample M-N (1188 F), for Section C, and that somewhat lesser depletion (17.7% chromium) was found during the analysis of Sample F-G (1154 F), for Section A.
- The variability in chromium depletion between Sections A, B, and C could not be correlated with: temperature, time at temperature, or metal loss rate.
- There was no evidence of grain boundary penetration. Neither was there evidence of internal sulfidation or oxidation.

In summary, it would appear that sulfur had a strong influence on both the formation and character of the surface scale. The high sulfur content at the scale/metal interface would seem to be particularly relevant. Evidence of potassium, iron, and sulfur in the deposit supports, to some extent, the role of coal ash corrosion as a component of the damage mechanism for this material. However, it should be noted that the potassium content was relatively low (0.96%) and no evidence was found in the deposit of other alkali metals.

Lastly, it should be noted, that while it was not the focus of this investigation, no evidence of metal loss could be found at the I.D. surface of Sample M-N. Also, the weld cross section for this material revealed no evidence of local corrosion in the vicinity of the weld. In fact, the Inconel 625 weld metal that was used to prepare the test sections for service appeared to be more resistant to coal ash corrosion than the 310 Ta test sample.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: 310 Ta

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• In assessing the data for Section B, it is important to understand that two of the three 310 Ta tube samples had to be removed from the section early due to excessive thinning. The schematic in Figure F-1 shows the relative positions of the TP 310 Ta samples in all three sections. Also, shown are the positions of all of the excessively thinned tubes that were removed and replaced in order to extend the life of Section C.• The first sample to be removed early was Sample F-G (1153 F). This sample was removed in June 2002, after 21.5 months of service.• The second sample to be removed early was Sample M-N (1176 F). This sample experienced about 28.5 months of service.• Sample X-Y (1092 F) survived for the full 37 month exposure period for Section B.• Sample F-G and Sample M-N were removed early and set aside for later analysis. The results of these analyses are included herein.• Also shown in Figure F-1 is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• During the Section A evaluation, detailed composition verification was undertaken for each tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample M-N confirmed that the correct material was used at this location.• For reference it should be noted Sample M-N was taken from Heat 17425.• The table in Figure F-2 also shows the "target" composition as reported by ORNL.

Material: 310 Ta

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance	<ul style="list-style-type: none">• Figure F-3 shows the typical appearance of the 310 Ta samples as delivered by ORNL.• Figures F-4 through F-6 document the appearance of the external surface for all three samples after service exposure. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the "o'clock" conventions described above, (with the 12 o'clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o'clock side of the tube faces downward, and the 6 o'clock orientation faces upward within the boiler.• Wastage is visible at 12 o'clock and 3 o'clock for all three samples.• Sample M-N (1176 F) had a thin brown/black deposit/scale at the 12 o'clock and 3 o'clock positions. It had a rust-red deposit/scale on the 6 o'clock side of the tube.• Sample F-G (1153 F) had a rust-red deposit/scale covering its surface.• Sample X-Y (1092 F) had a relatively thick deposit and scale which was thickest in the 6 o'clock view, and tapered around the tube in the 12 o'clock direction. The gray-white deposit typically associated with coal ash corrosion was most evident in the 3 o'clock view.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures F-7 through F-9 show the appearance of the external surface of the 301 Ta tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for all three samples show the appearance of general wastage due to fireside corrosion.• Pitting was observed in the 6 o'clock position for all three samples.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures F-10 through F-12.• The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost.• For all three tube samples, the minimum wall thickness in the cross section was not at one of the eight predetermined locations. In these cases, there were no "before" measurements for comparison. So, the average "before" wall thickness was used to calculate the wall thickness lost at these off-locations.

Material: 310 Ta

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss Rate Versus Average Surface Metal Temperature	<ul style="list-style-type: none"> • The chart in Figure F-13 plots the maximum wall thickness lost against the calculated average surface metal temperature for the three 310 Ta samples in all three test sections. • For Section A the wastage rate starts out high (120 mils/year) and generally maintains that level over the full temperature range. • For Sections B and C, the wastage rate generally increases with temperature. Starting in the range of 64 to 70 mils/year and ending in the range 110 to 131 mils/year for the highest temperature samples. •
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none"> • The chart in Figure F-14 plots metal loss as a function time. • Note that Sample F-G was removed early after 21.5 months for both Sections B and C. Sample M-N was removed early after 28.5 months for Section B, and that Sample X-Y was the only sample that survived for the full 37 month exposure period of Section B.
Metallurgical Analysis – SEM	<ul style="list-style-type: none"> • Sample M-N was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it had lost the most wall thickness of the three Section B tubes. (However, it might have been argued that Sample X-Y would have been a better choice in that it was the only sample 310 Ta sample to survive for the full 37 month exposure period of Section B.) • The focus of this investigation was in the region on Sample M-N where the maximum amount of material was lost. • Figure F-15 shows the appearance of the external scale/metal interface for the minimum wall thickness region of Sample M-N. • Figures F-16a, and b show the backscattered electron images of the scale/metal interface for Sample M-N. Five distinct regions are in evidence. These regions are, starting within the metal and working out: <ul style="list-style-type: none"> ○ <u>Base metal</u> – oxalic acid etch delineates grain boundaries, slip bands, inclusions and precipitates. ○ <u>Diffusion zone - dark etching</u> – this region is obvious as a dark-appearing band that is parallel to the metal surface, perhaps seen most clearly in Figures F- 16b. ○ <u>Diffusion zone – light etching</u> – this constitutes the leading edge of the grains as they interface with the scale. ○ <u>Adherent scale</u> – this feature is discontinuous along the surface, see Figure 15. ○ <u>Thick deposit</u> – upon outer surface of scale.

Material: 310 Ta

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">• Figure F-16a and 16b show numbered positions where EDS analyses were performed to characterize the scale/metal interface.• Figure F-17 shows the appearance of the microstructure at mid-wall in Sample M-N.• Figure F-18 shows the I.D. metal surface for Sample M-N. Minimal scale is noted along this surface.
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none">• Figure F-19 shows a longitudinal profile (at the 12 o'clock orientation) of the TP 310 Ta samples adjacent to the weld "X" in Section B.• An Inconel 625 weld metal was used throughout Section C. The cross sections show that the TP 310 Ta heat affected zones are not preferentially attacked, in fact, the wall thickness for the tube sample tapers from the weld toward the middle of the tube length.
EDS Analysis Results	<ul style="list-style-type: none">• The table in Figure F-20 provides a summary of the EDS analyses of the locations numbered in Figure F-16a and 16b. (Note: Figure 16b repeats many of the same numbers first identified in Figure 16a. The intent of Figure 16b is to provide additional clarification as the location for the various analyses.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Area 1: For the bulk deposit analysis</u> – the deposit is primarily comprised of the oxides of iron (60.2%), silicon (9.91%), nickel (5.08%), and aluminum 4.04%). A small amount of potassium (0.96%), and sulfur (0.27%) are indicated. Phosphorous (1.06%) and arsenic (2.915) also are present.• <u>Area 2: Bulk scale analysis</u> – the scale was primarily and oxide of chromium (50.5%) and iron (26.8%). A significant amount of sulfur (2.41%) was found. Lesser amounts of nickel (2.13%), manganese (2.88%) and silicon (1.20%) are indicated.• <u>Area 3: Scale adjacent to interface with metal</u> – The scale adjacent to the interface has a higher level of chromium (59.7%) and, perhaps more significantly, a very high sulfur level (13.4%). The iron (9.78%) and nickel (1.92%) content of the scale is decreased as is the manganese content (0.67%) and silicon content (0.85%). Tantalum (2.86%) also is present in this scale analysis.• <u>Areas 4 and 5: Diffusion zones</u> - These regions run parallel to the scale/metal interface. Each is much less than one grain wide. No evidence was found of chromium depletion in either zone. In fact, the composition in these regions was essentially identical to the bulk EDS analysis.• <u>Bulk EDS analysis</u> – this analysis was taken near mid-wall of the sample. It confirms that the sample is in fact 310 Ta.

Figure F-1: Schematic Drawing Showing Position of 310 Ta Tube Samples in Section B

1. Drawing shown in same relative orientation as per the actual installation.
2. This group of tube samples was removed from service in November 2001 - highlighted in red.
3. This group of tube samples was removed from service in June 2002 - highlighted in yellow.
4. This group of tube samples was removed from service in September 2003 - highlighted in blue.

Figure F-2 Semi-Quantitative Composition Verification for Type 310 Ta

Description: 20-25 Cr steel with improved creep strength due to addition of tantalum and nitrogen
Source: Oak Ridge National Laboratory (ORNL)
Reference Composition: “Target” Chemistry per ORNL (Reference 1).

Element	Reference Composition	Composition Heat 17425	Composition Heat 17426	Composition Heat 17431	Tube Sample F-G	Tube Sample M-N	Tube Sample X-Y
Ni	21.0	21.63	21.08	21.12	N/A	21.2	N/A
Cr	24.5	23.74	23.78	24.01	N/A	24.2	N/A
Fe	Balance	Balance	Balance	Balance	N/A	51.8	N/A
Mo	-	<0.01	<0.01	<0.01	N/A	--	N/A
Co	-	0.02	0.02	0.02	N/A	--	N/A
C	0.05	0.063	0.063	0.060	N/A	--	N/A
N	0.22	0.22	0.22	0.24	N/A	--	N/A
B	0.005	(a)	(a)	(a)	N/A	--	N/A
Mn	2.00	1.74	1.66	1.89	N/A	1.39	N/A
Si	0.25	0.25	0.24	0.27	N/A	--	N/A
Al	-	<0.01	<0.01	<0.01	N/A	--	N/A
Ti	-	<0.01	<0.01	<0.01	N/A	--	N/A
Nb	-	<0.01	<0.01	<0.01	N/A	--	N/A
Ta	1.75	1.18	1.03	1.24	N/A	1.39	N/A
Nb+Ta	-	-	-	-	N/A	--	N/A
V	-	<0.01	<0.01	<0.01	N/A	--	N/A
W	-	-	-	-	N/A	--	N/A
Cu	-	<0.01	<0.01	<0.01	N/A	--	N/A
Sn	-	-	-	-	N/A	--	N/A
P	-	0.008	0.009	0.013	N/A	--	N/A
S	-	0.006	0.006	0.006	N/A	--	N/A
O2	-	0.013	0.014	0.018	N/A	--	N/A

- a- Not analyzed.
b- By difference.

Reference 1: “Fabrication of Test Tubes for Coal Ash Corrosion Testing”, Sikka, V.K., Swindeman, R.W., Wright, I.G., Judkins, R.R., Johnson, R., Proc, 13th Annual Conf. on Fossil Energy Mat’ls, May 1999.

Sample M-N was from Heat 17425 N/A = Tube sample not analyzed.

Figure F-3: Appearance of 310 Ta Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure F-4 As-Received Appearance of Sample M-N (310 Ta)
(Average metal temperature: 1176 F)

Note: this tube was removed from service in September 2003

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure F-5 As-Received Appearance of Sample F-G (310 Ta)

(Average metal temperature: 1153 F)

Note: this tube was removed from service in June 2002

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure F-6 As-Received Appearance of Sample X-Y (310 Ta)

(Average metal temperature: 1092 F)

Note: this tube experienced the full 37 month exposure period.

12 O'Clock
(180 mils lost)

3 O'Clock
(197 mils lost)

6 O'Clock
(1 mils lost)

Figure F-7: OD Surface Appearance After Grit Blast

Material: 310 Ta

Sample: M-N

Note: this tube was removed from service in September 2003

12 O'Clock
(116 mils lost)

3 O'Clock
(152 mils lost)

6 O'Clock
(3 mils lost)

Figure F-8: OD Surface Appearance After Grit Blast

Material: 310 Ta
Sample: F-G

Note: this tube was removed from service in June 2002

12 O'Clock
(145 mils lost)

3 O'Clock
(47 mils lost)

6 O'Clock
(1 mils lost)

Figure F-9: OD Surface Appearance After Grit Blast

Material: 310 Ta
Sample: X-Y

Note: this tube experienced the full 37 month exposure period.

Material: 310 Ta
Sample Location: M-N
Maximum Rate: 110 mils/yr
Maximum Loss Orientation: Approx. 2:00 o'clock
Average metal Temperature: 1176 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.402	0.401	0.401	0.401	0.401	0.401	0.401	0.401	0.401	0.401
After	0.222	0.172	0.204	0.400	0.400	0.401	0.271	0.250		0.140
Delta	0.180	0.229	0.197	0.001	0.001	0.000	0.130	0.151		0.261

Figure F-10: Silhouette and Wall Thickness Measurements for Sample M-N

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Note: this tube was removed from service in September 2003

Material: 310 Ta
Sample Location: F-G
Maximum Rate: 106 mils/yr
Maximum Loss Orientation: Approx. 2:30 o'clock
Average metal Temperature: 1153 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.400	0.401	0.402	0.402	0.402	0.400	0.400	0.399	0.401	0.401
After	0.284	0.248	0.250	0.399	0.399	0.400	0.281	0.302		0.211
Delta	0.116	0.153	0.152	0.003	0.003	0.000	0.119	0.097		0.190

Figure F-11: Silhouette and Wall Thickness Measurements for Sample F-G

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Note: this tube was removed from service in June 2002

Material: 310 Ta
Sample Location: X-Y
Maximum Rate: 70 mils/yr
Maximum Loss Orientation: Approx. 9:30 o'clock
Average metal Temperature: 1092 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.399	0.400	0.400	0.400	0.401	0.400	0.400	0.399	0.400	0.400
After	0.254	0.272	0.353	0.397	0.400	0.395	0.221	0.244		0.185
Delta	0.145	0.128	0.047	0.003	0.001	0.005	0.179	0.155		0.215

Figure F-12: Silhouette and Wall Thickness Measurements for Sample X-Y

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Note: this tube experienced the full 37 month exposure period.

Figure F-13: Metal Loss Rate as a Function of Temperature

Material: 310 Ta

Note: In analyzing these data it is important to understand that the two of the three Section B samples were removed early due to excessive corrosion losses. Sample F-G (1153 F) was removed in June 2002. Sample M-N (1176 F) was removed in September 2003, and Sample X-Y (1092 F) experienced the full 37 month intended exposure period for Section B samples.

Figure F-14: Metal Loss as a Function of Time

Note: From the plot above it can be seen that, for Section B, Sample F-G was removed early (in June 2002) due to concerns about excessive metal loss. Sample M-N was removed early in September 2003, and Sample X-Y experienced the full 37 month exposure life.

Figure F-15: Low Magnification Image Showing External Surface at Thinnest Region of Sample M-N (310 Ta)

(a) External Scale/Metal Interface (BEI - Low Magnification)

(b) External Scale/Metal Interface (BEI - Intermediate Magnification)

Figure F-16: Microstructure: 310 Ta (Sample M-N)

Note: Numbers on photos indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

(BEI - Low Magnification)

Figure F-17: Mid-Wall Microstructure: 310 Ta (Sample M-N)

Note: Photomicrograph at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Internal Surface Appearance (BEI – High Magnification)

Figure F-18: Microstructure: 310 Ta (Sample M-N)

TP 310 Ta Adjacent to Weld "X"

Figure F-19: Longitudinal Cross-Section: 310 Ta Adjacent to Weld

Figure F-20: EDS Analysis of Deposit/Scale/Metal Interface for 310 Ta (Sample M-N)

Area	Description	Ni	Cr	Fe	Cu	Mn	Ta	Ti	Al	Si	C	O	Ca	K	Na	As	P	S
1	Bulk deposit analysis	5.08	--	60.2	--	--	0.42	0.34	4.04	9.91	--	14.8	--	0.96	--	2.91	1.06	0.27
2	Bulk scale analysis	2.13	50.5	26.8	--	2.88	--	--	--	1.20	--	14.1	--	--	--	--	--	2.41
3	Inner scale analysis	1.92	59.7	9.78	--	0.67	2.86	--	--	0.84	--	10.9	--	--	--	--	--	13.35
4	Metal at interface with scale	20.8	23.5	53.1	--	1.22	1.39	--	--	--	--	--	--	--	--	--	--	--
5	Deep etching zone near interface	20.4	23.9	52.9	--	1.30	1.54	--	--	--	--	--	--	--	--	--	--	--
	Bulk EDS analysis	21.2	24.2	51.8	--	1.39	1.39	--	--	--	--	--	--	--	--	--	--	--
	Reference bulk analysis.	21.0	24.7	51.2	--	1.72	0.73	--	0.002	0.24	0.07	--	--	--	--	--	0.003	0.007

Appendix G
Analysis of Performance
Section B
310 HCbN (HR3C)

Overview of Results: 310 HCbN (HR3C)

During the analysis of Section A, in 2002, dimensional measurements showed that, after approximately 15.5 months of exposure, 310 HCbN Sample G-H had lost 172 mils of its original 400 mil wall thickness. It thus had sustained a rate of wall thickness loss of 133 mils per year*. This high wastage rate raised concerns about the potential longevity of the 310 HCbN samples at the G-H positions in Sections B and C. So, the G-H samples were removed, after about 18.6 months of exposure, and replaced with a more corrosion resistant material. The intent was to ensure that neither Section C nor Section B would need to come out early.

Due to similar concerns about excessive metal loss, the tube samples at locations N-O and AA-BB were removed from Section B at the same time that the Section C sample was removed for evaluation, i.e. after 28.5 months of service. Only the 310 HCbN samples at the W-X location survived for the full 37 month exposure period for Section B. This history is summarized in the table below:

		Section A	Section C	Section B
	Full Exposure Period:	15.5 months	28.5 months	37 months
Sample	Nominal Temperature	Removed	Removed	Removed
N-O	1179 – 1190 F	15.5 months	28.5 months	28.5 months
G-H	1155 – 1167 F	15.5 months	18.6 months	18.6 months
W-X	1094 – 1106 F	15.5 months	28.5 months	37 months
AA-BB	1080 – 1092 F	15.5 months	28.5 months	28.5 months

The dimensional analysis of all four of the Section B tube samples (i.e. Sample N-O, Sample G-H, Sample W-X and Sample AA-BB) are included in this report. However, the metallurgical analysis focused on Sample N-O which had lost the greatest amount of wall thickness of any of the Section B samples (albeit it did not survive for the full 37 month exposure period). The “gray” colored boxes above show which sample was subjected to metallurgical analysis for each test section.

Review of the data revealed that the metal loss rate for the 310 HCbN samples was generally high and generally increased as a function of temperature, see Figure B-13. The figure below provides the locations for these samples.

Evaluation of the metallographic cross section for Sample N-O from Section B showed that, for the region where the corrosion rate was highest, the sample was denuded of deposit and that the surface scale was discontinuous. This is shown to some extent in the as-received condition that is documented in Figure G-4 where the 3 o'clock position is shown to have minimal deposit or scale. It is better shown in Figure G-18a (which was taken at 2:00 o'clock position on Sample N-O),

Evaluation of the metallographic cross section for Sample N-O revealed that, for the region where the corrosion rate was highest, the sample was almost completely bare of deposit and that the surface scale was discontinuous, see Figure G-18a.

An SEM/EDS evaluation of the surface scale found on one region of on Sample N-O for Section B reveals that the scale is predominantly a chromium-rich oxide (however, there also was a significant amount of iron and nickel in the scale), refer to Figure G-18b and the EDS results in Figure G-22. Of perhaps of particular importance in this analysis was the fact that the scale also contained a significant amount of sulfur, and that the sulfur content was particularly high (57.41%) at the interface between the scale and the metal, i.e. at Location 2 in Figure B-18b. This may well have contributed to the physical properties of the scale in this region, causing it to perhaps be more easily exfoliated.

Evaluation of the metal contiguous with the scale/metal interface of Sample N-O, Section B revealed no evidence of chromium depletion in this region. This is consistent with the for Sample G-H from Section A, but is at variance with the results for Sample G-H from Section C where significant chromium depletion was found. The reason for this variability has not been determined.

It should be noted, that while it was not the focus of this investigation, no evidence of metal loss could be found at the I.D. surface of Sample Y-Z. Also, for the one weld cross section evaluated, no evidence could be found of localized attack in the vicinity of the weld heat affected zone.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: 310 HCbN (HR3C)

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• In assessing the data for Section B, it is important to understand that three of the four 310 HCbN tube samples had to be removed from the section early due to excessive thinning. The schematic in Figure G-1 shows the positions of the 310 HCbN samples in all three sections. Also, shown are the positions of all of the excessively thinned tubes that were removed and replaced in order to extend the life of Section B.• Sample G-H was removed after 18.6 months of service due to concerns about excessive thinning. Samples N-O, AA-BB were removed early after 28.5 months. Sample W-X experienced the full 37 month exposure period for Section B.• The samples that were removed early were set aside for later analysis, and have been included in the current evaluation.• Also shown in this figure is the calculated average surface metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• The table in Figure G-2 provides the ASTM specified composition for this grade of material.• Sumitomo Metal Industries supplied tube from one heat of material for use in this program, Heat D8A0809. The composition for this heat also is provided in Figure G-2.• During the Section A evaluation, detailed composition verification was undertaken for each tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample N-O confirmed that the correct material was used at this location.

Material: 310 HCbN (HR3C)

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance	<ul style="list-style-type: none">• Figure G-3 shows the typical appearance of 310 HCbN sample on receipt from Sumitomo.• Figures G-4 through G-7 document the as-received appearance of the external surface of the Save 25 tube samples. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the "o'clock" conventions described above, (with the 12 o'clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o'clock side of the tube faces downward, and the 6 o'clock orientation faces upward within the boiler.• Wastage was visible at the 12 o'clock and 3 o'clock views for all four samples. A tan/black deposit/scale is noted in these views.• It was noted that all three samples had a rust-red deposit visible in the 6 o'clock view.• It was noted that Sample W-X had the thickest overall deposit. The chalky gray/white deposit typically associated with molten alkali-iron-sulfate accelerated attack is visible in the 3 o'clock view.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures G-8 through G-11 show the appearance of the external surface of the 310 HCbN tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for all four samples show the appearance of general wastage due to fireside corrosion.• The 6 o'clock position shows some evidence of pitting for Sample W-X and AA-BB; otherwise, it was relatively unaffected, and exhibited little or no wastage at this surface.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures G-12 through G-15.• The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost.• For all four tube samples, the minimum wall thickness in the cross section was not at one of the eight predetermined locations. In these cases, there was no "before" measurement for comparison. So, the average "before" wall thickness was used to calculate the wall thickness lost at these off locations.

Material: 310 HCbN (HR3C)

Summary of Findings, (continued)

Issue	Discussion
Rate of Wall Thickness Loss Versus Average Surface Metal Temperature	<ul style="list-style-type: none">• The chart in Figure G-16 plots the maximum rate of wall thickness loss against the calculated average surface metal temperature for each of the four 310 HCbN samples in Section B. The Section A and Section C data also are plotted.• Review of the data shows that wastage rate for Sample W-X and Sample AA-BB is lower than would be anticipated (based on temperature). This likely is due to the proximity of the samples to the boiler walls.
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure G-17 plots metal loss as a function of time for each sample location for all three sections.• The samples at the W-X location experienced the full intended exposure period for all three test sections.• For Section B, the samples at the N-O and AA-BB locations were removed early after 28.5 months. The sample at the G-H location was taken out early after only 18.6 months.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample N-O was selected for a detailed SEM/EDS assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it had lost the most total wall thickness among the four 310 HCbN samples (however, this sample did not survive for the full 37 month exposure period for Section B). The focus of this investigation was in the region of the tube where the maximum amount of material was lost.• Figures G-18a and 18b show the secondary electron images of the scale/metal interface for Sample N-O. Note from Figure G-18a that little or no deposit is noted along this interface, and that the presumably protective scale is not continuous.• Four distinct regions are in evidence in this cross section. These regions are, starting within the metal and working out:<ul style="list-style-type: none">○ <u>Bulk metal</u> – oxalic acid etch delineates grain boundaries and carbides.○ <u>Featureless grain region</u> – This constitutes the leading edge of the grains as they interface with the scale.○ <u>Dark etching scale along scale/metal interface</u> – this is seen continuous along the surface. EDS analysis will later show that this is a chromium-, nickel-, and iron-rich -oxide.○ <u>Bulk scale</u> – thick scale closer to original scale/deposit interface• Figures G-19 shows the appearance of the tube microstructure at mid-wall.• Figure G-20 shows the appearance of the internal metal surface for Sample N-O. Little if any oxide scale is visible at this surface.

Material: 310 HCbN (HR3C)

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none">• Figure G-21 shows a longitudinal profile (at the 12 o'clock orientation) of the 310 HCbN samples adjacent to the weld “X”.• An Inconel 625 weld metal was used throughout Section C. The cross sections show that the 310 HCbN heat affected zone is not preferentially attached, in fact, the wall thickness for the tube sample tapers from the weld toward the middle of the tube length.
EDS Analysis Results	<ul style="list-style-type: none">• The table in Figure G-22 provides a summary of the EDAX analyses of the locations numbered in Figure G-18b. Also shown in this table is a summary of the spectrographic analysis reported earlier, see Figure G-2.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Area 1: Bulk scale analysis</u> – No evidence could be found of deposit remnants in this region. This zone was predominantly comprised of oxides of chromium (54.2%), iron (19.3%), and nickel (7.07%). 13.6% of oxygen is indicated. No evidence was found of potassium or any of the other alkali metals. The sulfur content was relatively high (4.97%)• <u>Area 2: Scale adjacent to scale/metal interface</u> – This scale is further enriched in chromium (64.2%), and has relatively less iron (9.66%) and nickel (.1.13%). The oxygen content is somewhat higher (14.7%), and the sulfur content is significantly higher (7.41%)• <u>Area 3:– Metal along scale/metal interface</u> - This region etched only lightly, however, within the limits of EDS, the composition in this region is the same as that of the bulk analysis.• <u>Area 4: - Bulk metal analysis</u> – This analysis compares well with the reference emission spectrographic results.

Figure G-2 Semi-Quantitative Composition Verification for 310 HCbN (HR 3C)

Description: Nominal 25Cr/20Ni steel with Nb, Ta, and N added to provide creep strength.
Source: Sumitomo Metal Industries (SMI)
Reference Composition: “Specified” chemistry – ASTM A213 (TP310 HCbN).

Element	Reference Composition	Composition (a) Heat D8A0809	Tube Sample G-H	Tube Sample N-O	Tube Sample W-X	Tube Sample AA-BB
Ni	17.00-23.00	19.97	N/A	20.4	N/A	N/A
Cr	24.00-26.00	25.61	N/A	25.0	N/A	N/A
Fe	Balance	Balance	N/A	52.1	N/A	N/A
Mo	-	-	N/A	-	N/A	N/A
Co	-	-	N/A	-	N/A	N/A
C	0.04-0.10	0.05	N/A	-	N/A	N/A
N	0.15-0.35	0.24	N/A	-	N/A	N/A
B	-	-	N/A	-	N/A	N/A
Mn	2.00 max	1.18	N/A	1.13	N/A	N/A
Si	0.75 max	0.36	N/A	0.54	N/A	N/A
Al	-	-	N/A	-	N/A	N/A
Ti	-	-	N/A	-	N/A	N/A
Al+Ti	-	-	N/A	-	N/A	N/A
Nb	-	0.47	N/A	0.89	N/A	N/A
Ta	-	(c)	N/A	-	N/A	N/A
Nb+Ta	0.20-0.60	0.47	N/A	-	N/A	N/A
V	-	-	N/A	-	N/A	N/A
W	-	-	N/A	-	N/A	N/A
Cu	-	-	N/A	-	N/A	N/A
Sn	-	-	N/A	-	N/A	N/A
P	0.030 max	0.015	N/A	-	N/A	N/A
S	0.030 max	(c)	N/A	-	N/A	N/A

- a- Ladle analysis.
- b- By difference.
- c- Not detected.

N/A = Sample not analyzed.

Figure G-3: Appearance of 310 HCBN (HR3C) Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure G-4 As-Received Appearance of Sample N-O (310 HCbN)

(Average surface metal temperature: 1179°F)

Note: this tube was removed from service in September 2003

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure G-5 As-Received Appearance of Sample G-H (310 HCbN)

(Average surface metal temperature: 1155 °F)

Note: this tube was removed from service on June 2001.

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure G-6 As-Received Appearance of Sample W-X (310 HCbN)
(Average surface metal temperature: 1094 °F)

Note: this sample experienced the full intended 37 month exposure period for Section B

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure G-7 As-Received Appearance of Sample AA-BB (310 HCbN)

(Average surface metal temperature: 1080 °F)

Note: this tube was removed from service in September 2003

12 O'Clock
(149 mils lost)

3 O'Clock
(214 mils lost)

6 O'Clock
(0 mils lost)

Figure G-8: OD Surface Appearance After Grit Blast

Material: 310 HCBN (HR3C)
Sample: N-O

Note: this tube was removed from service in September 2003

12 O'Clock
(128 mils lost)

3 O'Clock
(151 mils lost)

6 O'Clock
(1 mil lost)

Figure G-9: OD Surface Appearance After Grit Blast

Material: 310 HCBN (HR3C)
Sample: G-H

Note: this tube was removed from service on June 2001.

12 O'Clock
(129 mils lost)

3 O'Clock
(54 mils lost)

6 O'Clock
(0 mils lost)

Figure G-10: OD Surface Appearance After Grit Blast

Material: 310 HCBN (HR3C)

Sample: W-X

Note: this sample experienced the full intended 37 month exposure period for Section B

12 O'Clock
(159 mils lost)

3 O'Clock
(52 mils lost)

6 O'Clock
(6 mils lost)

Figure G-11: OD Surface Appearance After Grit Blast

Material: 310 HCbN (HR3C)
Sample: AA-BB

Note: this tube was removed from service in September 2003

Material: 310 HCBN (HR3C)

Sample Location: N-O

Maximum Rate: 111 mils/yr

Maximum Loss Orientation: Approx. 2:00 o'clock

Average Surface Metal Temperature: 1179 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.399	0.402	0.402	0.398	0.400	0.399	0.397	0.398	0.399	0.399
After	0.250	0.150	0.188	0.398	0.400	0.397	0.267	0.239		0.135
Delta	0.149	0.252	0.214	0.000	0.000	0.002	0.130	0.159		0.264

Figure G-12: Silhouette and Wall Thickness Measurements for Sample N-O

Note: this tube was removed from service in September 2003

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Material: 310 HCBN (HR3C)

Sample Location: G-H

Maximum Rate: 121 mils/yr

Maximum Loss Orientation: Approx. 2:00 o'clock

Average Surface Metal Temperature: 1155 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.402	0.401	0.398	0.398	0.403	0.400	0.401	0.402	0.401	0.401
After	0.274	0.293	0.247	0.398	0.402	0.400	0.305	0.287		0.214
Delta	0.128	0.108	0.151	0.000	0.001	0.000	0.096	0.115		0.187

Figure G-13: Silhouette and Wall Thickness Measurements for Sample G-H

Note: this tube was removed from service in November 2001

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Material: 310 HcN (HR3C)

Sample Location:

W-X

Maximum Rate:

57 mils/yr

Maximum Loss Orientation:

Approx. 10:00 o'clock

Average Surface Metal Temperature: 1094 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.398	0.397	0.400	0.400	0.398	0.402	0.400	0.397	0.399	0.399
After	0.269	0.312	0.346	0.394	0.398	0.392	0.282	0.260		0.222
Delta	0.129	0.085	0.054	0.006	0.000	0.010	0.118	0.137		0.177

Figure G-14: Silhouette and Wall Thickness Measurements for Sample W-X

Note: this sample experienced the full intended 37 month exposure period for Section B

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Material: 310 HCBN (HR3C)

Sample Location: AA-BB

Maximum Rate: 101 mils/yr

Maximum Loss Orientation: Approx. 9:30 o'clock

Average Surface Metal Temperature: 1080 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.395	0.395	0.397	0.397	0.400	0.403	0.398	0.396	0.398	0.398
After	0.236	0.294	0.345	0.392	0.394	0.400	0.194	0.192		0.157
Delta	0.159	0.101	0.052	0.005	0.006	0.003	0.204	0.204		0.241

Figure G-15: Silhouette and Wall Thickness Measurements for Sample AA-BB

Note: this tube was removed from service in September 2003

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Figure G-16: Metal Loss Rate as a Function of Average Surface Metal Temperature

Material: 310 HCbN (HR3C)

Note: In analyzing these data it is important to understand that three of the four Section B samples were removed early due to excessive corrosion losses. Sample G-H (1155 F) was removed in November 2001, shortly after Section A was removed for evaluation. Sample N-O (1179 F) and Sample AA-BB (1080 F) were removed in September 2003. Sample W-X (1094 F) survived for the full 37 month exposure period of Section B.

Figure G-17: Metal Loss as a Function of Time

Material: 310 HcN (HR3C)

Note: From the plot above it can be seen that three of the four Section B samples were removed early due to excessive corrosion losses. Sample G-H was removed in November 2001, shortly after Section A was removed for evaluation. Sample N-O and Sample AA-BB were removed in September 2003. Sample W-X survived for the full 37 month exposure period of Section B.

(a) External Scale/Metal Interface (BEI - Low Magnification)

(b) External Scale/Metal Interface (SEI - Intermediate Magnification)

Figure G-18: Microstructure: 310 HCbN (Sample N-O)

Note: Numbers on photo indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

(BEI - Low Magnification)

Figure G-19: Mid-Wall Microstructure: 310 HCBN (Sample N-O)

Note: Photomicrograph at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Internal Surface Appearance (BEI - High Magnification)

Figure G-20: Microstructure: 310 HCBN (Sample N-O)

Figure G-21: Longitudinal Cross-Section: 310 HCBN Adjacent to Weld “X”

Figure G-22: EDS Analysis of Deposit/Scale/Metal Interface for 310 HCBN (Sample N-O)

Area	Description	Ni	Cr	Fe	Cu	Mn	Nb	Ti	Al	Si	C	O	Ca	K	Na	Mg	As	P	S
1	Outer scale that is detached	7.07	54.2	19.3	--	--	--	--	--	0.84	--	13.6	--	--	--	--	--	--	4.97
2	Adherent inner scale adjacent to interface	1.13	64.2	9.66	--	0.98	1.14	--	--	0.78	--	14.7	--	--	--	--	--	--	7.41
3	Light etching band of metal at interface	19.6	25.2	53.5	--	0.91	0.47	--	--	0.35	--	--	--	--	--	--	--	--	--
4	Bulk	20.4	25.0	52.1	--	1.13	0.89	--	--	0.54	--	--	--	--	--	--	--	--	--
	Reference bulk composition	20.0	25.6	Bal.	--	1.18	0.47	--	--	0.36	0.05	--	--	--	--	--	--	0.015	--

Appendix H
Analysis of Performance
Test Section B
HR 120

Overview of Results: HR 120

During the analysis of Section C, in 2004, dimensional measurements showed that, after approximately 28.5 months of exposure, the HR 120 Sample O-P had lost 295 mils of its original 400 mil wall thickness. It thus had sustained a rate of wall thickness loss of 124 mils per year*. This high wastage rate raised concerns about the potential longevity of the HR 120 sample at the O-P position in Sections B. So, this sample was removed and replaced with a more corrosion resistant material. The intent was to ensure that Section B would not need to come out early.

Sample V-W was the only HR 120 sample to survive for the full 37 month exposure period. While Sample DD-EE remained in position for the full 37 months, at some point in its service life it was weld overlay repaired. Thus the data for this sample was lost. This history is summarized in the table below:

		Section A	Section C	Section B
	Full Exposure Period:	15.5 months	28.5 months	37 months
Sample	Nominal Temperature	Removed	Removed	Removed
O-P	1183 – 1194 F	15.5 months	28.5 months	28.5 months
V-W	1099 – 1110 F	15.5 months	28.5 months	37 months
DD-EE	1077 – 1088 F	15.5 months	28.5 months	N/A

The dimensional analysis of all three of the Section B tube samples is included in this report. However, the metallurgical analysis focused on Sample O-P which had experienced the greatest wall thickness loss (237 mils) for the Section B samples. The “gray” colored boxes above show which sample was subjected to metallurgical analysis for each test section.

Review of the data for test Sections A and C (see Figure H-13) revealed that the metal loss rate for the HR 120 samples was generally high at both the high temperature (Sample O-P) and low temperature (Sample DD-EE) locations. The data for all three sections also revealed that the metal loss rate was reduced for the intermediate temperature location (Sample V-W).

Evaluation of the metallographic cross section for Sample O-P from Section B showed that, for the region where the corrosion rate was highest, the sample had a continuous (presumably protective) scale, with pockets of deposit on its outer surface. The scale appeared to be frangible, and variable in thickness, with layers peeling away leading to thinning of the total scale thickness.

Examinations of other high wastage rate materials revealed that these samples were bare of deposit, and had a discontinuous scale.

An SEM/EDS evaluation of the surface scale found on one region of on Sample O-P, Section B reveals that the scale is predominantly a chromium-rich oxide. However, there also was a significant amount of iron and nickel in the scale. Refer to Figure H-15b and the EDS results in Figure H-19. Perhaps of particular importance in this analysis was the fact that the scale also contained a significant amount of sulfur, and that the sulfur content was relatively high (3.32%). This may well have contributed to the physical properties of the scale in this region, causing it to perhaps be more easily exfoliated. EDS analysis of the deposit also revealed evidence the elemental constituents of the alkali-iron-trisulfate associated with coal ash corrosion. Evaluation of the metal contiguous with the scale/metal interface of Sample O-P, Section B revealed no evidence of some chromium depletion in this region. Significant chromium depletion was noted for Sample O-P in Section C (11.2% vs 24.1%). Only minimal (if any) depletion was noted for Sample O-P in Section A (23.1% vs 25.3%).

While it was not the focus of this investigation, no evidence of metal loss could be found at the I.D. surface of Sample O-P, nor was any scale in evidence at this location, see Figure H-17. Evaluation of the weld cross section in Figure H-18 revealed no evidence of localized corrosion. It also suggests that the Inconel 625 weld metal used to join tube samples to one another was more resistant to fire side corrosion than was the HR 120 tube metal.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: HR 120

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• The schematic in Figure H-1 shows the relative positions of the three HR 120 samples in Test Section B. Only Sample V-W survived the full 37 month exposure period for Section B.• Due to concerns about excessive wall losses, Sample O-P (1183 F) was removed early after 28.5 months of exposure. At some point in its service life, Sample DD-EE (1077 F) was weld overlay repaired, thus no data was available for this sample.
Composition Verification.	<ul style="list-style-type: none">• The HR 120 tubing for this program came from one heat of material (Heat 854487538) supplied from Haynes International, Inc.• The table in Figure H-2 provides a nominal HR 120 composition from Haynes literature. It also provides the reported heat analysis.<ul style="list-style-type: none">○ It is interesting to note that while the heat supplied met the constraints of the nominal composition, it was somewhat lean in alloying element additions: molybdenum (actual 0.23% versus 2.5% max nominal), cobalt (0.088% versus 3% max), and tungsten (not detectable versus 2.5% max).• During the Section A evaluation, detailed composition verification was undertaken for each tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample O-P confirmed that the correct material was used at this location.
As-Received Appearance	<ul style="list-style-type: none">• Figure H-3 shows the typical appearance of an HR 120 tube sample prior to service.• Figures H-4 through H-6 document the as-received appearance of the external surface of the HR 120 tube samples. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view opposite to the gas flow direction).

Material: HR 120

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance, Continued.	<ul style="list-style-type: none">• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the “o’clock” conventions described above, (with the 12 o’clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o’clock side of the tube faces downward, and the 6 o’clock orientation faces upward within the boiler.• Wastage is most evident at 12 o’clock and 3 o’clock for Sample O-P• The gray/white scale commonly associated with molten alkali-iron sulfate attack is visible at the 3 o’clock position in Sample V-W.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures H-7 through H-9 show the appearance of the external surface of the HR 120 tube samples after grit-blasting to remove deposit and scale. The 12 o’clock and 3 o’clock positions for samples show the appearance of general wastage due to fireside corrosion.• However, it is important to keep in mind that Sample DD-EE had been weld overlay repaired from roughly the 1 to 7 o’clock positions.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures H-10 through H-12.• The same relative “o’clock” positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost.• Note that the cross section for Sample DD-EE clearly shows the presence of the weld overlay repair, and accounts for the reason why dimensional measurements are not provided for this sample.• Note also that Sample O-P shows the presence of what appears to be a longitudinal weld seam whose cross section extends inward into the I.D. of the tube. This accounts for the fact that no measurement was taken for the 7:30 o’clock orientation.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure H-13 plots the wastage rate versus temperature for samples from all three the three sections. Three HR 120 samples are plotted for Sections A and C. Only two points are plotted for Section B (because Sample DD-EE was weld overlay repaired)..• Review of these data suggests that, for Section B, the highest temperature sample, Sample O-P, experienced the greatest rate of metal loss. Sample O-P experienced the highest wastage rate for Section C; however, for Section A the rate for Sample V-W was slightly higher, (109 mils/year vs 100 mils/year).• It also was noted that the rate of metal loss drops off for Sample V-W which experienced an intermediate exposure temperature.

Material: HR 120

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure H-14 plots metal loss as a function of time and location for each all three sections.• Note that, after 28.5 months of exposure, Sample O-P had 237 mils of its original 400 mil wall thickness. Based on this, and due to concerns about this high wastage rate, this sample was removed from Section B and did not experience the full 37 month exposure period.• Sample DD-EE had been weld overlay repaired, thus, no 37 month data was available.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample O-P was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it was experiencing metal wastage at about the maximum rate. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.• Figures H-15a and b show the secondary electron images of the scale/metal interface for Sample O-P.• Figure H-15a provides a low magnification view for this interface. It shows that the external scale is continuous with isolated pockets of deposit.• Five distinct regions are in evidence in Figure H-15. These regions are, starting within the metal and working out:<ul style="list-style-type: none">○ <u>Base metal</u> – oxalic acid etch delineates grain boundaries, carbides and inclusions.○ <u>Deep etching band</u> – base metal parallel to, but approximately one grain diameter removed from the interface○ <u>Shallow etching band</u> – This constitutes the leading edge of the grains as they interface with the scale.○ <u>Tightly adherent scale</u> – this is seen continuous along the surface.○ <u>Bulk Deposit</u> - located above what appears to be a wide and shallow pit in the metal surface.• Figure H-15b shows the four locations selected for EDAX analysis. The results of these follow• Figure H-16 shows the appearance of the mid-wall microstructure for HR 120. A slightly duplex grain structure is indicated. Blocky precipitates were randomly distributed, along with fine intra-and inter-granular precipitates.• Figure H-17 shows the internal metal surface for Sample O-P. While surface appears to have an irregular contour, no evidence was found to indicate internal scale formation or metal loss.

Material: HR 120

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none">• Figure H-18 shows a longitudinal profile (at the 12 o'clock orientation) of the HR 120 sample adjacent to the welds “V” in Section B.• An Inconel 625 weld metal was used throughout Section B. The cross sections show that the HR 120 heat affected zones are not preferentially attached, in fact, the wall thickness for the tube sample tapers from the weld toward the middle of the tube length.
EDS Analysis Results	<ul style="list-style-type: none">• The table in Figure H-19 provides a summary of the EDAX analyses of the numbered in Figure H-15b. Also shown in this table is a summary of the spectrographic analysis reported earlier, Figure H-2.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Area 1: Bulk deposit analysis</u> – The deposit was comprised primarily of the oxides of iron (43.2%), silicon (10.2%), nickel (8.60%), and aluminum (7.32 %). A significant amount of arsenic (9.36%) is indicated. Also present is significant amounts of potassium (2.18%), phosphorous (1.67%) and sulfur (0.85%).• <u>Area 2: Adherent scale</u> – The scale is comprised primarily of the oxides of the underlying metal, chromium (33.9%), iron (31.0%), and nickel (11.8%). Silicon (3.93%) and aluminum (1.34%) also were indicated. Some small amounts of potassium (0.18%), and arsenic (0.74%) and phosphorous (0.41%) were found. The sulfur content (3.32%) was significantly high in the scale.• <u>Areas 3 and 4: Light and dark etching metal bands adjacent to the scale/metal interface</u> – No evidence of chromium depletion was found. The composition in this region is the same as that for the bulk metal.• <u>Bulk EDS analysis</u> – This analysis, taken near mid-wall, compares well with the reference spectrographic analysis.

Figure H-1: Schematic Drawing Showing Position of HR 120 Tube Samples Within Test Section B

1. Drawing shown in same relative orientation as per the actual installation.
2. This group of tube samples was removed from service in November 2001 - highlighted in red.
3. This group of tube samples was removed from service in June 2002 - highlighted in yellow.
4. This group of tube samples was removed from service in September 2003 – highlighted in blue.

Figure H-2 Semi-Quantitative Composition Verification for HR 120

Description: Nominal 33Fe/25Cr/37Ni alloy with Co, W, and Nb added to provide creep strength.
Source: Haynes International, Inc.
Reference Composition: “Nominal” chemistry – per Haynes literature.

Element	Reference Composition	Composition Heat 854487538	Tube Sample O-P	Tube Sample V-W	Tube Sample DD-EE
Ni	37	37.61	38.0	N/A	N/A
Cr	25	25.28	25.3	N/A	N/A
Fe	Balance	Balance	35.6	N/A	N/A
Mo	2.5 max	0.33	-	N/A	N/A
Co	3 max	0.09	-	N/A	N/A
C	0.05	0.06	-	N/A	N/A
N	0.2	0.20	-	N/A	N/A
B	0.004	<0.002	-	N/A	N/A
Mn	0.7	0.68	0.50	N/A	N/A
Si	0.6	0.52	0.64	N/A	N/A
Al	0.1	0.06	-	N/A	N/A
Ti	-	0.02	-	N/A	N/A
Al+Ti	-	-	-	N/A	N/A
Nb	0.7	0.62	-	N/A	N/A
Ta	-	-	-	N/A	N/A
Nb+Ta	-	-	-	N/A	N/A
V	-	-	-	N/A	N/A
W	2.5 max	<0.10	-	N/A	N/A
Cu	-	0.10	-	N/A	N/A
Sn	-	-	-	N/A	N/A
P	-	0.016	-	N/A	N/A
S	-	<0.002	-	N/A	N/A
O2	-	-	-	N/A	N/A

N/A = Sample not analyzed.

Figure H-3: Appearance of HR 120 Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure H-4 As-Received Appearance of Sample O-P (HR 120)

(Average surface metal temperature: 1183 °F)

Note: this tube was removed from service in September 2003

12 O'Clock – Facing Gas Flow
 (Note: 3 o'clock is up in this image)

3 O'Clock
 (Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure H-5 As-Received Appearance of Sample V-W (HR 120)

(Average surface metal temperature: 1099 °F)

Note: this sample experienced the full intended 37 month exposure period for Section B

12 O'Clock – Facing Gas Flow
 (Note: 3 o'clock is up in this image)

3 O'Clock
 (Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure H-6 As-Received Appearance of Sample DD-EE (HR 120)

(Average surface metal temperature: 1077°F)

Note: at some point this sample was repaired using a weld overlay. As such it could not be used in this analysis.

12 O'Clock
(166 mils lost)

3 O'Clock
(191 mils lost)

6 O'Clock
(0 mils lost)

Figure H-7: OD Surface Appearance After Grit Blast

Material: HR 120
Sample: O-P

Note: this tube was removed from service in September 2003

12 O’Clock
(107 mils lost)

3 O’Clock
(60 mils lost)

6 O’Clock
(0 mils lost)

Figure H-8: OD Surface Appearance After Grit Blast

Material: HR 120

Sample: V-W

Note: this sample experienced the full intended 37 month exposure period for Section B

12 O'Clock
(N/A mils lost)

3 O'Clock
(N/A mils lost)

6 O'Clock
(N/A mils lost)

Figure H-9: OD Surface Appearance After Grit Blast

Material: HR 120
Sample: DD-EE

Note: at some point this sample was repaired using a weld overlay. As such it could not be used in this analysis.

Material:

HR 120

Sample Location:

O-P

Maximum Rate:

100 mils/yr

Maximum Loss Orientation:

Approx. 2:30 o'clock

Average Surface Metal Temperature:

1183 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.376	0.376	0.378	0.378	0.374	0.378	0.373	0.377	0.376	0.376
After	0.210	0.184	0.187	0.368	0.374	N/A**	0.242	0.213		0.139
Delta	0.166	0.192	0.191	0.010	0.000	N/A**	0.131	0.164		0.237

Figure H-10: Silhouette and Wall Thickness Measurements for Sample O-P

Note: this tube was removed from service in September 2003

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

** No data taken at this position due to internal weld bead.

Material:

HR 120

Sample Location:

V-W

Maximum Rate:

42 mils/yr

Maximum Loss Orientation:

Approx. 10:00 o'clock

Average Surface Metal Temperature:

1099 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.372	0.378	0.377	0.375	0.376	0.378	0.373	0.375	0.376	0.376
After	0.265	0.286	0.317	0.369	0.380	0.371	0.346	0.251		0.247
Delta	0.107	0.092	0.060	0.006	-0.004	0.007	0.027	0.124		0.129

Figure H-11: Silhouette and Wall Thickness Measurements for Sample V-W

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Note: this sample experienced the full intended 37 month exposure period for Section B

Material: HR 120

Sample Location: DD-EE
Maximum Rate: N/A mils/yr
Maximum Loss Orientation: N/A
Average Surface Metal Temperature: 1077 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.372	0.371	0.376	0.377	0.379	0.377	0.377	0.376	0.376	N/A
After	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A		N/A
Delta	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A		N/A

Figure H-12: Silhouette and Wall Thickness Measurements for Sample DD-EE

Note: at some point this sample was repaired using a weld overlay. As such it could not be used in this analysis.

Figure H-13: Metal Loss Rate as a Function of Average Surface Metal Temperature

Material: HR 120

Note: In analyzing these data it is important to understand that one of the three Section B samples was removed early due to excessive corrosion losses. Sample O-P (1183 F) was removed in September 2003. At one point in its life, Sample DD-EE (1077 F) was weld overlay repaired. Thus, it could not be used in this analysis. Sample V-W (1099 F) survived for the full 37 month exposure period of Section B.

Figure H-14: Metal Loss as a Function of Time

Material: HR 120

Note: In analyzing these data it is important to understand that for Section B, Sample O-P was removed in September 2003. At one point in its life, Sample DD-EE was weld overlay repaired. Thus, it could not be used in this analysis. Sample V-W survived for the full 37 month exposure period of Section B.

(a) External Scale/Metal Interface (BEI- Low Magnification)

(b) External Scale/Metal Interface (BEI - Intermediate Magnification)

Figure H-15: Microstructure: HR 120

Note: Numbers on photo indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

Internal Surface Appearance (BEI- Low Magnification)

Figure H-16: Mid-Wall Microstructure: HR 120

Note: Photomicrograph at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Internal Surface Appearance (BEI- High Magnification)

Figure H-17: Microstructure: HR 120

Figure H-18: Longitudinal Cross-Section: HR 120 Adjacent to Weld “V”

Figure H-19: EDS Analysis of Deposit/Scale/Metal Interface for HR 120 (Sample O-P)

Area	Description	Ni	Cr	Fe	Co	W	Mo	Mn	Nb	Ti	Al	Si	C	O	K	Ca	As	P	S
1	Outer deposit	8.60	0.31	43.2	--	--	--	--	--	0.48	7.32	10.2	--	15.4	2.18	0.35	9.36	1.67	0.85
2	Adherent scale	11.8	33.9	31.0	--	--	--	0.20	--	--	1.34	3.93	--	13.3	0.18	--	0.74	0.41	3.32
3	Light etching band of metal at interface	38.1	25.8	34.6	--	--	--	0.41	--	--	--	1.04	--	--	--	--	--	--	--
4	Dark etching band	37.2	25.9	35.6	--	--	--	0.61	--	--	--	0.65	--	--	--	--	--	--	--
	Weld metal composition	25.3	23.2	31.4	13.8	2.00	2.18	0.86	--	--	0.23	0.92	--	--	--	--	--	--	--
	Midwall	38.0	25.3	35.6	--	--	--	0.50	--	--	--	0.64	--	--	--	--	--	--	--
	Reference bulk composition	37.9	25.3	34.3	--	--	0.23	0.69	0.56	0.01	0.06	0.51	0.06	--	--	--	--	--	0.001

Appendix I
Analysis of Performance
Test Section B
Thermie

Overview of Results: Thermie

There were two Thermie samples included in each of the three test sections. One was located in a relatively high temperature location (Sample H-I), and the other at a relatively low temperature location (Sample HH-II). For Section B, Thermie experienced an intermediate wastage rate of 57 mils/year and 27 mils/year at locations H-I and HH-II respectively. It should be noted that sample H-I was removed early from service (after 18.6 months), and set aside for later analysis. However given its wastage rate, and its initial 400 mil wall thickness, had Sample H-I been left in service, it seems likely that it would have survived for the full 37 month exposure period of Section B. The sample removal history is summarized in the table below:

		Section A	Section C	Section B
	Full Exposure Period:	15.5 months	28.5 months	37 months
Sample	Nominal Temperature	Removed	Removed	Removed
H-I	1159 – 1185 F	15.5 months	18.6 months	18.6 months
HH-II	1056 – 1162 F	15.5 months	28.5 months	37 months

The dimensional analysis of both Section B tube samples is included in this report. However, the metallurgical analysis focused on Sample H-I which had experienced the greatest wastage rate. The “gray” colored boxes above show which sample was subjected to metallurgical analysis for each test section. The figure below provides the locations of the Thermie samples within Section B.

Evaluation of the metallographic cross section for Sample H-I reveals a higher wastage rate locations where the deposit and scale was intact, see Figures I-12a and I-12b. This region was the focus of a detailed further investigation. It should be noted that adjacent regions were relatively bare of deposit and scale. Analysis revealed that the deposit had significant amounts of potassium (as high as 5.27%) and sulfur (as high as 2.35%). EDS analyses focused on the deposit/scale and scale metal interface. Point-by-point, "dot maps", and "line scan" techniques were used in this investigation. Potassium and iron were noted in the deposit adjacent to the scale/metal interface. Of significance was evidence of a layered deposit, with an especially high sulfur concentration (7.54%) immediately adjacent to the scale/metal interface. It should be noted that no evidence could be found of diffusion zones in the tube metal adjacent to the interface.

It should be noted, that while it was not the focus of this investigation, no evidence of metal loss could be found at the I.D. surface of Sample H-I. Also, the weld cross section through Sample HH-II suggested that the Inconel 625 weld metal performed about as well as the adjacent Thermie tube metal.

* **Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: Thermie

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• In assessing the data for Section B, it is important to understand that some tube samples had to be removed from the section early due to excessive thinning. The schematic in Figure I-1 shows the relative positions of the Thermie samples in all three sections. Also, shown are the positions of all of the excessively thinned tubes that were removed and replaced in order to extend the life of Section B.• Thermie Sample H-I was removed early from Section B in November 2001. Sample HH-II survived for the full 37 month exposure period for Section B.• The Sample HH-II, that was removed early, was set aside for later analysis, and has been included in the current evaluation along with the other tube samples that made up Section B.• Also shown in this figure is the calculated average surface metal temperature at both locations.
Composition Verification.	<ul style="list-style-type: none">• Oak Ridge National Laboratory (ORNL) provided the Thermie samples that were used in this program. Samples H-I and HH-II were reported to be from different heats.• The table in Figure I-1 shows the ORNL “target” chemistry for these alloys along with the ORNL-provided analysis for both heats.• During the Section A evaluation, detailed composition verification was undertaken for each tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its’ proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of Sample HH-II confirmed that the correct material was used at this location.

Material: Thermie

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance	<ul style="list-style-type: none">• Figure I-3 shows the typical appearance of a Thermie tube sample prior to service• Figures I-4 and I-5 document the appearance of the external surface of the Thermie tube samples after service in Section B. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the "o'clock" conventions described above, (with the 12 o'clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o'clock side of the tube faces downward, and the 6 o'clock orientation faces upward within the boiler.• Sample H-I was observed to have a thick deposit at the 12 o'clock orientation, and to be relatively bare of deposit at the 3 o'clock and 6 o'clock orientations.• Note that, as is conventional, for Sample HH-II, a deposit was noted at the 6 o'clock orientation, and was bare of deposit in the other views.• Evidence of the gray/white scale associated with alkali-iron-trisulfate is in evidence for Sample H-I in the 12 o'clock view, Figure I-4.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures I-6 and I-7 show the appearance of the external surface of the Thermie tube samples after grit-blasting to remove deposit and scale.• The 12 o'clock and 3 o'clock positions for Samples H-I clearly show the appearance of general wastage due to fireside corrosion. The 6 o'clock position shows no evidence of wastage or pitting..• Wastage and pitting are somewhat less evident for Sample HH-II.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures I-8 and I-9.• The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure I-10 plots the maximum wastage rate against the calculated average metal temperature for the Thermie samples from all three sections.• These data suggest that the wastage rate for Thermie increases with increasing temperature.

Material: Thermie

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure I-11 plots metal loss as a function of time for each sample location for all three sections.• Tube Sample H-I was removed and replaced in Sections B and C after about 18.6 months of service. Measurements, at that time, revealed that the wastage rate for these samples was moderate. However, these samples were physically located within a series of samples that were experiencing a much higher corrosion rate, and the decision was made to extract and replace Sample H-I along with these other samples.• Sample HH-II demonstrated approximately the same maximum wall thickness loss for both Sections B and C. This suggests that the wastage rate is decreasing with time for this tube sample.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample H-I was selected for a detailed SEM/EDS assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it had a higher rate of metal loss than Sample HH-II.. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.• Figure I-12 shows backscattered electron images of the scale/metal interface for Sample H-I. In Figure I-12a, a deposit/scale coated pit is noted at the left side of this image. The interface to the right in this figure is relatively bare of deposit and scale.• Figure I-12b shows a higher magnification view of the pit shown in Figure I-12a. The numbered locations show the locations for the EDS analyses documented in the table in Figure I-14.
EDS Analysis Results	<ul style="list-style-type: none">• The table in Figure I-14 provides a summary of the EDS analyses of the locations numbered in Figures I-12b, and I-13. Also shown in this table is a summary of the spectrographic analysis reported earlier, see Figure I-2.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Area 1: Coarse outer deposit</u> – Major constituents of the deposit in this location are: iron (27.6%), nickel (22.5%), arsenic (18.4%), silicon (10.7%), oxygen (9.26%), and aluminum (5.48%). The following also were found in significant amounts: potassium (2.34%) and sulfur (1.78%).• <u>Area 2: Coarse outer deposit (broad scan)</u>: - Major constituents of the deposit at this location are: silicon (30.4%), oxygen (22.8%), iron (19.2%), aluminum (11.2%), nickel, (3.88%), and arsenic (1.65%). Potassium (5.27%) was increased at this location, as was sulfur (2.35%). Cobalt (0.43%) also was noted.

Material: Thermic

Summary of Findings, (continued)

Issue	Discussion
EDS Analysis Results, continued	<ul style="list-style-type: none">• <u>Area 3: Deposit adjacent to interface with scale</u> – Major constituents here were: nickel (27.9%), iron (22.9%), arsenic (13.0%), oxygen (12.2%), silicon (9.40%), and aluminum (4.19%). A significant amount of chromium (3.39%) was found and the cobalt content (1.85%) increased. The potassium (1.74%) was reduced somewhat, as was the sulfur (1.24%) content.• <u>Area 4: Bulk scale deposit composition</u> - The scale is found to be enriched in chromium (66.8%), niobium (5.51%), titanium (3.53%), and molybdenum (1.07%). The scale contained only a small amount of nickel (3.02%), cobalt (0.88%), and iron (0.78%).• <u>Area 5: Scale composition within grain boundary penetration</u> – Significant at this location is the increase of sulfur to (7.54%). Nickel (14.2%) and cobalt (7.79%) are increased relative to the bulk scale analysis. The chromium content (45.2%) is decreased but still high.• <u>Area 6: Metal at scale/metal interface</u> - composition of the metal adjacent to the scale/metal interface was virtually identical to that at mid-wall. No evidence of composition gradients could be found.
EDS Analysis Results – “Dot Maps” and “Line Scans”	<ul style="list-style-type: none">• Figure I-15 shows the results of EDS elemental “dot maps” to further investigate the corrosion attack that resulted in the pit shown in Figure I-13. Figures I-15d and I-15e shows that the outer regions of the scale are enriched in chromium and oxygen. Figure I-15f shows that the inner scale adjacent to the scale/metal interface is enriched in sulfur. No evidence of potassium enrichment could be found in the vicinity of the scale/metal interface.• Figure I-16 shows the results of EDS “dot maps” at a higher magnification along the same scale/metal interface. Figure I-16d emphasizes the relatively high content of chromium in the outer scale, and lower content in the inner scale adjacent to the interface. Figure I-16f shows the high concentration of sulfur immediately adjacent to the scale/metal interface.• Figure I-17 shows the results of EDS “line scans” that show elemental distributions across the same interface. Again, Figure I-17f, shows that the sulfur content is enriched at the scale/metal interface, while Figure I-17d shows that the chromium content is somewhat decrease. Figure I-17g and I-17h seem to indicate that the potassium and sodium contents are increased as the analysis progresses into the deposit.

Material: Thermie

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – Continued	<ul style="list-style-type: none">• Figure I-18 shows the microstructure at mid-wall in the Thermie tube.• Figure I-19 shows a longitudinal profile (at the 12 o'clock orientation) of Sample HH-II adjacent to the weld "II" in Section B.• In this cross section the Inconel 625 weld metal appears to have roughly equivalent corrosion resistant to the Thermie tube metal

Figure I-1: Schematic Drawing Showing Position of Thermie Tube Samples Within Test Section C

1. Drawing shown in same relative orientation as per the actual installation.
2. This group of tube samples was removed from service in November 2001 - highlighted in red.
3. This group of tube samples was removed from service in June 2002 - highlighted in yellow.
4. This group of tube samples was removed from service in September 2003 - highlighted in blue.

Figure I-2 Semi-Quantitative Composition Verification for Thermic

Description: Nominal 25Cr/20Co nickel alloy with additions of Nb and Ti to provide creep strength.
Source: Oak Ridge National Laboratory (ORNL)
Reference Composition: “Target” Chemistry per ORNL (Reference 1).

Element	Reference Composition	Composition Heat 17422	Composition Heat 17454	Tube Sample H-I	Tube Sample HH-II
Ni	48.0	49.06	48.92	48.4	N/A
Cr	24.0	23.08	23.63	23.3	N/A
Fe	2.0	2.06	2.11	2.24	N/A
Mo	0.5	0.43	0.42	-	N/A
Co	19.8	19.39	19.42	19.6	N/A
C	0.07	0.088	0.094	-	N/A
N	-	0.013	0.022	-	N/A
B	0.002 max	(a)	(a)	-	N/A
Mn	0.3	0.32	0.32	-	N/A
Si	0.5	0.51	0.49	0.52	N/A
Al	0.8	0.74	0.60	0.57	N/A
Ti	2.0	2.10	2.01	1.91	N/A
Al+Ti	-	-	-	-	N/A
Nb	2.0	2.20	1.95	3.43	N/A
Cu	-	<0.01	<0.01	-	N/A
Sn	-	-	-	-	N/A
P	-	<0.002	<0.002	-	N/A
S	-	0.003	0.009	-	N/A
O2	-	0.003	0.004	-	N/A
Zr	0.015 max	(a)	(a)	-	N/A
Mg	-	-	-	-	N/A

a- Not analyzed.
b- By difference.
c- Not found.

Reference 1: “Fabrication of Test Tubes for Coal Ash Corrosion Testing”, Sikka, V.K., Swindeman, R.W., Wright, I.G., Judkins, R.R., Johnson, R., Proc, 13th Annual Conf. on Fossil Energy Mat’ls, May 1999.

Note: Sample H-I was from Heat 17454 Sample HH-II was from Heat 17422 N/A = Sample not analyzed.

Figure I-3: Appearance of Thermie Tube Sample Prior to Service

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure I-4 As-Received Appearance of Sample H-I (Thermie)

(Average surface metal temperature: 1159 °F)

Note: this tube was removed from service in November 2001

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure I-5 As-Received Appearance of Sample HH-II (Thermie)
(Average surface metal temperature: 1056°F)

Note: this sample experienced the full intended 37 month exposure period for Section B

12 O'Clock
(62 mils lost)

3 O'Clock
(43 mils lost)

6 O'Clock
(1 mils lost)

Figure I-6: OD Surface Appearance After Grit Blast

Material: Thermie
Sample: H-I

Note: this tube was removed from service in November 2001

12 O'Clock
(72 mils lost)

3 O'Clock
(25 mils lost)

6 O'Clock
(2 mils lost)

Figure I-7: OD Surface Appearance After Grit Blast

Material: Thermie
Sample: HH-II

Note: this sample experienced the full intended 37 month exposure period for Section B

Material:

Thermie

Sample Location:

H-I

Maximum Rate:

57 mils/yr

Maximum Loss Orientation:

Approx. 2:00 o'clock

Average Surface Metal Temperature:

1159 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.400	0.401	0.403	0.402	0.401	0.400	0.398	0.398	0.400	0.400
After	0.338	0.321	0.360	0.402	0.400	0.399	0.368	0.348		0.311
Delta	0.062	0.080	0.043	0.000	0.001	0.001	0.030	0.050		0.089

Figure I-8: Silhouette and Wall Thickness Measurements for Sample H-I

Note: this tube was removed from service in November 2001.

Material:

Thermie

Sample Location:

HH-II

Maximum Rate:

27 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average Surface Metal Temperature:

1056 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.401	0.401	0.401	0.401	0.401	0.401	0.400	0.400	0.401	0.400
After	0.329	0.364	0.376	0.399	0.399	0.398	0.377	0.317		0.317
Delta	0.072	0.037	0.025	0.002	0.002	0.003	0.023	0.083		0.083

Figure I-9: Silhouette and Wall Thickness Measurements for Sample HH-II

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Note: this sample experienced the full intended 37 month exposure period for Section B.

Figure I-10: Metal Loss Rate as a Function of Average Surface Metal Temperature

Material: Thermie

Note: In analyzing these data it is important to understand that the one of the two Section B samples was removed early due to excessive corrosion losses. Sample H-I (1591 F) was removed in November 2001. Sample HH-II was removed with the remaining Section B samples.

Figure I-11: Metal Loss as a Function of Time

Material: Thermie

Note: From the plot above it can be seen that Section B Sample H-I was removed early, and Sample HH-II experienced the full exposure life.

(a) External Scale/Metal Interface (BEI - Low Magnification)

(b) External Scale/Metal Interface (BEI - Intermediate Magnification)

Figure I-12: Microstructure: Thermie (Sample H-I)

Note: Numbers on photo indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

(BEI - Intermediate Magnification)

Figure I-13: Microstructure at OD Surface
(At the Location Indicated by the No. 5 Box in Figure I-12b)

Figure I-14: EDS Analysis of Deposit/Scale/Metal Interface for Thermie (H-I)

Area	Description	Ni	Cr	Fe	Co	Mo	Mn	Ti	Nb	Al	Si	O	Ca	K	Na	Mg	As	P	S
1	Coarse outer deposit	22.5	0.54	27.6	--	--	--	0.95	--	5.48	10.7	9.26	--	2.34	0.37	--	18.4	--	1.78
2	Coarse outer deposit	3.88	0.48	19.2	0.43	--	--	1.52	--	11.2	30.4	22.8	--	5.27	0.84	--	1.65	--	2.35
3	Deposit adjacent to scale	27.9	3.39	22.9	1.85	--	--	1.00	--	4.19	9.40	12.2	--	1.74	0.09	--	13.0	1.02	1.24
4	Bulk scale composition	3.02	66.8	0.78	0.88	1.07	--	3.53	5.51	0.45	1.10	15.4	--	0.25	--	--	1.18	--	--
5	Scale within grain boundary penetration	14.2	45.2	0.88	7.79	--	--	3.80	5.18	1.51	1.38	12.5	--	--	--	--	--	--	7.54
6	Metal at scale/metal interface	48.9	23.5	2.18	19.2	--	--	1.90	2.95	0.71	0.65	--	--	--	--	--	--	--	--
	Midwall	48.4	23.3	2.24	19.6	--	--	1.91	3.43	0.57	0.52	--	--	--	--	--	--	--	--
	Reference bulk composition	48.9	23.6	2.11	19.4	0.42	0.32	2.01	1.95	0.60	0.49	--	--	--	--	--	--	0.002	0.009

Thermie 250x Maps

(a) Nickel Distribution

Thermie 250x Maps

(b) Iron Distribution

Figure I-15: EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution (Thermie, Sample H-I)

Thermie 250x Maps

(c) Cobalt Distribution

Thermie 250x Maps

(d) Chromium Distribution

Figure I-15, Cont.: EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution (Thermie, Sample H-I)

Thermie 250x Maps

(e) Oxygen Distribution

Thermie 250x Maps

(f) Sulfur Distribution

Figure I-15, Cont.: EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution (Thermie, Sample H-I)

Thermie 250x Maps

(g) Potassium Distribution

Thermie 250x Maps

(h) Sodium Distribution

Figure I-15, Cont.: EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution (Thermie, Sample H-I)

Thermie 1500x Interface Maps

(a) Nickel Distribution

Thermie 1500x Interface Maps

(b) Iron Distribution

Figure I-16: EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution (Thermie, Sample H-I)

Thermie 1500x Interface Maps

(c) Cobalt Distribution

Thermie 1500x Interface Maps

(d) Chromium Distribution

Figure I-16, Cont.: EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution (Thermie, Sample H-I)

Thermie 1500x Interface Maps

(e) Oxygen Distribution

Thermie 1500x Interface Maps

(f) Sulfur Distribution

Figure I-16, Cont.: EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution (Thermie, Sample H-I)

Thermie 1500x Interface Maps

(g) Potassium Distribution

Thermie 1500x Interface Maps

(h) Sodium Distribution

Figure I-16, Cont.: EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution (Thermie, Sample H-I)

(a) Nickel Distribution

(b) Iron Distribution

Figure I-17: EDS Line Scans of OD Scale/Metal Interface Showing Elemental Distribution (Thermic, Sample H-I)

(c) Cobalt Distribution

(d) Chromium Distribution

Figure I-17, Cont.: EDS Line Scans of OD Scale/Metal Interface Showing Elemental Distribution (Thermie, Sample H-I)

(e) Oxygen Distribution

(f) Sulfur Distribution

Figure I-17, Cont.: EDS Line Scans of OD Scale/Metal Interface Showing Elemental Distribution (Thermie, Sample H-I)

(g) Potassium Distribution

(h) Sodium Distribution

Figure I-17, Cont.: EDS Line Scans of OD Scale/Metal Interface Showing Elemental Distribution (Thermie, Sample H-I)

Midwall Microstructure (BEI - Intermediate Magnification)

Figure I-18: Midwall Microstructure: Thermite (Sample H-I)

Note: Electrolytic 10% oxalic acid etch, 9V OCP

ID Microstructure (BEI - High Magnification)

Figure I-19: ID Microstructure: Thermie (Sample H-I)

Note: Electrolytic 10% oxalic acid etch, 9V OCP

Figure I-20: Longitudinal Cross-Section: Thermie Adjacent to Weld “II”

Appendix J

Analysis of Performance

Test Section B

IN52 Weld Overlay

Overview of Results: IN52 Weld Overlay

There were two IN 52 weld overlay samples included in each of the three test sections. One was located in a relatively high temperature location (Sample R-S), and the other at a relatively low temperature location (Sample GG-HH). For Section B, IN 52 experienced an intermediate wastage rate of 31 mils/year and 59 mils/year at locations R-S and GG-HH respectively. Both samples survived for the full 37 month exposure period of Section B. The sample removal history is summarized in the table below:

		Section A	Section C	Section B
	Full Exposure Period:	15.5 months	28.5 months	37 months
Sample	Nominal Temperature	Removed	Removed	Removed
R-S	1195 – 1208 F	15.5 months	28.5 months	37 months
GG-HH	1062 – 1073 F	15.5 months	28.5 months	37 months

The dimensional analysis of both Section B tube samples is included in this report. However, the metallurgical analysis focused on Sample GG-HH which had experienced the greatest wastage rate. The “gray” colored boxes above show which sample was subjected to metallurgical analysis for each test section.

The chart in Figure J-10 plots wastage rate as a function of temperature. As can be seen, this chart shows that for all three test sections, the wastage rate was higher for the lower temperature Sample GG-HH (at 1062 F in Section B) than for the higher temperature Sample R-S (at 1195 F, in Section B). For the case of the IN 52 weld overlay specimens, Sample R-S was located closer to a wall, while Sample GG-HH was located near mid-span in the section. The figure below illustrates the positions of the IN 52 weld overlay specimens.

Evaluation of the metallographic cross section for Sample GG-HH reveals that the location selected for evaluation had a continuous scale but was devoid of deposit, see Figures J-12 and J-13. The IN 52 weld overlay was completely wasted away, and corrosion was continuing its penetration into the 800H substrate. Per the table in Figure J-16, EDS analysis revealed that the scale was rich in sulfur (3.24%). No evidence was found to verify the coal ash corrosion mechanism.

The EDS analysis also suggested that the composition of the weld overlay was modified somewhat due to the “dilution” that occurred during deposition of the IN 52 weld metal. Dilution involves mixing of the molten weld metal with a melted layer of the underlying 800H substrate.

This results in a change in the composition of the cladding that reflects the proportions of the molten weld metal and melted tube metal. In this case, dilution resulted in a weld overlay with an increased iron content (16.0% vs 8.99%), and a decreased nickel content (55.9% vs 61.8%). The chromium content remained about the same (27.3% vs 27.5%). While the chromium content has been established as a key indicator of corrosion resistance, earlier work in this program has suggested that the chromium plus nickel content is also an indicator. If this is true for the case at hand, then decreased dilution would lead to an improvement in corrosion resistance.

For the record, grain boundary separations were noted in the heat affected zone along the 800H interface with the weld overlay, see Figures J-12 and J-13. While the cause of these separations has not been fully investigated, based on their location (under the cladding and distant from the scale/metal interface), it seems likely that these separations occurred during the cladding operation. It should be noted however that this is the only instance where 800H heat affected zone cracking has been observed in this program.

It should also be noted, that while it was not the focus of this investigation, a cross section through the internal surface of Sample GG-HH revealed a thin internal scale accompanied by grain boundary penetrations, see Figure J-14.

Lastly, the weld cross section through Sample GG-HH (see Figure J-15) suggested that the Inconel 625 weld metal performed better than the adjacent IN 52 cladding.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: IN52 Weld Overlay

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• The schematic in Figure J-1 shows the relative positions of IN52 Weld Overlay samples in Test Section B. Note that both of the IN52 tube samples survived for the full 37 month exposure period.• Also, shown is the calculated average metal temperature at both locations.
Composition Verification.	<ul style="list-style-type: none">• The table in Figure J-2 provides the reference composition for the filler metal as per Special Metals Company (SMC) literature.• The table also shows the SMC heat analysis for the heat of filler wire used to deposit the cladding on these samples, Heat NX 9090JK.• During the Section A evaluation, detailed composition verification was undertaken for every tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample GG-HH confirmed that the correct material was used at this location.
As-Received Appearance	<ul style="list-style-type: none">• Figure J-3 shows the appearance of the IN52 Weld Overlay tube as delivered from SMC. Note the distinctive appearance of the weld cladding. The total wall thickness for this tube is approximately 290 mils. The clad layer is about 80 mils thick. The substrate is Incoloy 800H.• Figures J-4 and J-5 document the appearance of the external surface of the IN52 Weld Overlay tube samples after service in Test Section B. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).

Material: IN52 Weld Overlay

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance, Continued	<ul style="list-style-type: none">• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the “o’clock” conventions described above, (with the 12 o’clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o’clock side of the tube faces downward, and the 6 o’clock orientation faces upward within the boiler.• A thick rust-red deposit was noted in the 6 ‘clock view for both samples, as was some evidence of the gray/white scale typically associated with molten alkali-iron sulfate attack.• The 12 o’clock and 3 o’clock views showed intermittent deposit and a brown/black scale.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures J-6 through J-7 show the appearance of the external surface of the IN52 Weld Overlay tube samples after grit-blasting to remove deposit and scale. The 12 o’clock and 3 o’clock positions for both samples show the appearance of general wastage and pitting.• The 6 o’clock position, for tube Sample GG-HH, shows evidence of pitting attack. Very little attack is found at the 6 o’clock position for Sample R-S.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures J-8 and J-9.• The same relative “o’clock” positions were maintained as discussed earlier. Measurements were taken prior to service at eight evenly spaced locations about the tube circumference. To prepare for this, the external surface of the cladding was ground flush to minimize thickness variability due to surface contour. After-service attempts failed to find these predetermined locations. So a conservative approach was taken, and wall thickness measurements were taken at mid-specimen (as it was for the monolithic specimens).• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost. Note that in some cases, the delta is negative (e.g at the 6 o’clock position for Sample GG-HH). This is believed due to the difficulties (described above) in locating the exact location of the “before” measurement.
Wall Thickness Loss Rate Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure J-10 plots the maximum wall thickness lost against the calculated average metal temperature for each of the two IN52 Weld Overlay samples. The data for Sections A and C also are plotted.• The data in the chart suggest that the metal loss rate decreases with increased temperature for the IN52 Weld Overlay samples.

Material: IN52 Weld Overlay

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure J-11 plots metal loss as a function of time for both sample locations for all three sections.• Keep in mind that the initial IN 52 cladding thickness was roughly 80 mils. Based on this, It can be seen that, for both IN 52 clad samples, the cladding was totally penetrated at some point during the Section B exposure.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• The sample with the highest rate of metal loss (GG-HH) was selected for a detailed SEM/EDS assessment of the constituents and structure in the vicinity of the external and internal surfaces.• Unlike the analysis of other tube materials for Section C, the focus of this investigation was <u>not</u> in the region of the tube where the maximum amount of material was lost. The intent of this assessment was to focus on corrosion of the weld cladding, and the weld cladding had completely wasted away in the tube regions which experienced the most metal lost. Due to interest in the cladding, this investigation examined portions of the tube where the weld cladding remained.• Figures J-12a, b and c show backscattered electron images of the scale/metal interface for Sample GG-HH.• The numbers on Figures J-12c show the locations of EDS analyses that will later be reported.• Five distinct regions are in evidence in the microstructure near the interface. These regions are, starting within the adhering scale and working inward:<ul style="list-style-type: none">○ <u>Adherent Scale</u> – this scale is continuous along the scale/metal interface (for both the cladding and IN 800H), see Figure J-12a).○ <u>Light etching band along scale/metal interface with the cladding</u> – This is best shown in Figure J-12c. EDS analysis later will show this region is somewhat enriched in iron and depleted in nickel relative to the bulk cladding analysis.○ <u>Cladding</u>: – typical cladding microstructure is in evidence (Figure J-12c).○ <u>Weld heat affected zone in 800H</u> – Grain boundary cracking was noted in this region below the cladding (See Figures J-12c and J-13).○ <u>Unaffected 800H substrate</u>• Figure J-14 shows a 2 mil thick oxide scale along the internal metal surface of Sample GG-HH.

Material: IN52 Weld Overlay

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none">• Figure J-15 shows a longitudinal profile (at the 12 o'clock orientation) of the IN52 weld overlay sample adjacent to the weld “GG” in Section B, see Figure J-1 for location. This figure also shows (for comparison the condition of the IN 72 weld overlay sample that was adjacent to the same weld.• Examination of Figure J-14 reveals that the IN 52 weld cladding has been completely wasted away (while the IN 72 weld cladding has not). Also note that the Inconel 625 weld metal appears to have wasted to a lesser extent. In any case, the wall thickness adjacent to the weld is somewhat thicker and it tapers toward the middle of the tube length. This seems to lend validity to the dimensions taken from a ring that was extracted from the middle of this tube.
EDAX Analysis Results	<ul style="list-style-type: none">• The table in Figure J-15 provides a summary of the EDS analyses of the numbered locations in Figure J-12c. Also shown in this table is a summary of the spectrographic analysis reported earlier, see Figure J-2.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Area 1: Adherent scale</u> – The scale is primarily comprised of chromium (64.7%), oxygen (14.0%), nickel (10.4%), and iron (3.64%). The data also suggest a high concentration of sulfur (3.24%).• <u>Area 2: Cladding adjacent to scale/metal interface</u> – Relative to the bulk cladding composition, this region is slightly enriched in iron (16.0% vs 13.6%) otherwise its composition is similar to that of the bulk.• <u>Area 3: Weld overlay composition</u> - The cladding composition reflects dilution by the underlying 800H. Therefore, relative to the filler metal wire composition, the cladding composition is somewhat enriched in iron (13.6% vs 8.99%), and depleted in nickel (55.9% vs 61.8%). The chromium content was relatively unchanged (27.5% vs 27.3%).

Gas Flow
Direction

North End

South End

Figure J-1: Schematic Drawing Showing Position of IN52 Weld Overlay Tube Samples Within Test Section B

1. Drawing shown in same relative orientation as per the actual installation.
2. This group of tube samples was removed from service in November 2001 - highlighted in red.
3. This group of tube samples was removed from service in June 2002 - highlighted in yellow.
4. This group of tube samples was removed from service in September 2003 - highlighted in blue.

Figure J-2 Semi-Quantitative Composition Verification for Inco 52 / 800 HT (Weld clad duplex tubing)

Description: Nominal 30 Cr nickel alloy cladding for oxidation/corrosion protection. Incoloy 800HT substrate provides creep strength.
Source: Special Metals Corporation (SMC)
Reference Composition: Filler wire “limiting chemical composition” – Per SMC literature. (ANSI AWS 5.14M-97 Class ERNiCrFe-7)

Element	Reference Composition for Weld Cladding	Composition Heat NX 9090JK	Tube Sample R-S	Tube Sample GG-HH
Ni	Balance	60.48	N/A	55.9
Cr	28.0 – 31.5	28.97	N/A	27.5
Fe	7.0 – 11.0	8.86	N/A	13.6
Mo	0.50 max	0.01	N/A	-
Co	-	0.01	N/A	-
C	0.04 max	0.02	N/A	-
N	-	-	N/A	-
B	-	-	N/A	-
Mn	1.0 max	0.24	N/A	0.24
Si	0.50 max	0.14	N/A	0.27
Al	1.10 max	0.69	N/A	1.30
Ti	1.0 max	0.58	N/A	1.17
Al+Ti	1.5 max	1.27	N/A	2.47
Nb	0.10 max	0.01	N/A	-
Ta	-	<0.01	N/A	-
Nb+Ta	-	0.02	N/A	-
V	-	-	N/A	-
W	-	-	N/A	-
Cu	0.30 max	0.01	N/A	-
Sn	-	-	N/A	-
P	0.020 max	0.004	N/A	-
S	0.015 max	<0.001	N/A	-
O2	-	-	N/A	-
Others	0.50 max	<0.50	N/A	-

N/A = Sample not analyzed.

Note: Reference composition is for filler wire, not as-deposited.

Figure J-3: Appearance of IN52 Weld Overlay Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure J-4: As-Received Appearance of Sample R-S (IN52 Weld Overlay)

(Average surface metal temperature: 1195 °F)

Note: this sample experienced the full intended 37 month exposure period for Section B

12 O'Clock – Facing Gas Flow
 (Note: 3 o'clock is up in this image)

3 O'Clock
 (Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure J-5: As-Received Appearance of Sample GG-HH (IN52 Weld Overlay)

(Average surface metal temperature: 1062 °F)

Note: this sample experienced the full intended 37 month exposure period for Section B.

12 O'Clock
(37 mils lost)

3 O'Clock
(21 mils lost)

6 O'Clock
(0 mils lost)

Figure J-6: OD Surface Appearance After Grit Blast

Material: IN52 Weld Overlay
Sample: R-S

Note: this sample experienced the full intended 37 month exposure period for Section B.

12 O'Clock
(105 mils lost)

3 O'Clock
(20 mils lost)

6 O'Clock
(0 mils lost)

Figure J-7: OD Surface Appearance After Grit Blast

Material: IN52 Weld Overlay
Sample: GG-HH

Note: this sample experienced the full intended 37 month exposure period for Section B.

