Mechanism and prevention of localized corrosion of recovery boiler tubes at air ports

Lad Falat

ABSTRACT: This work studied the localized thinning of the stainless layer of composite tubes at air port openings in two large 1500-psi recovery boilers. Weld overlay repair patches of nickel applied to corroding areas on air port tubes survived less than six months of operation. This suggests that a previously presented sodium hydroxide mechanism is not sufficient to explain the localized thinning. Corrosion by molten flowing smelt in direct contact with the tube surface is an alternate mechanism that is consistent with experimental observations. Air port redesign to minimize the localized loss of a protective frozen smelt layer is a promising long term preventive measure.

KEYWORDS: Air jets, bibliographies, composites, corrosion prevention, openings, over lays, recovery furnaces, smelt, sodium hydroxide, tubes, welding.

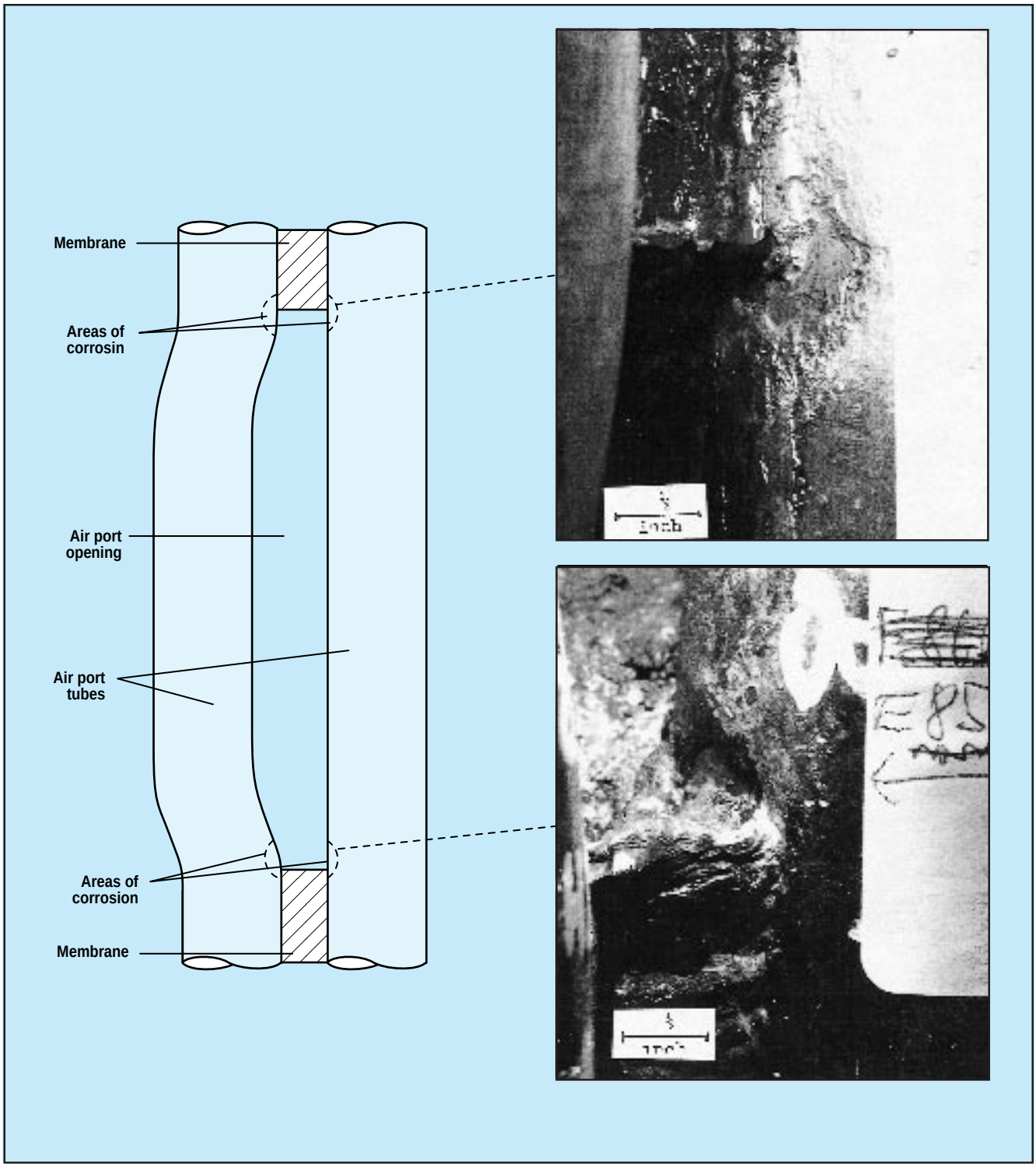
Before the late 1970s, the standard industry material for recovery boiler tubing was carbon steel. Typical recovery boilers of the time operated at 600–900 psi steam pressure. Because power generation efficiency is greater at higher steam pressure, however, the trend in the last 15 years has been to build high-pressure recovery boilers—1500 psi or greater. The higher temperature flue gas present in high-pressure boilers corrodes carbon steel boiler tubes faster. This resulted in development of a composite boiler tubing with a strong, thick, carbon steel inner wall and a thin corrosion-resistant Type 304L stainless steel outer layer. Although the installed cost of this composite tubing is much more than that of conventional carbon steel tubing, it was anticipated at the time that the composite tubing will outlast the design life of the boiler. Both steel tubing and composite tubing rely on a thin layer of solidified smelt for insulation and protection from the very corrosive hot molten smelt.

