CORROSION AND CRACKING IN RECOVERY BOILERS

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ABSTRACT

The different chemical environments in different parts of a recovery boiler cause many different types of corrosion. They can also aggravate thermal and mechanical cracking. This paper discusses how tubes corrode and crack in each environment. Implementing proven strategies developed to reduce corrosion rates and inhibit cracking reduces the risks of smelt-water explosions, extends the service life of a boiler and reduces its operating cost.

INTRODUCTION

Recovery boilers can be divided into at least eight different zones that have distinctly different chemical environments (1, 2). Tubes respond to each combination of chemical, mechanical and thermal parameters in different ways. Understanding the causes of corrosion and cracking enables us to develop and implement strategies that reduce corrosion rates and inhibit cracking. This reduces the risks of smelt-water explosions, extends the service life of a boiler and reduces its operating costs.

CORROSION OF FLOOR TUBES AND LOWER FURNACE TUBES

Corrosion and cracking in lower furnace tubes is of particular concern because this area of the boiler is the greatest source of smelt-water explosions (3). Oxygen partial pressures in the lower furnace are too low to stabilize protective oxides on carbon steel tubes, although the reduced sulfur gases in the furnace are able to form iron sulfide scales on these tubes. The resulting corrosion rates depend primarily on the surface temperatures of the tubes, which in turn depend on the operating pressure of the boiler. At the temperatures of boiler tubes in units with operating pressures below about 900 psi, carbon steel tubes corrode slowly enough to have an acceptably long life. In higher pressure boilers the corrosion rates are significantly higher. Until the early 1970s, all recovery boilers operated at relatively low pressures and used carbon steel tubes. But since the 1960s there had been increasing numbers of reports of accelerated corrosion in newer boilers that were designed to recover more heat from the liquor by operating at higher pressure. For example, when the operating pressure exceeds 1000 psi the corrosion rate typically exceeds 0.018" per year. This gives carbon steel tubes an unacceptably short life.

Corrosion protection strategies developed to extend tube life include using pin studs to anchor an insulating layer of frozen smelt on the surface of carbon steel tubes and using tubes with a corrosion-resistant layer added to their fireside surface. Laboratory results (4) showed that Type 304L stainless steel has good corrosion resistance in simulated boiler environments and composite tubes, co-extruded with an outer layer (typically 0.065" thick) of Type 304L stainless steel over an inner pressure-bearing layer of carbon steel, have performed well in recovery boilers. Composite wall tubes and floor tubes were first installed in Scandinavian boilers in the 1970's. About 100 North American recovery boilers now have composite water wall tubes installed in the lower furnace. They are generally maintenance-free, although specific problems of localized corrosion and of cracking of composite floor tubes and air port tubes will be discussed later.

Corrosion-resistant layers can also be applied to boiler tubes by thermal spray coating, and by diffusing chromium into the surface of carbon steel tubes (chromizing). The highest pressure recovery boilers currently in service use high chromium ferritic steel weld overlay coatings for corrosion resistance.

Floor tubes corrode less than wall tubes, because the frozen smelt layer on their surface has no tendency to fall away. The frozen smelt provides a physical barrier to the penetration of corrosive gases, and an insulating barrier that reduces the surface temperature of the tubes. As a result,

carbon steel usually provides adequate corrosion resistance for floor tubes. Composite floor tubes have been installed in some boilers, but are unnecessary and problematic except in smelt runs.

FIRESIDE CRACKING OF COMPOSITE FLOOR TUBES

About 65 of the approximately 340 recovery boilers in North America have composite floor tubes. Although fireside cracking of composite floor tubes had been found in about two-thirds of the European recovery boilers with composite floor tubes by 1992, it was not noticed in North American boilers until 1993. Cracking is not usually found in composite floor tubes unless it has been previously found in composite spout opening tubes and composite floor panel membranes in the same boiler. In sloped floor units, cracking is more likely to occur near the spout openings and where floor tubes bend down towards the supply header. Fortunately, when deep cracks reach the stainless steel-carbon steel interface, they either end in a corrosion pit in the carbon steel or turn and run parallel to the interface.

