

WHY DO KRAFT RECOVERY BOILER COMPOSITE FLOOR TUBES CRACK?

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ABSTRACT

Cracks were first reported in 1992 in co-extruded 304L stainless steel/SA210 Gd A1 carbon steel floor tubes of North American black liquor recovery boilers. Since then, a considerable amount of information has been collected on the tube environment, crack characteristics, the stress state of the tubes, and the crack initiation and propagation mechanisms. These studies have identified both operating procedures that apparently can greatly lessen the likelihood of crack formation in the stainless steel layer and alternate materials that appear to be much more resistant to cracking than is 304L stainless.

INTRODUCTION

Co-extruded 304L stainless steel/SA210 Gd A1 carbon steel (CS) was developed more than thirty years ago as a material that was more resistant to sulfidizing recovery boiler gases than carbon steel [1]. As it became established that the co-extruded (or composite, as they are commonly called) tubes performed better in boiler walls than those of carbon steel, it was logical to consider their use on recovery boiler floors because of the occasional corrosion-caused failure of carbon steel floor tubes. Use of composite tubes on recovery boiler floors was first implemented in Scandinavia around 1978, while the first use in North America occurred in the early 1980s [2,3]. A few years after composite tubes were adopted for use in recovery boilers, cracking was found in the stainless steel outer layer of tubes that formed smelt spout openings and, subsequently, in composite floor tubes. By 1992, it was apparent that cracking of the 304L layer in composite floor tubes was a widespread problem across the pulp and paper industry. Many research studies have since addressed aspects of this problem. This paper summarizes, in question and answer format, the results of the project on this topic funded primarily by the U.S.

WHERE ARE CRACKS FOUND?

The most common areas for floor tube cracking in slope-floored boilers are adjacent to the spout wall and in the smelt run areas adjacent to the side walls. Floor tube cracking in decanting-bottom boilers is generally found over a larger area; often randomly distributed over a large portion of the floor. Because many North American decanting-bottom boilers have composite tube walls, but not composite tube floors, reports often describe cracking in the wall-tube bends underneath the smelt bed.

On floors constructed with three inch tubes on four inch centers, transverse cracking in the 304L clad membrane, like that shown in **Figure 1**, is sometimes seen before cracking is found on the tubes. However, cracking is seen on both 2-1/2 and 3 inch composite tubes, and it is found in both slope-floored and decanting-type recovery boilers. Particularly on floors with the wider membrane, cracking can occur at the toe of the membrane to tube weld. Cracking is also found on both sizes of tubes away from the weld. This cracking sometimes is primarily circumferential in orientation (see **Figure 2**) while in other cases it will consist of a series of randomly-appearing interconnected cracks sometimes referred to as craze cracking like that shown in **Figure 3**. The different crack orientations most likely reflect the stress state (tensile or compressive for the axial and tangential directions) at the surface of the tubes at the time that cracking is occurs.

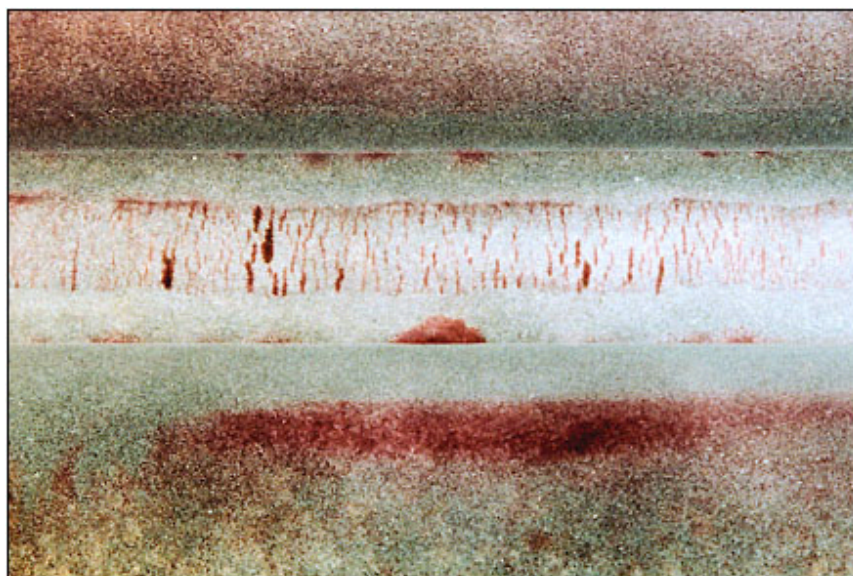


Figure 1. Transverse cracks like those shown are sometimes seen in the membrane of floor panels constructed with 76 mm (3 in.) diameter tubes on 102 mm (4 in.) centers.