Composite tubing has usually performed well. In 1985, however, after only two years of operation, a 1500-psi recovery boiler (Boiler A) evidenced a localized and atypical corrosion that was thinning the stainless layer at primary and secondary air port openings. After complete corrosion of the outer stainless steel layer, the underlying carbon steel did not corrode appreciably. This suggested that the air port environment is unlike that found in other parts of the lower furnace section. The 1985 and 1986 National Association of Corrosion Engineers (NACE) T-5H-1 Task Group meetings *(1, 2)* reported occurrences of composite tube corrosion at air ports in other high pressure recovery boilers. One participant reported corrosion of 304L in contact with simulated air port deposits consisting of sodium hydroxide and sodium carbonate *(2)*. Corrosion of carbon steel did not occur under these conditions. The experimental results supported a corrosion mechanism for air port tubes based on molten sodium hydroxide condensed from flue gas.

Barna and Rogan described their field and laboratory observations regarding composite tube corrosion. They speculated that hydroxide condenses on tube deposits and forms a

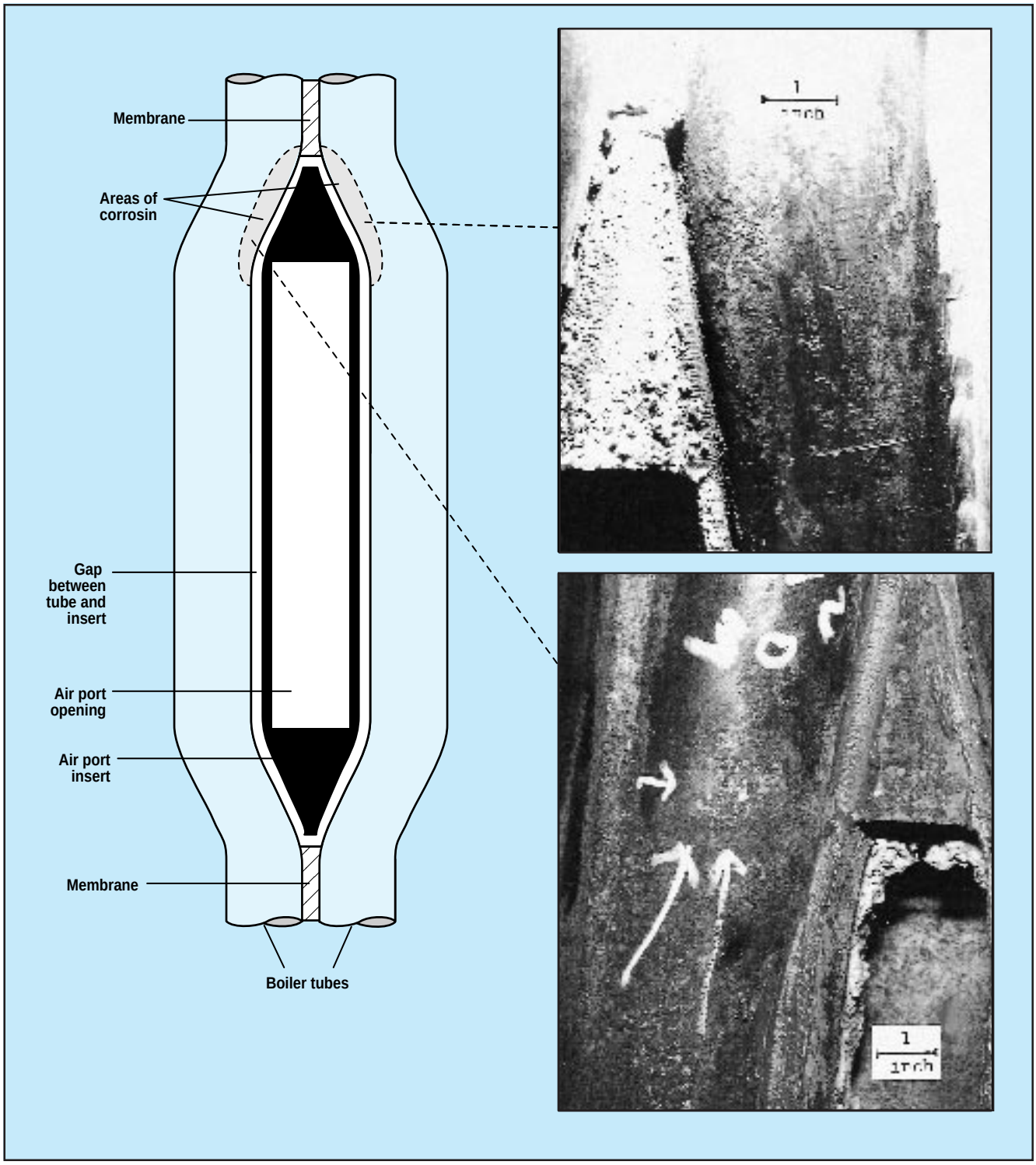
Falat is senior research chemist and corrosion team leader at Westvaco Corp., 11101 Johns Hopkins Rd., Laurel, MD 20723.

