CRACKING AND CORROSION OF COMPOSITE TUBES IN BLACK LIQUOR RECOVERY BOILERS


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ABSTRACT

Black liquor recovery boilers are an essential part of kraft mills. Their design and operating procedures have changed over time with the goal of providing improved boiler performance. These performance improvements are frequently associated with an increase in heat flux and/or operating temperature with a subsequent increase in the demand on structural materials associated with operation at higher temperatures and/or in more corrosive environments. Improvements in structural materials have therefore been required. In most cases the alternate materials have provided acceptable solutions. However, in some cases the alternate materials have solved the original problem but introduced new issues. This paper addresses the performance of materials in the lower portion of recovery boilers and, particularly, the problems associated with use of co-extruded tubes and the solutions that have been identified.

BACKGROUND

Co-extruded 304L stainless steel/SA210 carbon steel tubes were first used to make recovery boiler walls in Nordic countries in the early 1970s. Experience quickly showed these tubes to have improved resistance to environments that sometimes caused severe thinning of carbon steel tubes [1]. Consequently, by the end of the decade, application of composite tubes had been extended to service in many boilers as floor tubes, as well as wall tubes. A similar pattern of implementation of composite tubes in recovery boilers occurred in North America, but offset by nearly 10 years.

The increased operating experience gained with composite tubes in kraft recovery boilers soon led to the realization that these tubes could be subject to different corrosion problems and failure mechanisms than the carbon steel tubes they replaced. These included accelerated preferential corrosion of the stainless steel outer layer in recesses around port openings (“balding”), and cracking of the stainless layer in tubes that formed spout openings in some boilers. By the mid-1980s, cracking of the stainless steel layer of floor tubes was reported in the Nordic countries [2-5], and this was followed in the early-1990s by similar reports of cracking of the stainless steel cladding of floor tubes in North American boilers [6]. It was only a few years later that the first reports were received of cracking of 304L/SA210 composite tubes forming primary air port openings in some boilers [6].

As the widespread nature of the cracking problem in composite floor tubes first became apparent, a study funded primarily by the U.S. Department of Energy was undertaken to try to
identify the cracking mechanism and to identify solutions. A second program was eventually begun to determine why cracking and corrosion were occurring at primary air port openings. Both projects were led by Oak Ridge National Laboratory, and included the Pulp and Paper Research Institute of Canada (Paprican) and the Institute of Paper Science and Technology (now affiliated with Georgia Institute of Technology) as direct contributors. Many North American pulp and paper companies, two tube suppliers, and five boiler manufacturers provided substantial assistance and in-kind support. Collaborations and information exchanges were also established with European engineering consulting firms and research laboratories, including Åbo Akademi and VTT in Finland, and AF-IPK in Sweden. For the second phase of work on primary air port tubes, Process Simulations Limited was added to the project team. This paper summarizes the findings from these extensive research efforts.

**RECOVERY BOILER COMPOSITE FLOOR TUBE CRACKING**

**Characterization of floor tube cracking**

The floors of many boilers were inspected, and cracked floor tubes removed from boilers in North America and Europe were examined metallographically to gain information for better characterization of floor tube cracks. Photos taken after dye penetrant inspection of composite tube floors are shown in Fig. 1, and examples of the appearance of cracked floor tubes that were removed for laboratory inspection are shown in Fig. 2. Cross-sections were cut from a large number of cracked tubes, and the sections were subjected to extensive metallographic examinations. From examination of these sections, as well as sections of as-fabricated tubes, some typical features were identified. The cracks generally had significant branching, or at least did not advance perpendicularly to the outer surface, and in many cases the features on opposite sides of a crack had matching patterns suggesting that the crack had been pulled open rather than material removed by corrosion (see Fig. 3). When the cracks advanced in the stainless steel as far as the stainless/carbon steel interface, the cracks typically terminated at that point or turned and followed the interface, as shown in Fig. 4, rather than advancing into the carbon steel. In only a few isolated cases were floor tube cracks observed to advance into the carbon steel. In these cases, the tubes were always adjacent to, or the second tube away from, the side wall in a location where water floor through the tube has sometimes been measured and/or reported to be less than desired or sometimes even flowing in the reverse direction.

Information about the thermal history of a tube can also be deduced from examining the stainless steel/carbon steel interface of a composite tube in cross-section. During fabrication, a decarburized region develops in the carbon steel adjacent to the interface, and a region containing chromium carbides develops in the stainless steel on the opposite side of the interface. In unexposed tubes, the decarburized region was generally about 80 \( \mu \)m thick and contained no visible carbides. In tubes that had experienced sustained high-temperature exposure, the decarburized region was generally wider, and the interface often contained an extensive layer of carbides or other precipitates. Examples of a typical as-fabricated tube and a tube exposed to excessive temperatures are shown in Fig. 5. Overall though, very few composite tubes with such evidence of overheating have been found among all of the cracked tubes removed from service and examined throughout the history of this research program. Therefore, it is a clear conclusion that overheating (at least to the point of leaving metallurgical evidence in the microstructure) is not a necessary precursor to cracking in the boiler floor.
Fatigue data for 304L stainless steel

Because of the significant difference in the thermal expansion coefficient between the components of composite tubing, 304L stainless steel and carbon steel, it is reasonable to expect that considerable stresses could develop when the tubing is subjected to thermal cycling. To determine whether composite floor tube cracking could be attributed to thermal fatigue that was caused by thermal cycling, a review of 304L stainless fatigue data was undertaken and laboratory studies were conducted to generate fatigue data that provided more information on the behavior of this alloy. The ASME Code Sect. III, Subsect. NH design curve provided information for coarse-grained 300 series stainless steels. Figure 6 shows this design curve for 427°C with mechanical and thermal fatigue data for 304H and 304L stainless. The results of laboratory tests are shown in Fig. 7 added to the same design curve [7]. If thermal cycles from 300 to 450°C are considered, the cyclic strains would be about 0.25%. According to the ASME design curves, the fatigue life for a composite tube subjected to cyclic strains of this magnitude would be expected to be at least 100,000 cycles. As discussed in a subsequent section of this paper, there is no evidence that a composite floor tube experiences anywhere close to that number of thermal cycles.

Microstructural examination was also used to gain some information about the mechanical and thermal cycling history of the tubes. The plastic deformation that occurs during exposure of an austenitic stainless steel, such as 304L, to severe thermal or mechanical cycling causes multiplication of microstructural line defects called dislocations. The back and forth movement of dislocations during any type of cycling provides opportunities for self-annihilation or dynamic recovery. Often, this recovery is manifested by development of a substructure in which walls of high dislocation density surround relatively dislocation-free areas. This substructure is unique to fatigue loading conditions and its presence is indicative of severe fatigue loading. Its absence could, but does not necessarily, indicate that fatigue loading did not occur [8].

In order to study these dislocation structures, a very high magnification technique like transmission electron microscopy (TEM) must be used. TEM studies of cracked floor tubes have shown that the stainless steel in these tubes did not develop the microstructures characteristic of fatigue. In contrast, specimens taken from cracked air port opening tubes showed more evidence of thermal cycling than floor tubes, but not as much as samples removed from spout opening tubes, which contained the same characteristic substructure as a laboratory-produced thermal fatigue sample (Fig. 8). These results were interpreted to indicate that the floor and air port opening tubes had been subjected to thermal cycling, but not a sufficient amount to cause thermal fatigue cracking [8,9].

Floor tube temperature measurements and thermal cycling studies

Another approach to determining whether thermal cycling plays a major role in floor tube cracking was to measure the temperature on the crown of floor tubes in areas with a history of cracking and in areas where little or no cracking had been observed. To make these measurements, a 5 x 5 array of thermocouples was installed near the spout wall of a slope-floored recovery boiler that had a history of cracking in the tubes very near the spout (front) wall. The method of thermocouple attachment is shown schematically in Fig. 9, and the location of the thermocouples is shown in Fig. 10 [10].