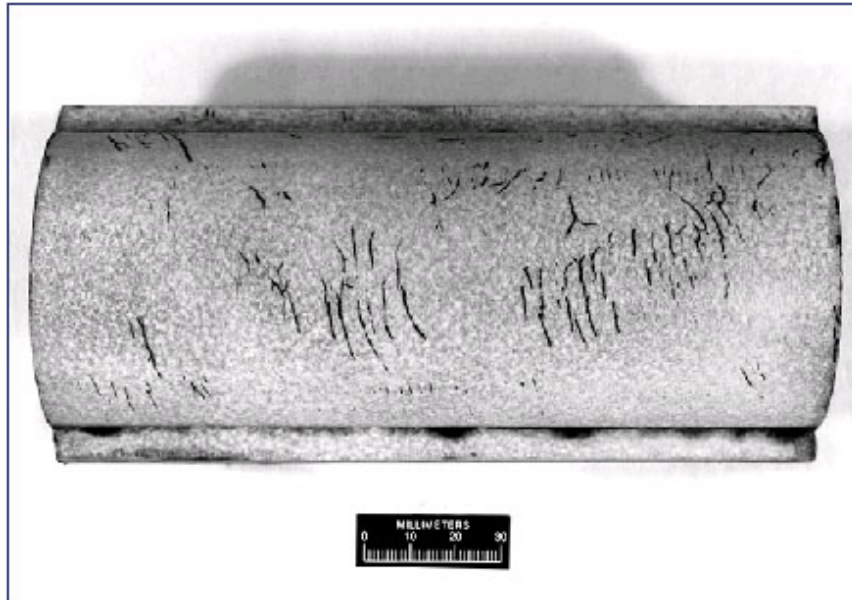


Figure 2. Circumferential cracks are found on some tubes indicating the tensile stresses on the tube are primarily axial.



Figure 3. The craze or interconnected cracking found on some tubes suggests that both axial and tangential stresses are tensile.

HOW DO I FIND CRACKS IN COMPOSITE TUBES?

The detection threshold for cracks is strongly dependent on the procedures used for inspection. In some circumstances, cracks may have grown to a stage where they can be found with a careful visual inspection. However, in most cases, extensive industry experience has found that careful surface preparation is required to positively identify cracks in composite tubes [4]. If the procedures are not optimized, cracks may not be detected.

Before any inspection is performed, debris and adherent deposits must be removed from the surface of the tubes. For floor tubes, this is facilitated by taking the time to completely burn out the smelt bed as the boiler is being shut down for inspection (**Figure 4**). There is an additional benefit to burning out the bed, since such action helps eliminate some of the conditions that can contribute to floor tube cracking. Some mills have used high pressure water lances inserted through the spout openings in the latter stages of a water wash to help remove the residual smelt bed from the floor.



Figure 4. Examples of a recovery boiler where the smelt bed has been nearly completely burned-out and a boiler where little effort was made to remove the bed before shut-down.

Effective non-destructive test (NDT) techniques are dye penetrant testing (PT) and eddy current. Surface preparation is especially critical for PT. To ensure detection of cracks, the most successful technique has been to use a flapper wheel (100-120 grit) to clean the surface as a final step before application of a visible dye penetrant. The flapper wheel serves to gently remove a

small amount of material from the surface of the tube, and leaves the crack in an optimal condition to absorb the dye. Wire-brushing alone tends to mask the mouths of tight, fine cracks and grinding may smear over the opening and also remove more material than desirable [4]. Less stringent requirements for tube cleanliness are needed for eddy current inspection. However, eddy current testing is dependent on the skill of the operator, and the sensitivity of the coils is such that it is common to identify many non-critical surface and subsurface irregularities as flaw indications. When indications are found with an eddy current technique, follow-up PT is usually performed to positively confirm the presence of cracks.