1. Diagram of a primary air port in Boiler A showing location of composite tube corrosion with corroded tubes appearing in inserts



molten phase at the deposit and tube interface. This then attacks 304L *(3)*. The hypothesis involving the condensation of hydroxide arose from previous work of Clement and Chassell *(4)* and Bruno *(5)*. These earlier investigators attributed corrosion on the casing side of carbon steel tangent tubes to condensed hydroxides. They postulated that hydroxide vapor migrated to the cold side of the tubes through gaps between tubes. It then condensed on the cooler surfaces. Wensley presented evidence that stainless layer wastage occurs at a temperature near the saturation steam temperature of 598°F for 1500 psi steam *(6)*. This observation sup-

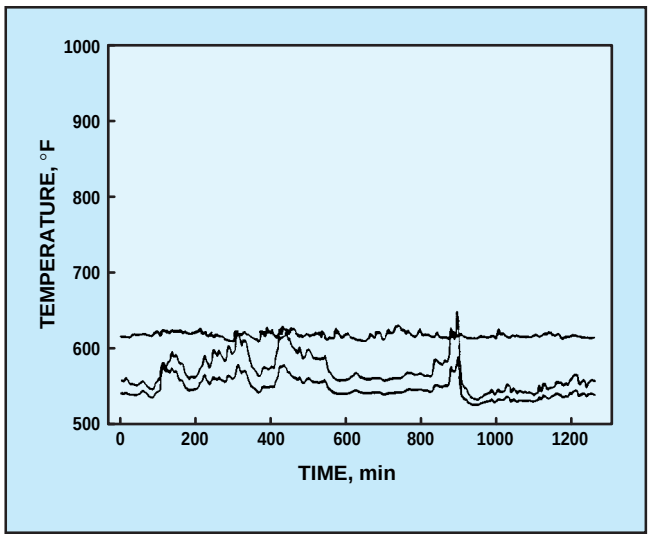
2. Diagram of a primary air port in Boiler B showing location of composite tube corrosion with corroded tubes appearing in inserts



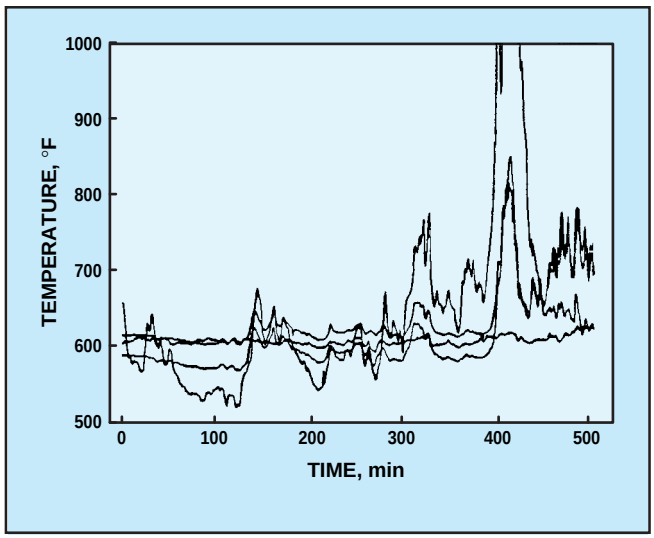
ports a hydroxide mechanism. Sodium hydroxide with a melting point of 605°F is one chemical in the boiler environment that can be molten at this temperature *(6)*.

Laboratory studies by Tran *(7)* showed that 304L dipped in molten NaOH and exposed to air at temperatures up to 750°F did not corrode. Any corrosion of 304L occurred only after air passing over the sample had undergone prescrubbing to remove carbon dioxide. This suggested that corrosion by hydroxide would require air free of carbon dioxide. Carbon steel showed no corrosion in Tran's experiments. He measured an

3. Representative temperature vs. time plots for thermocouples welded on a corroded composite air port tube surface in the recovery boiler showing a period of relative temperature stability



4. Representative temperature vs. time plots for thermocouples welded on a corroded composite air port tube surface in the recovery boiler showing large temperature excursions



electrochemical potential difference between carbon steel and 304L in molten NaOH that suggested possible galvanic effects in the corrosion of 304L. Lunn *et al.* concluded that the removal of cast port inserts and fins from the air ports in a 1500 psi recovery boiler (Boiler A) minimized the potential for sodium hydroxide condensation on the tubes *(7)*. Using the above described work and consultation with the boiler manufacturer, they removed all air port inserts. Inspections of the air ports in Boiler A over the subsequent three years did not reveal additional corrosion. Areas of air port tubes with exposure of the underlying carbon steel were discovered in 1990. Additional reports of "hydroxide" corrosion of air port composite tubes appear in the literature *(8–15)*.

Based on the popular hypothesis of hydroxide condensation, weld overlay patches of nickel were applied to some corroding areas on Boiler A air port tubes. Nickel is a very resistant alloy to molten alkali corrosion *(16–19)*. The complete consumption of the nickel patches within six months of operation indicated that a mechanism of corrosion by molten hydroxide was not sufficient to explain the thinning in this boiler. After this study had begun on Boiler A, a related problem surfaced on a new 1500-psi recovery boiler of a different design (Boiler B).