Material:

IN52 Weld Overlay

Sample Location:

R-S

Maximum Rate:

31 mils/yr

Maximum Loss Orientation:

Approx. 10:00 o'clock

Average Surface Metal Temperature:

1195 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.282	0.294	0.304	0.306	0.302	0.292	0.286	0.278	0.293	0.293
After	0.245	0.204	0.283	0.306	0.307	0.307	0.269	0.233		0.196
Delta	0.037	0.090	0.021	0.000	-0.005	-0.015	0.017	0.045		0.097

Figure J-8: Silhouette and Wall Thickness Measurements for Sample R-S

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Note: this sample experienced the full intended 37 month exposure period for Section B.

Material:

IN52 Weld Overlay

Sample Location:

GG-HH

Maximum Rate:

59 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average Surface Metal Temperature:

1062 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.291	0.280	0.274	0.274	0.282	0.294	0.300	0.300	0.287	0.300
After	0.186	0.260	0.254	0.288	0.294	0.284	0.231	0.119		0.119
Delta	0.105	0.020	0.020	-0.014	-0.012	0.010	0.069	0.181		0.181

Figure J-9: Silhouette and Wall Thickness Measurements for Sample GG-HH

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Note: this sample experienced the full intended 37 month exposure period for Section B.

Figure J-10: Metal Loss Rate as a Function of Average Surface Metal Temperature

Material: IN52 Weld Overlay

Figure J-11: Metal Loss as a Function of Time

Material: IN52 Weld Overlay

(a) External Scale/Metal Interface (SEI - Low Magnification)

(b) External Scale/Metal Interface (SEI - Intermediate Magnification)

Figure J-12 Microstructure: IN52 Weld Overlay (Sample GG-HH)

(c) External Scale/Metal Interface (SEI - Intermediate Magnification)

Figure J-12(Cont.): Microstructure: IN52 Weld Overlay (Sample GG-HH)

Note: Numbers on photos indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

(a) Cracking in 800H below scale (SEI - High Magnification)

(b) External Scale/Metal Interface (SEI - High Magnification)

Figure J-13 Microstructure: IN52 Weld Overlay (Sample GG-HH)

Internal Surface Appearance

**Figure J-14 Microstructure: 800H Substrate Internal Surface of Tube Having
IN52 Weld Overlay (Sample GG-HH)**

Note: Photomicrograph at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Figure J-15: Longitudinal Cross-Sections: IN52 Weld Overlay Adjacent to Weld "GG"

Note: None of the original weld overlay remains in this view, only 800H substrate.

Figure J-16: EDS Analysis of Deposit/Scale/Metal Interface for IN52 Weld Overlay (Sample GG-HH)

Area	Description	Ni	Cr	Fe	Cu	Mn	W	Ti	Al	Si	C	O	Ca	K	Na	Mg	As	P	S
1	Adherent external scale	10.4	64.7	3.64	--	0.88	--	1.18	1.51	0.42	--	14.0	--	--	--	--	--	--	3.24
2	Cladding adjacent to interface	55.9	26.7	16.0	--	0.30	--	0.32	0.56	0.21	--	--	--	--	--	--	--	--	--
3	Weld overlay composition	55.9	27.5	13.6	--	0.24	--	1.17	1.30	0.27	--	--	--	--	--	--	--	--	--
	At 800H crack under weld overlay	29.9	23.1	37	--	1.22	--	2.48	2.65	0.12	--	3.18	--	--	--	--	--	--	--
	Reference bulk composition	61.8	27.3	8.99	--	0.28	--	0.51	0.83	0.23	0.03	--	--	--	--	--	--	--	--

Appendix K
Analysis of Performance
Test Section B
Incoclad 671

Overview of Results: Incoclad 671

There were three Incoclad 671 samples included in each of the three test sections. These samples survived for the full intended exposure period for all three test sections. The sample removal history is summarized in the table below:

		Section A	Section C	Section B
	Full Exposure Period:	15.5 months	28.5 months	37 months
Sample	Nominal Temperature	Removed	Removed	Removed
P-Q	1191 – 1203 F	15.5 months	28.5 months	37 months
U-V	1109 – 1121 F	15.5 months	28.5 months	37 months
EE-FF	1067 – 1086 F	15.5 months	28.5 months	37 months

The chart in Figure K-13 plots wastage rate as a function of temperature. As can be seen from this chart, the wastage rate was greatest at the lowest temperature (i.e. for sample EE-FF). It was lowest at the intermediate temperature (i.e. for Sample U-V), then, rose slightly (or stayed the same) at the highest exposure temperature (i.e. for Sample P-Q). This performance was consistent for all three test sections.

For the case of the Incoclad 671 specimens, the high temperature sample (Sample P-Q) and especially the intermediate temperature sample (Sample U-V) were located closer to the walls, while the low temperature Incoclad 671 sample (Sample EE-FF) was located near mid-span in the section. The figure below illustrates the positions of the Incoclad 671 specimens.

The dimensional analysis of all three Incoclad 671 Section B tube samples is included in this report. However, the metallurgical analysis focused on Sample FF-GG which had experienced the greatest wastage rate. The “gray” colored boxes in the table above show which sample was subjected to metallurgical analysis for each test section.

Evaluation of the metallographic cross section for Sample FF-GG reveals that the location selected for evaluation had a continuous scale with a thin layer of deposit, see Figure K-15a. EDS analysis revealed that the scale has high levels of chromium (70.4%), sulfur (15.2%), and oxygen (10.1%), along with a small amount of nickel (2.82%). The table in Figure K-16 provides the results of EDS analyses for all of the microstructural features in the vicinity of the external scale/metal interface. Review reveals that distinct diffusion zone was present with ingress of corrosion along paths that appeared to be influenced by the local microstructure, see Figure K-15b. Pockets of internal sulfidation are indicated at the limits of the observed ingress, see Figure K-15c. It should be noted that the microstructure of the cladding involves two major constituents,

see Figure K-15d. Both constituents are comprised of nickel and chromium in different proportions. One constituent is nickel rich (69%), the other is chromium rich (72%). Internal sulfidation appears to be restricted to the nickel rich constituent.

Figure K-17 shows EDS elemental “dot maps” that further emphasize the results above. The non-homogeneous character of the cladding are best shown in the elemental dot map images for nickel and chromium that are provided in Figures K-17a and b. The typical structure of the cladding is emphasized toward the bottom of these images, where for the chromium map (in Figure K-17b), islands of chromium are indicated by high intensity white dots grouped in patches (indicating high local chromium content). These same patches show up as black regions in the nickel map (in Figure K-17a), indicating a lack of nickel in these same regions. The chromium, sulfur and oxygen rich scale are illustrated best by examining Figures K-17b, c, and d. The sulfur map in Figure K-17d also provides a view of the extent of internal sulfidation.

Figure K-18 shows a cross section of the internal surface. A thin scale is noted to line the surface of this Incoloy 800H substrate. Ingress of this scale appears to be microstructurally sensitive (and would lead to an irregular surface contour had the scale been exfoliated).

The weld longitudinal cross sections shown in Figure K-19 reveal that the Incoclad 671 appeared to provide better wastage resistance than did the Inconel 625 weld metal that was used to join the tube samples to one another. Figure K-19a shows that the Incoclad 671 provided wastage resistance that was roughly equivalent to the adjacent IN 72 weld overlay sample, and better than the adjacent HR 120 samples shown in Figures K-19b and c.

* **Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: Incoclad 671

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• The schematic in Figure K-1 shows the relative positions of the three Incoclad 671 samples in Test Section B. Note that all of the Incoclad 671 overlay samples survived for the full intended 37 month exposure period for Section B.• Also, shown is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• The table in Figure K-2 shows a reference nominal composition that was provided by the Special Metals Corporation (SMC).• No mill certificate or heat analysis was offered so it's not clear whether these samples came from one or multiple heats of material.• During the Section A evaluation, detailed composition verification was undertaken for every tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample EE-FF confirmed that the correct material was used at this location.
As-Received Appearance	<ul style="list-style-type: none">• Figure K-3 shows the typical appearance of the Incoclad 671 samples as they were received from SMC. This tube has a total wall thickness of about 260 mils, with a 75 mil thick outer layer of IN671 to provide corrosion resistance, and an inner supporting layer of 800H.• Figures K-4 through K-6 document the appearance of the external surface of the Incoclad 671 tube samples after they had been removed from service. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction..

Material: Inconel 671

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance, Continued	<ul style="list-style-type: none">• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the “o’clock” conventions described above, (with the 12 o’clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o’clock side of the tube faces downward, and the 6 o’clock orientation faces upward within the boiler.• The chalky white deposit/scale associated with molten alkali-iron sulfate attack can be seen on all three tube samples..• Sample P-Q (1191 F) and Sample U-V (1109 F) revealed a brown/red-brown deposit/scale on all three orientations, see Figure K-4.• Sample EE-FF also revealed a brown/red-brown deposit/scale on all three orientations; however, the 12 o’clock orientation was somewhat bare of deposit revealing an underlying black scale.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures K-7 through K-9 show the appearance of the external surface of the Inconel 671 tube samples after grit-blasting to remove deposit and scale.• Some minimal wastage is apparent at the 12 o’clock orientation for Sample U-V, see Figure K-8.• Sample EE-FF shows evidence of wastage at the 12 o’clock and 3 o’clock orientations, see Figure K-9.• Wastage is not apparent on the remaining surfaces.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures K-10 through K-12.• Measurements were taken at eight evenly spaced “o’clock” locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine wall thickness losses. In some cases, the delta is negative. This is believed due to wall thickness variability and difficulty in locating the exact location of the “before” measurement.
Wastage Rate Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure K-13 plots the maximum wastage rate versus the calculated average metal temperature for the three samples for all three test sections.• The wastage rate was low for all three samples; however, note that the sample having the lowest average exposure temperature (1074 F) had the highest wastage rate.

Material: Inconel 671

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure K-14 plots metal loss as a function of time for each sample location for all three sections.• The maximum wall thickness loss was unchanged as a function of time for Samples P-Q and U-V.• Maximum wall thickness loss increased (approximately) linearly with time for Sample EE-FF that was located near mid-span.
Metallurgical Analysis – SEM/EDS	<ul style="list-style-type: none">• Sample EE-FF was selected for a detailed SEM/EDS assessment of the constituents and structure at the external and internal surfaces.• Figures K-15a, b, and c show the external scale/metal interface for Sample EE-FF. The numbers on these figures show the locations of EDS analyses that are provided in the table in Figure K-16.• Figure K-15d shows the microstructure at mid-cladding. Figure K-15d shows that two constituents are apparent in the bulk tube metal. EDS analysis shows that the deeply etching constituent is nickel-rich (68.8% nickel, 30.8% chromium), and the shallow etching constituent is chromium-rich (72.0% chromium, 28.0% nickel).• Examination of the microstructure at the external scale/metal interface reveals the following features:<ul style="list-style-type: none">○ <u>External deposit/scale</u> - An aggregate deposit was noted. EDS analysis (Areas 1, 2, and 3 in Figure K-15a) reveals that the deposit was comprised of typical coal ash constituents: silicon, aluminum, iron, and arsenic. A small amount of potassium (0.96%) and sulfur (1.18%) also were in evidence.○ <u>Outer scale</u> – This region is located as Area 4 in Figure K-15a. EDS analysis shows that this scale is predominantly: chromium (87.1%), oxygen (5.88%), and iron (4.85%). Some small amount of nickel (0.57%) and sulfur (0.23%) also are present.○ <u>Bulk scale composition</u> – The bulk scale is comprised of: chromium (70.4%), oxygen (10.1%), and sulfur (15.2%). A small amount of nickel (2.82%) was indicated, but no iron was found. (This region is located as Area 5 in Figure K-15a.○ <u>Partially attacked cladding</u> – Corrosion ingress was noted beneath the scale, see Figure K-15b. EDS suggests that the chromium-rich component (Area 6 in Figure K-15b) shows evidence of oxidation (59.0% chromium, 33.0% nickel, 4.83% oxygen, and 1.72% nickel). The nickel-rich component (Area 7 in Figure K-15b) shows less oxygen (1.53%) and no sulfur.○ <u>Internal sulfidation</u> – Evidence of internal sulfidation was found at the extreme inward extent of the partially attacked region, see Area 8 in Figure K-15c where EDS shows that the nickel-rich phase is being attacked by sulfur, (57.6% nickel, 35.1% chromium, and 5.08% sulfur).

Material: Incoclad 671

Summary of Findings, (continued)

Issue	Discussion
EDS Analysis – Dot Maps	<ul style="list-style-type: none">• Figure K-17 shows EDS “dot maps” that show the distribution of selected elements in the vicinity of the scale metal interface.• Figure K-17a and K-17b show the distribution of nickel and chromium respectively. These together provide an indication of how these major alloying elements redistributed themselves near the interface. Figure K-17b shows a chromium depleted zone where diffusion fed chromium to a chromium-rich scale.• Figure K-17d shows the presence of sulfur within the scale and within the cladding due to internal sulfidation.
Metallurgical Analysis – Internal Surface	<ul style="list-style-type: none">• Figure K-18 shows the appearance of the internal surface for Sample EE-FF. Recall that Incoloy 800H provided the substrate for the IN 671 cladding, so, this image reflects the performance of 800H at this location. A thin scale is noted to coat the surface.
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none">• Figure K-17 shows a longitudinal profile (at the 12 o’clock orientation) of the Incoclad 671 samples adjacent to the welds in Section B. The welds in question are those identified as welds “Q”, “V”, and “EE”, see Figure L-1 for locations• Examination of Figure K-17a suggests that the Inconel 625 weld filler metal was less resistant to corrosion than the IN 671 cladding. IN 72 weld overlay appeared to provide roughly equivalent resistance to wastage, see Figure K-19a. HR 120 was inferior, see Figure K-19b and K-19c.• Note that for the Incoclad 671 sample adjacent to the “EE” weld, the Inconel 625 has wasted to the extent that the Incoloy 800H substrate is now exposed to fire side corrosive environment (at the interface between the weld and the cladding).

**Figure K-2 Semi-Quantitative Composition Verification for Incoclad 671 / 800 HT
(Co-extruded duplex tubing)**

Description: Nominal 50Cr/50 Ni alloy cladding for oxidation/corrosion protection.
Incoloy 800HT substrate to provide creep strength.
Source: Special Metals Corporation (SMC)
Reference Composition: Cladding “nominal” chemistry – per SMC literature.

Element	Reference Composition	Certified Composition (not provided)	Tube Sample P-Q	Tube Sample U-V	Tube Sample EE-FF
Ni	51.5		N/A	N/A	47.7
Cr	48.0		N/A	N/A	51.9
Fe	-		N/A	N/A	-
Mo	-		N/A	N/A	-
Co	-		N/A	N/A	-
C	0.05		N/A	N/A	-
N	-		N/A	N/A	-
B	-		N/A	N/A	-
Mn	-		N/A	N/A	-
Si	-		N/A	N/A	-
Al	-		N/A	N/A	0.20
Ti	-		N/A	N/A	0.18
Al+Ti	-		N/A	N/A	-
Nb	-		N/A	N/A	-
Ta	-		N/A	N/A	-
Nb+Ta	-		N/A	N/A	-
V	-		N/A	N/A	-
W	-		N/A	N/A	-
Cu	-		N/A	N/A	-
Sn	-		N/A	N/A	-
P	-		N/A	N/A	-
S	-		N/A	N/A	-
O2	-		N/A	N/A	-
Others	-		N/A	N/A	-

N/A = Sample not analyzed.

Figure K-3: Appearance of Inconelad 671 Tube Sample Prior to Service

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure K-4: As-Received Appearance of Sample P-Q (Inconel 671)
(Average surface metal temperature: 1191 °F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure K-5 As-Received Appearance of Sample U-V (Inconel 671)

(Average surface metal temperature: 1109 °F)

Note: this tube sample was 11-5/8-in. long.

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure K-6: As-Received Appearance of Sample EE-FF (Inconel 671)

(Average surface metal temperature: 1067°F)

12 O'Clock
(0 mils lost)

3 O'Clock
(0 mils lost)

6 O'Clock
(0 mils lost)

Figure K-7: OD Surface Appearance After Grit Blast

Material: Incoclad 671
Sample: P-Q

12 O'Clock
(3 mils lost)

3 O'Clock
(1 mils lost)

6 O'Clock
(2 mils lost)

Figure K-8: OD Surface Appearance After Grit Blast

Material: Incoclad 671

Sample: U-V

12 O’Clock
(2 mils lost)

3 O’Clock
(17 mils lost)

6 O’Clock
(0 mils lost)

Figure K-9: OD Surface Appearance After Grit Blast

Material: Incoclad 671
Sample: EE-FF

Material:

Incoclad 671

Sample Location:

P-Q

Maximum Rate:

1 mils/yr

Maximum Loss Orientation:

Approx. 9:00 o'clock

Average Surface Metal Temperature:

1191 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.260	0.256	0.250	0.254	0.257	0.261	0.264	0.263	0.258	0.264
After	0.260	0.256	0.254	0.254	0.257	0.259	0.261	0.261		0.261
Delta	0.000	0.000	-0.004	0.000	0.000	0.002	0.003	0.002		0.003

Figure K-10: Silhouette and Wall Thickness Measurements for Sample P-Q

Material:

Incoclad 671

Sample Location:

U-V

Maximum Rate:

1 mils/yr

Maximum Loss Orientation:

Approx. 1:30 o'clock

Average Surface Metal Temperature:

1109 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.260	0.261	0.260	0.260	0.259	0.260	0.261	0.260	0.260	0.261
After	0.257	0.257	0.259	0.257	0.257	0.256	0.259	0.258		0.257
Delta	0.003	0.004	0.001	0.003	0.002	0.004	0.002	0.002		0.004

Figure K-11: Silhouette and Wall Thickness Measurements for Sample U-V

Material:

Incoclad 671

Sample Location:

EE-FF

Maximum Rate:

11mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average Surface Metal Temperature:

1074 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.264	0.263	0.260	0.255	0.253	0.255	0.260	0.264	0.259	0.264
After	0.262	0.262	0.243	0.256	0.254	0.254	0.251	0.229		0.229
Delta	0.002	0.001	0.017	-0.001	-0.001	0.001	0.009	0.035		0.035

Figure K-12: Silhouette and Wall Thickness Measurements for Sample EE-FF

Figure K-13: Metal Loss Rate as a Function of Average Surface Metal Temperature

Material: Incoclad 671

Figure K-14: Metal Loss as a Function of Time

Material: Incoclad 67

(a) External Scale/Metal Interface (BEI – Intermediate Magnification)

(b) External Scale/Metal Interface at Box Indicated Above (BEI – High Magnification)

Figure K-15: Microstructure Incoclad 671 (Sample EE-FF)

(c) External Scale/Metal Interface (BEI – Intermediate Magnification)

(d) Microsturcture at Mid-Thickness of Cladding (BEI – Intermediate Magnification)

Figure K-15, Cont.: Microstructure Incoclad 671 (Sample EE-FF)

Figure K-16: EDS Analysis of Deposit/Scale/Metal Interface for Inconel 671 (EE-FF)

Area	Description	Ni	Cr	Fe	C	Mo	Mn	Ti	Nb	Al	Si	O	Ca	K	Na	Mg	As	P	S
1	Aggregate outer deposit	1.28	4.23	15.6	--	--	--	--	--	4.31	41.1	17.8	--	0.96	--	--	13.6	--	1.18
2	Light colored region in deposit	--	2.32	8.92	--	--	--	--	--	4.90	51.3	16.8	--	0.57	--	--	14.3	--	0.93
3	Dark colored region in deposit	--	--	1.36	--	--	--	--	--	11.6	38.0	18.9	--	0.41	--	--	27.0	2.58	--
4	Scale near interface with deposit	0.57	87.1	4.85	--	--	--	0.40	--	--	0.93	5.88	--	--	--	--	--	--	0.23
5	Bulk scale composition	2.82	70.4	--	--	--	--	0.92	--	0.63	--	10.1	--	--	--	--	--	--	15.2
6	Light region at partially attacked scale/metal interface.	33.0	59.0	--	--	--	--	1.19	--	0.30	--	4.83	--	--	--	--	--	--	1.72
7	Dark region at partially attacked scale/metal interface.	65.3	32.5	--	--	--	--	0.48	--	0.18	--	1.53	--	--	--	--	--	--	--
8	Subsurface dark etching constituent near interface	57.6	35.1	--	--	--	--	0.58	--	--	--	1.61	--	--	--	--	--	--	5.08
	Mid-cladding deeply etched component	68.8	30.8	--	--	--	--	0.32	--	--	--	--	--	--	--	--	--	--	--
	Mid-cladding lightly etched component	28.0	72.0	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	Mid-cladding bulk	47.7	51.9	--	--	--	--	0.18	--	0.20	--	--	--	--	--	--	--	--	--
	Reference bulk composition	51.5	48.0	--	0.05	--	--	--	--	--	--	--	--	--	--	--	--	--	--

IN671 1500x maps

(a) Nickel Distribution

IN671 1500x maps

(b) Chromium Distribution

Figure K-17: EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution (Inconel 671, Sample EE-FF)

IN671 1500x maps

(c) Oxygen Distribution

IN671 1500x maps

(d) Sulfur Distribution

Figure K-17, Cont.: EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution (Inconel 671, Sample EE-FF)

IN671 1500x maps

(e) Potassium Distribution

Figure K-17, Cont.: EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution (Inconel 671, Sample EE-FF)

ID Scale/Metal Interface (BEI - High Magnification)

**Figure K-18: Microstructure ID Scale/Metal Interface: of 800H Substrate
for Inconel 671 sample**

Note: Note EDS analysis reveals this internal scale to be an iron and nickel rich oxide.

(a) Incoclad 671 Adjacent to Weld "Q"

(b) Incoclad 671 Adjacent to Weld "V"

c) Incoclad 671 Adjacent to Weld "EE"

Figure K-19: Longitudinal Cross-Sections: Incoclad 671 Adjacent to Welds

Appendix L

Analysis of Performance

Test Section B

IN72 Weld Overlay

Overview of Results: IN72 Weld Overlay

There were two IN 72 weld overlay samples included in each of the three test sections. One was located in a relatively high temperature location (Sample Q-R), and the other at a relatively low temperature location (Sample FF-GG). For Section B, the IN 72 weld overlay samples experienced a low wastage rate, and survived for the full 37 month exposure period of Section B. The sample removal history is summarized in the table below:

		Section A	Section C	Section B
	Full Exposure Period:	15.5 months	28.5 months	37 months
Sample	Nominal Temperature	Removed	Removed	Removed
Q-R	1195 – 1208 F	15.5 months	28.5 months	37 months
FF-GG	1067 – 1079 F	15.5 months	28.5 months	37 months

The chart in Figure L-10 plots wastage rate as a function of temperature. As can be seen, this chart shows that for all three test sections, the wastage rate was greater for the lower temperature Sample FF-GG (at 1067 F in Section B) than for the higher temperature Sample Q-R (at 1195 F, in Section B). For the case of the IN 72 weld overlay specimens, Sample Q-R was located closer to a wall, while Sample FF-GG was located near mid-span in the section. The figure below illustrates the positions of the IN 72 weld overlay specimens.

The dimensional analysis of both Section B tube samples is included in this report. However, the metallurgical analysis focused on Sample FF-GG which had experienced the greatest wastage rate. The “gray” colored boxes in the table above show which sample was subjected to metallurgical analysis for each test section.

Evaluation of the metallographic cross section for Sample FF-GG reveals that the location selected for evaluation had a continuous scale but was devoid of deposit, see Figure L-12a, b, and c. A two-layer deposit was in evidence, see Figure L-12c.

A coarse and granular inner layer of scale is observed along the scale/metal interface (see position “1” in Figure L-12c). EDS analysis revealed that this layer of scale is comprised of nickel (52.2%), chromium (24.7%), and iron (5.70%) along with a significant amount of sulfur (11.1%) and oxygen (5.35%). A block and relatively coherent scale rests atop of the inner scale (see position “2” in Figure L-12c) and appears to be detached from it, and exfoliated from the surface in some locations (refer to Figure L-12a). EDS analysis revealed this layer was comprised primarily of chromium (75.5%) and oxygen (14.9%). A significant amount of sulfur (4.12%) and

potassium (1.98%) also were indicated in this layer. A summary of all of the EDS analyses is provided in Figure L-13.

Figure L-14 shows EDS elemental “dot maps” that further emphasize the results above. Figure L-14c and L-14d emphasize the presence of chromium and oxygen in the outer scale (and a significant reduction in chromium in the inner scale). Figure L-14e reveals a high concentration of sulfur in both the inner and outer scales. Figure L-14f shows a region in the outer scale where the potassium content is enriched.

The metallurgical analysis evidenced cited above seems to point toward formation of a frangible sulfur-rich inner scale that permits separation of an outer scale which is presumably a protective chromium oxide. Potassium (and iron, and sulfur) are indicated in the outer scale.

Metallography revealed that the IN 72 weld overlay contained numerous radial cracks that reduced the effective corrosion barrier thickness, see Figure L-15. The initial weld overlay thickness was roughly 80 mils, and an 11 mil surface-breaking crack was measured at one location. This thus reduced the effective cladding thickness by about 14%. Earlier analyses of these cracks revealed that they were located at roughly mid-thickness of the cladding and typically do not break the surface. This analysis suggested that these internal cracks likely are due to the welding procedure, and in fact, later modifications to the procedure appeared to alleviate this condition.

Figure L-16 shows a cross section of the internal surface. No scale was in evidence however the irregular line of the surface suggests the possibility that a scale had formed, and exfoliated from this surface. Note that in manufacturing these samples, IN 72 weld metal was overlain on a Incoloy 800H substrate, and that the performance along the internal surface represents that of the substrate rather than the overlay.

The weld longitudinal cross sections shown in Figure L-17 reveal that the IN 72 weld overlay appeared to provide somewhat better wastage resistance than did the Inconel 625 weld metal that was used to join the tube samples to one another. Figure L-17a shows that IN 72 compared favorably with IN 671 at this location. Figure L-17b shows that IN 72 performed much better than the IN 52 clad tube (where the cladding was completely wasted and the underlying 800H is now exposed to fire side conditions).

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: IN72 Weld Overlay

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• The schematic in Figure L-1 shows the relative positions of the two IN72 Weld Overlay samples in Test Section B. Both samples survived for the full intended service period for Section B.• Also, shown is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• The weld wire for cladding the IN 72 Weld Overlay samples used in this program was drawn from Special Metals Corporation (SMC) Heat UKL8138. The composition for this heat is provided in the table in Figure L-2 along with the target composition from SMC literature.• During the Section A evaluation, detailed composition verification was undertaken for every tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample FF-GG confirmed that the correct material was used at this location.• It was noted that the actual tube sample composition was higher in iron than the reported filler wire chemistry; however, is consistent with what would be expected for a weld deposit, and compares reasonable well the desired nominal chemistry in terms of chromium content.
As-Received Appearance	<ul style="list-style-type: none">• Figure L-3 shows the appearance of the archive sample for IN72 Weld Overlay material. This photograph documents the condition of the tube sample as it was delivered from SMC. The weld bead surface profile is clearly visible in this view. The cladding thickness was measured to be approximately 80 mils. Thus, it comprised about 27% of the total wall thickness of 292 mils.

Material: IN72 Weld Overlay

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance, Continued	<ul style="list-style-type: none">• Figures L-4 and L-5 document the appearance of the external surface of the IN72 Weld Overlay tube samples after service. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the "o'clock" conventions described above, (with the 12 o'clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o'clock side of the tube faces downward, and the 6 o'clock orientation faces upward within the boiler.• Sample Q-R was noted to have a relatively thick (red/brown) deposit and scale on all three orientations. The gray/white scale associated with molten alkali-iron sulfate attack is also noted at both the 12 o'clock and 6 o'clock orientations.• Sample FF-GG had a rust-red deposit and scale at the 6 o'clock orientation. The gray/white scale was also found in this orientation.• The other two orientations were relatively bare of deposit. A dark scale coated these surfaces.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures L-6 and L-7 show the appearance of the external surface of the IN 72 Weld Overlay tube samples after grit-blasting. The 12 o'clock and 3 o'clock positions for Sample FF-GG showed general wastage.• Sample Q-R appeared to be unaffected due to service.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures L-8 and L-9.• The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost. Note that in some cases, the delta is negative (particularly around the 6 o'clock position). This is believed due to wall thickness variability and difficulty in locating the exact location of the "before" measurement.• Sample FF-GG experienced the maximum wall thickness loss of 36 mils. Metallographic examination (reported later in this appendix) revealed internal radial weld cracking (apparently related to the cladding procedure). These cracks were as large as 11 mils in length in the cross section examined. This would bring the total loss to 47 mils, which is almost 60% of the cladding thickness.

Material: IN72 Weld Overlay

Summary of Findings, (continued)

Issue	Discussion
Wall Wastage Rate Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure L-10 plots the maximum wastage rate against the calculated average metal temperature for the two IN72 Weld Overlay samples in all three test sections.• <u>Note that these data do not take into account the additional wall thickness that would be lost due to internal weld cracking.</u>• The wastage rate for the Section B and Section C samples was slightly lower than the rate for Section A samples, but all were found to be very low.•
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure L-11 plots metal loss as a function of time for each sample location for all three test sections.• <u>Note again that these data do not take into account the additional wall thickness that would be lost due to internal weld cracking.</u>
Metallurgical Analysis – SEM/EDS	<ul style="list-style-type: none">• Sample FF-GG was selected for a detailed SEM/EDS assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected for evaluation due to its higher rate of corrosion based on diameter measurements.• Figures L-12a, b and c show the external scale/metal interface for Sample FF-GG.• The numbers on Figure L-12c show the locations of EDS analyses to further characterize the interface, (see the table in Figure L-13 for EDS results).• Based on examination the images in Figure L-12, four distinct regions are in evidence. These regions are, starting within the metal and working out:<ul style="list-style-type: none">○ <u>Base metal</u> – Oxalic acid etch faintly delineates grain boundaries, carbides, and inclusions.○ <u>Dark-Etching adjacent to the scale/metal interface</u> – This region (associated with EDS analysis point #3) was found to be slightly enriched in iron (3.14% vs 2.47%) and nickel (52.2% vs 50.5%). The chromium content (44.3%) was the same as that of the bulk cladding.○ <u>Granular scale along scale/metal interface</u> – Significant components of this scale include: nickel (50.5%), chromium (24.7%), iron (5.70%), and oxygen (5.35%). A significant amount of sulfur was present (11.1%) along with a small amount of potassium (0.26%).

Material: IN72 Weld Overlay

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM/EDS, Continued.	<ul style="list-style-type: none">○ <u>Detached (bulk) scale</u> – This scale was almost entirely comprised of chromium (75.7%), oxygen (14.9%), and sulfur (4.12%). Iron (1.46%) and nickel (0.93%) were present in small amounts. A significant amount of potassium (1.98%) was also noted.
Metallurgical Analysis EDS “Dot Maps”	<ul style="list-style-type: none">• Figure L-14 shows the results of EDS “dot maps” to further characterize the scale/metal interface shown to the left in these images.• Figure L-14c shows the lower levels of chromium in the coarse scale along the scale/metal interface. Figure L-14e depicts the enrichment in sulfur in this same location.• Figure L-14f shows an enrichment in potassium in the scale whose position appears to correlate well with iron at roughly the same location.
Metallurgical Analysis – Weld Cracking	<ul style="list-style-type: none">• Figure L-15 shows the appearance of cracking found within the cladding. These cracks are (in most cases) totally within the cladding and not connected to the surface. They are aligned in a radial direction, and as such, reduce the total barrier thickness provided by the cladding. The cracks appear to be along solidification grain boundaries.
Metallurgical Analysis – Internal Surface	<ul style="list-style-type: none">• Figure L-16 shows the appearance of the internal surface of Sample GG-HH. Recall that 800HT provides the substrate for this sample. No scale was found along this surface; however, the line of the internal surface appears to be irregular (suggestive of oxidation followed by scale exfoliation).
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none">• Figure L-17 shows a longitudinal profile (at the 12 o’clock orientation) of the IN72 Weld Overlay samples adjacent to the welds in Section C. The welds in question are those identified as welds “Q” and “GG”, see Figure L-1 for locations• Evaluation of the images in Figure L-17 suggests that the Inconel 625 weld filler metal was less resistant to corrosion than the adjacent IN72 weld overlay.• Figure L-17a shows that the IN 72 weld overlay sample fared well compared with the adjacent IN 671 sample.• Figure L-17b shows that the IN 72 weld overlay sample fared better than the adjacent IN 52 weld overlay.

Figure L-1: Schematic Drawing Showing Position of IN72 Weld Overlay Tube Samples Within Test Section B

1. Drawing shown in same relative orientation as per the actual installation.
2. This group of tube samples was removed from service in November 2001 - highlighted in red.
3. This group of tube samples was removed from service in June 2002 - highlighted in yellow.
4. This group of tube samples was removed from service in September 2003 - highlighted in blue.

Figure L-2 Semi-Quantitative Composition Verification for Inco 72 / 800 HT (Weld clad duplex tubing)

Description: Nominal 45Cr/55 Ni alloy cladding for oxidation/corrosion protection.
Incoloy 800HT substrate provides creep strength.

Source: Special Metals Corporation (SMC)

Reference Composition: Filler wire “nominal” chemistry – Per SMC literature.

Element	Reference Composition for Weld Cladding	Composition Heat UKL8138	Tube Sample Q-R	Tube Sample FF-GG
Ni	55	54.96	N/A	50.5
Cr	44	43.30	N/A	44.3
Fe	0.2	0.43	N/A	2.47
Mo	-	-	N/A	-
Co	-	-	N/A	-
C	0.05	0.02	N/A	-
N	-	-	N/A	-
B	-	-	N/A	-
Mn	0.1	0.03	N/A	-
Si	0.1	0.15	N/A	0.26
Al	-	0.20	N/A	-
Ti	0.6	0.66	N/A	0.54
Al+Ti	-	-	N/A	-
Nb	-	-	N/A	-
Ta	-	-	N/A	-
Nb+Ta	-	-	N/A	-
V	-	-	N/A	-
W	-	-	N/A	-
Cu	0.2	-	N/A	-
Sn	-	-	N/A	-
P	-	0.005	N/A	-
S	0.008	0.003	N/A	-
O	-	-	N/A	1.88
Others	<0.50	<0.50	N/A	-

N/A = Sample not analyzed.

Note: Reference composition is for filler wire, not as-deposited.

Figure L-3: Appearance of IN72 Weld Overlay Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure L-4: As-Received Appearance of Sample Q-R (IN72 Weld Overlay)

(Average surface metal temperature: 1195°F)

Note: this sample survived for the full 37 month exposure period for Section B.

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure L-5 As-Received Appearance of Sample FF-GG (IN72 Weld Overlay)

(Average surface metal temperature: 1067°F)

Note: this sample survived for the full 37 month exposure period for Section B.

12 O’Clock
(0 mils lost)

3 O’Clock
(0 mils lost)

6 O’Clock
(0 mils lost)

Figure L-6: OD Surface Appearance After Grit Blast

Material: IN72 Weld Overlay
Sample: Q-R

12 O’Clock
(20 mils lost)

3 O’Clock
(0 mils lost)

6 O’Clock
(0 mils lost)

Figure L-7: OD Surface Appearance After Grit Blast

Material: IN72 Weld Overlay
Sample: FF-GG

Material: IN72 Weld Overlay

Sample Location: Q-R
Maximum Rate: 1 mil/yr
Maximum Loss Orientation: 1:30 o'clock
Average Surface Metal Temperature: 1195 °F

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.285	0.289	0.293	0.298	0.296	0.295	0.290	0.285	0.291	0.289
After	0.285	0.286	0.292	0.298	0.298	0.294	0.291	0.288		0.286
Delta	0.000	0.003	0.001	0.000	-0.002	0.001	-0.001	-0.003		0.003

Figure L-8: Silhouette and Wall Thickness Measurements for Sample Q-R

Note: this sample survived for the full 37 month exposure period for Section B.

Material:

IN72 Weld Overlay

Sample Location:

FF-GG

Maximum Rate:

16 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average Surface Metal Temperature:

1067 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.301	0.296	0.292	0.288	0.287	0.289	0.292	0.295	0.293	0.295
After	0.261	0.276	0.276	0.289	0.287	0.288	0.283	0.244		0.244
Delta	0.040	0.020	0.016	-0.001	0.000	0.001	0.009	0.051		0.051

Figure L-9: Silhouette and Wall Thickness Measurements for Sample FF-GG

Note: this sample survived for the full 37 month exposure period for Section B.

Figure L-10: Metal Loss Rate as a Function of Average Surface Metal Temperature

Material: IN72 Weld Overlay

Figure L-11: Metal Loss as a Function of Time

Material: IN72 Weld Overlay

(a) External Scale/Metal Interface (BEI - Low Magnification)

(b) External Scale/Metal Interface (BEI - Intermediate Magnification)

Figure L-12: Microstructure: IN72 Weld Overlay

(c) Pit at External Scale/Metal Interface (BEI - Intermediate Magnification)

Figure L-12 (Cont.): Microstructure: IN72 Weld Overlay

Note: Numbers on photos indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

Figure L-13: EDS Analysis of Deposit/Scale/Metal Interface for IN 72 Weld Overlay (FF-GG)

Area	Description	Ni	Cr	Fe	C	Mo	Mn	Ti	Nb	Al	Si	O	Cu	K	Na	Mg	As	P	S
1	Detached scale/deposit	0.93	75.5	1.46	--	--	--	0.69	--	--	0.35	14.9	--	1.98	--	--	--	--	4.12
2	Coarse granular scale	50.5	24.7	5.70	--	--	--	1.28	--	0.60	0.51	5.35	--	0.26	--	--	--	--	11.1
3	Scale/metal interface	52.2	44.3	3.14	--	--	--	0.39	--	--	--	--	--	--	--	--	--	--	--
4	Scale/metal interface	43.4	52.8	2.85	--	--	--	0.35	--	0.26	0.33	--	--	--	--	--	--	--	--
5	Unaffected cladding	50.2	44.9	4.16	--	--	--	0.53	--	--	0.25	--	--	--	--	--	--	--	--
6	Dark etching boundary	39.5	53.7	4.61	--	--	--	0.39	--	--	--	1.82	--	--	--	--	--	--	--
	Mid-cladding bulk	50.5	44.3	2.47	--	--	--	0.54	--	--	0.26	1.88	--	--	--	--	--	--	--
	Reference bulk composition of cladding	55	44	0.2	0.05	0.1	--	0.6	--	--	0.1	--	0.2	--	--	--	--	--	0.008

IN72 1000x maps

(a) Nickel Distribution

IN72 1000x maps

(b) Iron Distribution

Figure L-14: EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution (IN 72 Weld Overlay, Sample FF-GG)

IN72 1000x maps

(c) Chromium Distribution

IN72 1000x maps

(d) Oxygen Distribution

Figure L-14, Cont.: EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution (IN 72 Weld Overlay, Sample FF-GG)

IN72 1000x maps

(e) Sulfur Distribution

IN72 1000x maps

(f) Potassium Distribution

Figure L-14, Cont.: EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution (IN 72 Weld Overlay, Sample FF-GG)

IN72 1000x maps

(g) Sodium Distribution

Figure L-14, Cont.: EDS Dot Maps of OD Scale/Metal Interface Showing Elemental Distribution (IN 72 Weld Overlay, Sample FF-GG)

(a) Cracks in Cladding (BEI - Low Magnification)

(b) Crack in Cladding Along Grain Boundary (Note pore at left)

Figure L-15: Weld Clad Cracking

Internal Surface Appearance

Figure L-16: Microstructure: IN72 Weld Overlay

(a) IN72 Weld Overlay Adjacent to Weld "Q"

(b) IN72 Weld Overlay Adjacent to Weld "GG"

Figure L-17: Longitudinal Cross-Sections: IN72 Weld Overlay Adjacent to Welds

ATTACHMENT 1

**TOPICAL REPORT – REMOVAL OF SECTION A
DATED NOVEMBER 2002**

COAL ASH CORROSION RESISTANT MATERIALS TESTING

Topical Report: Removal of Section “A”

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Date published: October 31, 2002

This report does not contain any Trade Secret/Proprietary Information.

This project was funded in part by the U. S. Department of Energy and the Ohio Coal Development Office, Department of Development, State of Ohio

U.S. Department of Energy Contract:
Ohio Coal Development Office Grant Agreement:
McDermott Technology, Inc. Contract:

DE-FC26-99FT40525
CDO/D-97-02
CRD 1392

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EXECUTIVE SUMMARY

In April 1999, three identical superheater test sections were installed into the Niles Unit #1. This boiler burns high sulfur (3% to 3.5%) coal, thus the superheater environment is aggressive. The test sections operated with an average surface metal temperature from 1047 °F to 1198 °F. This combination of aggressive environment and high temperature was appropriate for testing the performance of candidate tube materials. Analyses of the deposit and scale confirmed that the aggressive alkali-iron-trisulfate constituent was present at the metal surface and active in tube metal wastage. The test sections were constructed so that the response of twelve different candidate tube materials could be studied. The plan was to remove and evaluate one of the three test sections at time intervals of 1 year, 3 years, and 5 years. This would permit an assessment of performance of the twelve candidate materials as a function of time.

Test Section A, the first test section, was removed after about 24 months of service. During this 24 month period, the test section experienced an operating time at full temperature of about 15 months. This report documents the results of the evaluation of the performance of the candidate alloys in that test section. The evaluation described the condition of each tube sample after exposure. It then involved a determination of the rate of wall thickness loss for these samples. In cases where there was more than one sample of a candidate material in the test section, an assessment was made of the performance of the alloy as a function of temperature. Lastly, the microstructure of the scale/metal interface was examined to describe and record the characteristics of the attack for each material. Both the internal and external surfaces were examined, but obviously the focus was on the external surface.

The detailed results of the investigation are included in this report as a series of twelve appendices. Each appendix is devoted to the performance of one of the candidate alloys. The table below summarizes metal loss rate for the worst case sample of each of the candidate materials. The body of this report compares these in detail for all of the samples in the test section.

Maximum Metal Loss Rate for Each Candidate Material In Test Section A

In general, it can be stated that, while the sampling represented by these tests is small, the relative performance of the candidate alloys appears to have been strongly influenced by their total alloy content, in particular, the sum of their chromium plus nickel contents. It was less directly influenced by chromium content alone. This is indicated by the large amount of wall thickness loss variability in alloys having 20 to 25% chromium. The data also suggest that smaller grain size materials seem to benefit hot corrosion resistance; however, this influence is far outweighed by the influence of the alloy composition.

1.0 INTRODUCTION

The “Coal Ash Corrosion Resistant Materials Testing Program” is being conducted by the Babcock & Wilcox Company (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% and 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 use of coal. Figure 1 shows a comparison of the cost of electricity for subcritical and supercritical coal fired plants and a natural gas combined cycle (NGCC) plant based on an 85% capacity factor shows that at \$1.25/MBtu for coal, it is competitive with NGCC when gas is at \$3.40/MBtu or higher. An 85% capacity factor is realistic for a coal-fired plant but NGCC plants are currently only achieving about 60%. This gives coal an advantage if compared on the basis of cost per kW generated per year. When sub and supercritical plants are compared, supercritical is only slightly more costly than subcritical because the higher capital cost is nearly offset by the fuel savings resulting from the higher efficiency. Consequently, subcritical coal-fired plants would dominate the market were it not for environmental concern, especially CO₂.

Subcritical Coal Plant

- \$1100 / kW EPC
- O&M (non-Fuel) \$3.50 / MWh
- Avg. Heat Rate 9220 Btu/kWh

Supercritical Coal Plant

- \$1150 / kW EPC
- O&M (non-Fuel) \$3.50 / MWh
- Avg. Heat Rate 8550 Btu/kWh

Natural Gas Combined Cycle

- \$500 / kW EPC Cost
- O&M (non-fuel) \$2.50 / MWh
- Avg. Heat Rate 6,800 Btu/kWh

(Assumptions: 85% capacity factor, Tax life 20 years, book life 30 year, all heat rates HHV, levelized capital charge - EPRI Tag)

Figure 1: Comparison of Cost of Electricity

The superheaters in boilers, especially supercritical, operate under arduous conditions and the alloys from which they are constructed are exposed to high temperatures and corrosive conditions over long periods of time. From both environmental and cost considerations it is in the best interest of the nation and the power generation industry to operate coal fired power plants safely at the highest practical temperatures to increase plant efficiency and reduce emissions. This necessitates the use of more advanced creep and corrosion resistant alloys that can function safely for as long as possible without the need for costly outages for repair and maintenance.

The performance of new and existing alloys are often evaluated in laboratory scale tests which, while valuable in terms of providing a large bank of data under accelerated test conditions, do not accurately simulate the actual conditions within a boiler. Furthermore, laboratory tests often utilize specimens which do not experience the same stresses as components in service. Incorporating alloys in typical component dimensions within the coal-ash environment and the cyclic start-up and shut-down of a boiler enables a more accurate representation of their performance in real service conditions.

The objective of this program is to test and evaluate promising advanced materials to determine their resistance to fire-side coal-ash corrosion in an advanced supercritical boiler. To accomplish this, ten primary and two secondary advanced materials were incorporated into three identical test sections, cooled with reheat steam and installed in the Unit #1 boiler at Reliant Energy's Niles plant located in Niles, Ohio. To assess corrosion over time, the first section was originally intended to be removed and evaluated after about one (1) year of operation, the second after three (3) years of operation and the last after five (5) years of operation. It was also intended that the last section may be permitted to operate up to two years longer depending on previous experience and plant operations.

The benefits of having new reliable boiler tube alloys which promote advanced supercritical boilers are that they allow for greater usage of high sulfur coal with higher steam conditions and plant cycle efficiencies. The improved plant efficiency also reduces SO₂, NO_x and CO₂ emissions that make for a cleaner environment at a lower generating cost. In addition, these materials can be applied in numerous existing plants experiencing coal-ash corrosion, such as the Niles unit.

2.0 BACKGROUND

In recent years, there has been increasing interest in the performance and economic benefits of higher temperature and pressure pulverized coal plant cycles, i.e. advanced supercritical over conventional subcritical plants. Concerns about global warming and interest in nearer term solutions than sequestration or unproven energy conversion methods have magnified that interest. Subcritical plants operate at less than 3200 psi. Most conventional supercritical plants operate at 3600 psi and up to 1050/1050°F with cycle efficiencies of 37% to 39% depending on fuel and other factors. Advanced supercritical plants may operate at steam temperatures as high as 1200°F and pressures up to 6000 psi with cycle efficiencies as high as 45% with potential for even higher efficiencies as steam temperatures increase. Figure 2 shows the efficiency benefits of advanced steam conditions versus subcritical plants.

The increase in operating pressure, temperature, and efficiency results in significant benefits. These benefits include reductions in: coal burned per kilowatt of electricity produced which directly reduces gaseous emissions of SO₂, NO_x, and CO₂, as well as particulate emissions, and solid wastes generated (fly ash and SO₂ scrubber sludges). The economic benefits of the higher efficiency plants are also significant. Studies by B&W under the DOE sponsored Combustion 2000 LEBS Program and by EPRI for their State-of-the-Art Power Plant (SOAPP) project show that the capital costs for the new plants with high efficiency emissions control equipment are not much different than lower efficiency subcritical plants. In addition, the more efficient plants have significantly lower operating costs and some reductions in equipment costs because of reduced fuel consumption. These improvements provide a credible basis for advanced supercritical plants to compete internationally against less efficient designs as well as domestically against new gas turbine combined cycle plants, re-powering existing coal plants with natural gas fired options and other alternative plants.

Figure 2: Advanced Supercritical Plants versus Subcritical 2400psi/1000F/1000F.

The key drivers to increasing efficiency are reduced fuel cost and reduced CO₂ emissions. Because of the abundance and low cost of coal in the U.S., fuel cost savings do not provide as significant a motivation as in many other countries. Though not yet widely regulated in the U.S., greenhouse gas emissions and concern for global warming have recently sparked considerable interest in higher efficiency cycles. Figure 3 shows that CO₂ emissions can be significantly reduced by increasing plant efficiency (decreasing heat rate).

Figure 3: Impact of Heat Rate on CO₂ Emissions

However, as Figures 4, 5 and 6 show, improving efficiency has only a minimal impact on the other key emissions. Figure 4 shows the NO_x emissions in lb/MWh for selective catalytic reduction (SCR) removal rates of 25% to 95% and net plant heat rates varying from 9300 Btu/kWh (36.7% net plant efficiency) to 8050 Btu/kWh (42.4%). The graph shows that as a higher removal rate SCR is selected, the impact of the cycle heat rate declines. Although current removal rates are typically 90%, as high as 93% has been demonstrated, and even higher removal is possible with improved mixing and additional catalyst. At these high removal rates, improving heat rate (or cycle efficiency) has little impact on the further reduction of NO_x emissions.

Figure 5 shows the same comparison for SO₂. A typical removal in a wet scrubber is 90% with some today as high as 95% to 98%. Again, as the SO₂ removal rate in the scrubber increases, the effect of cycle heat rate improvement on further SO₂ removal decreases.

Figure 4: Impact of Heat Rate on NO_x Emissions

Figure 5: Impact of Heat Rate on SO₂ Emissions

Figure 6 shows the outlet particulate emission in lb/MWh as a function of the particulate in the flue gas in lb/MBtu. Again the conclusion is that as fabric filters and other particulate removal devices become more efficient, the impact of improved heat rates on emissions is nearly negligible. Figures 4 through 6 show that projects requiring low ambient air emissions will primarily achieve those low levels through the performance of the emissions control devices (SCR, scrubber, ESP/fabric filter); cycle heat rate has minimal impact.

Steam cycle efficiency is a function of the turbine cycle and boiler efficiencies and parasitic power requirements. Typically, about 11% of the cycle heat losses 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.

Figure 6: Impact of Heat Rate on Particulate Emissions

Figure 7: Impact of Steam Pressure on Heat Rate

As Figure 7 shows, 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 as shown in Figure 8. Increasing pressure also means that all pressure-parts get proportionately thicker resulting in higher costs for the entire boiler and metal temperatures requiring higher-grade alloys. Thus significant environmental value would be needed to economically justify increasing cycle pressure to gain a small amount of efficiency but increasing steam temperature is attractive.

Figure 8: Impact of Steam Temperature on Heat Rate

One reason many coal-fired power generators have not taken advantage of higher efficiency cycles for new plants is the lack of confidence in the adequacy of boiler superheater and reheater tube materials. As the steam temperature increases above 1000°F, the creep strength of most metals and alloys decreases and susceptibility to fireside corrosion increases rapidly. Though creep strength is a concern, high temperature fireside corrosion of superheater and reheater tubes has a much greater impact on the reliability of high temperature pulverized coal-fired boilers. This corrosion is caused by the formation of complex alkali-iron-sulfates on tube surfaces.

The general trend of fireside corrosion is shown in Figure 9. The corrosion rate for ferritic materials consistently increases with increasing temperature. For austenitic materials, which are required for the higher temperature areas of the boiler, there is a peak in the corrosion rate, generally between 1150°F and 1350°F. Above about 1400°F, the corrosive sulfates are unstable and do not condense to form corrosive liquids on tubes, while below 1000°F the coal ash is no longer molten.

In recent years, considerable progress has been made in developing materials with higher creep strength and resistance to steam side oxidation. These new materials permit the design and construction of reliable boilers which can be operated at supercritical pressures and steam temperatures in the range of 1100°F and higher. However, for the new materials, information is limited on high temperature corrosion in coal-fired boilers. High temperature materials testing is now being conducted in Europe and Japan, but with natural gas or very low sulfur coals. Credible data is

sorely needed in the corrosive environments experienced in many domestic and international boilers firing high sulfur coals.

Figure 9: Representative Corrosion Behavior of Boiler Alloys

2.1 The Host Boiler

The host unit is Reliant Energy plant, Niles Unit #1, a B&W cyclone fired boiler which is burning a high sulfur bituminous Ohio coal (about 3% sulfur as received). Though cooled with reheat steam, the location of the three test sections is in the second bank above the furnace exit within the secondary superheater (see Figure 10) where the existing secondary superheater sections are on a 1'-6" side spacing allowing insertion of the test sections in between. At this location the gas conditions are anticipated to be similar to those experienced by a secondary superheater in a large supercritical boiler.

Figure 10: Sectional Side View

3.0 MATERIAL SELECTION

The alloy selection process was performed by a team of metallurgists from ORNL, McDermott Technology Inc. (MTI) and Babcock and Wilcox (B&W) and representatives from the Department of Energy (DOE) and Ohio Coal Development Office (OCDO). The selection of alloys was primarily based on creep strength at 10^5 hours and corrosion resistance. Table 1 shows a list of potential alloys for inclusion in the program, along with (where available) the creep strength at 10^5 hours and the relative laboratory corrosion rate compared with alloy 347 where 0.5 is equivalent to half the corrosion rate of alloy 347 and 2 is equal to twice the corrosion rate. The alloys selected for inclusion in the test sections are given in Table 2

Table 1: Advanced and Reference Alloy Chemistries, Creep Life and Comparative Corrosion							
Alloy	Cr	Ni	Fe	Other	CAC/347 Index	700C (10⁵ksi)	Vendor
253MA	21	11	bal	Si	0.5		
310 clad	25	20	bal	- - -	~0.3	1.3	Generic
310HCbN (HR3C)	25	20	bal	NbN	0.3	6.8	Sumitomo
347H	18	11	bal	NbTa	1.0	7.4	Generic
347HFG	18	11	bal	NbTa	~1.0	10.0	Sumitomo
IN72 Weld Overlay (671 Clad)	48	bal	- -	- - -	0.2	3.4	INCO
IN52 Weld Overlay (690 clad)	30	bal	10		0.4		INCO
800H	21	32	bal	AlTi	0.4	8.0	INCO +
85H	18	15	bal	SiAl	0.6		ORNL experimental
8XA	21	32	bal	3.5AlTi			INCO developmental
AC66	27	31	bal	Nb			Mannesmann
Fe3Al+5Cr clad	5	- -	bal	17Al	0.3		ORNL experimental
HCM12	12	- -	bal	2WMo			Sumitomo
Thermic (Inconel 740)	25			20CoAlTiNb			INCO developmental
Inconel 617	22	bal	9	12CoAl	~1.0	17.0	INCO
MN25R	24	13	bal	MoN			Nippon Steel
NAC 35A clad	35	45	bal	Nb	~0.3	5.9	NKK
NF709	20	25	bal	NbMoTiN	0.5		Nippon Steel
NF709R	22.5	25	bal	Mo-lowC			Nippon Steel
Save 25	23	18	bal	CuNbN			Sumitomo
Super 304H	18	9	bal	CuNbN	~1.2	10.6	Sumitomo
T91 (SA213-T91)	9	- -	bal	MoV			
T92 (SA213-T92) (NF616)	9	- -	bal	MoWV			
310 Ta (Ta Modified 310)	25	20	bal	Ta	0.3		ORNL experimental
Tempaloy A1	18	10	bal	NbTi	~1.0	9.0	NKK
Tempaloy A3	22	15	bal	NbN			NKK
Tempaloy CR30A	30	51	bal	MoTiAl	~0.3	11.0	NKK
X-20 CrMoV121	12	- -	bal	MoV			
X3CrNiMoN17 13 (1.4910)	17	13	bal	MoN			
X8CrNiMoVNb1613 (1.4988)	16	13	bal	MoVN			

The chemical constituents of the selected alloys and coatings are given in Table 3. This table shows the specification limits, if available, otherwise, the nominal or “target” chemistry is provided. As shown, all alloys have high chromium content. A further criterion in alloy selection was the ability for the alloys to be formed into tube sections and welded to neighboring tubes. From a practical standpoint, alloy selection was also limited by availability. A number of the alloys were newly-established and undergoing evaluation, others were commercially available but not yet in use for superheater tubing and others were already in superheater service. A number of the alloys in this program were developmental, as described in the following section.

Table 2: Test Section Materials			
#	MATERIAL	SUPPLIER	ASME RECOGNIZED
1	Incoclad 671 – Core is Incoloy 800H	INCO	Code Case 1325
2	Thermie (Inconel 740)	ORNL	No
3	310HCbN (HR3C)	Sumitomo	Yes
4	310 Ta (Tantalum Modified 310)	ORNL	No
5	Modified 800H	ORNL	No
6	Save 25	Sumitomo	No
7	HR 120	Haynes	No
8	NF 709	Nippon Steel	No
9	Fe₃Al (Fe ₃ Al-2Cr/304H)	ORNL	Yes
10	347HFG – SA213TP347HFG	Sumitomo	Yes
11	Transition Piece – SA312TP304H		Yes
12	IN52 Weld Overlay (690 clad 800H)	INCO	No
13	IN72 Weld Overlay (671 clad 800H)	INCO	No
14	SA213TP310H		Yes

Table 3: Composition of Selected Advanced Materials

	Incoclad 671	Thermie (In 740)	310HCbN (HR3C)	310 Ta	Mod.8 00H	Save 25	HR120	NF709	Fe ₃ Al	347HF G	IN 52 Weld Overlay	IN 72 Weld Overlay
C	0.05	0.07	0.04-0.1	0.05	0.09	0.05-0.12	0.05	0.1 ^A	--	0.06- 0.10	0.04 ^A	0.05
Mn	--	0.3	2.00 ^A	2	2	2.0 ^A	0.7	1.5 ^A	--	2.0 ^A	1.0 ^A	0.1
P	--	--	0.03 ^A	--	--	0.03 ^A	--	0.03 ^A	--	0.04 ^A	0.020 ^A	--
S	--	--	0.03 ^A	--	--	0.01 ^A	--	0.01 ^A	--	0.03 ^A	0.015 ^A	0.008
Si	--	0.5	0.75 ^A	0.25	0.25	1.5 ^A	0.6	1.0 ^A	--	0.75 ^A	0.5 ^A	0.1
Ni	51.5	48	17-23	21	31	15-22	37	22-28	--	9.0- 13.0	Bal.	55
Cr	48	24	24-26	24.5	20	21-24	25	19-23	2.19	17-20	28-31.5	44
Mo	--	0.5	--	--	1.5	--	2.5 ^A	1.0-2.0	--	--	0.5 ^A	--
V	--	--	--	--	0.4	--	--	--	--	--	--	--
Nb	--	2	0.02-0.6*	--	0.25	0.03-0.60	0.7	0.1-0.4	--	0.48- 1.0*	0.01 ^A	--
Ti	--	2	--	--	0.25	--	--	0.02-0.20	--	--	1.0 ^A	0.6
W	--	--	--	--	--	0.8-2.8	2.5 ^A	--	--	--	--	--
Co	--	19.8	--	--	--	--	3 ^A	--	--	--	--	--
Cu	--	--	--	--	--	2.0-4.0	--	--	--	--	0.3 ^A	0.2
Al	--	0.8	--	--	--	--	0.1	--	15.93	--	1.1 ^A	--
Fe	--	2	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	7.0-11	0.2
N	--	--	0.15-0.35	0.22	--	0.15-0.30	0.2	0.10-0.25	--	--	--	--
Zr	--	0.015 ^A	--	--	--	--	--	--	--	--	--	--
Ta	--	--	--	1.75	--	--	--	--	--	--	--	--
B	--	0.002 ^A	--	--	0.005	--	--	0.002- 0.010	0.011	--	--	--
Others	--	--	--	--	--	--	--	--	--	--	0.5 ^A	0.5 ^A

*Nb+Ta

A = Maximum

4.0 FABRICATION OF TEST MATERIALS AND SECTIONS

The 12 test alloys selected for inclusion in the section are given in Table 2, along with the alloys for the inlet and outlet tubes, 304H and 310H. Due to availability, all but one of the 6 in. long specimens are 2.5 in. diameter with a wall thickness of 0.400". Since four (4) of the alloys were developmental, details of their fabrication are given in the following sub-section.

4.1 Fabrication of Test Materials

Of the twelve (12) test alloys, eight (8) were supplied by tube manufacturing companies and four (4) by Oak Ridge National Laboratory (ORNL) with the coating supplied by Pacific Northwest National Laboratory (PNNL). The alloys supplied by ORNL/PNNL included:

1. Type 304H stainless steel coated with ORNL-developed Fe_3Al alloy FAS. The coating was applied at PNNL by the electrospark discharge process.
2. 310 Ta – Type 310 stainless steel modified by adding tantalum to provide for high-strength at temperature.
3. Modified 800H, which is an ORNL modified version of Incoloy 800H developed by Special Metals Corporation (SMC).
4. Thermie (later re-named Inconel 740), a nickel-based alloy developed by SMC.

The production processes employed in fabricating the tube materials made at Oak Ridge National Laboratory are described to provide a sense of the effort and care taken in producing the advanced materials being tested.

Material 1: Type 304H Coated with ORNL's Fe_3Al Alloy FAS at PNNL

Type 304H tubing produced in Japan by Kobe Special Tube Company, Chofu-Kita Plant was procured from a commercial vendor. The tubing was manufactured to the ASTM A511-96 specification, hot-finished and annealed at 2012°F for 5 minutes followed by quenching in water. The chemical analysis was checked, and compared with the specifications and vendor's analysis in Table 4. The vendor's analysis showed that it met the ASTM specification, and the check analysis confirmed the vendor's analysis.

The as-received tube was cut into 6" long pieces, and its grain size showed a need for a grain coarsening treatment. This treatment consisted of heating the tubes in an argon-purged furnace to 2000°F, holding for 0.5 hours and cooling in air. The grain structure of the heat-treated tube at various locations was measured and is shown in Table 5. The observed 201 μm grain size or ASTM 1.7 suggests that the tubing was subjected to the proper heat treatment.

The electrospark discharge process was used at Pacific Northwest National Laboratory (PNNL) to apply the coating. For the tubes to be coated, a 1/8" diameter wire of the Fe_3Al alloy FAS composition was produced. Air-induction melting (AIM) was used to make a 10 lb. heat of the FAS composition (see Table 5 for specifications). The 1/8" ID Pyrex™ tubes used for vacuum suctioning of the wires broke from the thermal shock resulting in clean wires of the alloy. All of the 18" long wires had a good surface finish. After the wire was produced, a small chemistry sample was poured, and compared with the specifications. Table 4 shows that the content of aluminum matched extremely well with the specified value while chromium was a bit low. The lower chromium could have resulted from its oxidation because the wire suction process was carried out in air. It is the aluminum content that provides the sulfidation resistance, and its value is in good agreement with the specified value.

Table 4: Comparison of specification with vendor and actual analyses of type 304H stainless steel and FAS weld wire					
Weight percent					
		304H		FAS	
Element	Specification	Vendor	Actual	Target	Actual
C	0.08 (max)	0.05	0.054	--	0.008
Mn	2.00 (max)	1.81	1.76	--	<0.01
P	0.40 (max)	0.03	0.026	--	--
S	0.03 (max)	0.004	0.004	--	0.002
Si	1.00	0.41	0.41	--	<0.01
Ni	8.00-11.00	8.66	8.46	--	<0.01
Cr	18.00-20.00	18.44	18.47	2.19	1.59
Mo	--	--	0.26	--	0.01
V	--	--	0.05	--	<0.01
Cb	--	--	<0.01	--	<0.01
Ti	--	--	0.005	--	--
Co	--	--	0.21	--	<0.01
Cu	--	--	0.18	--	--
Al	--	--	0.01	15.93	15.79
Fe	--	--	<i>A</i>	<i>A</i>	<i>A</i>
N ₂	--	--	0.062	--	0.001
O ₂	--	--	0.005	--	0.005

^ABalance.

Table 5: Grain size of fabricated tubes of various alloys after heat treatment					
		Heat treatment		Grain size	
Alloy	Heat no.	(°C)	(h)	(μm)	(ASTM)
304 H	V80210	1093	0.5	201	1.7 ^A
310+Ta	17425	1200	2.0	123	3 ^B
310+Ta	17426	1200	2.0	133	3 ^B
310+Ta	17431	1200	2.0	70 ^B	4.7
Mod. 800	17423	1200	2.0	73	4.5 ^C
Mod. 800	17424	1200	2.0	63 ^C	5.0
Mod. 800	17433	1200	2.0	167 ^C	2.2
In 740	17421	1200	2.0	79 ^D	4.3
In 740	17422	1200	2.0	88 ^D	4.0
In 740	17454	1200	2.0	94 ^D	3.9

^AVery high annealing twin density, ^BLow annealing twin density., ^CNo annealing twins

^DAnnealing twinning near outside and inside diameters but very low density in the mid thickness
The weld wires of FAS were used at PNNL for the electrospark discharge coating process.

General Approach for Fabrication of Materials 2, 3, and 4

For the fabrication of Type 310+Ta, modified 800H and Thermie (Inconel 740), 50 lb. heats were melted by the AIM process. In each case, the heat was poured into an 8" long, 5½" diameter graphite

mold with a hot top. After cutting the hot tops, the ingots were machined to 5.40-in. OD (consistent with the extrusion press liner size at ORNL) and a 1½” diameter hole was drilled for incorporating a mandrel during hot extrusion. For type 310+Ta and modified 800H, the 1½” holes could be drilled by conventional tooling. However, the Thermie alloy required drilling by the electrodischarge machining process. For each alloy, the billets were heated to the appropriate temperature and hot extruded using a 1½” diameter mandrel and a 2¾” diameter opening die. Heated billets were glass-lubricated in each case prior to extrusion. All of the extrusions were carried out on a 1250-ton horizontal extrusion press available in the Materials Processing Group at ORNL.

Material 2: Type 310 Ta Stainless Steel

Billets from heats 17425, 17426, and 17431 were heated to 2102 °F for 3 hours in air followed by glass lubrication and hot extrusion to produce typically 36” long tubes. After cutting the nose and tail, they were given a solution annealing treatment at 2192 °F for 2 hours in an air furnace followed by forced air-cooling. The tubes were cut into 6 1/8” long pieces and a ring for chemical analysis and metallography was made. Each piece was machined to the final tube dimensions of 2 ½” OD x 0.400 thk x 6” long.

Table 6: Comparison of actual chemistry of type 310 stainless steel plus tantalum with target chemistry

Weight percent				
Element	Target	Heat 17425	Heat 17426	Heat 17431
C	0.05	0.063	0.063	0.060
Mn	2.00	1.74	1.66	1.89
P	--	0.008	0.009	0.013
S	--	0.006	0.006	0.006
Si	0.25	0.25	0.24	0.27
Ni	21.0	21.63	21.08	21.12
Cr	24.5	23.74	23.78	24.01
Mo	--	<0.01	<0.01	<0.01
V	--	<0.01	<0.01	0.01
Cb	--	<0.01	<0.01	<0.01
Ti	--	<0.01	<0.01	0.01
Co	--	0.02	0.02	0.01
Cu	--	<0.01	<0.01	<0.01
Al	--	<0.01	<0.01	--
Fe	--	<i>A</i>	<i>A</i>	<i>A</i>
N ₂	0.22	0.22	0.22	0.24
O ₂	--	0.013	0.014	0.018
Ta	1.75	1.18	1.03	1.24
B	0.005	<i>B</i>	<i>B</i>	<i>B</i>

^ABalance. ^BNot analyzed.

Figure 11: Optical Microstructure of Type 310 Ta (heat 17426)

Final anneal 2192 °F, 2 hour forced-air cooled. Transverse orientation.

The chemical analyses of rings from heats 17425, 17426, and 17431 of type 310 Ta are compared with the target chemistry in Table 6. All elements of type 310 Ta heats met the target chemistry extremely well except for tantalum. Somewhat lower values of tantalum were caused by its oxidation during the AIM process. However, based on the previous data¹ on heats of different tantalum levels, the observed tantalum levels are not expected to have a significant effect for the current test. Typical microstructure of a ring from a heat of type 310 Ta is shown in Figure 11, and the grain size of each heat is included in Table 5.

Material 3: Modified 800H

Billets from ORNL heats 17423 and 17424, billets were heated at 2147 °F for 3 hours and hot extruded through a 2¾" die over a 1½" diameter mandrel. The test billet of heat 17433 was held at 2192 °F in air for 16 hours for better homogenization. However, such an exposure resulted in an oxide scale nearly 1/8" thick, which made the billet too large to extrude. The oxide was machined off, and the billet was heated at 2147 °F for 3 hours and extruded in the same manner as the first two billets. After cutting the nose and tail, the extruded tubes were given a solution annealing treatment at 2192 °F for 2 hours in an air furnace followed by forced air cooling. The heat-treated tubes were cut into 6 1/8" long pieces and a ring for chemical analysis and metallography was made. Each piece was machined to the final dimensions of 2 ½" OD x 0.400 thick x 6" long.

The chemical analysis of rings from heats 17423, 17424, and 17433 of modified 800H are compared with the target chemistry in Table 7. All elements except titanium showed a good match with the target chemistry. Poor titanium recovery is caused by its oxidation during the AIM process. The lower titanium level is not expected to have any effect on its corrosion resistance. The optical microstructure of rings from each of the modified 800H alloy are shown in Figure 12, and the grain size of each heat is included in Table 5. The grain size of the tubing for the billet heated at 2192 °F for 16 hours for homogenization was nearly three times that of the grain size for tubes from the other two billets.

Table 7: Comparison of actual chemistry of modified 800H				
Weight percent				
Element	Target	Heat 17423	Heat 17424	Heat 17433
C	0.09	0.10	0.10	0.10
Mn	2.00	1.93	1.94	1.93
P	--	0.009	--	0.002
S	--	0.003	0.002	0.005
Si	0.25	0.24	0.24	0.26
Ni	31.0	30.74	31.04	31.10
Cr	20.0	19.89	19.98	19.91
Mo	1.5	1.50	1.52	1.51
V	0.4	0.38	0.23	0.37
Cb	0.25	0.26	0.26	0.25
Ti	0.25	0.11	0.15	0.03
Co	--	0.03	<0.01	<0.01
Cu	--	<0.01	<0.01	<0.01
Al	--	<0.01	<0.01	0.01
Fe	<i>A</i>	<i>A</i>	<i>A</i>	<i>A</i>
N ₂	--	0.026	0.029	0.018
O ₂	--	0.004	0.008	0.015
Ta	--	<0.01	--	1.24
B	0.005	<i>B</i>	<i>B</i>	<i>B</i>

^ABalance. ^BNot analyzed.

Figure 12: Optical Microstructure of Modified 800H (heat 17424)

Final anneal 2192°F, 2 hour forced-air cooled. Transverse orientation.

Material 4: Thermie Alloy

Billets from ORNL heats 17421, 17422, and 17454 were used to make the Thermie alloy pieces. After two unsuccessful extrusions at 2210 °F and 2282 °F, 2327 °F was used for successful extrusion of this alloy. All three billets were heated at 2327 °F for 3 hours in air and hot extruded through 2³/₄" diameter die over a 1¹/₂" diameter mandrel. Although the billets extruded to tube at 2327 °F, the tubes showed significant regions of surface irregularities. The extruded tubes were given a solution anneal treatment at 2192 °F for 2 hours followed by forced air cooling. The annealed tubes were cut into 6 1/8" long pieces and a ring for metallography and chemical analysis was made. The cut pieces were machined to the final dimensions of 2 1/2" OD x 0.400 thk x 6" long. The machined pieces of the Thermie alloy are shown in Figure 13. Metallography of the rings from each heat of In 740 alloy is shown in Figure 14, and the grain size measurements are presented in Table 4. The chemical analysis of the three heats of the Thermie alloy is compared with the target chemistry in Table 8. Except for slightly higher carbon, all other elements of the three Thermie alloy heats met all elements of the target chemistry. The slightly higher carbon level in these tubes is not expected to have any effect on the corrosion resistance of Thermie alloy.

Table 8: Comparison of actual chemistry of In 740 alloy with target chemistry

Weight percent				
Element	Target	Heat 17421	Heat 17422	Heat 17454
C	0.07	0.10	0.088	0.094
Mn	0.3	0.32	0.32	0.32
P	--	<0.002	<0.002	<0.002
S	--	0.005	0.003	0.009
Si	0.5	0.50	0.51	0.49
Ni	48.0	48.83	49.06	48.92
Cr	24.0	23.48	23.08	23.63
Mo	0.5	0.43	0.43	0.42
V	0.4	0.38	0.23	0.37
Cb	2.0	2.16	2.20	1.95
Ti	2.0	2.08	2.10	2.01
Co	19.8	19.22	19.39	19.42
Cu	--	<0.01	<0.01	<0.01
Al	0.08	0.75	0.74	0.60
Fe	2.0	2.11	2.06	2.11
N ₂	--	0.011	0.013	0.022
O ₂	--	0.002	0.003	0.004
B	0.002 ^A	<i>B</i>	<i>B</i>	<i>B</i>
Zr	0.015 ^A	<i>B</i>	<i>B</i>	<i>B</i>

^AMaximum. ^BNot analyzed

Figure 13: Photograph of Machined Tubes of In 740 Alloy

Figure 14: Optical Microstructure of Machined Thermie Alloy (heat 17427)

Final anneal 2192°F, 2 hour forced-air cooled. Transverse orientation.

Table 9: Summary of visual tube inspection and number of 310 Ta, modified 800H, and Thermie tubes shipped to Babcock & Wilcox from the Oak Ridge National Laboratory			
Alloy	Heat No.	Tube No.	Visual Observations
310 Ta	1742	1,2,3,4	All good. No defects
310 Ta	1742	1,2,3,4	All good. No defects
310 Ta	1743	1,2,3,4	All good. No defects
Total Pieces		12	
Total Shipped to MTI		12	
Mod 800H	1742	1,2	Both tube's OD surfaces showed very small flaws.
Mod 800H	1742	1,2,3	Tube's OD surfaces showed slight flaws.
	4	4	Tube showed larger flaw on OD surface. Sent for weld practice.
Mod 800H	1743	1,	Tube showed one small surface flaw.
	3	2,3	All good. No defects. Tube 3 saved at ORNL as archive.
		4	Surface flaw.
Total Pieces		10	
Total Shipped to MTI		9	
Thermie	1742	1	Two places on OD and an end did not clean up during machining
		3	Flaw on ID and one end.
		4	No defects
Thermie	1742	2	Bad machining job, saved at ORNL
	2	3	No defects.
Thermie	1745	1,2	No defects.
	4	3	Two places on OD and one end did not clean up during machining
Total Pieces		8	
Total Shipped to MTI		7	

Inspection and Shipments

All machined tubes of 310 Ta, modified 800H, and Thermie alloys were visually inspected and shipped with an inspection report. The inspection data and the number of tubes of each alloy shipped are shown in Table 8. Most of the tubes had no flaws. Minor flaws in the tubes are not expected to affect their corrosion resistance.

4.2 Fabrication of the Test Sections

The system consists of three identical sections, all alloy specimens have an OD of 2.5” and all but one (Inconelad 671 wall thickness 0.266”, availability issue) have a wall thickness 0.4”. All specimens are located in the top (hottest) two rows of the section and the balance of the section to which the test rows are connected is type 310H stainless steel with a wall thickness of 0.220”.

Each of the three (3) identical test sections contains ten (10) primary and two (2) secondary advanced material samples. The primary samples were placed in three different locations within the section (see Figure 15 and Table 2). The sequence of alloys in each section was based on their relative corrosion resistance and creep strength, as determined in laboratory-scale tests, with the most resistant being located at the hottest end of the section. However, slight alterations in the sequence were made to minimize the chances of dissimilar metal weld problems.

Figure 15: Test Section Arrangement

(see Table 2 for corresponding materials)

The three test sections were fabricated in two locations; the B&W manufacturing facility in West Point Mississippi, and at McDermott Technology Inc (MTI) research center in Alliance, Ohio. The West Point work scope involved the fabrication of the SA213 TP310H lower two rows not containing the test materials while the MTI work scope included the welding development and manufacture of the upper two rows which contain the advanced materials. Due to the experimental nature of the advanced material fabrication, it was deemed prudent to perform welding trials and section assembly in a location that could provide full metallurgical testing capabilities hence, final assembly was performed at MTI.

West Point Assembly

The work scope defined for West Point permitted fabrication to follow routine manufacturing practices. Generally, the SA213 TP310H tubes were received and weld preps were machined on the ends of the tubes for later fabrication. The tubes were cold bent to provide the 180° returns, and were subsequently annealed at 2000°F - 2100°F. The section pieces were then joined using orbital gas tungsten arc welding equipment. The baffle wall support lugs were then welded to the bends, all dimensions verified, and the assemblies were shipped to MTI for final assembly.

MTI Development

Prior to performing weld parameter development, consideration was given to the selection of several process variables, which would form the basis of the remaining weld development program. Key variables such as weld filler metal, weld groove geometry, and welding position were determined.

The selection of the filler metal revolved around two important characteristics. First, it was desired that the filler metal contain sufficient levels of chromium to avoid corrosion in excess of those levels expected for the tube material. Second, the filler metal needed to be compatible with the tube base materials being joined. It was also very desirable that only one filler metal be used for all the combinations of tube materials in order to greatly simplify the development activity. Alloy 625 (SFA 5.14, ERNiCrMo-3) was selected as meeting all of these major considerations. The chemical analysis of the actual heat of filler metal, along with its specified chemistry range, is shown in Table 10.

Table 10: Alloy 625 Filler Metal Chemistry															
	C	P	S	Si	Cr	Mn	Fe	Cu	Co	Mo	Al	Ti	Cb+Ta	Ni	Other
Range	0.10	0.20	0.015	0.50	20.0	0.50	5.0	0.50	NR	8.0-10.0	0.40	0.40	3.15	Bal	<0.50
	^A				23.0						^A	^A	4.15		
Actual	0.09	0.007	0.001	0.12	20.1	0.13	1.71	0.12	0.09	8.51	0.19	0.21	3.38	65.3	<0.50

^AMaximum.

Weld Groove and Welding Position

The original concept for fabrication was to assemble the test material using an orbital gas tungsten arc weld with the tube axis horizontal. This was the method used for the West Point scope of work and represents a conventional manufacturing approach. This concept was later modified for the work performed at MTI in order to keep the resultant weld inside diameter (ID) contour as flat as possible without evidencing any ID concavity. The control of ID contour was considered a significant process variable in order to determine heat transfer accurately during boiler operation.

In order to achieve a controlled ID contour, it was decided to weld with a stationary welding arc positioned at approximately 2 o'clock while rotating the tube beneath the arc. By maintaining the arc in one position, the contour of the root shape was consistently maintained. Also, the effects of gravity were minimized while the penetration into the root was optimized. Except for the final welds joining the test section pieces to each other, this was the method used throughout the assembly of the sections.

It should be noted that these measures were used to satisfy experimental criteria and would most likely not be necessary for commercial fabrication.

The weld prep selected was a standard weld groove used for automatic gas tungsten arc welding in many of B&W's manufacturing shops. The weld prep is as shown in Figure 16. One of the features of this prep is the extended 0.065" long land. This permits good penetration and sidewall fusion on the root bead, but allows shrinkage to occur in the axial direction, which enhances positive ID reinforcement and reduces the likelihood of ID concavity. The weld prep is also sufficiently narrow across the top, permitting all weld layers to be deposited as weld single beads.

Figure 16: Weld Preparation

Weld Parameter Development

Prior to starting fabrication, welding parameters were established for each of the base material combinations to be welded. Since the welding process, groove geometry and filler metal were common for all base material combinations, it was possible to develop one basic parameter set and then apply it to each material combination with very little change from one combination to the next. In fact, the greatest difference between welding programs was related to material thickness rather than material type. Minor changes in wire feed rate and voltage were occasionally found to be necessary between material types; however, these may have been caused simply by differences in machining dimensions or other non-material related factors. In any case, the parameter differences were small, and of a type normally seen in any welding operation.

The basic parameter sets were first developed through trial and error evaluation based on visual observation during mockup welding. Bead appearance, sidewall wetting, root penetration, and ID contour were the primary characteristics upon which the welds were evaluated. Once a final set of parameters was established, representative weld combinations were welded, radiographed, and metallographically examined in order to confirm the acceptability of the established welding parameters.

MTI Assembly

The first step in assembling the sections was to dimensionally inspect the tube thickness of each test piece and record the dimensions for later comparison when the test pieces are removed for final corrosion evaluation. Each test piece was punch marked on the tube ID to serve as a permanent location, or key, for future orientation of the recorded dimensions. The punch mark was also used to

maintain radial orientation of each test piece relative to the hot side of the section during boiler operation.

Following dimensional inspection, each test piece was fit, manual gas tungsten arc tack welded, and completely welded before adding a subsequent test piece to the assembly. During the assembly process, the test sections were fabricated as six independent legs as shown in Figure 17, two for each of the three sections. The exact sequencing of the welds was recorded for future use if needed. A scheme numbering the sequencing of the welds was developed and used for several purposes. First, the delivery of the test material took longer than originally planned which compressed the fabrication schedule such that it was necessary to alternate welding operations with radiographic inspection. By dividing the sections into six legs, it was possible to be welding on three legs while the other three legs were being radiographed. Second, by adding one 6" long test piece at a time, a visual inspection of the weld ID was more easily achieved. Since the weldability characteristics of the test materials were relatively unknown, it was important to visually inspect each root bead from both the ID and the OD of the weld before depositing subsequent weld layers. This inspection was to determine whether the weld contour was acceptable, to confirm freedom from cracking, and to assure good weld bead tie-in at the weld prep edges. Third, this method also permitted each material combination to be welded in groups of three, which simplified the equipment setup and weld program selection.

After each of the six legs was welded and radiographed, the sections were final assembled. This consisted of welding each of the legs to the SA213 TP310H bends and attaching a transition piece on the inlet and outlet ends to permit connecting the tube to the field installed external piping. Since these welds were also used to establish the over-all length of the assemblies, manual gas tungsten arc welding was performed for the root pass, and the weld completed using orbital welding. Following final assembly, all of the welds were dye penetrant inspected, and the completed sections hydrostatically tested per ASME Code requirements. MTI made a total of 116 welds, which were all radiographed and dye penetrant inspected with no indications.

Figure 17: Fabrication of Sections at MTI

5.0 DESCRIPTION OF TEST SYSTEM

The objective of the project is to test the resistance of several of the most promising new materials to coal ash corrosion conditions when operating at surface metal temperatures typical of a secondary superheater in a supercritical boiler with up to 1100°F steam temperatures (or higher if possible). To accomplish this objective, three identical sections were designed for installation in the gas path of the furnace of the Niles Unit #1 boiler within the existing secondary superheater banks as shown in Figure 10.

Test Sections

The sections are operated identically. The first section was initially expected to be removed and thoroughly evaluated after one year of operation, the second after three years and the third after about five years. This data is expected to provide the corrosion resistance information for the alloys needed to generate design criteria and permit the designer to select the best material.

The test system is supplied with steam from one of the two existing 14" carbon steel reheat inlet pipes that transport steam from the steam turbine to the boiler reheater. A new 6" carbon steel nozzle was installed in the existing 14" reheat inlet pipe on the left-hand side of the boiler (facing the frontwall). A 6" carbon steel feed pipe (see Figure 18) was routed to the front of the boiler to provide steam to the three parallel test sections.

Flow to each section is controlled to maintain the final outlet steam set temperature by the inlet flow control valve. Steam leaving the test sections at elevated temperature is injected via specially designed thermal nozzles into the right hand existing 16" alloy reheat outlet pipe. The steam is introduced into the pipe just above three existing equalization connections, which balance the pressure and flow between the two outlet pipes before the turbine. The relatively small flow mixes with the main flow from the boiler reheater on its way back to the steam turbine, and because of the small flow has little, if any, influence on the final reheat temperature.

Figure 18: System Schematic

Since these circuits are in parallel with the existing reheater, the existing reheat safety valves will protect the sections under normal conditions. However, if the section were to become isolated by closing the control and stop valves when there is a tube leak within the boiler setting, the steam trapped inside the circuit would continue to absorb heat and expand. To protect the portion of the sections outside the boiler from this increase in pressure, safety valves have been provided which are set at 600 psi. The safety valves vent into a large 10" closed vent pipe, which exhausts the steam to the atmosphere outside the building.

The three sections extend through the furnace front wall completely across the furnace up-pass. The sections are supported from the baffle wall at their rear and the furnace front wall at their front and the wall penetration is sealed with an insulated casing box. At each section, one wall tube was side bent (to the outside of the boiler wall) to provide passage for the section tubes and the gap between wall tubes will be closed in typical fashion.

To prevent the unlikely event of a tube failure in a test section from jeopardizing operation of the host unit, special alarms in the controls have been supplied to identify conditions that indicate the loss of steam from the section. Each test section is equipped to respond should such conditions be detected. If one condition is detected, the operator in the plant control room will be alerted to investigate and manually take appropriate action. If sufficient conditions are detected, the operator can elect to close the control valve at the inlet and the stop valve at the outlet to isolate the test section from the boiler. This will result in the destruction of that section due to overheating but will protect the host unit.