WHAT DO I DO IF I FIND CRACKS?

For many years, the immediate response to the discovery of cracks in recovery boiler composite floor tubes was to remove the cracks and repair the stainless steel layer. Removal of the cracks was almost always accomplished by grinding, and repair of the tubing was made by weld overlaying with an equivalent or similar weld metal. Subsequent observations that cracks sometimes originated in the repair welds led to a careful review of the use of weld repairs, and in some cases, a decision not to repair. Of the hundreds of floor tubes examined in this project, no cracks have been found to continue from the stainless steel into the carbon steel except for two cases with a chill tube (the tube adjacent to the side wall) in decanting floors and one case with a floor tube in the bend by the spout wall of a slope-floored boiler. The obvious conclusion is that it is very unusual for floor tube cracks to grow into the carbon steel much less be associated with a floor tube failure. Consequently, a decision will have to be made at each mill as to whether or not floor tube cracks will be ground out and repaired, ground out, or left alone and monitored.

WHAT CAUSES THE CRACKS?

In almost every case, cracks in composite floor tubes are initiated by a form of corrosion called stress corrosion cracking (SCC). This type of corrosion requires that tensile stresses be present on the tube surface at the same time as the tube is exposed to a specific liquid corrosive environment. Under exceptional circumstances, and in very few tubes, thermal fatigue might play a role in initiating cracks, but no such examples have been found in this study. Once a crack has initiated in a tube surface, it may continue to grow by SCC, by thermal fatigue, or a combination of both.

Substantial experimental evidence supports this conclusion. A technique known as transmission electron microscopy is capable of delineating microstructural features produced by thermal fatigue in the surface of the 304L layer of a composite tube. Relative to comparative standard test specimens subjected to thermal fatigue, floor tubes that have been examined by this technique do not possess microstructural features consistent with initiation of a crack by thermal fatigue [5]. Furthermore, comparing the fatigue behavior of fine-grained 304L stainless steel against standard design curves for thermal fatigue suggest that in excess of 100,000 cycles would be required to initiate fatigue cracks in 304L stainless steel, even with relatively extreme (150°C) temperature fluctuations. Careful monitoring of tube surface temperatures on a floor subject to substantial cracking has demonstrated that the tubes are exposed to an insufficient number of thermal cycles for a crack to initiate by thermal fatigue [6].

Modeling of residual stresses in composite tubes and panels made from composite tubes has revealed two circumstances under which tubes would be susceptible to SCC [7]. As the boiler initially heats up from ambient to operating temperatures, the difference in coefficients of thermal expansion and strength of the two materials in a composite tube subjects the outside surface of the 304L layer to sufficiently high compressive stresses that plastic yielding occurs. These stresses remain as long as the boiler operates normally. However, when the boiler is cooled from operating temperatures, the modeling predicts that the surface stresses will become tensile as the tubes cool about 50°C (90°F) below operating temperature, and will reach the yield stress of 304L after a temperature drop of about 90°C (160°F) [7]. Thus, in the ideal case of uniform heating and cooling, SCC only becomes possible as the tube cools below 250-270°C (480-520°F), depending on the operating pressure. Measurements of residual stresses in floor tube panels have verified the model predictions [8].

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. Laboratory experiments have demonstrated that SCC will occur over a temperature range of about 160°C to more than 220°C in hydrated mixtures of these salts (**Figure 5**) [9]. 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 [8,9]. Significantly, SCC has been induced in test samples exposed only to a moist salt mixture of sulfide and carbonate with no added hydroxide, at temperatures between about 160 and 200°C (320 and 390°F) – conditions which closely match those expected in the early stages of a water wash [9]. SCC will not occur at temperatures lower than about 160°C (320°F) within the concentration range of chemicals that might be expected during water washing, but has been demonstrated at temperatures as low as 60°C (140°F) in a highly concentrated or saturated solution of sulfide and hydroxide [8].

