CORROSION AND CRACKING IN CHEMICAL RECOVERY EQUIPMENT

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ABSTRACT

Causes of corrosion and cracking in individual items of chemical recovery equipment must be understood in order to minimize the lifetime costs of chemical recovery equipment. After reviewing these causes, this paper reviews appropriate materials of construction for major equipment items and proven strategies for extending the service life of existing equipment.

KRAFT LIQUORS

Basic Principles

The corrosivity of kraft liquors depends on their composition, their temperature and their rate of flow. At a given temperature and flow rate, the corrosion rate of carbon steel increases with the sulfidity and with the alkalinity of the liquor. As a result, white liquor is more corrosive than green liquor which is in turn more corrosive than black liquor. When sulfides are present, aeration of the liquor produces thiosulfates which accelerate the corrosion even more than sulfidity or alkalinity. This aeration effect causes accelerated corrosion of green and more particularly of white liquor at the waterline of storage tanks and clarifiers.

All liquors become more corrosive as their temperature is raised. However, this simple effect becomes more complicated in black liquor evaporators, where selective evaporation of more volatile components changes the liquor composition as evaporation proceeds. We will discuss these effects later.

The corrosion rate of stainless steels in kraft liquor environments depends on their chromium content. Figure 1 shows the thickness of seven weld overlay alloys applied at similar thicknesses to the wall of a digester and exposed to a year of batch cooks.. The corrosion resistance of these alloys was proportional to their chromium content, regardless of the other alloying elements they contained. Similar results have been obtained in other liquor environments.

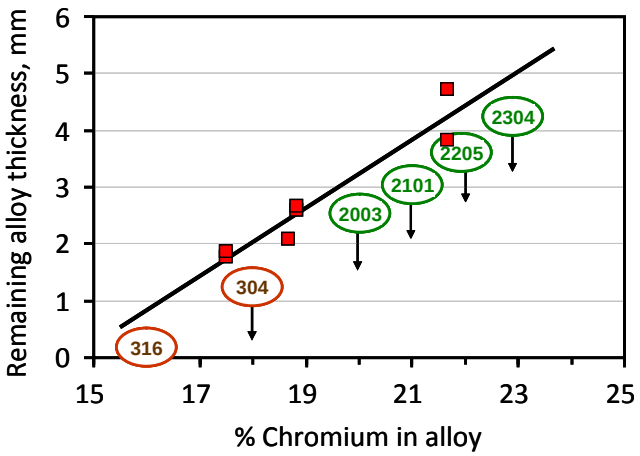


Figure 1: *Effect of chromium content on thickness of stainless alloys in kraft liquors. Common alloys superimposed according to their chromium content.*

The chromium content of candidate stainless alloys for kraft liquor service are also shown in Figure 1. Alloys 2003, 2101 and 2304 are commonly referred to as lean duplex stainless steels, while Alloy 2205 and more alloyed materials are simply called duplex stainless steels. The data in Figure 1 are consistent with pulp mill experience that Type 304 stainless steel (<18% Cr) and duplex stainless steels (e.g. Alloy 2003 (<20% Cr), Alloy 2101 (<21% Cr), Alloy 2205 (<22% Cr) and Alloy 2304 (<24% Cr) outperform Type 316 stainless steel (<16% Cr). . The ER 312 material commonly used for weld overlay repairs in digesters contains 28-32% Cr and typically produces overlays containing at least 25% Cr. In kraft liquor environments where carbon steel has an impractically short life, this relative performance indicator provides a useful starting point for materials selection decisions.

Black liquor

Black liquor is an aqueous solution of carbonates and sulfates that also contains a myriad of organic extractives dissolved from wood [1]. Its alkalinity is low and it can be handled and stored in carbon steel except where it is hot and fast-flowing. Oxidized black liquor is less corrosive than non-oxidized, so the liquor should be stored in the oxidized form where possible.

Although carbon steel can be used to handle weak black liquor at ambient temperatures, the hot and dilute liquors between the wash and extraction zones of softwood continuous digesters operating modern cooking processes can produce rapid thinning, especially where the caustic concentration is low [2] and temperatures, flow rates [3] and chloride concentrations [4] are high. The corrosive environments produced by hot dilute black liquors require high chromium duplex stainless steels [2].

To efficiently recover heat from the organic materials dissolved from wood chips in the pulping process, most of the water must first be removed from the black liquor by evaporation. Weak black liquor is stored at a concentration of about 15% solids and a temperature of about 170°F (77°C). The water is evaporated in a multiple stage steam-heated heat exchanger until the concentration reaches a target between 60% and 80% solids. The factors controlling corrosivity in evaporators are (a) the low molecular weight organic acids released in the low-solids stages and (b) the hot, concentrated alkali present in the small remaining aqueous phase in the high solids stages. The life of carbon steel in evaporator heads depends primarily on the organics present in the liquor and on the final liquor concentration and temperature. As a result some mills encounter corrosion at one end of the evaporator train and some at the other.