Figure 19: Shipment of Completed Sections from MTI to the Niles Facility

The 3 completed sections (Figure 19) were transported from MTI in Alliance to the Niles plant in April 1999 for installation into the boiler.

Data Acquisition System

Data collection is an automated process using a standard desktop personal computer (PC) located at the plant. Data is taken from the plant's control system every 4 minutes by a direct connection between the communication ports of the PC and the control cabinets. These data files are automatically stored on the computer's hard drive. There is one raw data file for each day of data collection. In addition, the data is averaged every 30 minutes and the averaged values are used by a Microsoft Visual Basic[®] program to calculate individual section steam flows, sample steam temperatures, sample metal temperatures and time of operation. Each section has one data file for each day of data collection stored on the local hard drive. All of this takes place automatically and without human intervention except in the rare occurrence of a problem with the computer system. In the unusual event of a system crash, the computer can easily be rebooted and all data collection and calculation programs resume automatically. Table 11 shows all data collected by the data acquisition program. Noticed there is other plant operating data as well as sample section data. This data is useful for correcting metal temperature calculations and understanding upsets in the system operation.

The data collection and section performance are closely monitored by both plant personnel and personnel from B&W in Barberton, Ohio. B&W monitors performance remotely via a phone modem and Laplink[®] software. Not only can real time performance of the loops be monitored but the data files stored on the hard drive can be accessed and reviewed at any time without interruption to the data collection. This is particularly useful for trouble shooting any operational problems that may arise. The software also allows the periodic transfer of data from the PC at the Niles plant to the hard drive of a PC in the Barberton offices. Once the data has been downloaded to the B&W office, it is duplicated again on 100 MB Zip discs. Recalculation of any or all data from the raw data files can also be performed in the office. This is particularly useful for recalculating files containing bad data caused by instrument failure such as an open thermocouple or the failure of the calculation program to run properly. Although infrequent, both have occurred.

Once the data has been collected, calculated and transferred to B&W, it must be put into a usable form for analysis. The metal temperatures for each sample are averaged into daily temperatures along with the total hours. Because little coal ash corrosion occurs at low metal temperatures, any time the section outlet metal temperature is below 1000 F, that particular temperature is not included in the average. This process is also automated by a specially created program and inputting the beginning and ending dates of interest.

Table 11: List of Data Collected at Niles

Tag#	Tag Description		Tag#	Tag Description
1	1A COAL FLOW		38	RH 1 LOOP DELTA P
2	1B COAL FLOW		39	RH 2 LOOP DELTA P
3	1C COAL FLOW		40	RH 3 LOOP DELTA P
4	1D COAL FLOW		41	RH 1 SOV DELTA P
5	WEST O2 PROBE		42	RH 2 SOV DELTA P
6	EAST O2 PROBE		43	RH 3 SOV DELTA P
7	E SH ATTEMP FLOW		44	RH 1 CV POS
8	W SH ATTEMP FLOW		45	RH 2 CV POS
9	RH ATTEMP FLOW		46	RH 3 CV POS
10	MAIN STEAM FLOW		47	RH INLET TEMP
11	FEEDWATER FLOW		48	RH 1 INTERMED TEMP
12	REHEAT STEAM FLOW		49	RH 2 INTERMED TEMP
13	TOTAL AIR FLOW		50	RH 3 INTERMED TEMP
14	MAIN STM PRESSURE		51	RH 1 OUTLET TEMP-A
15	FEEDWATER PRESSURE		52	RH 1 OUTLET TEMP-B
16	DRUM PRESSURE		53	RH 2 OUTLET TEMP-A
17	COLD RH PRESSURE		54	RH 2 OUTLET TEMP-B
18	HOT RH PRESSURE		55	RH 3 OUTLET TEMP-A
19	HOT RH TEMP		56	RH 3 OUTLET TEMP-B
20	COLD RH TEMP		57	CHORDAL TEMP A
21	E SEC SH IN TEMP		58	CHORDAL TEMP B
22	W SEC SH TEMP		59	OUTLET PIPE METAL TEMP
23	E MAIN STM TEMP		60	RH 1 SOV OPENED
24	W MAIN STM TEMP		61	RH 1 SOV CLOSED
25	E PRI SH OUT TEMP		62	RH 2 SOV OPENED
26	W PRI SH OUT TEMP		63	RH 2 SOV CLOSED
27	1A CYC AIR TEMP		64	RH 3 SOV OPENED
28	1B CYC AIR TEMP		65	RH 3 SOV CLOSED
29	1C CYC AIR TEMP		66	RH 1 CV DEMAND
30	1D CYC AIR TEMP		67	RH 1 SOV DEMAND
31	FEEDWATER TEMP		68	RH 2 CV DEMAND
32	ATTEMP WATER TEMP		69	RH 2 SOV DEMAND
33	GROSS MEGAWATTS		70	RH 3 CV DEMAND
34	RH INLET PRESSURE		71	RH 3 SOV DEMAND
35	RH 1 CV DELTA P		72	RH 1 AVG OUTLET TEMP
36	RH 2 CV DELTA P		73	RH 2 AVG OUTLET TEMP
37	RH 3 CV DELTA P		74	RH 3 AVG OUTLET TEMP

6.0 SYSTEM INSTALLATION, START-UP AND OPERATING HISTORY

6.1 Installation

In December 1998, a boiler performance test was conducted to determine the actual operating conditions of Unit 1. Prior to the test, a gas sampling and temperature measurement grid was installed at the boiler outlet. This grid provided accurate indications of the flue gas O₂ content and boiler exit (airheater inlet) gas temperature. Also installed were thermocouples at the exit of each of the three parallel gas paths in the downflow convection pass. These temperatures allowed a calculation of the amount of flue gas flowing over the reheat and primary superheater sections. To accurately predict total reheat steam flow, test thermocouples were installed around the two top feedwater heaters. This test instrumentation, along with data taken from the plant's existing control system, provided information such as furnace exit gas temperature (FEGT), main and reheat steam flow, and boiler efficiency which are necessary for understanding the boiler's operating conditions. In addition, the pressure drop between the reheat inlet and reheat outlet was measured using existing pressure taps in the pipes near the turbine. The pressure drop between the actual point on the reheat inlet pipe where steam is taken for the test sections and the point on the reheat outlet pipe where it is re-injected was back-calculated compensating for the reheat piping losses between points.

B&W Construction Company (BWCC) mobilized at the site on April 13, 1999 and by the end of the month had installed the safety valve vent piping, the feed piping and header, the inlet nozzle and outlet nozzles. On Wednesday April 28, 1999 the three test sections were lifted into place in the boiler (Figure 20). DOE, OCDO and B&W photographers were on hand to record the event. Installation of the piping, valves and instrumentation external to the boiler was subsequently completed. In parallel B&W configured and implemented the initial control logics in the plant's Digital Control System (DCS).

Figure 20: Installation of Sections into the Niles boiler

Difficulties encountered during installation caused BWCC concern about schedule and budget about half way through the outage. Upon completion, the events were reviewed and it was determined that

the following issues contributed to a significant cost overrun for this portion of the project. 1) Although a site visit was made, the impact of the tight space in which the equipment was installed was not fully appreciated during the estimating process. This affected the ability to efficiently schedule the crafts which reduced productivity. 2) Due to First Energy's collective bargaining agreement, which reduced labor rates, the lack of intended overtime initially (two shifts were planned) and other more lucrative projects at other area plants during the same time frame, BWCC experienced difficulty obtaining sufficient laborers. 3) In late March the outage length was reduced from 4 to 3 weeks. Considering items 1 and 2, this further exacerbated the situation. 4) During the installation on Unit 1, Unit 2 experienced two forced outages and at First Energy's request BWCC made repairs very quickly to get the unit back on line. This briefly distracted both labor and supervision from test section installation, further aggravating the situation. 5) One of the section outlet pipes had to be rerouted to avoid interference with a coal bunker stiffener not detected during site inspections made prior to the design. 6) Some minor errors were made and difficulty was experienced in obtaining acceptable welds in the outlet pipes. 7) Installation of the air supply piping and instrumentation piping was more time consuming than anticipated. Installation was completed on May 17, 1999, one day later than scheduled, and at significantly higher costs than budgeted.

6.2 Start-up

The sections and the Data Acquisition System ran through June 1999 with only one minor problem. One of the control valve position transmitters was providing an erroneous reading. The signal quality was good so it was thought to be a transmitter calibration or adjustment problem. Since this reading is used in a flow calculation as part of one of the tube leak alarms, one of the sections ran temporarily with an erroneous alarm indication (though it operated and controlled properly). Initial tuning of the controls was completed except for determination of the final set point for steam temperature and some changes to the control logic resulting from observing operation so far. These changes included reduction of the temperature increase rate on startup and the decrease rate on shutdown and the flow calculation used as part of the logic to detect a tube leak needed to be modified to avoid using the control valve position indication to improve reliability.

6.3 Operating History

1999

The steam temperature set point temperature needed to achieve the desired surface metal temperatures is a calculated value. Due to a lack of operating experience with the system it was initially set to 1000°F. To ensure accuracy, measurement of the gas temperature was necessary. When an attempt was made to take these measurements in early June, it was discovered that the access doors to be used to insert probes into the upper furnace were not functioning properly to insure safety. The Niles unit is pressurized and both aspirating and seal air are necessary to protect personnel when they are opened.

A brief outage in late June was used to make controls corrections and attempt to repair the furnace doors. Following restart only two of the doors would operate properly so gas temperature measurements were taken at two locations and the results were determined to be accurate enough to eliminate the need for the third location. Due to the brief outage length, a faulty control valve position indicator for Test Section "A" could not be examined. On restart of the boiler it operated properly for a while and then began giving false readings again. This behavior indicated a mechanical problem. Since the position indication was not a critical piece of information, repair was not deemed urgent.

As a result of initial calculations the steam temperature set point was increased to 1050°F in July. The system ran as expected during August. On September 2 a shorted outlet thermocouple (one of two) in the middle section, section B, caused a temperature excursion in which the steam temperature leaving the section went as high as 1220°F for about an hour and 45 minutes. After review by metallurgists, no damage to the materials was expected and due to the short duration of the incident there was no impact on the corrosion data. As a result of the effect of this shorted thermocouple connection, the control logics were modified again in early September to eliminate the possibility of one bad thermocouple producing an alarm where two are provided for redundancy. During the last week of the month the unit was shut down for a brief outage. In hopes of replacing the bad position indicator and repairing the shorted thermocouple, a replacement position transmitter was obtained from Fisher-Rosemont on the warranty. Unfortunately the plant was unable to complete this work. Thermocouple repair was completed the week after restart but replacement of the positioner had to wait until the next opportunity.

Just prior to the brief outage in late September Section "A" experienced two unexplained incidents where the control valve went open cooling the outlet temperature from its set point to 800F to 900F. Once an operator placed it into automatic mode, it controlled properly. After review of the data and the control logic, no explanation was found and the alarm listing was also reviewed but no cause was identified. Upon restart of the unit all three sections failed to go into automatic control mode. All were placed into automatic mode but both "A" and "B" sections experienced two or three incidents of the valve unexplainably opening and then returning to control.

During October the sections and the Data Acquisition System ran as expected with a steam temperature set point of 1050°F. Evaluation of increasing it to 1100°F was in progress but not completed due to resource availability and the recent control valve problem. Investigation of the unexplained problems with the control valves on Sections A and B revealed that the position controllers had failed due to overheating. The valve vendor replaced the controllers on these two valves during a brief outage. Higher temperature diaphragms (to 300°F) in all three actuators were installed in addition to a permanent cooling system and the position transmitter that had given erroneous readings almost since installation was replaced and returned on warranty.

The overheating of these controllers was caused by a rise in ambient temperature to over 200°F partially resulting from a cyclone burner casing failure. This was also repaired during the outage but failed again shortly after restarting of the boiler. A system for blowing cooling air over the valve electronic components was installed. The cooling system is functioned well and kept the valve temperatures at around 150°F (the design limit for the valve components is 175°F). Due to the brief

unplanned outage, a quick response from the valve vendor and some scrambling by B&W people, only a few days of operating time were lost for sections A and B while Section C ran normally.

Since the environment around these valves is much more severe than anticipated and worse than it should be, a meeting was held at the plant in November with plant personnel to discuss the repair of the control valves caused by overheating and the conditions the equipment is subjected to. Although some repairs to casing and insulation were expected in the next several months it was not certain whether they would significantly mitigate the severe temperature and dust conditions in the valve area (over 200°F). As a result, the importance of the cooling system operation, and the need for regular monitoring and backup was recognized. Removal of the first section was also discussed, and since there would not even be a year of operation at an operating temperature that had been gradually increased, it was decided that the first section would most likely be removed in the Fall of 2000 or in the Fall of 2001, depending on unit outage schedule.

A safety guard was installed on the cooling fan during a brief outage during November. Based on periodic readings (not continuously monitored) the cooling system maintained the temperature between of the controllers between 100°F and 155°F. The evaluation of steam temperature set point based on heat transfer analysis was completed in November and the steam temperature set point was increased to 1075°F.

During December 1999 some problems arose with control valve A which seemed to be heat related. During a very brief outage the valves were stroked and an inspection made. All worked and looked fine. Upon restart problems arose again with valve "A" (the control signal showed bad quality, the valve failed open and could not be controlled). Plant personnel routed cooler air from outdoors to the cooling system after which the valve began to respond and seemed to be working acceptably.

2000

In January, corrections were made to the data reduction program and calculation of a daily average was added as requested by MTI for future corrosion evaluations. All previous data was rerun and corrected and all data currently collected is using the new correlations.

In late February, Section A control valve electronics apparently overheated again causing the valve to operate in the wide-open position (section was running cool). During a brief outage for a tube leak on February 22, a cursory inspection of the sections for corrosion was made. Based on visual and tactile inspection, corrosion was minimal, as expected, and removal of the first section was delayed. There was some concern for the state of the inlet tubes that are 0.220 wall, SA-310 (they were not inspected). Though no problems were anticipated, the concern was due to the higher gas temperatures and furnace radiation the lowest tubes are exposed to which may be causing higher than expected surface metal temperatures and accelerated corrosion. If they were experiencing severe corrosion, we would have had to replace them with thicker tubes if available (the min wall is less than 0.1).

The annual maintenance outage began on March 4th and extended for six weeks. On March 22 the sections were inspected by a metallurgist to confirm whether: (1) the amount of wastage was sufficient to justify removal of a section for metallographic examination at this time, and (2) the test loops were likely to be serviceable through the coming 18 month period of operation before the next planned maintenance outage. A summary of results is shown in Table 12. It is important to note that all measurements were rough and should be interpreted qualitatively rather than quantitatively.

Of particular importance was an examination of the cooler inlet tubes (bottom of section) that are exposed to direct furnace radiation and flue gas impingement. Access to the full length of these inlet tubes was not possible but about four feet of the tubing near the center of each loop, where corrosion is worst, was examined. The inlet tubes are smooth with no flat areas, and ultrasonic thickness measurements indicated that the tube wall thickness is about 0.24 inch. Also, based on the initial 2.50 inch OD and caliper measurements of the current tube OD, there has been no significant corrosion of these tubes.

Table 12: Diameter Measurements		
	Top-to-Bottom	Side-to-Side
Hottest Save 25, West Loop (A)	2.45	2.42
Hottest Save 25, Middle Loop (B)	2.42	2.39
Hottest Save 25, East Loop (C)	2.41	2.38
Hottest NF790, East Loop (C)	2.44	2.43
Hottest 347HFG, East Loop (C)	2.45	2.41
Hottest 310HCbN, East Loop (C)	Rough, but no ridges	
2 nd Save 25 from steam outlet, East Loop (C)	More wear than adjacent 800Mod & NF709	
Bottom Tube, West Loop (A)	2.49	
Bottom Tube, Middle Loop (B)	2.49	
Bottom Tube, East Loop (C)	2.49	2.52

Some wastage occurred on several of the six-inch long specimens in the outlet legs (top of section) of the three test loops. There was generally a discontinuous transition from smooth top surfaces to roughened lower surfaces. However, with one exception, the maximum depth of corrosion was just a few mils (OD caliper measurements will be compared to measurements taken on the individual specimens before installation). As Table 12 shows, based on the nominal 2.50 inch OD, the depth of corrosion was only about 5 to 10 mils. The one material that appeared to have suffered somewhat more corrosion than the others was Save 25 (Fe-23%Cr-18%Ni). The hottest segment of this alloy had discernable flats on the bottom quadrants (centered at the 4 and 8 o'clock positions with 6 o'clock being the bottom, facing the gas flow). The flats are most pronounced on the segment in section A.

The corroded surfaces were rough so caliper measurements could not determine the maximum depth of wastage, which was probably about 30 mils deeper than indicated by the diameter measurements.

Around 60 mils of side-to-side loss were detected on the worst tube (these tubes are 400 mils thick, the minimum thickness required is about 80 mils). The cooler segment of Save 25 in the upper tube row of each loop showed less corrosion than the hottest segment, but more than the other nearby segments. The hottest segment of 310HCbN showed more corrosion roughening than adjacent alloys, but it was 18 inches closer to the outlet than the hottest Save 25 which experienced more corrosion. The 347HFG material was the only one on the test loops to have formed a distinct white layer similar to that formed on the ferritic materials in the SSH outlet elements. Inner layers on other alloys were generally black.

Following this inspection, a project status meeting was held on March 29 at the plant and based on the observations it was recommended that a section not be removed for metallographic examination until the next outage. There was too little corrosion to differentiate between most of the alloys. In addition, since there was already some discernable coal ash corrosion on some alloys and substantial corrosion on one alloy, the loop temperatures were not increased further.

Upon restart of the unit in mid-April after the spring outage, following replacement of the controller for control valve "A" and enveloping of all three controllers in "boxes" fed cooling air directly, control valve "A" exhibited the same behavior it had before the outage. It operated as expected for a day and then for no apparent reason went further closed than required until the temperature tripped the valve open. The valve was manually opened and locked out in that position until repairs could be made. Apparently the controller had not been the problem.

During a brief outage for a tube leak, Fisher visited the site on May 25, replaced control valve A's regulator, and moved it into a less hostile environment, which they thought was the problem. However, following restart of the unit the valve continued to malfunction. After plotting control signals and other data it appeared the problem was in the control system hardware since the signal to the valve was not correct but the valve seemed to be responding to the erroneous signal properly. In addition, the digital control system (DCS) periodically indicated brief bad quality on the signal to the valve that would explain why the valve had mysteriously gone into manual mode occasionally in the past. As a result, a visit was made to the plant on June 2 and a card in the DCS was found to be faulty. After replacement, the valve operated correctly and it was hoped this chronic problem had finally been solved. The positioner feedback for two of the valves was out of calibration with the demand signal which resulted in an inability to achieve the desired outlet temperature (two sections were running about 40F lower than the 1075F desired). This and calibration of a couple of pressure transmitters would be corrected at the next opportunity.

During a brief outage in late June, the control valve positioners for Sections A and B were adjusted to correspond to the control signal. When adjustment of valve B was attempted the controller did not respond so it was changed. Due to time they were unable to adjust valve C, which was the closest to being correct anyway. Valve C was tuned at the next opportunity. The pressure transmitters were reviewed and it was decided that re-calibration was not yet necessary.

Notification was received in April from First Energy that ownership of the Niles Plant was transferred to Duquesne as well as all obligations for the project. In early May we were verbally informed that ownership of the Niles Plant transferred to Orion Power Midwest on May 1 along with it all obligations for the project. A meeting was held on June 13 with the new plant manager, Mr. Keith Bastion, to introduce him to the project, its purpose and status. The meeting, attended by Larry Davison and the writer along with former plant manager (now Engineering Manager) Bob Johns, was productive and no impact on the project was expected as a result of Orion Energy's ownership.

In July we were still experiencing some difficulty in getting the valve positioners to agree with the demand signals. In addition the unit had been running at low loads (60 to 70 MWe) more than in the past. These differences and the low flow conditions in the reheater at low loads have caused us to decide to raise the load at which the valves begin controlling. At higher loads the valves control the outlet temperature to 1075°F well but at low loads the valve minimum position limit of 15% results in about 1000°F for the sections where the feedback from the positioner agrees with the demand well but the other section may continue to control to 1075°F. The concern is that at such low steam flows our ability to accurately calculate the surface metal temperature is marginal.

In August as a result of these operational issues, the load at which the valves open during load reduction was changed from 60 to 70 MWe and the load at which they begin controlling on load increases was changed from 65 to 75MWe. In addition, a request of the plant was made to inform us when the unit is down for an unplanned outage long enough to allow the unit to cool for entry for another inspection of the progress of corrosion.

In September the system ran as expected. The unit experienced two brief forced outages but there was insufficient time to inspect the sections. Ed Robitz, who has replaced Steve Kung as the MTI investigator, was brought up to speed on the data desired.

The plant notified B&W on a Saturday October 28 of a third brief opportunity to inspect the sections. However with only Monday for inspection, other commitments and circumstances prevented arrangement of the necessary personnel at B&W and at the plant. No opportunities to inspect the sections arose in November or December. On December 30 Orion Power personnel notified B&W that two of the control valves malfunctioned and were operating in the open position. This resulted in an outlet steam temperature of 780°F for sections A and B while section C outlet temperature remained at 1079°F. The cooling fan was in operation but the temperatures at these valve controllers was higher than desired (about 160°F) indicating there could be a breach in the cooling ductwork. Fisher (valve manufacturer) was brought to the site for repair at the next opportunity. With the exception of an infrequent computer lockup the DAS ran continuously (it was checked daily).

2001

No opportunities to inspect the sections arose in January. The electronic controllers for two valves failed in late December (probably due to overheating) causing the valves to open and the sections to run cool. In mid-January the third valve did the same. All three valves were open. This does no harm

to the unit or the sections but it does delay corrosion. Remedies were discussed with the plant for implementation at the next opportunity.

During a brief outage Fisher repacked and replaced the controllers for all of the three control valves on February 18. In addition, repairs were made to the system that cools the valve electronic components. Failure of a portion of the cooling system is believed to have contributed to the valve failures. Unfortunately, due to the brevity of the outage and other work inside the boiler, access to inspect the sections could not be arranged.

During a forced outage of the host boiler, B&W and MTI made a brief inspection of the test sections on March 12. The sections were examined for evidence of impending failures that could terminate the test before the scheduled Fall outage, when one of the sections is to be removed for metallography and the others are to be thoroughly measured to document relative corrosion rates.

All three sections were examined for areas of maximum wastage, where a through wall failure is most likely to occur. On each section, maximum wastage occurred on the outlet end of the top (outlet) row. Wastage has the appearance of classical coal ash corrosion, with flats occurring at the 7:00–9:00 and 3:00–5:00 clock positions around the tube circumference with 12:00 facing the gas flow (the bottom of the tube vertically). The alloys shown in the photograph (Figure 21) are NF709, 347HFG, Thermie, 310HCbN, and 310Ta from left to right.

Figure 21: Top Row of Section During March 12, 2001 Inspection

Table 13 shows the estimated maximum metal loss values for each tube segment in the outlet end of the top rows, beginning with the segment nearest the outlet. The next few alloy segment in sequence are 347HFG, Thermie, 310 HCBN, and 310Ta. All suffered substantial corrosion, but none more than the Save 25. Of the alloys shown, only Thermie (Fe-25Cr-20Co-Al-Ti-Nb) appears to have corroded distinctly less than the alloys to either side of it. There was no evidence of coal ash corrosion of the lower (inlet) leg.

The test loops have successfully accelerated coal ash corrosion of the advanced alloys, making comparison of their relative corrosion resistance to a high-sulfur Ohio coal possible. After about 20

months of operation at temperature, the maximum wall loss was about 200 mils. By the scheduled fall outage the wall loss was expected to reach about 260 mils. On that basis, the current operating temperature was maintained. At the fall outage one full loop was planned for removal and analysis. In addition, replacement of a small portion of the top row in the other two sections with Inconel clad material (sufficient material may already be in hand) was necessary to ensure completion of the test period.

Table 13: Estimated Maximum Metal Loss		
Specimen Number (dwg 259868D-03)	Material	Wastage
1	Inconel clad Incoloy 800	Negligible loss
12	Inconel 52 weld-clad Incoloy 800	Negligible loss
13	Inconel 72 weld-clad Incoloy 800	Negligible loss
1	Inconel clad Incoloy 800	Negligible loss
7	HR-120	50 mils
3	310HCbN	60 mils
4	310Ta	75 mils
5	Alloy 800 Modified	130 mils
6	Save25	200 mils
8	NF709	150 mils

Premature conclusion should not be drawn from the above wastage values. The alloy-to-alloy differences in corrosion rates are affected not just by alloy chemistry but also by temperature difference along the loop and possibly by proximity to the walls. For example, Save 25 could be less resistant than its neighbors, or it could simply be at the intermediate temperature where coal ash corrosion peaks.

During April and May the system ran as intended without event. On June 16 the control valve for Section "A" again failed (went open). Investigation during a brief outage later that week revealed a failure in the cooling air system. The failed components were repaired prior to returning the unit to service. Fisher was contacted to determine if there was a way to control the valves that could be located outside of the hostile environment and Fisher quoted pneumatic controllers. A meeting was arranged to ensure pneumatic controllers would resolve this issue.

We had learned that the fall outage would tentatively start in the first week of October 2001. Preparations for removal of the first section were initiated in June. It was decided that the half of Section "A" that contained the test specimens (top two rows) would be removed for evaluation and replaced with the more promising materials. The new half-section has the top row made of co-extruded Incoloy 800 core with Inconel 671 cladding and the second row made from Incoloy 800 core

with a Inconel 72 weld cladding. This section will be operated until the next outage to determine the impact of temperature on corrosion of these materials along their lengths. Due to the corrosion of the specimens at the center of the top row, a 3 ft. section was replaced in Sections "B" and "C". One was Incoloy 800 core with a Inconel 52 weld cladding and the other was TP310HCbN. These materials were available from the original fabrication of the test sections.

The system continued to run as intended through July without event. Preparations for removal of the first section progressed. Materials were obtained and plans for fabrication of a replacement loop for the top two rows of Section "A" and a three-foot section of the center of the top row in the remaining two sections were nearly completed. Fabrication was scheduled to begin in August. The three foot sections were being replaced since projections of the current corrosion rate for a couple of the samples in that portion of the Section indicated they would not last until the section is planned for removal.

The system continued to run as intended through August without event. On August 24 Orion Power Midwest advised of their decision to postpone the outage scheduled to begin in October until late January. This was about a 4-month delay but would not present any difficulties. Preparations for removal of the first section continued. Materials were obtained, drawings completed and fabrication of a replacement loop for the top two rows of Section "A" as well as a three-foot section of the center of the top row in the remaining two sections began. Delivery of all equipment was expected the first week in October. Mechanical positioners for the control valves were ordered and shipped from Fisher to the plant. These new positioners were to replace the electronic positioners and hopefully eliminate the failures we have experienced in the past due to overheating. Since they are mechanical, the valve response time may be slowed slightly and adjustment to the controls was expected.

The system continued to run as intended through September without event. In light of the delayed replacement of Section "A" and repair of the other two, an opportunity arose and an inspection of the three test sections occurred on September 26th. The original tube diameter was 2.5" and the wall thickness of the Save 25 and the majority of other tube segments was 400 mils. On each of the three sections the maximum corrosion loss was from the hottest Save 25 test segment. Because so much of the tube circumference was corroded, the amount of wall loss could no longer be accurately assessed by external measurement since there was insufficient un-corroded reference surface opposite areas of maximum corrosion. As close as could be determined, the maximum losses were; Section "A" (nearest the sidewall) is about 320 mils, leaving about 80 mils of remaining wall thickness, Section "B" (the middle Section) is about 290 mils, leaving about 110 mils and Section "C" (near center of the boiler) is about 300 mils, leaving about 100 mils.

The last inspection was March 12, 2001, after 20 months of service exposure. The maximum metal loss at that time was 200 mils, leaving 200 mils of remaining wall thickness. The additional loss over the last six months appeared to have been 90-120 mils, a loss rate of 15-20 mils per month. Much of what appeared to be an accelerated rate was actually because the Sections had operated almost steadily at temperature over the previous 6 months while several of the previous 20 months included time at reduced temperatures during startup or during valve problems. Since the outage was delayed until January 2002, it was decided to lock the control valves open to assure maximum cooling and slow the

progress of further coal ash corrosion as much as possible until these samples could be replaced, avoiding a possible tube failure which could ruin the samples.

On September 25 Reliant Resources Inc. announced their acquisition of Orion Power Holdings Inc. which will include the Niles Plant. According to the plant management, since they purchased the company and its obligations, no impact is expected.

The system continued to run as intended during October without event. However, during a brief outage for boiler tube leak repairs on October 15, a small hole was discovered in the SAVE25 sample in Section "C" (closest to the center of the boiler). The same samples in the other two sections showed major corrosion loss and were in jeopardy of breaking through as well. In response to this finding three 3 ft. sections of tubing (dutchmen) were taken to the plant with the intent of removing a 3 ft. portion of the top row containing the corroding samples and replace it with the dutchman. The dutchman that was planned for installation in Section "C" during the January 2002 outage was installed immediately. Due to system demand, however, no modifications were made to Sections "A" and "B" and the unit was back on line after a couple of days. Two additional dutchmen were left at the plant for installation into Sections "A" and "B" at the next opportunity.

On October 30 the completed replacement loop (top two rows) for Section "A" was transported to the plant with the intent that when the unit comes down again the top two rows containing the samples would be removed from Section "A" and replaced.

On November 6 the unit came down again due to a tube leak affording the opportunity to replace the top two rows of Section "A" and install the dutchman in Section "B". On November 8 the top two rows of Section "A" were removed and replaced. The two rows removed were transported to MTI for metallurgical evaluation, planned to begin in January. In addition, a dutchman was installed in the middle of the top row of Section "B" as planned. The only unfinished work was installation of the mechanical positioners to eliminate the nuisance failures of the electronic controllers.

On November 12 it was discovered that the electronic controller on control valve for Section "B" had failed. Mechanical controllers were in stock at the plant and the failed controller for Section B was replaced in an early December outage and has been working properly. The Section "A" valve was left in MANUAL OVERRIDE as it was prior to the unit coming off line to allow the new portion to settle in on the wall support.

On December 14 all valves were opened fully in response to some strange pressure drop readings across the outlet stop valves which would normally indicate a tube leak. The pressure transmitters were re-calibrated but the readings persisted. During an outage in mid December the sections were vacuum checked for leaks and none were found. During the brief outage Section A was inspected and the supports had seated as hoped. The strange pressure drops across the outlet stop valves will be further investigated during the January outage (transmitter calibration is still suspected as the cause). Subsequently, the manual override on sections "A" and "C" were released to AUTO and the steam

temperature returned to 1075°F above 70 MWe. The Section “B” control valve was left at 100% open in MANUAL OVERRIDE due to loss of the position feedback.

Procedures & Results

This section of the report documents the procedures and sequence of activities used to assess the condition of Test Section A after service. The primary focus is on determining the relative corrosion resistance of the candidate superheater tube alloys. Generalized results also are offered; however the detailed results are provided on a material-by-material basis in the appendices that follow.

Background:

Test Section A was removed from Niles Unit-1 after 29 months (approximately 21,200 hours), with an equivalent of 11,288 hours (1.29 years) of exposure 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. The ability to extend the exposure period was confirmed through physical measurements *in situ* in the boiler at approximately the one year interval.

Figure 22 provides a schematic showing the position of the welds that join samples to one another to form Test Section A. Note that each weld has been given a letter designation. Using these, the tube sample positions are indicated by the weld letter designations at either end of the sample. The same positions were occupied by the same candidate materials in all three test sections.

Table 14 provides the key to the sequence of candidate materials within the three test sections. In this table, the candidate alloys are listed in the sequence in which they are encountered in the test section as one progresses from the hottest location toward the coolest. This table includes the tube sample letter designations that are based on the weld lettering shown in Figure 22. Also provided is the calculated average surface metal temperature at each location.

Exposure Time

Initial exposure of the three test sections to flue gas occurred as Niles Unit-1 resumed operation in June of 1999, following a maintenance outage during which the sections were installed. Test Section A was removed in November of 2001, after a period of 29 calendar months in the boiler. During this time the boiler shifted load and cycled on and off line in normal response to power demand and boiler maintenance requirements.

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 is 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 surface metal temperature at the hot end of the test section (Point-T in Figure 22) was taken as the transition temperature above which the rate of coal ash corrosion is

significant and below which it is negligible. For Test Section A the accumulative time under conditions likely to cause coal ash corrosion was 11,288 hours, as compared to the total calendar time of approximately 21,200 hours.

Test Section Surface Metal Temperatures

As indicated in the introductory Description of Test Sections and Systems, desired test section temperatures are maintained by controlling the test section outlet steam temperature. The **outlet steam temperature** is the temperature of steam exiting the test section. It is constantly monitored by thermocouple measurement, and an arithmetic average outlet steam temperature is recorded at five minute intervals.

The external surface temperature of each alloy test segment is calculated at five minute intervals using the measured outlet steam temperatures, the average gas temperature, and a heat transfer model for the test section. In the following appraisals of coal ash corrosion, an average surface metal temperature is indicated for each test specimen. The indicated **average surface metal temperatures** are arithmetic averages of the calculated segment external surface metal temperatures for the 11,288 hours when the section was considered to be within the temperature range where coal ash corrosion is likely. The indicated arithmetic average provides a reasonable and practical approximation of the “isothermal equivalent temperature”, the isothermal temperature at which exposure for 11,288 hours would produce the observed extent of corrosion. The average surface metal temperature approximates the isothermal equivalent temperature to the extent that the corrosion rate is a linear function of temperature; and for this test, there is no basis for defining corrosion rate as a more complex function of temperature. Table 14 shows the estimated average surface metal temperatures for test segments in Section-A.

Temperatures were not isothermal. As gas, steam, and metal temperatures rose and fell at the beginning and end of each high-temperature boiler operating cycle, samples accumulated a few hours of coal ash corrosion below the target exposure surface metal temperature. Also, test section surface metal temperatures were low through an initial six month trial period. The full target section outlet steam temperature of 1075°F was only maintained after November of 1999. The temperature history of Section-A Segment “R-S” (Figure 23) illustrates the surface metal temperature variability. For this segment the average surface metal temperature over the duration of the test is 1198°F. As shown in Figure 23, surface metal temperatures are initially lower, averaging 1097°F in July of 1999. From July through December 1999, they climb to an average daily temperature of 1221F in December, and they remain near this temperature whenever the section is operational until it is removed in November of 2001. Figure 23 also illustrates the daily surface metal temperature variability. The wide spread in values is generally caused by transients when the unit is taken off line. The standard deviation for 24 hour periods averages about 17F°. The standard deviation of the daily average surface metal temperature about the long-term average temperature is 56F°.

Environment

The Niles cyclones burners are fired with Ohio bituminous coal having a sulfur content of approximately 3%. The sulfur in this coal is pyretic and organic, with little sulfate. Chlorine concentrations are typically less than 0.05%. Table 15 shows a representative coal analysis.

Documentation:

Test Section Appearance Upon Receipt After Exposure: Figures 24 and 25 show the appearance of Test Section A when it was received at MTI. Two figures were needed to document the entire length of the test section; however, there is some overlap between them. The weld lettering designations are noted in these figures. The schematic provides a representation of how each section was originally situated within the test section.

Tube Sample Surface Appearance: Close-up photographs were taken to document the condition of each tube sample. Three views were documented. The 12 o'clock position faced downward* into the oncoming gas flow. The 6 o'clock position was at the top of the tube on the side downstream of the gas flow direction. The 3 o'clock position was halfway between the two. These figures typically document the extent of deposit and scaling. In some cases where the scale and deposit have fallen away, evidence also is seen of the chalky white deposit associated with alkali sulfate hot corrosion. Figure 26 provides an example of this documentation for one tube sample. The rest of these are included in separate appendices to this report. Each appendix is devoted to a different candidate material.

- * By selecting the 12 o'clock orientation as the one facing directly into the gas flow direction, the resultant orientation yields an "upside-down" clock reference system relative to the physical position of the tube within the boiler, i.e. 12 o'clock faces downward.

Tube Sectioning:

Figure 27 provides a schematic that depicts how the tube sample was sectioned to extract specimens for evaluation. Figure 28 shows the sectioning plan for each tube sample. All cuts were made dry using a saw. As they were cut, samples were marked to maintain sample identity and tube orientation (i.e. 12 o'clock, 3 o'clock, and 6 o'clock).

Composition Verification:

A portion of the "extra material" indicated in Figure 28 was sent to a third-party laboratory for confirmatory chemical analysis. Most samples were analyzed by Koppel Steel Corporation using optical emission spectrometry per ASTM E 10-86, Stainless. The appropriate standards were not available at Koppel for all of the candidate materials. In these cases, the samples were sent to NSL Analytical Services, Inc.

The results of these analyses were compared with the reported heat analyses from the various providers of materials for test. They also were compared with material specifications if they were available. Otherwise, a "nominal" or "target" tube metal composition was used. The results of these analyses are included in the appendices for this report which provide detail on a material-by-material basis. Figure 29 shows a typical example.

Surface Condition:

Dimension rings (Identified as "RS-2" in Figure 28) were removed from the approximate centerline of each tube sample. These were grit blasted with aluminum oxide grit to remove deposit and scale. The surface condition of each ring was photographed, and is included in the appendices of this report.

These are intended to show and record the level and type of attack that was occurring at the external surface of these tubes (i.e. beneath the deposit/scale that are shown in Figure 26). Figure 30 shows a typical example. These figures also provide, as a reference, the amount of wall thickness measured at the position indicated. Dimensioning is discussed in more detail below. In general, it was the side of the tube that faced the gas flow that experienced most of the metal loss. The maximum wall thinning was typically between the 12 o'clock and 9 o'clock positions.

Dimensioning:

The grit blasted rings, then, were measured with certified micrometers that were accurate to ± 0.001 ". The measurements were taken at eight predetermined circumferential locations that were indicated by the "o'clock" positions: 12:00, 1:30, 3:00, 4:30, 6:00, 7:30, 9:00, and 10:30 o'clock. The "o'clock" positions were the same as those used above to express the orientation of the tube within the test section. Prior to service, measurements had been taken and recorded for each of these orientations for each of the tube samples. The measurements taken after service were compared with these and a "delta" calculated to express the wall thickness losses at each position. These are recorded for each candidate material in the appendices that follow. Figure 31 shows a typical example.

Note that an attempt was made to determine the maximum wall thickness loss for each tube sample. In some cases, it was clear that the minimum wall thickness was not at one of the eight predetermined locations, so, there was no "before service" measurement for use as a reference. In these cases, the average "before service" wall thickness measurement was determined and used as the reference measurement for determining the wall thickness lost. The location and value of the maximum are also documented in the appendices in tables such as the one shown in Figure 31.

Note also that it was not possible to take the "after service" measurements at the same axial position as the "before service" measurements, since these were taken at the tube ends, and the tube ends now were part of the welds that joined the tube samples to one another. Given the short lengths of the tube samples, and the overall consistency of the wall thickness measurements, it was judged that this 2 to 3-in. difference in axial location would have only a minor impact on the accuracy of the wall thickness measurements.

Metallography:

A full cross-section ring was polished and etched for each tube sample, (identified as RS-1 in Figure 28). The same electrolytic etching procedure was used for each material. It involved using a 10% oxalic acid etchant with a 9 volt open circuit potential. These then were examined using the scanning electron microscope (SEM), and optical microscopy.

SEM/EDAX:

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. Typically the examination was along the tube radius that extended through the thinnest wall for a given tube sample. Given the high level of resistance to steam-side oxidation for all of the candidate alloys, the focus of this analysis was on the deposit/scale/metal interface at the external surface of the tubes. Photographs were taken to record the

nature of the external scale and the condition of the underlying metal. These are recorded in the appendices along with comments regarding distinctive and/or unique features.

While in the SEM, EDAX (energy dispersive analysis by x-ray) analyses were made of selected regions of the deposit, scale, and underlying tube metal. These also are recorded in the appendices.

Optical Metallography:

Every sample was examined using optical microscopes. The major purpose of this was to verify that the sample that was selected for examination in the SEM truly was representative. The mid-wall (or cladding/overlay) microstructure was photographed for every sample. These are recorded in the appendices for each candidate material.

Weld Profile:

The weld profile for every tube sample was visually examined by looking at the external tube surface in the vicinity of each weld. The appearance of these areas can be seen in the tube sample surface appearance photographs shown in Figure 26, and documented in the appendices.

Two samples were selected to provide representative cross sections for examination. One represented the weld to a clad tube (where a capping pass was performed using the overlay material). The other represented the tubes without cladding. For these two samples, the weld was cross sectioned (as per sample RS-3 in Figure 28). These sections then were polished, etched and photographed to record their appearance. The results are shown in Figures 32 and 33. In both cases, the weld showed little evidence of general attack. However, localized attack was noted at the interface between the capping pass (of IN 72 weld metal) and the Incoclad 671 sample. This localized attack was restricted to the portion of the tube facing into the gas flow direction. Similar notching was also observed for the IN 52 and IN72 weld overlay samples. No similar attack was found elsewhere in the test section. The reason for this is unknown at this point.

Deposit Analysis:

A relatively thick and loosely adherent deposit was noted on the surface of Test Section A in the vicinity of the 6 o'clock position of Sample U-V. This was removed and subjected to inductively coupled plasma – optical emission spectrographic (ICP-OES) analysis. This deposit also was subjected to x-ray diffraction analyses to determine the identity of the molecular crystalline constituents present. Also noted on Sample U-V was the presence of the chalky-white scale that was tightly adherent and immediately adjacent to the metal surface. This chalky-white scale was expected to contain the aggressive species, and thus, was of particular interest. This scale was scraped from the surface and subjected to the same analyses as were used for the loosely adhering deposit.

In both cases, the ICP-OES analysis was used to determine the elemental constituents, which are reported as oxides. The results of the ICP-OES analysis are presented in Table 16. The x-ray diffraction analysis results are presented in Table 17.

Chlorine is a particularly aggressive corrodant, therefore, it merited a separate wet chemical analysis to determine whether it was present in either the deposit or the scale. The results of these analyses are reported in Table 18.

Lastly, EDAX analyses, performed during the SEM investigation, indicated the potential presence of carbon in both the deposit and in the tube metal adjacent to the scale/metal interface. Because carbon analysis by EDAX is not accurate, and because of the potential for contamination by the epoxy resin used as the mounting compound, a combustion-gravimetric analysis was performed to determine the presence of carbon in the deposit. The result of this analysis also is reported in Table 18.

Table 14: Tube Sample Designation and Average Surface Metal Temperature Based on Position in Test Section A

Sample Designation	Material	Average Surface Metal Temperature (F)
R-S	IN52 Weld Overlay	1198
Q-R	IN72 Weld Overlay	1198
P-Q	Incoclad 671	1193
O-P	HR 120	1184
N-O	310 HCbN (HR3C)	1180
M-N	310 Ta	1178
L-M	Modified 800H	1174
K-L	Save 25	1170
J-K	NF 709	1167
I-J	347 HFG	1164
H-I	Thermie	1160
G-H	310 HCbN (HR3C)	1157
F-G	310 Ta	1154
E-F	Modified 800H	1150
D-E	Save 25	1146
C-D	NF 709	1142
B-C	Fe3Al	1139
A-B	347 HFG	1137
Return Bend	TP 310	****
U-V	671 Clad	1110
V-W	HR 120	1100
W-X	310 HCbN (HR3C)	1095
X-Y	310 Ta	1092
Y-Z	Modified 800H	1088
Z-AA	Save 25	1084
AA-BB	310 HCbN	1081
BB-CC	NF 709	1077
CC-DD	347 HFG	1075
DD-EE	HR 120	1077
EE-FF	Incoclad 671	1075
FF-GG	IN72 Weld Overlay	1068
GG-HH	IN52 Weld Overlay	1062
HH-II	Thermie	1056
II-JJ	Save 25	1047

Table 15. Representative Analysis of Coal Burned in Niles Unit-1

<u>Coal Analysis</u>	
Moisture	5.0 %
Carbon	66.5 %
Hydrogen	4.9 %
Nitrogen	1.4 %
Sulfur	3.1 %
Alkali (as Na ₂ O)	0.2 %
Ash	12.3%
<u>Ash Analysis</u>	
SiO ₂	41.5 %
Al ₂ O ₃	19.5 %
TiO ₂	1.2 %
Fe ₂ O ₃	26.8 %
CaO	3.8 %
MgO	0.7 %
K ₂ O	1.6 %
Na ₂ O	0.5 %
SO ₃	3.3 %
P ₂ O ₅	0.6 %
BaO	0.1 %
Undetermined	0.3 %

Table 16: Deposit Analysis (ICP- Optical Emission Spectrographic Results)

Constituent*	Deposit Analysis, (wt%)	Chalky-White Scale Analysis, (wt%)
Silicon, SiO ₂	31.84	28.64
Aluminum, Al ₂ O ₃	14.11	9.66
Iron, Fe ₂ O ₃	22.99	12.85
Titanium, TiO ₂	1.06	0.60
Calcium, CaO	3.60	4.06
Magnesium, MgO	0.35	0.17
Sodium, Na ₂ O	0.70	0.96
Potassium, K ₂ O	1.82	3.82
Phosphorous, P ₂ O ₅	0.88	0.91
Sulfur, SO ₃	11.64	20.00

* It is customary for MTI, when doing deposit analyses, to report these constituents as oxides; however, the analyses are strictly elemental. The percent oxide is based on the elemental amount and an assumed oxide form.

Table 17: Deposit Analyses (X-Ray Diffraction Results)

Level	Range	Deposit Analysis	Chalky-White Scale Analysis
Major	>25%	----	<ul style="list-style-type: none"> • Cristobalite, syn, SiO₂
Medium	10 – 25%	<ul style="list-style-type: none"> • Hematite, syn, Fe₂O₃ • Cristobalite, syn, SiO₂ 	<ul style="list-style-type: none"> • Potassium Aluminum Sulfate, KAl (SO₄)₂
Minor	5 – 10%	<ul style="list-style-type: none"> • Potassium Aluminum Sulfate, KAl (SO₄)₂ • Quartz, syn, SiO₂ • Mullite, syn Al₆Si₂O₁₃ 	<ul style="list-style-type: none"> • Hematite, syn, Fe₂O₃
Trace	<5%	<ul style="list-style-type: none"> • Anhydrite, syn, CaSO₄ 	<ul style="list-style-type: none"> • Analcite, NaAl(SiO₃)₂ • Sillimanite, Al₂SiO₅ • Anhydrite, syn, CaSO₄ • Wollastonite–2M, CaSiO₃

Table 18: Carbon and Chlorine Analysis Results

Constituent	Deposit Analysis, (wt%)	Chalky-White Scale Analysis, (wt%)
Carbon	0.06	---
Chlorine	0.04	0.07

Figure 23: Daily Average Surface Metal Temperatures (F) for Tube Segment "R-S"

Figure 24: Appearance of Test Section A After Removal From Service (Part 1)

- Note:
- 1) The region highlighted in the schematic drawing of the test section is shown in the photograph below.
 - 2) The letters adjacent to the photograph indicate the positions of the various welds used to construct the test section. These letters also are used to identify the candidate metal samples that lie between them. For instance, Sample A-B lies between welds A and B. It was manufactured from 347 HFG. Sample B-C was manufactured from Fe₃ Al, etc.

Figure 25: Appearance of Test Section A After Removal From Service (Part 2)

Note: 1) The region highlighted in the schematic drawing of the test section is shown in the photograph below

12 O'Clock – Facing Gas Flow
 (Note: 3 o'clock is up in this image)

3 O'Clock
 (Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure 26: Typical Documentation of As-Received Appearance for Tube Sample

Note: The chalky alkali-iron trisulfate scale is noted toward the left-hand side at the 6 o'clock position.

Figure 27: Schematic Depicting Sectioning to Remove Tube Sample From the Test Section

Key	
Sample	Purpose
RS-1	Metallography ring
RS-2	Dimension ring
RS-3	Weld profile
RS-4, 5, 6	Extra material

Note:

- 1) Cut B - B' is at the approximate center of the tube sample
- 2) Specimens RS-1, RS-2, RS-3 are all about 1/2" thick

Figure 28: Schematic Depicting Sectioning of Tube Sample

Figure 29: Typical Composition Verification Report (for Modified 800H)

Description: Nominal 20Cr/30Ni steel with improved creep strength due to addition of V, Nb, Ti, and B
Source: Oak Ridge National Laboratory (ORNL)
Reference Composition: “Target” Chemistry per ORNL (Reference 1).

Element	Reference Composition	Composition Heat 17423	Composition Heat 17424	Composition Heat 17433	Tube Sample E-F	Tube Sample L-M	Tube Sample Y-Z
Ni	31.0	30.74	31.04	31.10	30.93	30.85	30.88
Cr	20.0	19.89	19.98	19.91	19.97	20.03	19.99
Fe	Balance	-	-	-	44.5	44.4	44.4
Mo	1.5	1.50	1.52	1.51	1.52	1.52	1.52
Co	-	0.03	<0.01	<0.01	(a)	(a)	(a)
C	0.09	0.10	0.10	0.10	0.10	0.10	0.11
N	-	0.026	0.029	0.018	(a)	(a)	(a)
B	0.005	-	-	-	0.005	0.005	0.005
Mn	2.00	1.93	1.94	1.93	1.94	1.96	2.00
Si	0.25	0.24	0.24	0.26	0.23	0.24	0.24
Al	-	<0.01	<0.01	<0.01	(a)	(a)	(a)
Ti	0.25	0.11	0.15	0.03	<0.01	0.093	0.13
Nb	0.25	0.26	0.26	0.25	0.25	0.25	0.25
Ta	-	<0.01	(a)	(a)	(a)	(a)	(a)
Nb+Ta	-	-	-	-	(a)	(a)	(a)
V	0.4	0.38	0.23	0.37	0.37	0.37	0.23
Cu	-	<0.01	<0.01	<0.01	(a)	(a)	(a)
Sn	-	-	-	-	-	-	-
P	-	0.009	(a)	0.002	(a)	(a)	(a)
S	-	0.003	0.002	0.005	(a)	(a)	(a)
O2	-	0.004	0.008	0.015	(a)	(a)	(a)

- a- Not analyzed.
b- By difference.

Reference 1: “Fabrication of Test Tubes for Coal Ash Corrosion Testing”, Sikka, V.K., Swindeman, R.W., Wright, I.G., Judkins, R.R., Johnson, R., Proc, 13th Annual Conf. on Fossil Energy Mat’ls, May 1999.

Note: Sample E-F was from Heat 17433
Sample L-M was from Heat 17423
Sample Y-Z was from Heat 17424

12 O'Clock
(112 mils lost)

3 O'Clock
(62 mils lost)

6 O'Clock
(0 mils lost)

Figure 30: Typical Example of OD Surface Appearance After Grit Blast

Note: This particular example is for modified 800H, Sample Y-Z.

Material:

Modified 800H

Sample Location:

Y-Z

Maximum Rate:

154 mils/yr

Maximum Loss Orientation:

Approx. 10 o'clock

Average metal Temperature:

1088 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.400	0.403	0.401	0.402	0.402	0.400	0.400	0.399	0.401	0.401
After	0.288	0.337	0.339	0.400	0.402	0.402	0.322	0.228	0.340	0.202
Delta	0.112	0.066	0.062	0.002	0.000	-0.002	0.078	0.171	0.061	0.199

Figure 31: A Typical Silhouette with Wall Thickness Measurements Showing Metal Loss as a Function of Position

Tube Sample:
Material:

N-O
310 HCBN

O-P
HR 120

Figure 32: Weld Profile Through Monolithic Tube Sample

Tube Sample:
Material:

O-P
HR 120

P-Q
Inconel 671

Figure 33: Weld Profile Through Clad Tube Sample

Discussion

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

Surface Metal Temperature: The average surface metal temperature, from the hot to the cooler end of the test section, ranged from 1198°F to 1047°F. As was discussed earlier, over this temperature range, all things being equal, the corrosion rate for a given austenitic alloy is expected to increase with increasing temperature. Recall that at about 1000°F, the coal ash becomes molten, and in its' molten form is much more aggressive. The upper limit to this would be roughly 1300°F where the stability of the complex sulfates generally begins to decrease and the corrosion rate ebbs.

Flue Gas Temperature: The flue gas temperature has a significant impact on the wastage rate for superheater tube materials in that it directly influences the average surface metal temperature. The flue gas temperature in the region of interest in Niles Unit #1 was estimated to be 2114°F. FEGT is a calculated average temperature based on performance data.

Internal Pressure: It is understood that the internal pressure for the test section was low, at approximately 300 psig. This has the benefit that almost the full wall thickness of the tube was available as a "corrosion allowance". Though it does not impose pressure stresses typical of a supercritical boiler, it offered the advantage that a candidate tube sample would not need to be pulled from service almost up to the point that the full thickness corrosion resistant material had wasted away.

Tube Sample Location Within Test Section: Based on the above, and considering the fact that the boiler was burning high-sulfur coal, it can be argued that the service of Test Section A provided an aggressive environment that 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.

Wastage Rate Results: Table 19 provides the wastage rate (mils of wall thickness lost per year) as a function of position within the Test Section A. Figure 34 presents this same information graphically. Table 20 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 35 shows a plot of wastage as a function of average service temperature for

each of the twelve candidate materials. It can be seen from these data that some materials evidenced an increase in wastage rate at intermediate temperatures (e.g. modified 800H, NF 709, 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 decrease with increasing temperature for the nickel-base alloys (IN 52, IN72, and Inconel 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.

Wastage Rate Assessment:

Recall that the intent was, in follow-on phases of this program, to examine tube samples in Test Sections B and C. This would allow one to gain an understanding as to how the twelve candidate superheater tube materials perform at greater time intervals. To facilitate this, the three test sections were built to be identical in terms of the placement of the candidate alloy tube samples. Then, they were installed side-by-side within Niles Unit #1, on the assumption that they would experience essentially the same exposure conditions. The tube samples in Test Section B were intended to be removed and examined after 42 months of exposure. The samples in Test Section C were intended to be examined after 60 months of exposure.

Review of the wastage rate data illustrated in Figure 34 raised concerns as to whether the tube samples in Test Sections B and C would survive for the full testing periods. Recall that due to such concerns, the six-tube sample length between welds “G” and “M” was removed from these test sections and replaced with a continuous length of IN72 weld overlay material. (These IN 72 lengths were excess material that was left over from the original construction of the test sections). These suggest that, now that Test Section A data is available, it would be prudent to assess the projected life expectancy for the various tube samples in Test Sections B and C, and act accordingly.

Rationale for Relative Alloy Performance:

The question naturally arises as to the reason(s) why one candidate alloy performed better than another. While this was not the thrust of this program, and it has not been studied in depth, review of these data indicates some general trends.

It should be noted that the test section designer’s thoughts focused on the chromium content as being a strong indicator of life expectancy. This is technically substantiated by the chromium-rich scale that forms on the surface of these high-chromium alloys. This sort of scale in the past has been demonstrated to provide protection from further corrosion in that, once formed, it provides a barrier that the reactant species must overcome in order to further consume the underlying tube metal. An example of such a

scale might be seen in the scanning electron microscope (SEM) images of the scale/metal interface for candidate material NF 709, (see “Areas 4 and 5 in Figure D-16 in Appendix D). The character of this scale further is substantiated by the results of EDAX analysis for these areas (see the table in Figure D-19) where chromium and oxygen are shown to be the predominant elemental constituents of the scale. The logic of a high chromium content being good, and a higher chromium content better, to a great extent guided selection of the candidate alloys.

The relationship between chromium content and performance generally was consistent with the Test Section A service experience results. Figure 36 plots maximum wastage rate against chromium content. It can be seen in Figure 36a that while the trend holds that higher chromium contents generally result in reduced wastage rates, the data spread is excessive versus the linear regression trend line, particularly in the 20 to 30 wt % range. The data appear better to fit a logarithmic trend line, see Figure 36b. However, even for this case the spread at the low end appears excessive.

The observation was made that the wastage response of these materials appeared to be inversely related to the total alloy content in these alloys, in particular, the sum of the nickel plus chromium contents. Figure 37 shows a plot of this sum versus maximum wastage rate. The linear regression trend line appears to fit these data well, (perhaps with Save 25 as an outlier to the high side). While it is granted that the sampling in question is not statistically significant, the data suggest that the correlation between chromium plus nickel content and wastage rate merits additional study.

In spite of the fact that the tube with Fe₃Al coating will likely fail earlier than some of the other candidate materials, it is not entirely clear that this coating has had a fair assessment within the test section. If the experience of Test Section A is an indicator, at this point, it is likely that this sample within Test Sections B and C is completely void of coating. Thus, they should be wasting away at a rate consistent with that of the underlying TP 304H stainless steel substrate. Given the low chromium and nickel contents of this stainless steel it likely is currently wasting away faster than the wastage rate indicated in Table 2. The fact that this sample is performing better than candidate materials with a higher alloy content, (e.g. Save 25, modified 800H, 347 HFG and NF 709), suggests that before the coating exfoliated from the tube surface (or was consumed by the aggressive environment), it provided a barrier to initiating of the attack on the underlying stainless steel. The extent of this protection is unknown because it is not known how long the coating lasted, nor is the current wastage rate known for the stainless steel. Nonetheless, examination of the initial condition of this coating revealed that it was very thin (on the order of 1 mil), and that it was discontinuous on the surface. This leaves one to wonder what the results might have been had the coating been thicker, continuous, and able to adhere to the surface for an extended period of time.

Scale/Metal Interface Issues:

Both the internal and external scale/metal interfaces were examined for every tube sample. Part of the reason for this was to verify that the tube thickness was not further reduced by grain boundary and/or other local penetrations. Another reason for this was that a representative sample of each candidate material was selected as the focus for a more detailed study. The focus typically centered on the one sample for each candidate material that experienced the greatest amount of wastage. The results of these analyses are recorded in the separate appendices for each candidate material.

Examination of the microstructure revealed that wastage-sensitive materials seemed to have some common characteristics at the external scale/metal interface. These are illustrated in the sketch shown in Figure 38. Typically five different regions are found; however, the characteristics of these can change somewhat from sample-to-sample. In general, the characteristics are as-follows.

Region	Description:
A	This coal ash deposit is fairly consistent from material to material (as would be expected). Table 5 shows the results of averaging the EDAX analyses for (11) of the (12) samples. As was mentioned earlier, oxides of silicon, aluminum, an iron predominate, but also present are significant amounts of the alkali metals and sulfur. Arsenic also was found, but is believed to have little or no impact on the wastage rate. The high level of carbon content indicated by EDAX is suspect in that the combustion-gravimetric method suggests that the carbon content of the deposit is less than one percent. Lastly, the significance of chlorine is noteworthy, but was only found in small amounts in one of the (11) samples analyzed.
B	This scale with embedded deposit (typically evidenced as spheres) was likely generated as the scale grew outward from the underlying metal surface. In almost every case there is a line of separation between this scale and a tightly adhering scale that lies beneath it. Region “3” in Figure A-16 provides a good example of the appearance of this region. The EDAX analysis of this region can reflect the combined composition of the commingled deposit and scale. However, depending upon the region scanned the analysis can be biased toward one or the other.

Region	Description:
C	Region C is the tightly-adherent scale immediately in contact with the underlying metal. It typically is a chromium-rich oxide; however, it can contain significant levels of both nickel- and iron- oxides. This presumably is a function of the composition of the underlying metal, but it may also reflect diffusion kinetics at or near to the surface. Also of significance in this region is that it often contains a significant amount of sulfur; however, none of the alkali metals was found in this region for any of the alloys investigated.
D	Region D appears to be a diffusion zone. It typically is 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. If it is real, one might conjecture that the carbon might be able to tie-up chromium, diminishing the total amount available to form the chromium-rich oxide scale. Sulfur is found in some cases in grain boundary penetrations into this region. Some have questioned whether Region D is in fact the first layer of scale. The fact that EDAX shows very little oxygen in this region, when combined with the appearance of grain boundaries contiguous with the underlying metal argue against this interpretation of the structure.
E	Region E is a deeply etching band that is parallel to the metal surface. It typically is at most a grain diameter in width. This may be interpreted as an etching “edge effect” in some cases; however, EDAX in most cases (but not all) suggests chromium depletion in this region.

Figure 39 shows these same five regions as they appear for NF 709. The appendices provide more detail for this and each of the other materials. As can be seen from these the evidence for each sample has been documented in detail; however, the implications of the evidence have not been fully explored.

Material	Tube Sample	Rate Metal Lost* (mils/yr)	Average Surface Metal Temperature, (F)
52 Weld Overlay	R-S	44	1198
72 Weld Overlay	Q-R	10	1198
Incoclad 671	P-Q	4	1193
HR 120	O-P	102	1184
310 HCBN	N-O	108	1180
310 Ta	M-N	123	1178
800 Mod	L-M	169	1174
Save 25	K-L	259	1170
NF 709	J-K	170	1167
347 HFG	I-J	174	1164
Thermie	H-I	53	1160
310 HCBN	G-H	133	1157
310 Ta	F-G	136	1154
800 Mod	E-F	178	1150
Save 25	D-E	224	1146
NF 709	C-D	136	1142
Fe3Al	B-C	145	1139
347 HFG	A-B	83	1137
Incoclad 671	U-V	2	1110
HR 120	V-W	61	1100
310 HCBN	W-X	98	1095
310 Ta	X-Y	120	1092
800 Mod	Y-Z	154	1088
Save 25	Z-AA	208	1084
310 HCBN	AA-BB	129	1081
NF 709	BB-CC	145	1077
347 HFG	CC-DD	176	1075
HR 120	DD-EE	109	1077
Incoclad 671	EE-FF	13	1075
72 Weld Overlay	FF-GG	21	1068
52 Weld Overlay	GG-HH	77	1062
Thermie	HH-II	31	1056
Save 25	II-JJ	67	1047

Table 19: Wastage as a Function of Position in Test Section A

Note: The tube samples are listed in their proper sequence within the test section, with the hottest sample at the top of the list, and proceeding downward.

* Metal loss rate is based on time at temperature, not total time within the boiler.

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

Table 20: Rankings Per Material Based on Rate of Metal Loss Within Test Section A

Note: The groupings above are intended to facilitate an understanding the performance of a given candidate material

* Metal loss rate is based on time at temperature, not total time within the boiler.

Table 21: Deposit Composition

Average Composition, per EDAX (11 Samples)

Element	Wt. %
Oxygen	33.2
Carbon	21.4
Iron	13.6
Silicon	12.5
Aluminum	6.31
Arsenic	4.71
Sulfur	1.89
Potassium	1.85
Phosphorous	0.83
Nickel	0.77
Calcium	0.75
Titanium	0.49
Sodium	0.43
Chromium	0.11
Chlorine	0.03

Of note:

1. Chlorine was found in (2) of the (11) samples, with a maximum of 0.28 wt. %.
2. Carbon, sulfur, and phosphorous were found in significant levels in all (11) samples.
3. At least one of the alkali metals were found in all (11) samples.
4. The oxygen content was very consistent for all samples.

Figure 34: Wastage Rate as a Function of Position in Test Section A

Note: The materials are listed in sequence according to their position within the test section, with the hottest end of the test section to the left, and the coolest end of the test section to the right.

Figure 35: Wastage as a Function of Average Surface Metal Temperature for the Twelve Candidate Alloys in Test Section A

**Figure 36a: Chromium Content Versus Wastage Rate
With Linear Regression Trend Line**

**Figure 36b: Chromium Content Versus Wastage Rate
With Logarithmic Trend Line**

**Figure 37: Chromium Plus Nickel Content Versus Wastage Rate
With Linear Regression Fit trend Line**

Figure 38: Common Characteristics at Scale/Metal Interface

Figure 39: Illustrates the Characteristic Microstructural Regions Found at the Scale/Metal Interface for Many of the Candidate Materials.

Note: These photographs are of the scale/metal interface for NF 709.

Observation and 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 Incoclad 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.

INDEX TO APPENDICES

<u>Appendix</u>	<u>Material</u>
A	Save 25
B	Modified 800H
C	347 HFG
D	NF 709
E	Fe ₃ Al
F	310 Ta
G	310 HCBN (HR3C)
H	HR 120
I	Thermie
J	IN52 Weld Overlay
K	Incoclad 671
L	IN72 Weld Overlay

Appendix A

Analysis of Performance

Test Section A

Save 25

Overview of Results: Save 25

Save 25 experienced the highest rate of metal loss for any of the candidate alloys, 259 mils/yr*. Given that Test Section A experienced a total time at temperature of 1.29 years, the total maximum wall thickness lost was measured to be 334 mils. This represents a loss of approximately 83% of the original wall thickness of 401 mils.

The reasons for this poor performance have not been resolved at this juncture. Typically, Save 25 would be expected to perform similar to the candidate alloys that have a similar level of chromium, i.e. approximately 20 to 25%. Candidate alloys having this chromium level include 310 Ta and 310 HCbN (HR3C). These Type 310 stainless steel based alloys performed near in the middle relative to the remainder of the Test Section A alloys, having a maximum rate of metal loss of 136 mils/yr and 133 mils/yr respectively.

The most significant difference between Save 25 and the Type 310-based alloys appears to be that Save 25 includes the addition of a significant amount of copper (up to 4%), while copper is primarily a residual element in the other two alloys. It has been speculated that copper may act to either inhibit formation of the protective chromium oxide scale, or it may facilitate de-cohesion between the scale and the underlying metal. Neither of these hypotheses have been proven.

Also of potential significance is that Save 25 has tungsten and niobium additions for grain refinement, while 310 Ta utilizes primarily tantalum, and 310 HCbN employs primarily niobium in this regard. For the record, the grain size of the 310 HCbN was significantly less than that of either 310 Ta or the Save 25, which were roughly equivalent.

Examination of the four Save 25 samples revealed that metal loss increased continuously with increased temperature. It should be noted, however, that there was a significant increase (from 67 mils/yr to 209 mils/yr) associated with the increase of average surface metal temperature from 1047 °F to 1084 °F. The reason for this dramatic increase merits further study. It seems likely that it is associated with fusion of a low melting point constituent in the deposit and/or scale.

Another area that may merit further study is the precipitation reaction that was evidenced in the Save 25 samples that experienced the higher average surface temperatures of 1170 F and 1146 °F. However, it should be noted that significant metal loss was experienced in the sample that was exposed at 1084 °F, this in spite of the fact that this reaction was not evident for this sample. The sample exposed at 1046 °F experienced neither the reaction nor excessive metal loss.

Analysis of deposit on the surface revealed that it had the known aggressive combination of species, namely iron, oxygen, the alkali metals, and sulfur. The presence of significant amounts of arsenic was unexpected, and its' significance is unclear. Examination and analysis of the scale adjacent to the metal surface revealed the chalky-white appearance associated with Alkali-iron-sulfates. Spectrographic ICP analysis confirmed this. Thus, the required corrosive elements were available to test the performance limits of this alloy.

Finally, the analysis of the deposit and the metal surface immediately adjacent to the interface revealed the presence of carbon. While carbon determinations using EDAX are unreliable, the implications of carbon in the deposit are worthy of additional consideration, as is the potential for carbon ingress from the deposit into the abutting metal.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: Save 25

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">The schematic in Figure A-1 shows the relative positions of Save 25 samples in Test Section A. Also, shown is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">The table in Figure A-2 provides the composition of the four tube samples after exposure. All four samples were taken from a single heat of material, Heat D621901. The table also shows the specified composition and ladle analysis as reported on the Sumitomo mill certificate that accompanied the material.It was noted that the actual tube sample composition was higher in copper content and lower in chromium and nickel content than was reported for the ladle analysis.It was noted that, for three of the four tube samples, the actual tube composition does not comply with the specified composition in that it is slightly high in copper relative to the maximum allowable of 4 wt%.The significance of these deviations is not clear in that the role of copper in this alloy is uncertain.
As-Received Appearance	<ul style="list-style-type: none">Figure A-3 documents the appearance of the Save 25 tube prior to exposure. Figures A-4 through A-7 document the as-received appearance of the Save 25 tube samples after service. Three views are provided for each tube: 12 o'clock (the view that faces downward into the on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).Wastage is visible at the 12 o'clock for all four samples.A relatively thick rust-red back-side scale and deposit build-up is seen at the 6 o'clock position on all four samples but is most readily apparent in samples Z-AA and II-JJ.A relatively thin red-brown deposit is seen on all other surfaces.A region where the deposit/scale has fallen away on the 6 o'clock position on Sample II-JJ shows evidence of the gray/white scale associated with molten alkali-iron sulfate attack. It is anticipated that if the red deposit/scale were scraped away it would reveal evidence of a gray/white scale in other locations.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">Figures A-8 through A-11 show the appearance of the external surface of the Save 25 tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for Samples K-L, D-E, and Z-AA show the appearance of general wastage due to fireside corrosion.The 6 o'clock position for Samples K-L and D-E show that significant pitting occurred on the back-side of these samples. For Sample K-L a 27 mil deep pit accounted for all of the reported wall thickness lost at this position. For sample D-E, a 24 mil deep pit accounted for most of the 28 mils lost at the 6 o'clock position.

Material: Save 25

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures A-12 through A-15.• The same relative “o’clock” positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost. Note that in some cases, the delta is negative (particularly on the back-side. 6 o’clock position). This is believed due to wall thickness variability and difficulty in locating the exact location of the “before” measurement.• In some cases, the minimum wall thickness in the cross section was not at one of the eight predetermined locations, (Samples K-L and II-JJ are examples). In these cases, there was no “before” measurement for comparison. So, the average “before” wall thickness was used to calculate the wall thickness lost at these off locations.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure A-16 plots the maximum wall thickness lost against the calculated average metal temperature for each of the four Save 25 samples.• As a general trend, it is apparent that the rate of attack increases continuously as the temperature is raised from 1047°F to 1170°F.• It also was noted that Save 25 suffers minimal wall reduction at 1040°F, but that the rate of metal loss increases dramatically when the temperature is raised to 1084°F.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample K-L was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it had lost the most wall thickness of all of the Save 25 samples. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.

Material: Save 25

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">Figure A-17 shows the appearance of the tube profile in the section containing the minimum wall thickness for Sample K-L. Note a scale/deposit on the external surface of approximately 10 to 15 mils in thickness. No scale is evident on the internal surface at this magnification.Figures A-18a, b, c and d, show the appearance of the scale/metal interface for Sample K-L. Figure A-18a and A-18b show secondary electron images (SEI) of the interface. Six distinct regions are in evidence. These regions are, starting within the metal and working out:<ol style="list-style-type: none"><u>Base metal</u> – oxalic acid etch delineates grain boundaries and carbides.<u>Deeply etching base metal</u> – this region is obvious as a light-appearing band that is parallel to the metal surface, perhaps see most clearly in Figure A-18a. Figure A- 18b shows that this band is approximately one-half grain wide, and affects only those grains contiguous with the surface. This may be an etching “edge effect”, however, it may also reflect composition differences due to diffusion in this region.<u>Featureless grain surface</u> – this constitutes the leading edge of the grains as they interface with the scale. EDAX analysis later shows that this zone seems related to diffusion of alloying elements both into and out of the metal surface as scale formation progresses. Perhaps the most significant of these is the suggested potential for chromium egress and carbon ingress in this region. (see the composition for Area 4 in the table that follows).<u>Thin porous, loosely adhering scale</u> – this is seen continuous along the surface. EDAX analysis will later show that this is predominantly chromium-oxide. The scale is approximately 0.3 mils thick.<u>Thin fused-deposit layer</u> – This characteristic is inferred from the fact that the spherical components of the outer deposit appear to be imbedded in a continuous layer of solid material. This is perhaps best shown in the higher magnification view provided in the higher magnification back scattered electron image (BEI) shown in Figure A-18d.<u>Thick and very porous deposit/scale conglomerate</u> – many spherical particles are noted along with what appears to be islands of scale (metal oxides).Figures A-18c and A-18d show backscattered images (BEI) of the scale/metal interface for Sample K-L. The BEI images provide better resolution of compositional differences. Also, noted on Figure A-18d are the four locations selected for EDAX analysis. The results follow.

Summary of Findings, (continued)

Material: Save 25

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none"> Figure A-19 shows the appearance of the internal metal surface for Sample K-L. A thin oxide scale is noted to cover the surface. The observed porosity is due to an etching edge effect in that no porosity was observed in the as-polished state for this sample.
Metallurgical Analysis – Light Optics.	<ul style="list-style-type: none"> Figures A-20a, b, c, and d show the appearance of the mid-wall microstructure for each of the tube samples. Examination of these reveals the presence of islands of a precipitate that are apparent in the two higher temperature samples K-L and D-E, but not in the lower temperature samples. The identity of this precipitate has not been determined, and its' significance is unclear. The tube/scale interface was examined for both the internal and external surfaces on all four Save 25 tube samples. The three samples that experienced heavy metal losses all had similar appearances. The one sample that did not, Sample II-JJ, had what appeared to be a continuous, non-porous, adherent, chromium oxide scale over its' entire external surface. Minor grain boundary penetrations also were noted on the three samples that experienced heavy metal losses. This appeared to be ingress of the featureless diffusion zone. These penetrations did not exceed one grain boundary in depth. Also, examined, for the samples having heavy metal loss, were the pitted regions on the back side (6 o'clock position) of the samples. The pitted regions were unique in that the featureless diffusion zone was markedly thinner. It also appeared as if the deposit within the pit was acting to inhibit or dissolve the chromium oxide scale in that the scale was particularly thin at the base of the pit. This was not further explored.
EDAX Analysis Results	<ul style="list-style-type: none"> The table in Figure A-21 provides a summary of the EDAX analyses of the locations numbered in Figure A-18d. Also shown in this table is the EDAX analysis of the bulk deposit, an EDAX analysis near mid-wall of the tube, and a summary of the spectrographic analysis reported earlier, see Figure A-2. Review of this table suggests the following: <ul style="list-style-type: none"> <u>Area A: Bulk deposit/scale analysis</u> – Alkali metals are present. Sulfur and phosphorous are present in an increased amount compared to the base metal. An iron oxide is likely, as are aluminum, silicon and titanium oxides. Carbon content is relatively high, however, EDAX is reliable qualitatively but not quantitatively for light elements such as carbon. This suggests that carbon is present, but the exact amount is unknown.

Summary of Findings, (continued)

Material: **Save 25**

Issue	Discussion
EDAX Analysis Results, Continued	<ul style="list-style-type: none"><li data-bbox="548 493 1372 657">• <u>Area 1: At scale/metal interface</u> – The large amounts of Ni, Cr, Fe, and Cu and smaller amount of oxygen suggests that this analysis overlapped the metal considerably. Again of significance here is the presence of sulfur and carbon. Note the lack of any alkali metals at this location.<li data-bbox="548 661 1333 758">• <u>Area 2: Chromium-rich oxide scale</u> – This is the scale that is immediately adjacent to the metal surface. Again high sulfur is indicated.<li data-bbox="548 762 1333 896">• <u>Area 3: Fused deposit with imbedded spherical particles</u> – This layer is immediately above the chromium-rich oxide scale. It appears to contain an iron-rich oxide with significant levels of arsenic, phosphorous, and sulfur.<li data-bbox="548 900 1372 997">• <u>Area 4: Diffusion zone in metal abutting the metal/scale interface</u> – Of potential significance here is the presence of increased levels of carbon.<li data-bbox="548 1001 1320 1098">• <u>Area 5: Tube metal composition</u> – Given its limitations this EDAX analysis compares favorably with that of the reference spectrographic analysis below it.

Figure A-1: Schematic Drawing Showing Position of Save 25 Tube Samples Within Test Section A

Note: Drawing shown in same relative orientation as per the actual installation.

Figure A-2 Composition Save 25

Description: Nominal 22Cr/18Ni steel with Nb and N added to provide creep strength.
Source: Sumitomo Metal Industries (SMI)
Reference Composition: “Specified” chemistry – per SMI certificate.

Element	Reference Composition	Composition (a) Heat D621907	Tube Sample D-E	Tube Sample K-L	Tube Sample Z-AA	Tube Sample II-JJ
Ni	15.00 – 22.00	19.80	19.18	19.25	19.05	19.73
Cr	21.00 – 24.00	22.60	21.88	21.85	21.81	22.02
Fe	Balance	Balance	51.17 (b)	51.25 (b)	51.31 (b)	50.99 (b)
Mo	-	-	0.12	0.12	0.11	0.11
Co	-	-	0.22	0.22	0.22	0.22
C	0.05 – 0.12	0.07	0.076	0.074	0.074	0.069
N	0.15 – 0.30	0.22	0.20	0.19	0.19	0.19
B	-	-	0.0037	0.0035	0.0034	0.0032
Mn	2.0 max	0.64	0.66	0.66	0.67	0.64
Si	1.5 max	0.23	0.24	0.24	0.24	0.23
Al	-	-	0.017	0.016	0.017	0.016
Ti	-	-	0.008	0.008	0.008	0.007
Al+Ti	-	-	-	-	-	-
Nb	0.30 – 0.60	0.45	0.49	0.49	0.48	0.45
Ta	-	-	0.090	0.090	0.090	0.090
Nb+Ta	-	-	-	-	-	-
V	-	-	0.069	0.069	0.069	0.064
W	0.80 – 2.80	1.31	1.35	1.35	1.34	1.35
Cu	2.00 – 4.00	3.31	4.2	4.1	4.3	3.8
Sn	-	-	0.004	0.004	0.005	0.004
P	0.030 max	0.022	0.017	0.018	0.017	0.018
S	0.010 max	(c)	0.001	0.001	0.001	0.001
O2	-	-	-	-	-	-

a – Ladle analysis
b- By difference
c- Not detected

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure A-4: As-Received Appearance of Sample K-L (Save 25)

(Average surface metal temperature: 1170°F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure A-5: As-Received Appearance of Sample D-E (Save 25)
(Average surface metal temperature: 1146°F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure A-6: As-Received Appearance of Sample Z-AA (Save 25)

(Average surface metal temperature: 1084°F)

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure A-7: As-Received Appearance of Sample II-JJ (Save 25)

(Average surface metal temperature: 1047 °F)

Note: This was a 24-in. long specimen. Weld “JJ” would be to the right of this image.

12 O'Clock
(257 mils lost)

3 O'Clock
(228 mils lost)

6 O'Clock
(27 mils lost)

Figure A-8: OD Surface Appearance After Grit Blast

Material: Save 25
Sample: K-L

12 O’Clock
(133 mils lost)

3 O’Clock
(191 mils lost)

6 O’Clock
(28 mils lost)

Figure A-9: OD Surface Appearance After Grit Blast

Material: Save 25
Sample: D-E

12 O’Clock
(131 mils lost)

3 O’Clock
(131 mils lost)

6 O’Clock
(0 mils lost)

Figure A-10: OD Surface Appearance After Grit Blast

Material: Save 25
Sample: Z-AA

12 O’Clock
(52 mils lost)

3 O’Clock
(55 mils lost)

6 O’Clock
(0 mils lost)

Figure A-11: OD Surface Appearance After Grit Blast

Material: Save 25
Sample: II-JJ

Material:

Save 25

Sample Location:

K-L

Maximum Rate:

259 mils/yr

Maximum Loss Orientation:

Approx. 10 o'clock

Average Surface Metal Temperature:

1170°F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.401	0.397	0.400	0.401	0.400	0.401	0.401	0.403	0.401	0.401
After	0.144	0.197	0.172	0.403	0.373	0.404	0.105	0.142	0.242	0.067
Delta	0.257	0.2	0.228	-0.002	0.027	-0.003	0.296	0.261	0.158	0.334

Figure A-12: Silhouette and Wall Thickness Measurements for Sample K-L

Material:

Save 25

Sample Location:

D-E

Maximum Rate:

224 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average metal Temperature:

1146°F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.405	0.404	0.405	0.405	0.404	0.399	0.400	0.399	0.403	0.399
After	0.272	0.181	0.214	0.272	0.376	0.403	0.391	0.110	0.277	0.110
Delta	0.133	0.223	0.191	0.133	0.028	-0.004	0.009	0.289	0.125	0.289

Figure A-13: Silhouette and Wall Thickness Measurements for Sample D-E

Material:

Save 25

Sample Location:

Z-AA

Maximum Rate:

209 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average metal Temperature:

1084°F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.389	0.391	0.394	0.391	0.392	0.386	0.384	0.387	0.389	0.387
After	0.258	0.174	0.263	0.384	0.392	0.392	0.373	0.118	0.294	0.118
Delta	0.131	0.217	0.131	0.007	0.000	-0.006	0.011	0.269	0.095	0.269

Figure A-14: Silhouette and Wall Thickness Measurements for Sample Z-AA

Material:

Save 25

Sample Location:

II-JJ

Maximum Rate:

67 mils/yr

Maximum Loss Orientation:

Approx. 11:30 o'clock

Average metal Temperature:

1047°F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.429	0.431	0.430	0.424	0.417	0.416	0.420	0.423	0.424	0.424
After	0.377	0.380	0.375	0.413	0.422	0.419	0.418	0.347	0.394	0.337
Delta	0.052	0.051	0.055	0.011	-0.005	-0.003	0.002	0.076	0.030	0.087

Figure A-15: Silhouette and Wall Thickness Measurements for Sample II-JJ

Figure A-16: Metal Loss as a Function of Average Surface Metal Temperature

Material: Save 25

Figure A-17:

Low Magnification Image Showing Cross-Section Through Thinnest Region of Sample K-L (Save 25)

Figure A-18: SEM Microstructure: Save 25

(c) External Scale/Metal Interface (BEI - Intermediate Magnification)

Note: Niobium-rich constituent (light colored) at grain boundary triple points.

(d) External Scale/Metal Interface (BEI - High Magnification)

Figure A-18 (cont.) SEM Microstructure: Save 25

Note: Numbers on Figure (d) indicate distinct areas characterized by the visual assessment and EDAX analyses that follow.

Figure A-19: SEM Microstructure: Save 25

(a) Sample K-L (1170 °F)

(b) Sample D-E (1146 °F)

Figure A-20: Optical Microstructures Save 25 Mid-Wall

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

(c) Sample Z-AA (1084 °F)

(d) Sample II-JJ (1047 °F)

Figure A-20 (cont.): Optical Microstructures - Save 25 Mid-Wall

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Figure A-21: EDAX Analysis of Deposit/Scale/Metal Interface for Save 25 (Sample K-L)

Area	Description	Visual Appearance	Ni	Cr	Fe	Cu	Mn	W	Ti	Al	Si	C	O	Ca	K	Na	As	P	S
A	Bulk deposit/ scale analysis	Rust red deposit marbled with spherical particles.	--	--	30.0	--	--	--	0.43	4.71	9.51	9.70	36.4	1.19	1.49	0.73	4.06	0.59	1.06
1	At the scale- metal interface	Near to grain boundary interface with surface.	22.1	22.4	33.5	3.06	--	--	--	0.42	0.18	5.43	11.2	--	--	--	--	--	1.59
2	Adherent chromium- oxide scale.	Pink/white deposit. No evidence of adjacent grain structure.	2.48	44.93	15.4	--	--	--	--	--	0.49	--	34.5	--	--	--	--	--	2.14
3	Scale with imbedded spherical particles.	Spherical particles likely associated with deposited material.	5.95	0.83	55.1	--	--	--	--	0.41	0.45	--	33.5	--	--	--	2.79	0.27	0.69
4	Diffusion zone.	Relatively featureless metal adjacent to surface.	20.5	19.2	51.9	2.85	0.71	--	--	0.31	0.37	4.17	--	--	--	--	--	--	--
	Base Metal	Primary grain structure.	20.2	21.8	52.8	3.34	--	1.87	--	--	--	--	--	--	--	--	--	--	--
	Reference bulk composition		19.2	21.8	51.2	4.1	0.66	1.35	0.008	0.016	0.24	0.07	--	--	--	--	--	0.018	0.001

Appendix B

Analysis of Performance

Test Section A

Modified 800H

Overview of Results: Modified 800H

Modified 800H experienced a relatively high rate of metal loss under Test Section A service conditions. The initial wall thickness for the modified 800H samples was nominally 400mils. The maximum rate of metal loss was 178 mils per year*, with the rate calculated based on time at temperature rather than total time in the boiler.

The microstructural differences associated with the modified 800H sample at the E-F position for Test Section A may have contributed to the poor performance of this particular sample. The heat used to make up the E-F sample, Heat 17433, exhibited an excessively large grain size relative to the other modified 800H samples in Test Section A. If the microstructure is believed to be a major contributor, then, this might be confirmed in later examinations of tube samples from the same heat in other test sections.