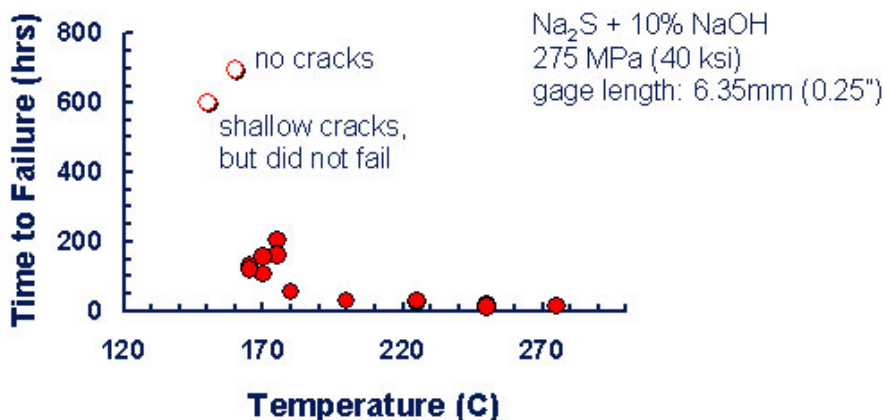


Figure 5. Effect of temperature on cracking of 304L stainless steel in a sodium sulfide 10% sodium hydroxide solution. Note that cracking occurs at temperatures above about 160°C.

These 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. 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 **Figure 6**. 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. A particularly dangerous situation for cracking exists when a residual bed of wet smelt is left on the boiler floor during a dry-out fire (**Figure 6b**). Floor tube temperatures can remain within the range of maximum susceptibility to SCC for several hours during a dry-out fire [10].

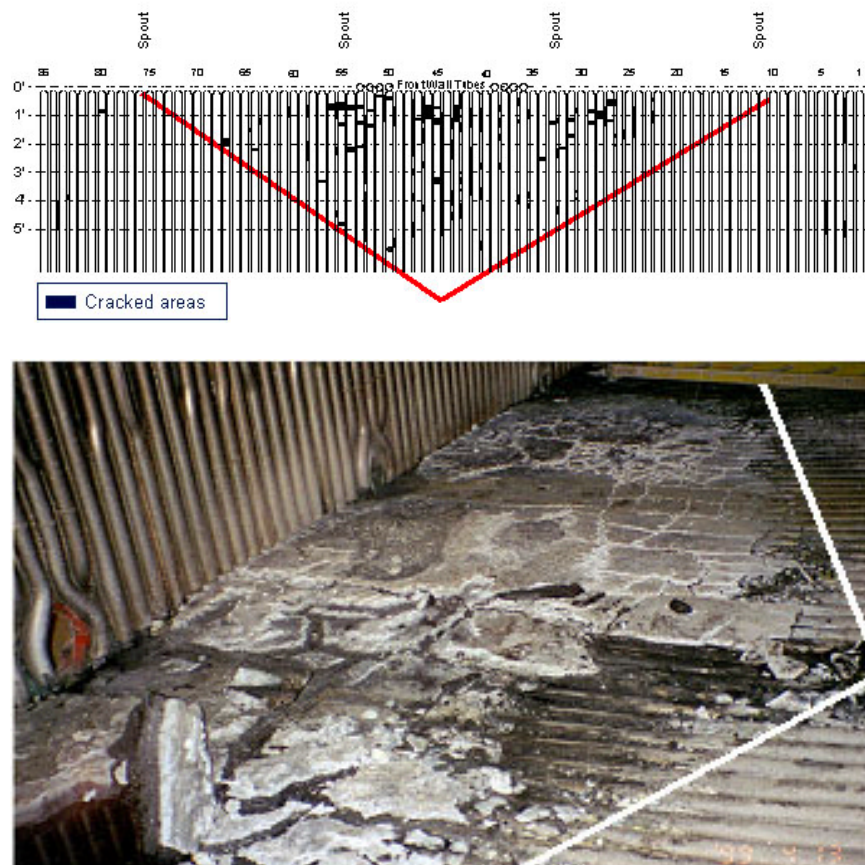


Figure 6. a) Schematic of recovery boiler floor showing location of cracking found in the tubes and membranes and b) photograph of recovery boiler floor showing the residual smelt bed that was present during a shut down. Note that both the cracking pattern and the residual bed have a "V" shape.