The alkaline salts that remain in very high solids liquor are concentrated within the very small remaining aqueous fraction. Their concentration in this aqueous fraction can be high enough to cause corrosion or stress-corrosion cracking on 300-series austenitic stainless steels. For this reason, process changes that increase black liquor solids have produced many corrosion and stress-corrosion cracking failures in Type 316 stainless steel equipment [5]. For additional corrosion resistance, replacement equipment handling concentrated liquors should be fabricated from a duplex stainless steel containing significantly more chromium [6]. Thinning and stress-corrosion cracking of 300-series stainless steels should be anticipated if black liquor concentrations are raised above about 75% solids and temperatures above about 285°F (140°C), because of the high alkalinity of the remaining aqueous fraction. Duplex stainless steels resist corrosion in hot concentrated black liquor (see Figure 1) and are almost immune to stress-corrosion cracking. In extreme cases, super-duplex alloys such as Alloy 2507 have been used. Foul condensates are normally handled in Type 316 stainless steel or Alloy 2205.

Evaporator tubes are routinely cleaned to remove carbonate scales. The least expensive (and most damaging) cleaning chemical is muriatic (hydrochloric) acid. This attacks Type 304 stainless steel and lean (low-molybdenum) duplex stainless steels and can cause stress-corrosion cracking in Type 304 stainless under high tensile stress (e.g. where the residual stress is high at weld intersections). To minimize this corrosion during acid cleaning, some mills have replaced Type 304 stainless steel tubes with Type 316. However, Type 316 is less resistant to corrosion in the process environment (see Figure 1). If Type 304 is used, it should be cleaned with formic acid or sulfamic acid [7]. If muriatic acid cleaning cannot be avoided, a better approach is to fabricate the evaporator from an SCC-resistant duplex stainless steel such as Alloy 2205.

Green Liquor

Dissolution of smelt from the recovery boiler into weak wash to form green liquor is a violent reaction that produces irregular and unpredictable thinning in the dissolving tank. Associated pressure pulses can propagate cracks at stress-raisers. Dissolving tanks should therefore be designed to be very strong, but not too rigid.

Stored green liquor is particularly corrosive at the waterline where aeration converts sulfides to thiosulfates and accelerates active dissolution. The presence of abrasive suspended solids (dregs) causes thinning where these materials scrape along the surface e.g. on the bottom of a clarifier or dregs washer, on the outside of pipe bends and on the bottom of piping. Piping should be made from lean duplex stainless steel. Lean duplex alloys are the material of choice for storage tanks also, when lifetime costs are considered.

Slaker, Causticizer and White Liquor Storage

Lime from the kiln must be slaked (converted to lime, i.e. calcium hydroxide) before it can be used to convert the sodium carbonate of the green liquor into the sodium hydroxide required for pulping. Good mixing is required to produce a uniform product. The lime particles are very abrasive and the mixing produces more abrasion than corrosion. The slaking reaction is rapid and strongly exothermic. It generates steam. The temperature increase accelerates the subsequent causticizing reaction and increases the proportion of calcium hydroxide converted to calcium carbonate (causticizing efficiency).

The hot white liquor that is produced is one of the most corrosive liquors in a chemical recovery plant. Its pH is greater than 13 and temperatures are normally above 200°F (93°C). Corrosion rates of carbon steel increase with pH, sulfidity, temperature, flow rate and aeration.

Corrosion rates of carbon steel in white liquor increase in proportion to the rate of liquor flow up to rates of about 2 m/s, after which it becomes independent of flow. Suspended “lime mud” (calcium carbonate) particles, which will be separated out in white liquor clarifiers, accelerate thinning by corrosion/erosion. Because carbon steel piping would have an impractically short service life, duplex stainless alloys are used for piping. Air oxidation of liquor sulfides to thiosulfate produces axi-symmetric accelerated thinning at the waterline of storage tanks and clarifiers.

50 to 60 years ago, when low-silicon steel grades were used to fabricate liquor tanks, carbon steel was widely used for handling and storing white liquor. The higher silicon content of today's structural steels (and weld filler metals) produces corrosion rates about three times faster than on the old low-silicon grades, so the service lives of modern carbon steel tanks have been reduced to 10 to 20 years. Because conventional grades of structural carbon steel have only marginally acceptable corrosion resistance for white liquor tanks, most mills are fabricating new white liquor tanks from lean duplex stainless steels. Those few mills that made their liquor tanks from low-silicon steel continue to obtain a reasonable service without upgrading to stainless steel.

Many different approaches have been used to repair aging liquor tanks. Gunnite (sprayed concrete) linings are inexpensive and long-lasting but make it impossible to visually inspect the process side of the tank wall for corrosion damage. Baked phenolic and other organic linings can extend tank life [8]. Electrochemical protection systems, which counterbalance the tendency of the steel to corrode, have achieved tenfold reductions in corrosion rate but need diligent monitoring and maintenance [9].