It is interesting to compare the composition of modified 800H with that of the Save 25 alloy which performed so poorly. The Save 25 had a slightly higher chromium content (22.5 % vs 20%), but its' total alloy content was lower due to its' low nickel content relative to the modified 800H (20% vs 30%). This in addition to the fact that modified 800H contains a significant amount of molybdenum (roughly 1.5%), while Save 25 contains almost none. Taking all of the alloying elements into account, then it can be determined that the total alloy content of Save 25 is relatively low compared to that of the modified 800H.

Due to the lack of deposit in the section examined, no deposit analysis was performed on modified 800H, however, it is reasonable to infer that the same deposit was found everywhere on Test Section A. This being the case, it is likely that the same alkali-iron-sulfate that gave rise to attack elsewhere in the test section cause the wastage observed for the modified 800H.

It is noted that the modified 800H developed a continuous adherent chromium-oxide scale covering the external surface of the tube. While this scale was thin, 2 to 4 mils, it was much less porous than that of the Save 25, (compare Figure B-15b with Figure A-18d). This may also have contributed to the relative performance of these two alloys.

* **Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time in the boiler.**

Material: Modified 800H

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">The schematic in Figure B-1 shows the relative positions of the Modified 800H samples in Test Section A. Also, shown is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">The table in Figure B-2 provides the composition of the three tube samples after exposure. Each of the three samples was taken from a different heat of Modified 800H. A correlation between the sample identification and heat number is provided in the figure. The table also shows the “target” composition and heat analyses as per Oak Ridge National Laboratory (ORNL).Both heat and “after exposure” analyses compared reasonably well with one another and with the stated “target” chemistries.
As-Received Appearance	<ul style="list-style-type: none">Figure B-3 documents the typical appearance of this material when it was received from ORNL. This image was taken from an archive sample.Figures B-4 through B-6 document the as-received appearance of the external surface of the tube samples after service exposure. Three views are provided for each tube: 12 o’clock (the view that faces on-coming gas flow), 3 o’clock (the view where the gas flow is tangent to the surface), and 6 o’clock (the view that shows the back-side of the tube relative to the gas flow direction).External tube wastage is visible for all three samples; however, this is more clearly shown in the tube silhouette images that follow.A relatively thick rust-red back-side scale and deposit build-up is seen at the 6 o’clock position on all three samples but is most readily apparent in samples YZ (Figure B-6).A relatively thin red-brown deposit is seen on all other surfaces.There is no clear evidence in these figures of the gray/white scale associated with molten alkali-iron sulfate attack. However, scraping to remove the red scale revealed evidence of a gray/white scale immediately adjacent to the metal surface throughout the test section.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">Figures B-7 through B-9 show the appearance of the external surface of the Modified 800H1 tube samples after grit-blasting to remove deposit and scale. The 12 o’clock and 3 o’clock positions for all three samples show the appearance of general wastage due to fireside corrosion.The 6 o’clock position for Samples L-M and E-F show that evidence of shallow but extensive pitting on the back-side of these samples.

Material: Modified 800H

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures B-10 through B-12.• The same relative “o’clock” positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost. Note that one case, the delta is negative (i.e. 7:30 o’clock for Sample Y-Z). This is believed due to wall thickness variability and difficulty in locating the exact location of the “before” measurement.• In some cases, the minimum wall thickness in the cross section was not at one of the eight predetermined locations, (Samples L-M and Y-Z are examples). In these cases, there was no “before” measurement for comparison. So, the average “before” wall thickness was used to calculate the wall thickness lost at these off locations.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure B-13 plots the maximum wall thickness lost against the calculated average metal temperature for each of the three Modified 800H samples.• The rate of attack was high for all three samples but was a maximum in Sample E-F which saw an average metal temperature of 1146°F. It dropped off for the sample at 1169 °F, and also for the sample at 1084 °F. The cause for this apparent peak temperature for accelerated attack is not clear.• It should be noted that, given a starting wall thickness of 400 mils, then a rate of wall thickness loss of approximately 180 mils/yr would predict that, all things being equal, the wall would be completely penetrated in less than 2-1/2 years. Based on this, it seems likely that tubes of this material would need to be removed from service before the next examination cycle (i.e. before 36 months of exposure).
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample E-F was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it had lost the most wall thickness of all of the Modified 800H samples. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.

Material: Modified 800H

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">Figure B-14 shows the appearance of the tube profile in the section containing the minimum wall thickness for Sample E-F. Note a scale/deposit on the external surface of approximately 4 mils in thickness. Most of this was in the form of scale with very little deposit at this location.Figures B-15a, b, and c show the secondary electron images of the scale/metal interface for Sample E-F. Four distinct regions are in evidence. These regions are, starting within the metal and working out:<ol style="list-style-type: none"><u>Base metal</u> – oxalic acid etch delineates grain boundaries and carbides.<u>Deeply etching base metal</u> – this region is obvious as a light-appearing band that is parallel to the metal surface, perhaps see most clearly in Figure B-15a (see the area marked with a “4” in this photo). This band is clearly less than one-half grain wide, and affects only those grains contiguous with the surface. This deeper etch likely reflects composition differences due to diffusion in this region.<u>Featureless grain surface</u> – This constitutes the leading edge of the grains as they interface with the scale (see the area marked with a “3” in Figure 15a. EDAX analysis will later show that this zone seems related to diffusion of alloying elements in the vicinity of the metal surface as scale formation progresses. Perhaps the most significant of these is the suggested potential for chromium egress from the metal at this point.<u>Thin adhering scale</u> – this is seen continuous along the surface. EDAX analysis will later show that this is predominantly chromium-oxide. This is most clearly seen in Figures 15b and 15c.Figure B-16 shows the appearance of the internal metal surface for Sample E-F. A thin oxide scale is noted to cover the surface. This region seems relatively unaffected due to service exposure.
Metallurgical Analysis – Light Optics.	<ul style="list-style-type: none">Figures B-17a, b, c, and d show the appearance of the mid-wall microstructure for each of the tube samples. The microstructure of Samples L-M and Y-Z were similar to one another. The grain boundaries etched deeply, as did copious amounts of both large and small precipitates. Sample E-F on the other hand exhibited a much larger grain size, and was relatively clear of precipitates relative to the other two samples.It is not clear whether the microstructural differences noted above contributed to the relatively poorer performance of Sample E-F.It seems unlikely that the observed microstructural differences were due to service exposure. Rather, it is postulated that these were inherent in the material as-received from ORNL. Recall that three different heats of Modified 800H were used in Test Section A.

Summary of Findings, (continued)

Material: **Modified 800H**

Issue	Discussion
Metallurgical Analysis – Light Optics, Continued.	<ul style="list-style-type: none"> While minor notching was apparent at grain boundaries, little or no grain boundary penetration was observed in any region of the samples.
EDAX Analysis Results	<ul style="list-style-type: none"> The table in Figure B-18 provides a summary of the EDAX analyses of the locations numbered in Figure B-15a. Also shown in this table is an EDAX analysis near mid-wall of the tube, and a summary of the spectrographic analysis reported earlier, see Figure B-2. No bulk analysis of external deposit could be performed since very little was present. Review of this table suggests the following: <ul style="list-style-type: none"> <u>Area 1: For the scale at the out surface (Area 1 in Figure 15a)</u> – There was no evidence of the alkali metals. Nor were sulfur and phosphorous present.. Sulfur and phosphorous are present in an increased amount compared to the base metal. The scale is comprised primarily of chromium oxide. Carbon content is relatively high, however, EDAX is reliable qualitatively but not quantitatively for light elements such as carbon. This suggests that carbon is present, but the exact amount is unknown. <u>Area 2: For the scale near the interface with the base metal (Area 2 in Figure 15a)</u> – This is primarily a chromium oxide layer. No carbon found in this region. <u>Area 3: For the featureless diffusion zone in the metal at the interface (Area 3 in Figure 15a)</u> - This zone is depleted in chromium relative to the matrix (roughly 15% as opposed to 20%). This zone also was noted to be depleted in vanadium and silicon. <u>Area 4: For the deeply etching grain region (Area 4 in Figure 15a)</u>. This zone had a composition very similar to that of the base metal at mid-wall. However, silicon and aluminum were low relative to the base metal, and vanadium was slightly high. <u>Base metal</u> – The EDAX base metal analysis compared very closely to the results of the spectrographic analysis shown earlier in Figure B-2 of this appendix.

Figure B-1: Schematic Drawing Showing Position of Modified 800H Tube Samples Within Test Section A

Note: Drawing shown in same relative orientation as per the actual installation.

Figure B-2 Composition Modified 800H

Description: Nominal 20Cr/30Ni steel with improved creep strength due to addition of V, Nb, Ti, and B
Source: Oak Ridge National Laboratory (ORNL)
Reference Composition: “Target” Chemistry per ORNL (Reference 1).

Element	Reference Composition	Composition Heat 17423	Composition Heat 17424	Composition Heat 17433	Tube Sample E-F	Tube Sample L-M	Tube Sample Y-Z
Ni	31.0	30.74	31.04	31.10	30.93	30.85	30.88
Cr	20.0	19.89	19.98	19.91	19.97	20.03	19.99
Fe	Balance	-	-	-	44.5	44.4	44.4
Mo	1.5	1.50	1.52	1.51	1.52	1.52	1.52
Co	-	0.03	<0.01	<0.01	(a)	(a)	(a)
C	0.09	0.10	0.10	0.10	0.10	0.10	0.11
N	-	0.026	0.029	0.018	(a)	(a)	(a)
B	0.005	-	-	-	0.005	0.005	0.006
Mn	2.00	1.93	1.94	1.93	1.94	1.96	2.00
Si	0.25	0.24	0.24	0.26	0.23	0.24	0.24
Al	-	<0.01	<0.01	<0.01	(a)	(a)	(a)
Ti	0.25	0.11	0.15	0.03	<0.01	0.093	0.13
Nb	0.25	0.26	0.26	0.25	0.25	0.25	0.25
Ta	-	<0.01	(a)	(a)	(a)	(a)	(a)
Nb+Ta	-	-	-	-	-	-	-
V	0.4	0.38	0.23	0.37	0.37	0.37	0.23
Cu	-	<0.01	<0.01	<0.01	(a)	(a)	(a)
Sn	-	-	-	-	-	-	-
P	-	0.009	(a)	0.002	(a)	(a)	(a)
S	-	0.003	0.002	0.005	(a)	(a)	(a)
O2	-	0.004	0.008	0.015	(a)	(a)	(a)

- a- Not analyzed.
b- By difference.

Reference 1: “Fabrication of Test Tubes for Coal Ash Corrosion Testing”, Sikka, V.K., Swindeman, R.W., Wright, I.G., Judkins, R.R., Johnson, R., Proc, 13th Annual Conf. on Fossil Energy Mat’ls, May 1999.

Note: Sample E-F was from Heat 17433
Sample L-M was from Heat 17423
Sample Y-Z was from Heat 17424

Figure B-3: Appearance of Modified 800H Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
 (Note: 3 o'clock is up in this image)

3 O'Clock
 (Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure B-4 As-Received Appearance of Sample L-M (Modified 800H)

(Average surface metal temperature: 1174°F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure B-5 As-Received Appearance of Sample E-F (Modified 800H)

(Average surface metal temperature: 1150 °F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure B-6 As-Received Appearance of Sample Y-Z (Modified 800H)

(Average surface metal temperature: 1088 °F)

12 O'Clock
(100 mils lost)

3 O'Clock
(138 mils lost)

6 O'Clock
(6 mils lost)

Figure B-8 OD Surface Appearance After Grit Blast

Material: Modified 800H
Sample: E-F

12 O'Clock
(112 mils lost)

3 O'Clock
(62 mils lost)

6 O'Clock
(0 mils lost)

Figure B-9 OD Surface Appearance After Grit Blast

Material: Modified 800H
Sample: Y-Z

Material:

Modified 800H

Sample Location:

L-M

Maximum Rate:

169 mils/yr

Maximum Loss Orientation:

Approx. 11 o'clock

Average Surface Metal Temperature:

1174 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.399	0.399	0.399	0.401	0.402	0.402	0.401	0.399	0.400	0.400
After	0.276	0.251	0.236	0.333	0.399	0.400	0.392	0.196	0.310	0.182
Delta	0.123	0.148	0.163	0.068	0.003	0.002	0.009	0.203	0.090	0.218

Figure B-10: Silhouette and Wall Thickness Measurements for Sample L-M

Material:

Modified 800H

Sample Location:

E-F

Maximum Rate:

178 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average Surface Metal Temperature:

1150 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.402	0.401	0.402	0.403	0.401	0.401	0.401	0.400	0.401	0.400
After	0.302	0.238	0.264	0.318	0.395	0.396	0.400	0.170	0.310	0.170
Delta	0.100	0.163	0.138	0.085	0.006	0.005	0.001	0.230	0.091	0.230

Figure B-11: Silhouette and Wall Thickness Measurements for Sample E-F

Material:

Modified 800H

Sample Location:

Y-Z

Maximum Rate:

154 mils/yr

Maximum Loss Orientation:

Approx. 10 o'clock

Average Surface Metal Temperature:

1088°F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.400	0.403	0.401	0.402	0.402	0.400	0.400	0.399	0.401	0.401
After	0.288	0.337	0.339	0.400	0.402	0.402	0.322	0.228	0.340	0.202
Delta	0.112	0.066	0.062	0.002	0.000	-0.002	0.078	0.171	0.061	0.199

Figure B-12: Silhouette and Wall Thickness Measurements for Sample Y-Z

Figure B-13: Metal Loss as a Function of Average Surface Metal Temperature

Material: Modified 800H

Figure B-14: Low Magnification Image Showing Cross-Section Through Thinnest Region of Sample E-F (Modified 800H)

Note: 1) Numbers indicate distinct areas characterized by the visual assessment and EDAX analyses that follow.

Figure B-15: Microstructure: Modified 800H

(c) External Scale/Metal Interface (Intermediate Magnification)

Figure B-15 (Cont.): Microstructure: Modified 800H

Internal Surface Appearance

Figure B-16: Microstructure: Modified 800H

(a) Sample L-M (1174°F)

(b) Sample E-F (1150°F)

Figure B-17: Optical Microstructures Modified 800H Mid-Wall

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

(c) Sample Y-Z (1088 °F)

Figure B-17 (Cont.): Optical Microstructures Modified 800H Mid-Wall

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Figure B-18: EDAX Analysis of Deposit/Scale/Metal Interface for Modified 800H (Sample E-F)

Area	Description	Visual Appearance	Ni	Cr	Fe	Mn	Mo	V	Al	Si	C	O
1	Coal ash deposit mixed with scale.	Rust red marbled deposit	7.32	19.2	10.0	1.48	--	--	0.47	2.23	25.0	32.9
2	Adherent chromium-oxide scale.	Pink/white deposit. No evidence of adjacent grain structure.	3.78	42.5	14.9	4.27	--	--	--	0.54	--	31.4
3	Diffusion zone depleted in Cr, Si, and V.	Generally featureless, however, grain boundaries continuous with underlying metal.	35.0	14.9	47.3	2.39	0.47	--	--	--	--	--
4	Diffusion zone.	Deep etching primary grain structure.	31.8	19.8	45.2	1.68	0.89	0.40	0.30	--	--	--
	Base Metal	Primary grain structure.	31.2	19.8	45.2	1.69	1.04	0.29	0.46	0.30	--	--
	Reference bulk composition per spectrographic analysis.		30.6	20.4	44.4	2.13	1.33	0.36	0.02	0.28	--	--

Appendix C

Analysis of Performance

Test Section A

347 HFG

Overview of Results: 347 HFG

Test Section A 347 HFG tube samples experienced a rate of metal loss that ranged from 83 to 176 mils per year*. The reasons for this poor performance have not been resolved; however, it is noted that this material has a relatively low chromium content (18%) and a relatively low total alloying element content (with a high balance iron content of about 65%). Based on the poor results for Save 25 and modified 800H, this level of alloying would predict relatively poor performance in this service environment. That fact that 347 HFG performed on par with these more highly alloyed materials may have been due to the fine grain size inherent in this material. It is postulated that the fine grain size would facilitate delivery of chromium to the metal surface and thus enhance formation of the protective chromium-rich scale.

Examination of the three 347 HFG tube samples suggested that the rate of corrosion was suppressed at an intermediate exposure temperature. It was 83 mils per year at 1137 °F, while it was about twice that (174 and 176 mils per year) at temperatures above (1164 °F) and below that (1075 °F). The reason for this sort of performance has not been resolved. However, it does not appear to be related to alloy content or microstructural differences in that these appeared to be the same for all three samples.

Analysis of deposit on the surface revealed that it contained the known aggressive combination of species, namely iron, oxygen, the alkali metals, and sulfur. The presence of significant amounts of arsenic was unexpected, and its' significance is unclear. Examination and analysis of the scale adjacent to the metal surface revealed the chalky-white appearance associated with Alkali-iron-sulfates. Spectrographic ICP analysis seemed to confirm this. Thus, the required corrosive elements were available to test the performance limits of this alloy.

Finally, the analysis of the deposit and the metal surface immediately adjacent to the interface revealed the presence of carbon. While carbon determinations using EDAX are unreliable, the implications of carbon in the deposit are worthy of additional consideration, as is the potential for carbon ingress from the deposit into the abutting metal.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: 347 HFG

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">The schematic in Figure C-1 shows the relative positions of 347 HFG samples in Test Section A. Also, shown is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">The table in Figure C-2 provides the composition of the three tube samples as determined after removal from Test Section A. It should be noted that all three samples were taken from a single heat of material, Heat D892703.The table also shows the specified composition as per the ASTM A213 specification. Also shown is the Sumitomo heat analysis which compares very well with the specification and with the analysis performed on the tube sample after service.
As-Received Appearance	<ul style="list-style-type: none">Figure C-3 shows the typical appearance of the 347 HFG material prior to service.Figures C-4 through C-6 document the as-received appearance of the external surface of the 347 HFG tube samples after they had been removed from service. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).Wastage is visible at the 12 o'clock for all three samples, however, this is most readily apparent on Samples I-J and CC-DD.A relatively thick rust-red back-side scale and deposit build-up is seen at the 6 o'clock position on all three samples but is most readily apparent in Sample CC-DD.A relatively thin red-brown deposit is seen on all other surfaces.There is no clear evidence in these figures of the gray/white scale associated with molten alkali-iron sulfate attack. However, scraping to remove the red scale revealed evidence of a gray/white scale immediately adjacent to the metal surface.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">Figures C-7 through C-9 show the appearance of the external surface of the 347 HFG tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for all three samples show the appearance of general wastage due to fireside corrosion. However this is most clearly shown for Sample I-J, Figure C-7.No significant pitting was found on the back-side of any of these samples.

Material: 347 HFG

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures C-10 through C-12.• The same relative “o’clock” positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost. Note that in one case, the delta is negative (at the 6 o’clock position for Sample CC-DD). This is believed due to wall thickness variability and difficulty in locating the exact location of the “before” measurement.• In some cases, the minimum wall thickness in the cross section was not at one of the eight predetermined locations, (Samples I-J and A-B are examples). In these cases, there was no “before” measurement for comparison. So, the average “before” wall thickness was used to calculate the wall thickness lost at these off-locations.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure C-13 plots the maximum wall thickness lost against the calculated average metal temperature for each of the three 347 HFG samples.• It was noted that the maximum rate of metal loss was about the same for the samples at the lowest and highest temperatures (174 mils per year at 1164 °F, and 176 mils per year at 1075 °F), but that the maximum metal loss rate dipped significantly at an intermediate temperature (83 mils per year at 1137 °F). The reason for this is not clear.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample I-J was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it had lost material at the maximum rate. The focus of this investigation was in the region of the tube where the maximum amount of material was lost, i.e. in the thinnest section.

Material: 347 HFG

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">• Figure C-14 shows the appearance of the tube profile in the section containing the minimum wall thickness for Sample I-J. Note a scale/deposit on the external surface of approximately 2 to 5 mils in thickness. No scale is evident on the internal surface at this magnification.• Figures C-15a, b, c and d, show the appearance of the scale/metal interface for Sample I-J. Figure C-15a, C-15b, and 15d show secondary electron images (SEI) of the interface. Five distinct regions are in evidence. These regions are, starting within the metal and working out:<ol style="list-style-type: none">1. <u>Base metal</u> – oxalic acid etch delineates grain boundaries and carbides.2. <u>Deeply etching base metal</u> – this region is somewhat less obvious than in either Save 25 or modified 800H. It can be seen as the relatively light-appearing band that is parallel to the metal surface in Figure C-15a. Figure C-15b shows that this band is approximately two grains wide, and appears related to etchant attack along the grain boundaries of those grains that are near to the interface with the scale. This likely reflects composition differences due to diffusion in this region. Extensive grain boundary decoration is noted.3. <u>An adherent scale</u> – this is shown to be continuous along the interface with the underlying metal. This is highlighted with the number “1” in the backscattered electron image shown in Figure C-15c. This scale was about 0.4 mils thick.4. <u>A separated, loosely adhering scale</u> – this also is seen continuous along the surface. This scale varied in thickness up to about 1.2 mils. EDAX analysis will later show that this and the adherent scale were predominantly chromium-oxide.5. <u>Thick and very porous deposit/scale conglomerate</u> – many spherical particles are noted along with what appears to be islands of scale (metal oxides).• Figure C-15c shows a backscattered image (BEI) of the scale/metal interface for Sample I-J. The BEI images provide better resolution of compositional differences. Also, noted on Figure C-15c are three of the locations selected for EDAX analysis. Figure C-15d shows a high magnification SEI image providing the locations of the other three locations for EDAX analyses. The results of these analyses follow.

Summary of Findings, (continued)

Material: 347 HFG

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none"> Figure C-16 shows the appearance of the internal metal surface for Sample I-J. An extremely thin oxide scale is noted to cover the surface. The observed porosity was determined to be due to an etching edge effect, in that, the as-polished specimen showed no evidence of porosity in this location.
Metallurgical Analysis – Light Optics.	<ul style="list-style-type: none"> Figures C-17a, b, c, and d show the appearance of the mid-wall microstructure for each of the tube samples. These samples are very similar to one another in terms of both microstructure and grain size. The tube/scale interface was examined at both the internal and external surfaces on all three 347 HFG tube samples. In spite of metal loss rate differences, all three samples evidenced similar interface appearance. Minor grain boundary penetrations were noted at the back side (6 o'clock position). These were relatively shallow and did not exceed one grain diameter for this fine grained material.
EDAX Analysis Results	<ul style="list-style-type: none"> The table in Figure C-18 provides a summary of the EDAX analyses of the locations numbered in Figures C-15c and C-15d. Also shown in this table is an EDAX analysis near mid-wall of the tube, and a summary of the spectrographic analysis reported earlier, see Figure C-2. The “areas” below correspond to the numbered locations indicated in the C-15 figures. Review of this table suggests the following: <ul style="list-style-type: none"> <u>Area 1: For the bulk deposit analysis</u> – Alkali metals are present. Sulfur and phosphorous are present in an increased amount compared to the base metal. An iron oxide is likely, as are aluminum, silicon and titanium oxides. Carbon content is relatively high, however, EDAX is reliable qualitatively but not quantitatively for light elements such as carbon. Further complicating this is the fact that the analysis may well be picking up carbon from the epoxy resin that is used in mounting the sample. Separate analysis suggests that the total carbon content of the deposit is low. <u>Area 2: Loosely adherent scale</u> – this region appears to be primarily a chromium / iron oxide. <u>Area 3: Adherent scale</u> – this region which is contiguous with the underlying metal appears to be comprised of a chromium-rich oxide. Also of note is the relatively high sulfur content in this area adjacent to the metal surface. <u>Area 4: Particle at scale/metal interface</u> – this appears to be a niobium-rich inclusion. <u>Area 5: Grain boundary at scale/metal interface</u> – of note is that this analysis suggests the presence of sulfur and oxides.

Summary of Findings, (continued)

Material: 347 HFG

Issue	Discussion
EDAX Analysis Results, Continued	<ul style="list-style-type: none"><li data-bbox="548 422 1377 781">• <u>Area 6: Base metal in grain abutting the interface</u> – the analysis here is very similar to that of the bulk spectrographic analysis for the base metal. The most significant difference is that this region appears to show the presence of increased carbon content. As discussed earlier, interpretation of this based on EDAX is difficult at best. However, it is very unlikely that, at this location, EDAX is picking up the epoxy compound used to mount the tube cross section. Based on this, it is likely that there is an increase in carbon content in the layer of metal immediately adjacent to the scale/metal interface. The implications of this have not been fully explored.

Figure C-1: Schematic Drawing Showing Position of 347 HFG Tube Samples Within Test Section A

Note: Drawing shown in same relative orientation as per the actual installation.

Figure C-2 Composition 347 HFG

Description: Nominal 18Cr/11Ni steel with Nb and Ta added to provide creep strength.
Source: Sumitomo Metal Industries (SMI)
Reference Composition: “Specified” chemistry – per ASTM A213 (TP347 HFG).

Element	Reference Composition	Composition (a) Heat D892703	Tube Sample A-B	Tube Sample I-J	Tube Sample CC-DD
Ni	9.00 – 13.0	11.98	12.00	11.89	11.88
Cr	17.0 – 20.0	18.4	18.64	18.61	18.61
Fe	Balance	Balance	64.8 (b)	64.8 (b)	64.9 (b)
Mo	-	-	0.24	0.24	0.24
Co	-	-	0.24	0.24	0.24
C	0.06 – 0.10	0.09	0.097	0.099	0.098
N	-	-	0.056	0.056	0.056
B	-	-	0.0027	0.0027	0.0026
Mn	2.00 max	1.46	1.46	1.48	1.47
Si	0.75 max	0.41	0.38	0.39	0.38
Al	-	-	0.013	0.014	0.014
Ti	-	-	0.001	0.002	0.002
Al+Ti	-	-	-	-	-
Nb	-	-	0.90	0.91	0.91
Ta	-	-	0.008	0.008	0.008
Nb+Ta	(8 x C) min- 1.0 max	0.9	0.908	0.909	0.909
V	-	-	0.065	0.067	0.066
W	-	-	0.009	0.010	0.009
Cu	-	-	0.19	0.20	0.19
Sn	-	-	0.008	0.008	0.008
P	0.040 max	0.027	0.023	0.023	0.023
S	0.030 max	0.001	0.002	0.002	0.002
O2	-	-	-	-	-

a – Product analysis
b – By difference.

Figure C-3: Appearance of 347 HFG Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
 (Note: 3 o'clock is up in this image)

3 O'Clock
 (Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure C-4 As-Received Appearance of Sample I-J (347 HFG)

(Average surface metal temperature: 1164°F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure C-5 As-Received Appearance of Sample A-B (347 HFG)

(Average surface metal temperature: 1137°F)

Note: This was a 17-5/8-in. long specimen. Weld “A: would be to the left of this image.

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure C-6 As-Received Appearance of Sample CC-DD (347 HFG)

(Average surface metal temperature: 1075 °F)

12 O'Clock
(159 mils lost)

3 O'Clock
(181 mils lost)

6 O'Clock
(1 mil lost)

Figure C-7: OD Surface Appearance After Grit Blast

Material: 347 HFG
Sample: I-J

12 O'Clock
(85 mils lost)

3 O'Clock
(20 mils lost)

6 O'Clock
(1 mil lost)

Figure C-8: OD Surface Appearance After Grit Blast

Material: 347 HFG
Sample: A-B

12 O'Clock
(101 mils lost)

3 O'Clock
(105 mils lost)

6 O'Clock
(0 mils lost)

Figure C-9: OD Surface Appearance After Grit Blast

Material: 347 HFG
Sample: CC-DD

Material:

347 HFG

Sample Location:

I-J

Maximum Rate:

174 mils/yr

Maximum Loss Orientation:

Approx. 9:30 o'clock

Average Surface Metal Temperature:

1164 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.401	0.403	0.402	0.398	0.397	0.401	0.403	0.402	0.401	0.401
After	0.242	0.307	0.221	0.394	0.396	0.395	0.196	0.250	0.300	0.177
Delta	0.159	0.096	0.181	0.004	0.001	0.006	0.207	0.152	0.101	0.224

Figure C-10: Silhouette and Wall Thickness Measurements for Sample I-J

Material: 347 HFG

Sample Location: A-B

Maximum Rate: 83 mils/yr

Maximum Loss Orientation: Approx. 9:30 o'clock

Average Surface Metal Temperature: 1137 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.446	0.444	0.439	0.435	0.432	0.435	0.440	0.444	0.439	0.439
After	0.361	0.415	0.419	0.43	0.431	0.435	0.366	0.384	0.405	0.332
Delta	0.085	0.029	0.02	0.005	0.001	0	0.074	0.06	0.034	0.107

Figure C-11: Silhouette and Wall Thickness Measurements for Sample A-B

Material:

347 HFG

Sample Location:

CC-DD

Maximum Rate:

176 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average Surface Metal Temperature:

1075°F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.401	0.402	0.399	0.397	0.397	0.399	0.399	0.398	0.399	0.398
After	0.300	0.207	0.294	0.395	0.400	0.397	0.383	0.170	0.318	0.170
Delta	0.101	0.195	0.105	0.002	-0.003	0.002	0.016	0.228	0.081	0.228

Figure C-12: Silhouette and Wall Thickness Measurements for Sample CC-DD

Figure C-13: Metal Loss as a Function of Average Surface Metal Temperature

Material: 347 HFG

C-14: Low Magnification Image Showing Cross-Section Through Thinnest Region of Sample I-J (347 HFG)

C-15: Microstructure: 347 HFG

C-15 (Cont.): Microstructure: 347 HFG

Note: 1) Numbers on photos indicate distinct areas characterized by the visual assessment and EDAX analyses that follow.

Internal Surface Appearance

Figure C-16: Microstructure: 347 HFG

(a) Sample I-J (1164°F)

(b) Sample A-B (1137°F)

Figure C-17: Optical Microstructures 347 HFG Mid-Wall

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

(c) Sample CC-DD (1075 °F)

Figure C-17 (cont.): Optical Microstructures – 347 HFG Mid-Wall

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Figure C-18: EDAX Analysis of Deposit/Scale/Metal Interface for 347 HFG (Sample I-J)

Area	Description	Visual Appearance	Ni	Cr	Fe	Cu	Mn	Nb	Mo	Al	Si	C	O	Ca	K	Na	As	P	S
1	Bulk deposit/ scale analysis	Spherical particles embedded in deposit.	--		28.34	--	--	--	--	4.30	7.90	19.5	34.8	0.52	0.96	--	2.34	0.34	0.99
2	Scale separated from underlying material.		--	22.0	42.3	--	--	--	--	--	0.69	--	35.0	--	--	--	--	--	--
3	Adherent chromium- oxide scale.	Adjacent to metal surface.	.078	39.4	21.6	--	--	--	--	--	0.81	--	35.0	--	--	--	--	--	2.37
4	Particle at scale/ metal interface.		11.2	7.35	41.3	--	--	40.1	--	--	--	--	--	--	--	--	--	--	--
5	Grain boundary at scale/metal interface.		3.84	38.34	35.99	--	--	--	--	--	1.02	2.96	16.4	--	--	--	--	--	1.42
6	Base Metal in grain abutting surface.	.	10.7	16.7	64.3	--	2.12	0.82	--	--	0.35	4.99	--	--	--	--	--	--	--
	Reference bulk composition		11.9	18.6	64.8	0.20	1.48	0.91	0.24	0.014	0.39	0.10	--	--	--	--	--	--	--

Appendix D

Analysis of Performance

Test Section A

NF 709

Overview of Results: NF 709

NF 709 tube samples consistently experienced a high rate of metal loss due to service exposure in Test Section A. The maximum rate of metal loss ranged from 136 mils per year to 170 mils per year. The reasons for this poor performance have not been fully characterized; however, it is interesting to compare the composition of NF 709 with that of the other alloys that performed poorly in Test Section A. NF 709 is similar in chromium content to Save 25 (at about 22%). However, in contrast to Save 25, it has about 1.5% molybdenum; otherwise these alloys are chemically very similar to one another. NF 709 has an higher chromium content than either modified 800H or 347 HFG (which are at about 20% and 19% respectively). Having an iron content of about 49%, the total alloy content of NF 709 ranks intermediate to that of the other poorly performing candidate alloys, i.e. the respective iron contents are: 51% for Save 25, 44% for modified 800H, and 65% for 347 HFG.

Examination revealed that the rate of metal loss was high for all three NF 709 samples, but a slight dip in the rate is indicated at the intermediate temperature, see Figure D-13. The cause for, and the significance of, this is not clear.

Analysis of deposit on the surface revealed that it had the known aggressive combination of species, namely iron, oxygen, the alkali metals, and sulfur. The presence of significant amounts of arsenic was unexpected, and its' significance is unclear. Examination and analysis of the scale adjacent to the metal surface revealed the chalky-white appearance associated with alkali-iron-sulfates. Spectrographic ICP analysis seemed to confirm this. Thus, the required corrosive elements were available to test the performance limits of this alloy.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: NF 709

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">The schematic in Figure D-1 shows the relative positions of NF 709 samples in Test Section A. Also, shown is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">The table in Figure D-2 provides the composition of the three tube samples after exposure. All three samples were taken from a single heat of material, Heat E58733. The table also shows the specified composition and heat analysis as reported on the Nippon Steel Corporation (NSC) mill certificate that accompanied the material.Review of the table reveals that the chemistries of all three samples were consistent with one another and with the heat analysis reported by NSC.
As-Received Appearance	<ul style="list-style-type: none">Figure D-3 shows the typical appearance of this tube material as it came from NSC.Figure D-4 through D-6 document the as-received appearance of the external surface after service in Test Section A. Three views are provided for each of the three tube samples: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).Wastage is visible at the 12 o'clock for all three samples.A relatively thick rust-red back-side scale and deposit build-up is seen at the 6 o'clock position on all three samples but is most readily apparent in sample BB-CC.A relatively thin red-brown deposit is seen on all other surfaces.Evidence of the gray/white scale associated with molten alkali attack can be seen in the location where the deposit has flaked off from the surface of sample BB-CC, in Figure D-6, 6 o'clock image. This is assumed to be present at the scale/metals interfaces throughout the test section.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">Figures D-7 through D-9 show the appearance of the external surface of the NF 709 tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for all three samples show the appearance of general wastage due to fireside corrosion.The 6 o'clock position for Samples J-K and C-D show the pitting that occurred on the back-side of these samples. Only minimal pitting was noted at the 6 o'clock position for Sample BB-CC. The pitting on Sample J-K accounted for 17 of the 18 mils lost at this position.

Material: NF 709

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures D-10 through D-12.• The same relative “o’clock” positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost. Note that in some cases (for Samples J-K and BB-CC), the delta is negative (particularly on the back-side, 6 o’clock position). This is believed due to wall thickness variability and difficulty in locating the exact location of the “before” measurement.• For Sample J-K, the minimum wall thickness in the cross section was not at one of the eight predetermined locations. In this case, there were no “before” measurement for comparison to determine the “delta”. So, the average “before” wall thickness was used to calculate the wall thickness lost at these off-locations.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure D-13 plots the maximum wall thickness lost against the calculated average metal temperature for the three NF 709 samples.• It was noted that the maximum rate of metal loss was high for all three samples, although it is somewhat lower for the sample at an intermediate temperature, i.e. 136 mils per year for Sample C-D.• It was noted that, similar to 347 HFG, the metal loss rate for the intermediate temperature (1142°F) was lower than that for the samples exposed at higher (1167 °F) and lower (1077 °F) temperatures. The reason for this is not clear.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample J-K was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it had lost the most wall thickness of all of the NF 709 samples. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.

Material: NF 709

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">• Figure D-14 shows the appearance of the tube profile in the section containing the minimum wall thickness for Sample J-K. Note a scale/deposit on the external surface of approximately 7 to 12 mils in thickness. No scale is evident on the internal surface at this magnification.• Figures D-15a, b, and c show secondary electron images that depict the appearance of the scale/metal interface for Sample J-K at increasing magnifications. Six distinct regions are in evidence. These regions are, starting within the metal and working out:<ol style="list-style-type: none">1. <u>Base metal</u> – oxalic acid etch delineates grain boundaries and carbides.2. <u>Deeply etching base metal</u> – this region is obvious as a light-appearing band that is parallel to the metal surface, perhaps see most clearly in Figure D-15a. Figure D- 15b shows that this band is a little more than one grain wide, and affects only those grains that are within a grain or two of the interface. This likely is due to composition differences related to diffusion in this region, although EDAX analysis appears to show very little difference between this location and the bulk metal analysis.3. <u>Featureless grain surface</u> – This constitutes the leading edge of the grains as they interface with the scale. EDAX analysis seems to show that this region is slightly depleted in chromium relative to the bulk metal analysis; however, there is no indication of carbon ingress here as had been suggested by EDAX analyses for other materials.4. <u>Tightly adhering scale</u> – this scale is continuous along the scale/metal interface. EDAX analysis shows it to be a chromium-rich oxide, and that it contains a significant amount of sulfur. It is approximately 2 mils thick.5. <u>Loosely adhering scale</u> – EDAX analysis will later show that this is comprised of chromium-, iron-, and nickel-rich oxides. The scale is approximately 2 mils thick.6. <u>Thick and very porous deposit/scale conglomerate</u> – many spherical particles are noted along with what appears to be islands of scale.• Figures D-16a and D-16b show backscattered images (BEI) of the scale/metal interface for Sample J-K. The BEI images provide better resolution of compositional differences. These images also show the ten locations selected for EDAX analysis. The results of these follow

Summary of Findings, (continued)

Material: NF 709

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none"> Figure D-17 shows the appearance of the internal metal surface for Sample J-K. A very thin oxide scale is noted to cover the surface. The observed porosity was confirmed to be due to an etching edge effect.
Metallurgical Analysis – Light Optics.	<ul style="list-style-type: none"> Figures D-18a, b, and c show the appearance of the mid-wall microstructure for each of the tube samples. These are very similar to one another in terms of grain size, and in terms of the numbers and sizes of precipitates and inclusions. The tube/scale interface was examined for both the internal and external surfaces on all three NF 709 tube samples. No significant differences were noted. No evidence of grain boundary penetrations was found on either the external or internal surfaces. Back side pitting was examined and found to be minor.
EDAX Analysis Results	<ul style="list-style-type: none"> The table in Figure D-19 provides a summary of the EDAX analyses of the locations numbered in Figure D-16a and D-16b. Also shown in this table is an EDAX analysis near mid-wall of the tube, and a summary of the spectrographic analysis, see Figure D-2. Review of this table suggests the following: <ul style="list-style-type: none"> <u>Area 1: For the bulk deposit analysis</u> – Alkali metals are present. Sulfur and phosphorous are present in an increased amount compared to the base metal. An iron oxide is likely, as are aluminum, silicon and titanium oxides. Carbon content appears to be relatively high, however, as stated earlier EDAX is not reliable for carbon, and this is exacerbated by the fact that there may be epoxy resin from the mounting compound impregnating this relatively loose-packed area. <u>Area 2: Layer within deposit/scale</u> – This layer is comprised almost entirely of nickel and sulfur, suggestive of a nickel sulfide corrosion product. <u>Areas 3 through 8 show scale analyses at various locations:</u> These suggest that the scale is comprised of chromium-, iron-, and nickel-rich oxides. Of significance in all of these is the presence of sulfur, particularly in the scale immediately adjacent to the interface. <u>Area 9: metal grains abutting the interface</u> – this area is somewhat depleted in chromium, suggestive of a diffusion zone. <u>Area 10: the “deep etching” band</u> – this area appears to be similar in composition to the bulk base metal, although it may be somewhat enriched in silicon. <u>Bulk EDAX analysis</u> – compares well with optical spectrograph results.

Figure D-1: Schematic Drawing Showing Position of NF 709 Tube Samples Within Test Section A

Note: Drawing shown in same relative orientation as per the actual installation.

Figure D-2 NF709

Description: Nominal 20Cr/25Ni steel with Nb and Ti added to provide creep strength.
Source: Nippon Steel Corporation (NSC)
Reference Composition: “Specified” chemistry – per NSC inspection certificate for heat delivered.

Element	Reference Composition	Composition Heat E58733	Tube Sample C-D	Tube Sample J-K	Tube Sample BB-CC
Ni	22.00 - 28.00	24.87	24.86	24.78	24.77
Cr	19.00 – 23.00	22.29	22.66	22.61	22.67
Fe	-	-	48.83 (a)	48.91 (a)	48.85 (a)
Mo	1.00 – 2.00	1.42	1.39	1.40	1.40
Co	-	-	0.16	0.16	0.16
C	0.1 max	0.02	0.033	0.033	0.033
N	0.100 – 0.250	0.176	0.17	0.18	0.17
B	0.0020 – 0.0100	0.0044	0.0044	0.0045	0.0045
Mn	1.50 max	0.97	1.00	1.00	1.01
Si	1.00 max	0.40	0.37	0.38	0.38
Al	-	-	0.032	0.034	0.033
Ti	0.02 - 0.20	0.05	0.036	0.035	0.036
Al+Ti	-	-	-	-	-
Nb	0.10 – 0.40	0.23	0.24	0.25	0.25
Ta	-	-	0.091	0.090	0.091
Nb+Ta	-	-	-	-	-
V	-	-	0.074	0.075	0.075
W	-	-	-	-	-
Cu	-	-	0.03	0.04	0.04
Sn	-	-	0.003	0.003	0.003
P	0.030 max	0.010	0.010	0.010	0.011
S	0.010 max	0.001	0.002	0.002	0.002
O2	-	-	-	-	-

a – By difference

Figure D-3: Appearance of NF 709 Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure D-4 As-Received Appearance of Sample J-K (NF 709)

(Average surface metal temperature: 1167°F)

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure D-5 As-Received Appearance of Sample C-D (NF 709)

(Average surface metal temperature: 1142 °F)

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure D-6 As-Received Appearance of Sample BB-CC (NF 709)

(Average surface metal temperature: 1077°F)

12 O'Clock
(139 mils lost)

3 O'Clock
(143 mils lost)

6 O'Clock
(18 mil lost)

Figure D-7: OD Surface Appearance After Grit Blast

Material: NF 709
Sample: J-K

12 O'Clock
(63 mils lost)

3 O'Clock
(96 mils lost)

6 O'Clock
(4 mils lost)

Figure D-8: OD Surface Appearance After Grit Blast

Material: NF 709
Sample: C-D

12 O'Clock
(111 mils lost)

3 O'Clock
(79 mils lost)

6 O'Clock
(0 mils lost)

Figure D-9: OD Surface Appearance After Grit Blast

Material: NF 709
Sample: BB-CC

Material: NF 709

Sample Location: J-K

Maximum Rate: 170 mils/yr

Maximum Loss Orientation: Approx. 9:30 o'clock

Average Surface Metal Temperature: 1167°F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.394	0.396	0.399	0.398	0.399	0.396	0.396	0.395	0.397	0.397
After	0.255	0.283	0.256	0.4	0.381	0.397	0.219	0.253	0.306	0.178
Delta	0.139	0.113	0.143	-0.002	0.018	-0.001	0.177	0.142	0.091	0.219

Figure D-10: Silhouette and Wall Thickness Measurements for Sample J-K

Material: NF 709

Sample Location: C-D

Maximum Rate: 136 mils/yr

Maximum Loss Orientation: Approx. 10:30 o'clock

Average Surface Metal Temperature: 1142 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.399	0.400	0.399	0.399	0.400	0.397	0.400	0.399	0.399	0.399
After	0.336	0.282	0.303	0.362	0.396	0.396	0.393	0.224	0.337	0.224
Delta	0.063	0.118	0.096	0.037	0.004	0.001	0.007	0.175	0.063	0.175

Figure D-11: Silhouette and Wall Thickness Measurements for Sample C-D

Material: NF 709

Sample Location: BB-CC

Maximum Rate: 145 mils/yr

Maximum Loss Orientation: Approx. 10:30 o'clock

Average Surface Metal Temperature: 1077 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.400	0.400	0.397	0.396	0.396	0.398	0.400	0.400	0.398	0.400
After	0.289	0.272	0.318	0.397	0.399	0.400	0.386	0.213	0.334	0.213
Delta	0.111	0.128	0.079	-0.001	-0.003	-0.002	0.014	0.187	0.064	0.187

Figure D-12: Silhouette and Wall Thickness Measurements for Sample BB-CC

Figure D-13: Metal Loss as a Function of Average Surface Metal Temperature

Material: NF 709

Figure D-14: Low Magnification Image Showing Cross-Section Through Thinnest Region of Sample J-K (NF 709)

Figure D-15: Microstructure: NF 709

(c) External Scale/Metal Interface (SEI - High Magnification)

Figure D-15 (Cont.): Microstructure: NF 709

Figure D-16: Microstructure: NF 709

Note: 1) Numbers on photos indicate distinct areas characterized by the visual assessment and EDAX analyses that follow.

Internal Surface Appearance

Figure D-17: Microstructure: NF 709

(a) Sample J-K (1167°F)

(b) Sample C-D (1142°F)

Figure D-18: Optical Microstructures NF 709 Mid-Wall

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

(c) Sample BB-CC (1077 °F)

Figure D-18: Optical Microstructures NF 709 Mid-Wall

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Figure D-19: EDAX Analysis of Deposit/Scale/Metal Interface for NF 709 (Sample J-K)

Area	Description	Visual Appearance	Ni	Cr	Fe	Cu	Mn	Nb	Ti	Al	Si	C	O	Ca	K	Cl	As	P	S
1	Bulk deposit analysis	Particulate deposit	0.77	--	6.11	--	--	--	0.52	6.23	13.1	28.4	32.1	0.57	1.75	0.28	6.76	1.63	1.78
2	Layer within deposit/scale.		69.0	0.70	0.61	--	--	--	--	--	--	--	--	--	--	--	--	--	29.7
3	Scale separated from underlying material.		17.7	30.2	14.4	--	--	--	--	--	0.74	--	33.4	--	--	--	--	--	3.56
4	Adherent scale near metal interface.		3.74	52.7	4.20	--	--	--	--	--	0.73	--	37.3	--	--	--	--	--	1.40
5	Adherent scale near metal interface..		4.58	41.5	15.2	--	--	--	--	--	0.68	--	34.4	--	--	--	--	--	3.65
6	Scale immediately adjacent to metal interface	.	1.59	42.2	16.79	--	--	--	--	--	0.74	--	35.0	--	--	--	--	--	3.66
7	Scale immediately adjacent to metal interface	Appears to be in line with adjacent grain boundary.	12.2	38.2	21.7	--	--	--	--	--	0.48	--	23.3	--	--	--	--	--	4.13
8	Scale immediately adjacent to metal interface	Closer to metal. Still in line with grain boundary.	29.6	20.6	29.6	--	--	--	--	--	0.49	--	16.2	--	--	--	--	--	3.36

Figure D-19 (Cont.): EDAX Analysis of Deposit/Scale/Metal Interface for NF 709 (Sample J-K)

Area	Description	Visual Appearance	Ni	Cr	Fe	Cu	Mn	Mo	Ti	Al	Si	C	O	Ca	K	Cl	As	P	S
9	Grains abutting the metal/scale interface.	Featureless diffusion zone.	28.0	19.4	52.1	--	--	--	--	--	0.16	--	--	--	--	--	--	--	0.32
10	Grains near to but not abutting interface.	Deep etching band.	26.1	22.0	50.3	--	--	1.15	--	--	0.50	--	--	--	--	--	--	--	--
	Bulk base metal per EDAX		25.4	22.1	49.4	--	1.12	1.3	--	0.38	0.28	--	--	--	--	--	--	--	--
	Reference bulk composition.	Per optical spectrograph .	24.8	22.6	48.9	0.04	1.00	1.40	0.035	0.034	0.38	0.03	--	--	--	--	--	0.010	0.002

Appendix E

Analysis of Performance

Test Section A

Fe₃Al / TP 304H

Overview of Results: Fe₃Al / TP 304H

The single Fe₃Al / TP 304H tube sample (B-C) in Test Section A experienced a relatively high rate of metal loss (145 mils per year)*. The reasons for this poor performance seem to be related to loss of the protective Fe₃Al coating at some point during the life of Sample B-C. Once this coating was gone, only TP 304H tube material remained, and the tube performance at that point would be related to the resistance of 304H to wastage. It seems likely from comparing metal losses with the other tube materials that the Fe₃Al coating provided protection while it was in place; however, at this point it is difficult to say how long it lasted. Further testing to determine the rate of metal loss for 304H would help establish this. However, considering the initial thin layer of coating, and its' "spotty" initial condition, (see Figure E-12a), it is likely that the coating failed to provide protection early-on.

Once again, analysis of deposit on the surface revealed that it had the known aggressive combination of species, namely iron, oxygen, the alkali metals, and sulfur. Examination and analysis of the scale adjacent to the metal surface also revealed the chalky-white appearance associated with alkali-iron-sulfates.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: Fe₃Al / TP 304H

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">The schematic in Figure E-1 shows the position of Fe₃Al / TP 304H sample in Test Section A. Also, shown is the calculated average metal temperature at this location.
Composition Verification.	<ul style="list-style-type: none">The table in Figure E-2 provides the composition of tube Sample B-C after exposure. A concerted effort was made to find and analyze the composition of the iron-aluminide coating on the “after service” samples, but after exposure, it was nowhere to be found on the surface of Sample B-C. It is assumed that the coating either spalled-off or was corroded away from the surface at some point during exposure in Test Section A.The table in Figure E-2 provides EDAX analyses of the Fe₃Al coating prior to service. Numerous samplings were made and found to be highly variable. The reported results are for material at the extreme outer surface. A bulk analysis was also attempted and reported. The significance of deviations from the target chemistry is unclear.Examination of the composition of Sample B-C reveals that it compares well with the specified limits of the ASME SA 213 TP304H specification, and at this point should be considered as such.
As-Received Appearance	<ul style="list-style-type: none">Figure E-3 shows the appearance of the surface of the Fe₃Al coated tube prior to service.Figure E-4 documents the appearance of the external surface of Sample B-C after service. Three views are provided for this tube: 12 o’clock (the view that faces on-coming gas flow), 3 o’clock (the view where the gas flow is tangent to the surface), and 6 o’clock (the view that shows the back-side of the tube relative to the gas flow direction).Wastage is visible at the 12 o’clock position for Sample B-C.A relatively thick rust-red back-side scale and deposit build-up is seen at the 6 o’clock position on Sample B-C.A relatively thin red-brown deposit is seen on all other surfaces.The gray/white scale associated with molten alkali-iron sulfate attack is somewhat visible at the left centerline at 3 o’clock in Figure E-4.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">Figure E-5 shows the appearance of the external surface of the Fe₃Al / TP 304H tube samples after grit-blasting to remove deposit and scale. The 12 o’clock and 3 o’clock positions clearly show the appearance of general wastage due to fireside corrosion.The 6 o’clock position shows very little evidence of attack.

Material: **Fe₃Al / TP 304H**

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss, Continued	<ul style="list-style-type: none">• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure E-7 plots the maximum wall thickness lost against the calculated average metal temperature for Sample B-C.• Obviously, no trends can be determined as there is only one data point. However, it should be noted that the maximum rate of metal loss of 145 mils per year at 1139 °F compares well with the performance of NF 709 which demonstrated a maximum rate of metal loss of 136 mils per year at 1142 °F. The fact that these performed similarly suggests that the Fe₃Al coating provided some level of protection before the coating was lost. This is deduced from the fact that NF 709 is more highly alloyed than the TP 304H and therefore should have performed better.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample B-C was subjected to a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.• Figure E-8 shows the appearance of the tube profile in the section containing the minimum wall thickness. An approximately 10 mil thick deposit/scale is noted on the external surface. A scale as thick as 7 mils was also found on the internal surface.• Figure E-9a, b and c show secondary electron images (SEI) of the external surface. There is no clear evidence of an adherent protective chromium-rich scale on this surface. Instead wastage appears to be progressing by separating of individual grains away from the surface through a grain boundary mechanism. This is most clearly shown in Figure E-9b. It is also shown to some extent in the back scattered electron image provided in Figure E-10. In this case, a grain appears to be suspended above the surface as it is carried up into the scale. This can be seen above and to the left of, and above, the number “4” in this figure.• The numbered locations in Figure E-10 show the locations of the EDAX analyses that follow.• Figure E-11 shows the appearance of the internal metal surface for Sample B-C. Local penetrations into the surface are observed as are penetrations along grain boundaries.

Material: Fe₃Al / TP 304H

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – Light Optics.	<ul style="list-style-type: none">• Figure E-12a shows the condition of the Fe₃Al coating prior to service. It can be seen that this coating is roughly 2 mils thick on average, but at some locations (i.e. near the middle of the image) it is completely missing.• Figures E-12b shows the microstructure of the tube sample near mid-wall. This highly is as would be expected for TP 304H.
EDAX Analysis Results	<ul style="list-style-type: none">• The table in Figure E-13 provides a summary of the EDAX analyses of the locations numbered in Figure E-10. Also shown in this table is an EDAX analysis near mid-wall of the tube, and a summary of the spectrographic analysis reported earlier, see Figure E-2.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Area 1: For the bulk deposit analysis</u> – Alkali metals are present. Sulfur and phosphorous are present in an increased amount compared to the base metal. An iron oxide is likely, as are aluminum, silicon and titanium oxides. The reported analysis suggests a relatively high carbon content for the deposit; however, as is discussed elsewhere, the EDAX is not reliable for carbon in general, and for this region in particular.• <u>Area 2: Scale adjacent to the interface</u> – this scale appears to be comprised of iron-, chromium-, and nickel-rich oxides. Also of significance here is the presence of sulfur and potassium, both of which are constituents of the alkali-iron-sulfate known to be a particularly aggressive agent.• <u>Area 3: in a grain that appears to be separated from the surface</u> – This separated grain is very similar to the bulk deposit chemistry.• <u>Area 4: in a grain that abuts the scale/metal interface</u> – this analysis suggests some loss of chromium, but otherwise it also is very similar to the bulk EDAX analysis.• <u>The bulk metal analysis</u> – is fairly consistent with the spectrographic analysis of the same material, see Figure E-2 if additional detail is desired.

Figure E-1: Schematic Drawing Showing Position of Fe₃Al Tube Sample Within Test Section A

Note: Drawing shown in same relative orientation as per the actual installation.

Figure E-2 Fe₃Al / TP 304H

Description: Commercially available iron Aluminide alloy (FAS) electrospark discharge coated onto Type 304H stainless steel (roughly 30 to 60 mils thick)..

Source: FAS developed by Oak Ridge National Laboratory (ORNL), applied by Pacific Northwest National Laboratory (PNNL)

Reference Composition: “Target” chemistry for coating – per Reference 1.

Element	Reference Composition of Coating	Composition (a) Heat 17433	EDAX of Coating at Outer Surface	EDAX of Bulk Coating		Element	Reference Composition SA 213 TP 304H	Tube Sample B-C
Ni	-	<0.01	1.22	3.99		Ni	8.00-11.0	8.51
Cr	2.19	1.59	3.92	10.8		Cr	18.0-20.0	18.8
Fe	Balance	-	79.5	67.8		Fe	-	69.4 (b)
Mo	-	0.01	-	-		Mo	-	0.42
Co	-	<0.01	-	-		Co	-	0.030
C	-	0.008	-	-		C	0.04-0.10	0.051
N ₂	-	0.001	-	-		N ₂	-	0.064
B	0.011	0.010	-	-		B	-	<0.001
Mn	-	<0.01	-	1.34		Mn	2.00 max	1.77
Si	-	<0.01	-	-		Si	0.75 max	0.37
Al	15.93	15.79	11.7	5.22		Al	-	0.007
Ti	-	-	-	-		Ti	-	0.002
Al+Ti	-	-	-	-		Al+Ti	-	-
Nb	-	<0.01	3.65	10.8		Nb	-	0.006
Ta	-	-	-	-		Ta	-	0.007
Mo	-	-	-	-		Nb+Ta	-	-
V	-	<0.01	-	-		V	-	0.047
W	-	-	-	-		W	-	0.028
Cu	-	-	-	-		Cu	-	0.17
Sn	-	-	-	-		Sn	-	0.006
P	-	-	-	-		P	0.040 max	0.029
S	-	0.002	-	-		S	0.030 max	0.001

a – Reported analysis of wire used in deposition process by PNNL.

b- By difference.

Figure E-3: Appearance of Fe₃Al Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure E-4 As-Received Appearance of Sample B-C (Fe_3Al)

(Average surface metal temperature: 1139 °F)

12 O’Clock
(79 mils lost)

3 O’Clock
(83 mils lost)

6 O’Clock
(7 mils lost)

Figure E-5: OD Surface Appearance After Grit Blast

Material: **Fe₃Al**
Sample: **B-C**

Material:

Fe₃Al

Sample Location:

B-C

Maximum Rate:

145 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average Surface Metal Temperature:

1139 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.395	0.395	0.394	0.392	0.392	0.392	0.393	0.394	0.393	0.394
After	0.316	0.255	0.311	0.355	0.385	0.383	0.378	0.207	0.324	0.207
Delta	0.079	0.14	0.083	0.037	0.007	0.009	0.015	0.187	0.070	0.187

Figure E-6: Silhouette and Wall Thickness Measurements for Sample B-C

Figure E-7: Metal Loss as a Function of Average Surface Metal Temperature

Material: Fe_3Al

Figure E-8: Low Magnification Image Showing Cross-Section Through Thinnest Region of Sample B-C (Fe_3Al / TP 304H)

Note: The Fe_3Al coating was completely missing from the sample surface after service exposure.

Note: 1) Numbers indicate distinct areas characterized by the visual assessment and EDAX analyses that follow.

Figure E-9: Microstructure: Fe₃Al / TP 304H

(c) External Scale/Metal Interface (SEI - High Magnification)

Figure E-9 (Cont.): Microstructure: Fe₃Al / TP 304H

Note: 1) Numbers indicate distinct areas characterized by the visual assessment and EDAX analyses that follow.

Figure E-10: Microstructure: Fe_3Al / TP 304H

Figure E-11: Microstructure: Fe_3Al / TP 304H

(a) Sample B-C

This photograph shows the as-deposited Fe_3Al layer before it was put into service. Approximate thickness: 0.002-in. None of this coating remained on the surface after exposure in service.

(b) Sample B-C (1139°F)

This photograph shows the microstructure in the underlying TP 304H stainless steel.

Figure E-12: Optical Microstructures Fe_3Al

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Figure E-13: EDAX Analysis of Deposit/Scale/Metal Interface for Fe₃Al / TP304H (Sample B-C)

Area	Description	Visual Appearance	Ni	Cr	Fe	Cu	Mn	W	Ti	Al	Si	C	O	Ca	K	Na	As	P	S
1	Bulk deposit analysis	Rust red deposit marbled with spherical particles.	--	--	8.63	--	--	--	0.59	6.33	13.4	24.9	22.5	0.64	2.90	1.10	2.50	0.99	4.53
2	Adherent chromium-oxide scale.		6.72	20.0	33.9	--	1.48	--	--	--	0.42	4.49	30.2	--	0.16	--	--	--	2.59
3	In grain separated from surface.	Grain boundary attack caused separation.	8.36	18.2	71.2	--	1.99	---	--	--	0.26	--	--	--	--	--	-	--	--
4	In grain abutting metal/ scale interface.		7.91	15.0	74.6	--	2.43	--	--	--	--	--	--	--	--	--	--	--	--
	Bulk EDAX analysis.		9.25	18.5	70.2	--	1.89	--	--	--	0.22	--	--	--	--	--	--	--	--
	Reference analysis		8.51	18.8	69.4	0.17	1.77	0.028	0.002	0.007	0.37	0.05	--	--	--	--	--	0.029	0.001

Appendix F
Analysis of Performance
Test Section A
310 Ta

Overview of Results: 310 Ta

Type 310 Ta experienced a high rate of metal loss at all three locations. These ranged from 120 mils per year to 136 mils per year*. This poor performance is consistent with that of those other alloys having approximately 20% to 25% chromium. It is also noteworthy that, based on iron content, the total alloy content for this material is intermediate to some of the poorly performing materials (i.e. 44% Fe for modified 800H, 49% Fe for NF 709, **51% Fe for 310 Ta**, 51% Fe for Save 25, , 65% Fe for 347 HFG) but perhaps much less than those that performed well (i.e. 9% for IN52, 2% for Thermie, 2% IN72, and <1% for Inconel 671).

Examination of the three 310 Ta samples revealed that metal loss was fairly consistent over the three locations; however, it appeared to peak at the intermediate temperature. The significance of this is unclear.

Analysis of deposit on the surface revealed that it had the known aggressive combination of species, namely iron, oxygen, the alkali metals, and sulfur. The presence of significant amounts of arsenic was unexpected, but consistent with the other samples tested. Examination and analysis of the scale adjacent to the metal surface revealed the chalky-white appearance associated with Alkali-iron-sulfates. Furthermore high sulfur was consistently indicated in this area.

Finally, the analysis of the deposit and the metal surface immediately adjacent to the interface revealed the presence of carbon. While carbon determinations using EDAX are unreliable, the implications of carbon in the deposit are worthy of additional consideration, as is the potential for carbon ingress from the deposit into the abutting metal.

* **Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: 310 Ta

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">The schematic in Figure F-1 shows the relative positions of 310 Ta samples in Test Section A. Also, shown is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">The table in Figure F-2 provides the composition of the three tube samples after exposure. Samples F-G and M-N were taken from the same heat, Heat 17425. Sample X-Y was taken from Heat 17426. No significant composition differences were noted between these heats.The table also shows the “target” composition as reported by ORNL. Composition limits were not provided; however, taken at face value, it is noted that the levels of chromium, manganese, and tantalum fell somewhat short of their target values. The significance of these deviations is not known.
As-Received Appearance	<ul style="list-style-type: none">Figure F-3 shows the typical appearance of the 310 Ta samples as delivered by ORNL.Figures F-4 through F-6 document the appearance of the external surface for all three samples after service exposure. Three views are provided for each tube: 12 o’clock (the view that faces on-coming gas flow), 3 o’clock (the view where the gas flow is tangent to the surface), and 6 o’clock (the view that shows the back-side of the tube relative to the gas flow direction).Wastage is visible at the 12 o’clock and 3 o’clock positions for all three samples, as was a relatively thick red-brown deposit/scale.A relatively thick rust-red back-side scale and deposit build-up is seen at the 6 o’clock position for Sample X-Y.A relatively thin red-brown deposit is seen covering other surfaces.Small areas of gray/white scale are visible in areas where the outer deposit/scale has fallen away, (such as near the center-line at the 12 o’clock position for sample X-Y, Figure F-6). This scale has been associated with molten alkali-iron sulfate attack. If the remainder of the deposit were removed, then it is anticipated that one would find a significant amount of gray/white scale immediately adjacent to the metal surface.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">Figures F-7 through F-9 show the appearance of the external surface of the 301 Ta tube samples after grit-blasting to remove deposit and scale. The 12 o’clock and 3 o’clock positions for all three samples show the appearance of general wastage due to fireside corrosion.The 6 o’clock position for Sample F-G shows that significant pitting occurred on the back-side. A 10 mil deep pit accounted for all of the wall reduction at the 6 o’clock measurement location.

Material: 310 Ta

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures F-10 through F-12.• The same relative “o’clock” positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost. Note that, in some cases, the delta is negative (for example at the 6 o’clock position in Sample M-N). This is believed due to wall thickness variability and difficulty in locating the exact location of the “before” measurement.• In some cases, the minimum wall thickness in the cross section was not at one of the eight predetermined locations, (Samples M-N and X-Y). In these cases, there was no “before” measurement for comparison. So, the average “before” wall thickness was used to calculate the wall thickness lost at these off-locations.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure E-13 plots the maximum wall thickness lost against the calculated average metal temperature for the three 310 Ta samples.• This shows that 310 Ta experienced a high rate of metal loss at all three locations, ranging from 120 mils per year in Sample X-Y to 136 mils per year in Sample F-G.• If wastage were to continue at this rate, then, given an initial wall thickness of 400 mils, and after 36 months of exposure, the full wall thickness would be gone at position F-G, and only 10% of the wall would remain at position X-Y.• Since 310 Ta remains in these positions in both Test Sections B and C, these should be examined in advance of the 36 month exposure period to verify the wall thickness.• It is also noted that, similar to the modified 800H candidate material, 310 Ta exhibited an accelerated rate of wastage at the intermediate temperature. The significance of this is unclear.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample F-G was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it had lost the most wall thickness of all of the 310 Ta samples. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.

Material: 310 Ta

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">Figure F-14 shows the appearance of the tube profile in the section containing the minimum wall thickness for Sample F-G. Note that the external surface scale/deposit thickness is highly variable. In general, there is very little deposit/scale evident on the external tube surface, but in image shown the maximum thickness of the deposit/scale is about 30 mils. Otherwise, the maximum adherent scale thickness is about 5 mils. No scale is evident on the internal surface at this magnification.Figures F-15a, b, and c show the secondary electron images of the scale/metal interface for Sample F-G. Six distinct regions are in evidence. These regions are, starting within the metal and working out:<ol style="list-style-type: none"><u>Base metal</u> – oxalic acid etch delineates grain boundaries, slip bands, inclusions and precipitates.<u>Deeply etching base metal</u> – this region is obvious as a light-appearing band that is parallel to the metal surface, perhaps see most clearly in Figure F- 15a. Figure F- 15b shows that this band is approximately one-half grain wide, and affects only those grains contiguous with the surface. This likely reflects composition differences due to diffusion in this region.<u>Featureless grain surface</u> – This constitutes the leading edge of the grains as they interface with the scale. This is clearly shown in the grains adjacent to the scale/metal interface in Figures F-15b and F-15c. As EDAX analysis later shows that this zone seems related to diffusion of alloying elements both into and out of the metal surface as scale formation progresses. Perhaps the most significant of these is the suggested potential for chromium egress and carbon ingress in this region. (see the composition for Area 7 in the table that follows.<u>Adherent scale</u> – this is seen more or less continuous along the surface. EDAX analysis will later show that this scale is likely a chromium-, iron- and nickel-rich oxide. The adherent scale is approximately 0.7 mils thick.<u>Scale with embedded deposit</u> – This scale characteristic occurs as oxide grows out from the metal surface and envelops the coal ash deposit that is attached to the surface. The region number “2” in Figure 15-a shows the appearance of this scale.<u>Thick and very porous deposit/scale conglomerate</u> – many spherical particles are noted along with what appears to be islands of scale (metal oxides).Figures F-15a and F-15c show numbered positions where EDAX analyses were performed to characterize the materials in the vicinity of the scale/metal interface.

Summary of Findings, (continued)

Material: 310 Ta

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none"> Figure F-16 shows the appearance of the internal metal surface for Sample F-G. An extremely thin oxide scale is noted to cover the surface.
Metallurgical Analysis – Light Optics.	<ul style="list-style-type: none"> Figures F-17a, b, c, and d show the appearance of the mid-wall microstructure for each of the tube samples these all are similar to one another having highly defined grain boundaries with “clouds” of precipitates in local regions along the boundaries. The tube/scale interface was examined for both the internal and external surfaces on all three 310 Ta tube samples. No evidence of grain boundary penetration was found at either surface.
EDAX Analysis Results	<ul style="list-style-type: none"> The table in Figure F-18 provides a summary of the EDAX analyses of the locations numbered in Figure F-15a and F-15c. Also shown in this table is the EDAX analysis of the bulk deposit, an EDAX analysis near mid-wall of the tube, and a summary of the spectrographic analysis reported earlier, see Figure F-2. Review of this table suggests the following: <ul style="list-style-type: none"> <u>Area 1: For the bulk deposit analysis</u> – Alkali metals are present. Sulfur and phosphorous are present in an increased amount compared to the base metal. An iron oxide is likely, as are aluminum, silicon and titanium oxides. Carbon content is relatively high, however, EDAX is not reliable quantitatively, in general, and qualitatively in this specific instance due to the potential for pick-up of the epoxy resin mounting compound. <u>Area 2: Deposit with imbedded particles</u> - The analysis here was similar to that of the bulk deposit except that carbon is no longer present and the iron content is significantly increased. <u>Area 3: Scale separated from underlying metal</u> – This is predominantly a chromium-rich scale having a significant sulfur content. <u>Areas 4 and 5: Tightly adhering scale</u> – This scale immediately adjacent to the metal/scale is iron-, chromium-, and nickel-rich. Also, of significance is the relatively high level of sulfur in this region. <u>Area 6: Particle embedded in tightly adhering scale</u> – The EDAX analysis is suggestive of a tantalum oxide. <u>Area 7: Grains abutting the scale/metal interface</u> – This region is less than one grain boundary wide. The results of the analysis suggests that this is a diffusion zone that is depleted in chromium and enriched in carbon. Again, the reader is cautioned regarding the accuracy of carbon analyses by EDAX; however, it should be noted that the lack of carbon in the bulk analysis seems to confirm that this is a region of higher content than elsewhere.

Figure F-2 Type 310 Ta

Description: 20-25 Cr steel with improved creep strength due to addition of tantalum and nitrogen
Source: Oak Ridge National Laboratory (ORNL)
Reference Composition: “Target” Chemistry per ORNL (Reference 1).

Element	Reference Composition	Composition Heat 17425	Composition Heat 17426	Composition Heat 17431	Tube Sample F-G	Tube Sample M-N	Tube Sample X-Y
Ni	21.0	21.63	21.08	21.12	21.49	21.47	21.49
Cr	24.5	23.74	23.78	24.01	24.16	24.16	24.21
Fe	Balance	Balance	Balance	Balance	51.0	51.0	50.9
Mo	-	<0.01	<0.01	<0.01	(a)	(a)	(a)
Co	-	0.02	0.02	0.02	(a)	(a)	(a)
C	0.05	0.063	0.063	0.060	0.062	0.063	0.062
N	0.22	0.22	0.22	0.24	0.22	0.22	0.22
B	0.005	(a)	(a)	(a)	0.007	0.007	0.008
Mn	2.00	1.74	1.66	1.89	1.68	1.68	1.68
Si	0.25	0.25	0.24	0.27	0.24	0.24	0.23
Al	-	<0.01	<0.01	<0.01	(a)	(a)	(a)
Ti	-	<0.01	<0.01	<0.01	(a)	(a)	(a)
Nb	-	<0.01	<0.01	<0.01	(a)	(a)	(a)
Ta	1.75	1.18	1.03	1.24	1.11	1.12	1.13
Nb+Ta	-	-	-	-	-	-	-
V	-	<0.01	<0.01	<0.01	(a)	(a)	(a)
W	-	-	-	-	-	-	-
Cu	-	<0.01	<0.01	<0.01	(a)	(a)	(a)
Sn	-	-	-	-	-	-	-
P	-	0.008	0.009	0.013	(a)	(a)	(a)
S	-	0.006	0.006	0.006	(a)	(a)	(a)
O2	-	0.013	0.014	0.018	(a)	(a)	(a)

- a- Not analyzed.
b- By difference.

Reference 1: “Fabrication of Test Tubes for Coal Ash Corrosion Testing”, Sikka, V.K., Swindeman, R.W., Wright, I.G., Judkins, R.R., Johnson, R., Proc, 13th Annual Conf. on Fossil Energy Mat’ls, May 1999.

Sample F-G and M-N were from Heat 17425
Sample X-Y was from Heat 17426

Figure F-3: Appearance of 310 Ta Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure F-4 As-Received Appearance of Sample M-N (310 Ta)

(Average surface metal temperature: 1178°F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure F-5 As-Received Appearance of Sample F-G (310 Ta)

(Average surface metal temperature: 1154 °F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure F-6 As-Received Appearance of Sample X-Y (310 Ta)

(Average surface metal temperature: 1092 °F)

12 O’Clock
(68 mils lost)

3 O’Clock
(93 mils lost)

6 O’Clock
(0 mils lost)

Figure F-7: OD Surface Appearance After Grit Blast

Material: 310 Ta
Sample: M-N

12 O’Clock
(60 mils lost)

3 O’Clock
(87 mils lost)

6 O’Clock
(10 mils lost)

Figure F-8: OD Surface Appearance After Grit Blast

Material: 310 Ta
Sample: F-G

12 O’Clock
(69 mils lost)

3 O’Clock
(38 mils lost)

6 O’Clock
(0 mils lost)

Figure F-9: OD Surface Appearance After Grit Blast

Material: 310 Ta
Sample: X-Y

Material: 310 Ta

Sample Location: M-N

Maximum Rate: 123 mils/yr

Maximum Loss Orientation: Approx. 10 o'clock

Average Surface Metal Temperature: 1178°F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.399	0.400	0.400	0.401	0.400	0.399	0.399	0.400	0.400	0.400
After	0.331	0.322	0.307	0.336	0.401	0.402	0.401	0.263	0.345	0.242
Delta	0.068	0.078	0.093	0.065	-0.001	-0.003	-0.002	0.137	0.054	0.158

Figure F-10: Silhouette and Wall Thickness Measurements for Sample M-N

Material: 310 Ta

Sample Location: F-G
Maximum Rate: 136 mils/yr
Maximum Loss Orientation: Approx. 10:30 o'clock
Average Surface Metal Temperature: 1154 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.401	0.402	0.403	0.402	0.401	0.401	0.400	0.399	0.401	0.399
After	0.341	0.347	0.316	0.367	0.391	0.401	0.401	0.250	0.352	0.224
Delta	0.060	0.055	0.087	0.035	0.010	0.000	-0.001	0.149	0.048	0.175

Figure F-11: Silhouette and Wall Thickness Measurements for Sample F-G

Material: 310 Ta

Sample Location: X-Y

Maximum Rate: 120 mils/yr

Maximum Loss Orientation: Approx. 10 o'clock

Average Surface Metal Temperature: 1092 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.401	0.401	0.400	0.400	0.400	0.400	0.400	0.401	0.400	0.400
After	0.332	0.371	0.362	0.400	0.400	0.400	0.319	0.270	0.357	0.245
Delta	0.069	0.030	0.038	0.000	0.000	0.000	0.081	0.131	0.044	0.155

Figure F-12: Silhouette and Wall Thickness Measurements for Sample X-Y

Figure F-13: Metal Loss as a Function of Temperature

Material: 310 Ta

Figure F-14: Low Magnification Image Showing Cross-Section Through Thinnest Region of Sample F-G (310 Ta)

Figure F-15: Microstructure: 310 Ta

(c) External Scale/Metal Interface (SEI - High Magnification)

Figure F-15 (Cont.): Microstructure: 310 Ta

Note: 1) Numbers on photos indicate distinct areas characterized by the visual assessment and EDAX analyses that follow.

Internal Surface Appearance

Figure F-16: Microstructure: 310 Ta

(a) Sample M-N (1178°F)

(b) Sample F-G (1154°F)

Figure F-17: Optical Microstructures 310 Ta Mid-Wall

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

(b) Sample X-Y (1092 °F)

Figure F-17 (Cont.): Optical Microstructures 310 Ta Mid-Wall

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Figure F-18: EDAX Analysis of Deposit/Scale/Metal Interface for 310 Ta (Sample F-G)

Area	Description	Visual Appearance	Ni	Cr	Fe	Cu	Mn	Ta	Ti	Al	Si	C	O	Ca	K	Na	As	P	S
1	Bulk deposit analysis	Rust red deposit with spherical particles.	6.00	--	22.3	--	--	--	0.42	4.39	7.58	12.6	36.3	2.27	1.62	--	2.87	0.95	2.66
2	Fused deposit with embedded particles.		9.03	--	44.1	--	--	--	0.34	3.02	5.29	--	35.4	--	0.44	--	--	2.02	0.32
3	Scale separated from underlying material.		4.41	40.9	5.51	--	--	--	--	0.29	0.82	--	41.9	0.24	1.96	--	--	--	3.94
4	Tightly adhering scale.		11.4	23.6	28.3	--	--	--	--	--	0.69	--	35.6	--	--	--	--	--	0.34
5	Tightly adhering scale.	Immediately adjacent to metal.	14.2	25.9	28.3	--	1.51	--	--	0.37	0.94	--	26.5	--	--	--	--	--	2.34
6	Particle in adhering scale.		1.68	2.91	5.88	--	5.83	59.4	--	--	--	--	24.3	--	--	--	--	--	--
7	Grains abutting interface.		22.5	17.7	52.4	--	1.27	1.50	--	--	--	4.67	--	--	--	--	--	--	--
	Bulk EDAX analysis.		21.2	23.1	51.1	--	2.11	2.49	--	--	--	--	--	--	--	--	--	--	--
	Reference bulk analysis.		21.0	24.7	51.2	--	1.72	0.73	--	0.002	0.24	0.07	--	--	--	--	--	0.003	0.007

Appendix G
Analysis of Performance
Test Section A
310 HCbN (HR3C)

Overview of Results: 310 HCbN (HR3C)

While it tested better than a number of materials in this study, the 310 HCbN samples experienced a high rate of metal loss at all locations in Test Section A, with the maximum being 133 mils per year*.

While its' overall performance was poor, it can be stated that 310 HCbN appeared to have performed somewhat better than other candidate materials having approximately the same level of chromium (26%) and total alloy content (50% Fe). It is speculated that the relatively small grain size for this material may have facilitated chromium diffusion to form and maintain the protective scale.

No trends could be identified to correlate the rate of metal loss with the average service temperature. High corrosion rates were experienced at both higher and lower temperatures (133 mils per year at 1157 °F for Sample G-H) and (129 mils per year at 1081 °F for Sample AA-BB).

Analysis of deposit on the surface revealed that it had the known aggressive combination of species, namely iron, oxygen, the alkali metals, and sulfur. Examination and analysis of the scale adjacent to the metal surface revealed the chalky-white appearance associated with alkali-iron-sulfates. Thus, the required corrosive constituent was available to test the performance limits of this alloy.

Finally, the analysis of the deposit and the metal surface immediately adjacent to the interface revealed the presence of carbon. While carbon determinations using EDAX are unreliable, the implications of carbon in the deposit are worthy of additional consideration, as is the potential for carbon ingress from the deposit into the abutting metal.

* **Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: 310 HCbN (HR3C)

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• The schematic in Figure G-1 shows the relative positions of 310 HCbN samples in Test Section A. Also, shown is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• The table in Figure G-2 provides the composition of the three tube samples after exposure. All four samples were taken from a single heat of material, Heat D8A0809. The table also shows the specified composition and ladle analysis as reported on the Sumitomo mill certificate that accompanied the material.• It was noted that the actual tube sample composition compared well with the ladle analysis, and that all were consistent with the specified composition.
As-Received Appearance	<ul style="list-style-type: none">• Figure G-3 shows the typical appearance of 310 HCbN sample on receipt from Sumitomo.• Figures G-4 through G-7 document the as-received appearance of the external surface of the Save 25 tube samples. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).• Wastage was visible at the 12 o'clock for all four samples; however, it was obscured to some extent by deposit on those surfaces..• A relatively thick rust-red back-side scale and deposit build-up is seen at the 6 o'clock position on Samples W-X and AA-BB. The backside positions of Samples G-H and N-O were relatively free from deposit.• Also seen at the 6 o'clock position for Sample W-X and AA-BB is evidence of a chalky gray/white deposit in an area where the deposit has flaked away from the surface. It is anticipated that this deposit would be pervasive immediately adjacent to the scale/metal interface everywhere on the 310 HCbN samples, and that it readily would be visible if the outer deposit were stripped away. This of course is consistent with molten alkali-iron-sulfate accelerated attack.• A relatively thick red-brown deposit is seen at all of the 12 and 6 o'clock surfaces.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures G-8 through G-11 show the appearance of the external surface of the 310 HCbN tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for all four samples show the appearance of general wastage due to fireside corrosion.• The 6 o'clock position was unaffected for all four samples, and exhibited little or no wastage at this surface.

Material: 310 HCbN (HR3C)

Summary of Findings, (continued)

Issue	Discussion
Grit-Blasted Surface Appearance, Continued	<ul style="list-style-type: none">Also of note in viewing these grit blasted surfaces is that the surface contour is highly variable in those regions of excessive attack. .
Wall Thickness Loss Determined	<ul style="list-style-type: none">Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures G-12 through G-15.The same relative “o’clock” positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost. Note that in some cases, the delta is negative (particularly on the back-side, 6 o’clock position). This is believed due to wall thickness variability and difficulty in locating the exact location of the “before” measurement.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">The chart in Figure G-16 plots the maximum wall thickness lost against the calculated average metal temperature for each of the four 310 HCbN samples.From this chart it can be seen that the metal loss rate was high in all four tube samples.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">Sample G-H was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it had lost the most wall thickness of all of the 310 HCbN samples. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.Figure G-17 shows the appearance of the tube profile in the section containing the minimum wall thickness for Sample G-H. Note a scale/deposit on the external surface of variable thickness. This ranged from approximately 2 to 20 mils in thickness. No scale is evident on the internal surface at this magnification.

Material: 310 HCBN (HR3C)

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">• Figures G-18a, b, c and d, show the secondary electron images of the scale/metal interface for Sample G-H. Six distinct regions are in evidence. These regions are, starting within the metal and working out:<ol style="list-style-type: none">1. <u>Base metal</u> – oxalic acid etch delineates grain boundaries and carbides.2. <u>Deeply etching base metal</u> – this region is obvious as a light-appearing band that is parallel to the metal surface, perhaps see most clearly in Figure G-18a. Figure G- 18b shows that this band is approximately two grains wide, and affects only those grains close to the surface. This likely reflects composition differences due to diffusion in this region.3. <u>Featureless grain surface</u> – This constitutes the leading edge of the grains as they interface with the scale. As EDAX analysis later shows that this zone seems related to diffusion of alloying elements both into and out of the metal surface as scale formation progresses. Perhaps the most significant of these is the suggested potential for carbon ingress in this region. (see the composition for Area 5 in the table that follows.4. <u>Tightly adhering scale</u> – this is seen continuous along the surface. EDAX analysis will later show that this is predominantly chromium-oxide. The scale is approximately 4 mils thick.5. <u>Loosely adhering scale with imbedded deposit</u> – This characteristic is inferred from the fact that the spherical components of the outer deposit appear to be imbedded in a continuous layer of solid material. This is perhaps best shown in the View provided in the back scattered electron image (BEI) shown in Figure G-19a (in the region marked with the number “2”.6. <u>Thick and very porous deposit/scale conglomerate</u> – many spherical particles are noted along with what appears to be islands of scale (metal oxides).• Figures G-19a and b show backscattered images (BEI) of the scale/metal interface for Sample G-H. The BEI images provide better resolution of compositional differences. Also, noted on Figure G-19a are the five locations selected for EDAX analysis. The results of these follow• Figure G-20 shows the appearance of the internal metal surface for Sample G-H. Little if any oxide scale is visible at this surface. The observed porosity along the internal surface was confirmed to be due to an etching effect in that no porosity was observed in the as-polished condition.

Summary of Findings, (continued)

Material: 310 HCbN (HR3C)

Issue	Discussion
Metallurgical Analysis – Light Optics.	<ul style="list-style-type: none">Figures G-21a, b, c, and d show the appearance of the mid-wall microstructure for each of the tube samples. Examination of these reveals them to be similar in terms of grain size and level of precipitation.The external and internal surfaces were examined for all four 310 HCbN samples. No evidence of grain boundary penetration or other irregularities was noted.
EDAX Analysis Results	<ul style="list-style-type: none">The table in Figure G-22 provides a summary of the EDAX analyses of the locations numbered in Figure G-19a. Also shown in this table is an EDAX analysis near mid-wall of the tube, and a summary of the spectrographic analysis reported earlier, see Figure G-2.Review of this table suggests the following:<ul style="list-style-type: none"><u>Area 1: For the bulk deposit analysis</u> – Alkali metals are present. Sulfur and phosphorous are present in an increased amount compared to the base metal. An iron oxide is likely, as are aluminum, silicon and titanium oxides. Carbon content is relatively high, however, EDAX is not reliable quantitatively, in general, and qualitatively in this specific instance due to the potential for pick-up of epoxy resin mounting compound.<u>Area 2: Scale with embedded particles</u> – This appears to be an iron-, chromium-, nickel-rich oxide. Also significant is the presence of sulfur in this layer.<u>Areas 3 and 4: Tightly adhering scale</u> – This scale is predominantly a chromium-rich oxide. Once again a relatively high level of sulfur is noted adjacent to the surface.<u>Area 5: Grains abutting the scale/metal interface</u> – These are similar in composition to the bulk analysis with the exception that a high carbon level is indicated.