The surface of composite tubes may be put into tension during normal operation when the tube surface is subject to a sudden localized high thermal transient. When this happens, the heating and subsequent cooling of the tube back to operating temperature leaves the outer surface of the composite tube in tension [11]. Sufficiently large thermal transients appear to occur only infrequently but do happen on many locations in the floor. Typically, the smelt bed in contact with the floor tubes during operation is frozen, and a liquid phase capable of causing SCC should not be present. However, indirect evidence for the presence of a liquid polysulfide-rich phase on the surface of some boiler floor tubes has been found [12-14]. It has yet to be shown that SCC will occur in the presence of this compound.

ARE SOME TUBE MATERIALS MORE RESISTANT TO CRACKING?

Considerable information has been generated, both in the laboratory and in the field, on the cracking behavior of alternatives to the standard 304L stainless steel/SA210 Gd A1 carbon steel composite floor tubes. Alternatives include other co-extruded systems such as Alloy 825/CS and Alloy 625/CS or similar alloys with slightly modified compositions, systems where the outer layer is applied using a weld overlay method (most commonly with alloy 625), and chromized tubes. Evaluation methods have ranged from laboratory residual stress measurements, finite element modeling of residual stresses, and laboratory stress corrosion cracking tests to field tests of single tubes, small test panels and significantly larger panels [7].

As mentioned previously, in order for cracks to occur in a tube, whether by thermal fatigue, corrosion fatigue or stress corrosion cracking, tensile stresses have to be present on the surface of the tube. Studies have been conducted to measure the surface residual stresses as well as the stresses at the carbon steel/stainless steel interface on room temperature composite tubes [7]. Stress measurements have been made on single, as-fabricated tubes of co-extruded 304L/CS, co-extruded alloy 825/CS, co-extruded alloy 625/CS, weld overlaid alloy 625/CS and chromized carbon steel. Finite element modeling was then used to predict the stresses that would develop at operating temperature based on the measured room temperature values. Because of their higher yield strength and better match with carbon steel's thermal expansion coefficient, alloy 825 and, particularly alloy 625, do not have their stress state strongly affected by temperature changes.

Finite element modeling to predict the stress state that would be developed in a series of alloys with a wide range of yield strengths and thermal expansion coefficients indicates that, as shown in **Figure 7**, alloys with the properties of alloy 825 and alloy 625 in combination with carbon steel require more severe conditions for the stresses to become tensile in the floor tube panels.

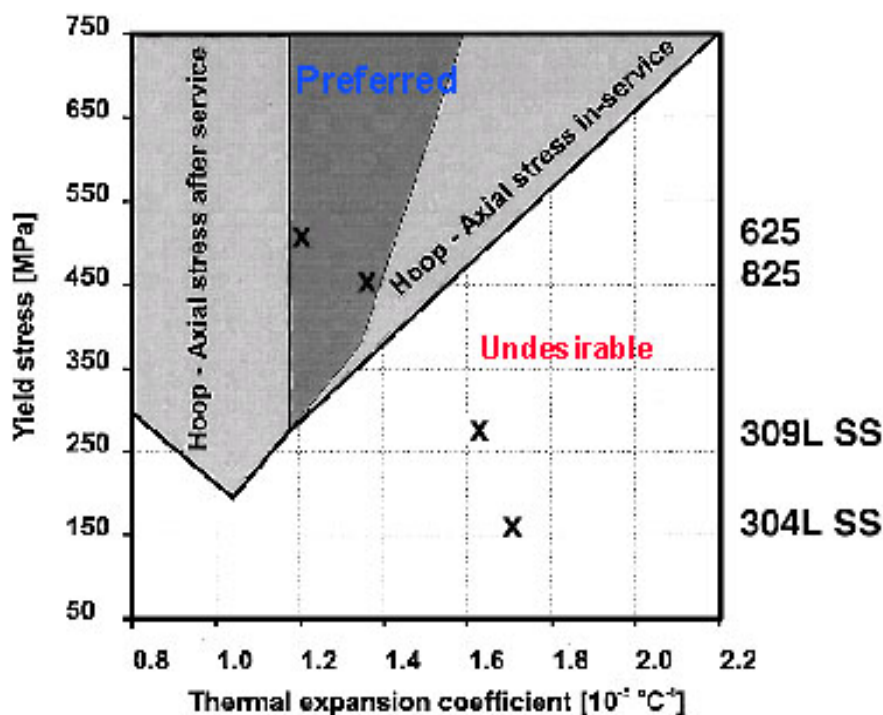


Figure 7. Plot of the stresses generated in co-extruded tube material when the outer, clad layer has the thermal expansion coefficient and yield stress shown on the axes of this plot. This plot indicates that alloys 625 and 825 have properties that result in less severe stresses being developed than would be seen with 304L and 309L stainless steels.