Analysis of the data, which was collected every ten seconds for each thermocouple, showed temperature fluctuations occurred at most locations, and the duration for these “spikes” was
generally on the order of a minute or two. A plot showing one of these temperature spikes is given in Fig. 11, and a depiction of the temperature variations for the entire thermocouple array is given in Fig. 12 [10]. In this latter figure, each of the 25 thermocouples is represented by the point where the grid lines intersect, and the temperature measured by each thermocouple is represented by the color at the intersection point. When two adjacent thermocouples are significantly different in temperature, the plotting program assumes a smooth variation in temperature in the region between the two thermocouples. Within the figure, each of the six displays shows the temperatures at a particular time as indicated above each display. This shows a spike occurring on tube 50 in the second row of thermocouples from the spout wall (~0.9 m), and this spike decays within about 90 seconds.

The collected temperature data were also used to determine the number of spikes occurring on each thermocouple during a six month period. The measurements included numbers for spikes of at least 50°C at each location and for spikes of at least 100°C. For both parameters, the greatest number of spikes occurred on the thermocouples on tubes 53 and 56 at the greatest distance (1.8 m) from the spout wall [10]. There are two important findings to be drawn from these data. First, based on the spike frequency and the available information on fatigue cracking of stainless steel, the number of spikes over the operating period of the boiler does not project to be enough for thermal fatigue to be the cause of the cracking. Secondly, the area of the floor where cracking of the tubes was the greatest is an area where temperature spikes are the fewest. This study did show that timing of the temperature fluctuations correlated fairly well with the operation of the first row of sootblowers that cleaned the screen tubes and the first bank of superheater tubes. This strongly suggests that the thermal fluctuations on the floor tubes in this boiler are caused by debris falling from the screen and superheater tubes.

Characterizing the boiler environment

Smelt bed during operation - As part of a comprehensive effort to identify the mechanism of composite floor tube cracking, studies were conducted to define the chemical environment experienced by the tubes. Under operating conditions with adequate flow of water in the tubes, the outer surface of the tubes should only be in contact with solidified smelt. Several attempts were made by European collaborators to collect and characterize the composition of smelt against the surface of floor tubes [11]. In a decanting floor boiler, significant enrichment of sulfur was reported in a thin layer of smelt directly against the tube surface. This was taken as evidence for the existence of sodium polysulfide, which would be liquid within the temperature range experienced by the floor tubes. It proved impossible to confirm whether similar enrichment could occur in sloped floor boilers where the turnover of the bed material would be expected to occur more rapidly, thus preventing enrichment of sulfur against the tube.

Water washes - During the water washing of the boiler, a liquid phase will be in contact with the tubes, and for at least some of the time, the temperature will be somewhat elevated. In order to characterize the solution in contact with the tubes, samples of wash water solutions were collected from several mills as a function of time during the water washing of the boiler [12]. These samples were analyzed to determine the dissolved species. The results of the analyses of one set of samples collected from a southeastern U.S. mill are listed in Table 1. These results show that the pH of the wash solution remained fairly constant and in the range of 11.5 to 11.9, but the concentration of many components decreased with time. The concentrations of potassium and chloride decreased very rapidly while sodium, carbonate, sulfate and sulfide decreased much more slowly. Despite the relatively low concentrations for some of these components, concentrations would be expected to increase as pools of water collected in some
areas or heating of the boiler caused some of the water to evaporate. To answer the question of what the composition would be if the amount of water were limited, laboratory studies were conducted in which smelt was dissolved in controlled amounts of water.

The study of the solubility of smelt constituents in a limited amount of water produced some surprising results. The test was conducted by putting 1000 gm of smelt in controlled amounts of water (250, 500, 750, 1000 and 2000 ml) then holding the mixture for 48 hours at room temperature. After the 48 hour exposure, the water was collected and analyzed. As shown in Fig. 13, it was found that with the smallest amount of water (250 ml), sodium hydroxide and sodium sulfite were the components present in greatest concentration. As the amount of water was increased, the concentration of these two components decreased while the concentrations of sodium carbonate and sodium sulfate increased. The presence of significant amounts of sodium hydroxide was not expected, but these results provided information that had to be considered during selection of the salt compositions for stress corrosion cracking tests.

Circumstantial evidence suggesting that the presence of residual smelt on the floor during washing plays a part in the development of floor tube cracks is shown in Fig. 14. The pattern of cracking found on the floor of this boiler closely matches the location of the smelt left after the bed was burned down and the boiler water washed. As discussed below, 304L stainless is particularly susceptible to SCC within a temperature range of 160 to above 220°C. A particularly dangerous situation for cracking would therefore exist when a residual bed of wet smelt is left on the boiler floor during a dry-out fire. Floor tube temperatures can remain within the range of maximum susceptibility to SCC for several hours during a dry-out fire [12].

Laboratory studies of cracking in solutions containing hydrated salts

Since thermal fatigue was largely eliminated as a source of cracking for composite floor tubes on the basis of the above arguments, attention was turned to environments capable of causing stress corrosion cracking (SCC) of 304L stainless steel. One key requirement for SCC is the presence of a liquid phase in contact with the metal surface. As discussed above, it was difficult to imagine this condition being fulfilled during normal operation of a boiler, which left water washing as one of the few occasions in the life of a recovery boiler when the floor tubes would be exposed to a liquid phase. The key questions were whether the water wash environment could cause SCC, and if so, was the time of exposure long enough to initiate cracks in the tubes?

As discussed in the previous section, water washing a recovery boiler subjects the hot floor tubes to a chemical environment rich in sulfide, carbonate, hydroxide, sulfate and other oxidized sulfur compounds. This is particularly the case when a large residual bed is left in contact with the floor tubes without being burned down. Constant stress tests were used to expose tensile and ASTM G-30 U-bend specimens to mixtures of sulfide, hydroxide and carbonate at temperatures between 100°C and 250°C. Early experiments demonstrated quite conclusively that SCC of 304L stainless steel will occur over a temperature range between about 160°C to more than 220°C in hydrated mixtures of these salts (Fig. 15) [13]. Furthermore, cracks were initiated in very short times (<60 mins) in some of these tests. The presence of sulfide was found to be essential for SCC, and cracking was more severe as the content of hydroxide in the salt was increased [13,14]. Significantly, SCC was induced in test samples exposed only to a moist salt mixture of sulfide and carbonate with no added hydroxide, also at temperatures between about 160 and 200°C – conditions which closely match those expected in the early stages of a water wash. SCC will not occur at temperatures lower than about 160°C within the
concentration range of chemicals that might be expected during water washing, but has been demonstrated at temperatures as low as 60°C in a highly concentrated or saturated solution of sulfide and hydroxide [13]. It is noteworthy that the stress-corrosion cracks formed in these laboratory tests were branched and transgranular and very similar to those reported in metallographic examinations of cracked composite tubes removed from recovery boiler floors [8,13,15].

The SCC data suggest that a narrow window of susceptibility to cracking exists when the boiler floor tubes are still hot, and covered by a relatively thick insulating layer of smelt. In the early stages of a water wash, saturated wash water will pass over the tubes, or moisten the smelt in contact with the tubes, forming the perfect environment for initiation of SCC.

If 304L was so readily susceptible to SCC in these environments, the obvious question to ask was whether or not other alloys were more resistant. Significantly, laboratory tests showed that no alloy available for manufacture as composite tubes is immune to SCC in these environments. ASTM G-30 U-bend specimens made from generic alloys were exposed to a simulated water-wash environment consisting of mixtures of either 75 wt% Na₂S + 25 wt% NaOH at 180ºC or 20 wt% Na₂S + 80 wt% Na₂CO₃ at 160 ºC. The former environment is thought to be severe relative to typical boiler exposure, while the latter environment is considered to be more realistic, and typical of many boilers [16]. In both cases, a nitrogen-fed atomizer was used to maintain a continuous mist of water over the surface of the salt mixture to maintain the presence of a liquid phase in contact with the U-bend specimen.

Note that data from U-bend tests are subject to considerable variability, and the results should be interpreted accordingly. Nonetheless, significant differences in resistance to stress corrosion cracking were observed across the range of alloys evaluated. Test data for the less aggressive test conditions are not shown. In those tests, only 304L cracked in a substantial fashion. Small incipient cracks (no more than one or two grains deep) were found on the alloy 825 specimens, and no cracks were observed in the alloy 625 specimens.

