# Could biomass-fueled boilers be operated at higher steam temperatures? Part 2: Field tests of candidate superheater alloys

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**ABSTRACT:** Operating superheater tubes of biomass-fired boilers at considerably higher temperatures than can be tolerated by commonly used structural materials could improve boiler efficiency. However, corrosion of the superheater tubes promoted by interaction with the relatively low melting point deposits that accumulate on the tubes becomes a major issue. The objective of this study was to use field exposures to determine if there are materials acceptable for use as superheater tubes that can operate at temperatures at least 100 Celsius degrees above the current maximum superheater temperature.

Corrosion probes containing multiple specimens of nine different alloys were exposed for at least 2000 h in the superheater area of three biomass boilers where the deposits were determined to be enriched in potassium or chlorine. Similar specimens were also exposed in a boiler co-firing coal and wood. For the probes, specimen temperatures ranged from a low of less than 400°C to temperatures above 600°C for all but one case. Following exposure, a section was taken from each specimen and examined using light microscopy and scanning electron microscopy. Results of the examination of these specimens showed some alloys performed considerably better than others, but the corrosion resistance could not be related to chromium or molybdenum content of the alloys.

***Application:*** The results of this study provide guidance on the selection of superheater tube alloys for applications where it is desired to operate in hostile environment at temperatures as much as 100 Celsius degrees higher than normally used in that environment.

It is generally recognized that more efficient utilization of biomass or biomass-derived fuels would provide a means to reduce consumption of imported petroleum and to decrease the production of greenhouse gases, because the carbon dioxide produced during burning of biomass is roughly offset in a fairly short time by the carbon dioxide consumed during regrowth of biomass. However, the relatively low melting point alkali metal salts and chlorine compounds released during burning of biomass can cause accelerated corrosion and fouling of superheater tubes at fairly moderate temperatures. Consequently, increased superheater tube corrosion may be a result of efforts to increase boiler efficiency by increasing the maximum steam temperature. The detrimental effects of the alkali metals and chlorine have been well documented, as have the efforts to identify a means to limit the severity of tube degradation [1-10]. Extensive reference lists that provide additional sources of information on biomass-related corrosion and corrosion prevention are included in the latter two of these documents.

In a project competitively selected and subsequently funded by the United States Department of Energy, studies have been conducted with four goals: 1) characterizing the superheater system designs and construction materials used outside North America; 2) determining the economic benefits or penalties of operating boilers at a significantly higher temperature (50-100 Celsius degrees) than currently used; 3) conducting laboratory corrosion studies with candidate tube materials using salt mixtures simulating those in selected boilers; and 4) conducting field studies with corrosion probes to measure the corrosion rates of alternate superheater tube alloys in four particularly aggressive biomass-fired boiler environments at temperatures as much as 100 Celsius degrees above the normal maximum superheater tube temperature. Results from studies conducted for the first three of these tasks have been or will be reported elsewhere [11-14].

Before exposing the corrosion probes, in order to get an indication of the composition of the superheater deposits, air-cooled sampling probes were exposed in three of the four environments. These sampling probes were exposed for a relatively short time – generally 7-10 days – and care was taken in recovering the deposits from the top and bottom surfaces of the probes. Results obtained from analysis of these deposits helped determine the test compositions for the laboratory studies.

In order to assess the performance of the selected alloys under the most severe environments that might be encountered during combustion of biomass, four boilers were selected as examples of what would be expected to be particularly hostile biomass boiler environments. These environments include a recovery boiler in Covington, VA, USA, that processes black liquor derived primarily from hardwood, thus yielding deposits particularly high in potassium content. A hogged fuel boiler in Crofton, BC, Canada, that primarily burns bark obtained from seawater-floated logs was expected to have deposits that are high in chlorine content. Another hogged fuel boiler in Port Mellon, BC, Canada, burns fuel consisting primarily of wood from beetle-killed pine trees, but also uses bark from seawater-floated logs and construction and demolition (C&D) waste, which together could result in superheater deposits containing some heavy metal as well as some chlorine. The fourth environment was a power boiler in Gadsden, AL, USA, that normally burns coal but supplemented the coal with wood for the period of these studies. This resulted in an environment containing sulfur from the coal, as well as the alkali metal salts from the wood. This study summarizes the results from the four corrosion probes that were exposed in the boiler superheater areas of particularly hostile, but significantly different, boiler environments.

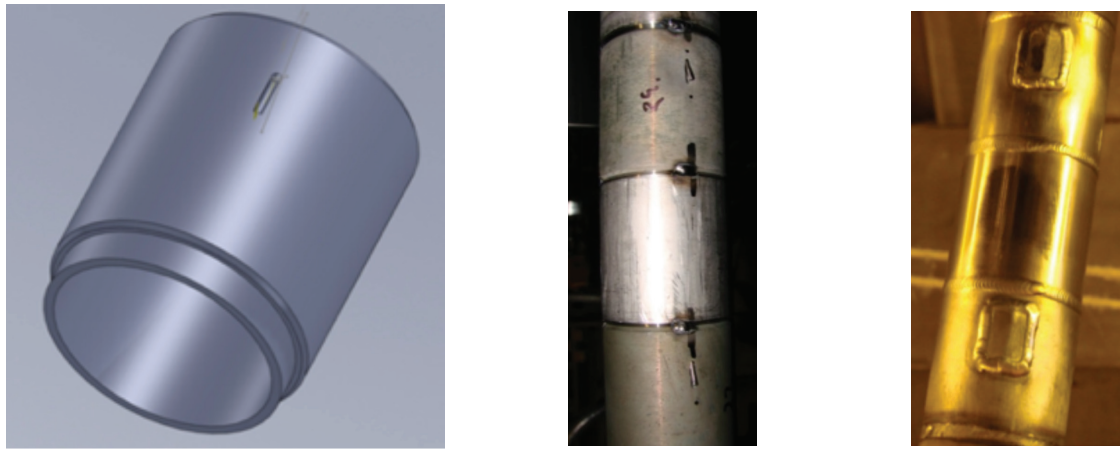
## EXPERIMENTAL PROCEDURE

### *Deposit sampling*

Deposit sampling probes were exposed in the recovery boiler and the two hogged fuel boilers. The sampling probes in the two hogged fuel boilers were prepared, exposed, and analyzed by the FPInnovations collaborators. The sampling probe exposed in the Covington boiler was air cooled and had ten thermocouples spaced every 15 cm (6 in.) along the length of the probe. These thermocouples alternated between the "top" and "bottom" of the probe, so temperatures measured on the bottom of the probe reflected the effects of radiant heating while temperatures measured on the top are more representative of the gas temperature. At the end of the approximately one week exposure period, the deposit sampling probe was removed from the boiler, allowed to cool, and then wrapped with plastic wrap to keep the deposits in place on the surface of the probe. Once the probe was safely returned to Oak Ridge National Laboratory (ORNL) in Oak Ridge, TN, USA, samples of the deposits were removed from both the top and bottom of the probe for analysis.