A goal of this study was to characterize the corrosive environment responsible for the localized thinning of the composite layer on air port tubes. An additional goal was to identify a cost-effective repair method. The approach involved the following:

- Measuring the air port tube surface temperature at various points
- Sampling the chemical environment of the air ports with condensing probes
- Recording the flow patterns of suspended particles, liquid, or both near air port tubes
- Testing candidate materials for permanent repairs.

Experimental results

Location of the composite layer thinning

The localized thinning of the 304L composite layer on tubes in Boiler A occurred at the top and bottom of port openings indicated in **Fig. 1**. The thinning resulted equally toward the fireside and the casing side of the tube. Thinning of the carbon steel substrate after the outer 304L layer had corroded away was not measurable. It is necessary to qualify the observation by the fact that the corroded areas were weld overlayed before the exposed carbon steel reached one square inch. The exposure time of the carbon steel was therefore subject to a limitation. While thinning of the stainless layer occurred on tubes of many air ports, tubes at some adjacent air ports remained unaffected. On many primary air port tubes, thinning occurred at the top and at the bottom of the port opening. Some primary port tubes showed thinning only at the top or the bottom. Significant thinning in Boiler A occurred at the bottom of only the primary air ports and at the tops of the primary and secondary air ports and some inspection ports. The spout wall and one side wall had the highest numbers of affected tubes. Although the other two walls did not have as many corroded air port tubes, the severity or rate of thinning on individual tubes did not relate to location.

Thinning of the stainless layer on air port tubes in Boiler B occurred only toward the fireside as **Fig. 2** shows. This boiler has air port inserts. Minor attack occurred opposite the corners of the rectangular port insert openings as the figure shows. There was no clear correlation between thinning rate and wall position in this boiler.

Boiler air port tube surface temperatures

Initial measurement of boiler tube surface temperatures on dozens of air ports in Boiler A used a specially designed contact probe. Temperatures substantially above the stauration steam temperature or approximately 600°F for 1500 psi steam were measured with intermittent excursion above 900°F. Measurements at the bottom of the primary ports indicated that molten and burning smelt was contacting the temperature probe and the tube surface. Ten 1/8 in. diameter Inconel 600 sheathed thermocouples were subsequently welded to the tube surface in four primary air ports in Boiler A. The thermocouples were welded to the upper and lower corners of the air port opening where corrosion was taking place. Nine of the thermocouples provided data for several months. **Figures 3 and 4** show that tube surface temperature generally varied between 500–700°F with excursions up to 1100°F lasting up to 60 min. Each trace represents data from one thermocouple. The excurcions were presumably caused by molten and burning smelt in direct contact with both the thermocouple and the tube surface. Periodic manual rodding of the bare tube surfaces in this boiler would likely ease the melting of the insulating layer of frozen smelt. The observed temperature excursions several hundred degrees above the steam saturation temperatures allow consideration of corrosion mechanisms other than the one based on hydroxide condensation.

Material evaluation

Areas of composite air port tubes in Boiler A where corrosion had exposed the underlying carbon steel underwent weld overlaying with Type 309L stainless steel. **Table I** provides this composition. It is a ductile welding electrode material commonly used for overlaying carbon steel and for joining carbon steel to stainless steel. Over a two year period, some 309L repairs showed measurable corrosion but at a fraction of the rate of the 304L layer. There was no observation of significant thinning of the underlying carbon steel where exposed. The carbon steel did not have exposure for longer than 6–8 months. Moskal reported 0.005–0.007 in./year corrosion on the underlying carbon steel after exposure of a palm-size area *(15, 20)*.

Several 309L repairs in Boiler A were weld-overlayed with patches of nickel. After less than seven months of service, the nickel patches were preferentially consumed to the fusion boundary with the 309L as **Fig. 5** shows.

Three corroding primary air ports on the right wall of Boiler A were completely coated with a 30% Cr and 70% Fe (30Cr70Fe) thermal spray. The metallic coating was intact in areas of air port tube corrosion after 18 months of service. Significant deterioration of this coating occurred after 27 months of service. Four test coatings were applied to a pair of boiler tubes comprising one primary air port for installation in Boiler A. Of these four test coatings and the 30Cr70Fe coating installed in the boiler, only the 30Cr70Fe remained intact in the area susceptible to corrosion for longer than 12 months. Table I summarizes all coating compositions and performance.

Eight locations on primary air port tubes that had the most thinning in Boiler B were weld-overlayed using two patches of 1 $in.^2$ each of Inconel 625, Hastelloy-X, 309L, and 310L. After one year of service, only the 309L patches showed any evidence of thinning. There is a possibility that the locations for application of the other materials became less corrosive because of better sealing of the air gap between the port tubes and the port inserts. This requires consideration and further investigation. A substantial reduction of the stainless steel thinning rate in Boiler B resulted from better sealing between the air gaps and the inserts.

Deposits collected at air ports in Boiler A

An air-cooled probe collected molten and condensible materials near air ports. Infrared (IR) spectrophotometric analyses of the materials from the area most susceptible to corrosion indicated spectra similar to those of a sample of molten smelt collected about 6 in. from the air port toward the center of the furnace. This showed that the chemical species at the corroding site were essentially those of the smelt. Chemical analysis of smelt drippings from a corroded site on an inspection port tube at the liquor gun port elevation yielded similar results.