Selected data are shown in Fig. 16 for the more severe test environment. Overall, 304L was observed to be very susceptible to SCC in all metallurgical conditions, while alloy 825 and alloy 625 were successively more resistant to cracking in their wrought forms. When the alloys were sensitized by heat treatment, there was only a small change in crack propagation observed for each alloy, relative to the non-heat treated specimens.

Specimens subjected to cold-work proved to be least resistant to SCC. In particular, U-bends made from 50% cold-worked alloy 825 and alloy 625 were as susceptible to stress corrosion as 304L in these tests. All cracking was found to be transgranular, with the exception of the cold-worked alloy 625. In this latter case, the cracks were found to have propagated intergranularly. This mode of crack propagation is consistent with reported cracking of alloy 625 composite tubes in the field [12].

**Effect of stress state on composite floor tube cracking**

**Modeling of stresses in floor tubes** - In order for essentially all cracking mechanisms to be operative, the stresses on the component must be tensile during some stage of its operation. In order to estimate the stresses on the surface of the stainless steel portion of composite tubes, finite element modeling and residual stress measurements were used to provide information on the stress state of the tubes as well as validation for the model predictions.
The finite element modeling utilized the commercial software ABAQUS [17] to predict the stresses that developed when composite tubes, with previously measured fabrication residual stresses, were welded to a clad membrane to produce the tube panels [18]. The model was extended to account for the effects of tube pressurization and the application of heat on one side to produce a temperature gradient across the tube wall on the fireside of the boiler. This modeling predicted that before being heated the first time, the axial stresses were compressive and the circumferential or hoop stresses were tensile in the stainless steel layer on the tubes in the tube panel. However, as shown in Fig. 17, both became compressive as the panel was heated from room temperature to the operating temperature, but when the panel was cooled to room temperature the axial and hoop stresses became tensile. As will be described in the next section, room temperature stress measurements confirmed these stress predictions.

Finite element modeling of stresses in the carbon steel layer near the interface on the fireside showed that axial stresses are compressive, thereby tending to prevent cracks from propagating into the carbon steel layer of a tube. However, in the membrane axial stresses are tensile in both 304L and carbon steel layers near the interface, so that transverse cracks can advance into the carbon steel layer as has been observed in some floor membranes.

In order to evaluate materials that might be considered alternatives to the 304L in composite tubes, the modeling studies were repeated for alloy 625/carbon steel and modified alloy 825/carbon steel composite tubes. Manufacturing stresses in these composite tubes were assigned based on X-ray and neutron diffraction measurements. Modeling of welding to make the tube panels showed development of tensile hoop stress and compressive axial stress at the tube crown. Upon heating to operating temperature, stresses changed in magnitude but not in sign. Upon cooling of the tube to room temperature, the stresses returned to their original values indicating that they remained elastic through the entire cycle. An important aspect of these results is that axial stresses for both modified alloy 825 and alloy 625 remain compressive throughout the cycle. Observations of cracked floor tubes revealed that most cracks were circumferential and hence their growth would be aided by axial tensile stresses. On this basis, it would appear that modified alloy 825 and alloy 625 are better choices than 304L stainless for the outer material of composite tubes.

The information used to draw the conclusion on alternate materials was from a generic modeling study where stresses were calculated for model alloys as a function of yield stress and thermal expansion coefficient. In order to avoid stress conditions under which stress corrosion cracking or thermal fatigue could occur, tensile stresses on the tube surface should be avoided and stresses should not exceed the elastic limit anytime during service. These modeling results were used to generate a plot showing regions in the yield stress vs thermal expansion coefficient graph where the constraints on stress were satisfied. As shown in Fig. 18, the properties of alloys 625 and 825 put both materials in the “preferred” region where the stress conditions are more desirable [18].

**Stress measurements on unexposed and exposed floor tubes** - The measurement of residual stresses in composite tubes has been accomplished using two techniques [19]. X-ray diffraction can provide information on the residual stresses on or very near the surface of a sample. This technique takes advantage of any shift in the location of diffraction peaks to determine if there is any change in lattice parameters resulting from compressive or tensile stresses on the component being examined. In order to make stress measurements well below the surface of the component, more penetrating radiation has to be used. This has been done using neutron radiation generated by a research-oriented nuclear reactor.
Measurement of residual stresses on the surface of unexposed 304L stainless/carbon steel composite tubes from both major manufacturers showed both axial and circumferential stresses were compressive but a cyclic stress pattern was measured along the length of the tube. This cyclic pattern was attributed to the straightening operation that is the final fabrication step used by at least one of the tube manufacturers.

Residual stress measurements were also made on sections of previously exposed composite tubes that were part of a tube panel removed from a recovery boiler floor, and as predicted by the finite element model, the axial and circumferential surface stresses were found to be tensile. These measurements provide validation for the composite tube residual stress modeling. Field measurements of residual stresses were made on modified alloy 825 clad floor tubes before start-up of the boiler and after about a year’s service. The measured stresses remained compressive as predicted by the finite element modeling.

To provide experimental results on the stresses in tubes at operating temperatures and higher, neutron diffraction was used to measure the stresses in the stainless steel layer of a composite tube while the tube was being heated. As the tube was heated from room temperature to a nominal operating temperature of about 300°C, the stresses at mid-thickness of the stainless layer changed from tensile to compressive as predicted by the finite element model.

Conclusions for composite floor tube cracking

- Cracking of composite 304L stainless steel/carbon steel floor tubes has been seen in every type of recovery boiler employed in North America. Of the hundreds of cracked tubes examined during this project, almost no cracks were found that progressed past the stainless steel/carbon steel interface in any of the floor tubes examined. The few exceptions to this observation were in tubes that were adjacent to the side walls of the boiler in a location where water circulation has sometimes been observed to be poor.

- The information collected does not support the idea that thermal fatigue is the mechanism responsible for composite floor tube cracking. It is more likely that a stress corrosion mechanism that involves sodium sulfide at a somewhat elevated temperature (≥160°C) is an essential component in the mechanism. Laboratory tests have shown that exposure of stainless steel in hydrated sodium sulfide can cause fairly rapid cracking if the temperature is sufficiently high and the stresses in the tube are tensile.

- For stress corrosion cracking (SCC) or a mode that incorporates some aspect of SCC, there are some conditions that must be met for the mechanism to be operative: sufficient tensile stress, proper temperature range, and appropriate chemical environment. The studies indicate that all of these conditions are satisfied only when the boiler is being cooled during a water wash, heated during a dry-out firing, or heated after a shutdown. Consequently, cracking can be avoided by completely burning out the bed before beginning a water wash, by delaying the start of the wash until the tube surfaces are cooler than 150°C, and removing moist (hydrated) smelt or concentrated wash water from the floor before heating the tubes above 150°C.

- Finite element modeling and residual stress measurements have established that the stresses in the stainless steel layer of a composite tube change from compressive to tensile as the tube is cooled below operating temperature and change from tensile to compressive.
compressive when the tube is heated to near the operating conditions. These studies show that modified alloy 825 and alloy 625 do not develop tensile stresses during normal operation, and these alloys, at least on this basis, are suitable alternatives to 304L stainless steel for composite floor tubes.

**CRACKING OF SMELT SPOUT OPENING TUBES**

Cracking in the tubes that form smelt spout openings or the tubes adjacent to the opening tubes were reported fairly soon after composite tubes were first used in wall panels [6]. The environment around smelt spouts might be expected to be especially severe because of the intermittent splashing that occurs as the smelt drains through the spout.

**Field observations of cracking in smelt spout opening tubes**

Although this project has not concentrated on the cracking seen in smelt spout opening tubes to the extent that floor tube and primary air port opening tube cracking has been examined, there have been opportunities to examine cracked tubes in the field and in the laboratory. Examples of cracked smelt spout opening tubes observed during boiler inspections are shown in Fig. 19. Both craze and circumferential cracks have been observed. In some cases the cracking is fairly shallow, but in other cases the cracks have been found to continue into the carbon steel indicating the stress state at the stainless steel carbon steel interface of spout opening tubes is different from that in floor tubes.