### *Corrosion probe design*

Each air-cooled corrosion probe was designed to contain 30 samples each at 5.08 cm (2 in.) long fabricated from 1.5 in. schedule 40 pipe or the equivalent. The samples were fabricated so that they were interlocking and each had a slot machined in the surface to accommodate a 0.0625 in. dia. sheathed thermocouple. Temperatures were measured by twenty-four thermocouples so that four of every five samples had a thermocouple attached. These thermocouples were fed through the inner diameter (ID) of the corrosion probe. The corrosion sample design, which is shown in **Fig. 1**, provides for about 1 cm of the thermocouple to be in contact with the outer surface of the sample. This design was intended to minimize the cooling effect on the thermocouples of the air flowing through the probe, thus making the measured temperature representative of the temperature of the outer surface of the samples. To assure that each thermocouple maintained full contact with the sample surface, a piece of 0.78 mm (0.031 in.) stainless steel shim stock was welded to the sample so that the shim stock held the thermocouple tightly against the sample. Pictures of the thermocouple arrangement without and with the shim stock are also included in Fig. 1. Besides showing the



*1. Schematic of the corrosion samples (left); photo of samples tack welded with thermocouples protruding from the surface of the samples (center); and photo of samples welded together and with shim stock welded in place to hold thermocouples on the surface of the samples (right).*

| Product Name | UNS No. | Fe | Ni | Cr | Mo | Co | Mn | Al | Si | Ti | C | Others |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 310H SS | S31009 | Bal | 19.10 | 24.30 | 0.25 | | 1.17 | | 0.55 | | 0.045 | |
| Haynes 214 | N07214 | 3.56 | Bal | 16.08 | | 0.03 | 0.21 | 4.22 | 0.12 | | 0.04 | Y=0.004, Zr=0.011 |
| Sanicro 28* | N08028 | 35 | 31 | 27 | 3.5 | | 1.8 | | 0.2 | | 0.01 | |
| 602CA | N06025 | 9.60 | 62.20 | 25.30 | | | 0.02 | 2.30 | 0.03 | 0.10 | 0.170 | Y=0.07, Zr=0.09 |
| HR160 | N12160 | 0.63 | Bal | 28.00 | 0.27 | 30.20 | 0.48 | | 2.75 | 0.48 | 0.056 | |
| Inconel 690* | N06690 | 9 | 62 | 29 | | | | | | | 0.02 | |
| HR120 | N08120 | 36.26 | 36.68 | 24.74 | 0.07 | 0.11 | 0.68 | 0.16 | 0.73 | | 0.057 | N=0.21 |
| Esshete 1250* | S21500 | 72 | 10 | 15 | 1 | | 6.3 | | 0.5 | | 0.1 | Nb=1, V=0.25, B=0.006 |
| 347H SS | S34709 | Bal | 9.02 | 17.21 | | | 1.31 | | 0.57 | | 0.048 | |

* Nominal values.

***I. Composition of alloys selected for exposure in the corrosion probes.***

shim stock that was welded in place over each thermocouple, this figure also shows the tack welds that were used to position and align the samples before application of the circumferential welds that rigidly connect adjacent samples. To provide additional support for the probe, which extended at least 2.1 m (7 ft) from the boiler wall, a 0.5 in. dia. stainless rod ran the length of the probe inside the corrosion samples (along with the thermocouples). A stiff spring was placed between the rod and the outside base of the corrosion probe in order to allow for thermal expansion that was expected to differ between the array of welded samples and the stainless steel support rod that was cooled by the air flowing through the probe.

For the laboratory corrosion study, eleven alloys were exposed to synthetic environments similar to those encountered in the biomass-fired boilers. The three co-investigators and the project participants selected eight of these alloys plus 347H stainless steel for exposure in the corrosion probe. These alloys and their compositions are listed in **Table I**. Nominal compositions are given for three of the alloys, while the other compositions are from actual heat analyses. The selected alloys included two alumina-forming alloys, as well as seven more traditional chromia-forming alloys. Alloy S31009 was chosen because it is currently used in the hottest areas of the Covington recovery boiler's superheater. Two other alloys (S21500 and S34709) were chosen because of good experience from similar superheater studies conducted in Europe. The two alumina-forming alloys were preoxidized at 1000°C to promote formation of the alumina layer, while the chromia-forming alloys were not given any pretreatment. Prior to assembly into the corrosion probe, the wall thickness of each sample was measured in several locations around the circumference.

The thirty samples on each corrosion probe were arranged in a repeating pattern so that samples of all but two of the materials (N06690 and N12160) were exposed to a range of temperatures. Four samples of each of the other seven alloys were positioned so that one sample of each material was near the hotter end of the probe, one sample was near the cooler end, and the other two samples of each material experienced intermediate temperatures. In addition to the effect resulting from a sample's position on the corrosion probe, the temperature of a sample varied from "top" to "bottom" in that one side was heated by the incident gas, and in some cases radiant heat from the lower boiler; so, in one case, it was observed that one side was as much as 80 Celsius degrees hotter than the other side. The arrangement of samples on the corrosion probe and the identification of thermocouple locations are shown in **Table II**, and **Fig. 2** shows a typical corrosion probe with alloy locations identified. Instrumentation for data collection and process control along with a computer were provided with the corrosion probe. A variable flow valve controlled air flow to the corrosion probe, and the setting of the variable flow valve was determined by computer software that adjusted the flow to maintain the temperature of a particular thermocouple in a selected range. Generally, a thermocouple experiencing one of the highest temperatures was selected for this control function, and this was usually a thermocouple on the bottom side near the hot end of the probe. In addition to enabling the remotely-located operator to select the reference thermocouple, the computer's display panel also permitted the operator to select the control range for this thermocouple and the data collection rate.