Figure G-1: Schematic Drawing Showing Position of 310 HcBn (HR3C) Tube Samples Within Test Section A

Note: Drawing shown in same relative orientation as per the actual installation.

Figure G-2 Composition 310 HCbN (HR 3C)

Description: Nominal 25Cr/20Ni steel with Nb, Ta, and N added to provide creep strength.
Source: Sumitomo Metal Industries (SMI)
Reference Composition: “Specified” chemistry – ASTM A213 (TP310 HCbN).

Element	Reference Composition	Composition (a) Heat D8A0809	Tube Sample G-H	Tube Sample N-O	Tube Sample W-X	Tube Sample AA-BB
Ni	17.00-23.00	19.97	19.91	20.01	19.97	19.93
Cr	24.00-26.00	25.61	25.95	26.01	25.98	26.00
Fe	Balance	Balance	50.52 (b)	50.40 (b)	50.45 (b)	50.51 (b)
Mo	-	-	0.11	0.11	0.11	0.10
Co	-	-	0.40	0.40	0.40	0.40
C	0.04-0.10	0.05	0.067	0.068	0.067	0.065
N	0.15-0.35	0.24	0.25	0.25	0.25	0.25
B	-	-	0.0015	0.0015	0.0015	0.0014
Mn	2.00 max	1.18	1.20	1.18	1.19	1.19
Si	0.75 max	0.36	0.35	0.33	0.34	0.33
Al	-	-	0.017	0.016	0.016	0.016
Ti	-	-	0.008	0.008	0.009	0.008
Al+Ti	-	-	-	-	-	-
Nb	-	0.47	0.47	0.47	0.47	0.46
Ta	-	(c)	0.090	0.091	0.091	0.091
Nb+Ta	0.20-0.60	0.47	0.560	0.561	0.561	0.551
V	-	-	0.077	0.076	0.076	0.075
W	-	-	<0.001	<0.001	<0.001	<0.001
Cu	-	-	-	-	-	-
Sn	-	-	0.003	0.003	0.003	0.004
P	0.030 max	0.015	0.014	0.015	0.014	0.015
S	0.030 max	(c)	0.001	0.002	0.001	0.002
O2	-	-	-	-	-	-
Others	-	-	-	-	-	-

- a- Ladle analysis.
- b- By difference.
- c- Not detected.

Figure G-3: Appearance of 310 HCBN (HR3C) Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure G-4 As-Received Appearance of Sample N-O (310 HCbN)

(Average surface metal temperature: 1180 °F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure G-5 As-Received Appearance of Sample G-H (310 HCBN)

(Average surface metal temperature: 1157 °F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure G-6 As-Received Appearance of Sample W-X (310 HCbN)

(Average surface metal temperature: 1095 °F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure G-7 As-Received Appearance of Sample AA-BB (310 HCbN)

(Average surface metal temperature: 1081 °F)

12 O'Clock
(53 mils lost)

3 O'Clock
(101 mils lost)

6 O'Clock
(0 mils lost)

Figure G-8: OD Surface Appearance After Grit Blast

Material: 310 HCbN (HR3C)
Sample: N-O

12 O'Clock
(63 mils lost)

3 O'Clock
(95 mils lost)

6 O'Clock
(2 mils lost)

Figure G-9: OD Surface Appearance After Grit Blast

Material: 310 HCbN (HR3C)
Sample: G-H

12 O’Clock
(33 mils lost)

3 O’Clock
(24 mils lost)

6 O’Clock
(0 mils lost)

Figure G-10: OD Surface Appearance After Grit Blast

Material: 310 HCBN (HR3C)

Sample: W-X

12 O’Clock
(78 mils lost)

3 O’Clock
(68 mils lost)

6 O’Clock
(0 mils lost)

Figure G-11: OD Surface Appearance After Grit Blast

Material: 310 HCbN (HR3C)
Sample: AA-BB

Material: 310 HCBN (HR3C)

Sample Location: N-O

Maximum Rate: 108 mils/yr

Maximum Loss Orientation: Approx. 10:30 o'clock

Average Surface Metal Temperature: 1180 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.396	0.398	0.400	0.398	0.398	0.401	0.398	0.397	0.398	0.397
After	0.343	0.323	0.299	0.400	0.402	0.398	0.396	0.258	0.352	0.258
Delta	0.053	0.075	0.101	-0.002	-0.004	0.003	0.002	0.139	0.046	0.139

Figure G-12: Silhouette and Wall Thickness Measurements for Sample N-O

Material:

310 HCBN (HR3C)

Sample Location:

G-H

Maximum Rate:

133 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average Surface Metal Temperature:

1157 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.404	0.398	0.397	0.404	0.403	0.402	0.402	0.400	0.401	0.400
After	0.341	0.324	0.302	0.329	0.401	0.403	0.401	0.228	0.341	0.228
Delta	0.063	0.074	0.095	0.075	0.002	-0.001	0.001	0.172	0.060	0.172

Figure G-13: Silhouette and Wall Thickness Measurements for Sample G-H

Material:

310 HcN (HR3C)

Sample Location:

W-X

Maximum Rate:

98 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average Surface Metal Temperature:

1095 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.399	0.399	0.398	0.398	0.398	0.399	0.398	0.396	0.398	0.396
After	0.366	0.338	0.374	0.398	0.398	0.397	0.398	0.269	0.367	0.269
Delta	0.033	0.061	0.024	0.000	0.000	0.002	0.000	0.127	0.031	0.127

Figure G-14: Silhouette and Wall Thickness Measurements for Sample W-X

Material: 310 HCBN (HR3C)

Sample Location: AA-BB

Maximum Rate: 129 mils/yr

Maximum Loss Orientation: Approx. 10:30 o'clock

Average Surface Metal Temperature: 1081 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.396	0.398	0.400	0.401	0.401	0.398	0.396	0.400	0.399	0.400
After	0.318	0.278	0.332	0.399	0.402	0.399	0.393	0.234	0.344	0.234
Delta	0.078	0.120	0.068	0.002	-0.001	-0.001	0.003	0.166	0.054	0.166

Figure G-15: Silhouette and Wall Thickness Measurements for Sample AA-BB

Figure G-16: Metal Loss as a Function of Average Surface Metal Temperature

Material: 310 HCbN (HR3C)

Figure G-17: Low Magnification Image Showing Cross-Section Through Thinnest Region of Sample G-H (310 HCbN)

Figure G-18: Microstructure: 310 HCbN

(c) External Scale/Metal Interface (SEI - High Magnification)

Figure G-18 (Cont.): Microstructure: 310 HCbN

Note: 1) Numbers on photos indicate distinct areas characterized by the visual assessment and EDAX analyses that follow.

Figure G-19: Microstructure: 310 HCbN

Internal Surface Appearance

Figure G-20: Microstructure: 310 HCBN

(a) Sample N-O (1180°F)

(b) Sample G-H (1157°F)

Figure G-21: Optical Microstructures 310 HCbN (HR3C) Mid-Wall

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

(c) Sample W-X (1095 °F)

(d) Sample AA-BB (1081 °F)

Figure G-21 (Cont.): Optical Microstructures 310 HCBN (HR3C) Mid-Wall

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Figure G-22: EDAX Analysis of Deposit/Scale/Metal Interface for 310 HCbN (HR3C) (Sample G-H)

Area	Description	Visual Appearance	Ni	Cr	Fe	Cu	Mn	Nb	Ti	Al	Si	C	O	Ca	K	Na	As	P	S
1	Bulk deposit analysis	Rust red deposit with spherical particles.	--	--	8.37	--	--	--	0.78	6.06	13.7	22.2	35.1	0.45	2.14	0.48	6.16	1.04	3.57
2	Fused deposit with embedded particles.		10.5	3.96	37.6	--	--	--	--	0.92	6.24	5.21	35.0	--	--	--	--	0.34	0.24
3	Tightly adhering scale.		4.68	46.99	7.04	--	--	--	--	--	0.75	--	39.4	--	0.15	--	--	--	0.93
4	Tightly adhering scale.	Immediately adjacent to metal.	4.16	42.0	15.1	--	--	--	--	--	0.61	--	36.1	--	--	--	--	--	2.04
5	Grains abutting interface.		20.3	25.6	51.4	--	--	--	--	--	--	2.74	--	--	--	--	--	--	--
	Reference bulk analysis.		19.9	26.0	50.5	--	1.20	0.47	0.008	0.017	0.35	0.07	--	--	--	--	--	0.014	0.001

Appendix H
Analysis of Performance
Test Section A
HR 120

Overview of Results: HR 120

HR 120 experienced a high rate of metal loss at two of the three sample positions within Test Section A. The maximum rate was being 109 mils per year* at the DD-EE position in Test Section A.

HR 120 has a chromium content (about 25%) that is similar to other candidate materials that performed poorly. However, its' total alloy content is higher, and perhaps this explains the somewhat better performance of this material relative to the 310-based alloys.

HR 120 was noted to have suffered from boundary penetrations in all three tube samples. This was generally restricted to a depth of one grain diameter. This small loss of material was not taken into account in calculating the metal loss rate as it was mathematically and practically insignificant. It is suggested however that further study of this local attack may yield a better understanding of the performance of this alloy in general and merits further investigation.

Analysis of deposit on the surface revealed that it had the known aggressive combination of species, namely iron, oxygen, the alkali metals, and sulfur. Examination and analysis of the scale adjacent to the metal surface revealed the chalky-white appearance associated with alkali-iron-sulfates. Spectrographic ICP analysis confirmed this. Thus, the required corrosive constituents were available to test the performance limits of this alloy.

Finally, the analysis of the deposit and the metal surface immediately adjacent to the interface revealed the presence of carbon. While one must proceed with caution in interpreting these results, the implications of carbon in the deposit are worthy of additional consideration, as is the potential for carbon ingress from the deposit into the abutting metal.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: HR 120

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">The schematic in Figure H-1 shows the relative positions of the HR 120 samples in Test Section A. Also, shown is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">The table in Figure H-2 provides the composition of the three tube samples after exposure. All four samples were taken from a single heat of material, Heat 854487538. The table also shows the nominal composition per Haynes International literature, and the heat analysis as reported on the mill certificate that accompanied the material.It was noted that the tube sample composition compared well with one another and with the reported heat analysis.It also was noted that all compared well with the nominal composition. Although, it was somewhat surprising to see that the actual chemistries fell far short of the maximum allowable for molybdenum (0.23% versus 2.5% max), cobalt (0.088% versus 3% max), and tungsten (not detectable versus 2.5% max).
As-Received Appearance	<ul style="list-style-type: none">Figure H-3 shows the typical appearance of an HR 120 tube sample prior to service.Figures H-4 through H-6 document the as-received appearance of the external surface of the HR 120 tube samples. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).Wastage on these tubes is, for the most part, obscured by deposit on the 12 o'clock and 3 o'clock positions.A relatively thick rust-red back-side scale and deposit build-up is seen at the 6 o'clock position on Sample H-5, and to some extent on Sample DD-EE.A relatively thin red-brown deposit is seen elsewhere.The cut at mid-section on Sample DD-EE was made during removal of the test section from the boiler.The gray/white scale commonly associated with molten alkali-iron sulfate attack is seen most readily in the DD-EE sample. It is visible along the cut at the 3 o'clock position. It also is visible on the surface at the 6 o'clock position where it appears that deposit and scale may have been jarred loose during test section removal activities..
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">Figures H-7 through H-9 show the appearance of the external surface of the HR 120 tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for all three samples show the appearance of general wastage due to fireside corrosion.No evidence of damage is noted at the back side, 6 o'clock, position for any of the three samples.

Material: HR 120

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures H-10 through H-12.• The same relative “o’clock” positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost. Note that in some cases, the delta is negative (particularly on the back-side, 6 o’clock position). This is believed due to wall thickness variability and difficulty in locating the exact location of the “before” measurement.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure H-13 plots the maximum wall thickness lost against the calculated average metal temperature for each of the three HR 120 samples.• Review of these data suggests that samples at positions O-P and DD-EE experienced a high rate of metal loss (102 mils per year and 109 mils per year respectively).• It is noted that the rate of metal loss appears to drop off at an intermediate temperature (1100 °F). The reason for this is unclear at this point.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample O-P was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it was experiencing metal wastage at about the maximum rate. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.• Figure H-14 shows the appearance of the tube profile in the section containing the minimum wall thickness for Sample O-P. A thin scale/deposit having a thickness of approximately 2 to 5 mils. Shallow scale penetrations are evident on the internal surface however they are too small to be seen at this magnification.

Material: HR 120

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">Figures H-15a, b, c and d, show the secondary electron images of the scale/metal interface for Sample O-P. Six distinct regions are in evidence. These regions are, starting within the metal and working out:<ol style="list-style-type: none"><u>Base metal</u> – oxalic acid etch delineates grain boundaries, carbides and inclusions..<u>Deeply etching base metal</u> – this region is obvious as a light-appearing band that is parallel to the metal surface, perhaps see most clearly in Figure H-15a. This band is approximately one-half grain wide, and affects only those grains contiguous with the surface. This likely reflects composition differences due to diffusion in this region.<u>Featureless grain surface</u> – This constitutes the leading edge of the grains as they interface with the scale. As EDAX analysis later shows that this zone seems related to diffusion of alloying elements both into and out of the metal surface as scale formation progresses. Perhaps the most significant of these is the suggested potential for chromium egress and carbon ingress in this region. (See the composition for Area 7 in the table that follows.<u>Tightly adherent scale</u> – this is seen continuous along the surface. EDAX analysis will later show that this is predominantly chromium-oxide. The scale is approximately 2 mils thick.<u>Thick and very porous deposit/scale conglomerate</u> – many spherical particles are noted along with what appears to be islands of scale (metal oxides).Figure H-15c and are the seven locations selected for EDAX analysis. The results of these followFigure H-16 shows the appearance of the internal metal surface for Sample O-P. A local scale penetration was noted at one location. This appears to be an incipient pit.
Metallurgical Analysis – Light Optics	<ul style="list-style-type: none">Figures H-17a, b, and c, show the appearance of the mid-wall microstructure for each of the tube samples. No obvious differences were noted between samples.The tube/scale interface was examined for both the internal and external surfaces for all three HR 120 samples. Of particular note was the presence of grain boundary penetrations that extended to a depth of less than one grain boundary. These appeared to be rich in oxides and sulfur similar to the adherent scale, see Areas 4 and 5 in the table that follows.

Summary of Findings, (continued)

Material: HR 120

Issue	Discussion
EDAX Analysis Results	<ul style="list-style-type: none">• The table in Figure H-18 provides a summary of the EDAX analyses of the Locations number in Figure H-15c and d. Also shown in this table is the EDAX analysis near mid-wall of the tube, and a summary of the spectrographic analysis reported earlier, see Figure H-2.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Area 1: Bulk deposit/scale analysis</u> – Alkali metals are present. Sulfur and phosphorous are present in an increased amount compared to the base metal. An iron oxide is likely, as are aluminum, silicon and titanium oxides. The analysis suggests that the carbon content is relatively high, however, these results need to be considered carefully given the inherent inaccuracies in EDAX carbon analysis and the possibility that this region in infused with the epoxy resin mounting compound.• <u>Area 2: Nodule within the deposit</u> – This appears to be primarily iron oxide.• <u>Areas 3 - 5: Chromium-rich oxide scale</u> – This is the scale that is immediately adjacent to the metal surface. Again high sulfur is indicated.• <u>Area 6: Diffusion zone in metal abutting the metal/scale interface</u> – Of potential significance here is the presence of increased levels of carbon.• <u>Area 7: Deeply etching region in grains abutting the metal/scale interface</u> – The presence of a high level of sulfur is the only distinguishing feature of this region.• <u>Bulk EDAX analysis</u> – This analysis compares well with the reference spectrographic analysis.

Figure H-1: Schematic Drawing Showing Position of HR 120 Tube Samples Within Test Section A

Note: Drawing shown in same relative orientation as per the actual installation.

Figure H-2 HR 120

Description: Nominal 33Fe/25Cr/37Ni alloy with Co, W, and Nb added to provide creep strength.
Source: Haynes International, Inc.
Reference Composition: “Nominal” chemistry – per Haynes literature.

Element	Reference Composition	Composition Heat 854487538	Tube Sample O-P	Tube Sample V-W	Tube Sample DD-EE
Ni	37	37.61	37.9	37.9	37.6
Cr	25	25.28	25.3	25.4	25.4
Fe	Balance	Balance	34.3 (a)	34.2 (a)	34.6 (a)
Mo	2.5 max	0.33	0.23	0.23	0.23
Co	3 max	0.09	0.088	0.089	0.090
C	0.05	0.06	0.059	0.061	0.058
N	0.2	0.20	0.17	0.18	0.17
B	0.004	<0.002	0.0030	0.0032	0.0029
Mn	0.7	0.68	0.69	0.69	0.69
Si	0.6	0.52	0.51	0.51	0.49
Al	0.1	0.06	0.064	0.063	0.076
Ti	-	0.02	0.01	0.01	0.01
Al+Ti	-	-	-	-	-
Nb	0.7	0.62	0.56	0.57	0.53
Ta	-	-	0.025	(b)	(b)
Nb+Ta	-	-	-	-	-
V	-	-	0.050	0.050	0.051
W	2.5 max	<0.10	(b)	(b)	(b)
Cu	-	0.10	-	-	-
Sn	-	-	0.003	0.003	0.003
P	-	0.016	0.018	0.018	0.018
S	-	<0.002	0.001	0.001	0.001
O2	-	-	-	-	-

a – By difference
b- Not detected

Figure H-3: Appearance of HR 120 Tube Sample Prior to Service

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure H-4 As-Received Appearance of Sample O-P (HR 120)

(Average surface metal temperature: 1184°F)

12 O'Clock – Facing Gas Flow
 (Note: 3 o'clock is up in this image)

3 O'Clock
 (Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure H-5 As-Received Appearance of Sample V-W (HR 120)

(Average surface metal temperature: 1100 °F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure H-6 As-Received Appearance of Sample DD-EE (HR 120)

(Average surface metal temperature: 1077 °F)

12 O’Clock
(59 mils lost)

3 O’Clock
(82 mils lost)

6 O’Clock
(0 mils lost)

Figure H-7: OD Surface Appearance After Grit Blast

Material: HR 120
Sample: O-P

12 O’Clock
(30 mils lost)

3 O’Clock
(27 mils lost)

6 O’Clock
(0 mils lost)

Figure H-8: OD Surface Appearance After Grit Blast

Material: HR 120
Sample: V-W

12 O’Clock
(95 mils lost)

3 O’Clock
(67 mils lost)

6 O’Clock
(0 mils lost)

Figure H-9: OD Surface Appearance After Grit Blast

Material: HR 120
Sample: DD-EE

Material:

HR 120

Sample Location:

O-P

Maximum Rate:

102 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average Surface Metal Temperature:

1184 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.376	0.377	0.376	0.376	0.376	0.379	0.374	0.377	0.376	0.377
After	0.317	0.311	0.294	0.365	0.383	0.375	0.375	0.245	0.333	0.245
Delta	0.059	0.066	0.082	0.011	-0.007	0.004	-0.001	0.132	0.043	0.132

Figure H-10: Silhouette and Wall Thickness Measurements for Sample O-P

Material:

HR 120

Sample Location:

V-W

Maximum Rate:

61 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average Surface Metal Temperature:

1100 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.376	0.380	0.376	0.378	0.373	0.379	0.378	0.380	0.378	0.380
After	0.346	0.352	0.349	0.378	0.376	0.375	0.366	0.301	0.355	0.301
Delta	0.030	0.028	0.027	0.000	-0.003	0.004	0.012	0.079	0.022	0.079

Figure H-11: Silhouette and Wall Thickness Measurements for Sample V-W

Material:

HR 120

Sample Location:

DD-EE

Maximum Rate:

109 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average Surface Metal Temperature:

1077 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.376	0.377	0.378	0.373	0.377	0.376	0.377	0.377	0.376	0.377
After	0.281	0.301	0.311	0.373	0.379	0.378	0.371	0.237	0.329	0.237
Delta	0.095	0.076	0.067	0.000	-0.002	-0.002	0.006	0.140	0.048	0.140

Figure H-12: Silhouette and Wall Thickness Measurements for Sample DD-EE

Figure H-13: Metal Loss as a Function of Average Surface Metal Temperature

Material: HR 120

Figure H-14: Low Magnification Image Showing Cross-Section Through Thinnest Region of Sample O-P (HR 120)

Figure H-15: Microstructure: HR 120

Figure H-15 (Cont.): Microstructure: HR 120

Note: 1) Numbers on photos indicate distinct areas characterized by the visual assessment and EDAX analyses that follow.

Internal Surface Appearance

Figure H-16: Microstructure: HR 120

(a) Sample O-P (1184°F)

(b) Sample V-W (1100 °F)

Figure H-17: Optical Microstructures HR 120 Mid-Wall

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

(c) Sample DD-EE (1077°F)

Figure H-17 (Cont.): Optical Microstructures HR 120 Mid-Wall

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Figure H-18: EDAX Analysis of Deposit/Scale/Metal Interface for HR 120 (Sample O-P)

Area	Description	Visual Appearance	Ni	Cr	Fe	Mo	Mn	Nb	Ti	Al	Si	C	O	Ca	K	Na	As	P	S
1	Bulk deposit analysis	Rust red deposit with spherical particles.	--	0.44	10.9	--	--	--	1.21	8.91	17.8	12.1	38.2	1.09	2.68	0.59	3.87	0.97	1.25
2	Nodule within deposit..		--	0.60	64.33	--	--	--	--	--	--	--	35.7	--	--	--	--	--	--
3	Scale separated from material beneath it.		2.10	47.7	8.87	--	--	--	--	--	1.01	--	39.4	--	0.22	--	--	--	0.68
4	Tightly adhering scale.	Near interface aligned with grain boundary.	3.81	38.6	18.1	--	--	0.95	--	--	0.99	--	35.7	--	--	--	--	--	1.86
5	Tightly adhering scale.	At interface.	9.85	42.1	12.3	--	--	--	--	--	1.51	--	30.1	--	--	--	--	--	4.09
6	Grains abutting interface.		38.8	23.1	34.9	--	--	--	--	--	0.21	2.98	--	--	--	--	--	--	--
7	Grains abutting interface.	Deeply etched grains.	36.8	26.1	34.8	--	--	--	--	--	0.38	--	--	--	--	--	--	--	1.91
	Bulk EDAX Analysis		37.0	25.3	36.2	--	--	1.26	--	--	0.29	--	--	--	--	--	--	--	--
	Reference bulk analysis.		37.9	25.3	34.3	0.23	0.69	0.56	0.01	0.064	0.51	0.06	--	--	--	--	--	--	0.001

Appendix I
Analysis of Performance
Test Section A
Thermie

Overview of Results: Thermie

Thermie experienced an intermediate rate of metal loss of 53 and 31 mils per year* at positions H-I and HH-II respectively.

Thermie seems to have benefited from a high total alloy content. Its' chromium content is similar to that of the candidate alloys that performed poorly (i.e. 25%); however, Thermie has a high total alloy content where the sum of chromium, nickel, and cobalt total almost 100%. This likely is the source of Thermie's resistance to scaling in this unit.

It was noted that the microstructures of Samples H-I and HH-II differ significantly in grain size. The impact of this is unclear at this point; however, contrary to conventional understanding, the sample having the larger grain size performed better. This of course could more reflect the lower temperature of the HH-II sample. This issue remains to be resolved.

Examination of both samples revealed no evidence of local grain boundary penetrations. The internal surface had only an extremely thin oxide scale.

Analysis of deposit on the surface revealed that, like all of the other samples investigated, the deposit on the Thermie samples had the known aggressive combination of species, namely iron, oxygen, the alkali metals, and sulfur. Examination and analysis of the scale adjacent to the metal surface revealed the chalky-white appearance associated with alkali-iron-sulfates. Thus, the required corrosive elements were available to test the performance limits of this alloy.

Finally, the analysis of the deposit and the metal surface immediately adjacent to the interface revealed the presence of carbon. While carbon determinations using EDAX are unreliable, the implications of carbon in the deposit are worthy of additional consideration, as is the potential for carbon ingress from the deposit into the abutting metal.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: Thermie

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">The schematic in Figure I-1 shows the relative positions of Save 25 samples in Test Section A. Also, shown is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">The table in Figure I-2 provides the composition of the two tube samples after exposure. Samples H-I and HH-II were taken from two different heats provided by Oak Ridge National Laboratory (ORNL). The table also shows the target composition and heat analysis as reported by ORNL.It is noted from these analyses that Thermie has a chromium content that is similar to candidate materials which experienced a high rate of metal loss (about 25%). However, in contrast to those samples, Thermie has a very high total alloy content. It might be argued that the alloy constituents in Thermie are not equally protective (48% Ni – 24% Cr – 20% Co), nonetheless this particular combination appears to have performed reasonably well.
As-Received Appearance	<ul style="list-style-type: none">Figure I-3 shows the typical appearance of a Thermie tube sample prior to serviceFigures I-4 and I-5 document the appearance of the external surface of the Thermie tube samples after service in Test Section A. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).Note that the cut in Sample H-I was created during removal of Test Section A from the boiler. This sample is substantially complete. It lacks only the kerf associated with the cut.The cuts in the 12 o'clock and 3 o'clock positions for Sample HH-II were created during removal of ring specimens for dimensioning, metallography and chemical analysis. These portions of the tube thus are not shown.Any wastage in these samples is obscured by deposit on the surface..A rust-red back-side scale and deposit build-up is seen at the 6 o'clock position on Sample HH-II. The 6 o'clock position is relatively free from deposit in Sample H-IEvidence of the gray/white scale associated with molten alkali-iron sulfate attack can be seen in Figure I-4, near the center of the 12 o'clock image. It is anticipated that scraping to remove the red scale would reveal evidence of a gray/white scale immediately adjacent to the metal surface for both samples.

Material: Thermie

Summary of Findings, (continued)

Issue	Discussion
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">Figures I-6 and I-7 show the appearance of the external surface of the Thermie tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for Samples HI clearly show the appearance of general wastage due to fireside corrosion. Some level of pitting also is suggested at this position. Wastage is less evident for Sample HH-II.Minimal or no pitting was observed at the 6 o'clock position for either sample.
Wall Thickness Loss Determined	<ul style="list-style-type: none">Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures I-8 and I-9.The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost. Note that for Sample HH-II, the delta is negative (particularly on the back-side, 6 o'clock position). This is believed due to wall thickness variability and difficulty in locating the exact location of the "before" measurement.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">The chart in Figure I-10 plots the maximum wall thickness lost against the calculated average metal temperature for each of the two Thermie samples.From this limited data it appears as if the rate of metal loss increases with increasing temperature.

Material: Thermie

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample H-I was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it had lost the most wall thickness of all of the two Thermie samples. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.• Figure I-11 shows the appearance of the tube profile in the section containing the minimum wall thickness for Sample H-I. Note a scale/deposit on the external surface of approximately 1 to 15 mils in thickness. No scale is evident on the internal surface at this magnification.• Figures I-12a, b, c and d, show secondary electron images of the scale/metal interface for Sample H-I. Six distinct regions are in evidence. These regions are, starting within the metal and working out:<ol style="list-style-type: none">1. <u>Base metal</u> – Oxalic acid etch delineates grain boundaries, carbides, and inclusions.2. <u>Deeply etching base metal</u> – This region is relatively faint, but can be seen in Figure I-12a and b. This affects only those grains immediately adjacent to the scale/metal interface.3. <u>Tightly adhering scale</u> – this is seen continuous along the scale/metal interface. EDAX analysis will later show that this is predominantly a chromium-rich oxide. The scale is approximately 0.5 mils thick.4. <u>Thick and porous deposit/scale conglomerate</u> – many spherical particles are noted along with what appears to be islands of scale (metal oxides). This can be seen most clearly in Figure I-12b.• Figures I-13a and b show backscattered images (BEI) of the scale/metal interface for Sample H-I. The BEI images provide better resolution of compositional differences. Also, noted on these figures are the eight locations selected for EDAX analysis. The results of these follow• Figure I-14 shows the appearance of the internal metal surface for Sample H-I. Little or no scale is noted on this surface.
Metallurgical Analysis – Light Optics	<ul style="list-style-type: none">• Figures I-15a and b show the appearance of the mid-wall microstructure for the two Thermie tube samples. The etch clearly delineates grain boundaries and carbides. Titanium carbides are clearly distinguishable. Differences in grain size are the most obvious differences between these two samples, with Sample HH-II having a much larger grain size than that of Sample H-I. The significance of this difference is not clear.• The tube/scale interface was examined for both the internal and external surfaces on both samples. No grain boundary penetrations were noted anywhere on these samples. No scale was visible on the internal surface.

Summary of Findings, (continued)

Material: Thermic

Issue	Discussion
EDAX Analysis Results	<ul style="list-style-type: none">• The table in Figure I-16 provides a summary of the EDAX analyses of the locations numbered in Figures I-13a and b. Also shown in this table a bulk EDAX analysis taken near mid-wall of the tube, and a summary of the spectrographic analysis reported earlier, see Figure I-2.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Area 1: Bulk deposit/scale analysis</u> – Alkali metals are present. Sulfur and phosphorous are present in an increased amount compared to the base metal. An iron oxide is likely, as are aluminum, silicon and titanium oxides. The analysis suggests that the carbon content is relatively high; however, this needs to be considered with caution given the accuracy of EDAX with respect to this element, and given the potential for contamination by the epoxy resin mounting compound.• <u>Areas 2 through 5: External scale</u> – The presence of a chromium-, nickel-, cobalt-, and iron-rich scale is indicated. Again of significance here is the presence of sulfur and carbon. Potassium (an alkali metal) is also in evidence at this location.• <u>Area 6: Grains abutting the scale/metal interface</u> - This regions appears to be somewhat depleted in alloying elements. Carbon is indicated. Evidence of oxygen suggests that the analyzed area overlaps the adjacent adherent scale. Compare this analysis with that of Area 7 where the focus is an oxide penetration into the metal surface.• <u>Area 7: Scale penetration into metal surface</u> – This analysis is very similar to that of Area 6 with an increase in oxygen and sulfur noted.• <u>Area 8: Particle near interface</u> – This is a niobium-rich precipitate.• <u>Bulk metal compositon</u> – Given its limitations, this EDAX analysis compares favorably with that of the reference spectrographic analysis below it.

Figure I-1: Schematic Drawing Showing Position of Thermie Tube Samples Within Test Section A

Note: Drawing shown in same relative orientation as per the actual installation.

Figure I-2 Thermie

Description: Nominal 25Cr/20Co nickel alloy with additions of Nb and Ti to provide creep strength.
Source: Oak Ridge National Laboratory (ORNL)
Reference Composition: “Target” Chemistry per ORNL (Reference 1).

Element	Reference Composition	Composition Heat 17421	Composition Heat 17422	Composition Heat 17454	Tube Sample H-I	Tube Sample HH-II
Ni	48.0	48.83	49.06	48.92	48.6	47.3
Cr	24.0	23.48	23.08	23.63	23.70	24.20
Fe	2.0	2.11	2.06	2.11	1.93	2.02
Mo	0.5	0.43	0.43	0.42	0.48	0.48
Co	19.8	19.22	19.39	19.42	19.88	20.37
C	0.07	0.10	0.088	0.094	0.092	0.088
N	-	0.011	0.013	0.022	(a)	(a)
B	0.002 max	(a)	(a)	(a)	<0.001	<0.001
Mn	0.3	0.32	0.32	0.32	0.31	0.31
Si	0.5	0.50	0.51	0.49	0.36	0.36
Al	0.8	0.75	0.74	0.60	0.67	0.94
Ti	2.0	2.08	2.10	2.01	1.93	1.92
Al+Ti	-	-	-	-	-	-
Nb	2.0	2.16	2.20	1.95	2.07	2.05
Cu	-	<0.01	<0.01	<0.01	(a)	(a)
Sn	-	-	-	-	-	-
P	-	<0.002	<0.002	<0.002	(a)	(a)
S	-	0.005	0.003	0.009	(a)	(a)
O2	-	0.002	0.003	0.004	(a)	(a)
Zr	0.015 max	(a)	(a)	(a)	<0.01	<0.01
Mg	-	-	-	-	-	-

- a- Not analyzed.
b- By difference.
c- Not found.

Reference 1:

“Fabrication of Test Tubes for Coal Ash Corrosion Testing”, Sikka, V.K., Swindeman, R.W., Wright, I.G., Judkins, R.R., Johnson, R., Proc, 13th Annual Conf. on Fossil Energy Mat’ls, May 1999.

Note: Sample H-I was from Heat 17454
Sample HH-II was from Heat 17422

Figure I-3: Appearance of Thermie Tube Sample Prior to Service

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure I-4 As-Received Appearance of Sample H-I (Thermie)

(Average surface metal temperature: 1160 °F)

Note: Sample cut at Weld “H” prior to photo.

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure I-5 As-Received Appearance of Sample HH-II (Thermie)

(Average surface metal temperature: 1056 °F)

Note: The 12 and 3 o'clock views were photographed at a much later date and after the sectioning operation. Material is missing from between the cut near weld HH and the middle of the specimen, and that is the reason why these images are shorter than the 6 o'clock image.

12 O’Clock
(42 mils lost)

3 O’Clock
(38 mils lost)

6 O’Clock
(4 mils lost)

Figure I-6: OD Surface Appearance After Grit Blast

Material: Thermie
Sample: H-I

12 O'Clock
(32 mils lost)

3 O'Clock
(22 mils lost)

6 O'Clock
(0 mils lost)

Figure I-7: OD Surface Appearance After Grit Blast

Material: Thermic
Sample: HH-II

Material:

Thermie

Sample Location:

H-I

Maximum Rate:

53 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average Surface Metal Temperature:

1160 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.404	0.402	0.402	0.404	0.405	0.406	0.404	0.403	0.404	0.403
After	0.362	0.380	0.364	0.401	0.401	0.401	0.387	0.335	0.379	0.335
Delta	0.042	0.022	0.038	0.003	0.004	0.005	0.017	0.068	0.025	0.068

Figure I-8: Silhouette and Wall Thickness Measurements for Sample H-I

Material:

Thermie

Sample Location:

HH-II

Maximum Rate:

31 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average Surface Metal Temperature:

1056°F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.399	0.399	0.400	0.399	0.399	0.399	0.399	0.400	0.399	0.400
After	0.367	0.386	0.378	0.399	0.400	0.400	0.399	0.360	0.386	0.360
Delta	0.032	0.013	0.022	0.000	-0.001	-0.001	0.000	0.040	0.013	0.040

Figure I-9: Silhouette and Wall Thickness Measurements for Sample HH-II

Figure I-10: Metal Loss as a Function of Average Surface Metal Temperature

Material: Thermie

Figure I-11: Low Magnification Image Showing Cross-Section Through Thinnest Region of Sample H-I (Thermie)

Figure I-12: Microstructure: Thermie

(c) External Scale/Metal Interface (SEI - Magnification)

Figure I-12 (Cont.): Microstructure: Thermie

Figure I-13: Microstructure: Thermie

Note: Numbers on photos indicate distinct areas characterized by the visual assessment and EDAX analyses that follow.

Internal Surface Appearance

Figure I-14: Microstructure: Thermie

(a) Sample H-I (1160°F)

(b) Sample HH-II (1056°F)

Figure I-15: Optical Microstructures Thermie Mid-Wall

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Figure I-16: EDAX Analysis of Deposit/Scale/Metal Interface for Thermie (Sample H-I)

Area	Description	Visual Appearance	Ni	Cr	Fe	Co	Mo	Nb	Ti	Al	Si	C	O	Ca	K	Na	As	P	S
1	Bulk deposit analysis	Rust red deposit with spherical particles.	--	--	9.33	--	--	--	0.35	7.12	15.3	29.2	31.1	0.38	2.09	0.65	3.05	--	1.49
2	Scale separated from material beneath it.		7.40	37.5	2.60	5.14	--	2.49	2.69	0.92	0.73	--	36.2	--	0.30	--	--	--	4.08
3	Tightly adhering scale.		9.15	39.8	1.01	5.93	--	--	2.85	1.18	0.78	--	32.6	--	--	--	--	--	6.71
4	Tightly adhering scale.	Near interface.	9.15	35.1	1.86	6.29	--	2.43	2.77	1.34	0.87	--	35.7	--	0.38	--	--	--	4.06
5	Tightly adhering scale.	At interface.	24.8	30.6	3.28	9.29	--	1.94	2.66	1.24	0.49	--	23.8	--	--	--	--	--	1.97
6	Grains abutting interface.		42.7	22.1	1.97	16.46	0.51	1.39	1.63	0.92	0.47	6.70	5.15	--	--	--	--	--	--
7	Scale penetration into metal		41.3	21.5	2.64	14.76	--	1.67	2.14	1.17	0.21	3.47	10.5	--	--	--	--	--	0.68
8	Particle near interface.		10.7	10.4	0.47	3.89	--	54.4	19.4	0.68	--	--	--	--	--	--	--	--	--
	Bulk EDAX Analysis		48.2	23.5	2.42	20.6	--	1.82	2.00	1.05	0.40	--	--	--	--	--	--	--	--
	Reference bulk analysis.		52.9	20.5	1.72	18.9	0.58	1.91	1.78	0.66	0.47	0.08	--	--	--	--	--	0.006	0.004

Appendix J

Analysis of Performance

Test Section A

IN52 Weld Overlay

Overview of Results: IN52 Weld Overlay

The IN52 Weld Overlay experienced an intermediate rate of metal loss (77 mils per year to 44 mils per year*) in the service environment of Test Section A. The overlay thickness is about 80 mils, or a little less than one-third of the total wall thickness. Once the overlay is breached, the performance of this material will be based on the scaling resistance of the underlying 800H base metal.

It should be noted that the composition of the IN52 Weld Overlay provides for a reasonably high level of chromium (28%) and for a high total alloy content. The high total alloying element content likely accounts for the good performance of this material. Penetrations along grain boundaries are likely due to segregation and/or a preferred diffusion path. These, however, seem inconsequential given their small size.

The reason why the wastage rate for this material decreased with increasing temperature is unclear at this point, but from the surface appearance seems real.

Analysis of deposit on the surface revealed that it had the known aggressive combination of species, namely iron, oxygen, the alkali metals, and sulfur. Examination and analysis of the scale adjacent to the metal surface revealed the chalky-white appearance associated with alkali-iron-sulfates. Thus, the required corrosive elements were available to test the performance limits of this alloy.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: IN52 Weld Overlay

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">The schematic in Figure J-1 shows the relative positions of IN52 Weld Overlay samples in Test Section A. Also, shown is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">The table in Figure J-2 provides the composition of the two tube samples after exposure. Both samples were manufactured using a single heat of filler wire, Heat NX 9090JK.The reference composition in this table is the specified composition for the filler wire. Both the wire heat composition and the cladding compositions comply with this specification; however, it is noted that the cladding is depleted in chromium and enriched in iron, as would be expected due to reactions in the arc and dilution from the base metal.
As-Received Appearance	<ul style="list-style-type: none">Figure J-3 shows the appearance of the IN52 Weld Overlay tube as delivered from Special Metals Corporation (SMC). Note the distinctive appearance of the weld cladding. The total wall thickness for this tube is approximately 290 mils. The clad layer is about 80 mils thick. An inner layer of 800H provides support.Figures J-4 and J-5 document the appearance of the external surface of the IN52 Weld Overlay tube samples after service in Test Section A. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).No wastage is visible on either sample, but this likely is obscured by the deposit/scale at the 12 o'clock and 3 o'clock positions on both samples.The back side, 6 o'clock position is relatively clear of deposit for both samples, with the R-S sample being somewhat cleaner than the GG-HH sampleA relatively red-brown deposit/scale is seen on almost all surfaces.Figure J-5 shows some small hints (in the 3 o'clock view) of the gray/white scale associated with molten alkali-iron sulfate attack. It is likely that scraping to remove the red scale would reveal evidence of the gray/white scale immediately adjacent to the metal surface at other locations.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">Figures J-6 through J-7 show the appearance of the external surface of the IN52 Weld Overlay tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for both samples show the appearance of general wastage due to fireside corrosion. Some pitting is also suggested at these locations.The 6 o'clock position for both samples show little or no evidence of attack. The original weld bead appearance is still visible at this location.

Material: IN52 Weld Overlay

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures J-8 and J-9.• The same relative “o’clock” positions were maintained as discussed earlier. Measurements were taken prior to service at eight evenly spaced locations about the tube circumference. To prepare for this, the external surface of the cladding was ground flush to minimize thickness variability due to surface contour. After-service wall thickness measurements were taken at these same locations then compared with the initial thickness.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost. Note that in some cases, the delta is negative (particularly on the back-side. 6 o’clock position for both samples). This is believed due to wall thickness variability and difficulty in locating the exact location of the “before” measurement.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure J-10 plots the maximum wall thickness lost against the calculated average metal temperature for each of the two IN52 Weld Overlay samples.• The data in the chart suggest that the metal loss rate decreases with increased temperature for the IN52 Weld Overlay samples.• A significant metal loss rate (of 77 mils per year) was experienced for the sample in the R-S position. This rate was adequate to breach the cladding thickness (80 mils), and the underlying Incoloy 800H was exposed to the corrosive elements.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• The sample with the highest rate of metal loss (R-S) was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.• Figure J-11 shows the appearance of the tube profile in the section containing the minimum wall thickness for Sample R-S. Note a scale/deposit on the external surface of approximately 2 to 20 mils in thickness. No scale is evident on the internal surface at this magnification.

Material: IN52 Weld Overlay

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">Figures J-12a, c and d, show secondary electron images of the scale/metal interface for Sample R-S. Note that the cladding has been completely wasted away at this location, to the metal at the interface is the underlying 800H.Six distinct regions are in evidence. These regions are, starting within the metal and working out:<ol style="list-style-type: none"><u>Base metal</u> – Oxalic acid etch delineates grain boundaries and carbides.<u>Deeply etching base metal</u> – this region is obvious as a light-appearing band that is parallel to the metal surface, perhaps see most clearly in Figure J-12a. Figure J-12c shows that this band is approximately one-half grain wide, and affects only those grains contiguous with the surface. This may be an etching “edge effect”; however, it may also reflect composition differences due to diffusion in this region.<u>Featureless grain surface</u> – This constitutes the leading edge of the grains as they interface with the scale. EDAX provides no evidence that this constitute a diffusion zone.<u>Scale</u> – this is seen continuous along the surface. EDAX analysis will later show that this is predominantly a nickel-and/or chromium-oxide. The scale is approximately 10 mils thick in the image shown in Figure J-12a and b.<u>Thick and very porous deposit/scale conglomerate</u> – many spherical particles are noted along with what appears to be islands of scale (metal oxides).Figures J-12 b shows backscattered images (BEI) of the scale/metal interface for Sample R-S. The BEI images provide better resolution of compositional differences. Also, noted on Figure J-12b are the ten locations selected for EDAX analysis. The locations for these are also shown in more detail in the higher magnification image provided in Figure J-12c. The results of the EDAX analyses followFigure J-13 shows the appearance of the internal metal surface for Sample R-S. An oxide scale is noted to cover the surface. Some deeper penetrations are also noted with the possibility of internal oxidation at one location; however, it is more likely that this scale is the result of an oxide penetration that is connected to the surface out of the plane of this image. In general, the scale is approximately 1 mil thick.
Metallurgical Analysis – Light Optics.	<ul style="list-style-type: none">Figures J-14a and b show the appearance of the weld overlay microstructure and the mid-wall microstructure for the underlying 800H material for Sample R-S. Figures J-15a and b show the same images for Sample GG-HH.Of particular note in these are the grain boundary penetrations that are evident at the scale/metal interface. These are about 0.5 mils deep.

Summary of Findings, (continued)

Material: IN52 Weld Overlay

Issue	Discussion
Metallurgical Analysis – Light Optics, Continued.	<ul style="list-style-type: none">• It should be noted that these penetrations are associated with extension of the “featureless” grain region into the underlying weld metal microstructure, rather than scale penetrations at that point.
EDAX Analysis Results	<ul style="list-style-type: none">• The table in Figure J-15 provides a summary of the EDAX analyses of the numbered locations in Figure J-12b and c. Also shown in this table is a summary of the spectrographic analysis reported earlier, see Figure J-2.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Areas 1 and 2: Bulk deposit/scale analysis</u> – Alkali metals are present. Sulfur and phosphorous are present in an increased amount compared to the base metal. An iron oxide is likely, as are aluminum, silicon and titanium oxides. The analysis suggests that the carbon content is relatively high, however, caution is urged in that EDAX analysis of carbon is inherently inaccurate, and there exists the possibility of contamination by the underlying epoxy resin mount material.• <u>Areas 3 through 6: Scale analysis</u> – The scale is predominantly a nickel-, chromium-, and iron-rich oxide. Also of significance is the relatively high levels of sulfur at a location adjacent to the metal surface.• <u>Area 7 through 10: Grain abutting interface</u> - This region shows some evidence of diffusion both into and out of the surface however this is not conclusive.

South End

Note: Drawing shown in same relative orientation as per the actual installation.

Figure J-2 Inco 52 / 800 HT (Weld clad duplex tubing)

Description: Nominal 30 Cr nickel alloy cladding for oxidation/corrosion protection. Incoloy 800HT substrate provides creep strength.
Source: Special Metals Corporation (SMC)
Reference Composition: Filler wire “limiting chemical composition” – Per SMC literature. (ANSI AWS 5.14M-97 Class ERNiCrFe-7)

Element	Reference Composition for Weld Cladding	Composition Heat NX 9090JK	Tube Sample R-S	Tube Sample GG-HH
Ni	Balance	60.48	61.8 (a)	60.80 (a)
Cr	28.0 – 31.5	28.97	27.29	27.99
Fe	7.0 – 11.0	8.86	8.99	9.44
Mo	0.50 max	0.01	<0.05	<0.05
Co	-	0.01	<0.05	<0.05
C	0.04 max	0.02	0.032	0.032
N	-	-	-	-
B	-	-	<0.001	<0.001
Mn	1.0 max	0.24	0.28	0.28
Si	0.50 max	0.14	0.23	0.22
Al	1.10 max	0.69	0.83	0.69
Ti	1.0 max	0.58	0.51	0.52
Al+Ti	1.5 max	1.27	1.34	1.21
Nb	0.10 max	0.01	<0.05	<0.05
Ta	-	<0.01	-	-
Nb+Ta	-	0.02	-	-
V	-	-	<0.05	<0.05
W	-	-	-	-
Cu	0.30 max	0.01	<0.05	<0.05
Sn	-	-	<0.001	<0.001
P	0.020 max	0.004	0.011	0.009
S	0.015 max	<0.001	0.010	0.017
O2	-	-	-	-
Others	0.50 max	<0.50	(b)	(b)

- a- By difference.
b- Not determined.

Note: Reference composition is for filler wire, not as-deposited.

Figure J-3: Appearance of IN52 Weld Overlay Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure J-4: As-Received Appearance of Sample R-S (IN52 Weld Overlay)

(Average surface metal temperature: 1198 °F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure J-5: As-Received Appearance of Sample GG-HH (IN52 Weld Overlay)

(Average surface metal temperature: 1062 °F)

12 O’Clock
(19 mils lost)

3 O’Clock
(0 mils lost)

6 O’Clock
(0 mils lost)

Figure J-6: OD Surface Appearance After Grit Blast

Material: IN52 Weld Overlay
Sample: R-S

12 O’Clock
(43 mils lost)

3 O’Clock
(39 mils lost)

6 O’Clock
(4 mils lost)

Figure J-7: OD Surface Appearance After Grit Blast

Material: IN52 Weld Overlay
Sample: GG-HH

Material:

IN52 Weld Overlay

Sample Location:

R-S

Maximum Rate:

44 mils/yr

Maximum Loss Orientation:

Approx. 12 o'clock

Average Surface Metal Temperature:

1198°F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.303	0.299	0.293	0.288	0.283	0.285	0.290	0.302	0.293	0.303
After	0.246	0.276	0.271	0.294	0.290	0.283	0.283	0.287	0.279	0.246
Delta	0.057	0.023	0.022	-0.006	-0.007	0.002	0.007	0.015	0.014	0.057

Figure J-8: Silhouette and Wall Thickness Measurements for Sample R-S

Material:

IN52 Weld Overlay

Sample Location:

GG-HH

Maximum Rate:

77 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average Surface Metal Temperature:

1062°F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.293	0.297	0.296	0.292	0.286	0.280	0.281	0.286	0.289	0.286
After	0.225	0.227	0.252	0.281	0.281	0.287	0.292	0.187	0.226	0.187
Delta	0.068	0.070	0.044	0.011	0.005	-0.007	-0.011	0.099	0.063	0.099

Figure J-9: Silhouette and Wall Thickness Measurements for Sample GG-HH

Figure J-10: Metal Loss as a Function of Average Surface Metal Temperature

Material: IN52 Weld Overlay

Figure J-11 Low Magnification Image Showing Cross-Section Through Thinnest Region of Sample R-S (IN52 Weld Overlay)

Figure J-12 Microstructure: IN52 Weld Overlay

Note: Numbers on photos indicate distinct areas characterized by the visual assessment and EDAX analyses that follow.

Note: Numbers on photos indicate distinct areas characterized by the visual assessment and EDAX analyses that follow.

Figure J-12(Cont.): Microstructure: IN52 Weld Overlay

Internal Surface Appearance

Figure J-13 Microstructure: IN52 Weld Overlay

(a) Sample R-S (1198°F)

This photograph shows the appearance of the weld overlay microstructure.

(b) Sample R-S (1198°F)

This photograph shows the microstructure at mid-wall for the underlying 800H.

Figure J-14 Optical Microstructures IN52 Weld Overlay

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

(a) Sample GG-HH (1062 °F)

This photograph shows the appearance of the weld overlay microstructure.

(b) Sample GG-HH (1062 °F)

This photograph shows location with the underlying 800H exposed to the surface..

Figure J-14 (Cont.): Optical Microstructures IN52 Weld Overlay

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Figure J-15: EDAX Analysis of Deposit/Scale/Metal Interface for IN52 Weld Overlay (Sample R-S)

Area	Description	Visual Appearance	Ni	Cr	Fe	Co	Mn	Nb	Ti	Al	Si	C	O	Ca	K	Na	As	P	S
1	Bulk deposit analysis	Rust red deposit with spherical particles.	1.66	--	11.0	--	--	--	0.73	8.59	13.2	23.4	31.5	--	2.97	0.59	4.24	0.97	1.07
2	Deposit / scale analysis		18.3	--	24.9	--	--	--	0.27	2.67	3.44	7.11	31.8	--	0.30	--	10.1	0.75	0.32
3	Loosely adhering scale		8.28	45.4	4.87	--	--	--	0.81	0.94	0.27	--	37.8	--	--	--	--	--	1.68
4	Tightly adhering scale.		4.75	49.7	0.44	--	--	--	0.70	1.31	0.23	--	40.4	--	--	--	--	--	2.43
5	Tightly adhering scale.	Near interface	67.9	2.36	1.73	--	--	--	--	--	--	--	23.1	--	--	--	--	--	4.95
6	Tightly adhering scale.	At interface	9.67	33.6	15.9	--	--	--	1.10	1.44	0.19	--	36.0	--	--	--	--	--	2.09
7	Grain abutting interface.		60.6	27.7	10.2	--	--	--	0.61	0.78	--	--	--	--	--	--	--	--	--
8	Grain abutting interface.	Deep etching.	49.0	28.45	8.51	--	--	--	0.55	4.21	--	--	9.24	--	--	--	--	--	--
9	Scale penetration into metal	At interface	56.5	23.4	10.2	--	--	--	0.89	1.05	--	--	6.26	--	--	--	--	--	1.68
10	Grain near interface	Normal etched appearance	58.3	27.9	9.46	--	--	--	0.45	0.86	0.17	--	2.88	--	--	--	--	--	--
	Reference bulk analysis.		61.8	27.3	8.99		0.28		0.51	0.83	0.23	0.03	--	--	--	--	--	--	--

Appendix K
Analysis of Performance
Test Section A
Incoclad 671

Overview of Results: Incoclad 671

Incoclad 671 experienced a low rate of metal loss due to Test Section A exposure. The maximum rate was determined to be 13 mils per year*. The chromium and overall alloy content of this material seem to account for its' good performance in this environment. This further would be assisted by the fine grain size of the cladding which likely would facilitate the diffusion that would aid in the formation of a protective chromium-rich scale.

The reason for the somewhat increased corrosion rate at lower temperatures is not entirely clear; however, it seems likely due to the local environment at this position in the test section. Analysis of deposit on the surface revealed that it had the known aggressive combination of species, namely iron, oxygen, the alkali metals, and sulfur. Thus, the required corrosive elements were available to test the performance limits of this alloy. The significance of the presence of chlorine on these surfaces is unclear, and should be further pursued as increased chlorine contents in the deposit could further accelerate corrosion.

* **Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: Inconel 671

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">The schematic in Figure K-1 shows the relative positions of the three Inconel 671 samples in Test Section A. Also, shown is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">The table in Figure K-2 provides the composition of the tube samples after exposure. No pedigree was offered for these materials so it's not clear whether these came from one or multiple heats of material. Nonetheless, the tube sample analyses are consistent with one another and compare well with the nominal composition provided by the Special Metals Corporation (SMC).
As-Received Appearance	<ul style="list-style-type: none">Figure K-3 shows the typical appearance of the Inconel 671 samples as they were received from SMC. This tube has a total wall thickness of about 260 mils, with a 75 mil thick outer layer of IN671 to provide corrosion resistance, and an inner supporting layer of 800H.Figures K-4 through K-6 document the appearance of the external surface of the Inconel 671 tube samples after they had been removed from service. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).Note that the 3 o'clock image of Sample P-Q was taken after rings of material had been removed for dimensioning, microstructure, and chemical analysis. As such, material is missing between Weld P and the center of the specimen. Thus, accounting for the shorten image at this orientation.Note also that tube Sample U-V was approximately twice as long as the others. The entire length of this longer specimen is shown in this figure.Wastage is not visible in any of these three tubes in any orientation.A relatively thick deposit/scale and deposit build-up is seen in all views of Sample U-V. Also visible in the 12 o'clock and 3 o'clock views is evidence of the chalky white scale associated with molten alkali-iron sulfate attack.Sample PQ is relatively free from deposit.Sample EE-Ff has a substantial deposit/scale visible in all three orientations.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">Figures K7 through K-9 show the appearance of the external surface of the Inconel 671 tube samples after grit-blasting to remove deposit and scale. The 12 o'clock position on Sample EE-FF shows the appearance of general wastage due to fireside corrosion.Wastage is not apparent in viewing the remaining surfaces.

Material: Inconel 671

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures K-10 through K-12.• Measurements were taken at eight evenly spaced “o’clock” locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost. Note that in some cases, the delta is negative (for instance, at the 1:30 position on all three samples). This is believed due to wall thickness variability and difficulty in locating the exact location of the “before” measurement.• For all three tube samples, the minimum wall thickness in the cross section was not at one of the eight predetermined locations. In these cases, there was no “before” measurement for comparison. So, the average “before” wall thickness was used to calculate the wall thickness lost at these off-locations.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure K-13 plots the maximum wall thickness lost against the calculated average metal temperature for the three Inconel 671 samples.• The wastage rate was low for all three samples; however, it is interesting to note that the sample having the lowest average exposure temperature (1075 °F) had the highest wastage rate. This confirms the appearance of the grit blasted surface of this sample, see Figure K-9.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample P-Q was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces.• Figure K-14 shows the appearance of the tube profile for Sample P-Q. The scale/deposit on the external surface is approximately 5 mils thick. No scale is evident on the internal surface at this magnification.

Material: Inconel 671

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">Figures K-15a, b, c and d, show secondary electron images of the scale/metal interface for Sample P-Q. Four distinct regions are in evidence. These regions are, starting within the metal and working out:<ol style="list-style-type: none"><u>Inconel 671 Base metal</u> – Oxalic acid etch delineates grain boundaries and carbides. Of particular note is the extremely fine grain size in the cladding material.<u>Metal at the Interface</u> – A very narrow zone of pitting/porosity is noted at this interface. It is not clear whether this is an etching edge effect or otherwise. In any case, this zone is very small at approximately 0.7 mils in thickness.<u>Adherent scale with embedded deposit</u> – this is seen continuous along the surface. EDAX analysis will later show that this is predominantly a chromium-rich oxide. The scale also is about 0.7 mils thick.<u>Thick and very porous deposit/scale conglomerate</u> – many spherical particles are noted along with what appears to be islands of scale (metal oxides).Figures K-16a and b show backscattered images (BEI) of the scale/metal interface for Sample K-L. The BEI images provide better resolution of compositional differences. Also, noted in these figures are the nine locations selected for EDAX analysis. The results of these followFigure K-17 shows the appearance of the internal metal surface for Sample P-Q. A thin oxide scale (about 1.5 mils) is noted to cover the surface. Also noted are local penetrations into the underlying material. Oxide islands are noted at more than a grain diameter into the metal. The nature of these was not explored.
Metallurgical Analysis – Light Optics	<ul style="list-style-type: none">Figures K-18a, b, and c show the appearance of the Inconel 671 microstructure for each of the tube samples. These again emphasize the consistently fine grain size for this cladding material.The tube/scale interface was examined for both the internal and external surfaces on all three Inconel 671 samples. Nothing was found of note.

Summary of Findings, (continued)

Material: Incoclad 671

Issue	Discussion
EDAX Analysis Results, Continued	<ul style="list-style-type: none">• The table in Figure K-19 provides a summary of the EDAX analyses of the numbered locations in Figure K-16a and b. Also shown in this table is an EDAX analysis to determine the bulk cladding composition, and a summary of the spectrographic analysis reported earlier, see Figure K-2.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Areas 1 and 2: Bulk deposit/scale analysis</u> – Alkali metals are present. Sulfur and phosphorous are present in an increased amount compared to the base metal. An iron oxide is likely, as are aluminum, silicon and titanium oxides. Of particular note is the presence of chlorine in this deposit, as it is know to be a particularly aggressive agent. Its’ significance in this case is unclear since this is the only analysis to suggest its’ presence. This analysis also suggests that the carbon content is relatively high, however, caution is urged in that EDAX analysis for carbon is inherently inaccurate, and there exists the possibility of contamination by the underlying epoxy resin material.• <u>Areas 3 and 4: Scale adjacent to the scale/metal interface</u> – It is noted that this is a predominantly chromium-rich oxide in spite of the fact that this material is more than 50% nickel. Also of note here is the presence of sulfur.• <u>Areas 5 through 8: Scale and other materials in the vicinity of the interface</u> – This appear to be a variety of chromium- and nickel-rich oxides. Again of note is the presence of sulfur.• <u>Area 9: Potential diffusion zone within metal surface</u> – This area is depleted in chromium and enriched in nickel.• <u>Bulk clad metal analysis</u> – Given its limitations this EDAX analysis compares favorably with that of the reference spectrographic analysis below it.

Figure K-2 Incoclad 671 / 800 HT (Co-extruded duplex tubing)

Description:

Nominal 50Cr/50 Ni alloy cladding for oxidation/corrosion protection. Incoloy 800HT substrate to provide creep strength.

Source:

Special Metals Corporation (SMC)

Reference Composition:

Cladding “nominal” chemistry – per SMC literature.

Element	Reference Composition	Certified Composition (not provided)	Tube Sample P-Q	Tube Sample U-V	Tube Sample EE-FF
Ni	51.5		51.10	51.00	51.50
Cr	48.0		47.73	47.85	47.35
Fe	-		0.140	0.093	0.100
Mo	-		0.033	0.033	0.033
Co	-		0.24	0.25	0.24
C	0.05		0.053	0.048	0.057
N	-		-	-	-
B	-		<0.001	<0.001	<0.001
Mn	-		0.001	<0.001	<0.001
Si	-		0.018	0.014	0.012
Al	-		0.23	0.27	0.29
Ti	-		0.38	0.39	0.38
Al+Ti	-		-	-	-
Nb	-		<0.001	<0.001	<0.001
Ta	-		-	-	-
Nb+Ta	-		-	-	-
V	-		0.011	0.012	0.011
W	-		-	-	-
Cu	-		0.003	0.003	0.002
Sn	-		<0.001	<0.001	<0.001
P	-		<0.001	<0.001	<0.001
S	-		0.010	0.024	0.052
O2	-		-	-	-
Others	-		-	-	-

Figure K-3: Appearance of Incoclad 671 Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
 (Note: 3 o'clock is up in this image)

3 O'Clock
 (Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure K-4: As-Received Appearance of Sample P-Q (Inconel 671)

(Average surface metal temperature: 1193 °F)

Note the 3 o'clock view was photographed at a much later date and after the sectioning operation. Material is missing from between the cut near weld P and the middle of the specimen, and that is the reason why this image is shorter than the other two.

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure K-5 As-Received Appearance of Sample U-V (Inconel 671)

(Average surface metal temperature: 1110 °F)

Note: this tube sample was 11-5/8-in. long.

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure K-6: As-Received Appearance of Sample EE-FF (Inconel 671)

(Average surface metal temperature: 1075 °F)

12 O’Clock
(0 mils lost)

3 O’Clock
(0 mils lost)

6 O’Clock
(5 mils lost)

Figure K-7: OD Surface Appearance After Grit Blast

Material: Incoclad 671
Sample: P-Q

12 O’Clock
(0 mils lost)

3 O’Clock
(0 mils lost)

6 O’Clock
(0 mils lost)

Figure K-8: OD Surface Appearance After Grit Blast

Material: Incoclad 671
Sample: U-V

12 O’Clock
(9 mils lost)

3 O’Clock
(1 mils lost)

6 O’Clock
(4 mils lost)

Figure K-9: OD Surface Appearance After Grit Blast

Material: Incoclad 671
Sample: EE-FF

Material:

Incoclad 671

Sample Location:

P-Q

Maximum Rate:

4 mils/yr

Maximum Loss Orientation:

Approx. 6 (and 7) o'clock

Average Surface Metal Temperature:

1193 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.257	0.252	0.253	0.258	0.260	0.265	0.266	0.262	0.259	0.260
After	0.263	0.259	0.254	0.253	0.255	0.260	0.264	0.264	0.259	0.255
Delta	-0.006	-0.007	-0.001	0.005	0.005	0.005	0.002	-0.002	0.000	0.005

Figure K-10: Silhouette and Wall Thickness Measurements for Sample P-Q

Material:

Incoclad 671

Sample Location:

U-V

Maximum Rate:

2 mils/yr

Maximum Loss Orientation:

Approx. 9 o'clock

Average Surface Metal Temperature:

1110 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.257	0.256	0.256	0.261	0.262	0.262	0.262	0.258	0.259	0.262
After	0.259	0.257	0.257	0.261	0.262	0.261	0.259	0.259	0.259	0.259
Delta	-0.002	-0.001	-0.001	0	0	0.001	0.003	-0.001	0.000	0.003

Figure K-11: Silhouette and Wall Thickness Measurements for Sample U-V

Material:

Incoclad 671

Sample Location:

EE-FF

Maximum Rate:

13 mils/yr

Maximum Loss Orientation:

Approx. 11 o'clock

Average Surface Metal Temperature:

1075°F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.261	0.256	0.255	0.254	0.258	0.260	0.266	0.266	0.260	0.260
After	0.252	0.260	0.254	0.251	0.254	0.258	0.261	0.265	0.257	0.243
Delta	0.009	-0.004	0.001	0.003	0.004	0.002	0.005	0.001	0.003	0.017

Figure K-12: Silhouette and Wall Thickness Measurements for Sample EE-FF

Figure K-13: Metal Loss as a Function of Average Surface Metal Temperature

Material: Incoclad 671

Figure K-14: Low Magnification Image Showing Cross-Section Through Thinnest Region of Sample P-Q (Inconel 671)

Figure K-15: Microstructure: Incoclad 671

(c) External Scale/Metal Interface (SEI - High Magnification)

Figure K-15 (Cont.): Microstructure: Incoclad 671

Figure K-16: Microstructure: Incoclad 671

Note: Numbers on photos indicate distinct areas characterized by the visual assessment and EDAX analyses that follow.

Internal Surface Appearance

Figure K-17: Microstructure: Incoclad 671

(a) Sample P-Q (1193°F)

(b) Sample U-V (1110 °F)

Figure K-18: Optical Microstructures Incoclad 671

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

(c) Sample EE-FF (1075 °F)

Figure K-18 (Cont.): Optical Microstructures Incoclad 671

Note: Photomicrographs at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Figure K-19: EDAX Analysis of Deposit/Scale/Metal Interface for Incoclad 671 (Sample P-Q)

Area	Description	Visual Appearance	Ni	Cr	Fe	Co	Mn	V	Ti	Al	Si	C	O	Ca	K	Cl	As	P	S
1	Bulk deposit analysis	Rust red deposit with spherical particles.	--	0.36	3.56	--	--	--	--	5.03	12.4	32.6	31.0	1.19	--	.034	11.6	0.58	1.33
2	Deposit / scale analysis		--	9.17	11.4	--	--	--	--	5.18	14.1	--	45.6	--	--	--	13.7	0.76	--
3	Scale with embedded coal ash.		--	70.0	7.50	--	--	0.59	0.47	0.52	1.97	--	18.5	--	--	--	--	--	0.48
4	Tightly adhering scale.	Near interface	3.18	53.7	3.18	--	--	--	0.86	1.28	0.33	--	40.2	--	--	--	--	--	0.42
5	Partially consumed metal	Within interface zone	32.1	52.3	--	--	--	--	0.30	2.37	--	--	13.0	--	--	--	--	--	--
6	Dark etching material.	Within interface zone	20.2	47.4	0.99	--	--	--	0.75	10.6	--	--	19.5	--	--	--	--	--	0.46
7	Partially consumed metal	Within interface zone	32.7	46.0	--	--	--	--	0.50	2.91	--	--	17.6	--	--	--	--	--	0.31
8	Internal corrosion product	In metal near interface	31.5	32.2	0.55	--	--	--	3.33	11.6	--	--	20.4	--	--	--	--	--	0.30
9	Base metal diffusion zone	Near interface	65.8	33.7	--	--	--	--	0.51	--	--	--	--	--	--	--	--	--	--
10	Bulk base metal analysis	Normal etched appearance	47.7	50.81	--	--	--	--	0.40	1.10	--	--	--	--	--	--	--	--	--
	Reference bulk analysis		51.1	47.7	.014	0.24	0.001	0.011	0.38	0.23	0.02	0.05	--	--	--	--	--	--	0.01

Appendix L
Analysis of Performance
Test Section A
IN72 Weld Overlay

Overview of Results: IN72 Weld Overlay

IN72 Weld Overlay experienced a low rate of metal loss due to Test Section A exposure. The maximum rate was determined to be 21 mils per year*. This rate has been adjusted to take into account metal thickness lost due to grain boundary penetrations.

As was true for the other nickel-base alloys, the chromium and overall alloy content of this material likely account for the good performance of the IN72 Weld Overlay in this environment. Also, like the other nickel-base materials, the corrosion rate appears to be higher at the lower exposure temperature (1068 °F for IN72, 1062 °F for IN52, and 1075°F for Inconel 671). The reason for the somewhat increased corrosion rate at lower temperatures has not been determined.

Analysis of deposit on the surface revealed that it had the known aggressive combination of species, namely iron, oxygen, the alkali metals, and sulfur. Thus, the required corrosive elements were available to test the performance limits of this alloy.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: IN72 Weld Overlay

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">The schematic in Figure L-1 shows the relative positions of the two IN72 Weld Overlay samples in Test Section A. Also, shown is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">The table in Figure L-2 provides the composition of the two tube samples after exposure. Both samples were taken from Heat UKL8138. The table also shows the filler wire nominal composition as reported in literature from the supplier, Special Metals Corporation (SMC). Also shown is the heat chemistry for the filler wire.It was noted that the actual tube sample composition was slightly lower in chromium and higher in iron than the reported filler wire chemistry; however, these differences are in line with what would be expected for a weld deposit, and compares reasonable well the desired nominal chemistry.
As-Received Appearance	<ul style="list-style-type: none">Figure L-3 provides the typical appearance of the IN72 Weld Overlay material as it was delivered from SMC. The weld bead surface profile is clearly visible in this view. The cladding thickness was measured to be approximately 80 mils. Thus, it comprised about 27% of the total wall thickness of 292 mils.Figures L-4 and L-5 document the appearance of the external surface of the IN72 Weld Overlay tube samples after service. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).No wastage is visible in these views. The original weld bead profile is somewhat obscured by deposit on Sample FF-GG (Figure L-5); however, it is clearly visible on Sample Q-R (Figure L-4) which is relatively free from scale.A relatively thick rust-red back-side scale and deposit build-up is seen at the 3 o'clock and 6 o'clock positions on Sample FF-GG.A relatively thin red-brown deposit is seen on all other surfaces.The 12 o'clock position for Sample FF-GG shows evidence of the gray/white scale associated with molten alkali-iron sulfate attack. This is also in evidence in the 3 o'clock view for Sample Q-R). It is anticipated that scraping to remove the red scale would reveal evidence of a gray/white scale immediately adjacent to the metal surface in most locations.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">Figures L-6 and L-7 show the appearance of the external surface of the IN 72 Weld Overlay tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for Sample FF-GG show the appearance of general wastage due to fireside corrosion.The "pit" shown in the 12 o'clock position for Sample Q-R is likely a weld imperfection.

Material: IN72 Weld Overlay

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures L-8 and L-9.• The same relative “o’clock” positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost. Note that in some cases, the delta is negative (particularly on the back-side). This is believed due to wall thickness variability and difficulty in locating the exact location of the “before” measurement.• Sample FF-GG experienced the maximum wall thickness reduction of 21 mils per year.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure L-10 plots the maximum wall thickness lost against the calculated average metal temperature the two IN72 Weld Overlay 25 samples.• Similar to the other high-nickel candidate alloys (IN52 Weld Overlay and Inconel 671), the wastage rate was low, but found to be higher at the lower exposure temperature (1068 F). The reason for this has not been explored but examination of the grit blast surface appearances in Figures L-6 and L-7 further substantiate that the sample at the higher average exposure temperature fared better.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample Q-R was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. This image shows the profile (in the welding direction) of the interface between the cladding and the underlying 800H material. The cladding thickness is seen to be fairly consistent in this plane.

Material: IN72 Weld Overlay

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">• Figure L-11 also shows that there is a minimal deposit/scale at the external surface. No scale is evident on the internal surface at this magnification.• Figures L-12 a, b, and c show secondary electron images (SEI) of the scale/metal interface for Sample O-R. High magnification back scattered electron images (BEI) of these same regions are provided in Figures L-13a and b. The SEI images provide better resolution of the visible features of the interface. The BEI images provide less resolution but allow one better to resolve compositional differences. Based on examination of these, five distinct regions are in evidence. These regions are, starting within the metal and working out:<ol style="list-style-type: none">1. <u>Base metal</u> – Oxalic acid etch delineates grain boundaries, carbides, and inclusions.2. <u>Grain boundary attacked base metal</u> – This region can best be seen in the higher magnification view provided in Figures L-12b and 13a. These grain boundary penetrations extend approximately 3 mils into the external surface. Counting these as lost wall thickness would not change the calculated “zero” wastage for Sample Q-R because of the variability in the original measurements, (see the data provided in Figure L-8). Counting these penetrations as lost wall thickness does make a difference in the calculated lost wall thickness for sample FF-GG, and the maximum rate has been adjusted by 3 mils per year to take this into account.3. <u>Reaction zone in metal</u> – This constitutes the leading edge of the grains as they interface with the scale. Scale and metal are intermingled in this area.4. <u>Tightly adherent scale</u> – this is seen continuous along the surface. EDAX analysis will later show that this is predominantly a chromium-rich oxide, (see the composition for Area 3 in the table that follows). The scale is approximately 0.3 mils thick.5. <u>Thick and very porous deposit/scale conglomerate</u> – many spherical particles are noted along with what appears to be islands of scale (metal oxides).• Figure L-14 shows the appearance of the internal metal surface for Sample Q-R. An oxide scale is noted to cover the surface and to be penetrating along some boundaries.
Metallurgical Analysis – Light Optics.	<ul style="list-style-type: none">• Figures L-15a and b show the appearance of the cladding microstructure for Sample Q-R. Figure L-15a clearly shows the grain boundary penetrations discussed earlier• Figures L-16a and b show the appearance of the cladding microstructure for Sample FF-GG. Figure 16b shows a penetration believed to be a weld imperfection.

Summary of Findings, (continued)

Material: IN72 Weld Overlay

Issue	Discussion
EDAX Analysis Results	<ul style="list-style-type: none">• The table in Figure L-17 provides a summary of the EDAX analyses of the nine locations numbered in Figure L-13a and b. Also shown in this table is a bulk EDAX analysis of the weld overlay, and a summary of the spectrographic analysis reported earlier, see Figure L-2.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Areas 1 and 2: Bulk deposit/scale analysis</u> – Alkali metals are present. Sulfur and phosphorous are present in an increased amount compared to the base metal. An iron oxide is likely, as are aluminum, silicon and titanium oxides. The analysis suggests that the carbon content is relatively high, however, caution is warranted in assessing this result in that EDAX is inherently inaccurate in analyzing carbon content and there is also the possibility for contamination by infiltrated epoxy resin mounting compound.• <u>Areas 3, 4, 6 and 9: At scale/metal interface</u> – These show evidence of a predominantly chromium-rich oxide scale (particularly in Area 3). Also significant here is the presence of sulfur.• <u>Area 7: Base metal adjacent to interface</u> – This metal adjacent to the interface compares well with the bulk analysis.• <u>Areas 5 and 8: Inclusion and corrosion product in grain boundary</u> – The inclusion appears to be titanium-rich. Of significance within these boundaries is the presence of high levels of sulfur (and perhaps carbon).• <u>Bulk Overlay Analysis:</u> – Given its limitations this EDAX analysis compares favorably with that of the reference spectrographic analysis below it.

Figure L-1: Schematic Drawing Showing Position of IN72 Weld Overlay Tube Samples Within Test Section A

Note: Drawing shown in same relative orientation as per the actual installation.

Figure L-2 Inco 72 / 800 HT (Weld clad duplex tubing)

Description: Nominal 45Cr/55 Ni alloy cladding for oxidation/corrosion protection. Incoloy 800HT substrate provides creep strength.
Source: Special Metals Corporation (SMC)
Reference Composition: Filler wire “nominal” chemistry – Per SMC literature.

Element	Reference Composition for Weld Cladding	Composition Heat UKL8138	Tube Sample Q-R	Tube Sample FF-GG
Ni	55	54.96	54.8	54.7
Cr	44	43.30	41.81	41.92
Fe	0.2	0.43	1.85	1.94
Mo	-	-	0.008	0.008
Co	-	-	0.094	0.092
C	0.05	0.02	0.029	0.088
N	-	-	-	-
B	-	-	0.004	0.003
Mn	0.1	0.03	0.10	0.10
Si	0.1	0.15	0.19	0.16
Al	-	0.20	0.24	0.17
Ti	0.6	0.66	0.59	0.60
Al+Ti	-	-	-	-
Nb	-	-	0.14	0.12
Ta	-	-	-	-
Nb+Ta	-	-	-	-
V	-	-	0.011	0.008
W	-	-	-	-
Cu	0.2	-	0.038	0.038
Sn	-	-	<0.001	<0.001
P	-	0.005	<0.005	<0.001
S	0.008	0.003	0.019	0.024
O2	-	-	-	-
Others	<0.50	<0.50	(a)	(a)

a- Not determined.

Note: Reference composition is for filler wire, not as-deposited.

Figure L-3: Appearance of IN72 Weld Overlay Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure L-4: As-Received Appearance of Sample Q-R (IN72 Weld Overlay)

(Average surface metal temperature: 1198 °F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure L-5 As-Received Appearance of Sample FF-GG (IN72 Weld Overlay)

(Average surface metal temperature: 1068 °F)

12 O'Clock
(0 mils lost)

3 O'Clock
(0 mils lost)

6 O'Clock
(0 mils lost)

Figure L-6: OD Surface Appearance After Grit Blast

Material: IN72 Weld Overlay
Sample: Q-R

12 O’Clock
(14 mils lost)

3 O’Clock
(0 mils lost)

6 O’Clock
(4 mils lost)

Figure L-7: OD Surface Appearance After Grit Blast

Material: IN72 Weld Overlay
Sample: FF-GG

Material: IN72 Weld Overlay

Sample Location: Q-R
Maximum Rate: 10 mils/yr*
Maximum Loss Orientation: 7:30 o'clock
Average Surface Metal Temperature: 1198 °F

* Increased by 3 mils per year based on evidence of grain boundary penetration.

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.294	0.286	0.284	0.284	0.292	0.299	0.300	0.299	0.292	0.299
After	0.300	0.296	0.288	0.285	0.284	0.290	0.297	0.300	0.292	0.290
Delta	-0.006	-0.010	-0.004	-0.001	0.008	0.009	0.003	-0.001	0.000	0.009

Figure L-8: Silhouette and Wall Thickness Measurements for Sample Q-R

Material:

IN72 Weld Overlay

Sample Location:

FF-GG

Maximum Rate:

21 mils/yr *

Maximum Loss Orientation:

Approx. 12 o'clock

Average Surface Metal Temperature:

1068 °F

* Increased by 3 mils per year based on evidence of grain boundary penetration.

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.288	0.291	0.289	0.294	0.297	0.296	0.290	0.287	0.292	0.288
After	0.264	0.282	0.287	0.294	0.298	0.295	0.291	0.286	0.287	0.264
Delta	0.024	0.009	0.007	0.000	-0.001	0.001	-0.001	0.001	0.005	0.024

Figure L-9: Silhouette and Wall Thickness Measurements for Sample FF-GG

Figure L-10: Metal Loss as a Function of Average Surface Metal Temperature

Material: IN72 Weld Overlay

Figure L-11: Low Magnification Image Showing Cross-Section Through Thinnest Region of Sample Q-R (IN72 Weld Overlay)

Figure L-12: Microstructure: IN72 Weld Overlay

(c) External Scale/Metal Interface (SEI - High Magnification)

Figure L-12 (Cont.): Microstructure: IN72 Weld Overlay

Figure L-13: Microstructure: IN72 Weld Overlay

Note: Numbers on photos indicate distinct areas characterized by the visual assessment and EDAX analyses that follow.

Internal Surface Appearance

Figure L-14: Microstructure: IN72 Weld Overlay

(a) Sample Q-R (1198 °F) Approx. 200X

(b) Sample Q-R (1198 °F) Approx. 50X

Figure L-15: Optical Microstructures IN72

Note: Electrolytic 10% oxalic acid etch, 9V OCP

(a) Sample FF-GG (1068 °F)

Approx. 200X

(b) Sample FF-GG (1068 °F)

Approx. 50X

Figure L-16: Optical Microstructures IN72

Note: Electrolytic 10% oxalic acid etch, 9V OCP

Figure L-17: EDAX Analysis of Deposit/Scale/Metal Interface for IN72 Weld Overlay (Sample Q-R)

Area	Description	Visual Appearance	Ni	Cr	Fe	Co	Mn	V	Ti	Al	Si	C	O	Ca	K	Na	As	P	S
1	Bulk deposit analysis	Rust red deposit with spherical particles.	--	0.40	11.57	--	--	--	0.39	7.78	13.7	20.7	35.6	--	1.73	0.63	4.37	1.03	1.07
2	Deposit / scale analysis		--	0.50	4.70	--	--	--	--	4.79	16.0	22.9	36.3	--	--	--	12.5	1.91	0.37
3	Tightly adhering scale.	Near interface	0.76	50.7	5.45	--	--	--	0.67	0.51	0.22	--	39.6	--	--	--	1.47	--	0.65
4	Scale in grain boundary	Near interface	52.5	21.5	2.80	--	--	--	7.43	0.99	--	5.57	7.17	--	--	--	--	--	2.03
5	Scale in grain boundary	Near interface	40.3	20.3	1.71	--	--	--	0.75	5.30	--	6.81	24.3	--	--	--	--	--	0.51
6	Partially consumed metal	Within interface zone	56.9	20.0	3.78	--	--	--	0.64	--	--	5.70	12.4	--	--	--	--	--	0.61
7	Base metal near interface.	Near interface	50.5	46.5	1.80	--	--	--	1.21	--	--	--	--	--	--	--	--	--	--
8	Inclusion and corrosion product at grain boundary	Near interface	48.1	41.8	1.45	--	--	--	3.02	2.12	--	--	--	--	--	--	--	--	3.45
9	Partially consumed metal	Within interface zone	53.4	19.8	3.53	--	--	--	0.68	1.14	--	4.78	15.8	--	--	--	--	--	0.83
	Bulk overlay analysis	Normal etched appearance	52.0	44.4	2.37	--	--	--	0.73	0.58	--	--	--	--	--	--	--	--	--
	Reference bulk analysis		54.8	41.8	1.85	0.09	0.10	0.01	0.59	0.24	0.19	0.03	--	--	--	--	--	--	0.019

ATTACHMENT 2

**TOPICAL REPORT – REMOVAL OF SECTION C
DATED JUNE 2004**

COAL ASH CORROSION RESISTANT MATERIALS TESTING

Topical Report: Removal of Section “C”

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Date published: June 2004

This report does not contain any Trade Secret/Proprietary Information.

This project was funded in part by the U. S. Department of Energy and the Ohio Coal Development Office, Department of Development, State of Ohio

U.S. Department of Energy Contract:
Ohio Coal Development Office Grant Agreement:
The Babcock & Wilcox Company Contract:

DE-FC26-99FT40525
CDO/D-97-02
CRD 1392

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EXECUTIVE SUMMARY

In April 1999, three identical superheater test sections were installed into the Niles Unit #1 for the purpose of testing and ranking the coal ash corrosion resistance of candidate superheater alloys. The Niles boiler burns high sulfur coal (3% to 3.5%) that has a reasonably high alkali content, thus the constituents necessary for coal ash corrosion are present in the ash. The test sections were controlled to operate with an average surface metal temperature from approximately 1060 °F to 1210 °F which was well within the temperature range over which coal ash corrosion occurs. Thus, this combination of aggressive environment and high temperature was appropriate for testing the performance of candidate corrosion-resistant tube materials. Analyses of the deposit and scale confirmed that the aggressive alkali-iron-trisulfate constituent was present at the metal surface and active in tube metal wastage. The test sections were constructed so that the response of twelve different candidate tube and/or coating materials could be studied. The plan was to remove and evaluate one of the three test sections at time intervals of 1 year, 3 years, and 5 years. This would permit an assessment of performance of the candidate materials as a function of time.

Test Section A was removed in November 2001 after about 24 months of service at the desired steam temperature set point, with about 15.5 months of exposure at full temperature. A progress report, issued in October 2002, was written to document the performance of the candidate alloys in that test section. The evaluation described the condition of each tube sample after exposure. It involved a determination of the rate of wall thickness loss for these samples. In cases where there was more than one sample of a candidate material in the test section, an assessment was made of the performance of the alloy as a function of temperature.

Test Sections B and C were examined during the November 2001 outage, and it was decided that, due to excessive wastage, certain tube samples needed to be removed and replaced in order to ensure that Test Sections B and C would have a chance of remaining in the boiler for their intended exposure period. These suspect tube samples were replaced and the two remaining test sections were put back into service. The tube samples that were removed from Test Sections B and C were set aside for later analysis at the end of the planned exposure period.

Test Sections B and C were again examined approximately six months later. At that time, measured wall thickness losses raised concerns about additional tube samples. These suspect samples were also removed, set aside for later analysis, and replaced. The test sections then went back into service until the end of the second exposure period, which was concluded in May 2003 when, due to evidence of excessive wastage, the valves were opened effectively stopping corrosion. In August 2003, Test Sections B and C were removed for closer examination. Section C had experienced about 42 months of service at the desired steam temperature set point with 28.5 months at full temperature. Test Section B was re-installed into the boiler (at the location originally occupied by Section C), and will remain in service until the end of the program.

This report provides the results of the evaluation of Test Section C, including the samples that remained in the Test Section for the full exposure period as well as those that were removed early. The analysis of Test Section C followed much the same protocol that was employed in the assessment of Test Section A. Again, the focus was on determining and documenting the relative corrosion rates of the candidate materials. The detailed results of the investigation are included in

this report as a series of twelve appendices. Each appendix is devoted to the performance of one of the candidate alloys. The table below summarizes metal loss rate for the worst case sample of each of the candidate materials for both Test Sections A and C. The body of this report compares these for all of the samples in the test section.