Visual observations of flow patterns at air ports

Direct visual observations of the primary air port tube surface during boiler operation was not possible. The light intensity from the smelt bed and the 4-ft distance from the observation sight glass to the boiler tubes prevented observation. A video camera recorded the flowing, freezing, and melting of smelt at 8–12X magnification taken from the sight glass. The recordings revealed that smelt flows almost continuously over the corroding areas at the tops of the ports. It spills from the smelt bed over the corroding areas at the bottom of the primary air ports closest to the floor of the boiler. The top of the smelt bed in Boiler A frequently coincided with the bottom of the primary air ports. After air port

5. Remains of a patch of nickel weld overlay on a corroded air port tube after six months of operation in a recovery boiler

rodding, a new deposit of smelt solidified on the tubes in seconds to minutes. During periods of heavy smelt flow over a given area, the solidified smelt became partially molten and sloughed off the tube surface to be replaced by another solidifying smelt layer. This very dynamic freezing and melting of smelt deposits repeated often in the minutes after rodding a port. Smelt flowing and dripping from the membrane between the tubes and spilling from the smelt bed over the primary air port bottoms was red-hot. It looked like it was burning. The entire air port resembled a blow torch with the base of the flame originating at the tube surface. These high temperature excursions recorded are consistent with the removal and formation of smelt deposits from the tube surface.

Corrosion mechanism

Examination of the NaOH mechanism

Results of laboratory evaluation of materials in sodium hydroxide and mixed hydroxide melts *(12)* confirmed that nickel is very resistant to molten hydroxide. High nickel alloys are the typical selection for strong alkaline service with unalloyed nickel being the best. Odelstam *et al.* used an Inconel 600 (15Cr 76Ni8Fe) crucible for corrosion studies in molten hydroxide with no evidence of corrosion *(9)*. Even if the nickel weld overlay patches applied in Boiler A were grossly diluted by the underlying 309L, the patches would have had a nickel content above the minimum for Inconel 600 and should have resisted the corrosion. The selective attack of nickel weld overlay on air port tubes in this boiler is a convincing argument against a mechanism based exclusively on hydroxide. The preferential and complete consumption of nickel points to "hot corrosion" by molten salts (smelt) with possible high temperature sulfidation, oxidation, or both. Nickel has little resistance to corrosion by aggressive sulfur compounds *(17, 21)*.

The hydroxide mechanism gained acceptance largely because hydroxide eutectics are among the few chemical species that can be present and remain molten on the tube surface. This assumes that the tube surface is in thermal equilibrium with the saturation steam temperature. Data in Figs. 3 and 4 show that the surface tube temperatures at the corroding sites undergo excursions several hundred degrees Fahrenheit above the temperature of the saturated steam. Crowe measured similar temperature excursions at air ports with a surface contact thermocouple *(22)*. Measurement and confirmation of large temperature excursions on the surface of air port tubes indicate that the corrosion mechanism in this area does not have the limitation of a low temperature hydroxide mechanism as Wensley argued *(6)*. Chordal thermocouple measurements made by Wensley represent bulk tube temperatures and not localized transient surface temperatures.

For the hydroxide attack to be possible, the hydroxide vapor must migrate to and condense in a cool, carbon dioxide free area on the port tube. The location of air port corrosion in either boiler studied does not appear to support the conditions required for hydroxide condensation. This is especially the case in Boiler B where the area of composite layer thinning orients toward the fireside in the outer region of the air jet from the primary ports.

According to equilibrium calculations for the gas composition in the lower furnace *(23)*, appreciable concentrations over 100 ppm of sodium hydroxide can only form in the furnace at temperatures exceeding 1800°F. At these temperatures and at the high concentration of carbon dioxide in the lower furnace atmosphere, any trace amounts of gas phase sodium hydroxide rapidly undergo carbonation. The corrosion mechanism implicating sodium hydroxide relies entirely on the premise that a sufficient concentration of sodium hydroxide vapor formed in the furnace escapes reaction with carbon dioxide in the lower furnace. It diffuses into the primary and the secondary air port openings against a bulk flow of combustion air, mixes with the combustion air, and cools to a temperature at which the conversion to carbonate is slow *(9)*. Crowe and Cameron *(24)* concluded that there is a very low probability that NaOH could condense from the boiler flue gas without forming carbonate. Tran *et al.* published data showing that the rate of hydroxide carbonation is negligible in air to 570°F *(14)*. In contrast, Fonder and Colwell have shown that a thin film of sodium hydroxide above its melting point of 605°F readily reacts in air to form carbonate *(27)*. It is difficult to envision migration or diffusion of hydroxide vapor against the air jet at the primary air ports. It is even more unlikely against the higher pressure air jet at the secondary air level. Hydroxide vapor migration might be possible to an inspection port where the air flow would be very low. Hydroxide vapor migration to the cooler side of boiler tubes described by Chassell and Clement *(4)* and Bruno *(5)* is plausible for tangent tube boilers. It is unlikely for membraned or sealed boilers like the two in this study.

There were reports of hydroxides in air port tube deposits collected after a water wash of the boiler *(5, 7, 9)*. Others have questioned the validity of the analytical techniques used, however, citing two ways in which hydroxides may be an artifact of the analyses *(23)*. There has been no detection of hydroxide in significant quantities in deposits collected in the current study.