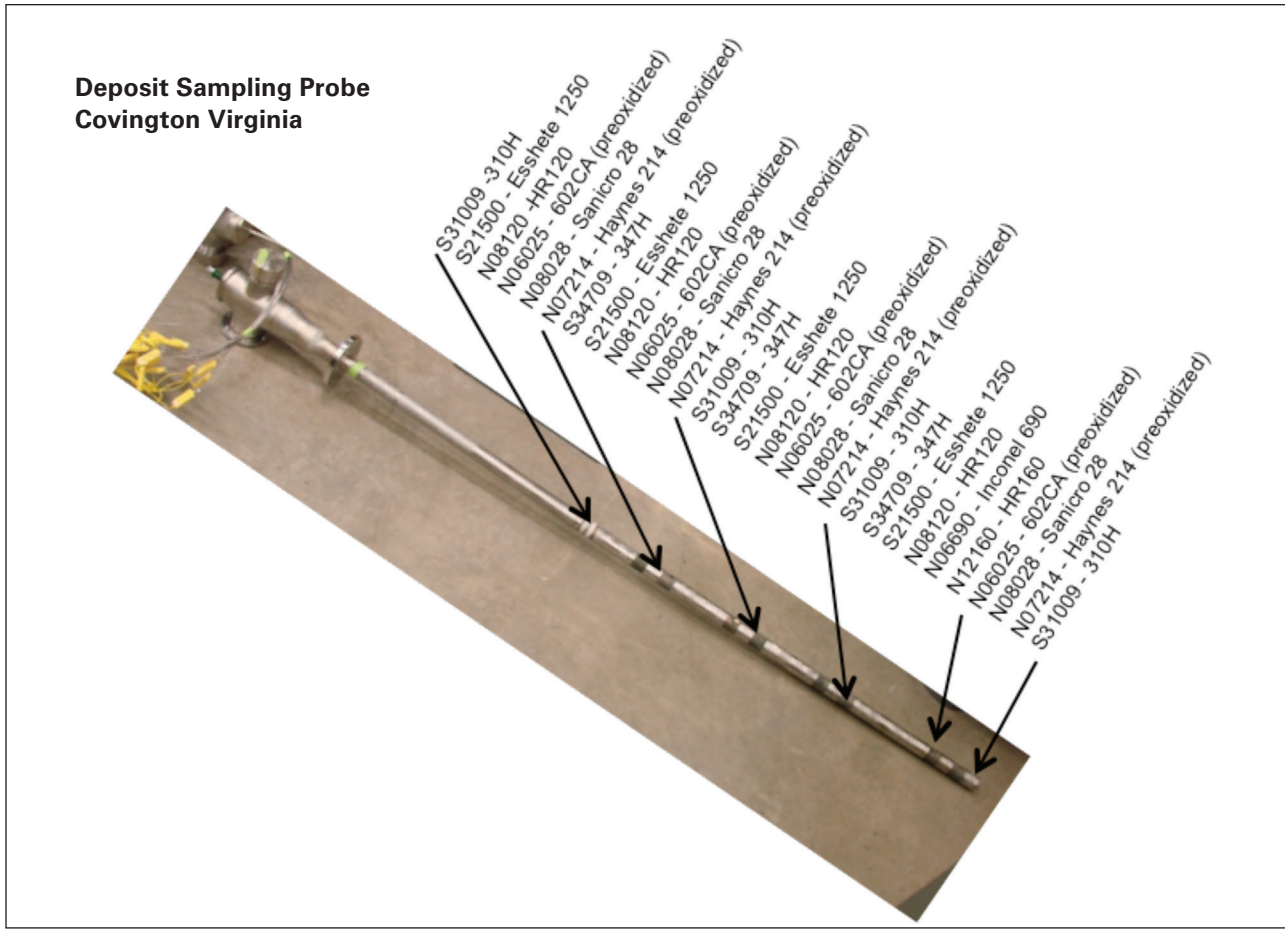
Although the computer software permitted the operator to

| Position | UNS No./Alloy | Thermocouple No. (on top of sample) | Thermocouple No. (on bottom of sample) |
|---|---|---|---|
| 1 | S31009/310H SS | 24 | |
| 2 | N07214/Haynes 214 | | 23 |
| 3 | N08028/Sanicro 28 | 22 | |
| 4 | N06025/602CA | | 21 |
| 5 | N12160/HR160 | 20 | |
| 6 | N06690/Inconel 690 | | |
| 7 | N08120/HR120 | | 19 |
| 8 | S21500/Esshete 1250 | 18 | |
| 9 | S34709/347H SS | | 17 |
| 10 | S31009/310H SS | | |
| 11 | N07214/Haynes 214 | 16 | |
| 12 | N08028/Sanicro 28 | | 15 |
| 13 | N06025/602CA | 14 | |
| 14 | N08120/HR120 | | |
| 15 | S21500/Esshete 1250 | | 13 |
| 16 | S34709/347H SS | 12 | |
| 17 | S31009/310H SS | | 11 |
| 18 | N07214/Haynes 214 | | |
| 19 | N08028/Sanicro 28 | 10 | |
| 20 | N06025/602CA | | 9 |
| 21 | N08120/HR120 | 8 | |
| 22 | S21500/Esshete 1250 | | |
| 23 | S34709/347H SS | | 7 |
| 24 | S31009/310H SS | 6 | |
| 25 | N07214/Haynes 214 | | 5 |
| 26 | N08028/Sanicro 28 | | |
| 27 | N06025/602CA | 4 | |
| 28 | N08120/HR120 | | 3 |
| 29 | S21500/Esshete 1250 | 2 | |
| 30 | S31009/310H SS | | 1 |

***II. Arrangement of samples on the corrosion probe and location of thermocouples.***

select the data collection rate, all four computers were set to record the temperature of each thermocouple once a minute during their entire operating periods. On a daily basis, the temperatures and valve setting data were transferred via a telephone connection from the on-site computer to a computer at ORNL. Plots of each day's temperature data were made and evaluated to be certain there were no operational issues. About once a week, the temperature plots were sent to the boiler operators.

At the completion of the exposure, the probe was removed from the boiler with as little loss of the deposits as was possible. Once the probe had cooled, the portion of the probe with the thirty samples was wrapped tightly with plastic to retain as much of the deposits as possible. When the probe was received at the laboratory, the orientation was carefully noted, then samples of the deposits were collected and each metal sample was cut off the probe. An example of the thirty samples is shown in **Fig. 3**. For the metallographic examination, a complete ring was cut from the approximate center of each sample and its orientation during exposure was noted. So that the exposed cross-section would be representative of the true thickness of the sample, every effort was made to make the cuts perpendicular to the axis of each sample. Any error introduced if cuts were not perpendicular would result in the remaining thickness being overestimated; thus, any error would be on the conservative side. Using the micrographs from the metallographic examinations, the thickness of remaining unaffected metal was determined for the top and bottom of each sample. Scanning electron microscopy was used to determine the extent of subsurface degradation and to collect compositional information for the reaction products on and near the surface, particularly for the samples exposed at the highest temperatures.




*2. Typical corrosion probe showing the arrangement of samples as they were assembled on the probe.*

## RESULTS

Results from examination of samples from the various corrosion probes are summarized in the following sections. The order of presentation is the order in which the probes were inserted in the respective boilers.

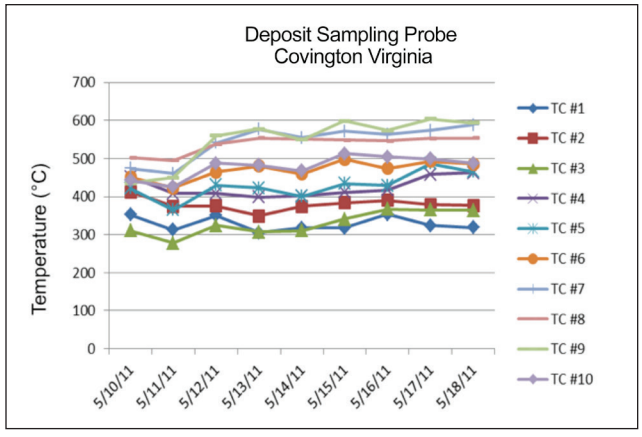
### *Covington recovery boiler deposit probe*

**Figure 4** shows the average daily temperature of the ten thermocouples over the approximately eight day exposure period of the deposit sampling probe in the Covington recovery boiler. The measured temperatures ranged from about 300°C to about 600°C [11]. Analysis of the deposits using X-ray diffraction provided results that indicated the potassium-rich compound, $K_3Na(SO_4)_2$, was among the components of the deposit [11].