**Laboratory observations of cracked tubes**

A number of cracked smelt spout opening tubes have been examined to get some indication of the depth of cracks. In addition to the conventional 304L/carbon steel composite tubes, co-extruded tubes with an outer layer of modified alloy 825 or alloy 625 have been examined. It is worth noting that cracking was seen in all the openings examined. A number of tubes made with modified alloy 825 were examined, but the cracking in those tubes was sometimes quite shallow. The observation of shallow cracks matched the reports from some mills that cracks on modified alloy 825 tubes could sometimes be removed with light buffing. Only one opening fabricated with alloy 625 tubes was examined, and, as shown in Fig. 20, intergranular cracking was found on those tubes. All of these alloys have been observed to corrode when used as smelt spout opening tubes.

**CRACKING OF PRIMARY AIR PORT OPENING COMPOSITE TUBES**

During the latter stages of the study of composite floor tube cracking, it was noted that an increasing number of mills were reporting cracking of the tubes that form primary air port openings [9,21]. Both craze and circumferential cracks were reported, and in all cases the cracks were limited to the lower portion of the air ports. Most frequently, the cracks were on or very near the bent portion of the tubes at the bottom of the port, but the cracks were sometimes seen some distance below the bottom of the port. The most significant aspect of this cracking was that, unlike floor tube cracks, some of the cracks continued through the stainless/carbon steel interface into the carbon steel. This was reason for serious concern and an indication that this cracking was not totally like that seen on composite floor tubes. Consequently, as the study of composite floor tubes reached a conclusion, the research efforts were directed toward determining the cause of, and solutions for, cracking of the primary air port tubes.
Field observations of cracking of primary air port tubes

Members of this research team visited many North American mills to observe the inspection of the composite tubes and particularly the tubes forming primary air ports. Cracking was seen on air port tubes for most boiler types utilized in North America. Examples of cracking are shown in Fig. 21. In this figure, examples of craze and circumferential cracking are shown on air ports with cast inserts, and circumferential cracking is shown on air ports with welded sleeves. It is important to note that cracks in air port tubes were not always easy to detect. Cracks were most likely to be found if, prior to dye penetrant inspection, the surface corrosion products were removed from the tube by cleaning with a 120 (or smaller) grit “flapper wheel” until shiny metal could be seen [22,23].

Laboratory observations of cracked air port tubes

A number of recovery boiler owners/operators have provided sections of wall panels that were removed in order to replace primary air ports. These sections were subjected to a dye penetrant examination, then samples were removed from areas where crack indications were found. These samples were mounted so that the cross section of the tube wall could be viewed, and the samples were carefully ground and polished, and when considered appropriate, etched with an acid solution to highlight microstructural features. Examination of these cross-sections provided information about crack characteristics and whether the cracks continued into the carbon steel. Any evidence of excessive heating of the tube would also be revealed by this examination.

Figures 22-24 show cracks in tubes revealed by dye penetrant inspection along with views of cracks in the tube cross-sections that were selected on the basis of the dye penetrant examination. The 304L stainless steel clad tube used for the primary air port opening shown in Fig. 22 had severe circumferential cracking just below the bottom of the air port. As shown in the figure, metallographic examination of cross section samples showed that some of the cracks advanced into the carbon steel. The primary air port shown in Fig. 23 was taken from a different recovery boiler, but the opening tubes were also fabricated with 304L stainless steel. The cross sections of cracks that are shown in Fig. 23 reveal that cracks advanced to the stainless steel/carbon steel interface, but no significant penetration into the carbon steel occurred. Alloy 625 co-extruded tubing was used to form the air port shown in Fig. 24, and as shown in the micrographs significant cracking occurred in the tubes. The laboratory examination did not find any cracks that advanced into the carbon steel.

Temperature studies

Since thermocouples were successfully used to obtain information on the temperature variations experienced by floor tubes, it was a logical extension to consider installing thermocouples on air port tubes. It was not clear that temperature variations should be expected, but it was initially decided to install thermocouples on primary air port tubes in three mills - two with a history of primary air port tube cracking and one new boiler nearly identical to one of the other two, but with no history of cracking. In the two boilers where air port tube cracking had been observed, thermocouples were installed on air ports with a history of cracking and air ports where no cracking had been previously observed. In both cases, thermocouples were mounted in the lower portion of an air port on the bent portion of the tubes in the general area where cracking was most often seen. Photos of typical thermocouple installations are shown in Fig. 25.
An example of the results for one of the mills is shown in Fig. 26 where it can be seen that the temperature fluctuations were much larger in amplitude on the air port where cracking had previously been observed [9]. This pattern of larger fluctuations occurring on air ports where cracking had been observed was also seen at the second mill. In the third boiler where no cracking had been observed, some fluctuations were seen but there was no preferred pattern and no regular pattern of large fluctuations.

Ultimately, thermocouples were installed on primary air ports in ten different boilers. Table 2 lists the ten boilers, provides some of the specifications for each and tells which experienced cracking of the primary air port tubes [24].

In one of the mills, in addition to the thermocouples installed near the bottom of the air port, thermocouples were installed at a number of other locations around the air port opening. The locations of these installation points are shown on the left side of Fig. 27. It was found that the largest fluctuations occurred in the areas where cracking was generally most severe (locations 1 and 2), while the smallest fluctuations were consistently in the area the farthest from the opening (location 11). The thermocouples at the top of air ports (locations 5, 6, 7 and 8) consistently ran hotter than the lower thermocouples but had fewer fluctuations with smaller amplitude. Thermocouples near the opening, but at or below the midpoint (locations 3, 9 and 12) sometimes showed considerable activity but had very little activity at other times. The right side of Fig. 27 shows some of the typical temperature patterns for several of the thermocouples around an opening. A few other mills had thermocouples in some of these locations, particularly positions 5 and 6, and there was good consistency between boilers with respect to the patterns likely to be observed at any one location.

To resolve whether the measured temperatures were truly representative of the temperatures at the tube surface, a tube with a modified version of chordal thermocouples, was also instrumented with thermocouples like those used on the air port opening tubes. Since chordal thermocouples (which are embedded in the tube wall) are considered to give representative indications of tube wall temperatures, they were used as a reference for thermocouples mounted on the tube surface. The tube was air cooled and the surface was heated with high-intensity lamps to simulate the sudden application of a heat pulse. Although the surface and chordal thermocouples did not give exactly the same temperatures, the measured values were substantially equivalent such that the surface thermocouple measurements could be considered representative of the actual conditions on the surface of the tube.

A further effort was made to characterize the severity of temperature fluctuations on the tube surfaces [25]. The parameters defined as a result of this study are identified as cycles and excursions. A cycle is defined as a temperature increase of at least 75 C° from the previous minimum temperature followed by a decrease of at least the same magnitude from the previous maximum temperature. The choice of this particular temperature change was based on finite element modeling studies showing 75 C° as approximately the temperature change required to take the 304L stainless steel layer on a composite tube from the yield state in compression to the yield state in tension. An excursion is defined as a data point for which the temperature is at least 450°C. Since data points are collected every ten seconds, six excursion data points would be interpreted as representing operation at a temperature of at least 450°C for an accumulated time of one minute. Selection of the 450°C temperature was based on many observations of instrumented air port tubes. Thorough documentation of each boiler showed that instrumented ports that were cracked experienced significant periods where the temperature was above 450°C. Consequently, that temperature was selected as the lower limit for the definition of
excursions.

In addition to the temperatures around the primary air port openings questions were raised about whether temperature fluctuations would occur on the secondary air ports in a boiler experiencing primary air port cracking or on the windbox side of the primary air port tubes. Temperature fluctuations at the secondary level would indicate the environment causing the heat pulses also exists at the secondary level, and fluctuations on the windbox side of opening tubes might indicate disturbances in the flow of pressurized water in the tube as a result of local heating on the fireside. To address both of these issues, thermocouples were installed on the bent portion of the opening tubes at the bottom of four secondary air ports and near the top of primary air ports on the windbox side of two tubes. As shown in Fig. 28, surface temperatures of tubes forming secondary air port openings showed very few fluctuations. The cleaning of the openings by the port rodders appeared to cause the greatest variations in temperature. The thermocouples on the windbox side of air port tubes similarly showed very little variation in temperature (see Fig. 29) indicating that any flow disturbances were not intense enough to be reflected by temperatures on the windbox side of the tubes.