Maximum Wastage Rate for Each Candidate Material In Test Sections A and C

Review of this chart reveals that, with few exceptions, the results for Test Section C (20,832 hour exposure at corrosive temperatures) were very similar to those earlier determined for Test Section A (11,288 hour exposure). In general, it can be stated that, while the sampling represented by these tests is small, the relative performance of the candidate alloys appears to have been strongly influenced by their total alloy content, in particular, the sum of their chromium plus nickel contents.

Maximum Wastage Rate as a Function of Chromium Plus Nickel

Two areas of caution also were identified with regard to some of the more resistant materials. First, the IN 52 Weld Overlay samples went into service with an 80 mil thick cladding for corrosion protection, but by the end of the Test Section C exposure period, the cladding was completely wasted away, and the underlying substrate was exposed to the corrosive environment. Given the fact that the 800H substrate is much less corrosion resistant than the cladding, the wastage rate is expected to increase significantly for this material. Second, it was determined that the IN 72 Weld Overlay, while being very corrosion resistant also had experienced a weld

cracking phenomenon that may impact its service life. Preliminary investigations suggest that the cladding may have contained small, and difficult to detect, internal cracks prior to service exposure. Preliminary investigations also suggest that the extent of cracking within the IN 72 Weld Overlay may increase in quantity and in length as a function of time at temperature. This issue however has not yet been fully resolved. So, at this point, for the sake of comparison, the data illustrated in the charts above only take corrosion wastage into account. If the wall thickness lost due to the observed cracking had been included in the wastage rate calculations, then the wastage rate would have increased by about 50%. However, if this additional 50% were taken into account, the total wall thickness lost for the IN 72 Weld Overlay still would be small relative to some of the other materials. Nonetheless, it must be remembered that the IN 72 Weld Overlay samples initially had only 80 mils of cladding to act as a corrosion barrier. Once the cladding is breached, as was noted for the IN 52 Weld Overlay, the wastage rate is expected to increase considerably.

Of particular concern regarding the damage found in IN 72 Weld Overlay, is the fact that, while these samples are in service, the surface deposit and scale may hide the fact that the underlying metal is not sound. The extent of damage is normally monitored by visual inspection and dimensional measurements in situ within the boiler without disturbing the surface condition of the tubes. If the cladding is breached by a cracking mechanism, and the underlying metal is corroding away beneath the cladding, then, this condition may not be discernable by standard inspection methods. Obviously, this could lead to a false sense of security regarding the soundness of a test section. Given this concern, the otherwise good corrosion resistance of this material, and the usefulness of weld cladding as an inexpensive means of achieving this corrosion resistance, suggests that elimination of this cracking is an area worthy of further study.

1.0 INTRODUCTION

This report represents the second in a series of three topical reports that document progress toward completion of the DOE-sponsored program to compare and rank the coal ash corrosion resistance of twelve candidate superheater tube materials (and/or coatings). (Contract No. DE-FC26-99FT40525).

The first topical report, issued on October 31, 2002, addressed the evaluation of Section A which was the first test section to be removed from the boiler. The Section A report provided the full details of the project background, material selection, fabrication of test materials and sections, description of the test system, and system installation and startup. The report also provided the operating history through 2001 along with the results of the evaluation of the candidate materials within the section. That information will not be repeated here. The reader is directed to "Topical Report: Removal of Section A" if this information is needed.

This second topical report addresses herein the evaluation of test Section C which was removed for evaluation in August 2003. Section C was the second test section to be removed from the boiler. The results of the evaluation of each candidate material in Section C are contained in the twelve separate appendices that accompany this report. The main body of this report integrates this information and draws preliminary observations and conclusions based on the results to date. Annex 1 of this report documents the operating history of the test sections beginning where the Section A report left off at the end of 2001. This annex thus provides a timeline of activities

throughout 2002 and 2003. Annex 1 can be found following the “Observations and Conclusions” section of this report.

At this point in time, test Section B continues in service, and likely will be removed for evaluation within the next twelve months. At that time a third topical report will be issued to cover the evaluation of test Section B after it has been removed from service. Once all three sections have been evaluated, and the topical reports issued, the program will be brought to completion, and a final report will be issued that integrates and summarizes observations and conclusions that can be drawn from all of the data collected in this program.

2.0 BACKGROUND

Procedures & Results

This section of the report documents the procedures and sequence of activities used to assess the condition of Test Section C after service. The primary focus is on determining the relative coal ash corrosion resistance of the candidate superheater tube alloys. General results also are offered in this section of the report. Detailed results are provided on a material-by-material basis in the attached appendices.

Background:

At the beginning of the program, three identical test sections were installed side-by-side in the Niles Unit-1 boiler. These were identified as Test Sections A, B, and C. The intent was to remove and evaluate a section after each of three increasingly longer exposure increments. The purpose was to demonstrate how the candidate tube alloys performed as a function of time. Test Section A was to be removed after one year. Section B was to be removed after three years of exposure, and Test Section C was to be removed at the end of the program, after approximately 5 years of exposure.

Due to various practical issues, and due to the fact that some of the candidate alloys corroded much more rapidly than expected, as the program progressed, it became necessary to deviate from the original plan. Test Section A was removed and analyzed first as planned. However, when it came time to remove the second test section for analysis, examination revealed that Section C was distorted (due to in situ maintenance), while Section B was relatively unaffected. Based on this, it was decided to evaluate Section C and to reinstall Section B. The results of the analysis of Section C are the subject of this report. Test Section B remains in the boiler, and will continue in service until the end of the program.

Test Section A was removed from Niles Unit-1 in November 2001, after 28.5 calendar months (approximately 21,200 hours) from start-up, 24 months with the desired steam temperature set point, and an equivalent of 11,288 hours (15.5 months) of exposure under conditions likely to cause coal ash corrosion. At the time that Section A was removed for analysis, it became apparent that some of the tube samples in Sections B and C (particularly the Save 25 samples) would not survive the additional time required to reach the next planned exposure increment. In an effort to ensure that Sections B and C would not fail prior to their scheduled removal time, it was decided that questionable tube samples should be removed from the test sections and replaced with “dutchmen” tube lengths. The dutchmen were intended to provide the wall

thickness and corrosion resistance needed to extend the life of the section. Six contiguous tubes (between welds G and M) were removed from both Sections B and C and replaced. The dutchman for Section B was made from a single length of Alloy 800H which was clad with Inco 52 weld metal. The dutchman for Section C was made from two lengths of 310 HCbN that were joined together to cover the width of the gap.

Sections B and C went back into service with the dutchmen in place. When they were re-examined about six months later, it was noted that additional tube samples needed to be replaced due to excessive corrosion. So, in June 2002, for both sections, three contiguous tube samples (between welds D and G) were removed and replaced with Inco 52 clad dutchmen. When these repairs were made both sections went back into service until the outage in May 2003 when, due to evidence of excessive wastage, the valves were opened effectively stopping corrosion.

In August 2003, both sections were removed and visually evaluated. This examination revealed that Section C had become distorted due to field maintenance difficulties while Section B was relatively unaffected, see figures below for comparison.

Section B – As Removed

Section C – As Removed

Furthermore, inspection of both sections revealed evidence of tube wastage that suggested that additional tube samples would need to be replaced if either section were to survive to the completion of the program. Based on this, it was decided to remove and replace all of the questionable samples from Section B, then, to put it back into service. It further was decided to use the samples from Section C for the current evaluation. It should be noted that Section B was re-installed into the boiler at the location previously occupied by Section C.

Section C Lay-Out

Figure 1 provides a schematic showing the position of the welds that join samples to one another to form Test Section C. Note that each weld has been given a letter designation. Using these, the tube sample positions are indicated by the weld letter designations at either end of the sample. As was mentioned earlier, the three test sections were identical, so, the same positions were occupied by the same candidate materials in all three test sections.

Figure 1 also shows the positions of the dutchmen in Section C at the time of its' removal from service. As was mentioned above, the tube samples at these locations were removed early due to excessive corrosion, so they did not experience the full exposure interval for Section C. Nonetheless, the samples from these locations were set aside (at the time of their removal) and their assessment will be included in the analysis of Section C. The only sample that could not be fully analyzed was the Save 25 sample at location D-E. This was due to the fact that at some

point, the D-E sample leaked, was repaired with a weld pad, and put back into service. Otherwise the full sequence of tube samples is included in this analysis.

Table 1 provides the key to the sequence of candidate materials within the three test sections. In this table, the candidate alloys are listed in the sequence in which they are encountered in the test section as one progresses from the hottest location toward the coolest. This table includes the tube sample letter designations that are based on the weld lettering shown in Figure 1. Included in this table are calculated Test Section C average surface metal temperature at each location and the total exposure time for each sample.

Exposure Time

Initial exposure of the three test sections to flue gas occurred when Niles Unit-1 resumed operation in June of 1999, following a maintenance outage during which the sections were installed. Test Section C was removed from service in May of 2003, after a period of 47 calendar months in the boiler, 42 months at desired steam temperature set point and about 28.5 months at full temperature under conditions likely to cause coal ash corrosion. During this time the boiler shifted load and cycled on and off line in normal response to power demand and boiler maintenance requirements.

It is well understood that the rapid metal loss associated with coal ash corrosion of austenitic materials occurs over a temperature range between approximately 1,000 F and 1,300 F. The intent of this work was to control the test sample average surface metal temperatures to fall within this range over the full length of the test section. This required that the boiler be operated at sufficiently high load to assure reasonably constant gas temperatures. At low loads, reheat steam pressure and/or furnace exit gas temperature is 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 surface metal temperature at the hot end of the test section (Point-T in Figure 22) was taken as the transition temperature above which the rate of coal ash corrosion is significant and below which it is negligible. For Test Section C the accumulative time at full temperature under conditions likely to cause coal ash corrosion was 20,832 hours.

Test Section Surface Metal Temperatures

As indicated above, desired test section temperatures are maintained by controlling the temperature of steam exiting the test section. It is constantly monitored by thermocouple measurement, and an arithmetic average outlet steam temperature is recorded at five minute intervals.

The external surface temperature of each alloy test segment is calculated at five minute intervals using the measured outlet steam temperatures, the average gas temperature, and B&W's heat transfer model for the test section. In the following appraisals of coal ash corrosion, an average surface metal temperature is determined for each test specimen. The indicated average surface metal temperatures are arithmetic averages of the calculated segment external surface metal

temperatures for the time that the sample was exposed to the coal ash corrosion temperature range. Most of the tube samples within Section C experienced the full 20,832 hours at full temperature. The average surface metal temperatures for samples that were removed early were calculated based on the exposure temperatures during their time in the boiler. For all of these samples, the indicated arithmetic average provides a reasonable and practical approximation of the “isothermal equivalent temperature”, i.e. the isothermal temperature at which exposure over time would produce the observed extent of corrosion. The average surface metal temperature approximates the isothermal equivalent temperature to the extent that the corrosion rate is a linear function of temperature. This simplification is justified at this point due to the limited amount of available data, but the data seems to suggest that the corrosion rate may be departing from linearity for some of the materials under investigation. Table 1 shows the estimated average surface metal temperatures for test segments in Section C.

Temperatures were not constant. As gas, steam, and metal temperatures rose and fell at the beginning and end of each high-temperature boiler operating cycle, samples accumulated a few hours of coal ash corrosion below the target exposure surface metal temperature. Also, test section surface metal temperatures were low throughout an initial six month shakedown period. The full target section outlet steam temperature of 1075°F was only maintained after November of 1999. The temperature history of Section C, Segment “R-S” (Figure 2) illustrates the surface metal temperature variability. For this segment the average surface metal temperature over the duration of the test is 1208°F. As shown in Figure 2, surface metal temperatures are initially low. Then from July through December 1999, they climb to an average surface metal temperature appropriate for testing, and remain near this temperature whenever the section is operational until it is removed in from service May of 2003. Figure 2 also illustrates the daily surface metal temperature variability. The wide spread in values is generally caused by transients when the unit is taken off line.

Environment

The Niles cyclone boiler is fired with Ohio bituminous coal having a sulfur content of approximately 3% to 3.5%. The sulfur in this coal is pyretic and organic, with little sulfate. Chlorine concentrations are typically less than 0.05%. Table 2 shows a representative coal analysis. This same coal has been used to date throughout the program.

Documentation:

Test Section Appearance Upon Receipt After Exposure: Figures 3 and 4 show the appearance of Test Section C when it was received at the Research Center. Two figures were needed to document the entire length of the test section; however, there is some overlap between them. The weld lettering designations are noted in these figures. The schematic provides a representation of how each tube sample was originally situated within the test section.

Tube Sample Surface Appearance: Close-up photographs were taken to document the condition of each tube sample. Figure 5 provides an example of this documentation for one tube sample. Three views were documented. The 12 o'clock position faced downward* into the oncoming gas flow. The 6 o'clock position was at the top of the tube on the side downstream of the gas flow direction. The 3 o'clock position was halfway between the two. These figures typically document the extent of deposit and scaling. In some cases where the scale and deposit have

fallen away, evidence also is seen of the chalky white deposit associated with alkali-iron-trisulfate hot corrosion. The rest of these are included in separate appendices to this report. Each appendix is devoted to a different candidate material.

Tube Sectioning:

Figure 6 provides a schematic that depicts how the tube sample was sectioned to extract specimens for evaluation. Figure 7 shows the sectioning plan for each tube sample. All cuts were made dry using a saw. As they were cut, samples were marked to maintain sample identity and tube orientation (i.e. 12 o'clock, 3 o'clock, and 6 o'clock).

Composition Verification:

For Test Section A, removed and analyzed earlier, a portion of the “extra material”, identified as RS-4 in Figure 7, was sent to a third-party laboratory for confirmatory chemical analysis, primarily by optical emission spectrometry. The results of these analyses were compared with the reported heat analyses from the various providers of materials for test. They were also compared with material specifications if they were available. Otherwise, a “nominal” or “target” tube metal composition was used.

The results of these spectroscopic analyses for Test Section A, confirmed that the correct tube material had been used at each location in the test section, and that the tube material complied with its' intended chemical composition. The scanning electron microscope (SEM) also was used to perform a semi-quantitative chemical analysis (using the energy dispersive x-ray spectrometry (EDS)) for each of the twelve different material types in Test Section A. These results compared well with the somewhat more accurate optical emission spectrometry analyses as can be seen from reviewing the data in the appendices to the final report covering the Section A analysis.

With alloy identification confirmed for Test Section A, it was decided that only representative sampling would be used to verify that the correct materials were at their proper location within Test Section C. It also was decided to use EDS as the analytical method, and that OES would be used as a fall-back if problems arose. To this end, twelve samples were chosen for analysis. Each of the twelve represented the most aggressively attacked sample of each material type. The EDS analyses confirmed that all twelve samples were of the proper material type.

The results of these analyses are included in the appendices of this report which provide detail on a material-by-material basis. Figure 8 shows a typical example.

Surface Condition:

Dimension rings (identified as “RS-2” in Figure 7) were removed from the approximate centerline of each tube sample. These were grit blasted with aluminum oxide grit to remove deposit and scale. The surface condition of each ring was photographed, and is included in the appendices of this report. Figure 9 shows a typical example. These are intended to show and

* By selecting the 12 o'clock orientation as the one facing directly into the gas flow direction, the resultant orientation yields an “upside-down” clock reference system relative to the physical position of the tube within the boiler, i.e. 12 o'clock faces downward.

record the level and type of attack that was occurring at the external surface of these tubes (i.e. beneath the deposit/scale that are shown in Figure 5).

Figure 10 shows a typical example of a dimension ring cross section and associated measurements. Such figures provide, as a reference, the amount of wall thickness measured at the position indicated. Dimensioning is discussed in more detail below. In general, it was the side of the tube that faced the gas flow that experienced most of the metal loss. The maximum wall thinning was typically between the 12 o'clock and 9 o'clock (or 3 o'clock) positions.

Dimensioning:

The grit blasted rings were measured with certified micrometers that were accurate to ± 0.001 ". The measurements were taken at eight predetermined circumferential locations that were indicated by the "o'clock" positions: 12:00, 1:30, 3:00, 4:30, 6:00, 7:30, 9:00, and 10:30 o'clock. The "o'clock" positions were the same as those used above to express the orientation of the tube within the test section. Prior to service, measurements had been taken and recorded for each of these orientations for each of the tube samples. The measurements taken after service were compared with these and a "delta" calculated to express the wall thickness losses at each position. These are recorded for each candidate material in the appendices that follow.

Note that an attempt was made to determine the maximum wall thickness loss for each tube sample. In some cases, it was clear that the minimum wall thickness was not at one of the eight predetermined locations, so, there was no "before service" measurement for use as a reference. In these cases, the average "before service" wall thickness measurement was determined and used as the reference measurement for determining the wall thickness lost. The location and value of the maximum are also documented in the appendices in tables such as the one shown in Figure 10.

Note also that it was not possible to take the "after service" measurements at the same axial position as the "before service" measurements, since these were taken at the tube ends, and the tube ends now were part of the welds that joined the tube samples to one another. Given the short lengths of the tube samples, and the overall consistency of the wall thickness measurements, it was judged that this 2 to 3-in. difference in axial location would have only a minor impact on the accuracy of the wall thickness measurements.

Metallography:

A full cross-section ring was polished and etched for one tube sample for each material type, (i.e. the ring identified as RS-1 in Figure 7). The same electrolytic etching procedure was used for each material. It involved using a 10% oxalic acid etchant with a 9 volt open circuit potential. These then were examined using the scanning electron microscope (SEM).

SEM/EDS:

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. Typically the examination was along the tube radius that extended through the thinnest wall for a given tube sample. Given the high

level of resistance to steam-side oxidation for all of the candidate alloys, the focus of this analysis primarily was on the deposit/scale/metal interface at the external surface of the tubes. Nonetheless, the condition at the scale/metal interface also was documented for the internal surface of the tube. For both surfaces, photographs were taken to record the nature of the scale and the condition of the underlying metal. These are recorded in the appendices along with comments regarding distinctive and/or unique features.

While in the SEM, EDS(energy dispersive spectroscopy) analyses were made of selected regions of the deposit, scale, and underlying tube metal. These also are recorded in the appendices.

Weld Profile:

Welds of every material type were cross sectioned (as per sample RS-3 in Figure 7) and evaluated. The purpose of this was to investigate the condition of the welds and weld heat affected zones relative to the remainder of the tube. The weld cross sections were polished, etched and photographed to record their appearance. Typical results are shown in Figures 11, 12 and 13.

Deposit Analysis:

Deposit was scraped and removed from outside surfaces and submitted for elemental and compound identification by chemical analysis and x-ray diffraction respectively. The deposit was tight and adherent and did not contain the heavy outer deposit that is sometimes seen on superheater tubes. Deposits were subjected to inductively coupled plasma – optical emission spectrographic (ICP-OES) analysis. The results are provided in Tables 3 and 4.

Lastly, EDS analyses, performed during the SEM investigation, indicated the potential presence of carbon in both the deposit and in the tube metal adjacent to the scale/metal interface, see Table 5. Because carbon analysis by EDS is not accurate, and because of the potential for contamination by the epoxy resin used as the mounting compound, a combustion-gravimetric analysis was performed to determine the presence of carbon in the deposit. The result of this analysis also is reported in Table 5 which also provides the chlorine content of the inner and outer layers of the deposit.

Table 1: Tube Sample Designation, Average Surface Metal Temperature, and Exposure Time Based on Position in Test Section C

Sample Designation	Material	Average Surface Metal Temperature (F)	Exposure Time (hrs)
S-T	Incoclad 671	1219	20,832
R-S	IN52 Weld Overlay	1208	“
Q-R	IN72 Weld Overlay	1208	“
P-Q	Incoclad 671	1203	“
O-P	HR 120	1194	“
N-O	310 HCbN (HR3C)	1190	“
M-N	310 Ta	1188	“
L-M	Modified 800H	1185	13,590
K-L	Save 25	1180	“
J-K	NF 709	1178	“
I-J	347 HFG	1174	“
H-I	Thermie	1171	“
G-H	310 HCbN (HR3C)	1167	“
F-G	310 Ta	1166	15,807
E-F	Modified 800H	1162	“
D-E	Save 25	1158	“
C-D	NF 709	1153	20,832
B-C	Fe3Al	1149	“
A-B	347 HFG	1147	“
Return Bend	TP 310	****	
U-V	671 Clad	1121	“
V-W	HR 120	1110	“
W-X	310 HCbN (HR3C)	1106	“
X-Y	310 Ta	1103	“
Y-Z	Modified 800H	1099	“
Z-AA	Save 25	1096	15,807
AA-BB	310 HCbN	1092	20,832
BB-CC	NF 709	1088	“
CC-DD	347 HFG	1086	“
DD-EE	HR 120	1088	“
EE-FF	Incoclad 671	1086	“
FF-GG	IN72 Weld Overlay	1079	“
GG-HH	IN52 Weld Overlay	1073	“
HH-II	Thermie	1067	“
II-JJ	Save 25	1058	“
JJ-KK	NF709	1048	“

Table 2. Representative Analysis of Coal Burned in Niles Unit-1

<u>Coal Analysis</u>	
Moisture	5.0 %
Carbon	66.5 %
Hydrogen	4.9 %
Nitrogen	1.4 %
Sulfur	3.1 %
Alkali (as Na ₂ O)	0.2 %
Ash	12.3%
<u>Ash Analysis</u>	
SiO ₂	41.5 %
Al ₂ O ₃	19.5 %
TiO ₂	1.2 %
Fe ₂ O ₃	26.8 %
CaO	3.8 %
MgO	0.7 %
K ₂ O	1.6 %
Na ₂ O	0.5 %
SO ₃	3.3 %
P ₂ O ₅	0.6 %
BaO	0.1 %
Undetermined	0.3 %

Table 3: Deposit Analysis

Constituent	Section A Outer Layers (wt%)	Section A Inner Layers (wt%)	Section C Outer Layers (wt%)	Section C Inner Layers (wt%)
Silicon, SiO ₂	31.84	28.64	23.39	20.51
Aluminum, Al ₂ O ₃	14.11	9.66	11.49	7.90
Iron, Fe ₂ O ₃	22.99	12.85	14.39	12.26
Titanium, TiO ₂	1.06	0.60	0.66	0.53
Calcium, CaO	3.60	4.06	4.26	7.61
Magnesium, MgO	0.35	0.17	0.84	0.76
Sodium, Na ₂ O	0.70	0.96	2.06	1.88
Potassium, K ₂ O	1.82	3.82	6.92	5.64
Phosphorous, P ₂ O ₅	0.88	0.91	1.02	0.89
Sulfur, SO ₃	11.64	20.00	--	--
Sulfur, SO ₄	--	--	34.79	41.84
Strontium, SrO	--	--	0.07	0.05
Manganese, MnO	--	--	0.06	0.06
Barium, BaO	--	--	0.06	0.07

Table 4: Deposit Analyses (X-Ray Diffraction Results)

Level	Scale Analysis
Major	<ul style="list-style-type: none">• Cristobalite, syn, SiO₂• αQuartz, SiO₂
Minor	<ul style="list-style-type: none">• Ferrinatriite (Na₃Fe(SO₄)₃(H₂O)₃)• Potassium Dihydrogen Phosphate (KH₂PO₃)• Tamarugite (NaAl(SO₄)₂(H₂O)₆)
Trace	<ul style="list-style-type: none">• Hohmannite (Fe₂(H₂O)₄(SO₄)₂O(H₂O)₄)

Table 5: Carbon and Chlorine Analysis Results

Constituent	Outer Layers, (wt%)	Inner Layers, (wt%)
Carbon	0.27	0.58
Chlorine	0.05	0.05

Figure 1: Schematic of Test Section Showing Position of Welds and Location of Dutchmen (i.e. samples removed early)

Note:

1. The welds are indicated as circles in the schematic above. A letter designation is associated with each weld. The candidate tube samples lie between the welds and are designated by the weld at either end of the sample.
2. The “hot leg” of this test section is toward the top in this schematic. The hottest position in the test section is at position S-T. Accordingly, the coolest position in the test section is at position JJ-KK at the inlet to the “cold leg” of the test section.
3. Tube samples removed and replaced by “dutchmen” in November 2001 are highlighted in red.
4. Tube samples removed and replaced by “dutchmen” in June 2002 are highlighted in yellow.

Figure 2: Daily Average Surface Metal Temperatures (F) for Tube Segment "R-S

Figure 3: Appearance of Test Section C After Removal From Service (Part 1)

- Note:
- 1) The region highlighted in the schematic drawing of the test section is shown in the photograph below.
 - 2) The letters adjacent to the photograph indicate the positions of the various welds used to construct the test section. These letters also are used to identify the candidate metal samples that lie between them. For instance, Sample A-B lies between welds A and B. It was manufactured from 347 HFG. Sample B-C was manufactured from Fe_3Al , etc.

Figure 4: Appearance of Test Section C After Removal From Service (Part 2)

Note: 1) The region highlighted in the schematic drawing of the test section is shown in the photograph below

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure 5: Typical Documentation of As-Received Appearance for Tube Sample Y-Z (Modified 800H)

Note: The chalky alkali-iron trisulfate scale is noted in all three orientations. Differences in coloration are primarily due to lighting effects, with the 3 o'clock orientation being the most accurate in this regard.

Figure 6: Schematic Depicting Sectioning to Remove Tube Sample From the Test Section

Key	
Sample	Purpose
RS-1	Metallography ring
RS-2	Dimension ring
RS-3	Weld profile
RS-4, 5, 6	Extra material

Note:

- 1) Cut B - B' is at the approximate center of the tube sample
- 2) Specimens RS-1, RS-2, RS-3 are all about $\frac{1}{2}$ " thick

Figure 7: Schematic Depicting Sectioning of Tube Sample

Figure 8: Typical Semi-Quantitative Composition Verification for Modified 800H

Description: Nominal 20Cr/30Ni steel with improved creep strength due to addition of V, Nb, Ti, and B
Source: Oak Ridge National Laboratory (ORNL)
Reference Composition: “Target” Chemistry per ORNL (Reference 1).

Element	Reference Composition	Composition Heat 17423	Composition Heat 17424	Composition Heat 17433	Tube Sample E-F	Tube Sample L-M	Tube Sample Y-Z
Ni	31.0	30.74	31.04	31.10	31.0	N/A	N/A
Cr	20.0	19.89	19.98	19.91	19.1	N/A	N/A
Fe	Balance	-	-	-	46.0	N/A	N/A
Mo	1.5	1.50	1.52	1.51	1.41	N/A	N/A
Co	-	0.03	<0.01	<0.01		N/A	N/A
C	0.09	0.10	0.10	0.10		N/A	N/A
N	-	0.026	0.029	0.018		N/A	N/A
B	0.005	-	-	-		N/A	N/A
Mn	2.00	1.93	1.94	1.93	1.68	N/A	N/A
Si	0.25	0.24	0.24	0.26	0.38	N/A	N/A
Al	-	<0.01	<0.01	<0.01		N/A	N/A
Ti	0.25	0.11	0.15	0.03		N/A	N/A
Nb	0.25	0.26	0.26	0.25		N/A	N/A
Ta	-	<0.01	(a)	(a)		N/A	N/A
Nb+Ta	-	-	-	-		N/A	N/A
V	0.4	0.38	0.23	0.37	0.42	N/A	N/A
Cu	-	<0.01	<0.01	<0.01		N/A	N/A
Sn	-	-	-	-		N/A	N/A
P	-	0.009	(a)	0.002		N/A	N/A
S	-	0.003	0.002	0.005		N/A	N/A
O2	-	0.004	0.008	0.015		N/A	N/A

a- Not analyzed.

b- By difference.

Reference 1:

“Fabrication of Test Tubes for Coal Ash Corrosion Testing”, Sikka, V.K., Swindeman, R.W., Wright, I.G., Judkins, R.R., Johnson, R., Proc, 13th Annual Conf. on Fossil Energy Mat’ls, May 1999.

Note: Sample E-F was from Heat 17433
Sample L-M was from Heat 17423
Sample Y-Z was from Heat 17424

N/A = Tube sample not analyzed.

12 O’Clock
(N/A mils lost)

3 O’Clock
(106 mils lost)

6 O’Clock
(0 mils lost)

Figure 9: Typical Example of OD Surface Appearance After Grit Blast

Note: This particular example is for IN52 Weld Overlay, Sample GG-HH.

Material: Modified 800H
Sample Location: Y-Z
Maximum Rate: 79 mils/yr
Maximum Loss Orientation: Approx. 9:30 o'clock
Average metal Temperature: 1099 F

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.402	0.401	0.401	0.400	0.400	0.401	0.401	0.401	0.401	0.401
After	0.253	0.226	0.294	0.389	0.390	0.387	0.233	0.294		0.212
Delta	0.149	0.175	0.107	0.011	0.010	0.014	0.168	0.107		0.189

Figure 10: A Typical Silhouette with Wall Thickness Measurements Showing Metal Loss as a Function of Position

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Note: Fe_3Al material to the right of the weld in this image and 347 HFG to the left.

Figure 11: Weld Profile Through Tube Sample Showing Good Corrosion Resistance in the Vicinity of the Weld

**Figure 12: Weld Profile Through Clad Tube Sample
Incoclad 671 Adjacent to Weld "V" in Section C (at 1121 F)**

**Figure 13: Weld Profile Through Clad Tube Sample
Inconel 671 Adjacent to Weld “P” (at 1203 F) in Section C**

Discussion:

The primary goal of this program is to rank the relative performance of candidate superheater tube alloys for use in boilers fired with corrosive high-sulfur coals. The operational history for Niles Unit #1 demonstrates that the service conditions provide an environment within the boiler that is aggressive enough to test the ability of these materials to resist coal ash corrosion, and to provide an adequate ranking of their relative performance.

Surface Metal Temperature: The average surface metal temperature, from the hot to the cooler end of the test section, ranged from about 1210°F to 1060°F. As was discussed earlier, over this temperature range, the coal ash corrosion rate for a given austenitic alloy is generally expected to increase with increasing temperature. Recall that at about 1000°F, alkali-iron trisulfates in the coal ash become molten, and this molten constituent is very aggressive. The upper limit to this is about 1300°F where the stability of the complex sulfates decreases and the corrosion rate ebbs. The exact temperature range over which the sulfates are molten depends on the ash, gas and scale chemistries.

Flue Gas Temperature: The flue gas temperature has a significant impact on the wastage rate for superheater tube materials in that it directly influences the average surface metal temperature. The flue gas temperature in the region of interest in Niles Unit #1 was estimated to be 2114°F.

Internal Pressure: It is understood that the internal pressure for the test section was low, at approximately 300 psig. This has the benefit that almost the full wall thickness of the tube was available as a “corrosion allowance”. Though it does not impose pressure stresses typical of a supercritical boiler, it offered the advantage that a candidate tube sample would not need to be pulled from service almost up to the point that its full wall thickness had wasted away.

Candidate Alloy Rankings Based on Corrosion Resistance: Based on the above, and considering the fact that the boiler was burning high-sulfur coal, the service of Test Section C provided an aggressive environment that was suitable for ranking candidate superheater materials with respect to their resistance to coal ash corrosion. That the environment is aggressive is further confirmed by the fact that some of the candidate tube materials corroded at a very high rate, and that this resulted in the need to replace tube segments in Section C before the full exposure period was completed.

Table 6 provides the wastage rate (mils of wall thickness lost per year) as a function of position within the Test Section C. Figure 14 presents this same information graphically. Table 7 provides the wastage rate with all of the samples of a given material grouped separately. Examination of these results allows one to determine the maximum wastage rate for each of the candidate materials. These maximum rates, shown in Table 8, are the limiting case for any of the candidate materials when exposed to the coal ash corrosion conditions for Section C. Thus, these rates can be used to rank the performance of these materials relative to one another. From this it can be seen that Inconel 671 and IN 72 Weld Overlay exhibited the lowest maximum corrosion rates based on Section C exposure. These same materials also exhibited the best corrosion resistance based on Section A exposure. It should also be noted that Save 25 exhibited the highest maximum corrosion rate for both test sections. The other materials performed between these two extremes. However, almost all of these candidate materials exhibited a maximum

corrosion rate in excess of 50 mils per year. Figure 15 provides a graphical comparison of these maximum wastage rates for both Sections A and C.

Wastage Rate as a Function of Temperature: Figure 16 shows a plot of wastage as a function of average service temperature for each of the twelve candidate materials in Section C. Interpretation of these data is complicated by the fact that, while some materials behaved as one would have expected, others did not. The data show that for some materials the wastage rate increased with temperature, e.g. Save 25 and 800 Mod. Some materials exhibited an apparent decrease in wastage rate at intermediate temperatures, e.g. 347 HFG and HR 120. Other materials exhibited an apparent increase in wastage rate at an intermediate temperature, e.g. 310 HCbN and 310 Ta. Finally, the more resistant high-chromium, high-nickel alloys appeared to exhibit a decrease in rate as temperature increased, e.g. Inconel 671, IN 72 WO, and IN 52 WO. It further should be understood that, for the most part, performance was consistent in that the candidate materials exhibited this same sort of performance in both Sections A and C, compare Figures 16 and 17.

It is tempting, but risky at this point, to draw inferences from the corrosion rate versus temperature data. For instance, the data that showed a reduced corrosion rate at an intermediate temperature might be taken to infer that two corrosion mechanisms were active, one mechanism acting to accelerate corrosion at the lower temperature, and the other mechanism acting to accelerate corrosion at the highest temperature. However, before drawing such inferences, one must also take into consideration the fact that the normal operating conditions within this region of the boiler are not as controllable as might attain during laboratory testing. As an example, when the location of tube samples are “mapped” to show their position within the test section, it becomes apparent that those samples that are located at either end of the test section tend to evidence a lower than expected wastage rate. This suggests the possibility that the physical location of the samples within the test section may influence their wastage rate. It has been speculated, but not confirmed, that the lower than expected wastage rate for the samples at either end of the section may be due to the possibility that the actual surface metal temperatures in these locations are cooler than the calculated average surface metal temperatures that have been used in this investigation. Several practical boiler operational issues can be postulated that might account for this. To date this issue has not been fully explored. It is, however, interesting to note that the Section C analysis revealed that the candidate materials performed similarly to those from Section A, e.g. 347 HFG experienced a decrease in wastage rate at an intermediate temperature in both cases. This and the results for the other materials suggest that the test sections appear to be performing in a consistent manner.

Additional Issues for Consideration:

There are a few issues that should be taken into account in assessing the wastage data in the tables and figures above. First, some of the candidate materials relied on a surface coating that had been breached at some point, perhaps early on, during the Section C exposure period. With the coating breached, it can no longer provide resistance to corrosion, and the remaining tube life would be determined by the corrosion resistance of the underlying substrate material.

Analysis of Section A showed that the coating on the Fe₃Al-coated specimen was breached early during the exposure period, and that corrosion was wasting away the underlying Type 304 H

stainless steel substrate. This also was true for Section C, in fact, no evidence could be found of the original Fe_3Al coating.

Analysis of Section C revealed that IN 52 Weld Overlay tube segments appear to have done well based on the calculated wastage rate. However, it should be noted that within the timeframe of the Section C exposure, the original 80 mil thick protective cladding was completely breached, and that only the 800 H substrate remained to provide corrosion resistance for these specimens. Note from Table 8 that 800 H has to date demonstrated one of the higher maximum wastage rates. Thus, now that the protective coating has been wasted away, one would expect that the calculated wastage rate would increase for the IN 52 Weld Overlay samples that remain in the boiler.

Finally, based on calculated wastage rates, the IN 72 Weld Overlay tube segments consistently have demonstrated excellent corrosion resistance, see Table 8. However, this material appears also concurrently to be suffering from a time-dependent cracking problem. The cracking problem does not appear related to the hot-side corrosion mechanism for this material; however, in at least one case, corrosion had removed enough material to reveal and penetrate along an underlying crack. If this additional loss of wall thickness had been taken into account, the calculated corrosion rate would have increased by more than fifty percent. The extent of the IN 72 Weld Overlay cracking problem was first discovered when the material was examined in the SEM along with the other eleven candidate materials. Figure 18 shows an SEM image of one region where underlying cracks intersected the tube surface.

The cracking shown in Figure 18 spurred further investigation. Figure 19 shows evidence of cracking at other locations in this tube segment. Note that the cracking appears to be at roughly the mid-point of the 72 Weld Overlay cladding, and does not contain a corrosion product. Similar cracking was found for both 72 Weld Overlay test segments in Section C. Closer examination of Section A samples revealed the same sort of sub-surface cracking, but to a somewhat lesser extent. Finally, examination of an archive 72 Weld Overlay tube sample revealed a few similar internal cracks, see Figure 20.

The implications of the 72 Weld Overlay cracking problem are not clear. The fact that Incoclad 671, which has a very similar composition to that of 72 Weld Overlay, and appears to be performing well without cracking, suggests that this may be more of a process-related problem than a material chemistry issue. Additional work would be required to resolve this.

Wastage Rate as a Function of Time

Recall that one goal of this program was to characterize wastage as a function of time for each of the candidate materials. To facilitate this, the three test sections were built to be identical in terms of the placement of the candidate alloy tube samples. Then, they were installed side-by-side within Niles Unit #1, on the assumption that they would experience essentially the same exposure conditions. The tube samples in Test Section A were removed and examined after 15.5 months of exposure at full temperature. For Section C, samples were removed after 18.6, 21.6 and 28.5 months at full temperature. As was explained earlier, excessive corrosion caused the need for early removal of samples from Section C. 28.5 months is considered to be the full exposure period.

Table 9 presents the corrosion rate data for both Section A and Section C together. It should be noted from this that the wastage rates at higher temperatures (above about 1150 F) remained nearly constant or increased as a function of time. At lower temperatures, rates stayed the same or decreased with time. This decrease in rate with time suggests the possibility that built-up scale is providing some level of protection against further wastage.

The chart in Figure 21 was constructed by plotting the maximum wall thickness lost as a function of time for the materials from Section A and Section C. Then a straight-line was fit to the two data points for each material. As was indicated above, this is not to suggest that the corrosion rate was linear for these materials. Inspection of this chart, and given the fact that most of these materials started with an initial 400 mil wall thickness, the reason for the early removal of some of these materials becomes readily apparent.

Rationale for Relative Alloy Performance:

While this has not been considered in depth, the analysis of the data for Section A provided some insight as to why one candidate alloy performed better than another. The Section A analysis provided further confirmation of the initial assumption that high chromium content would result in good performance under coal ash corrosion conditions. Section C data now also are available, and Figure 22 shows the maximum corrosion rate plotted against chromium content for both test sections. Logarithmic fit lines are plotted for both sets of data. Examination of these suggests that the materials behaved similarly in both test sections. While a relatively good fit is indicated, the data spread at lower chromium contents appears to be excessive.

Figure 23 plots the maximum corrosion rate against the sum of the chromium plus nickel contents. In this case, the linear fit lines almost completely overlap, and the data spread appears to be more reasonable, particularly at the lower chromium plus nickel contents.

This leads once again to the observation that the wastage response of these materials appeared to be inversely related to the total alloy content in these alloys, in particular, the sum of the chromium plus nickel contents. While it is granted that the sampling in question is not statistically significant, the data suggest that the correlation between chromium plus nickel content and wastage rate merits additional study.

Scale/Metal Interface Issues:

Both the internal and external scale/metal interfaces were examined in detail for each candidate material. The focus typically centered on the one sample for each candidate material that experienced the greatest amount of wastage. The results of these analyses are recorded in the separate appendices for each candidate material.

Examination of the microstructure revealed that the less corrosion resistant materials seemed to have characteristics in common at the external scale/metal interface. These are illustrated in the sketch shown in Figure 24. Figure 25 shows an example of the five regions typically found for corrosion sensitive materials. These would include a high-chromium scale adhering to the tube surface, and a distinct chromium-depleted diffusion zone in the metal below the scale.

It should be noted that in some cases the appearance of the scale/metal interface was somewhat more complicated. Figure 26 shows the appearance of the interface at the external surface of an

IN52 Weld Overlay sample. Here, once again, an adherent high-chromium scale is found along the interface (Region 1 in Figure 26). However, below the interface is a fairly homogeneous band of material that is somewhat depleted in chromium (Region 2), and beyond that, one can see evidence of internal corrosion penetration into and along interdendritic regions. The significance of this is beyond the scope of this effort and has not fully been explored. However, it should be noted that the IN72 Weld Overlay, also developed similar interface characteristics.

For all of the candidate alloys, examination of the internal scale/metal interfaces revealed minimal conclusive evidence of scale or corrosion penetration. In most cases, the internal scale thickness and corrosion penetration were non-existent or less than 1 mil. This may have been due to some minimal exfoliation after these scales had formed. Figure 27 shows typical examples of the appearance of these interfaces.

Material	Tube Sample	Rate Metal Lost* (mils/yr)	Average Surface Metal Temperature, (F)
52 Weld Overlay	R-S	48	1208
72 Weld Overlay	Q-R	6	1208
Incoclad 671	P-Q	2	1203
HR 120	O-P	124	1194
310 HCbN	N-O	133	1190
310 Ta	M-N	131	1188
800 Mod	L-M	183	1185
Save 25	K-L	>259	1180
NF 709	J-K	181	1178
347 HFG	I-J	204	1174
Thermie	H-I	77	1171
310 HCbN	G-H	141	1167
310 Ta	F-G	127	1166
800 Mod	E-F	176	1162
Save 25	D-E	N/A**	1158
NF 709	C-D	114	1153
Fe3Al	B-C	100	1149
347 HFG	A-B	76	1147
Incoclad 671	U-V	1	1121
HR 120	V-W	46	1110
310 HCbN	W-X	52	1106
310 Ta	X-Y	64	1103
800 Mod	Y-Z	79	1099
Save 25	Z-AA	148	1096
310 HCbN	AA-BB	79	1092
NF 709	BB-CC	100	1088
347 HFG	CC-DD	120	1086
HR 120	DD-EE	79	1088
Incoclad 671	EE-FF	10	1086
72 Weld Overlay	FF-GG	14***	1079
52 Weld Overlay	GG-HH	63	1073
Thermie	HH-II	34	1067
Save 25	II-JJ	56	1058

Table 6: Maximum Wastage Rate as a Function of Position in Test Section C

* Metal loss rate is based on time at temperature, not total time within the boiler.

** N/A = Sample overlain with weld metal, thus no data available.

*** The calculated rate is based solely on wall thickness measurements and does not take into account that corrosion had removed sufficient material to connect an underlying weld crack with the surface.

Key: Sample removed from service November 2001 -----
Sample removed from service June 2002 -----
Sample remained in service until the end of Section C exposure in May 2003 -----

Material	Tube Sample	Maximum Rate Metal Lost* (mils/yr)	Average Surface Metal Temperature, (F)
Save 25	K-L	>259	1180
Save 25	D-E	N/A**	1158
Save 25	Z-AA	148	1096
Save 25	II-JJ	56	1058
800 Mod	L-M	183	1185
800 Mod	E-F	176	1162
800 Mod	Y-Z	79	1099
347 HFG	I-J	204	1174
347 HFG	CC-DD	120	1086
347 HFG	A-B	76	1147
NF 709	J-K	181	1178
NF 709	C-D	114	1153
NF 709	BB-CC	100	1088
Fe3Al	B-C	100	1149
310 Ta	M-N	131	1188
310 Ta	F-G	127	1166
310 Ta	X-Y	64	1103
310 HCbN	G-H	141	1167
310 HCbN	N-O	133	1190
310 HCbN	AA-BB	79	1092
310 HCbN	W-X	52	1106
HR 120	O-P	124	1194
HR 120	DD-EE	79	1088
HR 120	V-W	46	1110
Thermie	H-I	77	1171
Thermie	HH-II	34	1067
52 WO	GG-HH	63	1073
52 WO	R-S	48	1208
72 WO	FF-GG	14***	1079
72 WO	Q-R	6	1208
671 Clad	EE-FF	10	1086
671 Clad	P-Q	4	1203
671 Clad	U-V	1	1121

Table 7: Rankings Per Material Based on Rate of Metal Loss in Test Section C

* Metal loss rate is based on time at temperature, not total time within the boiler.

** N/A = Sample overlain with weld metal, thus no data available.

*** The calculated rate is based solely on wall thickness measurements and does not take into account that corrosion had removed sufficient material to connect an underlying weld crack with the surface.

Key: Sample removed from service November 2001 -----
Sample removed from service June 2002 -----
Sample remained in service until the end of Section C exposure in May 2003 ----

Material	Tube Sample	Surface Metal Temperature (F)	Section C Maximum Rate of Metal Loss (mils/yr)
Save 25	K-L	1180	>259
347 HFG	I-J	1174	204
800 Mod	L-M	1185	183
NF 709	J-K	1178	181
310 HCbN	G-H	1167	141
310 Ta	M-N	1188	131
HR 120	O-P	1194	124
Fe3Al	B-C	1149	100
Thermie	H-I	1171	77
IN 52 WO	GG-HH	1073	63
IN 72 WO	FF-GG	1079	14*
671 Clad	EE-FF	1086	10

* Note: this rate does not take wall loss due to internal cracking in this weld overlay material.

Table 8: Maximum Rate of Metal Loss for Each Candidate Material

Material	Tube Sample	Section A Rate Metal Lost* (mils/yr)	Section A Exposure Temperature (F)	Section C Rate Metal Lost* (mils/yr)	Section C Exposure Temperature (F)
52 Weld Overlay	R-S	44	1198	48	1208
72 Weld Overlay	Q-R	10	1198	6	1208
Inconclad 671	P-Q	4	1193	2	1203
HR 120	O-P	102	1184	124	1194
310 HCbN	N-O	108	1180	133	1190
310 Ta	M-N	123	1178	131	1188
800 Mod	L-M	169	1174	183	1185
Save 25	K-L	259	1170	>259	1180
NF 709	J-K	170	1167	181	1178
347 HFG	I-J	174	1164	204	1174
Thermie	H-I	53	1160	77	1171
310 HCbN	G-H	133	1157	141	1167
310 Ta	F-G	136	1154	127	1166
800 Mod	E-F	178	1150	176	1162
Save 25	D-E	224	1146	N/A**	1158
NF 709	C-D	136	1142	114	1153
Fe3Al	B-C	145	1139	100	1149
347 HFG	A-B	83	1137	76	1147
Inconclad 671	U-V	2	1110	1	1121
HR 120	V-W	61	1100	46	1110
310 HCbN	W-X	98	1095	52	1106
310 Ta	X-Y	120	1092	64	1103
800 Mod	Y-Z	154	1088	79	1099
Save 25	Z-AA	208	1084	148	1096
310 HCbN	AA-BB	129	1081	79	1092
NF 709	BB-CC	145	1077	100	1088
347 HFG	CC-DD	176	1075	120	1086
HR 120	DD-EE	109	1077	79	1088
Inconclad 671	EE-FF	13	1075	10	1086
72 Weld Overlay	FF-GG	21	1068	14***	1079
52 Weld Overlay	GG-HH	77	1062	63	1073
Thermie	HH-II	31	1056	34	1067
Save 25	II-JJ	67	1047	56	1058

Table 9: Maximum Wastage Rate as a Function of Time and Position

Note: Those test segments highlighted in blue experienced an increase in wastage rate with time.

* Metal loss rate is based on time at temperature (up to 11,288 hours for Section A and up to 20,832 hours for Section C, not total time within the boiler.

** N/A = Sample overlain with weld metal, thus no data available.

*** The calculated rate is based solely on wall thickness measurements and does not take into account that corrosion had removed sufficient material to connect an underlying weld crack with the surface.

Figure 14: Maximum Wastage Rate as a Function of Position within Section C

Note:

1. The materials are listed in sequence according to their position within the test section, with the hottest end of the test section to the left, and the coolest end of the test section to the right.
2. No data provided for Save 25 tube segment at position D-E because this segment had been overlain with weld metal

Figure 15: Maximum Wastage Rate for Each Candidate Material in Both Sections

Figure 16: Wastage as a Function of Average Surface Metal Temperature for the Twelve Candidate Alloys in Test Section C

Figure 17: Wastage as a Function of Average Surface Metal Temperature for the Twelve Candidate Alloys in Test Section A

Figure 18: Weld Cracks Intersecting External Corrosion for 72 WO Test Segment

Approx. 20x

Figure 19: Internal Cracking in 72 Weld Overlay Test Segment from Section C

Figure 20: Internal Cracking in 72 Weld Overlay Archive Material

Figure 21: Maximum Wastage as a Function of Time for the Candidate Materials

Figure 22: Chromium Content Versus Wastage Rate for Both Sections A and C With Logarithmic Trend Line

Figure 23: Chromium Plus Nickel Content Versus Wastage Rate With Linear Regression Fit trend Line

Figure 24: Common Characteristics at External Scale/Metal Interface

Figure 25: Illustrates the Characteristic Microstructural Regions Found at the External Scale/Metal Interface for Many of the Candidate Materials.

Note: These photographs are of the scale/metal interface for NF 709.

Figure 26: Characteristics of External Scale/Metal Interface for IN52 Weld Overlay

Internal Scale/Metal Interface for Type 310 Ta

Internal Scale/Metal Interface for HR 120

Internal Scale/Metal Interface for Save 25

Figure 27 Typical Examples of the Condition of the Internal Scale/Metal Interface after Service

Observations and Conclusions:

Evaluation of tubes removed from Section C suggests the observation that the candidate materials performed very similarly in both Sections A and C.

- The relative rankings of the candidate materials (based on wastage rate) are very similar for Section A (with 15.5 months of exposure) and Section C (after 28.5 months of exposure).

- The same materials showed the best resistance to coal ash corrosion: Incoclad 671, IN72 Weld Overlay, Thermie, and IN52 Weld Overlay.
- The same materials performed poorly: Save 25, Modified 800H, 347 HFG, and NF 709.
- The same materials demonstrated a reduced wastage rate at intermediate temperatures: 347 HFG, NF 709, and HR 120.

Evaluation of the materials which performed well suggests the following:

- Incoclad 671 continued to exhibit the best resistance to coal ash corrosion. This good performance was attributed to its' high levels of chromium and nickel (and low levels of iron).
- IN72 Weld Overlay exhibited good resistance to coal ash corrosion; however, it also showed evidence of an internal cracking problem that may increase in extent with increased time at temperature. The fact that IN72 has a chromium and nickel content similar to that of Incoclad 671 suggests that this problem may be process-related. However, it raises a serious concern in that the cracking is sub-surface and thus may not be visible during in situ visual examination of these tubes.
- It was noted that Incoclad 671 and IN72 Weld overlay both exhibited a decrease in corrosion rate with additional time at temperature. This suggests that a coherent protective scale is formed for these materials, and that this scale slows further wastage.

- Thermie also exhibited a increased wastage rate as a function of time. The rate for this material was ten-fold greater than that of either the Incoclad 671 or the IN 72 Weld Overlay.
- IN52 Weld Overlay exhibited moderate resistance to coal ash corrosion; however, at this point (i.e. after 28.5 months at temperature in the corrosive environment of this boiler), the full 80 mil thickness of the weld overlay has been breached. With this corrosion barrier removed the wastage rate is expected to increase with continued exposure.

For the purpose of discussion, a line was drawn to define materials as moderate (or poor) performers if they demonstrated a wastage rate in excess of 100 mils/year, for at least one exposure temperature. The following comments apply to these materials:

- With the exception of 347 HFG, these materials are all highly alloyed, with a chromium content in the range of 20 to 25 wt% and a with a nickel content that ranged from as low as 17 to as high as 37. Type 347 HFG stainless steel is less highly alloyed.
- Preliminary plots of alloy content versus wastage show a good correlation between chromium content and performance, and a better correlation between chromium plus nickel content and performance.
- From this it is not clear why Save 25, with a chromium content of 21-24 wt%, and a total alloy content of between 36 and 46 wt% would perform more poorly than the less highly alloyed 347 HFG. However, it has been speculated (but not confirmed) that the high copper content of Save 25 may have had an adverse effect on its' ability to develop and/or maintain a protective chromium oxide scale.

Tube-to-tube weld investigations suggest the following:

- In general, the Inconel 625 weld metal (used to join the tubes to one another) performed well, and better than most of the candidate alloys in this investigation. Weld cross sections revealed that most tubes were thicker in the vicinity of these welds and decreased in wall thickness toward the mid-point of the tube segment. For these materials, there was no evidence that either the weld metal or the adjacent heat affected zone suffered from preferential corrosion.
- For the case of the best performing materials, at higher temperatures the Inconel 625 provided less resistance than the candidate material (i.e. Incoclad 671 and IN 72 Weld Overlay). In at least one case, the Inconel 625 weld metal had wasted to the extent that it exposed the material under the cladding to coal ash corrosion conditions, and corrosion was progressing inward at that point.

Annex 1 Program Timeline: 2002 - 2003

On October 31, 2002 a Topical Report providing the full details of the project background, material selection, fabrication of the test materials and sections, description of the test system, and system installation, start-up and operating history through 2001 was provided along with the results of evaluation of Section A removed in November of 2001. That information will not be repeated herein and the reader is referred to "Topical Report: Removal of Section A" for that information. The following provides the operating history of the sections beginning where the Section A report left off through the end of 2003. It is followed by the results of evaluation of the second section, Section C, removed in August 2003.

2002

During January Section C ran as intended with 1075°F outlet steam temperature while B control valve was kept open due to a failed position indicator and evaluation of the samples from the top two rows of Section A was initiated.

During the annual maintenance outage from February 17 through March 3, a mechanical positioner was installed on Section C. The position indicator on B was tested and worked properly during the outage. Changes were also made to the control logic to accommodate this new equipment. The unusual pressure drop across the outlet stop valves, discovered in November, is believed to be transmitter calibration and will be investigated further when the unit is operating. Evaluation of the samples from the top two rows of Section A continued.

After restart in early March the position indicator on Section B was not working (presumably related to heat) so the inlet valve was opened until the indicator could be replaced. Tuning of the temperature control logic will be necessary because the slower mechanical positioners caused the valves to 'hunt' to maintain the outlet temperature resulting in outlet temperature fluctuations of $\pm 25^\circ\text{F}$ (maximum temperature of 1100°F).

Samples from Section A were prepared and documentation (photographs) of the as-received condition was completed in April. Ring sections were cut for dimensioning and metallographic examination were polished, etched and their condition was documented. The dimension rings were de-scaled and measured at eight locations. The appearance of the de-scaled surfaces was photographed. The metallographic rings were mounted and ground flat and the chemistry was determined for all 33 tube samples. After some tinkering, the position indicator for Section B began working properly. Arrangements were made for the first week in May to adjust the control logics for all three valves to minimize the outlet temperature fluctuations caused by the more sluggish mechanical positioners. In May they were adjusted and the system ran as intended without incident.

Metallographic specimens through welds, chemical analysis and hardness for each ring specimen, dimensional comparison to as-received measurements and SEM evaluation of deposit and scale from selected samples began in May. Specimen photography, preparation of dimension rings, dimensional measurements, and light metallography were completed. Specimen alloy chemistries were verified by spectroscopic analyses. SEM work was initiated for one area on each alloy, a total of 12 specimens. Energy dispersive X-ray analyses were used to

document chemical compositions of the alloy, scale near the alloy scale interface, the inner layer of deposit, and the outermost layer of deposit that is still in-place on the tube surface and report writing began. In June SEM work was completed and report writing and data evaluation continued. A heavier sample of deposit from one area of the surface will be sent for analysis at a chemistry laboratory next month. Examination of metallographic sections through selected welds is yet to begin.

The unit was in a forced outage from July 10 to July 18 (not due to the sections). Otherwise, the system ran as intended during July and Topical report writing continued.

The unit experienced two forced outages from August 12 to August 18 and another from August 28 to August 31, neither due to the test sections. Otherwise, the system ran as intended during August. Examination of metallographic sections through selected welds was completed. A draft of the Topical Report for Section A was completed and released for internal review and some minor issues for further examination were identified as a result of analysis report writing.

Internal review of the draft report was completed in September and the missing and incomplete sections were written. A meeting is planned for the first week in October to review and consolidate comments with the objective of releasing the draft Topical Report to DOE and OCDO by the end of October. The sections continued to run at temperature without problems. The intermediate thermocouple on section "A" (which no longer contains any test materials) was reading abnormally high and inconsistent with adjacent thermocouples. On occasion it caused the control valve to switch to manual-open at low load but it was returned to auto by the operator.

The system ran as intended during October. The Topical Report for Section A was completed, internally reviewed, was reproduced for transmittal in early November. On October 8, the superheater test sections were briefly inspected (visually). All six return bends were dislodged from their support lugs. All three sections were carefully inspected for evidence of steam leakage, and there were no leaks. One alloy segment in Section B and in Section C had lost about 250 mils (about 60%) of the tube wall thickness. This is the 347HFG segment in the next to top leg of the test sections. Two other alloy segments in Sections B and C had lost about 200 mils from the wall thickness. One of these was the hottest HR120 segment adjoining the Inconel at the hot end of the outlet leg of the sections. The other was the NF709 near the lower temperature end of the top leg. The Topical Report for Section A was released on October 31, 2002 for review and comment.

The system ran as intended during November and December.

2003

The system ran as intended January through June with no incidents. A visit was made to the plant on May 27 to inspect the existing tubes while the boiler was down. One tube sample in both B & C Sections was found to be severely corroded. Due to the ash on the tubes and the access and lighting conditions during the inspection, some confusion existed as to which alloy was corroded but it was decided that the samples would be replaced at the next opportunity and the corroded specimens returned for examination. Meanwhile the control valves were locked open to keep the sections cool and minimize further corrosion until then.

A visit was made to the plant on June 19 to inspect the existing tubes in more detail. Both supports on the baffle wall of all three Sections had moved off the support lugs. The lower test row of Section C was bowed downward and was touching the adjacent 3rd row (from the top). The upper row of Section C had significant wastage in two of the samples (310Ta and 310HCbN). Most of the unclad samples in Section B showed significant wastage as well. There was concern that the thinning walls of Sections B and C would not last until the fall outage so two bends were weld prepped and plans were made so the plant could remove the top two rows of both Sections, ship them to Alliance, Ohio for evaluation, and install the bends to connect the top two rows. Once the top two rows were removed the valves would be left open (run cool) until the fall outage when the two new Sections will be installed for the USC Materials Project (DE-FG26-01NT41175 and OCDO D-00-20). If Section B could be sufficiently ‘repaired’ by replacing the corroded samples with new ones to be confident it could operate for another 1.5 to 2 years it would be reinstalled.

The system ran through July with the control valves locked open to keep the sections cool and minimize further corrosion. As planned, the top two rows of both of the remaining sections (B&C) were removed in August during a brief unscheduled outage and replaced with the bends sent in early July. Both Sections were transported to the B&W Research Center (BWRC) and metal loss was preliminarily assessed using calipers. Based on those measurements the remaining life of each specimen was considered in regard to operating an additional 18 months. Since the Section taken from the C position (farthest from the boiler sidewall) was badly distorted but the one from the B (middle) location is in good condition, it was decided to replace the specimens in Section B whose remaining life would not be expected to achieve 18 more months and reinstall it in the boiler in the C location during the fall outage to obtain additional operating time.

Section B – As Removed

Section C – As Removed

The Niles unit came down for its fall outage on September 24th. Plans for evaluation of the specimens in Section C were initiated and the unacceptable specimens in Section B were removed and the remaining portions weld prepped. After further review of the corrosion, one additional sample was marked for removal leaving (15) of the original (33) specimens for further exposure. Segments of left over IncoClad and some HR3C material were used to replace the removed specimens. These were installed in the two-row portion of Section B in early October and it was returned to the plant for reinstallation in location C during the outage.

In November the repaired Section B was re-installed in the C location. Section C segments were disassembled and measurements and sample preparations made at BWRC. All (33) thirty-three of the tube samples from Section C were sectioned to yield dimension rings, and specimens for metallography and composition verification including the specimens that were part of the

original installation, and those that were added later to replace samples that had evidenced excessive wall losses. The dimension rings were lightly grit-blasted, thickness was measured at eight different o'clock positions, and the data was compared with the original wall thickness at these locations to determine the amount metal lost. In Section A, it was noted in some cases that the weld heat affected zones may have been more aggressively attached than the remainder of the tube sample. To evaluate this, weld cross sections have been prepared to evaluate the weld heat affected zone for each of the candidate materials.

In December, the insulation damaged when accessing some instrumentation was repaired and the unit restarted on December 22 and controls verification planned for early January 2004 after which Section B (in the C location) will be operated at full temperature. Full cross section rings from Section C were polished and are prepared for evaluation using the scanning electron microscope at the First Energy Beta Labs. First Energy Beta Labs have been contracted to perform an analysis of the deposit for comparison with the analysis for Section A. It is also planned to use the energy dispersive (semi-quantitative) analysis capabilities of the scanning electron microscope at First Energy Beta Labs to verify that the correct alloys were in their proper locations.

Note that removal of the last Section is currently shown as October (fall) of 2004. The actual removal date will depend on the outage dates set by Reliant Energy and may extend to the spring of 2005 which will delay the Report from the current schedule. It was also discovered after restart (in January 2004) that the section outlet thermocouples (which are used for control of the outlet steam temperature) were not properly installed. Actual operation at desired temperatures must be delayed until they can be repaired. Once repaired and the system is operating properly, the operating time and schedule will be reevaluated.

COAL ASH CORROSION RESISTANT MATERIALS TESTING

Topical Report: Removal of Section “C”

APPENDICES

U.S. Department of Energy Contract:
Ohio Coal Development Office Grant Agreement:
The Babcock & Wilcox Company Contract:

DE-FC26-99FT40525
CDO/D-97-02
CRD 1392

INDEX TO APPENDICES

<u>Appendix</u>	<u>Material</u>
A	Save 25
B	Modified 800H
C	347 HFG
D	NF 709
E	Fe ₃ Al
F	310 Ta
G	310 HCBN (HR3C)
H	HR 120
I	Thermie
J	IN52 Weld Overlay
K	Incoclad 671
L	IN72 Weld Overlay

Appendix A
Analysis of Performance
Test Section C
Save 25

Overview of Results: Save 25

The metal loss rate for the Save 25 samples increased with average surface metal temperature over the range of exposure for Section C, i.e. from 1058 F to 1180 F. The rate of metal loss at the highest temperature, in excess of 259 mils per year*, was adequate to perforate the tube wall within 18.6 months of exposure. This was the highest rate of metal loss for any of the candidate alloys. Save 25 continued to demonstrate poor resistance to corrosion down to an average surface metal temperature of about 1096 F. Sample II-JJ, which saw exposure at 1058 F, experienced a moderate rate of metal loss of 58 mils per year. More than half of the wall thickness remained at the end of the Section C exposure period for this sample.

As was stated in the Section A report, typically, Save 25 would be expected to perform similar to the candidate alloys that have a similar level of chromium, i.e. approximately 20 to 25%%. Candidate alloys having this chromium level include 310 Ta and 310 HCbN (HR3C). These Type 310 stainless steel based alloys performed near in the middle of the pack relative to the other candidate alloys. The most significant difference between Save 25 and the Type 310-based alloys appears to be that Save 25 includes the addition of a significant amount of copper (up to 4%). It has been speculated that copper may act to either inhibit formation of the protective chromium oxide scale, or it may facilitate de-cohesion between the scale and the underlying metal. Neither of these hypotheses has been proven.

Analysis of deposit on the surface of tube sample II-JJ revealed that the deposit had the known aggressive combination of species, namely iron, oxygen, the alkali metals, and sulfur. The presence of significant amounts of arsenic was unexpected, and its' significance is unclear. Examination and analysis of the scale adjacent to the metal surface revealed the chalky-white appearance associated with Alkali-iron-sulfates. Thus, the required "bad actor" was available to test the performance limits of this alloy.

The analysis of the deposit and the metal surface immediately adjacent to the interface revealed the presence of carbon. While carbon determinations using EDS are unreliable, the implications of carbon in the deposit are worthy of additional consideration, as is the potential for carbon ingress from the deposit into the abutting metal.

Finally, while it was not the focus of this investigation, the internal surface condition was briefly examined for sample II-JJ.

* **Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: Save 25

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• In assessing the data for Section C, it is important to understand that some tube samples had to be removed from the section early due to excessive thinning.• The schematic in Figure A-1 shows the positions of the tube lengths that were removed early. In November 2001, a length was removed that comprised six tube specimens. In June 2002, two lengths were removed. One length comprised three tube specimens. The other involved only one specimen.• Figure A-1 also shows the positions of the four Save 25 samples within Section C when it was initially installed. Examination of this figure reveals that three of the four Save 25 specimens were removed early, Sample K-L in November 2001, Samples D-E and Z-AA in June 2002. The lowest temperature sample, Sample II-JJ, survived until the end of the Section C exposure period.• The samples that were removed early were set aside for later analysis, and have been included in the current evaluation along with the other tube samples that made up Section C. However, it should be noted that it was not possible to analyze Sample D-E extensively due to the fact that it was overlaid with weld metal during its service life.• Also shown in Figure A-1 is the calculated average surface metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• The Save 25 tube samples for this program were manufactured from one heat of material (Heat D621907) by Sumitomo Metals Industries (SMI). The table in Figure A-2 provides a “specified” composition and ladle analysis per the SMI-provided materials certificates.• Previous analysis of the Save 25 samples from Section A showed that for three of the four tube samples, the actual tube composition did not comply with the specified composition in that it is slightly high in copper relative to the maximum allowable of 4 wt%.• However, for Section C, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample II-JJ confirmed that the correct material was used at this location.

Material: Save 25

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance	<ul style="list-style-type: none">• Figure A-3 documents the appearance of the Save 25 tube prior to exposure.• Figures A-4 through A-7 document the as-received appearance of the Save 25 tube samples after service. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the "o'clock" conventions described above, (with the 12 o'clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o'clock side of the tube faces downward, and the 6 o'clock orientation faces upward within the boiler.• The 12 and 3 o'clock positions for Sample K-L show that this tube was perforated by corrosion near mid-length.• Figure A-5 shows the weld cladding repair to Sample D-E and provides the reason why further analysis of this sample would be fruitless.• Sample II-JJ shows evidence of the gray/white scale associated with molten alkali-iron sulfate attack.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures A-8 through A-11 show the appearance of the external surface of the Save 25 tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for all four samples show the appearance of general wastage due to fireside corrosion.• With the exception of Sample II-JJ, all of the Save 25 samples showed significant pitting at the 6 o'clock position.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures A-12 through A-15.• The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost.• In some cases, the minimum wall thickness in the cross section was not at one of the eight predetermined locations, (Samples K-L and II-JJ are examples). In these cases, there was no "before" measurement for comparison. So, the average "before" wall thickness was used to calculate the wall thickness lost at these off locations.• For Sample K-L, the wall was completely perforated, so, it was not possible to determine an accurate maximum rate of metal loss.

Material: Save 25

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure A-16 plots the maximum wall thickness lost against the calculated average surface metal temperature for each of the four Save 25 samples.• As a general trend, it is apparent that the rate of attack increases continuously as the temperature is raised over the interval of roughly 1040 F to 1180 F.• It also was noted that Save 25 suffers minimal wall reduction at 1040 F, but that the rate of metal loss increases dramatically when the temperature is raised to 1080 F.• The observed high rate of metal loss provides the reason that all of the Save 25 samples that saw an exposure of 1080 F and above have been removed from service. At this point only the II-JJ sample (at 1040 F) remains in service for Section B.
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure A-17 plots metal loss as a function of time for three of the four sample locations Sections A and C, with samples from Section C having experienced generally longer exposure times. Note: Sample D-E data was not plotted because this sample had been overlain with weld metal in Section C, so, no data was available for this sample.• The (401 mils) data point for Sample K-L represents complete penetration of the wall.• While the data is very limited, data for Sample Z-AA suggest that the corrosion rate slowed with time after an initial rapid loss of wall thickness.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample II-JJ was selected for a detailed SEM/EDS assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected because it was the only Save 25 sample to survive for the full exposure period of Section C.• Figures A-18a and b show the appearance of the scale/metal interface for Sample K-L. Six distinct regions are in evidence. These regions are, starting within the metal and working out:<ul style="list-style-type: none">○ <u>Base metal</u> – etch shows grain boundaries and carbides.○ <u>Diffusion zone – light etching</u> - This region is obvious as a light-appearing band that is parallel to the metal surface, perhaps see most clearly in Figure A-18b. .○ <u>Diffusion zone – dark etching</u> – This constitutes the leading edge of the grains as they interface with the scale. As EDS analysis later shows, this zone is depleted in chromium and possibly enriched in carbon.○ <u>Thin porous, loosely adhering scale</u> – this is seen continuous along the surface. EDS analysis will later show that this is predominantly chromium-oxide.○ <u>Bulk deposit</u> – EDS analysis will show that this region contains know aggressive species, including iron, sulfur, chlorine, and alkali metals.

Summary of Findings, (continued)

Material: **Save 25**

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">• Figure A-19 shows the appearance of the microstructure at mid-wall.• Figure A-20 shows the appearance of the internal surface for Sample II-JJ. Little evidence of an oxide scale was found. While it cannot be stated conclusively without further investigation, the irregular surface contour at the internal surface suggest that this surface had experienced metal loss due to steam-side oxidation, but that the scale subsequently had spalled away from the surface.
EDS Analysis Results	<ul style="list-style-type: none">• The table in Figure A-21 provides a summary of the EDS analyses of the locations numbered in Figure A-18b. Also shown in this table is a summary of the spectrographic analysis reported earlier, in Figure A-2.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Area 1: Bulk deposit/scale analysis</u> – Alkali metals are present. Sulfur and phosphorous are present in an increased amount compared to the base metal. An iron oxide is likely, as are aluminum, silicon and titanium oxides. Carbon content is relatively high, however, EDS is reliable qualitatively but not quantitatively for light elements such as carbon. This suggests that carbon is present, but the exact amount is unknown.• <u>Area 2: Adherent scale</u> – This appears to be comprised of an chromium-, iron-, and nickel-rich oxide. Again of significance here is the presence of sulfur and carbon.• <u>Area 3: Diffusion zone – dark etching</u> - This is leading edge of the metal adjacent to the scale/metal interface. This region is depleted in chromium. Oxygen and perhaps carbon ingress are suggested by this analysis.• <u>Area 4: Diffusion zone – light etching</u> – The analysis here is practically indistinguishable from that of the bulk tube alloy.• <u>Area 5: Tube metal composition</u> – Given its limitations this EDS analysis compares favorably with that of the reference spectrographic analysis below it.

Figure A-1: Schematic Drawing Showing Position of Save 25 Tube Samples Within Section C

1. Drawing shown in same relative orientation as per the actual installation.
2. This group of tube samples was removed from service in November 2001 - highlighted in red.
3. This group of tube samples was removed from service in June 2002 - highlighted in yellow.

Figure A-2 Semi-Quantitative Composition Verification for Save 25

Description: Nominal 22Cr/18Ni steel with Nb and N added to provide creep strength.
Source: Sumitomo Metal Industries (SMI)
Reference Composition: “Specified” chemistry – per SMI certificate.

Element	Reference Composition	Composition (a) Heat D621907	Tube Sample D-E	Tube Sample K-L	Tube Sample Z-AA	Tube Sample H-JJ
Ni	15.00 – 22.00	19.80	N/A	N/A	N/A	19.6
Cr	21.00 – 24.00	22.60	N/A	N/A	N/A	22.0
Fe	Balance	Balance	N/A	N/A	N/A	52.8
Mo	-	-	N/A	N/A	N/A	-
Co	-	-	N/A	N/A	N/A	-
C	0.05 – 0.12	0.07	N/A	N/A	N/A	-
N	0.15 – 0.30	0.22	N/A	N/A	N/A	-
B	-	-	N/A	N/A	N/A	-
Mn	2.0 max	0.64	N/A	N/A	N/A	0.44
Si	1.5 max	0.23	N/A	N/A	N/A	0.18
Al	-	-	N/A	N/A	N/A	-
Ti	-	-	N/A	N/A	N/A	-
Al+Ti	-	-	N/A	N/A	N/A	-
Nb	0.30 – 0.60	0.45	N/A	N/A	N/A	-
Ta	-	-	N/A	N/A	N/A	-
Nb+Ta	-	-	N/A	N/A	N/A	-
V	-	-	N/A	N/A	N/A	-
W	0.80 – 2.80	1.31	N/A	N/A	N/A	1.86
Cu	2.00 – 4.00	3.31	N/A	N/A	N/A	3.24
Sn	-	-	N/A	N/A	N/A	-
P	0.030 max	0.022	N/A	N/A	N/A	-
S	0.010 max	(c)	N/A	N/A	N/A	-
O2	-	-	N/A	N/A	N/A	-

a – Ladle analysis
b- By difference
c- Not detected

N/A = Sample not analyzed.

Figure A-3: Appearance of Save 25 Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
 (Note: 3 o'clock is up in this image)

3 O'Clock
 (Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure A-4: As-Received Appearance of Sample K-L (Save 25)

(Average metal temperature: 1180 F)

Note: this tube sample was removed from service on 11/6/01

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure A-5: As-Received Appearance of Sample D-E (Save 25)

(Average metal temperature: 1158 F)

Note: this tube sample was surface clad to extend life.
This tube sample was removed from service on 6/10/02

12 O'Clock – Facing Gas Flow
 (Note: 3 o'clock is up in this image)

3 O'Clock
 (Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure A-6: As-Received Appearance of Sample Z-AA (Save 25)

(Average metal temperature: 1096 F)

Note: this sample was removed from service prematurely on 6/10/02

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure A-7: As-Received Appearance of Sample II-JJ (Save 25)

(Average metal temperature: 1058 F)

12 O’Clock
(289 mils)

3 O’Clock
(274 mils)

6 O’Clock
(2 mils lost)

Figure A-8: OD Surface Appearance After Grit Blast

Material: Save 25
Sample: K-L

12 O’Clock
(N/A)

3 O’Clock

(Not this shows the condition of the weld overlay build-up, not the original surface.)

6 O’Clock

(The weld overlay can be seen to the left in this image. The original surface is to the right.)

Figure A-9: OD Surface Appearance After Grit Blast

Material: Save 25

Sample: D-E

12 O'Clock
(253 mils lost)

3 O'Clock
(207 mils lost)

6 O'Clock
(0 mils lost)

Figure A-10: OD Surface Appearance After Grit Blast

Material: Save 25
Sample: Z-AA

12 O’Clock
(106 mils lost)

3 O’Clock
(74 mils lost)

6 O’Clock
(6 mils lost)

Figure A-11: OD Surface Appearance After Grit Blast

Material: Save 25
Sample: II-JJ

Material: SAVE 25

Sample Location: K-L
Maximum Rate: >259 mils/yr
Maximum Loss Orientation: Approx. 2:30 o'clock
Average metal Temperature: 1180 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.398	0.402	0.404	0.402	0.403	0.404	0.399	0.397	0.401	0.401
After	0.109	0.029	0.130	0.389	0.401	0.287	0.040	0.130		0.000
Delta	0.289	0.373	0.274	0.013	0.002	0.117	0.359	0.267		0.401

Figure A-12: Silhouette and Wall Thickness Measurements for Sample K-L

Note: this tube sample was removed from service on 11/6/01

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Material: SAVE 25
Sample Location: D-E
Maximum Rate: N/A mils/yr
Maximum Loss Orientation: N/A
Average metal Temperature: 1158 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.399	0.399	0.401	0.403	0.404	0.401	0.401	0.404	0.402	0.402
After	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A		N/A
Delta	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A		N/A

Figure A-13: Silhouette and Wall Thickness Measurements for Sample D-E

Note: this tube sample had a weld build-up applied in an effort to extend service; however, it ultimately was removed from service on 6/10/02.
 No measurements taken due to weld build-up.

Material:

SAVE 25

Sample Location:

Z-AA

Maximum Rate:

148 mils/yr

Maximum Loss Orientation:

Approx. 2:30 o'clock

Average metal Temperature:

1096 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.397	0.398	0.397	0.400	0.398	0.396	0.398	0.399	0.398	0.398
After	0.144	0.191	0.190	0.386	0.398	0.387	0.219	0.246		0.130
Delta	0.253	0.209	0.207	0.014	0.000	0.009	0.179	0.153		0.268

Figure A-14: Silhouette and Wall Thickness Measurements for Sample Z-AA

Note: this tube sample was removed from service on 6/10/02

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Material:

SAVE 25

Sample Location:

II-JJ

Maximum Rate:

56 mils/yr

Maximum Loss Orientation:

Approx. 2:30 o'clock

Average metal Temperature:

1058 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.420	0.424	0.426	0.428	0.425	0.423	0.421	0.420	0.423	0.423
After	0.314	0.311	0.352	0.416	0.419	0.421	0.370	0.306		0.290
Delta	0.106	0.113	0.074	0.012	0.006	0.002	0.051	0.114		0.133

Figure A-15: Silhouette and Wall Thickness Measurements for Sample II-JJ

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Figure A-16: Metal Loss Rate as a Function of Temperature

Material: Save 25

Note: In analyzing these data it is important to understand that the three of the four Section C samples were removed early due to excessive corrosion losses. Sample K-L (1180 F) was removed in November 2001, shortly after the Section A samples. At the same time, Sample D-E (1158 F) had its' wall thickness built-up using a weld overlay. It then was removed from service at the same time as Sample Z-AA in June 2002. The weld overlay destroyed wall thickness data for Sample D-E and accounts for the fact that no data is plotted for this sample for Section C. Sample II-JJ (1058 F) was removed with the remaining Section C samples in May 2003.

* - The wall thickness for this sample was completely penetrated; therefore, this data point represents a minimum rate of loss.

Figure A-17: Metal Loss as a Function of Time

Material: Save 25

Note: From the plot above it can be seen that Sample K-L from Section C, which was completely perforated, had somewhat more exposure than the Section A samples, even though it was removed at roughly the same time, i.e. November 2001. There was no data for the D-E sample from Section C due to the fact that it was overlain with weld metal. Sample Z-AA from Section C was removed in June 2002. Sample II-JJ experienced the full exposure life for both Sections A and C.

(a) External Scale/Metal Interface (SEI - Low Magnification)

(b) External Scale/Metal Interface (SEI - Intermediate Magnification)

Figure A-18: SEM Microstructure: Save 25

Note: Numbers on Figure (b) indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

Figure A-19: SEM Mid-Wall Microstructure: Save 25

Note: Photomicrograph at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

(a) Internal Surface (SEI - Intermediate Magnification)

(b) Internal Surface (SEI - High Magnification)

Figure A-20: SEM Microstructure: Save 25

Figure A-21: EDS Analysis of Deposit/Scale/Metal Interface for Save 25 (Sample II-JJ)

Area	Description	Ni	Cr	Fe	Cu	Mn	W	Ti	Al	Si	C	O	Ca	K	As	Cl	P	S
1	Bulk deposit/ scale analysis	1.88	0.30	13.2	--	--	--	0.24	5.11	4.87	50.0	16.8	0.49	0.73	5.09	0.29	--	1.14
2	Adherent scale.	11.8	32.4	28.8	--	0.54	--	--	0.69	1.17	3.56	14.6	--	--	--	--	--	6.38
3	Diffusion zone – dark etching along scale/metal interface.	24.5	11.1	56.6	2.79	0.36	--	--	--	0.52	2.30	1.85	--	--	--	--	--	--
4	Diffusion zone – light etching.	20.3	22.4	53.3	2.75	0.36	--	--	--	0.82	--	--	--	--	--	--	--	--
5	Base Metal	19.6	22.0	52.8	3.24	0.44	1.86	--	--	0.18	--	--	--	--	--	--	--	--
	Reference bulk composition	19.2	21.8	51.2	4.1	0.66	1.35	0.008	0.016	0.24	0.07	--	--	--	--		0.018	0.001

Appendix B
Analysis of Performance
Test Section C
Modified 800H

Overview of Results: Modified 800H

Analysis of Section A revealed that Modified 800H had sustained a maximum rate of 178 mils per year* of exposure to the corrosion-inducing service conditions within the Niles boiler. This resulted in a maximum measured wall reduction of 0.230 inches after 1.29 years of exposure within Section A. Time of exposure is based on time above a minimum average surface metal temperature of 1000F, not calendar time. So, given an initial wall thickness of about 0.400 inches, Section A results showed that one Modified 800H tube sample had lost almost 60 percent of its initial wall thickness after a relatively short exposure time. Consistent with this observation, shortly after Section A was removed from the boiler, the Modified 800H samples at location L-M were removed from both Sections B and C and replaced with a more corrosion resistant material. The Modified 800H samples at location E-F were replaced for both sections approximately six months later. For Section C, only one Modified 800H tube sample survived for the full length of time until the section was removed for evaluation, that was the sample at location Y-Z. This corresponded to the location within Section C having lowest average surface metal temperature for a Modified 800H sample.

It should be noted that the metal loss rates determined to date for both Section A and Section C all were based on a ring sample that was extracted from mid-length of each tube sample. In this analysis additional attention was focused on metal losses in the vicinity of welds. Representative samples were taken and it was determined that, for the Modified 800H samples evaluated, the Inconel 625 weld filler metal is reasonably resistant to coal ash corrosion and that the tube material immediately adjacent to the weld (i.e. the weld heat affected zone) was somewhat less affected by corrosion than was the remainder of the tube. Indeed the tube wall appeared to be progressively thinner toward the mid-point of the tube sample.

Due to the lack of deposit in the section examined, no deposit analysis was performed on modified 800H, however, it is reasonable to infer that the same deposit was found everywhere on Section C. This being the case, it is likely that the same alkali-iron-sulfate that gave rise to attack elsewhere in the section caused the wastage observed for the modified 800H.

Evaluation of the microstructure at the external scale/metal interface revealed that Modified 800H had developed a continuous adherent chromium-oxide scale covering the external surface of the tube. Similar results were found during the evaluation of the Modified 800H sample removed from Section A. The results of this assessment suggested that this material suffered rapid general metal loss that may be related to the degree of chromium depletion in the vicinity of the metal surface (as low as 9%). The evidence suggested also that progressive spalling of the chromium oxide scale that adheres to the surface may also have played an important role in influencing the poor performance of this material.

* **Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: Modified 800H

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• In assessing the data for Section C, it is important to understand that some tube samples had to be removed from the section early due to excessive thinning. The schematic in Figure B-1 shows the relative positions of the Modified 800H samples in all three sections. Also, shown are the positions of all of the excessively thinned tubes that were removed and replaced in order to extend the life of Section C.• Two modified 800H samples were removed early. Sample L-M was removed in November 2001. Sample E-F was removed in June 2002. Sample Y-Z survived for the full Section C exposure period.• The samples that were removed early were set aside for later analysis, and have been included in the current evaluation along with the other tube samples that made up Section C.• Also shown in this figure is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• The table in Figure B-1 provides a reference composition from Oak Ridge National Laboratory (ORNL) literature for this alloy.• ORNL provided material from three different heats of Modified 800H for assessment in this program. The composition for each of the three heats also is reported.• During the Section A evaluation, detailed composition verification was undertaken for each tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample E-F confirmed that the correct material was used at this location.

Material: Modified 800H

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance	<ul style="list-style-type: none">• Figure B-3 documents the typical appearance of this material when it was received from ORNL.• Figures B-4 through B-6 document the as-received appearance of the external surface of the tube samples after service exposure. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the "o'clock" conventions described above, (with the 12 o'clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o'clock side of the tube faces downward, and the 6 o'clock orientation faces upward within the boiler.• External tube wastage is visible for all three samples; however, this is more clearly shown in the tube silhouette images that follow.• A relatively thick rust-red scale and deposit build-up is seen on Samples L-M and Y-Z. This build up is not in evidence on Sample E-F. It is believed that the build-up was removed (perhaps for tube inspection purposes) after the tube was removed from service.• The gray/white scale associated with molten alkali-iron sulfate attack can be found at the 12 and 3 o'clock positions for Sample Y-Z.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures B-7 through B-9 show the appearance of the external surface of the Modified 800H tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for all three samples show the appearance of general wastage due to fireside corrosion.• The 6 o'clock position for all three tube samples shows that evidence of shallow but extensive pitting on the back-side.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures B-10 through B-12.• The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost.• For all three tube samples, the minimum wall thickness in the cross section was not at one of the eight predetermined locations. In these cases, there was no "before" measurement for comparison. So, the average "before" wall thickness was used to calculate the wall thickness lost at these off locations.