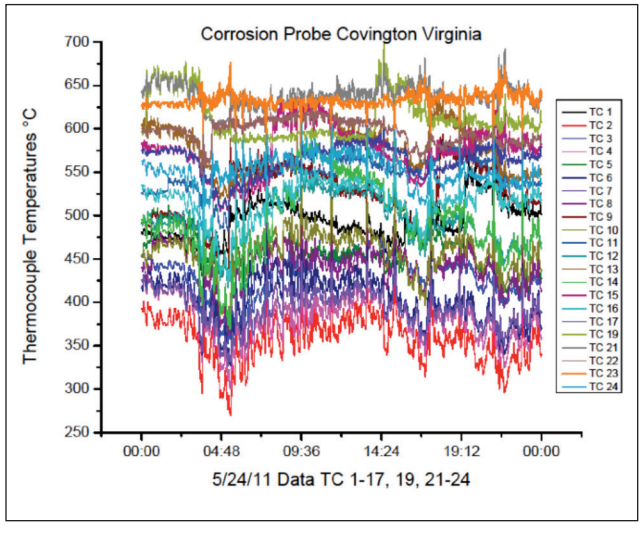
### *Covington recovery boiler corrosion probe*

The deposit sampling probe and the corrosion probe were inserted through a port on the rear wall (the side opposite the bull nose and the smelt spouts) on the 14th floor of the boiler, which was about 20 ft (6 m) below the roof of the boiler. This location was high enough in the boiler that the temperature could be controlled in the desired range with a reasonable air flow, and, because this location was well away from the superheater tubes, there were no sootblowers in the vicinity to affect or disrupt the accumulation of deposits on the probe. As noted previously, deposits from the sampling probe exposed in the Covington boiler confirmed the presence of significant amounts of potassium in the deposits.

*3. Photo of the 30 samples removed from one of the corrosion probes. Samples #6 and #10 still contain the spacers used to position the support rod in the center of the probe. Several other samples still contain the remnants of the thermocouple that was attached to the outer surface of most samples.*



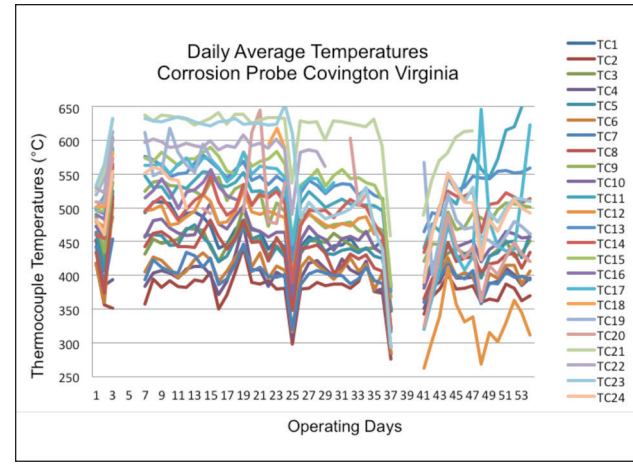

*4. Average daily temperatures for each of the ten thermocouples on the deposit sampling probe.*



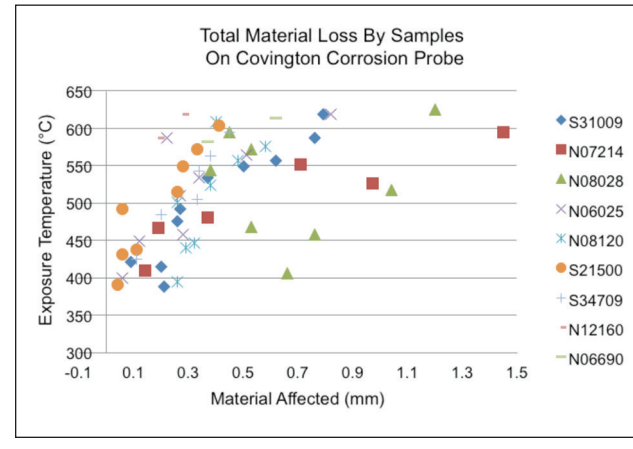

*5. Typical example of thermocouple temperatures from the corrosion probe exposed in the Covington recovery boiler. Note that the orange line shows the temperature of thermocouple #23 which was being used to control the flow of cooling air and thus the probe temperature.*

The corrosion probe was exposed for 2000 h (12 weeks), and the boiler operated under reasonably normal conditions for the great majority of that time. An example of the data collected for one day early in the exposure period is shown in **Fig. 5**. Unfortunately, several thermocouples failed during the latter part of the exposure period, so temperatures shown for some thermocouples do not cover the full 2000 h. At the conclusion of the probe exposure, the arithmetic mean temperature for each thermocouple on each day was calculated, and these results are shown in **Fig. 6**. From a plot of these average temperatures, an estimate was made for the average top and bottom temperature for each sample. During the 2000 h exposure, the temperature of every sample clearly varied considerably from the average value, so the meaning of exposure temperature is much different between the field exposures and the well-controlled laboratory tests.