Proposed mechanism

The following do not support a thinning mechanism using condensed molten hydroxide:

I. Composition and performance of test materials applied to corroding air port tubes

Material	Type	Nominal composition, % Cr	Ni	Fe	Mo	Others	Performance
Type 304L stainless steel	Composite layer of tube	18	8	*	-	-	Corrodes up to 0.040 in./year
Type 309L stainless steel	Weld overlay	23	13	*	-	1.5 Si, 2.0 Mn	Corrodes up to 0.005 in./year
Type 310L stainless steel	Weld overlay	25	20	*	-	1.5 Si, 2.0 Mn	No measurable corrosion surface attack noted
Inconel 625	Weld overlay	22	*	5	9	3.4 Cb + Ta	No measurable corrosion
Hastelloy-X	Weld overlay	22	*	19	9	1 W	No measurable corrosion
Nickel	Weld overlay	-	99.5	-	-	-	Corrodes rapidly
Coating #1	**	30	-	70	-	-	Deteriorated after 28 months of service
Coating #2	**	28	38	4	-	27 Co, 3 Si	Surface etching noted
Coating #3	**	43	55	-	-	2 Si	Corrodes up to 0.030 in./year
Coating #4	**	30	-	65	-	4 Al, 1 Y	Coating spalled
Hastelloy G-30 coating #5	**	29	42	15	5	3 Co, 2 Cu, 3 W	Coating spalled

* = balance
** = applied by high velocity oxy fuel process

- Observation of liquor and smelt flow on air port tubes during boiler operation
- The poor performance of nickel weld overlay on air port tubes
- Analysis of deposits condensed on an air cooled probe in contact with the corroding areas.

The finding of higher than expected tube surface temperature excursions no longer limits the mechanism to a low temperature one such as that based on hydroxide.

The corroding areas on tubes in Boiler A had one common feature. Corrosion occurred where reduced smelt flowing down the tube or membrane contacted air. This occurred at the top of primary and secondary air ports, the bottom of the primary air ports (corresponding to the smelt line), and at the bottom of one secondary air port with much less severity. Tertiary air ports at an elevation above the liquor guns did not experience an effect because much less smelt or liquor exists on the tubes at this elevation. Figure 2 shows discolorations and surface roughening indicative of the initial stages of this type of tube corrosion near the corners of the air port inserts in Boiler B.

When an air port is periodically rodded, frozen and semi-molten smelt is knocked off the port tubes, oftentimes exposing a bare tube surface. When the tubes of the air port undergo cleaning, there is also removal of frozen smelt from the membrane at the top and bottom of the port. Depending on the proximity of the bed and flow of air and thus temperature, observations in Boiler A indicate that the buildup of a frozen smelt layer can take from seconds to several minutes.

The main components of smelt and liquor flowing down the tube wall are sodium carbonate, sodium sulfide, and unburned organic materials. Carbon will have reduced sulfate originally present in the firing liquor in the boiler to sulfide. Sulfide remains in the reduced condition on the walls of the boiler until it contacts air. The sulfide rich smelt flowing down wall tubes and the membrane will first encounter oxygen at the termination of the membrane at the top of an air port—primary or secondary—or an inspection port that is not gas tight. When the reduced molten smelt encounters air, the sulfide rapidly and very exothermically oxidizes to sulfate. It is the oxidation of sulfide at the char particle surface and at the surface of the smelt bed that is the main source

of heat in the lower furnace *(25)*. It is hypothesized by this author that the oxidation of sulfide rich smelt at the membrane drip points—areas of corrosion—provides an energy source for the reported surface temperature excursions. Sulfide oxidation occurs rapidly and completely with sulfur going from an oxidation state of -2 to +6. Because sulfide continuously replenishes at the drip point and the combustion air flow is so turbulent, it is difficult to determine what percentage of the sulfur oxidizes at the drip point. If this complex dynamic environment oscillates between reducing (sulfide) and oxidizing (sulfate) conditions as believed, the stability of protective corrosion films formed under one condition may be disrupted under the opposite condition *(17, 21)*.

Crowe and Cameron proposed an alternative mechanism for corrosion based on pyrosulfate formation *(24)*. The presence of chlorides (a major volatile species in the lower furnace) *(26)*, sulfur trioxide, and oxygen at a temperature of 750–840°F would be necessary for a molten pyrosulfate mechanism *(23)*. The presence of sulfur trioxide does not appear likely, but it is not possible to exclude it. One cannot exclude corrosion by elemental sulfur itself from consideration, since the conditions for its formation are also present *(27)*. Elemental sulfur can form in situ by air oxidation of the large amounts of hydrogen sulfide volatilized by pyrolysis of liquor solids. Elemental sulfur may also be a short-lived intermediate species in the oxidation of sodium sulfide.