**Cause of temperature fluctuations**

Based on many years of temperature monitoring along with periodic boiler inspections, it became apparent that the magnitude of temperature fluctuations on thermocouples near the bottom of an air port were a good indicator of the likelihood of cracking occurring in the tubes that form the air port opening. Consequently, it became important to determine the source of the intense local heating that caused the abrupt temperature changes. In an effort to identify the heat source, several approaches were used. First, a specially developed camera that could be inserted into the boiler through a primary air port opening was used to try to characterize the activities on the surface of the air port tubes. Secondly, modeling of possible heat sources, particularly oxidation of sulfide to sulfate and combustion of liquor droplets, was performed. In addition, temperature patterns were monitored while changes in operating parameters were conducted as a means to estimate the effect of different boiler conditions.

**Video imaging of primary air port tubes** - The use of temperature patterns to monitor changes in the air port environment is being complemented by video imaging [26]. Team members have developed a cooled camera that is specially designed to be inserted through a primary air port into the boiler (see Fig. 30). Once in the boiler, the camera can be directed to observe what is occurring on the surface of the tubes. Figures 31 and 32 show the camera’s view of the air port tubes during a shutdown, and the view of the boiler during operation with a low and high bed. This camera has been used, along with the thermocouples, in an effort to determine what might be happening, physically and/or chemically, to cause the temperature changes. These studies have shown a thin coating of condensed and frozen material is always present on the fireside of the wall tubes and membranes. Molten salt frequently flows over the coated tube and membrane surfaces, and under some conditions, significant amounts flow across areas of the tubes where cracking has been observed. The camera studies have also shown black liquor particles in a wide range of consumption states (evaporation of water, volatilization of organic material or melting of inorganic material) with rapidly varying deposition rates on the tubes at the bottom of the primary air ports. Steady temperatures, close to the saturated water temperature of the steam/water in the tubes, were demonstrated to be largely due to a quiescent bed completely covering the surface of the thermocouple shields. Likewise, steady temperatures within a band approximately 80 to 100 C° higher were recorded when the bed was extremely low, and the thermocouple shields were completely exposed to the radiant
energy within the furnace cavity.

Temperature increases of up to ~100 C° above the baseline (just above water side temperatures), are associated with particle removal, exposing the thin coating on the tube surface. The particles are primarily removed either by an increase in molten salt flow down the surface of the tubes or a change in the balance between particle deposition and consumption rate. None of these conditions has been shown, by itself, to be the source of high temperature excursions above 450°C on the thermocouples.

Modeling of local heating - A three-dimensional finite element model was used to predict the temperature variations that might occur on a primary air port composite tube subjected to localized changes in the heat flux. In keeping with the observations from the camera work, two sources of heat release at the fireside surface of the tube were considered – combustion of black liquor droplets and oxidation of Na2S from the smelt layer [24].

For both cases, the model used the assumptions that the inside surface of the tube was in contact with water at 295°C and the increase in heat flux was assumed to occur over a 2 x 2 element area on the lower portion of the bent tube, as shown in Fig. 33. The area of localized heating is approximately 375 mm². Furthermore, it was assumed all of the heat generated by the combustion is directly felt by the tube surface, whereas in practice the tube fireside surface is nearly always covered by a thin layer of frozen smelt; this has been documented by the video camera.

For the case of heat release from the combustion of black liquor droplets on the tube surface, the contributions from the volatile combustion and the char burning stages were considered. It was assumed the total heat generated can be approximated by a heat flux profile which increases linearly over a fairly short period of time (1.5-2.5 s), before decreasing more gradually to the initial value. It was also assumed that the entire 2 x 2 element region of the tube surface was simultaneously under the influence of liquor droplets undergoing combustion. The variation in temperature at the tube surface due to the increased heat flux from the combustion of liquor droplets is shown in Fig. 34 for three different droplet sizes. The smaller the droplet size, the higher is the peak heat flux and the temperature increase, and also the faster is the drop in temperature to its initial value. Since the heat flux is computed using an area measure based on the initial diameter of the droplet, the smaller droplet leads to a greater heat flux. It should be noted the smaller droplet size causes a larger increase in temperature, but the duration is not very long.

The other source of heat for a localized increase in temperature considered in the analyses was the exothermic reaction of smelt oxidation, which converts Na2S to Na2SO4. The maximum heat generation by the oxidation of a smelt layer on the tube surface is also estimated. It is assumed sufficient oxygen is available so all the Na2S in the smelt is oxidized. In this case, the heat release was assumed to occur over a fixed period of 10 seconds, with a linear increase in heat flux over 3 seconds, followed by a linear decrease over the next 7 seconds. The heat flux increases with the thickness of the smelt layer as does the maximum temperature at the center of the heated region (Fig. 35). Similar to the previous case, all of the heat from the smelt oxidation is assumed to go into heating the tube surface.

The analyses described show smelt oxidation is capable of causing a fairly large increase in temperature, although the magnitudes shown are based on calculations with several simplifying assumptions. The possible insulation offered by the frozen smelt layer has not been included in
the analyses, and this would lower the maximum temperature during the localized heating. Nevertheless, the modeling results show smelt oxidation can lead to a fairly high heat flux and significant increase in temperature, while the combustion of black liquor droplets leads to a comparatively smaller temperature rise. Thermocouple data recorded at 10 second intervals show, in some instances, the tube surface experiences elevated temperatures for significant periods of time, whereas the temperature variations shown here last for less than a minute. However, these analyses only considered “single event” cases, and it may be important to consider sustained heat release due to smelt running down the tube surface or continuing delivery of black liquor droplets to the tube surface over much longer periods of time.

**Effect of stress state on primary air port cracking**

Measurement and modeling of residual stresses in floor tubes helped define the conditions when cracking could occur and provided an explanation for why cracks didn’t propagate into the carbon steel. Similar measurements and modeling have been conducted on primary air port tubes, but the more complex design (bent tubes, tubes out of the plane of the wall, etc.) made the air port work considerably more difficult. Nevertheless, some very useful information has been gained from the stress studies.

**Stress measurements on wall panels** - X-ray and neutron diffraction residual stress measurements have been made on unexposed bent tubes and on two air port sections, both removed from boilers constructed with 63.5 mm (2½ in.) tubes on 76 mm (3 in.) centers. One of the sections examined was fabricated from 304L stainless steel/carbon steel composite tubing while the other was made from alloy 625/carbon steel composite tubing. Both sections had cracks or were from an area in the boiler where cracking had been observed. As with the floor tubes, surface stresses were measured with x-ray diffraction techniques while neutron diffraction was used to measure stresses within the tube wall [16,24,27].

X-ray diffraction has been used to measure the surface stresses in the single, unexposed, bent tube shown in Fig. 36. To avoid most effects of surface cold-work, the surface was electropolished to remove about 0.04 mm in the areas where measurements were to be made. The bright circles on the side of the tube in Fig. 36 are the areas that were electropolished and used for surface stress measurements. Figure 37 shows the variation in axial residual stress measured along the length of the tube in the locations indicated. In the unbent portion of the tube, the axial stress is compressive, but as the measuring location moves around the “stretched” portion of the tube, the stresses become tensile. As the measuring location moves on to the “compressed” area of the tube, the stresses become highly compressive, then the sequence is reversed as the measuring location moves on to the second half of the tube.

Neutron diffraction measurements have also been made to determine the stresses within the stainless steel clad layer and within the ferritic carbon steel material. These measurements were made below the surface at approximately the same locations where the surface residual stress measurements were made. Figure 38 shows the results of the neutron diffraction residual stress measurements. These indicate that the axial strains in the carbon steel are compressive in the straight portion of the tube, but they become tensile in some of the bent regions of the tube. It has to be noted that these measurements were made at room temperature in unwelded tubing and represent an average over the thickness of the carbon steel shell. Nevertheless, there is a clear indication that significant changes occur in the strains (and stresses) when the tubes are bent at this radius. Plans call for measuring stresses in comparable locations in a single tube bent on a considerably larger radius. This might make it
possible to define the effect of bending radius on residual stresses.