In order to determine the performance of each alloy as a



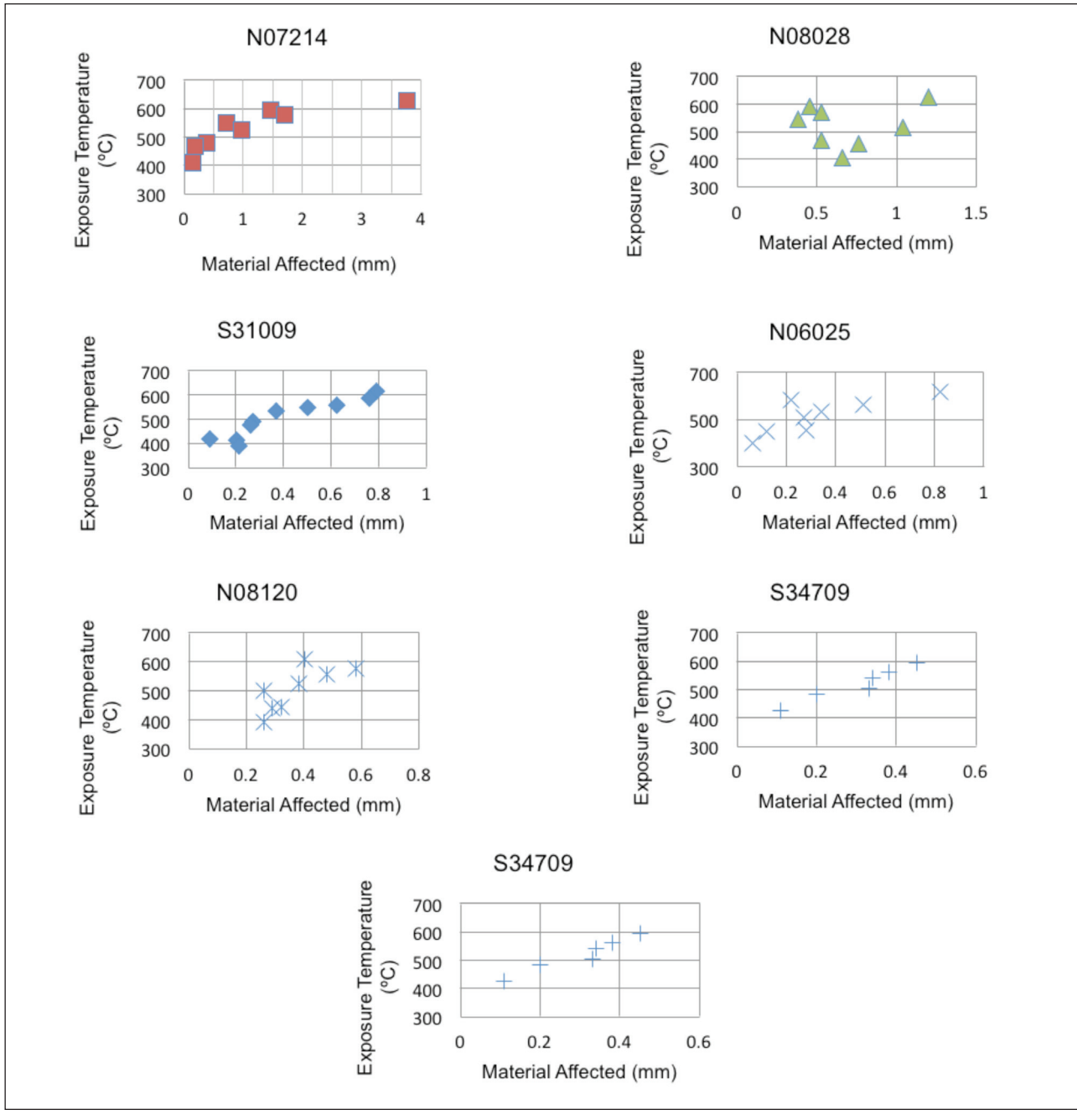

*6. Average daily temperatures of thermocouples in the Covington recovery boiler*




*7. Total affected material as a function of exposure temperature for samples exposed for 2000 h on the corrosion probe in the Covington recovery boiler*

function of average exposure temperature and to compare the performance of all the alloys, the depth of affected material (a sum of thickness loss and extent of subsurface attack) was plotted versus the estimated average temperature. Results for all the alloys exposed in the Covington boiler are shown in **Fig. 7**, and results for selected individual alloys are shown in **Fig. 8**. These results show there are several alloys that did not perform very well in this environment at and above 570°C (N07214, N08028, and S31009), while N12160 and S21500 were among the better performers. Alloy N06025 showed a very low rate of material affected around 590°C, but considerably higher rates at 560°C and 615°C.

As a means to compare the results of the corrosion probe exposure with actual boiler experience, it is important to note that S31009 has performed well under the current boiler operating conditions – presumably at a tube temperature of about 470°C. If it is assumed that the degradation rate observed at 470°C for S31009 exposed on the probe is acceptable, then it would seem reasonable that any alloy that demonstrates approximately the same rate at 570°C would be




***8. Total affected material versus exposure temperature for individual alloys exposed for 2000 h on the corrosion probe in the Covington recovery boiler***

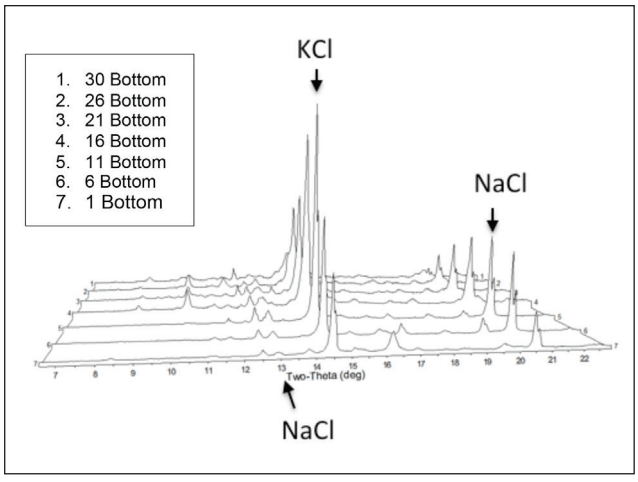
suitable for use at that temperature. On that basis, N12160 and S21500 would be expected to perform satisfactorily if used in a "high potassium" boiler operating with superheater tube temperatures around 570°C.

### *Crofton hogged fuel boiler*

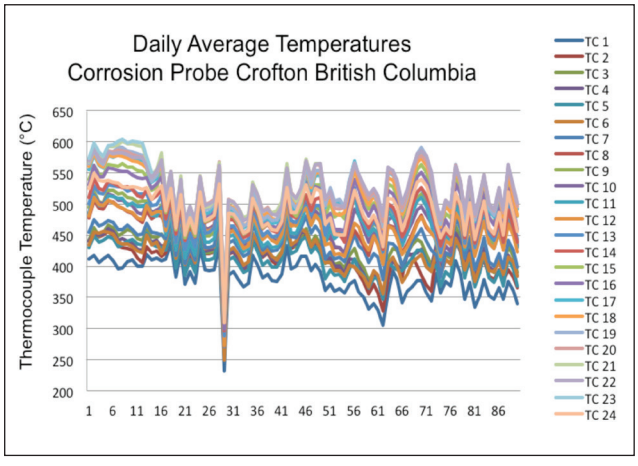
As previously noted, the hogged fuel boiler in Crofton, BC, was selected because bark from the seawater floated logs would result in a fuel with high chloride content. X-ray diffraction analysis of deposits collected from the surface of several corrosion probe samples showed a high concentration of NaCl. **Figure 9** shows the results of examination of several samples.

The corrosion probe in the Crofton boiler was inserted through a manway door in the superheater area less than an estimated 2 m below a sootblower. Consequently, some cleaning of the tube surface possibly occurred on a fairly regular basis. The probe was exposed for a total of about 2160 h, but the exposure was interrupted and the probe removed from the boiler because of a planned shutdown and water washing of the boiler about midway through the exposure period.

**Figure 10** shows the average daily temperatures for the 24 thermocouples on the corrosion probe that was exposed



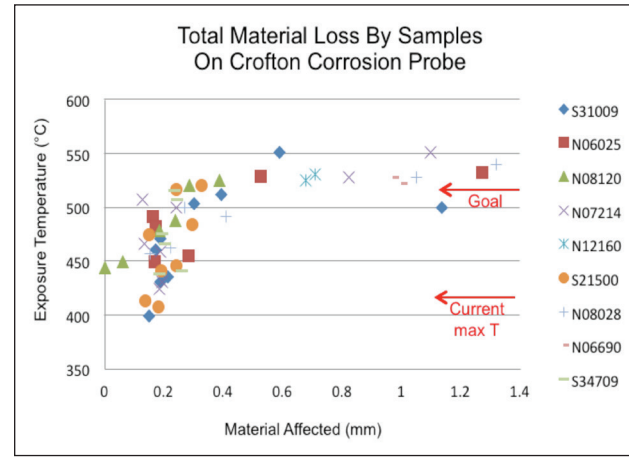

*9. Results of X-ray diffraction measurements of deposits collected from the bottom of 7 samples on the corrosion probe in the Crofton hogged fuel boiler.*




*10. Daily average temperature of thermocouples exposed about 2160 h on the corrosion probe in the Crofton hogged fuel boiler.*

in the Crofton boiler. The computer software was set to control the flow of cooling air on the basis of the temperature of thermocouple #24, but it is clear from Fig. 10 that the temperature of thermocouple #24 frequently dropped below the desired range. In these cases, the air flow was already reduced to a minimal level, so this resulted in the significant fluctuations in temperature shown in Fig. 10. An average value for the temperature of each sample was calculated, but it should be recognized that each sample experienced significant variations around the calculated value.