This author's observations suggest that the local environment at corroding areas on the composite tubing is similar to that of a smelt spout, although the temperature is higher. Circulating water cools the smelt spout. Corrosion at air ports appears to be "hot corrosion" by molten salts. It is in a sulfate, sulfide, and carbonate melt rather than in molten hydroxide, however. The observed rapid thinning of nickel and the minimal degradation after 18 months of service of a 30Cr70Fe coating in areas of previously active corrosion suggest high temperature sulfidation, perhaps alternating with oxidation. According to Lai *(17, 28)*, alloys containing 25% Cr and higher have superior sulfidation resistance. This is consistent with the improved performance of 309L (23% Cr) weld overlay in Boiler A compared with that of the 304L composite layer (18% Cr). The surface etching of coating #2 from Table I and the corrosion of the 45Cr55Ni coating indicate the even more severe action of molten compared to gaseous corrosive species, however. The wrought alloy with the composition of coating #2 is highly resistant in hot gaseous sulfidizing environments *(28)*. The 45Cr55Ni coating has shown sufficient resistance to lower furnace sulfidizing atmosphere. The 45Cr 55Ni coating does show corrosion, however, at the smelt spouts *(11, 29)*. No commercially available alloys will withstand corrosion by molten high temperature smelt for very long *(28)*. An alternately oxidizing and sulfidizing (reducing) localized environment would aggravate any molten salt corrosion. Surface films formed under one set of conditions would not be stable under the opposite conditions *(17, 21)*.

Several unexplained observations remain. It is puzzling why one air port has severe recurring corrosion while an adjacent air port served by the same windbox remains unattacked. Possible explanations include local differences in air and smelt flow patterns or rodding access and practice. Another puzzle is the much lower rate of dissolution of the underlying carbon steel after removal of the outer 304L layer. Colwell's proposed mechanism using the selective solubility of chromium oxides as a function of melt basicity *(12)* is consistent with the higher rate of thinning of the 304L composite layer compared to that of carbon steel. Colwell's laboratory experiments were in molten hydroxide melts which we believe are not representative of the localized environment near the air port tube. The basis for his work and proposed mechanism lies in more applicable earlier work performed in sodium sulfate and sodium carbonate melts *(12)*. Moskal observed that the exposed carbon steel thinned at a rate of 0.005–0.008 in./year after dissolution of a substantial area of the stainless composite layer *(20)*. Crowe and Cameron's proposed pyrosulfate mechanism appears similarly consistent with the lower rate of carbon steel corrosion *(24)*. Their hypothesis, however, predicts that higher levels of chromium will not necessarily improve the resistance of a candidate material. Materials testing on actual operating air port tubes does not support this. Lunn *et al. (7)* and Colwell *(12)* describe evidence in laboratory studies of preferential corrosion of 304L when galvanically coupled to carbon steel. Colwell concluded, however, that the small galvanic effect could not account for the large difference in corrosion rates.

In summary, the chemical environment at the recovery boiler air port is complex and dynamic. A hypothesis is that reduced or partially oxidized molten smelt, an excess of combustion air, and local hot spots caused by a loss of the insulating frozen smelt layer combine to degrade the composite tube surface locally. The flow of smelt, the mechanical action of rodding, and the exothermic oxidation of smelt contribute to localized melting of the frozen smelt layer.

Repair of corroded air port tubes

Three strategies exist for controlling the localized thinning of the stainless layer of composite tubes at air ports:

- Repeated weld overlay repair of exposed carbon steel

- Application of a thermal spray coating that is resistant to the environment
- Redesign of the port opening.

Each of these possibilities has advantages and disadvantages.

Weld overlay with a more resistant material than 304L such as 309L is the least costly repair option. The 309L corrodes at a fraction of the rate of the 304L composite layer. The 310L, Alloy 625, and Hastelloy-X weld overlay patches tested in Boiler B have not shown any signs of deterioration in six months of service. They appear to be suitable materials for repair. High chromium low nickel ductile welding electrodes (29Cr9Ni) may be the best repair material. There has been no confirmation through testing, however. Weld overlay appears the least costly option because the area for repair is small—typically one square inch maximum per affected tube. It is usually possible to do the repairs without affecting the outage length. Data is still necessary to determine if repeated weld overlay of the stainless layer of a composite tube damages the underlying pressure containing carbon steel portion of the tube in a way that the tube would no longer meet ASME Pressure Vessel Code strength and toughness criteria.

Since it had little deterioration in 18 months of service, the 30Cr70Fe thermally sprayed metallic coating is a viable repair option for the corroding air port tubes. Because of deterioration after 27 months of service, even this coating is not a permanent repair, however. Other thermally sprayed materials shown in Table I need further evaluation. One disadvantage of the thermal spray coating is the high cost of surface preparation of the tubes—grit blasting. It is necessary to do this from the fireside and the cold side. An extended outage would be necessary to implement this repair option.

A promising long-term strategy to eliminate the localized corrosion is air port redesign. The objective in this case is to prevent the smelt flowing down membrane and tube surfaces from coming into contact with combustion air directly on the tube surface. The strategy would be to maintain reducing conditions on the tube surface by directing combustion air further into the furnace without impinging directly on the tube surface. Such a design would incorporate air injection nozzles of an appropriate material sealed completely to the air port tubes and protruding into the furnace by several inches. The original Boiler A port design incorporated cast inserts. The inserts were removed in an attempt to eliminate corrosion of the tube surface under the insert *(7)*. The current ports on Boiler A incorporate no inserts and are susceptible to oxidation of smelt directly on the tube surface and to removal of the protective frozen smelt from the tube surface by rodding. Air port design on Boiler B incorporates cast inserts sealed to the port tubes with refractory. This design has been less susceptible to the localized corrosion provided the air gap between the air port insert and the tube remains sealed. A significant reduction in the composite layer thinning rate occurred in Boiler B after better sealing of that air gap. In retrospect, sealing the original cast inserts to the tubes on Boiler A may have eliminated the first corrosion problem *(7)* without creating the second problem.