There is increasing evidence that floor tube cracking is initiated during shut downs and water washes rather than during operation (5, 6). Laboratory testing has shown that the concentrated solutions of sodium sulfide and sodium hydroxide formed by dissolving a large amount of smelt in a small amount of water cause stress-corrosion cracking in the Type 304L stainless steel cladding in the temperature range160-200ºC (320-392ºF). To avoid the conditions that can produce cracking in composite floor tubes, do not begin to water wash until floor tube temperatures fall below 160ºC (320°F), and be sure that all the smelt is removed from the floor tubes before the boiler is fired up again.

Stress-corrosion cracking only occurs when tensile stresses are present. Finite element analysis has shown that the surface of composite tubes is in compression when a boiler is at its operating temperature. However, temperature monitoring has shown that floor tubes can experience brief temperature spikes of several hundred degrees. Stress modeling shows that these temperature spikes develop tensile stresses in the stainless surface layer that remain when the boiler cools to room temperature in a shutdown. It also shows that tubes clad with Alloy 825 and Alloy 625 develop much lower tensile stresses than conventional tubes clad with Type 304L stainless steel. Therefore, tubes clad with these alloys should be used as replacements in boilers with floor tube cracking problems.

Temperature spikes in floor tubes that develop tensile stresses in the surface of composite tubes propagate cracks by thermal fatigue. This can be minimized by installing a layer of packed refractory or interlocking tile over the floor tubes. Since floor tubes are not designed to supply much of the heat to the boiler water, the loss of steaming capacity of the boiler will be small.

LOCALIZED CORROSION OF AIR PORT TUBES

Both carbon steel and composite tubes suffer localized corrosion in the corners of port openings in high pressure boilers (7). Localized wastage on the furnace side of air port tubes is caused by high temperatures produced by the exothermic combustion of unburnt liquor on these tubes in the jet of air entering the boiler from the port.

The windbox side of air port tubes can also suffer localized corrosion. This has been attributed to the presence of molten sodium hydroxide in stagnant areas where it has not reacted to form sodium carbonate. Corrosion products that would otherwise protect carbon steel tubes (sodium ferrite) and composite tubes (chromic oxide) are fluxed (dissolved) away by molten sodium hydroxide, allowing rapid corrosion. On composite tubes, this fluxing can rapidly thin the stainless steel outer layer. Fortunately the thinning slows when the stainless steel outer layer is consumed and the underlying carbon steel is exposed. Typical corrosion rates might be 0.01 - 0.05" per year on the stainless steel layer but only 0.03 - 0.08" per year on the exposed carbon steel. Because the corrosion rate slows down when the underlying carbon steel is exposed, it produces expanding (but not deepening) bald spots that expose the underlying carbon steel, beginning at the top inner

corners of air port tubes. This balding can be weld-repaired with Alloy 625 before serious damage is done.

THERMAL FATIGUE CRACKING OF WALL TUBES BESIDE SMELT SPOUTS AND AIR PORTS

Thermal fatigue cracking has been reported in both carbon steel tubes and composite tubes at (primary) air ports and spout openings since about 1983. Around air ports the cracking is generally limited to the tubes that form the port opening itself, while around spout openings the cracking can spread to several tubes on either side. These tubes experience temperature excursions when the insulating frozen smelt layer is removed by rodding and when molten smelt washes up against the tubes. Cracking in tubes that form air ports is aggravated by residual tensile stresses from the forming of tube bends and from attachment welds. Although the fireside cracks in composite floor tubes discussed below turn at the base of the clad layer and propagate parallel to the tube surface, cracks in air port tubes and smelt spout tubes can continue to propagate into the carbon steel layer. This propagation appears to be driven by residual stresses introduced during the formation of the air port tube bends. Because the cracks can penetrate the carbon steel portion of these tubes this type of cracking must be inspected and repaired with particular care.

Recent work by Tran and others (8) shows that improved firing practices can eliminate tube cracking by reducing the occurrence of thermal spikes. If improved operational control does not eliminate the cracking, the cracked wall tubes should be replaced with Alloy 825-clad or Alloy 625-clad composite tubes.

MOLTEN SMELT ENVIRONMENTS

Molten smelt can dissolve carbon steel and composite tubes at rates equivalent to many inches per year. Fortunately the flow of water through boiler tubes keeps them cool, so the smelt freezes rapidly on them and insulates the tube surface from the corrosive effects of molten smelt. Flowing smelt produces higher corrosion rates than stagnant molten smelt. Student research at IPST has shown that rates up to the equivalent of 50" per year have been measured when the metal temperature is the same as the smelt temperature, simulating the case where tubes have boiled dry. Smelt flow across the tube surface accelerates the corrosion rate because the replenished smelt delivers more heat and wears away the insulating frozen smelt layer. To avoid this, smelt spouts are designed with internal water-cooling systems to keep their surface temperature low. Lowering the temperature of smelt spout cooling water 40°F can increase spout life four times. However, the temperature of spout cooling water must be kept above 140°F to avoid dew point condensation that could risk smelt-water explosions.