**Figure 11** shows the measured thickness of affected material versus exposure temperature for the samples exposed on the Crofton boiler probe. With the current maximum superheater tube temperature at about 415°C, the goal was to identify the materials with the lowest degradation rate at 515°C. This figure shows that most of the alloys had a fairly low degradation rate at 500°C, but many of the alloys showed rapid increases in degradation at slightly higher temperatures. This pattern is more clearly shown in the plots for individual




*11. Total affected material as a function of exposure temperature for samples exposed for 2160 h on the corrosion probe in the Crofton hogged fuel boiler.*

alloys displayed in **Fig. 12**. The two alumina forming alloys, N07214 and N06025, along with N08028 showed this type of behavior while S34709, N08120, and S21500 didn't appear to show such rapid increases when exposed to average temperature at and above 525°C.

### *Gadsden power boiler*

One of the boiler manufacturers participating in this project suggested that the coal fired boiler at Southern Company's power plant in Gadsden, AL, be considered for inclusion in the project because the boiler had previously been used for co-firing coal and biomass – both wood and switchgrass. After a description of the project was presented to power plant and administrative personnel, the power plant operators agreed to participate in the project and to operate the boiler continuously for an extended time with a blend of coal and wood. The original goal was to operate with up to 15% biomass, but that goal could not be achieved. The actual amount of biomass included in the coal-wood blend ranged from 8% to 15%.

This corrosion probe was inserted in a sootblower lane between superheater tube platens and is shown in **Fig. 13** just before it was removed. Deposits on the probe were a reddish color and were fairly limited in terms of the amount accumulated. Although there were a couple of interruptions in boiler operation during the early stages of the exposure, as shown in **Fig. 14**, the temperatures were far more constant than observed in the other three boilers that were studied. The total exposure period lasted for about 123 days, but the first several days were during a startup period when temperatures were low, and there were two short periods, clearly evident in Fig. 14, where the boiler briefly cooled, in one case to near room temperature. The probe was actually exposed to normal operating conditions for about 106 days or 2540 h.

The average temperatures for the top and bottom of each sample were calculated from the daily average temperatures. From these calculations, it was evident that the tops of the samples were 60-80 Celsius degrees hotter than the bottom

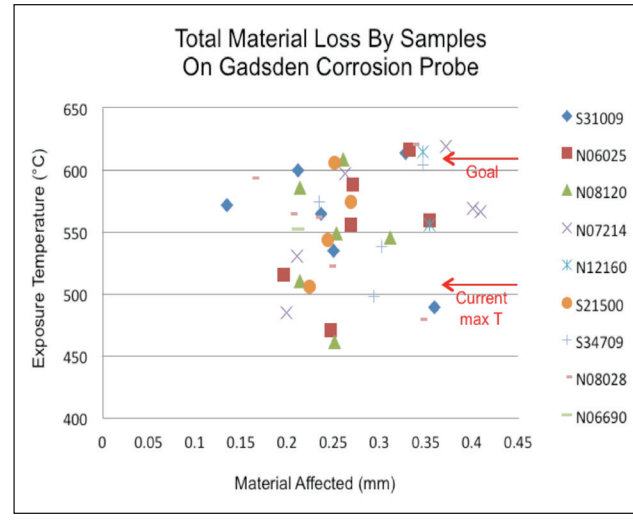

***12. Total affected material versus exposure temperature for individual alloys exposed for 2160 h on the corrosion probe in the Crofton hogged fuel boiler.***

of the samples. This is not the pattern generally seen in superheater tubes, but the boiler operators confirmed that this was the pattern to be expected for this location.

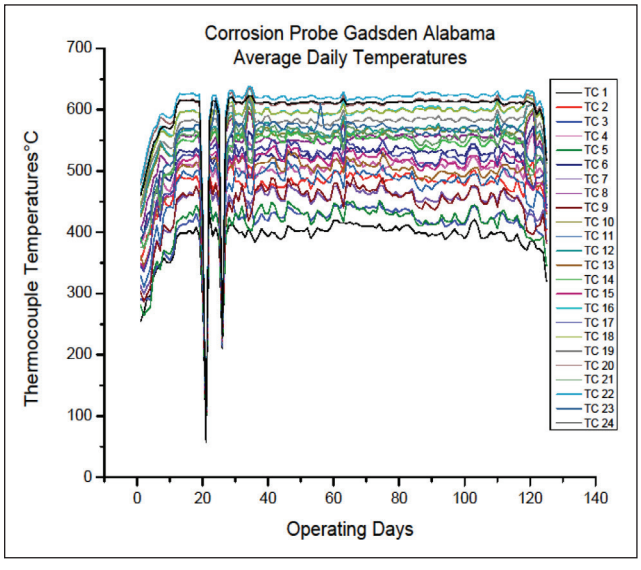
After the probe and the supporting structure were returned to ORNL, preparations were made to dispose of the portion of the probe that was just inside the boiler wall but did not include any samples. In making the routine but required check for evidence of radioactivity on the structure, it was found that low levels of lead and bismuth isotopes were present. These isotopes are decay products of uranium, and it is reasonable to assume that the low concentration of uranium in the coal resulted in deposition of these isotopes on the cooler portion of the corrosion probe. As a result, the nine samples on the cooler end of the probe could not be removed and examined. Deposits were removed from the samples on the hotter end of the corrosion probe, and the analyses identified mullite, quartz, cristobalite, hematite, and magnetite as the major components.

The 21 samples that could be examined were sectioned in the customary way, and the reduction in thickness was determined, as well as the subsurface attack. Results of those measurements are plotted as a function of exposure temperature

*13. Photo of the corrosion probe in the Gadsden power boiler just prior to its removal (photo courtesy of Billy Zemo, Southern Company).*




*15. Total affected material as a function of exposure temperature for samples exposed for 2540 h on the corrosion probe in the Gadsden power boiler.*




*14. Average daily temperatures of thermocouples on the corrosion probe exposed about 2540 h in the coal and wood co-fired Gadsden power boiler.*

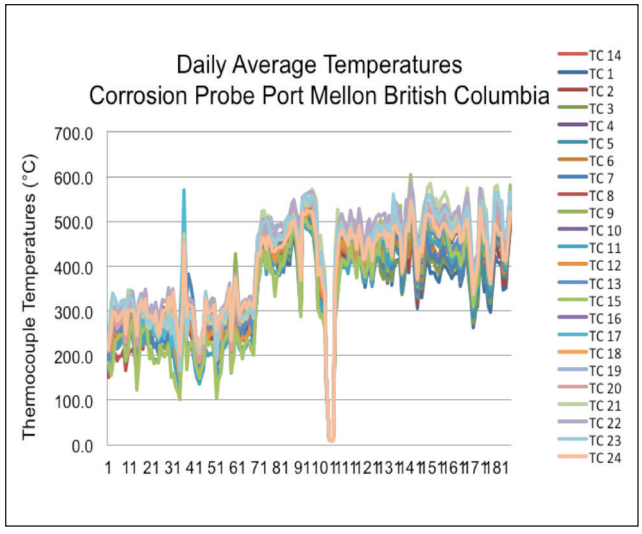
in **Fig. 15**. These results show that the degradation of the alloys in the coal-wood-fired environment was significantly less than seen for most of the alloys in the boilers fired exclusively with biomass. As can be seen from the figure, several alloys had losses in the 0.20 mm to 0.25 mm range for this exposure period.