Material: Modified 800H

Summary of Findings, (continued)

Issue	Discussion
Rate of Wall Thickness Loss Versus Average Surface Metal Temperature	<ul style="list-style-type: none">• The chart in Figure B-13 plots the maximum rate of wall thickness lost against the calculated average surface metal temperature for the three Modified 800H samples in Section C. Similar data from Section A also are provided on this chart.• Review of these data reveals a relatively high rate of metal loss for all locations, with one sample (Sample Y-Z from Section C) evidencing a somewhat lower rate.• For Section C, the rate of metal loss increased with temperature. These are similar to the results for Section A with the exception that, for Section A, the rate at 1150 F was somewhat higher than that at 1174 F.• It also was noted that Sample Y-Z experienced a much higher rate of metal loss in Section A than it did in Section C.• These inconsistencies are noted, however, they are not surprising given the relatively limited sampling of this program. Furthermore, it's pointed out that all of these data suggest an objectionably high rate for Modified 800H over the temperature range in question.
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure B-14 plots metal loss as a function of time for each sample location for Sections A and C. with samples from Section C having experienced generally longer exposure times.• Shortly after Section A was removed for analysis, the tube Sample L-M was also removed and replaced in Section C due to excessive metal loss.• Metal losses in Sample E-F as a function of time provide the reason that it was removed early from Section C.• In Section C, Sample Y-Z lost less wall thickness in 28.5 months of exposure, than it did in Section A in 18.6 months. This was in spite of the fact that the average surface metal temperature for Sample Y-Z in Section C exceeded that of the same sample location in Section A (1099 F vs 1088 F).
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample E-F was selected for a detailed SEM/EDS assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it had lost the most wall thickness of all of the Modified 800H samples. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.

Material: Modified 800H

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">Figures B-15a, and -15b show the secondary electron images of the scale/metal interface for Sample E-F. Three distinct regions are in evidence. These regions are, starting within the metal and working out:<ul style="list-style-type: none"><u>Base metal</u> – oxalic acid etch delineates grain boundaries and carbides.<u>Deeply etching base metal</u> – this region is obvious as a light-appearing band that is parallel to the metal surface, perhaps see most clearly in Figure B-15b (see the area marked with a “2” in this photo). This band is much less than one-half grain wide, and affects only those grains contiguous with the surface. This deeper etch likely reflects composition differences due to diffusion in this region. EDS will later show that this zone is depleted in chromium.<u>Thin adhering scale</u> – this is seen continuous along the surface. EDS analysis will later show that this is predominantly chromium-oxide.Figure B-16 shows the microstructure at mid-wall in Sample E-F.Figure B-17 shows the appearance of the internal metal surface for Sample E-F. A very thin oxide scale is noted along the surface. This region seems relatively unaffected due to service exposure.
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none">Figure B-18 shows a longitudinal profile (at the 12 o’clock orientation) of a Modified 800H sample adjacent to weld “Z” in Section C, see Figure F-1 for locationsAn Inconel 625 weld metal was used throughout Section C. The cross sections show that the TP 310 Ta heat affected zones are not preferentially attached, in fact, the wall thickness for the tube sample tapers from the weld toward the middle of the tube length.
EDS Analysis Results	<ul style="list-style-type: none">The table in Figure B-19 provides a summary of the EDS analyses of the locations numbered in Figure B-15b. Review suggests:<ul style="list-style-type: none"><u>Area 1: For the scale at the out surface (See Figure 15b)</u> – There was no evidence of the alkali metals. Nor were sulfur and phosphorous present. The scale is comprised primarily of a chromium-rich oxide.<u>Area 2: For the deeply diffusion zone in the metal at the interface (See Figure 15b)</u> - This zone is depleted in chromium relative to the matrix (roughly 9% as opposed to 20%). This zone also was noted to be depleted in vanadium and to some extent silicon.<u>Area 3: Base metal</u> – The EDS base metal analysis were used to confirm that the correct alloy had been used in this location. The results compared well with the results of the spectrographic analysis of this grade of material (as per the Section A report).

Figure B-2 Semi-Quantitative Composition Verification for Modified 800H

Description: Nominal 20Cr/30Ni steel with improved creep strength due to addition of V, Nb, Ti, and B
Source: Oak Ridge National Laboratory (ORNL)
Reference Composition: “Target” Chemistry per ORNL (Reference 1).

Element	Reference Composition	Composition Heat 17423	Composition Heat 17424	Composition Heat 17433	Tube Sample E-F	Tube Sample L-M	Tube Sample Y-Z
Ni	31.0	30.74	31.04	31.10	31.0	N/A	N/A
Cr	20.0	19.89	19.98	19.91	19.1	N/A	N/A
Fe	Balance	-	-	-	46.0	N/A	N/A
Mo	1.5	1.50	1.52	1.51	1.41	N/A	N/A
Co	-	0.03	<0.01	<0.01		N/A	N/A
C	0.09	0.10	0.10	0.10		N/A	N/A
N	-	0.026	0.029	0.018		N/A	N/A
B	0.005	-	-	-		N/A	N/A
Mn	2.00	1.93	1.94	1.93	1.68	N/A	N/A
Si	0.25	0.24	0.24	0.26	0.38	N/A	N/A
Al	-	<0.01	<0.01	<0.01		N/A	N/A
Ti	0.25	0.11	0.15	0.03		N/A	N/A
Nb	0.25	0.26	0.26	0.25		N/A	N/A
Ta	-	<0.01	(a)	(a)		N/A	N/A
Nb+Ta	-	-	-	-		N/A	N/A
V	0.4	0.38	0.23	0.37	0.42	N/A	N/A
Cu	-	<0.01	<0.01	<0.01		N/A	N/A
Sn	-	-	-	-		N/A	N/A
P	-	0.009	(a)	0.002		N/A	N/A
S	-	0.003	0.002	0.005		N/A	N/A
O2	-	0.004	0.008	0.015		N/A	N/A

- a- Not analyzed.
b- By difference.

Reference 1: “Fabrication of Test Tubes for Coal Ash Corrosion Testing”, Sikka, V.K., Swindeman, R.W., Wright, I.G., Judkins, R.R., Johnson, R., Proc, 13th Annual Conf. on Fossil Energy Mat’ls, May 1999.

Note: Sample E-F was from Heat 17433
Sample L-M was from Heat 17423
Sample Y-Z was from Heat 17424
N/A = Tube sample not analyzed.

Figure B-3: Appearance of Modified 800H Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure B-4 As-Received Appearance of Sample L-M (Modified 800H)

(Average metal temperature: 1185 F)

Note: this tube sample was removed from service on 11/6/01

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure B-5 As-Received Appearance of Sample E-F (Modified 800H)

(Average metal temperature: 1162 F)

Note: this tube sample was removed from service on 6/10/02)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure B-6 As-Received Appearance of Sample Y-Z (Modified 800H)

(Average metal temperature: 1099 F)

12 O'Clock
(198 mils lost)

3 O'Clock
(200 mils lost)

6 O'Clock
(5 mils lost)

Figure B-8 OD Surface Appearance After Grit Blast

Material: Modified 800H
Sample: L-M

12 O'Clock
(220 mils lost)

3 O'Clock
(251 mils lost)

6 O'Clock
(12 mils lost)

Figure B-8 OD Surface Appearance After Grit Blast

Material: Modified 800H
Sample: E-F

12 O'Clock
(149 mils lost)

3 O'Clock
(107 mils lost)

6 O'Clock
(10 mils lost)

Figure B-9 OD Surface Appearance After Grit Blast

Material: Modified 800H
Sample: Y-Z

Material:

Modified 800H

Sample Location:

L-M

Maximum Rate:

183 mils/yr

Maximum Loss Orientation:

Approx. 2:30 o'clock

Average metal Temperature:

1185 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.400	0.399	0.398	0.398	0.398	0.399	0.400	0.400	0.399	0.399
After	0.202	0.134	0.198	0.380	0.393	0.375	.0190	0.233		0.115
Delta	0.198	0.265	0.200	0.018	0.005	0.024	0.210	0.167		0.284

Figure B-10: Silhouette and Wall Thickness Measurements for Sample L-M

Note: this sample was removed from service on 11/6/01.

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Material:

Modified 800H

Sample Location:

E-F

Maximum Rate:

176 mils/yr

Maximum Loss Orientation:

Approx. 2:30 o'clock

Average metal Temperature:

1162 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.396	0.398	0.400	0.400	0.400	0.403	0.400	0.398	0.399	0.399
After	0.176	0.132	0.149	0.382	0.388	0.383	0.236	0.281		0.083
Delta	0.220	0.266	0.251	0.018	0.012	0.020	0.164	0.117		0.316

Figure B-11: Silhouette and Wall Thickness Measurements for Sample E-F

Note: this tube sample was removed from service on 6/10/02.

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Material:	Modified 800H
Sample Location:	Y-Z
Maximum Rate:	79 mils/yr
Maximum Loss Orientation:	Approx. 9:30 o'clock
Average metal Temperature:	1099 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.402	0.401	0.401	0.400	0.400	0.401	0.401	0.401	0.401	0.401
After	0.253	0.226	0.294	0.389	0.390	0.387	0.233	0.294		0.212
Delta	0.149	0.175	0.107	0.011	0.010	0.014	0.168	0.107		0.189

Figure B-12: Silhouette and Wall Thickness Measurements for Sample Y-Z

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Figure B-13: Metal Loss Rate as a Function of Temperature

Material: Modified 800H

Note: In analyzing these data it is important to understand that the three Section C samples were removed at different times, and so they experienced different lengths of exposure. Sample L-M (1185 F) was removed November 2001, shortly after the Section A samples. Sample E-F (1162 F) was removed in June 2002. Sample Y-Z (1099 F) saw was removed with the remaining Section C samples in May 2003.

Figure B-14: Metal Loss as a Function of Time

Material: Modified 800H

Note: Sample L-M was removed from Section C shortly after the Section A samples were removed. For Section C, Sample E-F was removed early due to excessive wall thickness losses (316 mils). Sample Y-Z experienced the full exposure life for both Sections A and C.

(a) External Scale/Metal Interface (Low Magnification)

(b) External Scale/Metal Interface (Intermediate Magnification)

Figure B-15: Microstructure: Modified 800H

Note: EDS analysis was performed at numbered locations. See Figure B-16 for results.

Midwall Microstructure

Figure B-16: Microstructure: Modified 800H

Internal Surface Appearance

Figure B-17: Microstructure: Modified 800H

Note: Photomicrograph at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Modified 800H Adjacent to Weld "Z"

Figure B-18: Longitudinal Cross-Section: Modified 800H Adjacent to Weld

Note: The weld shown above is not original with Section C. It was used in inserting a "dutchman" between welds Z and AA on June 10, 2002.

Figure B-19: EDS Analysis of Deposit/Scale/Metal Interface for Modified 800H (Sample E-F)

Area	Description	Visual Appearance	Ni	Cr	Fe	Mn	Mo	V	Al	Si	C	O
1	Adherent chromium-oxide scale.	Generally featureless, however, grain boundaries continuous with underlying metal.	3.78	42.5	14.9	4.27	--	--	--	0.54	--	31.4
2	Diffusion zone adjacent to scale/metal interface, depleted in Cr, Si, and V.	Featureless, dark etching grains.	38.9	9.06	50.1	1.55		--	--	0.33	--	--
3	Base Metal	Primary grain structure.	31.0	19.1	46.0	1.68	--	0.42	--	0.38	--	--
	Reference bulk composition per spectrographic analysis.		30.6	20.4	44.4	2.13	1.33	0.36	0.02	0.28	--	--

Appendix C
Analysis of Performance
Test Section C
347 HFG

Overview of Results: 347 HFG

The three Section C 347 HFG tube samples experienced rates of metal loss that ranged from 204, 120, and 76 mils per year*. Taking into consideration the initial 400 mil wall thickness tube Sample I-J, which experienced the highest rate of loss, was removed from service and replaced after only 1.55 years of exposure to corrosive conditions. The other two samples survived until the end of the Section C exposure period (about 2.38 years).

Comparison of the results for Sections A and C revealed that, for both sections, the sample which saw an intermediate temperature exposure (Sample A-B, at 1147 F in Section C) experienced a lower rate of metal loss than the samples in the section that were at a higher temperature (Sample I-J at 1174 F) and at a lower temperature (Sample CC-DD at 1086 F). The reason for this is not clear, but if it is real and not due to scatter, then, it suggests that more than one corrosion mechanism may be operating over the service temperature range. In any case, based on the Section A assessment, these differences in performance, do not appear to be related to alloying and/or microstructural differences in that all three samples appeared to be identical.

It should be noted that the metal loss rates determined to date for both Section A and Section C all were based on a ring specimen that was extracted from mid-length of each tube sample. In this analysis additional attention was focused on metal losses in the vicinity of welds. Representative samples were taken and it was determined that, for the 347 HFG samples evaluated, the Inconel 625 weld filler metal is reasonably resistant to coal ash corrosion and that the tube material immediately adjacent to the weld (i.e. the weld heat affected zone) was somewhat less affected by corrosion than was the remainder of the tube. Indeed the tube wall appeared to be progressively thinner toward the mid-point of the tube sample.

Analysis of deposit on the surface revealed that it contained the known aggressive combination of species, namely iron, oxygen, the alkali metals, chlorine and sulfur. Examination and analysis of the scale adjacent to the metal surface revealed the chalky-white appearance associated with Alkali-iron-sulfates. Thus, the required “bad actor” was available to test the performance limits of this alloy.

Finally, the analysis of the deposit and the metal surface immediately adjacent to the interface revealed the presence of carbon. While carbon determinations using EDS are unreliable, the implications of carbon in the deposit are worthy of additional consideration, as is the potential for carbon ingress from the deposit into the abutting metal.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: 347 HFG

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• In assessing the data for Section C, it is important to understand that some tube samples had to be removed from the section early due to excessive thinning. The schematic in Figure C-1 shows the relative positions of the 347 HFG samples in all three sections. Also, shown are the positions of all of the excessively thinned tubes that were removed and replaced in order to extend the life of Section C.• One 347 HFG sample was removed early. Sample I-J was removed in November 2001, (i.e. about the same time that Section A was removed from service for evaluation). The other two 347 HFG samples survived for the full Section C exposure period.• The sample that was removed early was set aside for later analysis, and has been included in the current evaluation along with the other tube samples that made up Section C.• Also shown in this figure is the calculated average surface metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• The table in Figure C-2 provides the specified composition from ASTM A213 (TP347 HFG).• Sumitomo supplied from one heat all of the 347 HFG tubing used in this program. The table in Figure C-2 provides the heat analysis reported by Sumitomo. The analysis compares well with the specification.• During the Section A evaluation, detailed composition verification was undertaken for every tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample CC-DD confirmed that the correct material was used at this location.

Material: 347 HFG

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance	<ul style="list-style-type: none">• Figure C-3 shows the typical appearance of the 347 HFG material prior to service.• Figures C-4 through C-6 document the as-received appearance of the external surface of the 347 HFG tube samples after they had been removed from service. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the "o'clock" conventions described above, (with the 12 o'clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o'clock side of the tube faces downward, and the 6 o'clock orientation faces upward within the boiler.• Wastage is visible for all three samples in all three orientations; however, it may most clearly be seen at the 12 o'clock position where the profile of the weld metal provides a reference.• A relatively thick rust-red back-side scale and deposit build-up is seen at the 6 o'clock position on all three samples.• A relatively thin red-brown deposit is seen on all other surfaces.• There is no clear evidence in these figures of the gray/white scale associated with molten alkali-iron sulfate attack. However, scraping to remove the red scale revealed evidence of a gray/white scale immediately adjacent to the metal surface.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures C-7 through C-9 show the appearance of the external surface of the 347 HFG tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for all three samples show the appearance of general wastage due to fireside corrosion.• No significant pitting was found on the back-side of these samples.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures C-10 through C-12.• The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost.• For all three samples, the minimum wall thickness in the cross section was not at one of the eight predetermined locations. In these cases, there was no "before" measurement for comparison. So, the average "before" wall thickness was used to calculate the wall thickness lost at these off-locations.

Material: 347 HFG

Summary of Findings, (continued)

Issue	Discussion
Rate of Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure C-13 plots the maximum wall thickness lost against the calculated average surface metal temperature for each of the three 347 HFG samples in Section C. Similar data for Section A also are plotted on this chart.• It was noted that, for both sections, the maximum rate of metal loss was greater at the low and high temperatures, and dipped significantly at an intermediate temperature. The reason for this is not clear; however, it may suggest the role of different corrosion mechanisms.• It should be noted that, given an initial wall thickness of 400 mils, then given the measured maximum rate of metal loss of between 204 and 174 mils per year, the samples at the highest exposure temperature (i.e. the samples at position I-J) would not be expected to survive for three years of exposure. This provides further justification as to why these samples were removed early from all three sections.
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure C-14 plots metal loss as a function of time for each sample location for both Sections A and C, with samples from Section C having experienced generally longer exposure times.• Sample I-J was removed from Section C and replaced at about the same time that Section A was removed for analysis, i.e. November 2001. It was noted that the rate of metal loss appears to be greater for the Sample I-J from Section C as compared with the same sample in Section A. This may have been due to the somewhat higher temperatures for the I-J position in Section C (1174 F vs 1164 F), but due to limited sampling it is difficult to draw this conclusion with certainty.• The chart shows a straight line fit to the maximum metal loss data points for Samples A-B and CC-DD for both Sections A and C. Evaluation of the rate of metal loss data depicted in Figure C-13 suggests that a straight line fit might well be appropriate for the samples at position A-B in that the rate of metal loss was the same at this location for both Section A and Section C.• For the samples at position CC-DD, the rate of metal loss drops off between Section A (176 mils/yr) and Section C (120 mils/yr), so, a straight-line fit would likely be less appropriate.

Material: 347 HFG

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">• Sample CC-DD was selected for a detailed SEM/EDS assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that, between the two samples that survived the full Section C exposure period, Sample CC-DD had lost material at the maximum rate. The focus of this investigation was in the region of the tube where the maximum amount of material was lost, i.e. in the thinnest section.• Figures C-15a and b show the appearance of the external scale/metal interface for Sample CC-DD. Five distinct regions are in evidence. These are highlighted by the numbered locations shown in Figure C-15b. These same locations were analyzed using the EDS capabilities of the SEM. The results are provided later.• A description of the regions is provided below, starting within the metal and working out:<ul style="list-style-type: none">○ <u>Base metal</u> – oxalic acid etch delineates grain boundaries and carbides.○ <u>Deeply etching base metal</u> – It can be seen as the relatively light-appearing band that is parallel to the metal surface in Figure C-15b. Figure C-15b shows that this band is approximately one-half grain wide, and appears related to etchant attack along the grain boundaries of those grains that are near to the interface with the scale. EDS analysis will show that this etching response reflects composition differences due to diffusion (primarily chromium) in this region.○ <u>Deep etching base metal (darker gray)</u> – EDS analysis showed that this region (2 to 3 grains wide) also is within the diffusion zone adjacent to the external surface.○ <u>An adherent scale</u> – this is shown to be continuous along the interface with the underlying metal. EDS analysis will show that this is a chromium-rich oxide.○ <u>Thick and very porous deposit/scale conglomerate</u> – many spherical particles are noted along with what appears to be islands of scale (metal oxides).• Figure C-16 documents the appearance of the mid-wall microstructure for Sample CC-DD.• Figure C-17 shows a cross section along the internal surface of Sample CC-DD. Little or no scale or metal loss was in evidence.

Summary of Findings, (continued)

Material: 347 HFG

Issue	Discussion
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none">• Figure C-18 shows a longitudinal profile (at the 12 o'clock orientation) of the 347 HFG samples adjacent to the welds in Section C. The welds in question are those identified as welds “B” and “DD”, see Figure C-1 for locations• An Inconel 625 weld metal was used throughout Section C. The cross sections show that the 347 HFG heat affected zones are not preferentially attached, in fact, the wall thickness for the tube sample tapers from the weld toward the middle of the tube length.
EDS Analysis Results	<ul style="list-style-type: none">• The table in Figure C-19 provides a summary of the EDS analyses of the locations numbered in Figure C-15b. The “areas” below correspond to the numbered locations indicated in the C-15 figures.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Area 1: For the bulk deposit analysis</u> – Potassium, sulfur, and chlorine are present as constituents of corrosion species. An iron-rich oxide is likely, as are aluminum and silicon oxides. Carbon content is relatively high, however, EDS is reliable qualitatively but not quantitatively for light elements such as carbon.• <u>Area 2: Adherent scale</u> – this region appears to be primarily a chromium / iron oxide.• <u>Area 3: Deep etching diffusion zone</u> – this region which is contiguous with the adherent scale appears to be depleted in chromium (5 wt% vs 20wt% in the base metal). This of course is consistent with the formation of the chromium-rich oxide scale.• <u>Area 4: – Gray etching diffusion zone</u> – this analysis confirms that the diffusion zone is approximately 2 grains wide for this sample. The chromium content in this region was measured to be 12 wt% versus 20 wt% in the base metal.• <u>Area 5: - Base metal</u> – Area 5 was used to determine the base metal composition.

Figure C-1: Schematic Drawing Showing Position of 347 HFG Tube Samples Within Section C

1. Drawing shown in same relative orientation as per the actual installation.
2. This group of tube samples was removed from service in November 2001 - highlighted in red. ☐
3. This group of tube samples was removed from service in June 2002 - highlighted in yellow. ☐

Figure C-2 Semi-Quantitative Composition Verification for 347 HFG

Description: Nominal 18Cr/11Ni steel with Nb and Ta added to provide creep strength.
Source: Sumitomo Metal Industries (SMI)
Reference Composition: “Specified” chemistry – per ASTM A213 (TP347 HFG).

Element	Reference Composition	Composition (a) Heat D892703	Tube Sample A-B	Tube Sample I-J	Tube Sample CC-DD
Ni	9.00 – 13.0	11.98	N/A	N/A	12.3
Cr	17.0 – 20.0	18.4	N/A	N/A	18.0
Fe	Balance	Balance	N/A	N/A	--
Mo	-	-	N/A	N/A	--
Co	-	-	N/A	N/A	--
C	0.06 – 0.10	0.09	N/A	N/A	--
N	-	-	N/A	N/A	--
B	-	-	N/A	N/A	--
Mn	2.00 max	1.46	N/A	N/A	1.05
Si	0.75 max	0.41	N/A	N/A	0.57
Al	-	-	N/A	N/A	--
Ti	-	-	N/A	N/A	--
Al+Ti	-	-	N/A	N/A	--
Nb	-	-	N/A	N/A	--
Ta	-	-	N/A	N/A	--
Nb+Ta	(8 x C) min- 1.0 max	0.9	N/A	N/A	N/D
V	-	-	N/A	N/A	--
W	-	-	N/A	N/A	--
Cu	-	-	N/A	N/A	--
Sn	-	-	N/A	N/A	--
P	0.040 max	0.027	N/A	N/A	--
S	0.030 max	0.001	N/A	N/A	--
O2	-	-	N/A	N/A	--

N/D = EDS technique (gold coating) precluded an accurate niobium determination.

N/A = Tube sample not analyzed.

Figure C-3: Appearance of 347 HFG Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure C-4 As-Received Appearance of Sample I-J (347 HFG)

(Average metal temperature: 1174 F)

Note: this tube sample was removed from service on 11/6/01.

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure C-5 As-Received Appearance of Sample A-B (347 HFG)

(Average metal temperature: 1147 F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure C-6 As-Received Appearance of Sample CC-DD (347 HFG)
(Average metal temperature: 1086 F)

12 O'Clock
(205 mils lost)

3 O'Clock
(281 mils lost)

6 O'Clock
(15 mil lost)

Figure C-7: OD Surface Appearance After Grit Blast

Material: 347 HFG
Sample: I-J

12 O'Clock
(142 mils lost)

3 O'Clock
(60 mils lost)

6 O'Clock
(15 mil lost)

Figure C-8: OD Surface Appearance After Grit Blast

Material: 347 HFG
Sample: A-B

12 O'Clock
(205 mils lost)

3 O'Clock
(229 mils lost)

6 O'Clock
(8 mils lost)

Figure C-9: OD Surface Appearance After Grit Blast

Material: 347 HFG
Sample: CC-DD

Material: 347 HFG
Sample Location: I-J
Maximum Rate: 204 mils/yr
Maximum Loss Orientation: Approx. 2:30 o'clock
Average metal Temperature: 1174 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.397	0.401	0.402	0.403	0.403	0.405	0.404	0.398	0.402	0.402
After	0.192	0.157	0.121	0.369	0.388	0.360	0.128	0.236		0.085
Delta	0.205	0.244	0.281	0.034	0.015	0.045	0.276	0.162		0.317

Figure C-10: Silhouette and Wall Thickness Measurements for Sample I-J

Note: this tube sample was removed from service on 11/6/01.

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Material: 347 HFG
Sample Location: A-B
Maximum Rate: 76 mils/yr
Maximum Loss Orientation: Approx. 10:00 o'clock
Average metal Temperature: 1147 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.441	0.438	0.436	0.436	0.439	0.441	0.443	0.443	0.440	0.440
After	0.299	0.327	0.376	0.423	0.424	0.424	0.274	0.355		0.259
Delta	0.142	0.111	0.060	0.013	0.015	0.017	0.169	0.088		0.181

Figure C-11: Silhouette and Wall Thickness Measurements for Sample A-B

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Material: 347 HFG
Sample Location: CC-DD
Maximum Rate: 120 mils/yr
Maximum Loss Orientation: Approx. 9:30 o'clock
Average metal Temperature: 1086 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.398	0.402	0.402	0.399	0.397	0.397	0.398	0.397	0.399	0.399
After	0.193	0.224	0.173	0.381	0.391	0.382	0.155	0.179		0.114
Delta	0.205	0.178	0.229	0.018	0.008	0.015	0.243	0.218		0.285

Figure C-12: Silhouette and Wall Thickness Measurements for Sample CC-DD

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Figure C-13: Metal Loss Rate as a Function of Temperature

Material: 347 HFG

Note: In analyzing these data it is important to understand that one of the three Section C samples was removed at an earlier date than the other two., and so they experienced different lengths of exposure. Sample I-J (1175 F) was removed in November 2001, at about the same time as the Section A samples. Sample A-B (1147 F) and Sample CC-DD were removed with the remaining Section C samples in May 2003.

Figure C-14: Metal Loss as a Function of Time

Note: From the plot above it can be seen that, for Section C, Sample I-J was removed from service due to excessive metal losses at about the same time that Section A was removed for evaluation. Samples CC-DD and A-B both experienced the full exposure life for both Sections A and C.

(a) External Scale/Metal Interface (SEI - Low Magnification)

(b) External Scale/Metal Interface (SEI - Intermediate Magnification)

C-15: Microstructure: 347 HFG

Note: 1) Numbers on photos indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

(SEI - Intermediate Magnification)

C-16: Mid-Wall Microstructure: 347 HFG

Note: Etchant - Electrolytic 10% oxalic acid etch, 9V OCP

SEI - Internal Surface Appearance

Figure C-17: Microstructure: 347 HFG

(a) 347 HFG Adjacent to Weld “B”

(b) 347 HFG Adjacent to Weld “DD”

Figure F-18: Longitudinal Cross-Sections: 347 HFG Adjacent to Welds

Figure C-19: EDS Analysis of Deposit/Scale/Metal Interface for 347 HFG (Sample I-J)

Area	Description	Ni	Cr	Fe	Cu	Mn	Nb	Mo	Al	Si	C	O	Cl	K	Zn	As	P	S
1	Bulk deposit analysis	0.52	2.15	49.6	--	--	--	--	1.21	2.82	31.1	11.4	0.31	0.58	1.01	--	0.13	0.13
2	Adherent chromium-oxide scale	3.12	43.3	30.6	--	--	--	--	--	1.10	--	19.1	--	0.28	--	--	--	1.42
3	Deep etching diffusion zone at scale/metal interface.	15.7	5.02	78.3	--	0.67	--	--	--	0.26	--	--	--	--	--	--	--	--
4	Gray etching diffusion zone near interface.	12.6	12.6	73.0	--	1.06	--	--	0.39	0.30	--	--	--	--	--	--	--	--
5	Base metal analysis.	12.3	18.0	68.1		1.05	--	--	--	0.57	--	--	--	--	--	--	--	--
	Reference bulk composition	11.9	18.6	64.8	0.20	1.48	0.91	0.24	0.014	0.39	0.10	--	--	--	--	--	--	--

Appendix D
Analysis of Performance
Test Section C
NF 709

Overview of Results: NF 709

NF 709 tube samples continued to evidence a high rate of metal loss due to service exposure. For samples in Section C the rate increased continuously with temperature, and ranged from 100 to 181 mils per year*. The fact that the starting wall thickness for these tubes was slightly less than 400 mils provides the reason why the sample with the highest corrosion rate (Sample J-K) had to be removed early to prolong the life of the section.

It should be noted that the metal loss rates determined to date for both Section A and Section C all were based on a ring sample that was extracted from mid-length of each tube sample. In this analysis additional attention was focused on metal losses in the vicinity of welds. Representative samples were taken and it was determined that, for the NF 709 samples evaluated, the Inconel 625 weld filler metal is reasonably resistant to coal ash corrosion and that the tube material immediately adjacent to the weld (i.e. the weld heat affected zone) was somewhat less affected by corrosion than was the remainder of the tube. Indeed the tube wall appeared to be progressively thinner toward the mid-point of the tube sample.

Analysis of deposit on the surface revealed that it had the known aggressive combination of species, namely iron, oxygen, the alkali metals, and sulfur. The presence of significant amounts of arsenic was unexpected, and its' significance is unclear. Examination and analysis of the scale adjacent to the metal surface revealed the chalky-white appearance associated with alkali-iron-sulfates.

* **Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: NF 709

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• In assessing the data for Section C, it is important to understand that some tube samples had to be removed from the section early due to excessive thinning. The schematic in Figure D-1 shows the relative positions of the NF 709 samples in all three sections. Also, shown are the positions of all of the excessively thinned tubes that were removed and replaced in order to extend the life of Section C.• One NF 709 sample was removed early. Sample J-K was removed in November 2001, (i.e. shortly after Section A was removed from service for evaluation). The other two NF 709 samples survived for the full Section C exposure period.• The sample that was removed early was set aside for later analysis, and has been included in the current evaluation along with the other tube samples that made up Section C.• Also shown in this figure is the calculated average surface metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• Tubes from one heat of NF 709 (Heat 58733) were provided by Nippon Steel Corporation (NSC) for testing in this program. NSC also provided the composition for Heat 58733, and a reference target composition that provided the tolerances for the alloying elements in this material. These are shown in the table in Figure D-2 along with the results of a semi-quantitative analysis that was used to verify the composition of one of the NF 709 tubes in Section C.• During the evaluation of Section A, detailed composition verification was undertaken for every tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample C-D confirmed that the correct material was used at this location.

Material: NF 709

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance	<ul style="list-style-type: none">• Figure D-3 shows the typical appearance of this tube material as it came from NSC.• Figure D-4 through D-6 document the as-received appearance of the external surface after service in Section C. Three views are provided for each of the three tube samples: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the "o'clock" conventions described above, (with the 12 o'clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o'clock side of the tube faces downward, and the 6 o'clock orientation faces upward within the boiler.• Wastage is most clearly visible at the 3 and 12 o'clock orientations for all three samples. The raised surface of the adjoining Inconel 625 weld metal provides a good reference for this.• Evidence of the gray/white scale associated with molten alkali attack can best be seen at the 3 o'clock orientations for Samples C-D and BB-CC.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures D-7 through D-9 show the appearance of the external surface of the NF 709 tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for all three samples show the appearance of general wastage due to fireside corrosion.• The 6 o'clock position for Samples J-K and C-D show the pitting that occurred on the back-side of these samples. Only minimal pitting was noted at the 6 o'clock position for Sample BB-CC.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures D-10 through D-12.• The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost.• For all three samples, the minimum wall thickness in the cross section was not at one of the eight predetermined locations. In these cases, there were no "before" measurement for comparison to determine the "delta". So, the average "before" wall thickness was used to calculate the wall thickness lost at these off-locations.

Material: NF 709

Summary of Findings, (continued)

Issue	Discussion
Rate of Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure D-13 plots the maximum wall thickness lost against the calculated average metal temperature for the three NF 709 samples. Similar data for Section A also are plotted on this chart.• For both sections, it was noted that there appears to be a “knee” in the plotted curve that comes about due to a significant increase in the rate of metal loss above an exposure temperature of about 1160 F.• As was mentioned earlier, Sample J-K was removed early due to excessive metal losses.
Metal Loss as a Function of Time at Each Location	<ul style="list-style-type: none">• The chart in Figure D-14 plots metal loss as a function of time for each sample location for both Sections A and C, with samples from Section C having experienced generally longer exposure times.• Shortly after Section A was removed for analysis, the tube Sample J-K was also removed and replaced in Section C.• The chart shows a straight line fit to the maximum metal loss data points for Samples C-D and BB-CC for both Sections A and C. Evaluation of the rate of metal loss data depicted in Figure D-13 suggests that a straight line fit might well be appropriate for these data in that the rate of metal loss was similar for both locations for both Section A and Section C.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample C-D was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it had lost the most wall thickness of the two NF 709 samples that survived the full exposure period for Section C. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.• Figures D-15a, and b show secondary electron images that document the appearance of the scale/metal interface for Sample C-D at increasing magnifications. Six distinct regions are in evidence. These regions are, starting within the metal and working out:<ul style="list-style-type: none">○ <u>Base metal</u> – oxalic acid etch delineates grain boundaries and carbides.○ <u>Light etching base metal</u> – this region is obvious as a light-appearing band that is parallel to the metal surface, perhaps see most clearly in Figure D-15b. This figure shows that this band is about one grain wide, and affects only those grains that are within a grain or two of the interface. This likely is due to composition differences related to diffusion in this

Summary of Findings, (continued)

Material: NF 709

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<p>region. EDS analysis suggests that this location is depleted in nickel and enriched in chromium and iron relative to the bulk metal analysis</p> <ul style="list-style-type: none"> ○ <u>Dark etching diffusion zone</u> – This constitutes the leading edge of the grains as they interface with the scale. EDS analysis suggests that this region is significantly depleted in chromium relative to the bulk metal analysis ○ <u>Tightly adhering scale</u> – This scale is continuous along the scale/metal interface. EDS analysis shows it to be a chromium-rich oxide, and that it contains a significant amount of sulfur. ○ <u>Thick and porous deposit/scale conglomerate</u> – many spherical particles are noted along with what appears to be islands of scale. EDS analysis shows both potassium and sulfur. <ul style="list-style-type: none"> • Figures D-16 shows the appearance of the mid-wall microstructure. • Figure D-17 shows the appearance of the internal metal surface for Sample C-D. A very thin oxide scale is noted to cover the surface.
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none"> • Figure D-18 shows a longitudinal profile (at the 12 o'clock orientation) of the NF 709 samples adjacent to the welds in Section C. The welds in question are those identified as welds “D” and “BB”, see Figure F-1 for locations • An Inconel 625 weld metal was used throughout Section C. The cross sections show that the TP 310 Ta heat affected zones are not preferentially attached, in fact, the wall thickness for the tube sample tapers from the weld toward the middle of the tube length.
EDS Analysis Results	<ul style="list-style-type: none"> • The table in Figure D-19 provides a summary of the EDS analyses of the locations numbered in Figure D-15b. Also shown for reference in this table are the results the spectrographic analysis that was performed during the assessment of Section A. • Review of this table suggests the following: <ul style="list-style-type: none"> • <u>Area 1: For the bulk deposit analysis</u> – Alkali metals are present. Sulfur and phosphorous are present in an increased amount compared to the base metal. An iron oxide is likely, as are aluminum, silicon and titanium oxides. Carbon content appears to be relatively high, however, EDS is not reliable for carbon. • <u>Area 2: Adherent scale</u> – This layer is comprised primarily of a chromium-rich oxide, although oxides of iron and nickel also are present. • <u>Area 3: Diffusion zone – dark etching</u> – this area is depleted in chromium, suggestive of a diffusion zone. • <u>Area 4: Diffusion zone – light etching</u> – this is depleted in nickel and enriched in chromium and iron relative to the base metal • <u>Area 5: Bulk EDS analysis</u> – compares well with optical spectrograph results.

Figure D-2 Semi_Quantitative Composition Verification for NF709

Description: Nominal 20Cr/25Ni steel with Nb and Ti added to provide creep strength.
Source: Nippon Steel Corporation (NSC)
Reference Composition: “Specified” chemistry – per NSC inspection certificate for heat delivered.

Element	Reference Composition	Composition Heat E58733	Tube Sample C-D	Tube Sample J-K	Tube Sample BB-CC
Ni	22.00 - 28.00	24.87	25.0	N/A	N/A
Cr	19.00 – 23.00	22.29	21.9	N/A	N/A
Fe	-	-	50.4	N/A	N/A
Mo	1.00 – 2.00	1.42	1.5	N/A	N/A
Co	-	-	-	N/A	N/A
C	0.1 max	0.02	-	N/A	N/A
N	0.100 – 0.250	0.176	-	N/A	N/A
B	0.0020 – 0.0100	0.0044	-	N/A	N/A
Mn	1.50 max	0.97	0.73	N/A	N/A
Si	1.00 max	0.40	0.41	N/A	N/A
Al	-	-	-	N/A	N/A
Ti	0.02 - 0.20	0.05	-	N/A	N/A
Al+Ti	-	-	-	N/A	N/A
Nb	0.10 – 0.40	0.23	N/D	N/A	N/A
Ta	-	-	-	N/A	N/A
Nb+Ta	-	-	-	N/A	N/A
V	-	-	-	N/A	N/A
W	-	-	-	N/A	N/A
Cu	-	-	-	N/A	N/A
Sn	-	-	-	N/A	N/A
P	0.030 max	0.010	-	N/A	N/A
S	0.010 max	0.001	-	N/A	N/A
O2	-	-	-	N/A	N/A

N/D = EDS technique (gold coating) precluded an accurate niobium determination.

N/A = Tube sample not analyzed.

Figure D-3: Appearance of NF 709 Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure D-4 As-Received Appearance of Sample J-K (NF 709)

(Average metal temperature: 1178 F)

Note: this tube was removed from service on 11/6/01.

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure D-5 As-Received Appearance of Sample C-D (NF 709)

(Average metal temperature: 1153 F)

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure D-6 As-Received Appearance of Sample BB-CC (NF 709)

(Average metal temperature: 1088 F)

12 O'Clock
(201 mils lost)

3 O'Clock
(224 mils lost)

6 O'Clock
(1 mil lost)

Figure D-7: OD Surface Appearance After Grit Blast

Material: NF 709
Sample: J-K

12 O'Clock
(208 mils lost)

3 O'Clock
(204 mils lost)

6 O'Clock
(13 mils lost)

Figure D-8: OD Surface Appearance After Grit Blast

Material: NF 709
Sample: C-D

12 O'Clock
(188 mils lost)

3 O'Clock
(207 mils lost)

6 O'Clock
(2 mils lost)

Figure D-9: OD Surface Appearance After Grit Blast

Material: NF 709
Sample: BB-CC

Material: NF 709
Sample Location: J-K
Maximum Rate: 181 mils/yr
Maximum Loss Orientation: Approx. 9:30 o'clock
Average metal Temperature: 1178 F

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.400	0.398	0.398	0.396	0.395	0.395	0.395	0.399	0.397	0.397
After	0.199	0.160	0.174	0.378	0.394	0.365	0.146	0.254		0.116
Delta	0.201	0.238	0.224	0.018	0.001	0.030	0.249	0.145		0.281

Figure D-10: Silhouette and Wall Thickness Measurements for Sample J-K

Note: this tube was removed from service on 11/6/01.

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Material: NF 709
Sample Location: C-D
Maximum Rate: 114 mils/yr
Maximum Loss Orientation: Approx. 2:30 o'clock
Average metal Temperature: 1153 F

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.399	0.399	0.398	0.399	0.401	0.400	0.400	0.402	0.400	0.400
After	0.191	0.163	0.194	0.386	0.388	0.394	0.219	0.297		0.128
Delta	0.208	0.236	0.204	0.013	0.013	0.006	0.181	0.105		0.272

Figure D-11: Silhouette and Wall Thickness Measurements for Sample C-D

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Material:	NF 709
Sample Location:	BB-CC
Maximum Rate:	100 mils/yr
Maximum Loss Orientation:	Approx. 9:30 o'clock
Average metal Temperature:	1088 F

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.398	0.397	0.399	0.397	0.396	0.400	0.399	0.398	0.398	0.398
After	0.210	0.237	0.192	0.385	0.398	0.384	0.190	0.238		0.159
Delta	0.188	0.160	0.207	0.012	0.002	0.016	0.209	0.160		0.239

Figure D-12: Silhouette and Wall Thickness Measurements for Sample BB-CC

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Figure D-13: Metal Loss Rate as a Function of Temperature

Material: NF 709

Note: In analyzing these data it is important to understand that the one of the three Section C samples was removed early due to excessive corrosion losses. Sample J-K (1178 F) was removed in November 2001, shortly after Section A was removed for analysis. Sample C-D (1153 F) and Sample BB-CC (1088 F) were removed with the remaining Section C samples in May 2003.

Figure B-14: Metal Loss as a Function of Time

Material: Modified NF 709

Note: From the plot above, Section C Sample J-K was removed shortly after Section A was removed for evaluation. Samples C-D and BB-CC experienced the full exposure life for both Sections A and C.

(a) External Scale/Metal Interface (SEI - Low Magnification)

(b) External Scale/Metal Interface (SEI - Intermediate Magnification)

Figure D-15: Microstructure: NF 709

Note: 1) Numbers on photos indicate distinct areas characterized by the visual assessment and EDAX analyses that follow.

Mid-Wall Microstructure (SEI - Low Magnification)

Figure D-16: Microstructure: NF 709

Note: Photomicrograph at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Internal Surface Appearance

Figure D-17: Microstructure: NF 709

(a) NF 709 Adjacent to Weld "D"

(b) NF 709 Adjacent to Weld "BB"

Figure D-18: Longitudinal Cross-Section: NF 709 Adjacent to Welds

Note: The weld shown in figure D-18a is not original with Section C. It was used in inserting a "dutchman" between welds D and G on June 10, 2002.

Figure D-19: EDS Analysis of Deposit/Scale/Metal Interface for NF 709 (Sample C-D)

Area	Description	Ni	Cr	Fe	Cu	Mn	Nb	Ti	Al	Si	C	O	Mo	K	Cl	As	P	S
1	Bulk deposit analysis	2.01	1.74	36.3	--	--	--	0.64	6.43	9.55	14.4	24.0	--	1.45	--	1.15	1.72	0.62
2	Adherent scale near metal interface.	6.21	50.6	13.2	--	0.51	--	--	--	1.39	--	17.9	--	--	--	--	--	10.2
3	Diffusion zone-dark etch	30.9	12.2	56.0	--	0.61	--	--	--	0.34	--	--	--	--	--	--	--	--
4	Diffusion zone-light etch	13.5	24.3	60.7	--	0.90	--	--	--	0.64	--	--	--	--	--	--	--	--
5	Bulk base metal per EDAX	25.0	21.9	50.4	--	0.73	--	--	--	0.40	--	--	1.51	--	--	--	--	--
	Reference Bulk Composition Per optical spectrograph.	24.9	22.7	48.8	0.04	1.00	1.40	0.036	0.032	0.37	0.03	--	1.39	--	--	--	0.010	0.002

Appendix E
Analysis of Performance
Test Section C
Fe₃Al / TP 304H

Overview of Results: Fe₃Al / TP 304H

The rate of metal loss for the Fe₃Al / TP 304H tube sample (B-C) in Section C was somewhat less than that for the same material in Section A, (i.e. 100 mils per year versus 145 mils per year*). The reason for this reduced wastage rate is not clear. For both samples, the protective Fe₃Al coating was not in evidence anywhere on the tube surface at the time of the analysis, and based on performance in Section A, it likely disappeared early during the life of the tube sample, (i.e. in less than 1.55 years). In any case, the limited number of Fe₃Al / TP 304H samples in this program, makes it difficult to draw substantive conclusions.

It should be noted that the metal loss rates determined to date for both Section A and Section C all were based on a ring specimen that was extracted from mid-length of each tube sample. In this analysis additional attention was focused on metal losses in the vicinity of welds. Representative samples were taken and it was determined that, for the Fe₃Al / TP 304H samples evaluated, the Inconel 625 weld filler metal is reasonably resistant to coal ash corrosion and that the tube material immediately adjacent to the weld (i.e. the weld heat affected zone) was somewhat less affected by corrosion than was the remainder of the tube. Indeed the tube wall appeared to be progressively thinner toward the mid-point of the tube sample.

* **Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: Fe₃Al / TP 304H

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">The schematic in Figure E-1 shows the position of the one Fe₃Al / TP 304H sample in Section C. Also, shown is the calculated average metal temperature at this location.
Composition Verification.	<ul style="list-style-type: none">The table in Figure E-2 provides the composition of tube Sample B-C after exposure. An attempt was made to find and analyze the composition of the iron-aluminide coating on the “after service” samples, but none could be found. It is assumed that the coating either spalled or was corroded away from the surface at some point during the 2.38 years of exposure in Section C. This is consistent with similar results for Section A, after 1.55 years of exposure.The table in Figure E-2 provides EDS analyses of the Fe₃Al coating prior to service. Numerous samplings were made and found to be highly variable. The reported results are for material at the extreme outer surface. A bulk analysis was also attempted and reported. The significance of deviations from the target chemistry is unclear.EDS semi-quantitative analysis at mid-wall for Sample B-C confirms that this material is consistent with TP 304H, thus it verifies that the correct sample was located at position B-C.
As-Received Appearance	<ul style="list-style-type: none">Figure E-3 shows the appearance of the surface of the Fe₃Al coated tube prior to service.Figure E-4 documents the appearance of the external surface of Sample B-C after service. Three views are provided for this tube: 12 o’clock (the view that faces on-coming gas flow), 3 o’clock (the view where the gas flow is tangent to the surface), and 6 o’clock (the view that shows the back-side of the tube relative to the gas flow direction).The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the “o’clock” conventions described above, (with the 12 o’clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o’clock side of the tube faces downward, and the 6 o’clock orientation faces upward within the boiler.Wastage is obscured by the heavy deposit and scale at the 3 and 12 o’clock orientations for Sample B-C.A relatively thin red-brown deposit is seen at the 6 o’clock orientation. The tube profile in this view also gives a sense of the extent of wastage.The gray/white scale associated with molten alkali-iron sulfate attack is clearly visible at the 3 and 12 o’clock orientations..
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">Figure E-5 shows the appearance of the external surface of the Fe₃Al / TP 304H tube samples after grit-blasting to remove deposit and scale. General wastage is most clearly shown at the 12 o’clock orientation.The 6 o’clock position shows very little evidence of attack.

Material: Fe₃Al / TP 304H

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. This is shown in silhouette in Figure E-6.• The same relative “o’clock” positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost.• For the sample in question, the minimum wall thickness in the cross section was not at one of the eight predetermined locations. So, there were no “before” measurement for comparison to determine the “delta”. To address this, the average “before” wall thickness was used to calculate the wall thickness lost at this off-location.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure E-7 plots the maximum wall thickness lost against the calculated average metal temperature for Sample B-C in both Sections A and C.• I was noted that the rate metal loss was somewhat greater for Section A than for Section C. It’s difficult to draw conclusions from this particularly given the fact that the iron-aluminide coating was likely gone from the Section C sample very early in its life.
Metal Loss as a Function of Time	<ul style="list-style-type: none">• The chart in Figure E-8 plots metal loss as a function of time.• Given the limited data, it’s difficult to justify the straight line fit shown, particularly in the light of the evidence of a decreasing metal loss rate as a function of time, per the data shown in Figure E-7.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample B-C was subjected to a detailed SEM/EDS assessment of the constituents and structure in the vicinity of the external and internal surfaces. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.• Figures E-9a and b show secondary electron images (SEI) of the external surface. A continuous scale was observed at the interface along with a relatively thin deposit.• The numbered locations in Figure E-9b show the locations of EDS analyses that follow. Location 1 was taken to represent the bulk TP 304H composition. Location 4 represented the continuous scale, and Location 5 represented the diffusion zone along the external surface.• Figure E-10 represents the microstructure at mid-wall in the tube.• Figure E-11 shows the appearance of the internal metal surface for Sample B-C. Local penetrations into the surface are observed. The numbered locations show the locations of additional EDS analyses that follow. Location 2 represents the composition of a corrosion penetration into the surface. Location 3 represents the ID scale.

Material: Fe₃Al / TP 304H

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none">• Figure E-12 shows a longitudinal profile (at the 12 o'clock orientation) of the Fe₃Al / TP 304H sample adjacent to weld “B” in Section C, see Figure E-1 for location.• An Inconel 625 weld metal was used throughout Section C. The cross sections show that the Fe₃Al / TP 304H heat affected zone is not preferentially attacked, in fact, the wall thickness for the tube sample tapers from the weld toward the middle of the tube length.
EDS Analysis Results	<ul style="list-style-type: none">• The table in Figure E-13 provides a summary of the EDS analyses of the locations numbered in Figures E-9 and E-11. Also shown in this table is a summary of the spectrographic analysis reported earlier.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Area 1: Bulk metal analysis for TP 304 H</u> – These results are taken as verification that the correct tube material was at position B-C• <u>Area 2: Scale penetration at ID surface</u> – The analysis suggests that this scale is a nickel-rich oxide.• <u>Area 3: Scale adhering along ID surface</u> – This analysis also suggests a nickel-rich oxide..• <u>Area 4: OD surface deposit/scale</u> – The analysis suggests that this is primarily an iron-rich oxide. Sulfur also is noted. The reason for the presence of copper is unclear.• <u>Area 5: OD diffusion zone</u> – This zone is depleted in chromium and thus enriched in nickel and iron.

Figure E-2 Semi-Quantitative Composition Verification for Fe₃Al / TP 304H

Description: Commercially available iron Aluminide alloy (FAS) electrospark discharge coated onto Type 304H stainless steel (roughly 30 to 60 mils thick)..

Source: FAS developed by Oak Ridge National Laboratory (ORNL), applied by Pacific Northwest National Laboratory (PNNL)

Reference Composition: “Target” chemistry for coating – per Reference 1.

Element	Reference Composition of Coating	Composition (a) Heat 17433	EDS of Coating at Outer Surface	EDS of Bulk Coating		Element	Reference Composition SA 213 TP 304H	Tube Sample B-C
Ni	-	<0.01	1.22	3.99		Ni	8.00-11.0	8.23
Cr	2.19	1.59	3.92	10.8		Cr	18.0-20.0	16.5
Fe	Balance	-	79.5	67.8		Fe	-	Balance
Mo	-	0.01	-	-		Mo	-	-
Co	-	<0.01	-	-		Co	-	-
C	-	0.008	-	-		C	0.04-0.10	-
N ₂	-	0.001	-	-		N ₂	-	-
B	0.011	0.010	-	-		B	-	-
Mn	-	<0.01	-	1.34		Mn	2.00 max	1.19
Si	-	<0.01	-	-		Si	0.75 max	0.50
Al	15.93	15.79	11.7	5.22		Al	-	-
Ti	-	-	-	-		Ti	-	-
Al+Ti	-	-	-	-		Al+Ti	-	-
Nb	-	<0.01	3.65	10.8		Nb	-	-
Ta	-	-	-	-		Ta	-	-
Mo	-	-	-	-		Nb+Ta	-	-
V	-	<0.01	-	-		V	-	-
W	-	-	-	-		W	-	-
Cu	-	-	-	-		Cu	-	-
Sn	-	-	-	-		Sn	-	-
P	-	-	-	-		P	0.040 max	-
S	-	0.002	-	-		S	0.030 max	-

a – Reported analysis of wire used in deposition process by PNNL.

b- By difference.

Figure E-3: Appearance of Fe₃Al Coated TP 304H Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure E-4 As-Received Appearance of Sample B-C (Fe_3Al / TP 304H)

(Average metal temperature: 1149 F)

12 O’Clock
(227 mils lost)

3 O’Clock
(194 mils lost)

6 O’Clock
(27 mils lost)

Figure E-5: OD Surface Appearance After Grit Blast

Material: **Fe₃Al / TP 304H**
Sample: **B-C**

Material:	Fe₃Al / TP 304H
Sample Location:	B-C
Maximum Rate:	100 mils/yr
Maximum Loss Orientation:	Approx. 2:30 o'clock
Average metal Temperature:	1149 F

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.392	0.391	0.392	0.389	0.388	0.389	0.391	0.392	0.390	0.390
After	0.165	0.194	0.198	0.356	0.361	0.364	0.190	0.236		0.151
Delta	0.227	0.197	0.194	0.033	0.027	0.025	0.201	0.156		0.239

Figure E-6: Silhouette and Wall Thickness Measurements for Sample B-C

Figure E-7: Metal Loss Rate as a Function of Temperature

Material: Fe₃Al / TP 304H

Figure E-7: Metal Loss as a Function of Time

Material: Fe₃Al / TP 304

(a) External Scale/Metal Interface (SEI - Low Magnification)

(b) External Scale/Metal Interface (SEI - Intermediate Magnification)

Note: Numbers indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

Figure E-9: Microstructure: Fe_3Al / TP 304H

(SEI - Low Magnification)

Figure E-10: Mid-wall Microstructure: Fe₃Al / TP 304H

Note: Photomicrograph at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

(SEI - Intermediate Magnification)

Figure E-11: Microstructure: Internal Scale/Metal Interface : Fe_3Al / TP 304H

Note: Numbers indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

Fe₃Al / TP 304H Adjacent to Weld "B"

Figure E-12: Longitudinal Cross-Section: Fe₃Al / TP 304H Adjacent to Weld

Figure E-13: EDS Analysis of Deposit/Scale/Metal Interface for Fe₃Al / TP304H (Sample B-C)

Area	Description	Ni	Cr	Fe	Cu	Mn	W	Ti	Al	Si	C	O	Cu	K	Na	As	P	S
1	Mid-wall bulk analysis TP 304H	8.23	16.5	73.6	--	1.19	--	--	--	0.50	--	--	--	--	--	--	--	--
2	ID surface scale.	47.2	8.58	33.7	--	1.04	--	--	1.59	--	--	7.86	--	--	--	--	--	--
3	ID surface scale.	20.4	16.8	44.9	--	2.14	--	--	--	0.79	--	15.0	--	--	--	--	--	--
4	OD surface deposit/scale.	--	0.81	69.7	--	--	--	--	4.89	5.16	--	13.6	4.02	--	--	1.37	--	0.50
5	OD diffusion zone.	10.2	8.47	79.5	--	1.19	--	--	--	0.59	--	--	--	--	--	--	--	--
	Reference analysis	8.51	18.8	69.4	0.17	1.77	0.028	0.002	0.007	0.37	0.05	--	--	--	--	--	0.029	0.001

Appendix F
Analysis of Performance
Test Section C
310 Ta

Overview of Results: 310 Ta

Type 310 Ta experienced a high rate of metal loss at two of the three locations in Section C. The metal loss rates for Samples M-N and F-G were 131 and 127 mils per year* respectively. These rates were very similar to those determined for the samples from Section A which had metal loss rates that ranged from 120 mils per year to 136 mils per year. This suggests a linear rate of metal loss for samples at these locations. It was noted that Sample F-G needed to be removed early from Section C due to concerns about excessive metal loss. This poor performance of TP 310 Ta is consistent with that of those other alloys having approximately 20% to 25% chromium.

The sample at the lowest temperature location, Sample X-Y, had a metal loss rate of 120 mils per year for Section A and 64 mils per year for Section C. The reason for this reduced rate is not clear, particularly given the fact that the average surface metal temperature for tube Sample X-Y is somewhat higher (calculated to be 11 °F) in Section C than in Section A, and otherwise the corrosion rate appears to increase with temperature over the temperature range in question.

It should be noted that the metal loss rates determined to date for both Section A and Section C all were based on a ring sample that was extracted from mid-length of each tube sample. In this analysis additional attention was focused on metal losses in the vicinity of welds. Representative samples were taken and it was determined that, for the TP 310 Ta samples evaluated, the Inconel 625 weld filler metal is reasonably resistant to coal ash corrosion and that the tube material immediately adjacent to the weld (i.e. the weld heat affected zone) was somewhat less affected by corrosion than was the remainder of the tube. Indeed the tube wall appeared to be progressively thinner toward the mid-point of the tube sample.

Analysis of deposit on the surface revealed that it had the known aggressive combination of species, namely iron, oxygen, the alkali metals, and sulfur. The presence of significant amounts of arsenic was consistent with the analysis of samples from Section A, and further is consistent with the other samples from Section C. Examination and analysis of the scale adjacent to the metal surface revealed the chalky-white appearance associated with Alkali-iron-sulfates. Furthermore high sulfur was consistently indicated in this area.

Finally, the analysis of the deposit and the metal surface immediately adjacent to the interface revealed the presence of carbon. While carbon determinations using EDS are unreliable, the implications of carbon in the deposit are worthy of additional consideration, as is the potential for carbon ingress from the deposit into the abutting metal.

* **Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: 310 Ta

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• In assessing the data for Section C, it is important to understand that some tube samples had to be removed from the section early due to excessive thinning. The schematic in Figure F-1 shows the relative positions of the TP 310 Ta samples in all three sections. Also, shown are the positions of all of the excessively thinned tubes that were removed and replaced in order to extend the life of Section C.• One TP 310 Ta sample was removed early. Sample F-G was removed in June 2002. Based on this, Sample F-G experienced approximately three additional months at service temperature than the Section A samples. It saw approximately seven less months at service temperature than full exposure period for samples in Section C.• Samples M-N and X-Y survived for the full Section C exposure period.• The Sample F-G that was removed early was set aside for later analysis, and has been included in the current evaluation along with the other tube samples that made up Section C.• Also shown in Figure F-1 is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• During the Section A evaluation, detailed composition verification was undertaken for each tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample M-N confirmed that the correct material was used at this location.• For reference it should be noted Sample M-N was taken from Heat 17425. Sample X-Y was taken from Heat 17426.• The table in Figure F-2 also shows the "target" composition as reported by ORNL.

Material: 310 Ta

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance	<ul style="list-style-type: none">• Figure F-3 shows the typical appearance of the 310 Ta samples as delivered by ORNL.• Figures F-4 through F-6 document the appearance of the external surface for all three samples after service exposure. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the "o'clock" conventions described above, (with the 12 o'clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o'clock side of the tube faces downward, and the 6 o'clock orientation faces upward within the boiler.• Wastage is visible at the 12 o'clock and 3 o'clock positions for all three samples, as was a relatively thick red-brown deposit/scale.• The gray-white deposit typically associated with coal ash corrosion can clearly been seen at the 3 o'clock position for Sample X-Y. EDS analysis will show that the aggressive species implied by this corrosion mechanism are also found in the scale of Sample M-N.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures F-7 through F-9 show the appearance of the external surface of the 301 Ta tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for all three samples show the appearance of general wastage due to fireside corrosion.• The 6 o'clock position for Samples M-N shows that significant pitting occurred on the back-side (i.e. the side of the tube opposite the gas flow direction).
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures F-10 through F-12.• The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost.• For all three tube samples, the minimum wall thickness in the cross section was not at one of the eight predetermined locations. In these cases, there were no "before" measurements for comparison. So, the average "before" wall thickness was used to calculate the wall thickness lost at these off-locations.

Material: 310 Ta

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss Rate Versus Average Surface Metal Temperature	<ul style="list-style-type: none"> • The chart in Figure F-13 plots the maximum wall thickness lost against the calculated average surface metal temperature for the three 310 Ta samples in Section C. These same data also are plotted for the tube samples from Section A. • It should be noted that, with one exception (Sample X-Y from Section C) the remaining samples exhibited a consistent rate of metal loss from section to section. These results typically would be suggestive of a linear rate of metal loss. • It is difficult to account for the lower rate of metal loss (64 mils per year) for Sample X-Y other than to note that it was situated at a relatively low temperature position.
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none"> • The chart in Figure F-13 plots metal loss as a function. Consistent with the rates above Samples M-N and F-G demonstrated a nearly linear rate of metal loss. • Also, apparent from this chart is that, while all three sample locations exhibited approximately the same rate of metal loss for Section A (i.e. after 18.6 months of service), Sample X-Y in Section C exhibited a reduced rate of metal loss.
Metallurgical Analysis – SEM	<ul style="list-style-type: none"> • Sample M-N was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it had lost the most wall thickness of the two tubes which survived the full exposure period for Section C. The focus of this investigation was in the region where the maximum amount of material was lost. • Figure F-14 shows the appearance of the tube profile in the section containing the minimum wall thickness for Sample M-N. • Figures F-15a, b, and c show the secondary electron images of the scale/metal interface for Sample F-G. Five distinct regions are in evidence. These regions are, starting within the metal and working out: <ul style="list-style-type: none"> ○ <u>Base metal</u> – oxalic acid etch delineates grain boundaries, slip bands, inclusions and precipitates. ○ <u>Diffusion zone - light etching</u> – this region is obvious as a light-appearing band that is parallel to the metal surface, perhaps seen most clearly in Figures F- 15b and c. ○ <u>Diffusion zone – dark etching</u> – this constitutes the leading edge of the grains as they interface with the scale. EDS analysis will later show that this region is depleted in chromium and enriched in sulfur. ○ <u>Adherent scale</u> – this feature is continuous along the surface. EDS analysis will later show that this scale is likely a chromium-, iron- and nickel-rich oxide. ○ <u>Thick and very porous deposit/scale conglomerate</u> – many spherical particles are noted along with what appears to be islands of scale (metal oxides).

Summary of Findings, (continued)

Material: 310 Ta

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none"> Figure F-15b shows numbered positions where EDS analyses were performed to characterize the materials in the vicinity of the scale/metal interface. Figure F-16 shows the appearance of the microstructure at mid-wall in the specimen. Figure F-17 internal metal surface for Sample M-N. An extremely thin oxide scale is noted to cover the surface.
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none"> Figure F-18 shows a longitudinal profile (at the 12 o'clock orientation) of the TP 310 Ta samples adjacent to the welds in Section C. The welds in question are those identified as welds “N” and “X”, see Figure F-1 for locations An Inconel 625 weld metal was used throughout Section C. The cross sections show that the TP 310 Ta heat affected zones are not preferentially attacked, in fact, the wall thickness for the tube sample tapers from the weld toward the middle of the tube length.
EDS Analysis Results	<ul style="list-style-type: none"> The table in Figure F-19 provides a summary of the EDS analyses of the locations numbered in Figure F-15b. Also shown in this table is a summary of the spectrographic analysis reported earlier. Review of this table suggests the following: <ul style="list-style-type: none"> <u>Area 1: For the bulk deposit analysis</u> – Alkali metals are present. Sulfur and phosphorous are present in an increased amount compared to the base metal. An iron oxide is likely, as are aluminum, silicon and titanium oxides. Carbon content is relatively high, however, EDS is not reliable quantitatively for low atomic number elements. <u>Area 2: Tightly adhering scale</u> – This scale immediately adjacent to the metal/scale is comprised predominantly of a chromium-rich oxide. Also, of significance is the relatively high level of sulfur in this region. <u>Area 3: Diffusion zone – dark etching</u> – This region, adjacent to the scale/metal interface, is less than one grain wide. The results of the analysis suggest that this is a diffusion zone that is depleted in chromium and enriched in iron and nickel. This is consistent with the chromium-rich oxide scale that adheres to the metal surface. <u>Area 4: Diffusion zone – light etching</u> - This region is approximately one grain wide. It appears to be slightly depleted in chromium. <u>Area 5: Bulk EDS analysis</u> – The analysis at this location served as the reference composition for verification of the sample identity.

Figure F-1: Schematic Drawing Showing Position of 310 Ta Tube Samples in Section C

1. Drawing shown in same relative orientation as per the actual installation.
2. This group of tube samples was removed from service in November 2001 - highlighted in red. ☐
3. This group of tube samples was removed from service in June 2002 - highlighted in yellow. ☐

Figure F-2 Semi-Quantitative Composition Verification for Type 310 Ta

Description: 20-25 Cr steel with improved creep strength due to addition of tantalum and nitrogen
Source: Oak Ridge National Laboratory (ORNL)
Reference Composition: “Target” Chemistry per ORNL (Reference 1).

Element	Reference Composition	Composition Heat 17425	Composition Heat 17426	Composition Heat 17431	Tube Sample F-G	Tube Sample M-N	Tube Sample X-Y
Ni	21.0	21.63	21.08	21.12	N/A	21.2	N/A
Cr	24.5	23.74	23.78	24.01	N/A	23.2	N/A
Fe	Balance	Balance	Balance	Balance	N/A	52.4	N/A
Mo	-	<0.01	<0.01	<0.01	N/A	--	N/A
Co	-	0.02	0.02	0.02	N/A	--	N/A
C	0.05	0.063	0.063	0.060	N/A	--	N/A
N	0.22	0.22	0.22	0.24	N/A	--	N/A
B	0.005	(a)	(a)	(a)	N/A	--	N/A
Mn	2.00	1.74	1.66	1.89	N/A	1.33	N/A
Si	0.25	0.25	0.24	0.27	N/A	0.18	N/A
Al	-	<0.01	<0.01	<0.01	N/A	--	N/A
Ti	-	<0.01	<0.01	<0.01	N/A	--	N/A
Nb	-	<0.01	<0.01	<0.01	N/A	--	N/A
Ta	1.75	1.18	1.03	1.24	N/A	1.72	N/A
Nb+Ta	-	-	-	-	N/A	--	N/A
V	-	<0.01	<0.01	<0.01	N/A	--	N/A
W	-	-	-	-	N/A	--	N/A
Cu	-	<0.01	<0.01	<0.01	N/A	--	N/A
Sn	-	-	-	-	N/A	--	N/A
P	-	0.008	0.009	0.013	N/A	--	N/A
S	-	0.006	0.006	0.006	N/A	--	N/A
O2	-	0.013	0.014	0.018	N/A	--	N/A

- a- Not analyzed.
b- By difference.

Reference 1: “Fabrication of Test Tubes for Coal Ash Corrosion Testing”, Sikka, V.K., Swindeman, R.W., Wright, I.G., Judkins, R.R., Johnson, R., Proc, 13th Annual Conf. on Fossil Energy Mat’ls, May 1999.

Sample M-N was from Heat 17425 N/A = Tube sample not analyzed.

Figure F-3: Appearance of 310 Ta Tube Sample Prior to Service

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure F-4 As-Received Appearance of Sample M-N (310 Ta)

(Average metal temperature: 1188 F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure F-5 As-Received Appearance of Sample F-G (310 Ta)

(Average metal temperature: 1166 F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure F-6 As-Received Appearance of Sample X-Y (310 Ta)

(Average metal temperature: 1103 F)

12 O’Clock
(212 mils lost)

3 O’Clock
(255 mils lost)

6 O’Clock
(0 mils lost)

Figure F-7: OD Surface Appearance After Grit Blast

Material: 310 Ta
Sample: M-N

12 O’Clock
(119 mils lost)

3 O’Clock
(188 mils lost)

6 O’Clock
(2 mils lost)

Figure F-8: OD Surface Appearance After Grit Blast

Material: 310 Ta
Sample: F-G

12 O'Clock
(105 mils lost)

3 O'Clock
(61 mils lost)

6 O'Clock
(0 mils lost)

Figure F-9: OD Surface Appearance After Grit Blast

Material: 310 Ta
Sample: X-Y

Material: 310 Ta
Sample Location: M-N
Maximum Rate: 131 mils/yr
Maximum Loss Orientation: Approx. 2:30 o'clock
Average metal Temperature: 1188 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.400	0.401	0.401	0.401	0.401	0.400	0.400	0.400	0.400	0.400
After	0.188	0.118	0.146	0.381	0.401	0.381	0.231	0.203		0.089
Delta	0.212	0.283	0.255	0.020	0.000	0.019	0.169	0.197		0.311

Figure F-10: Silhouette and Wall Thickness Measurements for Sample M-N

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Material: 310 Ta
Sample Location: F-G
Maximum Rate: 127 mils/yr
Maximum Loss Orientation: Approx. 2:30 o'clock
Average metal Temperature: 1166 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.402	0.402	0.402	0.401	0.402	0.399	0.398	0.399	0.401	0.401
After	0.283	0.207	0.214	0.399	0.399	0.395	0.270	0.333		0.173
Delta	0.119	0.195	0.188	0.002	0.003	0.004	0.128	0.066		0.228

Figure F-11: Silhouette and Wall Thickness Measurements for Sample F-G

Note: this tube was removed from service on 6/10/02.

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Material: 310 Ta
Sample Location: X-Y
Maximum Rate: 64 mils/yr
Maximum Loss Orientation: Approx. 9:30 o'clock
Average metal Temperature: 1103 F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.400	0.400	0.399	0.400	0.399	0.401	0.401	0.400	0.400	0.400
After	0.295	0.291	0.338	0.391	0.399	0.394	0.285	0.334		0.248
Delta	0.105	0.109	0.061	0.009	0.000	0.006	0.116	0.166		0.152

Figure F-12: Silhouette and Wall Thickness Measurements for Sample X-Y

* Measurement taken at "maximum loss orientation" noted above. The average "before" wall thickness was used to calculate the "delta".

Figure F-13: Metal Loss Rate as a Function of Temperature

Material: 310 Ta

Note: In analyzing these data it is important to understand that the one of the three Section C samples was removed early due to excessive corrosion losses. Sample F-G (1166 F) was removed in June 2002. Sample M-N (1188 F) and Sample X-Y (1103 F) were removed with the remaining Section C samples in May 2003.

Figure F-13: Metal Loss as a Function of Time

Note: From the plot above it can be seen that, for Section C, Sample F-G was removed early (in June 2002) due to concerns about excessive metal loss. Samples X-Y and M-N experienced the full exposure life for both Sections A and C.

Figure F-14: Low Magnification Image Showing Cross-Section Through Thinnest Region of Sample F-G (310 Ta)

(a) External Scale/Metal Interface (SEI - Low Magnification)

(b) External Scale/Metal Interface (SEI - Intermediate Magnification)

Figure F-15: Microstructure: 310 Ta

Note: Numbers on photos indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

(c) External Scale/Metal Interface (SEI - High Magnification)

Figure F-15 (Cont.): Microstructure: 310 Ta

(SEI - Low Magnification)

Figure F-16: Mid-Wall Microstructure: 310 Ta

Note: Photomicrograph at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Internal Surface Appearance

Figure F-17: Microstructure: 310 Ta

(a) TP 310 Ta Adjacent to Weld "N"

(b) TP 310 Ta Adjacent to Weld "X"

Figure F-18: Longitudinal Cross-Section: 310 Ta Adjacent to Welds

Figure F-19: EDS Analysis of Deposit/Scale/Metal Interface for 310 Ta (Sample M-N)

Area	Description	Ni	Cr	Fe	Cu	Mn	Ta	Ti	Al	Si	C	O	Ca	K	Na	As	P	S
1	Bulk deposit analysis	1.96	0.90	26.1				0.56	4.78	10.8	18.4	27.3		1.28		3.94	1.62	2.31
2	Tightly adhering scale..	3.48	54.5	18.2		1.98			0.26	1.39		15.2						4.98
3	Diffusion zone – dark etching adjacent to interface.	25.2	12.2	60.0		1.09	0.91			0.58								
4	Diffusion zone – light etching.	21.4	21.1	54.7		1.01	1.34			0.45								
5	Bulk EDS analysis	21.2	23.2	52.4		1.33	1.72			0.18								
	Reference bulk analysis.	21.0	24.7	51.2	--	1.72	0.73	--	0.002	0.24	0.07	--	--	--	--	--	0.003	0.007

Appendix G
Analysis of Performance
Test Section C
310 HCbN (HR3C)

Overview of Results: 310 HCbN (HR3C)

One 310 HCbN sample in Section C, Sample G-H experienced a significantly high rate of metal loss (141 mils per year*) that it was removed and replaced after 18.6 months of exposure, i.e. shortly after Section A was removed for examination. Sample N-O remained in Section C for continued testing and experienced a high rate of metal loss to the point where, less than 25% of the wall remained at the time that Section C was removed from service. The other two 310 HCbN samples, which experienced lower exposure temperatures, experienced little if any additional corrosion relative to the samples from Section A. The reason for this is not clear.

It should be noted that the metal loss rates determined to date for both Section A and Section C all were based on a ring specimen that was extracted from mid-length of each tube sample. In this analysis additional attention was focused on metal losses in the vicinity of welds. Representative samples were taken and it was determined that, for the 310 HCbN samples evaluated, the Inconel 625 weld filler metal is reasonably resistant to coal ash corrosion and that the tube material immediately adjacent to the weld (i.e. the weld heat affected zone) was somewhat less affected by corrosion than was the remainder of the tube. Indeed the tube wall appeared to be progressively thinner toward the mid-point of the tube sample.

Analysis of deposit on the surface revealed that it had the known aggressive combination of species, namely iron, oxygen, the alkali metals, and sulfur. Examination and analysis of the scale adjacent to the metal surface revealed the chalky-white appearance associated with alkali-iron-sulfates. Thus, the required corrosive constituent was available to test the performance limits of this alloy.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: 310 HCBN (HR3C)

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• In assessing the data for Section C, it is important to understand that some tube samples had to be removed from the section early due to excessive thinning. The schematic in Figure G-1 shows the relative positions of the 310 HCBN samples in all three sections. Also, shown are the positions of all of the excessively thinned tubes that were removed and replaced in order to extend the life of Section C.• One 310 HCBN sample was removed early. Sample G-H was removed in November 2001, (i.e. shortly after Section A was removed from service for evaluation). Samples N-O, W-X and AA-BB survived for the full Section C exposure period.• The sample that was removed early was set aside for later analysis, and has been included in the current evaluation along with the other tube samples that made up Section C.• Also shown in this figure is the calculated average surface metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• The table in Figure G-1 provides the ASTM specified composition for this grade of material.• Sumitomo Metal Industries supplied tube from one heat of material for use in this program, Heat D8A0809. The composition for this heat also is provided in Figure G-1.• During the Section A evaluation, detailed composition verification was undertaken for each tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS

	<p>would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.</p> <ul style="list-style-type: none"> • The results of the EDS analysis of tube sample N-O confirmed that the correct material was used at this location.
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Material: 310 HCbN (HR3C)

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance	<ul style="list-style-type: none"> • Figure G-3 shows the typical appearance of 310 HCbN sample on receipt from Sumitomo. • Figures G-4 through G-7 document the as-received appearance of the external surface of the Save 25 tube samples. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction). • The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the "o'clock" conventions described above, (with the 12 o'clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o'clock side of the tube faces downward, and the 6 o'clock orientation faces upward within the boiler. • Wastage was visible at the 12 o'clock for all four samples; however, it was obscured to some extent by deposit on those surfaces.. • A chalky gray/white deposit is clearly seen at the 3 o'clock position for Samples W-X and AA-BB. This of course is consistent with molten alkali-iron-sulfate accelerated attack.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none"> • Figures G-8 through G-11 show the appearance of the external surface of the 310 HCbN tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for all four samples show the appearance of general wastage due to fireside corrosion. • The 6 o'clock position shows some evidence of pitting for all four samples; otherwise, it was relatively unaffected, and exhibited little or no wastage at this surface.
Wall Thickness Loss Determined	<ul style="list-style-type: none"> • Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures G-12 through G-15. • The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure. • The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost.

	<ul style="list-style-type: none"> For all four tube samples, the minimum wall thickness in the cross section was not at one of the eight predetermined locations. In these cases, there was no “before” measurement for comparison. So, the average “before” wall thickness was used to calculate the wall thickness lost at these off locations.
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Material: 310 HCbN (HR3C)

Summary of Findings, (continued)

Issue	Discussion
Rate of Wall Thickness Loss Versus Average Surface Metal Temperature	<ul style="list-style-type: none"> The chart in Figure G-16 plots the maximum rate of wall thickness loss against the calculated average surface metal temperature for each of the four 310 HCbN samples in Section C. The Section A data also is plotted. Review of the data shows that the lower temperature samples in Section C experienced a lower than expected rate of metal loss. Otherwise, the rates are fairly consistent, and moderately high.
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none"> The chart in Figure G-17 plots metal loss as a function of time for each sample location for Sections A and C. with samples from Section C having experienced generally longer exposure times. Shortly after Section A was removed for analysis, the tube Sample G-H was also removed and replaced in Section C. It was noted that the rate of metal loss appears to be greater for the Sample G-H from Section C. This may have been due to the somewhat higher temperatures for the G-H position in Section C (1167 F vs 1157 F), but due to limited sampling it is difficult to draw this conclusion with certainty. It was noted that the tube sample at position AA-BB experienced only somewhat more metal loss, relative to the sample at the same position in Section A, after the full exposure period for Section C (i.e. 189 versus 166 mils total). The Sample W-X in Section C actually experienced less metal loss than the sample at the same position in Section A even though it saw approximately ten additional months at the service temperature.
Metallurgical Analysis – SEM	<ul style="list-style-type: none"> Sample N-O was selected for a detailed SEM/EDS assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it had lost the most wall thickness among the three 310 HCbN samples that survived the full exposure period for Section C. The focus of this investigation was in the region of the tube where the maximum amount of material was lost. Figures G-18a, b, c and d, show the secondary electron images of the scale/metal interface for Sample G-H. Six distinct regions are in evidence. These regions are, starting within the metal and working out: <ul style="list-style-type: none"> <u>Base metal</u> – oxalic acid etch delineates grain boundaries and carbides. <u>Diffusion zone – light etch</u> – this region is obvious as a light-

	<p>appearing band that is parallel to the metal surface, perhaps see most clearly in Figure G-18b.</p> <ul style="list-style-type: none"> ○ <u>Featureless grain surface</u> – This constitutes the leading edge of the grains as they interface with the scale. As EDS analysis later shows that this zone seems related to diffusion of alloying elements both into and out of the metal surface as scale formation progresses.
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Material: 310 HCBN (HR3C)

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none"> ○ <u>Tightly adhering scale</u> – this is seen continuous along the surface. EDS analysis will later show that this is a chromium-, nickel-, and iron-rich -oxide. ○ <u>Thick and very porous deposit/scale conglomerate</u> – many spherical particles are noted along with what appears to be islands of scale (metal oxides). • Figures G-19 shows the appearance of the tube microstructure at mid-wall. • Figure G-20 shows the appearance of the internal metal surface for Sample N-O. Little if any oxide scale is visible at this surface.
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none"> • Figure G-21 shows a longitudinal profile (at the 12 o'clock orientation) of the 310 HCBN samples adjacent to the welds in Section C. Three welds were cross sectioned. These were identified as “N”, “X” and “BB” in the schematic shown in Figure G-1. • An Inconel 625 weld metal was used throughout Section C. The cross sections show that the 310 HCBN heat affected zones are not preferentially attached, in fact, the wall thickness for the tube sample tapers from the weld toward the middle of the tube length.
EDS Analysis Results	<ul style="list-style-type: none"> • The table in Figure G-22 provides a summary of the EDAX analyses of the locations numbered in Figure G-18b. Also shown in this table is a summary of the spectrographic analysis reported earlier, see Figure G-2. • Review of this table suggests the following: <ul style="list-style-type: none"> • <u>Area 1: For the bulk deposit analysis</u> – Alkali metals are present. Sulfur and phosphorous are present in an increased amount compared to the base metal. An iron oxide is likely, as are aluminum, silicon and titanium oxides. Carbon content is relatively high, however, EDS is not reliable quantitatively. • <u>Area 2: Tightly adhering scale</u> – This appears to be an iron-, chromium-, nickel-rich oxide. Also significant is the presence of sulfur in this layer. • <u>Area 3:– Diffusion zone – dark etching</u> - This region of the tube metal is depleted in chromium relative to the bulk composition (roughly 9% versus 22% per EDS). • <u>Area 4: - Diffusion zone – light etching</u> – This region of is only somewhat depleted in chromium (roughly 20% versus 22% per EDS).

	<ul style="list-style-type: none">• <u>Area 5: Bulk metal analysis</u> – This analysis was used for composition verification.
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Figure G-1: Schematic Drawing Showing Position of 310 HCbN (HR3C) Tube Samples Within Test Section C

1. Drawing shown in same relative orientation as per the actual installation.
2. This group of tube samples was removed from service in November 2001 - highlighted in red.
3. This group of tube samples was removed from service in June 2002 - highlighted in yellow.

Figure G-2 Semi-Quantitative Composition Verification for 310 HCbN (HR 3C)

Description: Nominal 25Cr/20Ni steel with Nb, Ta, and N added to provide creep strength.
Source: Sumitomo Metal Industries (SMI)
Reference Composition: “Specified” chemistry – ASTM A213 (TP310 HCbN).

Element	Reference Composition	Composition (a) Heat D8A0809	Tube Sample G-H	Tube Sample N-O	Tube Sample W-X	Tube Sample AA-BB
Ni	17.00-23.00	19.97	N/A	21.1	N/A	N/A
Cr	24.00-26.00	25.61	N/A	22.1	N/A	N/A
Fe	Balance	Balance	N/A	55.6	N/A	N/A
Mo	-	-	N/A	-	N/A	N/A
Co	-	-	N/A	-	N/A	N/A
C	0.04-0.10	0.05	N/A	-	N/A	N/A
N	0.15-0.35	0.24	N/A	-	N/A	N/A
B	-	-	N/A	-	N/A	N/A
Mn	2.00 max	1.18	N/A	0.86	N/A	N/A
Si	0.75 max	0.36	N/A	0.28	N/A	N/A
Al	-	-	N/A	-	N/A	N/A
Ti	-	-	N/A	-	N/A	N/A
Al+Ti	-	-	N/A	-	N/A	N/A
Nb	-	0.47	N/A	-	N/A	N/A
Ta	-	(c)	N/A	-	N/A	N/A
Nb+Ta	0.20-0.60	0.47	N/A	-	N/A	N/A
V	-	-	N/A	-	N/A	N/A
W	-	-	N/A	-	N/A	N/A
Cu	-	-	N/A	-	N/A	N/A
Sn	-	-	N/A	-	N/A	N/A
P	0.030 max	0.015	N/A	-	N/A	N/A
S	0.030 max	(c)	N/A	-	N/A	N/A

- a- Ladle analysis.
- b- By difference.
- c- Not detected.

N/A = Sample not analyzed.

Figure G-3: Appearance of 310 HCBN (HR3C) Tube Sample Prior to Service

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure G-4 As-Received Appearance of Sample N-O (310 HCBN)

(Average surface metal temperature: 1190 °F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure G-5 As-Received Appearance of Sample G-H (310 HCbN)

(Average surface metal temperature: 1167°F)

Note: this tube was removed from service on 11/6/01.

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure G-6 As-Received Appearance of Sample W-X (310 HCbN)

(Average surface metal temperature: 1106 °F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure G-7 As-Received Appearance of Sample AA-BB (310 HCbN)

(Average surface metal temperature: 1092 °F)

12 O'Clock
(201 mils lost)

3 O'Clock
(205 mils lost)

6 O'Clock
(6 mils lost)

Figure G-8: OD Surface Appearance After Grit Blast

Material: 310 HCbN (HR3C)

Sample: N-O

12 O'Clock
(146 mils lost)

3 O'Clock
(173 mils lost)

6 O'Clock
(2 mils lost)

Figure G-9: OD Surface Appearance After Grit Blast

Material: 310 HCBN (HR3C)
Sample: G-H

12 O’Clock
(61 mils lost)

3 O’Clock
(45 mils lost)

6 O’Clock
(7 mils lost)

Figure G-10: OD Surface Appearance After Grit Blast

Material: 310 HCBN (HR3C)

Sample: W-X

12 O'Clock
(146 mils lost)

3 O'Clock
(148 mils lost)

6 O'Clock
(7 mils lost)

Figure G-11: OD Surface Appearance After Grit Blast

Material: 310 HCBN (HR3C)
Sample: AA-BB

Material: 310 HCBN (HR3C)

Sample Location: N-O

Maximum Rate: 133 mils/yr

Maximum Loss Orientation: Approx. 2 o'clock

Average Surface Metal Temperature: 1190 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.396	0.396	0.398	0.401	0.400	0.398	0.401	0.399	0.399	0.399
After	0.195	0.093	0.193	0.391	0.394	0.399	0.252	0.293		0.083
Delta	0.201	0.303	0.205	0.010	0.006	-0.001	0.149	0.106		0.316

Figure G-12: Silhouette and Wall Thickness Measurements for Sample N-O

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Material: 310 HCBN (HR3C)

Sample Location: G-H

Maximum Rate: 141 mils/yr

Maximum Loss Orientation: Approx. 2:30 o'clock

Average Surface Metal Temperature: 1167 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.404	0.401	0.399	0.402	0.400	0.399	0.400	0.402	0.401	0.401
After	0.258	0.221	0.226	0.401	0.398	0.399	0.232	0.311		0.182
Delta	0.146	0.180	0.173	0.001	0.002	0.000	0.168	0.091		0.219

Figure G-13: Silhouette and Wall Thickness Measurements for Sample G-H

Note: this tube was removed from service on 11/6/01.