A combination of stress measurement and finite element modeling suggest that the stresses developed in chromized carbon steel tubes are compressive and remain that way through the thermal cycles experienced in a recovery boiler floor [10]. This result is explained by the unique variation in the thermal expansion coefficient that occurs as a function of chromium content in chromized tubes.

Laboratory studies of stress corrosion cracking in various solutions, but particularly in environments containing hydrated sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), show that such solutions can cause cracking of 304L stainless steel when held in the 150-200°C temperature range (Ref 8). By comparison, these laboratory tests show that Alloys 625 and 825 are much more resistant to cracking. These tests have produced very minor cracking of 825, and, for 625, have only produced cracks in sensitized material.

A direct comparison of three compositions of co-extruded tubes and two compositions of weld overlaid carbon steel tubes is being made in a North American recovery boiler. Operating experience from this particular recovery boiler has shown that co-extruded 304L/CS and weld overlaid 309L on carbon steel cracked during the second year of exposure (see **Figure 8**) while co-extruded 825/CS, co-extruded 625/CS and weld overlaid 625 have not cracked after five years of exposure. Reports of operating experience in Scandinavian boilers also indicates that an alloy equivalent to alloy 825 has operated in a recovery boiler floor for at least eight years without cracking.

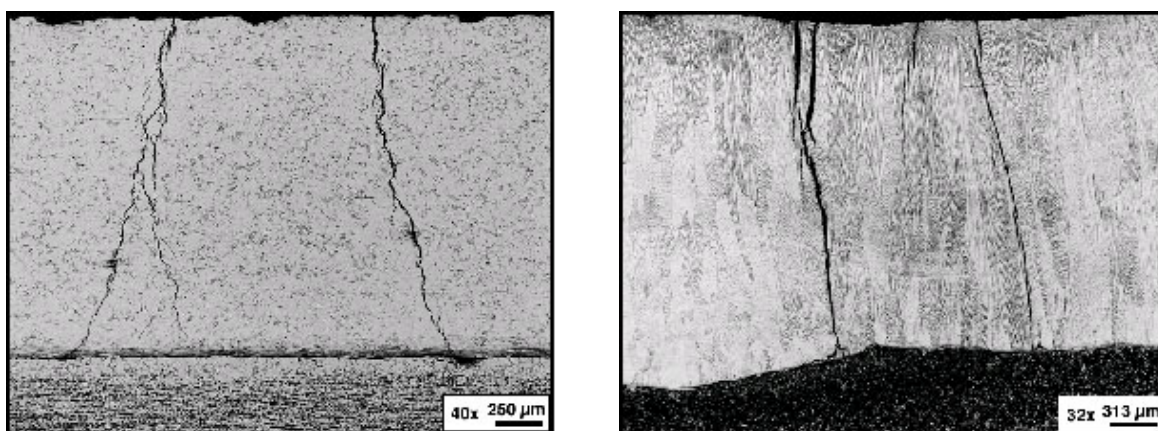


Figure 8. *Cross section of cracking in co-extruded 304L/carbon steel and 309L weld overlay tubing. Note that most cracks penetrate entirely through the stainless steel layer but do not continue into the carbon steel.*

It should be noted that these alloys are more resistant to the typical floor tube cracking problem, but they are, by no means, totally immune. Prudent use of these alloys would also involve following the operating procedures noted elsewhere in this report.

CAN I PREVENT FURTHER CRACKING OF EXISTING FLOOR TUBES?

To date, several mills have been able to avoid cracking the 304L/CS composite floor tubes in their recovery boilers. Based on their experience and our current understanding, it appears that

cracking is most likely to occur during water washes, dry-out fires, or other operating procedures which allow hydrated smelt to come in contact with the surface of the composite tubes at temperatures in the range of about 150-200°C (300-400°F). Cracking of 304L composite tubes would therefore be minimized by following an operating procedure during shutdowns in which the bed is burned out completely and water is not allowed to reach the floor until the floor tube surface temperature is below 150°C (300°F). The risk of cracking is greatly increased during a dry-out fire or a start-up if the floor is heated above 150°C (300°F) while in contact with hydrated smelt or concentrated wash water.