### *Port Mellon hogged fuel boiler*

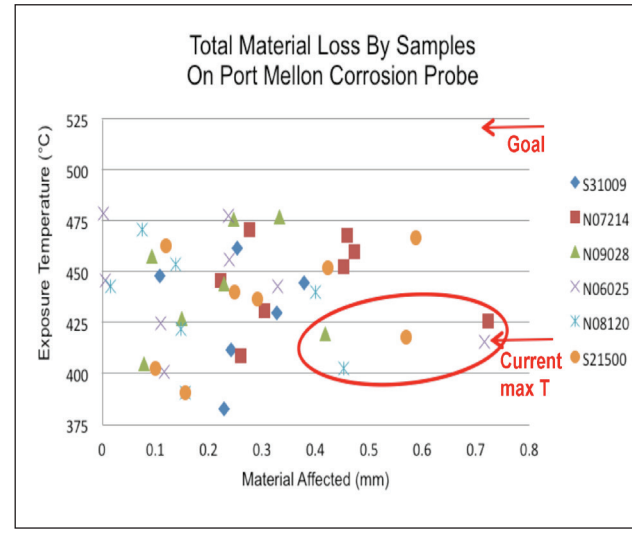
The fourth probe was inserted in a hogged fuel boiler in Port Mellon, BC, with the expectation that the boiler would be, like the Crofton boiler, firing bark from seawater floated logs. However, the infestation of pine beetles resulted in a ready availability of beetle-killed pine trees. Consequently, at the time of the corrosion probe exposure, the mill was using wood from beetle-killed pine trees, bark from seawater floated logs, and occasional barge loads of C&D waste from Vancouver. The latter of these three sources of biomass may have ultimately contributed some unexpected, but very interesting, results.

This boiler was converted to a fluidized bed system, which delayed insertion of the corrosion probe, so this was the last of the exposures to be started. Once the probe was inserted, there was a problem with the variable flow valve that made it impossible to reduce the flow of cooling air to less than the fully open position. This made it impossible to control the probe temperature, and consequently, these temperatures stayed well below the desired level. Eventually, the variable flow valve was replaced, and this permitted better control of the temperature. However, the site available for insertion of the probe was less than 30 cm (12 in.) above the bullnose, and this proximity to a water cooled surface apparently prevented the probe temperatures from reaching the desired levels. The average daily temperatures are shown in **Fig. 16**, and it is obvious that the temperatures stayed low until about the 70th day when the variable flow valve was replaced. Even after the valve replacement, for many days the highest temperatures were not much above 500°C. This resulted in not having sufficient data to predict degradation rates at and above 500°C. The exposure time at the higher temperature levels was about 118 days or about 2830 h.

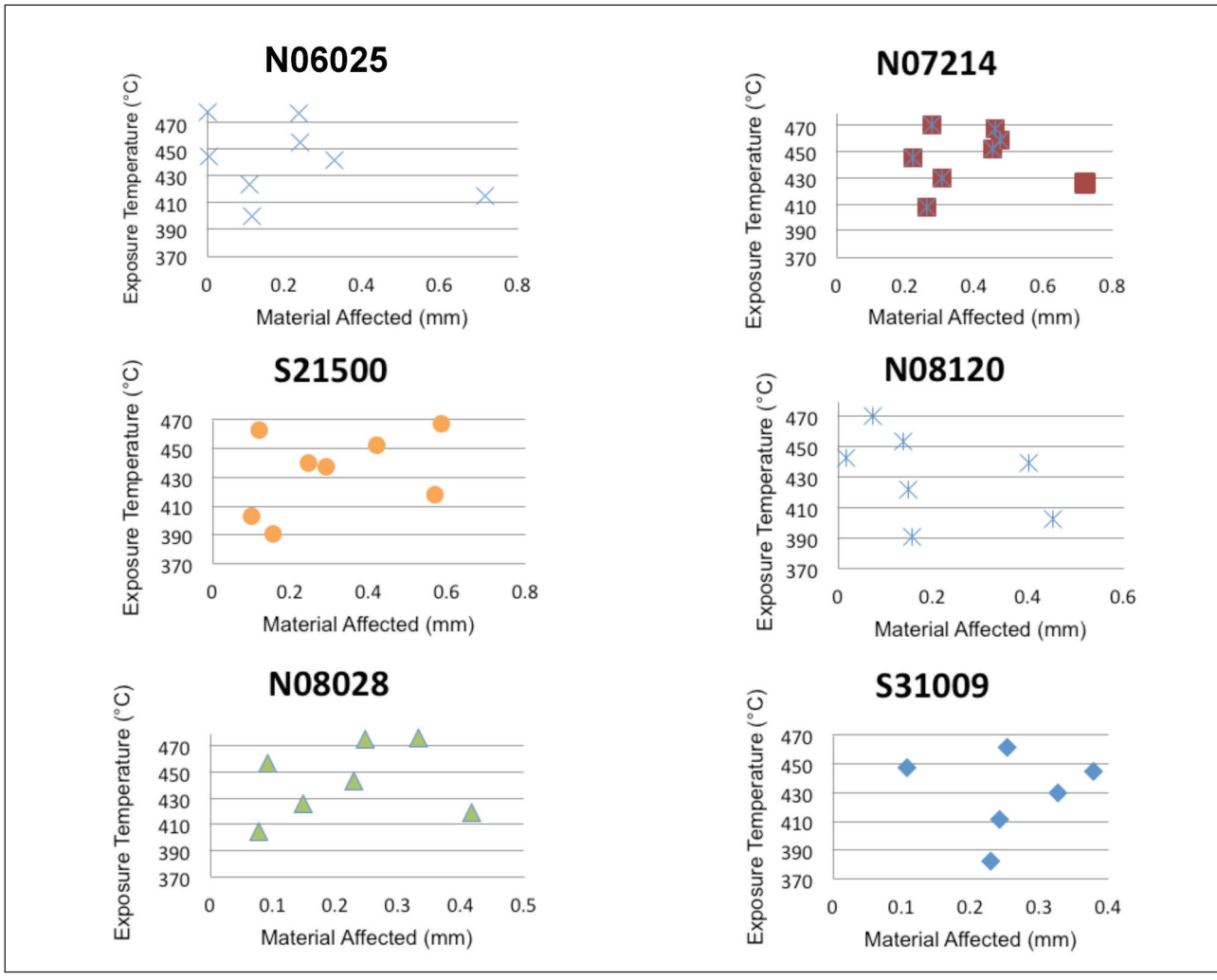
**Figure 17** shows the depth of affected material versus temperature for the various samples exposed in the Port Mellon boiler. In addition to the fact that the highest temperatures were lower than desired, it was of particular interest to note that most of the alloys showed a higher than expected degree of degradation in the 400°C-430°C temperature range. Note the data points inside the red oval in Fig. 17. The deviation from the expected degradation pattern is more evident in the plots in **Fig. 18**, which show




*16. Average daily temperatures of thermocouples on the corrosion probe exposed about 2830 h in the Port Mellon hogged fuel boiler.*




*17. Total affected material as a function of exposure temperature for samples exposed about 2830 h on the corrosion probe in the Port Mellon hogged fuel boiler.*




*18. Total affected material versus exposure temperature for individual alloys exposed for 2830 h on the corrosion probe in the Port Mellon hogged fuel boiler. Note the higher amount of material lost in the 400°C-430°C temperature range for most alloys.*

the variation in affected material versus temperature for six of the alloys exposed in this boiler.