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Material: 310 HCBN (HR3C)

Sample Location: W-X

Maximum Rate: 52 mils/yr

Maximum Loss Orientation: Approx. 9:30 o'clock

Average Surface Metal Temperature: 1106 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.398	0.398	0.398	0.401	0.399	0.397	0.400	0.397	0.398	0.398
After	0.337	0.322	0.353	0.398	0.392	0.396	0.301	0.346		0.273
Delta	0.061	0.076	0.045	0.003	0.007	0.001	0.099	0.051		0.125

Figure G-14: Silhouette and Wall Thickness Measurements for Sample W-X

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Material: 310 HCBN (HR3C)

Sample Location: AA-BB

Maximum Rate: 79 mils/yr

Maximum Loss Orientation: Approx. 9:30 o'clock

Average Surface Metal Temperature: 1092 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss*
Before	0.399	0.400	0.400	0.397	0.394	0.399	0.399	0.399	0.398	0.398
After	0.253	0.278	0.252	0.380	0.387	0.387	0.256	0.269		0.209
Delta	0.146	0.122	0.148	0.017	0.007	0.012	0.143	0.130		0.189

Figure G-15: Silhouette and Wall Thickness Measurements for Sample AA-BB

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Figure G-16: Metal Loss Rate as a Function of Average Surface Metal Temperature

Material: 310 HCBN (HR3C)

Note: In analyzing these data it is important to understand that the one of the three Section C samples was removed early due to excessive corrosion losses. Sample G-H (1167 F) was removed in November 2001, shortly after Section A was removed for evaluation. Sample N-O (1190 F), Sample W-X (1106 F), and Sample AA-BB (1092 F) were removed with the remaining Section C samples in May 2003.

Figure G-17: Metal Loss as a Function of Time

Material: 310 HCbN (HR3C)

Note: From the plot above it can be seen that, for Section C, the Sample G-H was removed shortly after Section A was removed for evaluation. The other three sample locations experienced the full exposure life for both Sections A and C.

(a) External Scale/Metal Interface (SEI - Low Magnification)

(b) External Scale/Metal Interface (SEI - Intermediate Magnification)

Figure G-18: Microstructure: 310 HCbN

Note: Numbers on photo indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

Figure G-19: Mid-Wall Microstructure: 310 HCBN

Note: Photomicrograph at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Internal Surface Appearance (SEI - Intermediate Magnification)

Figure G-20: Microstructure: 310 HCbN

(a) 310 HCBN Adjacent to Weld "N"

(b) 310 HCBN Adjacent to Weld "X"

Figure G-21: Longitudinal Cross-Sections: 310 HCBN Adjacent to Welds

(c) 310 HCBN Adjacent to Weld "BB"

Figure G-21, Continued: Longitudinal Cross-Sections: 310 HCBN Adjacent to Welds

Figure G-22: EDS Analysis of Deposit/Scale/Metal Interface for 310 HCBN (HR3C) (Sample G-H)

Area	Description	Ni	Cr	Fe	Cu	Mn	Nb	Ti	Al	Si	C	O	Ca	K	Na	As	P	S
1	Bulk deposit analysis	1.03	0.57	22.5	--	0.14	--	0.36	6.77	12.5	25.3	21.6	0.16	1.08	--	4.96	2.00	1.07
2	Tightly adhering scale..	18.9	20.3	42.1	--	--	--	--	0.17	0.51	--	13.7	0.54	--	--	--	--	3.74
3	Diffusion zone – dark etching adjacent to interface.	27.3	8.68	62.7	--	0.71	--	--	--	0.46	--	--	0.22	--	--	--	--	--
4	Diffusion zone – light etching.	21.5	19.9	57.3	--	0.96	--	--	--	0.31	--	--	--	--	--	--	--	--
5	Bulk tube metal analysis	21.1	22.1	55.6	--	0.86	--	--	--	0.28	--	--	--	--	--	--	--	--
	Reference bulk analysis.	19.9	26.0	50.5	--	1.20	0.47	0.008	0.017	0.35	0.07	--	--	--	--	--	0.014	0.001

Appendix H
Analysis of Performance
Test Section C
HR 120

Overview of Results: HR 120

Of the three HR 120 samples in Section C, Sample O-P experienced the highest rate of metal loss (124 mils per year). Given a total exposure period of 2.38 years, this metal loss rate resulted in a total wall loss of 295 mils at one location, i.e. 79% of the initial wall thickness was lost. This problem was exacerbated in that when the section was being manufactured, the wall thickness was reduced by machining to provide for a weld transition to an adjacent tube that had a thinner wall. The end result was that only a very thin ligament remained. Accordingly, this tube section was removed and replaced for Section B which is continuing in service to gain data beyond the 2.38 years associated with Section C.

It was also noted that, for both Section A and Section C, the sample that saw the lowest exposure temperature, Sample DD-EE had a higher metal loss rate than Sample V-W which saw an intermediate exposure temperature. While limited data is available, it might be postulated that somewhat different mechanisms are active at the low and high temperature locations.

It should be noted that the metal loss rates determined to date for both Section A and Section C all were based on a ring specimen that was extracted from mid-length of each tube sample. In this analysis additional attention was focused on metal losses in the vicinity of welds. Representative samples were taken and it was determined that, for the HR 120 samples evaluated, the Inconel 625 weld filler metal is reasonably resistant to coal ash corrosion. Two cases were noted wherein the wall thickness of the HR 120 was machined thinner to facilitate welding during construction of the test section. These areas must be taken into consideration during future in situ measurements of similarly designed samples.

Analysis of deposit on the surface revealed that it had the known aggressive combination of species, namely iron, oxygen, potassium, and sulfur. Examination and analysis of the scale adjacent to the metal surface revealed the chalky-white appearance associated with alkali-iron-sulfates. Thus the required corrosive constituent was available to test the performance limits of this alloy.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: HR 120

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• The schematic in Figure H-1 shows the relative positions of the three HR 120 samples in Test Section C. Note that none of the HR 120 samples were included in the tube lengths that were removed early and replaced, i.e. in November 2001 or in June 2002.• Also, shown is the calculated average surface metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• The HR 120 tubing for this program came from one heat of material (Heat 854487538) supplied from Haynes International, Inc.• The table in Figure H-2 provides a nominal HR 120 composition from Haynes literature. It also provides the reported heat analysis.<ul style="list-style-type: none">○ It is interesting to note that while the heat supplied met the constraints of the nominal composition, it was somewhat lean in alloying element additions: molybdenum (actual 0.23% versus 2.5% max nominal), cobalt (0.088% versus 3% max), and tungsten (not detectable versus 2.5% max).• During the Section A evaluation, detailed composition verification was undertaken for each tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample O-P confirmed that the correct material was used at this location.
As-Received Appearance	<ul style="list-style-type: none">• Figure H-3 shows the typical appearance of an HR 120 tube sample prior to service.• Figures H-4 through H-6 document the as-received appearance of the external surface of the HR 120 tube samples. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view opposite to the gas flow direction).

Material: HR 120

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance, Continued.	<ul style="list-style-type: none">• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the “o’clock” conventions described above, (with the 12 o’clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o’clock side of the tube faces downward, and the 6 o’clock orientation faces upward within the boiler.• Wastage on these tubes is, for the most part, obscured by deposit on the 12 o’clock and 3 o’clock positions.• The gray/white scale commonly associated with molten alkali-iron sulfate attack is seen most readily at the 3 o’clock position in Sample DD-EE.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures H-7 through H-9 show the appearance of the external surface of the HR 120 tube samples after grit-blasting to remove deposit and scale. The 12 o’clock and 3 o’clock positions for all three samples show the appearance of general wastage due to fireside corrosion.• Pitting was noted on at the 6 o’clock position for Sample O-P.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures H-10 through H-12.• The same relative “o’clock” positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost. Note that the delta is negative for the 6 o’clock position for Sample O-P. This is believed due to wall thickness variability and difficulty in locating the exact location of the “before” measurement.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure H-13 plots the maximum wall thickness lost against the calculated average metal temperature for each of the three HR 120 samples in Section C. Section A data also are plotted.• Review of these data suggests that the highest temperature sample, Sample O-P, experienced the greatest rate of metal loss for both sections.• It also was noted that the rate of metal loss appears to drop off for Sample V-W which experienced an intermediate exposure temperature. The reason for this has not been resolved but it suggests that different corrosion mechanisms are active at the higher and lower exposure temperatures.

Material: HR 120

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure H-14 plots metal loss as a function of time for each sample location for Sections A and C. with samples from Section C having experienced generally longer exposure times.• It was noted that metal loss rate increased as a function of time for Sample O-P at the highest exposure temperature. Likewise it was noted that the rate decreased with time for Samples V-W and DD-EE. This suggests that the straight line fit shown in Figure H-14 may pertain.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample O-P was selected for a detailed SEM/EDAX assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it was experiencing metal wastage at about the maximum rate. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.• Figures H-15a and b show the secondary electron images of the scale/metal interface for Sample O-P. Six distinct regions are in evidence. These regions are, starting within the metal and working out:<ul style="list-style-type: none">○ <u>Base metal</u> – oxalic acid etch delineates grain boundaries, carbides and inclusions.○ <u>Diffusion zone – light etching</u> – this region is obvious as a light-appearing band that is parallel to the metal surface, perhaps see most clearly in Figure H-15b. This band is approximately one-half grain wide, and affects only those grains contiguous with the surface. Later EDS analysis will show that this region is very similar in composition to the bulk tube, with the possible exception that the sulfur content may be somewhat increased in this area.○ <u>Diffusion zone – dark etching</u> – This constitutes the leading edge of the grains as they interface with the scale. EDS analysis later shows that this zone is depleted in chromium (11.2% versus roughly 24%).○ <u>Tightly adherent scale</u> – this is seen continuous along the surface. EDS analysis will later show that this is predominantly a chromium-rich oxide with a significant amount of sulfur present.○ <u>Bulk Deposit</u> - The deposit was comprised of oxides of iron, silicon, and aluminum. Arsenic was noted, as were sulfur and possibly carbon.• Figure H-15b shows the six locations selected for EDAX analysis. The results of these follow• Figure H-16 shows the appearance of the mid-wall microstructure for HR 120.• Figure H-17 shows the internal metal surface for Sample O-P. It appears to be coated with a 1 mil thick oxide.

Summary of Findings, (continued)

Material: HR 120

Issue	Discussion
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none"> Figure H-18 shows a longitudinal profile (at the 12 o'clock orientation) of the HR 120 samples adjacent to the welds in Section C. Three welds were cross sectioned. These were identified as “P”, “V” and “DD” in the schematic shown in Figure H-1. An Inconel 625 weld metal was used throughout Section C. The cross sections show that the HR 120 heat affected zones are not preferentially attached, in fact, the wall thickness for the tube sample tapers from the weld toward the middle of the tube length. An important point to notice is that welds “P” and “V” both joint HR 120 to Inconel 625 which had a thinner wall thickness (nominal 260 mils vs nominal 375 mils). In order to complete this joint successfully the wall thickness of the HR 120 tube had to be reduced considerably. This accounts for the weld cross section appearance in Figures H-18a and b. It is important to note from this that only a thin ligament remained for Sample O-P at the time that it was removed from service. This fact should be kept in mind during in situ measurements to determine the remaining wall thickness of similarly constructed test sections.
EDS Analysis Results	<ul style="list-style-type: none"> The table in Figure H-19 provides a summary of the EDAX analyses of the numbered in Figure H-15b. Also shown in this table is a summary of the spectrographic analysis reported earlier, Figure H-2. Review of this table suggests the following: <ul style="list-style-type: none"> <u>Area 1: Bulk deposit/scale analysis</u> – Potassium is present, as are sulfur and phosphorous. An iron oxide is likely, as are aluminum, silicon and titanium oxides. The analysis suggests that the carbon content is relatively high, however, these results need to be considered carefully given the inherent inaccuracies in EDS carbon analysis. <u>Area 2: Loosely adhering deposit/scale</u> – This appears to be chromium-, iron-, and nickel-rich oxide. Sulfur is present. <u>Area 3: Tightly adhering scale</u> - This is the chromium-rich scale that is immediately adjacent to the metal surface. Again high sulfur is indicated. <u>Area 4: Diffusion zone – dark etching</u> – This region that abuts the tightly adhering scale is depleted in chromium. <u>Area 5: Diffusion zone – light etching</u> – The presence of a significant amount of sulfur is the only thing that distinguishes this region from the bulk tube metal.. <u>Bulk EDS analysis</u> – This analysis compares well with the reference spectrographic analysis.

Figure H-2 Semi-Quantitative Composition Verification for HR 120

Description: Nominal 33Fe/25Cr/37Ni alloy with Co, W, and Nb added to provide creep strength.
Source: Haynes International, Inc.
Reference Composition: “Nominal” chemistry – per Haynes literature.

Element	Reference Composition	Composition Heat 854487538	Tube Sample O-P	Tube Sample V-W	Tube Sample DD-EE
Ni	37	37.61	38.2	N/A	N/A
Cr	25	25.28	24.1	N/A	N/A
Fe	Balance	Balance	36.5	N/A	N/A
Mo	2.5 max	0.33	-	N/A	N/A
Co	3 max	0.09	-	N/A	N/A
C	0.05	0.06	-	N/A	N/A
N	0.2	0.20	-	N/A	N/A
B	0.004	<0.002	-	N/A	N/A
Mn	0.7	0.68	0.46	N/A	N/A
Si	0.6	0.52	0.65	N/A	N/A
Al	0.1	0.06	-	N/A	N/A
Ti	-	0.02	-	N/A	N/A
Al+Ti	-	-	-	N/A	N/A
Nb	0.7	0.62	-	N/A	N/A
Ta	-	-	-	N/A	N/A
Nb+Ta	-	-	-	N/A	N/A
V	-	-	-	N/A	N/A
W	2.5 max	<0.10	-	N/A	N/A
Cu	-	0.10	-	N/A	N/A
Sn	-	-	-	N/A	N/A
P	-	0.016	-	N/A	N/A
S	-	<0.002	-	N/A	N/A
O2	-	-	-	N/A	N/A

N/A = Sample not analyzed.

Figure H-3: Appearance of HR 120 Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure H-4 As-Received Appearance of Sample O-P (HR 120)
(Average surface metal temperature: 1194 °F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure H-5 As-Received Appearance of Sample V-W (HR 120)
(Average surface metal temperature: 1110 °F)

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure H-6 As-Received Appearance of Sample DD-EE (HR 120)
(Average surface metal temperature: 1088 °F)

12 O'Clock
(204 mils lost)

3 O'Clock
(208 mils lost)

6 O'Clock
(0 mils lost)

Figure H-7: OD Surface Appearance After Grit Blast

Material: HR 120
Sample: O-P

12 O’Clock
(76 mils lost)

3 O’Clock
(43 mils lost)

6 O’Clock
(2 mils lost)

Figure H-8: OD Surface Appearance After Grit Blast

Material: HR 120
Sample: V-W

12 O'Clock
(131 mils lost)

3 O'Clock
(177 mils lost)

6 O'Clock
(11 mils lost)

Figure H-9: OD Surface Appearance After Grit Blast

Material: HR 120
Sample: DD-EE

Material:

HR 120

Sample Location:

O-P

Maximum Rate:

124 mils/yr

Maximum Loss Orientation:

Approx. 1:30 o'clock

Average Surface Metal Temperature:

1194 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.374	0.376	0.378	0.377	0.374	0.375	0.378	0.376	0.376	0.376
After	0.170	0.081	0.170	0.363	0.376	0.362	0.249	0.229		0.081
Delta	0.204	0.295	0.208	0.014	-0.002	0.013	0.129	0.147		0.295

Figure H-10: Silhouette and Wall Thickness Measurements for Sample O-P

Material:

HR 120

Sample Location:

V-W

Maximum Rate:

46 mils/yr

Maximum Loss Orientation:

Approx. 9:30 o'clock

Average Surface Metal Temperature:

1110 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.375	0.376	0.371	0.372	0.379	0.379	0.377	0.375	0.376	0.376
After	0.299	0.297	0.328	0.367	0.377	0.372	0.299	0.314		0.267
Delta	0.076	0.079	0.043	0.005	0.002	0.007	0.078	0.061		0.109

Figure H-11: Silhouette and Wall Thickness Measurements for Sample V-W

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Material:

HR 120

Sample Location:

DD-EE

Maximum Rate:

79 mils/yr

Maximum Loss Orientation:

Approx. 10:00 o'clock

Average Surface Metal Temperature:

1088 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.372	0.375	0.374	0.379	0.375	0.374	0.371	0.374	0.374	0.374
After	0.241	0.271	0.197	0.366	0.364	0.364	0.249	0.225		0.186
Delta	0.131	0.104	0.177	0.013	0.011	0.010	0.122	0.149		0.188

Figure H-12: Silhouette and Wall Thickness Measurements for Sample DD-EE

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Figure H-13: Metal Loss Rate as a Function of Average Surface Metal Temperature

Material: HR 120

Figure H-14: Metal Loss as a Function of Time

Material: HR 120

(a) External Scale/Metal Interface (SEI- Low Magnification)

(b) External Scale/Metal Interface (SEI - Intermediate Magnification)

Figure H-15: Microstructure: HR 120

Note: Numbers on photo indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

Internal Surface Appearance (SEI- Low Magnification)

Figure H-16: Mid-Wall Microstructure: HR 120

Note: Photomicrograph at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

Internal Surface Appearance

Figure H-17: Microstructure: HR 120

(a) HR 120 Adjacent to Weld “P”

(b) HR 120 Adjacent to Weld “V”

Figure H-18: Longitudinal Cross-Sections: HR 120 Adjacent to Welds

(c) HR 120 Adjacent to Weld "DD"

**Figure H-18, Continued: Longitudinal Cross-Sections: HR 120
Adjacent to Welds**

Figure H-19: EDS Analysis of Deposit/Scale/Metal Interface for HR 120 (Sample O-P)

Area	Description	Ni	Cr	Fe	Mo	Mn	Nb	Ti	Al	Si	C	O	Ca	K	Na	As	P	S
1	Bulk deposit analysis	6.74	0.25	26.0	--	--	--	0.39	8.17	11.9	20.9	19.1	--	2.30	--	2.96	0.85	0.48
2	Loosely adhering scale/deposit	12.7	47.7	19.1	--	--	--	--	--	3.74	--	15.8	--	--	--	--	--	0.87
3	Tightly adhering scale.	8.58	57.4	9.28	--	--	--	--	--	1.42	--	17.6	--	--	--	--	--	5.76
4	Diffusion zone – dark etching near scale/metal interface	47.1	11.2	40.6	--	0.64	--	--	--	0.54	--	--	--	--	--	--	--	--
5	Diffusion zone – light etching	37.3	25.6	35.5	--	0.48	--	--	0.13	0.68	--	--	--	--	--	--	--	0.31
6	Bulk EDS Analysis	38.2	24.1	36.5	--	0.46	--	--	0.65	--	--	--	--	--	--	--	--	--
	Reference bulk analysis.	37.9	25.3	34.3	0.23	0.69	0.56	0.01	0.064	0.51	0.06	--	--	--	--	--	--	0.001

Appendix I
Analysis of Performance
Test Section C
Thermie

Overview of Results: Thermie

Thermie experienced an intermediate rate of metal loss of 76 and 34 mils per year* at positions H-I and HH-II respectively. It was noted that Sample H-I was removed early, but given the metal loss rate above, it would have been able to survive for the 2.38 years required for the full Section C exposure period.

Metallographic examination of a Sample HH-II in Section C revealed evidence of significant grain boundary penetration at the external surface of the tube. It should also be noted that, for Section A, the metallographic examination focused on Sample H-I, instead of Sample HH-II, and that Sample HH-II has a much larger grain size than Sample H-I. It is not clear whether this difference in microstructure gave rise to the observed difference in mechanism.

It should be noted that the metal loss rates determined to date for both Section A and Section C all were based on ring specimens that were extracted from mid-length of each tube sample. In this analysis additional attention was focused on metal losses in the vicinity of welds. Representative samples were taken and it was determined that, for the Thermie samples evaluated, the Inconel 625 weld filler metal is reasonably resistant to coal ash corrosion and that the tube material immediately adjacent to the weld (i.e. the weld heat affected zone) was somewhat less affected by corrosion than was the remainder of the tube. Indeed the tube wall appeared to be progressively thinner toward the mid-point of the tube sample.

Visual examination of the scale adjacent to the metal surface revealed the chalky-white appearance associated with alkali-iron-sulfates. Thus, the required corrosive elements likely were available to test the performance limits of this alloy.

* **Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: Thermie

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• In assessing the data for Section C, it is important to understand that some tube samples had to be removed from the section early due to excessive thinning. The schematic in Figure I-1 shows the relative positions of the Thermie samples in all three sections. Also, shown are the positions of all of the excessively thinned tubes that were removed and replaced in order to extend the life of Section C.• One Thermie sample was removed early. Sample H-I was removed in November 2001, (i.e. at the same time that Section A was removed from service for evaluation). Sample HH-II survived for the full Section C exposure period.• The Sample HH-II, that was removed early, was set aside for later analysis, and has been included in the current evaluation along with the other tube samples that made up Section C.• Also shown in this figure is the calculated average surface metal temperature at both locations.
Composition Verification.	<ul style="list-style-type: none">• Oak Ridge National Laboratory (ORNL) provided the Thermie samples that were used in this program. Samples H-I and HH-II were reported to be from different heats.• The table in Figure I-1 shows the ORNL “target” chemistry for these alloys along with the ORNL-provided analysis for both heats.• During the Section A evaluation, detailed composition verification was undertaken for each tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its’ proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of Sample HH-II confirmed that the correct material was used at this location.

Material: Thermie

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance	<ul style="list-style-type: none">• Figure I-3 shows the typical appearance of a Thermie tube sample prior to service• Figures I-4 and I-5 document the appearance of the external surface of the Thermie tube samples after service in Section C. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the "o'clock" conventions described above, (with the 12 o'clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o'clock side of the tube faces downward, and the 6 o'clock orientation faces upward within the boiler.• Evidence of the gray/white scale associated with molten alkali-iron sulfate attack clearly in evidence for Sample HH-II, Figure I-5.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures I-6 and I-7 show the appearance of the external surface of the Thermie tube samples after grit-blasting to remove deposit and scale.• The 12 o'clock and 3 o'clock positions for Samples H-I clearly show the appearance of general wastage due to fireside corrosion. Some level of pitting also is suggested at the 6 o'clock position for this sample.• Wastage and pitting are much less evident for Sample HH-II.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures I-8 and I-9.• The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost.• Note that for some positions in Sample H-I, the delta is negative. This is believed due to wall thickness variability and difficulty in locating the exact location of the "before" measurement.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure I-10 plots the maximum wall thickness lost against the calculated average metal temperature for each of the two Thermie samples. Data for the Thermie samples in Section A also are included in this plot.• From these limited data it appears as if the rate of metal loss increases with increasing temperature.

Material: Thermie

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure I-11 plots metal loss as a function of time for each sample location for Sections A and C. with samples from Section C having experienced generally longer exposure times.• About the time that Section A was removed for analysis, the tube Sample H-I was also removed and replaced in Section C. Given the fact that these samples had an initial wall thickness of 400 mils, the metal loss rate for Sample H-I would have predicted that this sample should have been able to survive the 2.38 years the comprise the full exposure period for Section C. Nonetheless, this sample was located between a series of samples that were experiencing a much higher corrosion rate, and the decision was made to extract and replace Sample H-I along with these other samples.• Sample HH-II demonstrated approximately the same rate of metal loss for Section C as it did in Section A (34 mils per year vs 31 mils per year). Based on this, the linear data fit may well be appropriate. Additional data would be required to confirm this.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample HH-II was selected for a detailed SEM/EDS assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected based on the fact that it had seen the full exposure period for Section C. The focus of this investigation was in the region of the tube where the maximum amount of material was lost.• Figures I-12a and b show backscattered electron images of the scale/metal interface for Sample HH-II. The multiple zones evident for this material during the Section A analysis were not seen in this sample from Section C. A very thin scale was noted in isolated patches on the surface of the tube. Scale-filled cracks were noted along the surface of the tube. No diffusion zone was in evidence.• Figure I- 13 provides a view of the microstructure at mid-wall.• Figure I-14 shows a cross section at the internal surface of Sample HH-II. Little or no scale is noted on this surface.
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none">• Figure I-15 shows a longitudinal profile (at the 12 o’clock orientation) of Sample HH-II adjacent to the weld “HH” in Section C.• An Inconel 625 weld metal was used throughout Section C. The cross sections show that the Thermie weld heat affected zones are not preferentially attacked, in fact, the wall thickness for the tube sample tapers from the weld toward the middle of the tube length.• Of note in this cross section is the fact that, when Section C was being built, the wall thickness of the Thermie sample had to be reduced so that it could be attached to the thinner-walled IN 52 Weld Overlay specimen that was adjacent to it. It is important to remember this as we examine the Thermie samples that remain in service in Section B. In situ diameter measurements to estimate remaining wall thickness need to take into account this locally thinner wall adjacent to the weld.

Summary of Findings, (continued)

Material: Thermic

Issue	Discussion
EDS Analysis Results	<ul style="list-style-type: none">• The table in Figure I-16 provides a summary of the EDS analyses of the locations numbered in Figures I-12b. Also shown in this table is a summary of the spectrographic analysis reported earlier, see Figure I-2.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Area 1: Scale/metal interface</u> – Analysis of this region suggests the formation of a chromium-rich oxide; however, given the small volume of scale at this location, it seems likely that, to a great extent, this analysis reflects the composition of the tube metal adjacent to the interface.• <u>Areas 2: Corrosion product in crack near the surface</u> – This analysis suggests that the crack was lined with a chromium-rich oxide. A significant amount of sulfur also was found at this location.• <u>Area 3: Corrosion product in crack near the surface</u> - This analysis suggests the presence of a nickel-rich corrosion product.• <u>Area 4: Bulk metal analysis</u> – Given its limitations, this EDS analysis compares favorably with that of the reference spectrographic analysis below it.

Figure I-2 Semi-Quantitative Composition Verification for Thermic

Description: Nominal 25Cr/20Co nickel alloy with additions of Nb and Ti to provide creep strength.
Source: Oak Ridge National Laboratory (ORNL)
Reference Composition: “Target” Chemistry per ORNL (Reference 1).

Element	Reference Composition	Composition Heat 17422	Composition Heat 17454	Tube Sample H-I	Tube Sample HH-II
Ni	48.0	49.06	48.92	N/A	51.3
Cr	24.0	23.08	23.63	N/A	24.8
Fe	2.0	2.06	2.11	N/A	1.99
Mo	0.5	0.43	0.42	N/A	-
Co	19.8	19.39	19.42	N/A	18.4
C	0.07	0.088	0.094	N/A	-
N	-	0.013	0.022	N/A	-
B	0.002 max	(a)	(a)	N/A	-
Mn	0.3	0.32	0.32	N/A	-
Si	0.5	0.51	0.49	N/A	0.53
Al	0.8	0.74	0.60	N/A	0.66
Ti	2.0	2.10	2.01	N/A	2.22
Al+Ti	-	-	-	N/A	-
Nb	2.0	2.20	1.95	N/A	-
Cu	-	<0.01	<0.01	N/A	-
Sn	-	-	-	N/A	-
P	-	<0.002	<0.002	N/A	-
S	-	0.003	0.009	N/A	-
O2	-	0.003	0.004	N/A	-
Zr	0.015 max	(a)	(a)	N/A	-
Mg	-	-	-	N/A	-

- a- Not analyzed.
b- By difference.
c- Not found.

Reference 1:

“Fabrication of Test Tubes for Coal Ash Corrosion Testing”, Sikka, V.K., Swindeman, R.W., Wright, I.G., Judkins, R.R., Johnson, R., Proc, 13th Annual Conf. on Fossil Energy Mat’ls, May 1999.

Note: Sample H-I was from Heat 17454 Sample HH-II was from Heat 17422

N/A = Sample not analyzed.

Figure I-3: Appearance of Thermie Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
 (Note: 3 o'clock is up in this image)

3 O'Clock
 (Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure I-4 As-Received Appearance of Sample H-I (Thermie)

(Average surface metal temperature: 1171 °F)

Note: this tube was removed from service on 11/6/01.

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure I-5 As-Received Appearance of Sample HH-II (Thermie)
(Average surface metal temperature: 1067°F)

12 O’Clock
(86 mils lost)

3 O’Clock
(0 mils lost)

6 O’Clock
(6 mils lost)

Figure I-6: OD Surface Appearance After Grit Blast

Material: Thermic
Sample: H-I

12 O’Clock
(39 mils lost)

3 O’Clock
(55 mils lost)

6 O’Clock
(6 mils lost)

Figure I-7: OD Surface Appearance After Grit Blast

Material: Thermie
Sample: HH-II

Material:

Thermie

Sample Location:

H-I

Maximum Rate:

77 mils/yr

Maximum Loss Orientation:

Approx. 1:30 o'clock

Average Surface Metal Temperature:

1171 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.399	0.399	0.400	0.400	0.400	0.400	0.399	0.398	0.399	0.399
After	0.313	0.280	0.401	0.401	0.394	0.397	0.330	0.343		0.280
Delta	0.086	0.119	-0.001	-0.001	0.006	0.003	0.069	0.055		0.119

Figure I-8: Silhouette and Wall Thickness Measurements for Sample H-I

Note: this tube was removed from service on 11/6/01.

Material:

Thermie

Sample Location:

HH-II

Maximum Rate:

34 mils/yr

Maximum Loss Orientation:

Approx. 2:30 o'clock

Average Surface Metal Temperature:

1067 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.399	0.399	0.398	0.399	0.399	0.399	0.399	0.399	0.399	0.399
After	0.360	0.344	0.343	0.395	0.394	0.399	0.382	0.340		0.318
Delta	0.039	0.055	0.055	0.005	0.006	0.000	0.017	0.059		0.081

Figure I-9: Silhouette and Wall Thickness Measurements for Sample HH-II

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Figure I-10: Metal Loss Rate as a Function of Average Surface Metal Temperature

Material: Thermie

Note: In analyzing these data it is important to understand that the one of the two Section C samples was removed early due to excessive corrosion losses. Sample H-I (1171 F) was removed in November 2001. Sample HH-II was removed with the remaining Section C samples in May 2003.

Figure I-10: Metal Loss as a Function of Time

Material: Thermie

Note: From the plot above it can be seen that Section C Sample H-I was removed early . Sample HH-II experienced the full exposure life for both Sections A and C.

(a) External Scale/Metal Interface (BEI - Low Magnification)

(b) External Scale/Metal Interface (BEI - Intermediate Magnification)

Figure I-12: Microstructure: Thermie

Note: Numbers on photo indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

(SEI - Intermediate Magnification)

Figure I-13: Microstructure at OD Surface: Thermie

Note: Electrolytic 10% oxalic acid etch, 9V OCP

Internal Surface Appearance (SEI - Intermediate Magnification)

Figure I-14: Microstructure: Thermie

Thermie Adjacent to Weld "HH"

Figure I-15: Longitudinal Cross-Sections: Thermie Adjacent to Weld

Figure I-16: EDS Analysis of Deposit/Scale/Metal Interface for Thermie (Sample HH-II)

Area	Description	Ni	Cr	Fe	Co	Mo	Nb	Ti	Al	Si	C	O	Ca	K	Na	As	P	S
	Bulk deposit analysis – None found on sample.																	
1	Scale / metal interface near surface of tube	50.0	24.1	1.96	17.7	--	--	1.63	1.93	0.40	--	2.81	--	--	--	--	--	--
2	Corrosion product in crack near surface	6.96	59.0	1.13	4.20	--	--	3.29	1.85	1.47	--	15.4	--	--	--	--	--	6.61
3	Corrosion product in crack near surface	47.9	21.7	1.88	20.2	--	--	1.84	0.56	0.46	--	4.08	--	--	--	--	--	1.37
4	Bulk EDAX Analysis	51.3	24.8	1.99	18.4	--	--	2.22	0.66	0.53	--	--	--	--	--	--	--	--
	Reference bulk analysis.	52.9	20.5	1.72	18.9	0.58	1.91	1.78	0.66	0.47	0.08	--	--	--	--	--	0.006	0.004

Appendix J

Analysis of Performance

Test Section C

IN52 Weld Overlay

Overview of Results: IN52 Weld Overlay

The IN52 Weld Overlay experienced an intermediate rate of metal loss (48 mils per year to 63 mils per year*) in the service environment of Test Section C. The 80 mil thick IN 52 weld overlay was found to have been completely breached during their 2.38 years of exposure. Now that the overlay has been breached, the performance of this material will be based on the scaling resistance of the underlying 800H base metal. As this point, slightly more than half of the original wall thickness remains for Sample GG-HH which experienced a lower corrosion rate than Sample R-S which experienced a higher average surface metal temperature (1208 F vs 1073 F). This increased rate of metal loss at lower temperatures is consistent with the results found for the other high-nickel, high-chromium alloys provided by Special Metals Corporation.

Comparison of the IN 52 data with that for the more highly alloyed IN 72 clad overlay suggests that IN 72, having a maximum rate of wall loss of 14 mils per year, is significantly more resistant to corrosion in the environment of the Niles boiler. However, this result is somewhat mitigated by the fact that IN 72 was found to have suffered an internal cracking problem within the cladding that may make it a somewhat less desirable candidate cladding material. While the IN 52 cladding showed evidence of lack of fusion –type defects, no evidence could be found of the grain boundary cracking found in the IN 72 weld overlay material. This IN 72 cracking may take on additional importance as this program draws to an end in that examination of archive material along with material from Sections A and C suggest that the extent of internal cracking is increasing with increased exposure time.

It should be noted that the metal loss rates determined to date for both Section A and Section C all were based on a ring specimen that was extracted from mid-length of each tube sample. In the current analysis, additional attention was focused on metal losses in the vicinity of welds. Indeed examination revealed that, for the IN 52 samples, the IN 52 cladding material wasted away more rapidly than the Inconel 625 weld metal that was used to join the tube samples together to construct the section.

No significant amount of deposit was found on these samples. Analysis of the scale showed a high level of sulfur confirming the presence of a potentially aggressive environment. The loss of wall thickness in these samples further bears this out.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: IN52 Weld Overlay

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• The schematic in Figure J-1 shows the relative positions of IN52 Weld Overlay samples in Test Section A. Note that none of the IN52 overlay samples was within the tube lengths that were removed early, i.e. in November 2001 or in June 2002.• Also, shown is the calculated average metal temperature at both locations.
Composition Verification.	<ul style="list-style-type: none">• The table in Figure J-2 provides the reference composition for the filler metal as per Special Metals Company (SMC) literature.• The table also shows the SMC heat analysis for the heat of filler wire used to deposit the cladding on these samples, Heat NX 9090JK.• During the Section A evaluation, detailed composition verification was undertaken for every tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample GG-HH confirmed that the correct material was used at this location.
As-Received Appearance	<ul style="list-style-type: none">• Figure J-3 shows the appearance of the IN52 Weld Overlay tube as delivered from SMC. Note the distinctive appearance of the weld cladding. The total wall thickness for this tube is approximately 290 mils. The clad layer is about 80 mils thick. An inner layer of 800H provides support.• Figures J-4 and J-5 document the appearance of the external surface of the IN52 Weld Overlay tube samples after service in Test Section C. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).

Material: IN52 Weld Overlay

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance, Continued	<ul style="list-style-type: none">• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the “o’clock” conventions described above, (with the 12 o’clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o’clock side of the tube faces downward, and the 6 o’clock orientation faces upward within the boiler.• No wastage is visible on either sample, but this likely is obscured by the deposit/scale at the 12 o’clock and 3 o’clock positions on both samples.• Evidence of the gray/white scale associated with molten alkali-iron sulfate attack was found on both samples.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures J-6 through J-7 show the appearance of the external surface of the IN52 Weld Overlay tube samples after grit-blasting to remove deposit and scale. The 12 o’clock and 3 o’clock positions for both samples show the appearance of general wastage due to fireside corrosion. Some pitting is also suggested at these locations.• The 6 o’clock position, for tube Sample GG-HH, shows evidence of pitting attack. Very little attack is found at the 6 o’clock position for Sample R-S.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures J-8 and J-9.• The same relative “o’clock” positions were maintained as discussed earlier. Measurements were taken prior to service at eight evenly spaced locations about the tube circumference. To prepare for this, the external surface of the cladding was ground flush to minimize thickness variability due to surface contour. After-service wall thickness measurements were taken at these same locations then compared with the initial thickness.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine the amount of wall thickness lost. Note that in some cases, the delta is negative (e.g at the 6 o’clock position for Sample GG-HH). This is believed due to wall thickness variability and difficulty in locating the exact location of the “before” measurement.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure J-10 plots the maximum wall thickness lost against the calculated average metal temperature for each of the two IN52 Weld Overlay samples. The data for Section A also are plotted.• The data in the chart suggest that the metal loss rate decreases with increased temperature for the IN52 Weld Overlay samples.• A significant metal loss rate (of 63 mils per year for Sample GG-HH, and 48 mils per year for Sample R-S in Section C). This rate was adequate to breach the cladding thickness (80 mils) for both samples, exposing the underlying Incoloy 800H.

Material: IN52 Weld Overlay

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure J-11 plots metal loss as a function of time for each sample location for both Sections A and C, with samples from Section C having experienced generally longer exposure times.• Both tube samples experienced increased metal loss with time; however, the data above suggest the rate decreased as a function of time, so, a straight-line fit likely is not appropriate.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• The sample with the highest rate of metal loss (GG-HH) was selected for a detailed SEM/EDS assessment of the constituents and structure in the vicinity of the external and internal surfaces.• Unlike the analysis of other tube materials for Section C, the focus of this investigation was <u>not</u> in the region of the tube where the maximum amount of material was lost. The intent of this assessment was to focus on corrosion of the weld cladding, and the weld cladding had completely wasted away in the tube regions which experienced the most metal lost. Due to interest in the cladding, this investigation examined portions of the tube where the weld cladding remained.• Figures J-12a and b show backscattered electron images of the scale/metal interface for Sample GG-HH. Figure 12c shows a secondary electron image of the same region.• The numbers on Figures J-12a, b, and c show the locations of EDS analyses that will later be reported.• Four distinct regions are in evidence in the microstructure near the interface. These regions are, starting within the adhering scale and working inward:<ul style="list-style-type: none">○ <u>Adherent Scale</u> – this scale is continuous along the scale/metal interface. It is primarily a chromium-rich oxide with evidence of both carbon and sulfur being present.○ <u>Light etching band along scale/metal interface</u> - EDS analysis later will show this region is similar in composition to base metal with some ingress of oxygen and perhaps carbon.○ <u>Dark etching band parallel to the scale/metal interface</u>: – EDS analysis later will show evidence of oxygen (and perhaps carbon) ingress. This leads to internal oxidation and accounts for the darker grey appearance of this region. The scalloped shape of this region appears to be associated with the possibility that the dendrite cores, being richer in chromium, are more resistant to corrosion, while the interdendritic regions are not.○ <u>Weld metal deposit to form cladding</u> – This region exhibits classic weld metal microstructure with dendrites growing in a radial direction from the underlying 800H substrate.• Figure J-13 shows a 2 mil thick oxide scale along the internal metal surface of Sample GG-HH.

Summary of Findings, (continued)

Material: IN52 Weld Overlay

Issue	Discussion
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none"> Figure J-14 shows a longitudinal profile (at the 12 o'clock orientation) of the IN52 Weld Overlay samples adjacent to the welds in Section C. The welds in question are those identified as welds “R” and “HH”, see Figure J-1 for locations Examination of Figure J-14 reveals that in both cases the IN 52 weld cladding has been completely wasted away. Also note that the Inconel 625 weld metal appears to have wasted to a lesser extent. In any case, the wall thickness adjacent to the weld is somewhat thicker and it tapers toward the middle of the tube length. This seems to lend validity to the dimensions taken from a ring that was extracted from the middle of this tube.
EDAX Analysis Results	<ul style="list-style-type: none"> The table in Figure J-15 provides a summary of the EDS analyses of the numbered locations in Figure J-12. Also shown in this table is a summary of the spectrographic analysis reported earlier, see Figure J-2. Review of this table suggests the following: <ul style="list-style-type: none"> <u>Area 1: Adherent scale</u> – This is primarily a chromium-rich oxide. The data also suggest a high concentration of sulfur and perhaps carbon. <u>Area 2: Light etching band along scale interface</u> – The composition of this band is similar to that of the base metal with some ingress of oxygen and perhaps carbon. <u>Area 3: Dendrite core</u> - This analysis suggests that the dendrite core has a composition very similar to that of the bulk metal analysis. <u>Area 4: Inderdendritic region – corrosion possible</u> – This analysis suggests that the region between dendrites has a reduced level of nickel relative to the bulk metal analysis. Evidence of oxygen and perhaps carbon suggest that corrosion has affected this region that is located near to the scale/metal interface. <u>Area 5: Interdendritic region – not corroded</u> – This interdendritic region is further away from the scale/metal interface and shows no evidence of corrosion. <u>Area 6: Grain boundary that crosses corroded zone</u> – This region was chosen because it did not evidence corrosion while the adjacent grains did. Analysis shows that this boundary was enriched in chromium. <u>Area 7: Bulk metal analysis</u> – This analysis was used to verify that the weld cladding had a composition consistent with IN 52.

Figure J-1: Schematic Drawing Showing Position of IN52 Weld Overlay Tube Samples Within Test Section C

1. Drawing shown in same relative orientation as per the actual installation.
2. This group of tube samples was removed from service in November 2001 - highlighted in red.
3. This group of tube samples was removed from service in June 2002 - highlighted in yellow.

Figure J-2 Semi-Quantitative Composition Verification for Inco 52 / 800 HT (Weld clad duplex tubing)

Description: Nominal 30 Cr nickel alloy cladding for oxidation/corrosion protection. Incoloy 800HT substrate provides creep strength.
Source: Special Metals Corporation (SMC)
Reference Composition: Filler wire “limiting chemical composition” – Per SMC literature. (ANSI AWS 5.14M-97 Class ERNiCrFe-7)

Element	Reference Composition for Weld Cladding	Composition Heat NX 9090JK	Tube Sample R-S	Tube Sample GG-HH
Ni	Balance	60.48	N/A	59.9
Cr	28.0 – 31.5	28.97	N/A	29.2
Fe	7.0 – 11.0	8.86	N/A	9.25
Mo	0.50 max	0.01	N/A	-
Co	-	0.01	N/A	-
C	0.04 max	0.02	N/A	-
N	-	-	N/A	-
B	-	-	N/A	-
Mn	1.0 max	0.24	N/A	-
Si	0.50 max	0.14	N/A	0.36
Al	1.10 max	0.69	N/A	0.68
Ti	1.0 max	0.58	N/A	0.61
Al+Ti	1.5 max	1.27	N/A	1.29
Nb	0.10 max	0.01	N/A	-
Ta	-	<0.01	N/A	-
Nb+Ta	-	0.02	N/A	-
V	-	-	N/A	-
W	-	-	N/A	-
Cu	0.30 max	0.01	N/A	-
Sn	-	-	N/A	-
P	0.020 max	0.004	N/A	-
S	0.015 max	<0.001	N/A	-
O2	-	-	N/A	-
Others	0.50 max	<0.50	N/A	-

N/A = Sample not analyzed.

Note: Reference composition is for filler wire, not as-deposited.

Figure J-3: Appearance of IN52 Weld Overlay Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure J-4: As-Received Appearance of Sample R-S (IN52 Weld Overlay)

(Average surface metal temperature: 1208 °F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure J-5: As-Received Appearance of Sample GG-HH (IN52 Weld Overlay)

(Average surface metal temperature: 1073 °F)

12 O’Clock
(N/A mils lost)

3 O’Clock
(91 mils lost)

6 O’Clock
(3 mils lost)

Figure J-6: OD Surface Appearance After Grit Blast

Material: IN52 Weld Overlay
Sample: R-S

12 O’Clock
(N/A mils lost)

3 O’Clock
(106 mils lost)

6 O’Clock
(0 mils lost)

Figure J-7: OD Surface Appearance After Grit Blast

Material: IN52 Weld Overlay
Sample: GG-HH

Material:

IN52 Weld Overlay

Sample Location:

R-S

Maximum Rate:

48 mils/yr

Maximum Loss Orientation:

Approx. 2:30 o'clock

Average Surface Metal Temperature:

1208 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.287	0.285	0.290	0.295	0.302	0.301	0.293	0.286	0.292	0.292
After	N/A	0.223	0.199	0.291	0.299	0.299	0.296	0.249		0.178
Delta	N/A	0.062	0.091	0.004	0.003	0.002	-0.003	0.037		0.114

Figure J-8: Silhouette and Wall Thickness Measurements for Sample R-S

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Material:

IN52 Weld Overlay

Sample Location:

GG-HH

Maximum Rate:

63 mils/yr

Maximum Loss Orientation:

Approx. 10 o'clock

Average Surface Metal Temperature:

1073 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.284	0.282	0.282	0.287	0.293	0.294	0.293	0.289	0.288	0.288
After	N/A	0.213	0.176	0.283	0.295	0.283	0.247	0.162		0.138
Delta	N/A	0.069	0.106	0.004	-0.002	0.011	0.046	0.127		0.150

Figure J-9: Silhouette and Wall Thickness Measurements for Sample GG-HH

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Figure J-10: Metal Loss Rate as a Function of Average Surface Metal Temperature

Material: IN52 Weld Overlay

Figure J-11: Metal Loss as a Function of Time

Material: IN52 Weld Overlay

(a) External Scale/Metal Interface (BEI - Intermediate Magnification)

(b) External Scale/Metal Interface (BEI - High Magnification)

Figure J-12 Microstructure: IN52 Weld Overlay

Note: Numbers on photos indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

(c) External Scale/Metal Interface (SEI - Intermediate Magnification)

Figure J-12(Cont.): Microstructure: IN52 Weld Overlay

Note: Numbers on photos indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

Internal Surface Appearance

Figure J-13 Microstructure: 800H Substrate Internal Surface of Tube with IN52 Weld Overlay

Note: Photomicrograph at approximately 200X. Electrolytic 10% oxalic acid etch, 9V OCP

(a) IN52 Weld Overlay Adjacent to Weld “R”

(b) IN52 Weld Overlay Adjacent to Weld “HH”

Figure J-14: Longitudinal Cross-Sections: IN52 Weld Overlay Adjacent to Welds

Note: None of the original weld overlay remains in this view, only 800H substrate.

Figure J-15: EDS Analysis of Deposit/Scale/Metal Interface for IN52 Weld Overlay (Sample GG-HH)

Area	Description	Ni	Cr	Fe	Co	Mn	Nb	Ti	Al	Si	C	O	Ca	K	Na	As	P	S
1	Adherent scale	7.76	55.1	3.80	--	--	--	0.60	1.42	0.25	4.88	17.4	--	--	--	--	--	8.78
2	Light etching band along scale interface	57.2	25.3	9.16	--	--	--	0.26	0.36	--	5.15	2.53	--	--	--	--	--	--
3	Dendrite core	61.9	27.9	9.73	--	--	--	--	0.39	--	--	--	--	--	--	--	--	--
4	Interdendritic – corrosion possible.	49.8	28.0	7.13	--	--	--	0.51	0.80	0.24	7.02	6.44	--	--	--	--	--	--
5	Interdendritic – not corroded.	59.0	30.1	8.95	--	--	--	0.87	0.82	0.28	--	--	--	--	--	--	--	--
6	Grain boundary possible corroded zone	50.6	39.8	7.36	--	--	--	1.08	1.17	--	--	--	--	--	--	--	--	--
7	Bulk composition mid-overlay.	59.9	29.2	9.25	--	--	--	0.61	0.68	0.36	--	--	--	--	--	--	--	--
	Reference bulk analysis.	61.8	27.3	8.99	--	0.28	--	0.51	0.83	0.23	0.03	--	--	--	--	--	--	--

Appendix K
Analysis of Performance
Test Section C
Incoclad 671

Overview of Results: Incoclad 671

Incoclad 671 experienced a very low rate of metal loss due to exposure in Test Section C. The maximum rate was determined to be 10 mils per year*. The chromium and overall alloy content of this material seem to account for its' good performance in this environment. This further would be assisted by the fine grain size of the cladding which likely would facilitate the diffusion that would aid in the formation of a protective chromium-rich scale.

Examination revealed that, while the corrosion rate for Incoclad 671 was very low at all of the exposure temperatures, it was highest at the lowest exposure. The Section C data and the Section A data are consistent in this regard. The reason for the somewhat increased corrosion rate at lower temperatures is not entirely clear; however, the evidence of high sulfur in the reaction zone may give some guidance in this regard. It was noted that physical examination of the as-received tube surfaces showed evidence on the surface of all three tube samples of the alkali sulfates that are known to be particularly aggressive.

It should be noted that the metal loss rates determined to date for both Section A and Section C all were based on a ring specimen that was extracted from mid-length of each tube sample. In the current analysis, additional attention was focused on metal losses in the vicinity of welds. Indeed examination revealed that, for the Incoclad samples, the welds were the only regions where any significant corrosion occurred. Analysis showed that the Inconel 625 weld filler metal, that was used for joining tubes to one another, while being reasonably resistant to coal ash corrosion, was less resistant to corrosion than the adjacent Incoclad 671 material. This was particularly obvious for the Sample P-Q which experienced the highest exposure temperature (1203 F) of the three Incoclad 671 specimens. It is believed that dissolution of the Inconel 625 filler metal accounts for the local loss of cross section at the weld at location "P". This suggests that perhaps an IN72 filler metal may have been a better choice at this location.

* **Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: Inconel 671

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• The schematic in Figure K-1 shows the relative positions of the three Inconel 671 samples in Test Section C. Note that none of the Inconel 671 overlay samples was within the tube lengths that were removed early, i.e. in November 2001 or in June 2002.• Also, shown is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• The table in Figure K-2 shows a reference nominal composition that was provided by the Special Metals Corporation (SMC).• No mill certificate or heat analysis was offered so it's not clear whether these samples came from one or multiple heats of material.• During the Section A evaluation, detailed composition verification was undertaken for every tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample EE-FF confirmed that the correct material was used at this location.
As-Received Appearance	<ul style="list-style-type: none">• Figure K-3 shows the typical appearance of the Inconel 671 samples as they were received from SMC. This tube has a total wall thickness of about 260 mils, with a 75 mil thick outer layer of IN671 to provide corrosion resistance, and an inner supporting layer of 800H.• Figures K-4 through K-6 document the appearance of the external surface of the Inconel 671 tube samples after they had been removed from service. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction..

Material: Inconel 671

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance, Continued	<ul style="list-style-type: none">• The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the “o’clock” conventions described above, (with the 12 o’clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o’clock side of the tube faces downward, and the 6 o’clock orientation faces upward within the boiler.• Wastage is not visible in any of these three tubes in any orientation.• The chalky white scale associated with molten alkali-iron sulfate attack can be seen on all three tube samples..
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">• Figures K7 through K-9 show the appearance of the external surface of the Inconel 671 tube samples after grit-blasting to remove deposit and scale. The 3 and 12 o’clock positions on Sample EE-FF show the appearance of general wastage due to fireside corrosion.• Wastage is not apparent in viewing the remaining surfaces.
Wall Thickness Loss Determined	<ul style="list-style-type: none">• Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures K-10 through K-12.• Measurements were taken at eight evenly spaced “o’clock” locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.• The before and after measurements were documented in the table that accompanies each figure. These form the basis for the “delta” calculation to determine wall thickness losses. In some cases, the delta is negative. This is believed due to wall thickness variability and difficulty in locating the exact location of the “before” measurement.• For tube Sample EE-FF, the minimum wall thickness in the cross section was not at one of the eight predetermined locations. In this case, there was no “before” measurement for comparison. So, the average “before” wall thickness was used to calculate the wall thickness lost at these off-locations.
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure K-13 plots the maximum wall thickness lost against the calculated average metal temperature for the three samples. The data from Section A also are plotted.• The wastage rate was low for all three samples; however, note that the sample having the lowest average exposure temperature (1086 °F) had the highest wastage rate. This is confirmed by the appearance of the grit blasted surface of this sample, see Figure K-9.
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure K-14 plots metal loss as a function of time for each sample location for both Sections A and C, with samples from Section C having experienced generally longer exposure times.• The chart emphasizes the point that the higher temperature samples experienced little if any additional wall loss, while the low temperature sample, Sample EE-FF experienced increased metal loss with time.

Material: Incoclad 671

Summary of Findings, (continued)

Issue	Discussion
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample EE-FF was selected for a detailed SEM/EDS assessment of the constituents and structure at the external and internal surfaces.• Figure K-15 shows the appearance of the tube profile for Sample EE-FF. The scale/deposit on the external surface is approximately 2 mils thick. No scale is evident on the internal surface at this magnification.• Figures K-15a and b show secondary electron images of the scale/metal interface for Sample EE-FF. Figures 15 c and d show back-scattered electron images of this same region to enhance the appearance of local composition and topological differences.• The numbers on Figures K-15b and d show the locations of EDS analysis that will be reported later in this document.• Examination of the microstructure reveals four distinct regions:<ul style="list-style-type: none">○ <u>Incoclad 671 Base metal</u> – Oxalic acid etch delineates grain boundaries and carbides. Of particular note is the extremely fine grain size in the cladding material. Also note from, Figure 15d, that two phases are apparent in the bulk tube metal. Later EDS analysis will show that these phases contain nickel and chromium in different proportions. The chromium-rich phase is resistant to attack by the oxalic acid etchant, see point #5, Figure K-15d. The nickel-rich phase is less resistant, see point #6 in the same figure.○ <u>Metal at the Interface</u> – A very narrow diffusion zone is noted at the metal/scale interface. This is indicated at point #3 in Figure 15b, but perhaps is shown more clearly in Figure 15d. Examination reveals that the scale is progressing into the metal surface along this narrow zone. EDS analysis has shown that the zone is depleted in chromium.○ <u>Adherent scale with embedded deposit</u> – EDS analysis will later show that this is predominantly a chromium-rich oxide with a significant amount of sulfur present.○ <u>Thick and very porous deposit/scale conglomerate</u> – many spherical particles are noted along with what appears to be islands of scale (metal oxides).• Figure K-16 shows the condition of the tube wall at its internal surface. No evidence found of significant corrosion in this region.
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none">• Figure K-17 shows a longitudinal profile (at the 12 o'clock orientation) of the Incoclad 671 samples adjacent to the welds in Section C. The welds in question are those identified as welds “P”, “V”, and “FF”, see Figure L-1 for locations• Examination of Figure K-17a suggests that the Inconel 625 weld filler metal was less resistant to corrosion than the clad tube adjacent to the weld at location “P”. It is believed that dissolution of the Inconel 625 filler metal is the principle reason for the local loss of cross section at this weld. This suggests that a different filler metal may have been a better choice at this location.

Summary of Findings, (continued)

Material: Incoclad 671

Issue	Discussion
EDAX Analysis Results, Continued	<ul style="list-style-type: none">• The table in Figure K-18 provides a summary of the EDS analyses of the numbered locations in Figure K-15b and d. Also shown in this table is a summary of the spectrographic analysis reported earlier, see Figure K-2.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Areas 1: Bulk deposit/scale analysis</u> – Alkali metals and sulfur are present. The relatively high chromium content suggests that a significant percentage of the chromium-oxide scale was included in this analysis. The oxides of iron, aluminum, and titanium also are indicated. An iron oxide is likely, as are aluminum, silicon and titanium oxides.• <u>Area 2: Adherent scale</u>– This scale is predominantly a chromium-rich oxide with a significant amount of sulfur noted.• <u>Area 3: Diffusion zone - adjacent to the scale/metal interface</u> – This zone is depleted in chromium (21.7% vs roughly 50% in the bulk tube).• <u>Area 4: Bulk metal analysis</u> – This confirms that the sample was correctly identified as Incoclad 671.• <u>Area 5: Shallow etching region in cladding</u> – This constituent of the microstructure is rich in chromium (nominally 85% Cr / 15% Ni).• <u>Area 6: Deep etching region in cladding</u> – This constituent of the microstructure is rich in nickel (nominally 70% Ni / 30% Cr).

**Figure K-2 Semi-Quantitative Composition Verification for Incoclad 671 / 800 HT
(Co-extruded duplex tubing)**

Description: Nominal 50Cr/50 Ni alloy cladding for oxidation/corrosion protection.
Incoloy 800HT substrate to provide creep strength.
Source: Special Metals Corporation (SMC)
Reference Composition: Cladding “nominal” chemistry – per SMC literature.

Element	Reference Composition	Certified Composition (not provided)	Tube Sample P-Q	Tube Sample U-V	Tube Sample EE-FF
Ni	51.5		N/A	N/A	47.0
Cr	48.0		N/A	N/A	52.5
Fe	-		N/A	N/A	-
Mo	-		N/A	N/A	-
Co	-		N/A	N/A	-
C	0.05		N/A	N/A	-
N	-		N/A	N/A	-
B	-		N/A	N/A	-
Mn	-		N/A	N/A	-
Si	-		N/A	N/A	-
Al	-		N/A	N/A	0.23
Ti	-		N/A	N/A	0.24
Al+Ti	-		N/A	N/A	-
Nb	-		N/A	N/A	-
Ta	-		N/A	N/A	-
Nb+Ta	-		N/A	N/A	-
V	-		N/A	N/A	-
W	-		N/A	N/A	-
Cu	-		N/A	N/A	-
Sn	-		N/A	N/A	-
P	-		N/A	N/A	-
S	-		N/A	N/A	-
O2	-		N/A	N/A	-
Others	-		N/A	N/A	-

N/A = Sample not analyzed.

Figure K-3: Appearance of Inconel 671 Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure K-4: As-Received Appearance of Sample P-Q (Inconel 671)

(Average surface metal temperature: 1203 °F)

12 O’Clock – Facing Gas Flow
(Note: 3 o’clock is up in this image)

3 O’Clock
(Note: 6 o’clock is up in this image)

6 O’Clock – Opposite Gas Flow

Figure K-5 As-Received Appearance of Sample U-V (Inconel 671)

(Average surface metal temperature: 1121 °F)

Note: this tube sample was 11-5/8-in. long.

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure K-6: As-Received Appearance of Sample EE-FF (Inconel 671)
(Average surface metal temperature: 1086 °F)

12 O’Clock
(0 mils lost)

3 O’Clock
(0 mils lost)

6 O’Clock
(0 mils lost)

Figure K-7: OD Surface Appearance After Grit Blast

Material: Incoclad 671
Sample: P-Q

12 O’Clock
(3 mils lost)

3 O’Clock
(1 mils lost)

6 O’Clock
(0 mils lost)

Figure K-8: OD Surface Appearance After Grit Blast

Material: Incoclad 671

Sample: U-V

12 O’Clock
(4 mils lost)

3 O’Clock
(0 mils lost)

6 O’Clock
(0 mils lost)

Figure K-9: OD Surface Appearance After Grit Blast

Material: Incoclad 671
Sample: EE-FF

Material:

Incoclad 671

Sample Location:

P-Q

Maximum Rate:

2 mils/yr

Maximum Loss Orientation:

Approx. 10:30 o'clock

Average Surface Metal Temperature:

1203 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.259	0.264	0.262	0.258	0.256	0.255	0.256	0.259	0.259	0.259
After	0.259	0.261	0.263	0.261	0.258	0.256	0.253	0.254		0.254
Delta	0.000	0.003	-0.001	-0.003	-0.002	-0.001	0.003	0.005		0.005

Figure K-10: Silhouette and Wall Thickness Measurements for Sample P-Q

Material:

Incoclad 671

Sample Location:

U-V

Maximum Rate:

1 mils/yr

Maximum Loss Orientation:

Approx. 12 o'clock

Average Surface Metal Temperature:

1121 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.258	0.253	0.257	0.260	0.262	0.262	0.262	0.258	0.259	0.258
After	0.255	0.256	0.256	0.260	0.263	0.261	0.259	0.257		0.255
Delta	0.003	-0.003	0.001	0.000	-0.001	0.001	0.003	0.001		0.003

Figure K-11: Silhouette and Wall Thickness Measurements for Sample U-V

Material:

Incoclad 671

Sample Location:

EE-FF

Maximum Rate:

10 mils/yr

Maximum Loss Orientation:

Approx. 2 o'clock

Average Surface Metal Temperature:

1086 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max Loss
Before	0.256	0.258	0.260	0.263	0.261	0.259	0.257	0.255	0.259	0.259
After	0.252	0.235	0.260	0.263	0.263	0.260	0.256	0.248		0.234
Delta	0.004	0.023	0.000	0.000	-0.002	-0.001	0.001	0.007		0.025

Figure K-12: Silhouette and Wall Thickness Measurements for Sample EE-FF

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Figure K-13: Metal Loss Rate as a Function of Average Surface Metal Temperature

Material: Incoclad 671

Figure K-14: Metal Loss as a Function of Time

Material: Incoclad 67

Figure K-15: Low Magnification Image Showing Cross-Section Through Thinnest Region of Sample EE-Ff (Incoclad 671)

(a) External Scale/Metal Interface (SEI - Low Magnification)

(b) External Scale/Metal Interface (SEI - Intermediate Magnification)

Figure K-16: Microstructure: Incoclad 671

Note: Numbers on photos indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

(c) External Scale/Metal Interface (BEI - High Magnification)

(d) External Scale/Metal Interface (SEI - High Magnification)

Figure K-15 (Cont.): Microstructure: Incoclad 671

Internal Surface Appearance

Figure K-16: Microstructure: Incoclad 671

(a) Incoclad 671 Adjacent to Weld "P"

(b) Incoclad 671 Adjacent to Weld "V"

Figure K-17: Longitudinal Cross-Sections: Incoclad 671 Adjacent to Welds

(c) Incoclad 671 Adjacent to Weld FF”

**Figure K-17, Continued: Longitudinal Cross-Sections: Incoclad 671
Adjacent to Welds**

Figure K-18: EDS Analysis of Deposit/Scale/Metal Interface for Inconel 671 (Sample EE-FF)

Area	Description	Ni	Cr	Fe	Co	Mn	V	Ti	Al	Si	C	O	Ca	K	Cl	As	P	S
1	Bulk deposit analysis	1.25	75.6	3.26	--	--	--	1.07	1.13	--	--	17.0	0.11	0.18	--	--	--	0.56
2	Tightly adhering scale.	1.95	71.9	--	--	--	--	0.90	1.41	--	--	13.5	--	--	--	--	--	10.2
3	Diffusion zone – dark etching	72.6	21.7	--	--	--	--	--	0.45	--	--	2.24	--	--	--	--	--	3.01
4	Bulk tube analysis/	47.0	52.5	--	--	--	--	0.24	0.23	--	--	--	--	--	--	--	--	--
5	Shallow etching constituent in tube.	15.4	84.6	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
6	Deep etching constituent in tube.	68.3	31.0	--	--	--	--	0.30	0.36	--	--	--	--	--	--	--	--	--
	Reference bulk analysis	51.1	47.7	.014	0.24	0.001	0.011	0.38	0.23	0.02	0.05	--	--	--	--	--	--	0.01

Appendix L

Analysis of Performance

Test Section C

IN72 Weld Overlay

Overview of Results: IN72 Weld Overlay

IN72 Weld Overlay continued to demonstrate a low rate of metal loss due to hot side corrosion. The maximum rate, based on diameter measurements, was determined to be 14 mils per year* (for Sample FF-GG). However, perhaps of equal importance is the fact that the overlay material appears to have suffered from internal cracking some grain boundaries that lie at roughly mid-point in the cladding. These internal cracks were shown to range from about 10 to 30 mils in length and seemed to be concentrated in one-half of the tube circumference and almost totally absent in the other.

The evidence associated with this internal cracking seems to suggest that hot corrosion is not the only active degradation mechanism for this material. The cause for the cracking has not been conclusively determined to date. However, evidence of cracking deep within the cladding, and lacking evidence of corrosion within the cracks, suggests that these, at least initially, are two separate phenomena. This investigation was able to identify a number of internal cracks in both Section C specimens. These internal cracks generally were not filled with corrosion product, thus they were apparently not connected to the external surface of the tube. However, in at least one instance (for Sample FF-GG) hot corrosion had removed sufficient surface material to expose an internal crack that was approximately 20 mils long. This exposed crack showed evidence of corrosion along its length. If the additional 20 mils associated with this crack had been taken into account, then the calculated metal loss rate would have added 8 mils per year for Sample FF-GG. It should be noted that the cladding thickness was about 80 mils. So, for this case, the corrosion plus crack length breached about half of the cladding thickness.

To further explore the weld overlay cracking phenomenon, archive material was examined to verify determine whether the original material contained cracks. Dye penetrant and magnetic particle tests were performed on a piece of IN72 Weld Overlay archive material that had been set aside when the sections were originally constructed. Non-destructive testing of this six inch long sample showed no evidence of cracking. A ring section of the archive material was then cut and metallurgically examined. This showed evidence of a few small grain boundary cracks. When the Section A IN72 Weld Overlay samples were re-examined, it was found that these too had internal cracks that in only one case (noted in the Section A report) breached the surface. However, more importantly, more cracking was found in the Section A than in the archive material. Furthermore, Section C samples showed more cracking than the Section A samples. This suggests that service exposure may give rise to and grow additional cracks as a function of time.

Consideration of the evidence above suggests that IN72 Weld Overlay shows promise as to its ability to resist corrosion: however, serious consideration must be given to understanding the internal cracking phenomenon and its implications. If the internal cracking problem can be solved through processing or otherwise, then the IN72 Weld Overlay approach will offer a good practical solution toward addressing the problem of high temperature corrosion in similar applications. However, lacking an understanding of, and solution for, the observed internal cracking, and given the fact that cracking appears to be increasing with time at temperature, suggests that users would be well served in being cautious about employing this material. A major concern would be that the tubes may well show no visible evidence of underlying cracking during in situ inspection in the boiler.

Nonetheless, as was true for the other nickel-base alloys, the chromium and overall alloy content of this material likely account for the good corrosion resistance of the IN72 Weld Overlay in this environment. Also, like the other high-nickel, high-chromium materials, the corrosion rate

appears to be higher at the lower exposure temperature. The reason for the somewhat increased corrosion rate at lower temperatures has not been determined.

It should be noted that the metal loss rates determined to date for both Section A and Section C all were based on a ring specimen that was extracted from mid-length of each tube sample. In this analysis additional attention was focused on metal losses in the vicinity of welds. Representative samples were taken and it was determined that the Inconel 625 weld filler metal, that was used for joining tubes to one another, while being reasonably resistant to coal ash corrosion, was less resistant to corrosion than the adjacent IN72 weld overlay. It is believed that dissolution of the Inconel 625 filler metal is the principle reason for the local loss of cross section at the weld at location "R". This suggests that IN72 filler metal may have been a better choice at this location.

Analysis of deposit on the surface revealed that it had the known aggressive combination of species, namely iron, oxygen, the alkali metals, and sulfur. Thus, the required corrosive elements were available to test the performance limits of this alloy.

*** Note throughout this appendix, the reported metal loss rate was calculated based on time at temperature rather than total time within the boiler.**

Material: IN72 Weld Overlay

Summary of Findings

Issue	Discussion
Sample Location and Orientation.	<ul style="list-style-type: none">• The schematic in Figure L-1 shows the relative positions of the two IN72 Weld Overlay samples in Test Section C. Note that neither of the IN72 overlay samples was within the tube lengths that were removed early, i.e. in November 2001 or in June 2002.• Also, shown is the calculated average metal temperature at each location.
Composition Verification.	<ul style="list-style-type: none">• The weld wire for cladding the IN 72 Weld Overlay samples used in this program was drawn from Special Metals Corporation (SMC) Heat UKL8138. The composition for this heat is provided in the table in Figure L-2 along with the target composition from SMC literature.• During the Section A evaluation, detailed composition verification was undertaken for every tube sample that was removed from service. This served, in part, to verify that the each tube material was located at its' proper position within the test section.• Based on the good results for Section A, it was decided that it would be unnecessary to analyze each and every tube sample for composition verification. Rather, it was decided to select a representative sample from each tube material type for confirmatory analysis.• During the Section A evaluation, the energy dispersive spectrographic (EDS) capabilities of the scanning electron microscope (SEM) were used to perform semi-quantitative analyses of each of the twelve different candidate tube materials. Comparison of these EDS results showed reasonably good correlation with results obtained using quantitative analytical techniques, including optical emission spectrometry.• Based on this, it was decided that the accuracy provided by EDS would suffice for composition verification, but that more detailed analyses would be undertaken if questions arose.• The results of the EDS analysis of tube sample FF-GG confirmed that the correct material was used at this location.• It was noted that the actual tube sample composition was higher in iron than the reported filler wire chemistry; however, is consistent with what would be expected for a weld deposit, and compares reasonable well the desired nominal chemistry in terms of chromium content.
As-Received Appearance	<ul style="list-style-type: none">• Figure L-3 shows the appearance of the archive sample for IN72 Weld Overlay material. This photograph documents the condition of the tube sample as it was delivered from SMC. The weld bead surface profile is clearly visible in this view. The cladding thickness was measured to be approximately 80 mils. Thus, it comprised about 27% of the total wall thickness of 292 mils.

Material: IN72 Weld Overlay

Summary of Findings, (continued)

Issue	Discussion
As-Received Appearance, Continued	<ul style="list-style-type: none">Figures L-4 and L-5 document the appearance of the external surface of the IN72 Weld Overlay tube samples after service. Three views are provided for each tube: 12 o'clock (the view that faces on-coming gas flow), 3 o'clock (the view where the gas flow is tangent to the surface), and 6 o'clock (the view that shows the back-side of the tube relative to the gas flow direction).The reader should be alerted to the fact that, within the boiler, the gas flows upward over these tubes. This implies that for the "o'clock" conventions described above, (with the 12 o'clock orientation facing the gas flow direction), the actual physical orientation of these tubes is such that the 12 o'clock side of the tube faces downward, and the 6 o'clock orientation faces upward within the boiler.No wastage is visible in these views. The original weld bead profile is somewhat obscured by deposit on Sample FF-GG (Figure L-5); however, it is clearly visible on Sample Q-R (Figure L-4) which is relatively free from scale.All three views of Sample Q-R show evidence of the gray/white scale associated with molten alkali-iron sulfate attack. This is also in evidence in the 6 o'clock view for Sample FF-GG.
Grit-Blasted Surface Appearance	<ul style="list-style-type: none">Figures L-6 and L-7 show the appearance of the external surface of the IN 72 Weld Overlay tube samples after grit-blasting to remove deposit and scale. The 12 o'clock and 3 o'clock positions for Sample FF-GG show the appearance of general wastage due to fireside corrosion.Scattered pitting is in evidence at the 12 and 3 o'clock positions for Sample Q-R.
Wall Thickness Loss Determined	<ul style="list-style-type: none">Tube cross-sections were prepared to allow for measurement of wall thickness to determine metal loss due to exposure. These are shown in silhouette in Figures L-8 and L-9.The same relative "o'clock" positions were maintained as discussed earlier. Measurements were taken at eight evenly spaced locations about the tube circumference. These were then compared with measurements taken at these same locations prior to exposure.The before and after measurements were documented in the table that accompanies each figure. These form the basis for the "delta" calculation to determine the amount of wall thickness lost. Note that in some cases, the delta is negative (particularly around the 6 o'clock position). This is believed due to wall thickness variability and difficulty in locating the exact location of the "before" measurement.Sample FF-GG experienced the maximum wall thickness reduction due to corrosion of 14 mils per year. As was mentioned in the overview section of this report, an additional 8 mils per year would need to be included if one were to take into account weld cracking that intersects the external surface.

Material: IN72 Weld Overlay

Summary of Findings, (continued)

Issue	Discussion
Wall Thickness Loss Versus Average Metal Temperature	<ul style="list-style-type: none">• The chart in Figure L-10 plots the maximum wall thickness lost against the calculated average metal temperature for the two IN72 Weld Overlay samples in Section C. The data from the Section A samples also are plotted. <u>Note that these data do not take into account the additional wall thickness that would be lost due to internal weld cracking.</u>• The hot corrosion rate for the Section C samples was slightly lower than the rate for Section A samples, but both were found to be very low. Again it was noted that the rate was higher at the lower exposure temperature, as is consistent with the grit blasted surface images shown in Figures L-6 and L-7.
Wall Thickness Loss as a Function of Time and Location	<ul style="list-style-type: none">• The chart in Figure L-11 plots metal loss as a function of time for each sample location for both Sections A and C, with samples from Section C having experienced generally longer exposure times. <u>Note again that these data do not take into account the additional wall thickness that would be lost due to internal weld cracking.</u>• The chart shows a straight line fit to the maximum metal loss data points for Samples Q-R and FF-GG for both Sections A and C. Evaluation of the rate of metal loss data depicted in Figure L-10 suggests that a straight line fit would not likely be appropriate for these samples in that the rate of metal loss decreased from Section A to Section C for both samples under consideration.
Metallurgical Analysis – SEM	<ul style="list-style-type: none">• Sample FF-GG was selected for a detailed SEM/EDS assessment of the constituents and structure in the vicinity of the external and internal surfaces. This sample was selected for evaluation due to its higher rate of corrosion based on diameter measurements.• Figure L-12 shows back-scattered electron images (BEI) of the external surface of Sample FF-GG. This mode of imaging was chosen because it highlights differences in atomic weight.• Figures L-12a and b show BEI of the external scale/metal interface for Sample FF-GG. Also shown in this image are the scale-lined weld cracks that have intersected corrosion that is progressing inward from the external surface.• The numbers on Figure L-12b show the locations of EDS analyses to further characterize these regions. The results of these are provided in a later section of this report.• Figure L-12c provides the appearance of a shallow pit found on the surface of Sample FF-GG. These were found typically to be under a local build-up of deposit on the tube surface.

Summary of Findings, (continued)

Material: IN72 Weld Overlay

Issue	Discussion
Metallurgical Analysis – SEM, Continued.	<ul style="list-style-type: none">• Based on examination the images in Figure L-12, five distinct regions are in evidence. These regions are, starting within the metal and working out:<ul style="list-style-type: none">○ <u>Base metal</u> – Oxalic acid etch faintly delineates grain boundaries, carbides, and inclusions.○ <u>Dark-Etching Band Parallel to the Scale/Metal Interface</u> – This region is clearly indicated by the arrow associated with EDS analysis point #5 in Figure L-12b. Analysis reported later will suggest that this region has suffered internal oxidation (6.23% oxygen).○ <u>Light-Etching Band at the Scale/Metal Interface</u> – This region is clearly indicated by the arrow associated with the EDS analysis point #4 in Figure L-12b. Analysis reported later will suggest that this region is primarily unaffected tube metal with a lesser oxygen content (1.83% oxygen).○ <u>Tightly adherent scale</u> – this is seen continuous along the surface underneath the surface deposit. EDS analysis will later show that this is predominantly a chromium-rich oxide.○ <u>Thick and very porous deposit/scale conglomerate</u> – many spherical particles are noted along with what appears to be islands of scale (metal oxides).• Figure L-13 shows the appearance of the internal metal surface for Sample FF-GG. No oxide scale is in evidence.
Metallurgical Analysis – Weld Cross Section.	<ul style="list-style-type: none">• Figure L-14 shows a longitudinal profile (at the 12 o'clock orientation) of the IN72 Weld Overlay samples adjacent to the welds in Section C. The welds in question are those identified as welds “R” and “FF”, see Figure L-1 for locations• Evaluation of the images in Figure L-14 suggests that the Inconel 625 weld filler metal was less resistant to corrosion than the adjacent IN72 weld overlay. It is believed that dissolution of the Inconel 625 filler metal is the principle reason for the local loss of cross section at the weld at location “R”. This suggests that IN72 filler metal may have been a better choice at this location.

Summary of Findings, (continued)

Material: IN72 Weld Overlay

Issue	Discussion
EDS Analysis Results	<ul style="list-style-type: none">• The table in Figure L-15 provides a summary of the EDS analyses of the seven locations numbered in Figure L-12 b. Also shown in this table is a summary of the spectrographic analysis reported earlier, see Figure L-2.• Review of this table suggests the following:<ul style="list-style-type: none">• <u>Area 1: Bulk deposit/scale analysis</u> – Alkali metals are present. Sulfur also is present in an increased amount compared to the base metal. An iron oxide is likely, as are aluminum and silicon oxides.• <u>Area 2: Nodule in bulk deposit</u> – Iron-, aluminum-, and silicon-rich oxides are indicated. Again the corrosive combination of alkali metals and sulfur also are in evidence.• <u>Areas 3: Adherent scale</u> – The analysis suggest a chromium and nickel rich oxide. Again a significant amount of corrosive species are also indicated, particularly sulfur.• <u>Area 4: Light etching band at scale/metal interface</u> – The analysis suggest that this is a narrow zone of base metal showing some oxygen ingress.• <u>Areas 5: Dark etching band parallel to scale/metal interface</u> – The analysis suggests ingress of oxygen and formation of a chromium-bearing oxide at this location.• <u>Area 6: Scale within corrosion deposit within weld crack</u> – The crack is shown to be lined with a chromium-rich oxide.• <u>Area 7: Bulk analysis:</u> – Given its limitations this EDAX analysis compares favorably with that of the reference spectrographic analysis below it.

Figure L-1: Schematic Drawing Showing Position of IN72 Weld Overlay Tube Samples Within Test Section C

1. Drawing shown in same relative orientation as per the actual installation.
2. This group of tube samples was removed from service in November 2001 - highlighted in red.
3. This group of tube samples was removed from service in June 2002 - highlighted in yellow.

Figure L-2 Semi-Quantitative Composition Verification for Inco 72 / 800 HT (Weld clad duplex tubing)

Description: Nominal 45Cr/55 Ni alloy cladding for oxidation/corrosion protection.
Incoloy 800HT substrate provides creep strength.
Source: Special Metals Corporation (SMC)
Reference Composition: Filler wire “nominal” chemistry – Per SMC literature.

Element	Reference Composition for Weld Cladding	Composition Heat UKL8138	Tube Sample Q-R	Tube Sample FF-GG
Ni	55	54.96	N/A	53.0
Cr	44	43.30	N/A	42.9
Fe	0.2	0.43	N/A	3.21
Mo	-	-	N/A	-
Co	-	-	N/A	-
C	0.05	0.02	N/A	-
N	-	-	N/A	-
B	-	-	N/A	-
Mn	0.1	0.03	N/A	-
Si	0.1	0.15	N/A	0.26
Al	-	0.20	N/A	-
Ti	0.6	0.66	N/A	0.61
Al+Ti	-	-	N/A	-
Nb	-	-	N/A	-
Ta	-	-	N/A	-
Nb+Ta	-	-	N/A	-
V	-	-	N/A	-
W	-	-	N/A	-
Cu	0.2	-	N/A	-
Sn	-	-	N/A	-
P	-	0.005	N/A	-
S	0.008	0.003	N/A	-
O2	-	-	N/A	-
Others	<0.50	<0.50	N/A	-

N/A = Sample not analyzed.

Note: Reference composition is for filler wire, not as-deposited.

Figure L-3: Appearance of IN72 Weld Overlay Tube Sample Prior to Service

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure L-4: As-Received Appearance of Sample Q-R (IN72 Weld Overlay)

(Average surface metal temperature: 1208 °F)

12 O'Clock – Facing Gas Flow
(Note: 3 o'clock is up in this image)

3 O'Clock
(Note: 6 o'clock is up in this image)

6 O'Clock – Opposite Gas Flow

Figure L-5 As-Received Appearance of Sample FF-GG (IN72 Weld Overlay)

(Average surface metal temperature: 1079 °F)

12 O'Clock
(N/A mils lost)

3 O'Clock
(0 mils lost)

6 O'Clock
(0 mils lost)

Figure L-6: OD Surface Appearance After Grit Blast

Material: IN72 Weld Overlay
Sample: Q-R

12 O’Clock
(N/A mils lost)

3 O’Clock
(8 mils lost)

6 O’Clock
(0 mils lost)

Figure L-7: OD Surface Appearance After Grit Blast

Material: IN72 Weld Overlay
Sample: FF-GG

Material:

IN72 Weld Overlay

Sample Location:

Q-R

Maximum Rate:

6 mils/yr

Maximum Loss Orientation:

7:30 o'clock

Average Surface Metal Temperature:

1208 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.293	0.286	0.285	0.287	0.292	0.297	0.299	0.298	0.292	0.289
After	N/A	0.282	0.285	0.289	0.294	0.298	0.300	0.283		0.283
Delta	N/A	0.004	0.000	-0.002	-0.002	-0.001	-0.001	0.015		0.015

Figure L-8: Silhouette and Wall Thickness Measurements for Sample Q-R

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Material:

IN72 Weld Overlay

Sample Location:

FF-GG

Maximum Rate:

14 mils/yr

Maximum Loss Orientation:

Approx. 10 o'clock

Average Surface Metal Temperature:

1079 °F

12 O'Clock

3 O'Clock

Approx. 1.2X

Wall Reduction by Position (in.)

	12 o'clock	1:30	3:00	4:30	6:00	7:30	9:00	10:30	AVG	Max* Loss
Before	0.293	0.292	0.288	0.289	0.289	0.295	0.296	0.294	0.292	0.292
After	N/A	0.263	0.280	0.292	0.290	0.288	0.282	N/A		0.256
Delta	N/A	0.029	0.008	-0.003	-0.001	0.007	0.014	N/A		0.036

Figure L-9: Silhouette and Wall Thickness Measurements for Sample FF-GG

* Measurement taken at “maximum loss orientation” noted above. The average “before” wall thickness was used to calculate the “delta”.

Figure L-10: Metal Loss Rate as a Function of Average Surface Metal Temperature

Material: IN72 Weld Overlay

Figure L-11: Metal Loss as a Function of Time

Material: IN72 Weld Overlay

(a) External Scale/Metal Interface (BEI - Low Magnification)

(b) External Scale/Metal Interface (BEI - Intermediate Magnification)

Figure L-12: Microstructure: IN72 Weld Overlay

Note: Numbers on photos indicate distinct areas characterized by the visual assessment and EDS analyses that follow.

(c) Pit at External Scale/Metal Interface (BEI - Intermediate Magnification)

Figure L-12 (Cont.): Microstructure: IN72 Weld Overlay

Internal Surface Appearance

Figure L-13: Microstructure: IN72 Weld Overlay

(a) IN72 Weld Overlay Adjacent to Weld "R"

(b) IN72 Weld Overlay Adjacent to Weld "FF"

Figure L-14: Longitudinal Cross-Sections: IN72 Weld Overlay Adjacent to Welds

Figure L-15: EDS Analysis of Deposit/Scale/Metal Interface for IN72 Weld Overlay (Sample FF-GG)

Area	Description	Ni	Cr	Fe	Co	Mn	V	Ti	Al	Si	C	O	Ca	K	Na	Mg	P	S
1	Bulk deposit analysis	--	--	80.8	--	--	--	--	1.29	1.93	--	15.7	--	0.28	--	--	--	--
2	Nodule in bulk deposit	--	--	32.9	--	--	--	0.51	10.1	19.3	--	25.0	1.94	4.39	0.61	0.30	--	4.93
3	Adherent scale analysis	18.6	54.0	0.88	--	--	--	1.45	0.90	0.42	--	15.1	0.15	0.35	--	--	--	8.01
4	Light etching band parallel to scale interface	53.5	41.6	2.07	--	--	--	0.43	0.18	0.31	--	1.83	--	--	--	--	--	--
5	Dark etching band parallel to scale interface	39.7	46.7	1.64	--	--	--	0.54	5.16	--	--	6.23	--	--	--	--	--	--
6	Scale within weld crack.	1.43	73.2		--	--	--	--	--	0.18	--	18.7	--	--	--	--	--	6.22
7	Bulk overlay analysis	53.0	42.9	3.21	--	--	--	0.61	--	0.26	--	--	--	--	--	--	--	--
	Reference bulk analysis	54.8	41.8	1.85	0.09	0.10	0.01	0.59	0.24	0.19	0.03	--	--	--	--	--	--	0.019