At least three mills (all with sloped bottom boilers) that follow these practices have avoided cracking in their composite floor tubes. In sloped floor boilers with low spouts, it is relatively easy to completely burn out the bed before washing, and then remove the remaining smelt covering the floor tubes during the wash. In sloped bottom boilers with high spouts, and in decanting bottom boilers, it is more difficult to remove the smelt from the boiler, and the need to allow the remaining bed to cool before beginning a water wash becomes more critical.

In the event that exposure of the floor tubes to wash water under a still-hot bed is unavoidable, a key question becomes how long at temperatures over 150°C (300°F) can be tolerated before damage to the floor occurs. As shown in **Figure 9**, in laboratory tests cracks have been produced in 304L in about one hour's exposure at temperature to a mixture of sulfide and hydroxide.

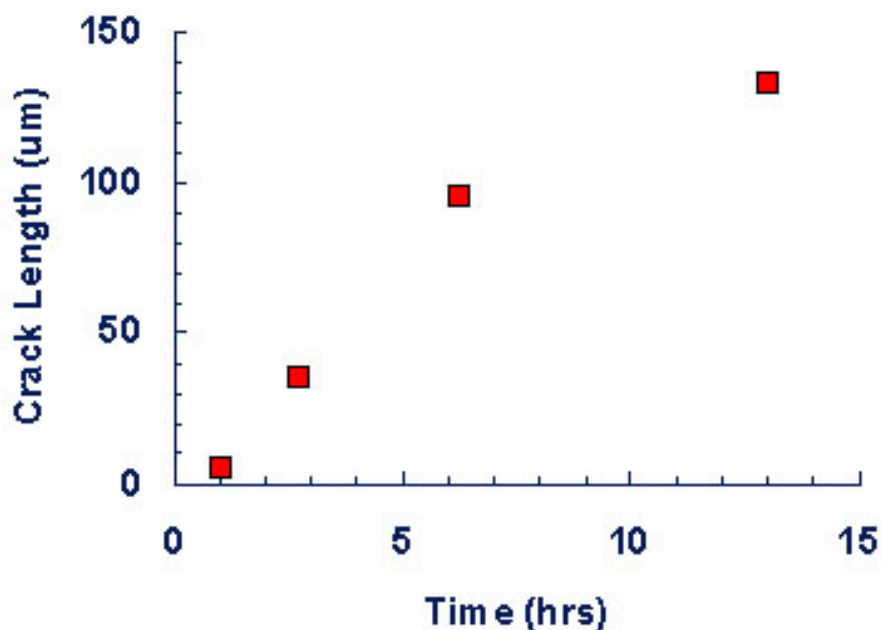


Figure 9. *Effect of exposure time on crack development in 304L stainless steel in a sodium sulfide 20% sodium hydroxide solution at 160°C. Note that short cracks are present after the first hour of exposure.*

The frequency of thermal fluctuations on floor tubes cannot be directly related to cracking, but elimination of these perturbations should prevent tensile stresses from developing on the tube surfaces at operating conditions, and this could have a beneficial effect on the progression of existing cracks via thermal cycling.

DO I ONLY HAVE TO WORRY ABOUT FLOOR TUBE CRACKING?

Cracking of floor tubes has been the principal focus of the existing research project. However, cracking of 304L composite tubing has been documented in air port and smelt spout openings as well as in floor tubes [3]. The same general principles apply for inspection of these areas for cracking as apply to floor tubes. While some aspects of the cracking in these other locations bear similarities to cracking in floor tubes, other features are very different. At present, our understanding of the causes of cracking in locations other than in floor tubes is insufficient to clearly identify solutions to the problem.

CONCLUSIONS

With care, cracking of 304L composite floor tubes in kraft recovery boilers can be minimized, or even prevented. However, when it is not possible to follow shut down and water wash procedures designed to minimize cracking, alternative materials to 304L composite tubes have been shown to substantially increase resistance to cracking. Some of these materials now have an extended history of successful operation in recovery boiler floors.

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