In an effort to determine why higher rates of degradation were seen at relatively low temperatures, more thorough analysis was undertaken on deposits collected from the samples exposed in the particular temperature range. Both X-ray diffraction and Raman scattering were used to try to identify components of the deposits that were potentially responsible for low melting point compounds that might cause accelerated degradation in a fairly low temperature range. Results of the X-ray and Raman studies indicate the presence of zinc (Zn [II]) and/or lead (Pb [II]), either one of which could form relatively low melting point compounds. A more detailed review of the analysis results of the deposits collected from the sampling probe exposed by FPInnovations revealed zinc concentrations on the order of 0.2% and lead concentrations of about a third that level [15]. Studies conducted in Finland at Åbo Akademi have shown that heavy metal salts or oxides containing zinc and/or lead can cause accelerated corrosion of superheater tube alloys like 2¼Cr-1Mo steel and 347H stainless steel [16]. Based on this information, it appears likely that the higher degree of degradation seen in the 400°C -430°C range on the corrosion probe samples is due to the presence of these heavy metals that almost certainly were introduced into the boiler in the C&D waste. It will be of interest to learn if the lower temperature superheater tubes and the tubes in the bull nose of the Port Mellon boiler experience accelerated corrosion.

## SUMMARY

Four corrosion probes, each containing a total of 30 metallic samples of 9 different alloys, were each exposed in a boiler firing biomass. Three of the boilers were selected because of the extreme environment that was expected in each, and the fourth was chosen because it burned a mixture of coal and biomass.

The temperatures measured by the 24 thermocouples on each probe showed very significant variations during the exposures, which had durations of at least 2000 h.

In the potassium-rich environment of the Covington probe, two alloys (N06690 and S21500) seemed to demonstrate corrosion resistance that would suggest they would likely perform satisfactorily in a potassium-rich environment at a temperature 100°C above current operating temperatures.

For the chloride-rich environment of the Crofton boiler, essentially all alloys showed fairly low degradation rates when exposed at temperatures below about 500°C, but the six alloys that had samples exposed above about 525°C all showed greatly accelerated rates above that temperature. Both alumina forming alloys (N06025 and N07214) performed very well below about 510°C, but, as noted, both alloys had much higher rates above 525°C.

The environment of the Gadsden probe likely showed small variations as the amount of wood varied, but that variation was probably considerably less than that of the environment in the other boilers studied because of the expectation of consistent steam production from this power boiler. All samples exposed in the Gadsden boiler showed relatively low degradation rates, possibly because of the absence of significant amounts of alkali metals and chlorides.

The presence of zinc and/or lead in the environment of the Port Mellon boiler was not expected when the exposure sites were selected, but this provided some very interesting results. Essentially all the alloys (except S31009) showed higher degradation rates in the 400°C -430°C range, and this very likely can be attributed to the presence of Zn and/or Pb in the deposits. Even though the average sample temperatures on this corrosion probe were well below the desired range, enough information was collected to note that degradation rates for almost all alloys tended toward higher values even at 40 Celsius degrees or more below the temperature goal.

It is generally expected that the corrosion resistance of an alloy will improve with increasing chromium content. However, that was not a pattern that fits the results of the corrosion probe studies. Alumina forming alloys are sometimes an alternative to chromia forming alloys because of an improved resistance in some aggressive environments, but the alumina forming alloys did not consistently perform well on these corrosion probes. It is worth noting that the alumina forming alloys often perform better at considerably higher temperatures, and the temperatures to which the probes were exposed may not have been high enough to get the best features of the alumina forming alloys. **TJ**

## ACKNOWLEDGEMENTS

Dane F. Wilson's efforts in reviewing this document are recognized and appreciated. Adam Willoughby led the effort to assemble the probes and the data collection system; Tyson Jordan and Hu Longmire carried out the metallographic sample preparation and light microscopy examinations; Tracie Lowe conducted the scanning electron microscope examinations; Robbie Meisner performed the X-ray diffraction and Maggie Connatser the Raman examinations of the deposits. Employees of all four of the facilities where probes were exposed assisted with installation and removal of the probes, as well as helped in troubleshooting several problems that arose. In particular, the help provided by Curtis Clemmons at Covington, Bob Erickson at Crofton, Billy Zemo at Gadsden, and Peter Hildering at Port Mellon is appreciated. Neville Stead of FPInnovations provided considerable help in installation, maintenance, and removal of the Crofton and Port Mellon corrosion probes. Material for the corrosion samples was provided by Haynes International, Rolled Alloys, ThyssenKrupp VDM, and Sandvik Materials Technology, and other in-kind contributions were provided by Åbo Akademi University, Andritz Oy, Babcock & Wilcox, Catalyst Paper, Chalmers University of Technology, Domtar Corp., FM Global, FPInnovations, Foster Wheeler, Georgia Institute of Technology, Howe Sound Pulp & Paper, International Paper, MeadWestvaco, Metso Power, Outokumpu Stainless, SharpConsultant, Southern Company, Special Metals, University of Toronto Pulp and Paper Centre, Vattenfall Power, and

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## ABOUT THE AUTHORS

The efficiency of current biomass-fired boilers is severely limited because of corrosion associated with deposits that accumulate on superheater tubes. Identification of more corrosion resistant alloys and/or process changes that would permit boiler operation at considerably higher temperature would result in a significant improvement in efficiency.

Members of this research team have previously studied other boiler corrosion issues – floor and wall tube corrosion and cracking and superheater tube cracking and corrosion. Superheater corrosion studies conducted in Europe, primarily Finland, have produced results complementary to this latest work.

A major issue in this study was identifying biomass boilers with particularly aggressive superheater environments and then obtaining permission and suitable exposure sites in these boilers.

The severity of corrosion of some alloys in these environments was somewhat of a surprise, and we had not anticipated the apparent effect of Zn on superheater tube corrosion in the boiler burning a limited amount of construction/demolition waste.

If boiler operators want to make limited increases in superheater temperature, these results provide some guidance on selection of superheater tube materials.

***Keiser***

***Sharp***

***Singbeil***

Also, if a new boiler is being designed, these results provide guidance on what materials could be used for superheater tubes that could operate 100°C hotter than would conventionally be done.

We would like to continue our work with a more in-depth study of the more promising alloys in operating biomass-fired boilers.

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