Smelt that freezes across air ports or smelt spouts interferes with the operation of the boiler, and must be removed by rodding. The removal of this frozen smelt suddenly exposes the tubes to hot molten smelt, and cycles of sudden heating can produce thermal fatigue cracking on the metal surface. Washing of the smelt bed up and down against wall tubes causes similar heating cycles. Because the outer stainless layer of composite tubing is restrained by the inner carbon steel layer, composite tubes are more vulnerable than carbon steel tubes to thermal fatigue cracking, particularly at fireside attachment welds.

CORROSION OF UPPER FURNACE AND SCREEN TUBES

Corrosion rates on upper furnace wall tubes, roof tubes and furnace screen tubes are two to three times slower than on lower furnace tubes because the addition of secondary and tertiary combustion air raises the oxygen partial pressure enough to stabilize protective iron oxides on carbon steel tubes. Additionally, radiative heat fluxes are lower and gas temperatures are lower, so tube surface temperatures are slightly lower. For this reason, composite tubes are not required in the upper furnace water walls.

Upper furnace wall tubes that are not seal welded to one another can suffer cold-side corrosion on the side of the tubes that faces away from the furnace. Deep and isolated pits and irregular channels of corrosion running down the length of the tubes can be produced by cold-side deposits acidified by furnace gases where they are wetted by water washing. This cold side corrosion propagates when

moist furnace dusts remain on the tube surface for long periods (e.g. when a unit is water washed but not fired to dry the tubes during an extended outage). Laboratory measurements show that moist tube deposits will corrode carbon steel at about 0.001" per day at ambient temperatures.

Recovery boilers operated with relatively cool smelt beds and consequently high concentrations of SO_2 and SO_3 in the flue gases tend to form sodium bisulfate deposits in the upper furnace (9). These have low melting point temperatures. If the melting point temperature of a deposit is lower than the surface temperature of an upper furnace tube, the molten deposit will flux off the oxides that would otherwise protect the tube. The corrosion initiates as pits that can appear in parallel lines like cat's claw scratches. It is likely that this pitting initiates where stresses in the tube have cracked the mill scale.

Pitting in upper furnace tubes can also be caused by the reduced sulfur gases that exist under partially-burned liquor particles. This type of corrosion only occurs when the liquor droplets are incompletely burned in the lower furnace (i.e. in heavily loaded boilers with inadequate mixing of combustion air) where partially-burned liquor droplets carry over and are deposited on upper furnace tubes.

FATIGUE CRACKING OF GENERATING BANK TUBES AND PENDANT TUBES AT RESTRAINTS

Fireside fatigue cracking in generating bank tubes (10) and in pendant tubes at restraints is a significant cause of critical leaks. Cracks initiate at the node where a vibrating tube is held stationary, e.g.

- where a generating bank tube passes into a drum
- where an economizer tube is welded into a header
- where pendant tubes are held by vibration bar clamps

These fatigue cracks proceed inwards from the fireside of the tubes and are largely unaffected by corrosion processes. They often appear as pairs of cracks close to the restraint and on either side of the tube in the plane of vibration (11). Fatigue cracking is aggravated by locally severe restraints, such as sharp corners on vibration bars produced by flame cutting, and by thinning caused by external wear from loose components like worn vibration bars.

Empirical studies have concluded that generating bank vibration bars are more trouble than they are worth unless the drum-to-drum distance exceeds 31’ (12). Where vibration bars are required, making them from an oxidation resistant alloy such as Type 304L stainless steel extends their life.

Similar cracking can occur at attachment welds on pendant tubes in the upper part of the boiler. If these welds are subject to excessive stresses, e.g. as a result of the “freeze up” of sliding tube connectors, or as a result of unexpectedly high amplitude vibration of the tubes, fatigue cracks will nucleate adjacent to the attachment weld on the outside of the tube. Through-wall cracks can cause severe damage by directing jets of water onto adjacent tubes that thin large areas and produce fish-mouth ruptures.