Residual stress measurements made on two sections of exposed air port panels indicate stresses are different between the top and bottom of primary air ports. The stress measurement results shown in Fig. 39 for an air port fabricated from 304L stainless steel/carbon steel tubes indicate the stresses in the carbon steel are near neutral in certain areas at the bottom of the air port. Measurements of surface stresses on an air port section fabricated with co-extruded alloy 625/carbon steel show the room temperature stresses are different between the top and bottom of the air port. These results are shown in Fig. 40. It is important to note that electropolishing had to be done in order to remove the surface material that was likely cold-worked during the cleaning of the air port for the in mill inspection.

**Modeling of stresses in primary air port tubes** - As part of the overall effort to understand the cracking of composite tubes in primary air ports, modeling of the temperature and stress distributions in the composite tubes has been conducted using the commercial finite element program ABAQUS. The finite element mesh for the air port opening was generated using detailed measurements on primary air port sections provided by the mills. Based on the measurements, the geometry of the bent tube was approximated using a cubic spline. Assuming symmetry, only one side of the air port opening was discretized using shell elements for the tubes and membranes, and solid elements for the welds. The temperature values on the fireside surface were assigned based on the data from the various thermocouples. Representative values were assumed so that the temperature increased from 310°C at the bottom of the air port to 360°C at the top. The temperature was also assumed to be slightly higher at the crown of the tube compared to the membrane. Under normal operation, the inside surface of the tube is exposed to pressurized water at 295°C. The cold side of the panel was assumed to be exposed to air at about 100°C. Thermal analysis was used to determine the temperature distribution in the air port for these conditions [16,24,27].

The computed temperature distribution was used in subsequent mechanical analyses to determine the resulting changes in the stress distribution in the air port panel. Since collection of residual data for the primary air port tubes has not been completed, the panel was assumed to have no initial residual stresses. Analysis of a normal operating cycle, i.e., starting from room temperature and heating to normal operating condition followed by cooling back to room temperature, showed that the thermal expansion mismatch between 304L stainless steel and SA210 carbon steel resulted in the stress components at the surface of the 304L layer becoming tensile during cooling. (This result is similar to what was found earlier during analysis of the floor tubes see above and reference 18). The stress at the inside surface of the tube became compressive at the end of the operating cycle, as shown in Figure 41.

As noted earlier, there is a significant difference in the nature of cracking seen on recovery boiler floor tubes and the bent tubes that form primary air ports. Cracks initiate at the surface in both cases, but they rarely proceed past the interface into the carbon steel in the floor tubes. However, cracks have been observed to propagate into the carbon steel in the lower portion of the bent tubes of primary air ports. Earlier work on modeling of floor tubes showed compressive axial stresses in the carbon steel, thus limiting circumferential cracks to the clad layer. The model for the primary air port was used to examine the operating conditions under which the stresses in the carbon steel could become tensile, thus aiding crack propagation.

The thermocouple data being collected from several mills indicate that the majority of primary air ports experience fluctuations in temperature, which sometimes reach fairly high magnitudes.
These variations are often limited to the lower portions of the air port opening, and their duration in some cases is sufficiently long to possibly cause the development of steam in the section of the tube experiencing the temperature excursion. The effect of these localized temperature excursions and of the contact with steam was investigated through finite element modeling. The temperature rise was limited to a small section on the lower portion of the primary air port, while the balance of the tube remained under normal operating conditions (Fig. 42). The results of the modeling are presented at two locations in the carbon steel layer at the crown of the tube on the fireside since the interest is mainly in checking for development of tensile stresses in the carbon steel.

For a localized temperature excursion with a peak value of 450ºC, a fairly large temperature gradient develops through the tube wall since the inside surface of the tube is cooled by water at 295ºC. In the bent tube, the presence of steam was modeled during the temperature excursion, and the resulting stress variation is shown in Fig. 43. Contact with steam leads to almost uniform temperature through the tube wall. While the stress values undergo large changes due to this, the effect is reversed when contact with water is restored. Subsequent cooling to normal operation as well as back to room temperature causes the stresses to become slightly less compressive at the interface and more compressive at the inside surface.

A similar analysis was also conducted assuming a peak value of 600ºC during the localized temperature excursion. The overall trends are similar to the previous case with a 450ºC peak temperature, although the stress magnitudes are quite different. As in the previous case, the presence of steam (represented by greatly reduced transfer of heat to the fluid in the tube) causes large changes in stress values, which are reversed upon contact with water, as shown in Fig. 44. In this case, the stresses at the interface are slightly tensile after the temperature excursion, with a slight increase in magnitude upon shutdown. Stresses at the inside surface are compressive after the temperature excursion and even more so after shutdown.

It must be emphasized that the results presented here were obtained assuming no initial stresses in the primary air port, and the magnitude of stresses would clearly change if the initial stresses were known. However, the modeling does indicate certain trends in the stress variation, and shows the possibility for developing tensile stresses in the presence of sufficiently large localized temperature excursions. The large temperature gradient through the tube wall thickness appears to play the most significant role in development of the tensile stresses, with the presence of steam also contributing, but to a much smaller degree. The fact that tensile stresses develop at the interface would suggest that cracks that initiate in the clad layer could proceed into the carbon steel. However, the presence of compressive stresses at the inside surface would indicate that the cracks will most likely stop. The change in stress from approximately neutral near the interface to highly compressive at the inside surface is supported by experimental data using neutron diffraction measurements at the lower portion of the bent tube on an air port panel taken from service [9,21]. Measurements on the same bent tube at the top of the air port showed compressive axial stresses throughout the carbon steel layer, which is consistent with the results when the temperature excursions are absent or when the peak temperatures are not as high. The data from the primary air port thermocouples also show the occurrence of temperature excursions with greater frequency and magnitude at the lower portion of the bent tube.

Clearly, in addition to an association with cracking in the vicinity of the bottom of the air port, the temperature fluctuations, if severe enough, can make the tube vulnerable to penetration of the crack into the carbon steel. Experience from years of monitoring temperatures on primary air
port tubes on the ten boilers has shown the air port tubes that suffer from the cracking problem have occasional fluctuations that exceed 600°C; in fact, temperatures over 750°C have been recorded.

In view of this analysis, it is important to understand the cause of the temperature fluctuations and how this can be controlled without otherwise adversely affecting boiler operation. In addition, the residual stress state of tubes in other air port designs needs to be measured to determine if the air port design can play a major role in preventing crack propagation into the carbon steel.

**Effect of operating parameters on primary air port cracking**

Determination of the effect of operational parameters on the cracking of primary air port tubes has been approached in two ways – field studies and mathematical modeling.

**Field studies to evaluate operating parameter effects** - On several occasions during the past few years, team members from Paprican have worked with operators of a particular mill to systematically vary parameters of the fuel (black liquor) supply system and the combustion air delivery system. Monitoring of the pattern of temperature fluctuations during the time the operating parameters were being changed has made it possible to identify some conditions for which the magnitude of the fluctuations is significantly changed. Figure 45 illustrates the importance of the combined effect of both the air and liquor delivery system; it shows thermal cycles versus time for a period before and after a number of major changes were made to the operation of the boiler. Temperature cycles and excursions were high during initial operation, but cycle frequency subsequently decreased significantly following the changes that were made to boiler operation. Through this period, a number of key operational variables were changed nearly simultaneously, and subsequent trials have focused on quantifying the relative influence of the most important changes.

Analysis of the data from the trials is still in progress, but operating conditions have now been established that limit temperature fluctuations at the air port openings, relative to initial operation of the boiler and to fluctuations observed in other boilers with cracked tubes at air port openings. Parameters addressed included the liquor firing temperature, nozzle design, size, and gun angle. For the air distribution, the split between primary, secondary and tertiary air, windbox pressures, and secondary air interlacing patterns were covered in the recommendations. A general conclusion has been that liquor parameters have a stronger influence on temperature fluctuations at the primary air port level than any moderate modifications to the air delivery system in the boiler. For example, Fig. 46 shows that temperature fluctuations measured on the side wall thermocouples decreased slightly, but those on the front wall showed very little change when operators switched from a 5 versus 5 interlaced arrangement to a 3 versus 2 interlaced mode.