Conclusions

Using the observations noted in this paper, it is possible to draw the following conclusions:

- Visual observation of corroded regions, measurement of local high temperature swings, analysis of molten and solidified matter from corroded areas on air port tubes, and the performance of test materials indicate that chemical interaction of high temperature molten smelt with intermittently exposed tube surfaces causes the localized thinning of the outer stainless steel layer of composite recovery boiler air port tubes.
- The poor performance of nickel weld overlay and the specific location of the thinning seen in two recovery boilers do not support the previous hypothesis that condensed molten sodium hydroxide causes air port tube corrosion.
- The most promising strategy to prevent air port tube corrosion requires designing the port to prevent direct interaction of molten smelt with the composite tube surface. Smelt flow, air flow, and rodding procedures must be considerations in the design.
- Weld overlay is the least costly method of repairing corroded air port tubes. It is necessary to determine the impact of repeated welding on the integrity of the tube, however. TJ

Literature cited

1. Anon., *Minutes of Meeting of the T-5H-1 Task Group on Recovery Boiler Fireside Corrosion*, NACE, Houston, 1985.
2. Anon., *Minutes of Meeting of the T-5H-1 Task Group on Recovery Boiler Fireside Corrosion*, NACE, Houston, 1986.
3. Barna, J. L. and Rogan, J. B., *1986 TAPPI Engineering Conference Proceedings*, TAPPI PRESS, Atlanta, p. 377.
4. Clement, J. L. and Chassell, J. R., *Recovery Unit Corrosion: A Progress Report*, presented at the 22nd TAPPI Engineering Conference, Atlanta, Sept. 21, 1967.
5. Bruno, F., *4th International Symposium on Corrosion in the Pulp and Paper Industry Proceedings*, Swedish Corrosion Institute, Stockholm, 1983, p. 68.
6. Wensley, D. A., *Proceedings of NACE Corrosion 87*, NACE, Houston, 1987, p. 205.
7. Lunn, M. A., Sharp, W.B.A., Andrews, J. D., *et al.*, *Pulp and Paper Industry Corrosion Problems*, Finnish Pulp and Pa-

per Research Institute, Helsinki, 1989, vol. 6, p. 151.
8. Anon., *Minutes of Meeting of the T-5H-1 Task Group on Recovery Boiler Fireside Corrosion*, NACE, Houston, 1987.
9. Odelstam, T., Tran, H. N., Barham, D., *et al.*, *TAPPI 1987 Engineering Conference Proceedings*, TAPPI PRESS, Atlanta, p. 585.
10. Barna, J. L., Rogan, J. B., Mattia, R. J., *et al.*, *TAPPI 1989 Kraft Recovery Operations Seminar*, TAPPI PRESS, Atlanta, p. 267.
11. Sharp, W.B.A. and Tran, H. N., personal communication.
12. Colwell, J. A., *TAPPI 7th International Symposium on Corrosion in the Pulp and Paper Industry Proceedings*, TAPPI PRESS, Atlanta, 1992, p. 231.
13. Paul, L. D., Barna, J. L., Danielson, M. J., *et al.*, *TAPPI 1992 Engineering Conference Proceedings*, TAPPI PRESS, Atlanta, p. 321.
14. Tran, H., Mao, X., and Barham, D., *TAPPI 7th International Symposium on Corrosion in the Pulp and Paper Industry Proceedings*, TAPPI PRESS, Atlanta, 1992, p. 363.
15. Bruno, F., *TAPPI 7th International Symposium on Corrosion in the Pulp and Paper Industry Proceedings*, TAPPI PRESS, Atlanta, 1992, p. 341.
16. Craig, B. D., *Handbook of Corrosion Data*, ASM International, Metals Park, 1989, p. 516.
17. Lai, G. Y., *High-Temperature Corrosion of Engineering Alloys*, ASM International, Metals Park, 1990, p. 117-144.
18. Anon., *Corrosion Resistance of Nickel and Nickel-Containing Alloys in Caustic Soda and Other Alkalies*, INCO Inc., Huntington, 1973.
19. Tuthill, A. H., personal communication.
20. Moskal, M., personal communication.
21. Kofstad, P, *High Temperature Corrosion*, Elsevier Applied Science, London, 1988, pp. 425-464.
22. Crowe, D. C., personal communication.
23. Pejryd, L. and Hupa, M., *TAPPI 1984 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 579.
24. Crowe, D. C. and Cameron, J. H., *Institute of Paper Chemistry Technical Paper Series No. 299*, IPST, Atlanta, 1988.
25. Grace, T. M., *Chemical Recovery in the Alkaline Pulping Processes*, TAPPI PRESS, Atlanta, 1985, pp. 87-116.
26. Cameron, J. H., *Institute of Paper Chemistry Technical Paper Series No. 237*, IPST, Atlanta, 1987.
27. Colwell, J. and Fonder, G., personal communication.
28. Lai, G. Y., personal communication.
29. Luer, K., personal communications.

The author acknowledges the contributions of Babcock & Wilcox and Metalspray, Inc. in this investigation. He also thanks G. Lai (Haynes International), J. Colwell (IPST), J. Barna (Babcock & Wilcox), and H. Tran (Univ. of Toronto) for useful discussions on the subject.

Received for review June 21, 1994.

Accepted Oct. 10, 1994.