SUPERHEATER CORROSION

In the absence of molten deposits and unburned liquor carryover, rates of superheater corrosion depend only on the tube temperature and oxygen partial pressure. The corrosion rate is limited by the transport of reagents through the thickening surface oxide. Therefore, superheater materials can be made more corrosion-resistant by adding alloying elements that form oxides with lower solid state diffusion coefficients.

When a superheater temperature is high enough to produce unacceptably high corrosion rates on unalloyed carbon steel, tube materials with alloying additions of chromium are required. Although chromium oxidizes more readily than iron, chromium oxides have much lower diffusion coefficients than iron oxides. Commonly used superheater tube materials, in order of increasing corrosion resistance, are as follows:

Carbon steel
T11 steel (1% Cr)
T22 steel (2.25% Cr, 1% Mo)

Type 347 stainless steel (19% Cr)
Alloy 310 (25 % Cr)

Because the most corrosion-resistant of these alloys (the austenitic stainless steels like 347 and 310) would be vulnerable to waterside stress-corrosion cracking if the boiler water became contaminated by chlorides, some mills prefer to install composite superheater tubes with a Type 310 stainless steel (25% Cr) outer layer and a 2.25% Cr inner layer. These are more expensive than solid Type 347 superheater tubes, but combine the high oxidation resistance of the stainless steel outside layer with the high temperature strength and immunity to stress-corrosion cracking of the carbon steel inner layer.

Unburnt liquor particles carried over because of incomplete combustion (high loading and inadequate reaction with combustion air in the lower furnace) can destabilize protective oxides on the windward side of superheater tubes in the same way as was described earlier for screen tubes.

If the surface temperature of a superheater tube exceeds the melting point of the deposits on its surface, the surface oxides will dissolve rapidly into the molten deposits. For example, a 5°F increase in tube temperature (beyond the deposit melting point) can increase corrosion rates four- or five-fold. To avoid this rapid superheater corrosion, a mill should minimize the formation of molten bisulfates by reducing the excess volume of combustion air that produces SO_3, minimizing the S/Na_2 ratio in the flue gases and optimizing sootblower operation to keep the tubes clean.

The most aggressive conditions in superheaters are found at the front corner of the bottom bends in the hottest platens. These bends experience not only the highest heat flux but also erosion from particles entrained in the flue gases.

CORROSION AND EROSION IN GENERATING BANK TUBES

Since generating bank tubes are relatively cool and serve in a relatively oxidizing environment, corrosion allowances are generally small and sometimes zero. However, thinning can be caused by low melting point acidic sulfate deposits as on superheater and furnace screen tubes, and by erosion-corrosion caused by water droplets entrained in the sootblower steam.

Generating bank tubes often suffer "near drum thinning" (13). This is localized fireside thinning within about 0.5" of the outer surface of the mud drum. It produces an elliptical depression on the tube (shaped as if the tube was clay and you had pressed your thumb into it) where the tube faces the lowest sootblower. The thinning appears where dust particles are blown off the surface of the mud drum and against the tubes by sootblower jets. During each sootblower cycle, the dust particles scour a little oxide off the tube surface that was formed since the previous sootblowing cycle. Special ultrasonic equipment has been developed to detect and quantify this type of thinning from inside the tubes (14).

CAUSTIC STRESS-CORROSION CRACKING IN BOILER DRUMS

Slow leakage of boiler water out of boiler drums where generating bank tubes are not completely sealed into the drum can produce caustic stress-corrosion cracking. The leaking water flashes to steam when it reaches the outer surface of the drum, concentrating the water treatment chemicals. Caustic stress-corrosion cracking, also known as caustic embrittlement, occurs in carbon steel under tensile stress in caustic concentrations above about 5% at temperatures above about 300ºF. The tensile stresses may arise from operating pressures or from residual stresses produced by welding. The inside of the holes in a boiler drum contain residual tensile stresses from the rolling (inside-out expansion) of the tubes to seal them into the drum. The combination of hot concentrated caustic and tensile stress can drive caustic stress-corrosion cracks from hole to hole in a boiler drum and produce water leaks (15), particularly if the drum is made from high strength steel. Re-rolling generating bank tubes to improve the seal between tube and drum will eliminate the cracking only if every seal is perfect. Otherwise the additional rolling merely raises the tensile stresses that are driving the cracks. Seal welding leaking tubes to the drum is problematic also, because it introduces additional

stresses that tend to loosen the seals of adjacent tubes. A final solution to generating bank tube leaks often requires either very careful seal welding of all the tube seals or replacement of the generating bank tubes.