Other mills have conducted similar, but more limited, studies in which attempts have been made to limit the changes to a single parameter. Results of a test where the liquor temperature was changed are shown in Fig. 47, and this shows that increasing the liquor temperature in this particular boiler resulted in a decrease in thermocouple fluctuations. Factors such as carryover and rate of sulfate reduction were not measured, and it is likely that other boiler conditions, such as air system splits and distributions, were also changed with the liquor temperature change.

**Modeling studies to evaluate operating parameter effects** - Very detailed computational fluid
dynamics (CFD) models of recovery boilers have been developed to explore the dynamics of fuel and air flow within a recovery boiler. Over the past few years, attempts have been made to extend the use of these models to explain why some boilers are particularly prone to cracking at air port opening tubes, or why some portions of the boiler walls (particularly opposing corners) are more prone to cracking than others. To achieve these goals has proven to be quite complex, and requires that improvements be made to the models that better deal with how liquor is distributed off of the nozzles into the boiler, and how bed dynamics will affect will affect flow around the primary air ports. Progress is being made in both areas, but not to the point where definitive conclusions can be reached about boiler operating factors that affect cracking of tubes at air port openings.

Observations of cracking and corrosion on alternate tube materials

The great majority of the air ports studied were constructed of 304L stainless/carbon steel composite tubes, but there have been opportunities to examine ports fabricated with tubes that have other alloys as the outer layer [28]. Specifically, co-extruded tubes fabricated with alloy 625 and with modified alloy 825 have been studied as have been tubes with alloy 625 weld overlay. The studies have generally been limited to examination of the tubes while they were still in place in the boiler, but 625 weld overlay tubes from two boilers and co-extruded alloy 625 tubes from another boiler have been examined in the laboratory.

To date, no cracking and only one case of corrosion have been reported for modified alloy 825 co-extruded tubes in service as air port opening tubes, although minor cracking is common in spout opening tubes [28]. In contrast, substantial cracking of alloy 625 co-extruded tubes in air port openings has occurred. Minor cracking and substantial corrosion has been reported in weld overlaid alloy 625 tubes. Cracking has been observed at the top of primary air ports in weld overlaid 625 tubes as shown in Fig. 48, and it has also been seen in co-extruded 625 tubes. For the weld overlaid and co-extruded alloy 625, dye penetrant inspections were conducted in the laboratory to identify cracked areas, then samples were cut from selected tubes for metallographic examination. Examples of the cracking seen in the co-extruded 625 tubes are shown in Fig. 24. The cracking in these tubes was extensive. None of the cracks in the laboratory samples advanced into the carbon steel, but reports from the mill indicated that cracks were found that advanced into the carbon steel.

Studies have also been conducted to document the extent of localized corrosion on the air port tubes [28]. The thinning of the composite layer caused by this corrosion is generally limited to the areas at the top and/or bottom of the air ports, and sometimes it is observed on tubes along the edge of the castings. Thinning at the tops and/or bottoms of primary air ports is frequently seen on 304L stainless/carbon steel tubes, and thinning of tubes along the edge of the port castings has been observed on weld overlaid 625 tubes in several boilers. Examples of this thinning are shown in Fig. 49. Severe thinning of modified alloy 825/carbon steel tubes has only been seen in one boiler, but experience with this material is still somewhat limited.

Influence of air port design on cracking

Each boiler manufacturer has its own particular design for primary air port openings, and some manufacturers have used several different designs [29]. However, there are common features among air ports used in most boilers constructed with 2½ inch diameter tubes on 3 inch centers. The air port opening is formed by bending two adjacent tubes behind the plane defined by the tubes forming the boiler wall. Some manufacturers use a sleeve or lining inserted into the air
port while others use a removable casting. All of these are intended to provide some protection
to the tubes from the rodders used to clean deposits from the air ports as well as perform some
of the functions of a nozzle in guiding the incoming air. In one design, bending of the tubes
forming the opening is usually done on a radius on the order of 12-15 cm. In this paper, these
are described as the shorter, wider air port design. In contrast, the tubes forming the primary air
port openings of the other major design are bent on a radius of 25-30 cm. In comparison, these
ports are longer and narrower than those described above, and these openings are described
as the longer, narrower opening.

Among the many observations being made relating to temperature fluctuations and tube
 cracking, the information shown in Fig. 50 is of special interest. These temperature
measurements were taken from one of these boilers where the longer, narrower style of primary
air port was installed in all locations as part of the original construction. Clearly, these variations
are significantly less frequent and much smaller in magnitude than those shown in Figs. 26 and
27. This is true even for the data shown from a short, wide port opening with no history of
cracking.

Within North America, inspections have yet to discover cracks in the tubes forming the primary
air port openings of 10 boilers from a single manufacturer with a design of air port that
incorporates a long, narrow opening (and, thus, less severe bends for the tubes that form the
opening). However, limited cracking has been observed in a similar opening design installed as
a retrofit in another boiler. These observations suggest that while air port design may be an
important contributing factor to cracking, differences in air and liquor distribution and other
operating parameters are also important.

Taken together, all of these observations are promising, in that they suggest that cracking might
be minimized, or even prevented, by paying careful attention to the design and operation of both
the boiler and air port opening. Consequently, some of the modeling work being undertaken in
this project is being directed toward identifying the critical characteristics that define an opening
that is least susceptible to cracking.

**Conclusions related to primary air port tube cracking**

Cracking of primary air port tubes, although not yet at the stage of understanding of floor tube
cracking, may be minimized by adhering to one or more of the following recommendations on
alternate materials, air port designs, and changes in operating procedures.

- None of the existing alternatives to 304L/SA210 composite tubes represents a universal
  materials-related solution to cracking and corrosion problems experienced in the lower
  furnace of kraft recovery boilers. However, modified alloy 825 co-extruded tubes have, to
date, the more favorable performance history in both floor and air port opening
  applications. Alloy 625 tubes have provided crack-free service when used in boiler
  floors, but they have experienced both corrosion and cracking when used to make air
  port openings.

- Primary air port designs with the larger radius bends (25-30 cm) appear to be less prone
to cracking than ports constructed with smaller radius bends (12-15 cm), but cracking is
not totally eliminated by retrofitting these types of openings. Additional steps must also
be taken to address the cracking problem.
• Tube temperature fluctuations can be reduced by making certain changes in boiler operating parameters. These changes are primarily directed toward a common goal - a shift from burning liquor on the walls to burning in suspension and on the boiler floor. Studies have shown that changes in liquor characteristics and/or spray parameters, as well as secondary air patterns, can change the frequency and magnitude of temperature fluctuations. Consequently, it is expected that the cracking of primary air port tubes would be similarly influenced.

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Table 1. Composition of wash water samples from a southeastern U.S. mill as a function of floor tube temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Na⁺ (mg/g)</th>
<th>K⁺ (mg/g)</th>
<th>CO₃⁻ (%)</th>
<th>Cl⁻ (%)</th>
<th>Total S (%)</th>
<th>SO₄²⁻ (%)</th>
<th>S⁰ (%)</th>
<th>pH</th>
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<td>81</td>
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Table 2. Characteristics of recovery boilers instrumented with primary air port thermocouples.

<table>
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<tr>
<th>Boiler ID</th>
<th>Nominal capacity MLbDS/d</th>
<th>Operating pressure (psig)</th>
<th>Floor type</th>
<th>Primary air port type</th>
<th>Sleeve/insert type</th>
<th>Extent of PAP cracking</th>
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</thead>
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1. Sections of recovery boiler tube floors showing cracking on 304L stainless steel/carbon steel co-extruded tubes.