CORROSION IN ECONOMIZERS, PRECIPITATORS AND STACKS

Economizer tubes rarely suffer corrosion damage, although sootblower erosion can occur and external fatigue cracking has occasionally caused tube ruptures. Rates of thermal oxidation are low, and temperatures of water-filled economizer tubes are far below deposit melting temperatures. However, corrosion can be caused by dew point condensates. If surface metal temperatures in an economizer, precipitator or stack fall below the dew point temperature (typically 155-170°F), moisture will condense out of the flue gases onto these surfaces. This moisture will readily dissolve acid furnace gases (e.g. CO_2, NO_x, SO_x) and its pH can fall as low as 3.0 or 2.5. This acidic condensate will dissolve carbon steel. Dew point condensation generally occurs during low-load operation, where the flue gases are coolest, and in the winter. In precipitators it tends to occur first where shell heating or insulation are inadequate. Most boiler operators find it is more cost-effective to insulate or heat the precipitator shell than to raise the flue gas temperature. Where carbon steel precipitator or stack temperatures cannot be maintained above the dew point, Type 316L stainless steel or polymeric coatings provide useful protection.

WATERSIDE CORROSION

Corrosion damage on the waterside of boiler tubes is usually caused either by inadequate feedwater purity or by improper chemical cleaning. A well-monitored water treatment program and efficient deaerator operation are essential to avoid the corrosion damage and heating losses caused by insulating waterside deposits. Excessive waterside deposits cause two types of corrosion. They cause localized “oxygen pitting” under deposits where the environment is starved of oxygen, and they accelerate fireside corrosion by insulating the tube from the cooling effect of the water inside it which increases the fireside temperature. A related form of under-deposit corrosion can occur where sodium hydroxide becomes concentrated from the boiler water chemicals by a departure from nucleate boiling, by boiling under porous deposits or by waterline evaporation. Corrosion in concentrated caustic solutions under deposits is sometimes called caustic gouging. It produces localized corrosion with a smooth or wavy contour.

Waterside deposits are most likely to form where heat transfer is highest, i.e. on tubes at the smelt line (smelt-gas interface), around fuel burners, and under pin studs or other weld attachments that funnel heat into the tube. Tube samples are cut out of these regions to measure the deposit thickness and determine whether the boiler needs chemical cleaning,

Upset conditions that produce thick, insulating waterside deposits that restrict water flow can produce rapid fireside corrosion even on composite tubes.

The waterside of boiler tubes is also vulnerable to a form of corrosion fatigue cracking known as stress-assisted corrosion (16). During the first year when inspections for waterside cracking in recovery boilers became common (1992), nearly half the units inspected showed indications of cracking. In units over 12 years old, this percentage was over 80%. Cracks found in these inspections forced many companies to replace carbon steel lower furnace tubes. The cracking occurs on the waterside of tubes at locations where attachment welds are present on the outside of the tube. Despite cautionary bulleting from boiler manufacturers (17), pulp and paper companies had rarely, if ever, inspected for this type of cracking until a smelt-water explosion in the Stone Container Missoula, MT mill in May 1991 was traced to this cause. Recent research (18) has shown that stress-assisted corrosion is caused by local dissolution during water quality upsets at sites where the waterside oxide is fractured by tensile thermal stresses. Tensile residual stresses are generated within about 1” of attachment welds by temperature cycles to the boiler operating temperature and back (19). The locations most vulnerable to stress assisted cracking are floor-to-sidewall seals and

attachment welds at air ports and smelt spouts. Specialized radiographic techniques have been developed to detect these cracks and estimate their severity (20).

To minimize waterside stress-assisted corrosion, avoid excursions in feedwater quality. When recovery boilers are being built or rebuilt, make attachments to membranes rather than tubes wherever possible and avoid attachments that are localized and very strong. In units that have experienced waterside corrosion fatigue, use chelants rather than acids for scale removal and carefully monitor chemical cleaning operations, to avoid conditions that could damage the boiler.

Deaerators and deaerator storage tanks are vulnerable to stress-assisted corrosion beside welds in the pressure shell, particularly those below the water line. To prevent this cracking, control the feedwater chemistry and avoid water hammer. Also, carefully check design calculations and weld quality when purchasing a new deaerator.

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