2. Photographs of dye penetrant tested recovery boiler floor tube sections. The upper right tube is 309L stainless steel weld overlay tubing; the other tubes are 304L stainless steel/carbon steel co-extruded tubes.
3. Photomicrographs of cross-sections of cracked 304L stainless steel/carbon steel floor tubes showing branching and cracks with matching sides that suggest the crack has been pulled open.

4. Photomicrographs of cross-sections of cracked 304L stainless steel/carbon steel floor tubes showing cracks terminating at the stainless/carbon steel interface or turning and advancing along the interface.
5. Photomicrographs showing the stainless steel/carbon steel interface of two tubes. The upper pair of photos shows a tube that has been subjected to overheating; the decarburized zone is wider than normal and the interfacial precipitation is more than normal. The bottom pair of photos shows the interfacial area in a typical unexposed tube.

6. ASME fatigue design curve for 300 series stainless steels for 427°C. Additional data for 304H and 304L have been added to the plot.
7. ASME fatigue design curve for 300 series stainless steels for 427°C with additional laboratory-generated data included. Note that for cyclic strains of about 0.25%, the fatigue life is predicted to be about 100,000 cycles.

8. Photomicrographs generated with a transmission electron microscope showing the dislocation structure for four stainless steel samples. Note that the cracked primary air port tube has roughly the same degree of dislocation tangles as the control sample while the cracked floor tube has fewer tangles and the cracked smelt spout tube more tangles.
9. Sketch showing how thermocouples were attached to floor tubes. Strain gauges were mounted in six locations in the original set-up, and this sketch shows their position.

10. The arrangement of thermocouples installed near a spout wall on a recovery boiler floor that experienced floor tube cracking near the spout wall.
11. Plot of time versus temperature showing a temperature spike that measured by a floor tube thermocouple.

12. Depiction of the temperature pattern associated with a temperature spike. Note that a spike is seen in the top center frame by a thermocouple about 0.9 m (3 ft) from the spout wall on tube 50. The spike has significantly decreased in intensity 20 seconds after it was first noted.
13. Plot showing the relative amounts of smelt derived constituents dissolved in a given amount of water. Note that when the amount of water is severely limited the concentrations of NaOH and Na$_2$S$_2$O$_3$ are the greatest.

14. Photo and sketch showing the floor of a recovery boiler. The sketch indicates the area where cracking was seen and the photo shows the smelt bed remaining after the boiler was shutdown.
15. Plot of time to failure versus test temperature for 304L stainless steel samples subjected to a load of 275 MPa in a solution of Na$_2$S + 10% NaOH. Note that below about 160°C, the samples do not fail.

16. Maximum crack depth for alloys tested in various heat-treated and cold-worked states in a mixture of 75 wt% Na$_2$S + 25 wt% NaOH at 180°C.
17. Hoop and axial stresses predicted to develop on the fireside crown of a 304L stainless steel clad composite tube. Note that when the temperature is raised to operating conditions, the stresses are compressive and when the tube is cooled to room temperature, the stresses become tensile.

18. A plot of yield stress versus thermal expansion coefficient with the regions identified where the stresses that develop in the tube meet certain constraints. The “preferred” area defines a combination of yield stress and expansion coefficient where the stress conditions are more desirable.
19. Photographs of dye-penetrant tested, cracked smelt spout opening tubes.

20. Photomicrograph of cross-section of alloy 625 clad smelt spout opening tube showing the intergranular cracking of the alloy 625.
21. Examples of cracked primary air port opening tubes with (left to right) craze cracking, circumferential cracking, membrane cracking and cracking in the membrane to tube weld.

22. Cracks in a 304L stainless steel clad air port opening tube. The cracks in location 4 are shown in cross section in the micrographs on the right. Note that many of these cracks terminate in a corrosion "pit" at the stainless steel/carbon steel interface.
23. Cracks in 304L stainless steel clad tubes just below the air port opening. Micrographs of the cross section of the tube show that these cracks penetrate into the carbon steel.

24. Cracks in a alloy 625 clad air port opening tube. Many of these cracks continue through the alloy 625 layer to the interface. Note that the cracking is intergranular in nature.
25. Examples of the thermocouple installations used in the first three boilers equipped with thermocouples on the primary air port tubes.

26. Typical temperature data for a 24 hour period on an air port (left) that had previously experienced cracking and an air port (right) with no prior history of cracking.
27. Sketch showing the locations at which thermocouples were installed in one boiler to determine the variation in temperature patterns around the air port. Note that no air port had thermocouples installed at all the locations indicated. The plot on the right shows typical temperature patterns measured for the locations indicated.

28. Plot of the temperature fluctuations measured on the opening tubes near the bottom of four secondary air ports in a North American boiler that experienced severe primary air port tube cracking.
29. Plot of temperatures measured at two locations on the fireside of a primary air port tube (R24-1 and R24-5) and the temperatures measured at equivalent locations on the windbox side of the same tubes. Note that negligible fluctuations were measured on the windbox side of the tubes.

30. Photograph of video camera designed to go through a primary air port and record the activities on the fireside of a primary air port.
31. Video camera’s view of the bottom of a primary air port. Note the view of the casting and the two thermocouple shields.

32. Video camera’s view of the bottom of a primary air port during boiler operation. In the picture on the left, the bed is quite low while in the picture on the right the bed is near the bottom of the primary air port.
33. Schematic of the tubes that form half of a primary air port with the grid markings and the area subjected to increased heat flux for the modeling study of local heating.

34. Plot showing the variation in temperature at the tube surface as a result of combustion of a pulse of liquor droplets.
35. Plot showing the variation in temperature at the tube surface as a result of the oxidation of a given volume of smelt.

36. Photo of a 304L stainless steel clad tube bent in the shape required for the most common air port design used in North American boilers. The shiny circles are the electropolished areas where X-ray diffraction residual stress measurements were made.
37. Plot of the axial stresses measured along the surface of the tube shown in the previous figure. The results indicate that surface stresses are tensile in the “stretched” areas of the tube and compressive in the areas bent the other direction. Note that the patterns are equivalent for both ends of the tube.

38. Radial and axial strains measured in the stainless clad layer and the carbon steel base material using neutron diffraction techniques. Note that the strains in the carbon steel are compressive in the straight portion but tensile in some of the bent portions.
39. Axial strain measured at several points through the wall thickness of a previously exposed 304L stainless steel/carbon steel tube. The locations shown are near the bottom of the air port and the strains are near neutral near the interface. The strains measured at the top of the air port were more compressive.

40. Axial stresses measured using x-ray diffraction on the surface of alloy 625 clad tubes. Note that some material had to be removed by electropolishing to get below the work-hardened surface layer. Note that stresses on the bottom half of the air port opening tubes are more tensile than are those on the top half of the air port.
41. Plot of the axial and hoop stresses predicted on a 304L stainless clad tube for a normal cycle to operating conditions.

42. Schematic of the tubes that form half of a primary air port with the grid markings and the area where the temperature is temporarily raised to a higher than normal temperature.
43. Plot of the axial and hoop stresses developed in the carbon steel during a temperature excursion to 450°C for the area marked in the previous figure.

44. Plot of the axial and hoop stresses developed in the carbon steel during a temperature excursion to 600°C for the area marked in Figure 42.
45. Plot showing the cumulative totals of cycles and excursions for six thermocouples in continuous service in a recovery boiler that has experienced extensive primary air port tube cracking. In April 2000, the liquor temperature, the liquor gun type and the air distribution patterns were changed.

46. Plot of temperatures measured by primary air port thermocouples on the right hand side wall and the front wall when the secondary air pattern was changed from 5 versus 5 to 3 versus 2.
47. Plot of temperatures measured on the left hand side wall when the liquor temperature was repeatedly changed.

48. Photographs of cracking in alloy 625 weld overlay tubes at the top of primary air ports.
49. Examples of thinning on tubes forming primary air port openings. The photo on the left shows thinning of weld overlay 625 tubing along the casting; the center photo shows the decrease in the thickness of the alloy 625 overlay at the bottom of a primary air port, and the right photo shows complete loss of the 304L cladding on the tubes at the bottom of a primary air port.

50. Plot of temperature versus time for two thermocouples on primary air port opening tubes in a boiler originally equipped with the longer, narrower air port design.