Many mills have sought to repair locally-thinned areas of liquor tanks with surface patches of 1/16 in. (1.6 mm) or 1/8 in. (3.2 mm) thick stainless steel sheet, because such "wallpaper" repairs can be made quickly and relatively inexpensively. Although successful procedures have been developed for this type of repair in the flue gas desulfurization industry [10], the required precautions are very rarely followed in pulp and paper mills. As a result the welds attaching the wallpaper often crack and allow corrosion to proceed undetected in the thinned material under the patch. Through-wall holes in insulated tanks are difficult to find, expensive to repair and potentially dangerous. "Wallpaper" repairs should be avoided except for temporary patches scheduled for replacement by new full thickness repair plates.

For new white liquor tanks and clarifiers, lean duplex stainless steel is the most cost-effective material of construction. This type of material has the additional benefit that it is not vulnerable to caustic stress-corrosion cracking, which can be a problem at welds in carbon steel equipment.

LIME KILNS

Lime kilns roast the calcium hydroxide recycled from causticizers. The size of modern lime kilns presents substantial mechanical challenges to their materials of construction. For thermal efficiency the kiln length/diameter ratio must be much greater than 30 and its slope between ¼" and ½" per foot (between 20 and 40 mm per meter). Misalignment of the kiln and uneven wear of the bearing surfaces produces fatigue stresses and corresponding cracking.

The gas temperature at the hot (low) end of the kiln, typically 1150-1250°C (2100-2280°F), is too high for all but the most advanced aerospace alloys. Therefore the carbon steel kiln shell is lined with refractory bricks. The bricks are installed in four zones - charging, preheating, burning and discharge. Curtains of chains are attached inside the kiln transfer heat from the combustion gases to heat and dry the wet lime tumbling along the kiln. A wide range of chain materials is available. Most of these materials are variants of Type 304H stainless steel with alloying additions to improve their resistance to abrasion and oxidation. The choice of alloy depends on the operating temperature and the location of the bricks within the kiln. Mechanical damage to the refractory bricks caused by the chains rubbing against them can be detected during kiln operation by inspecting for hot spots using IR thermography. A lack of timely maintenance to damaged refractory will allow these hot spots to grow and cause shell buckling.

The refractories used to line lime kilns are generally magnesia-spinels ($MgO + MgO.Al_2O_3$). The magnesia makes the brick chemically basic so that it can survive the highly basic environment of the lime kiln. However, magnesia has a high coefficient of thermal expansion, high thermal conductivity, and poor thermal shock resistance. Spinel ($MgO.Al_2O_3$), which is a better insulator and has a lower coefficient of thermal expansion, is mixed into the brick material to dilute the magnesia and reduce its thermal expansion and thermal conductivity. The large difference in thermal expansion between the magnesia and the spinel improves thermal shock resistance by creating micro-cracks in the brick. Unfortunately the spinel portion of the brick is susceptible to corrosion because its alumina reacts readily with lime to form calcium-aluminates that have melting point temperatures below 2500°F (1370°C). Also if silicates are present e.g. from alumina-silicate bricks, low melting temperature calcium-aluminum-silicates can form. Installing an initial layer of lime forms a protective layer of lime refractory over the refractory bricks and extends their life.

60% to 70% alumina brick linings are often used in preheating zones and burning zones and 60% alumina brick is used in insulated zone linings.

Two-layer brick systems, with an outer layer of insulating bricks, enable the lime to be calcined at a lower temperature with a longer retention time by providing better insulation (heat retention). This avoids the formation of molten refractory reaction products. The disadvantage of two-layer brick systems is that they must be started up and cooled down more slowly than single layer systems.

RECOVERY BOILERS

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.

Recovery boilers can be divided into at least eight different zones that have distinctly different chemical environments [11, 12]. 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.

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 [13]. Oxygen partial pressures in the lower furnace are too low to stabilize protective oxides on carbon steel tubes, but the partial pressure of reduced sulfur gases in the furnace is high enough 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 (62 bars), carbon steel tubes corrode slowly enough to have an acceptably long life. Corrosion rates in higher pressure boilers are significantly higher. For example, when the operating pressure exceeds 1000 psi (69 bar) the corrosion rate typically exceeds 0.018" per year (0.46 mm per year), giving carbon steel tubes an unacceptably short life.

The first strategy developed to extend tube life in recovery boilers was to install pin studs to anchor an insulating layer of frozen smelt on the surface of carbon steel tubes. However, although studding continues to be widely used, careful studies have shown that the removal of studs does not increase the thinning rates of wall tubes [14].

Forty years ago, laboratory tests [15] showed that Type 304L stainless steel had good corrosion resistance in simulated recovery boiler environments. Composite tubes, co-extruded with an outer layer (typically 0.065" (1.65 mm) thick) of Type 304L stainless steel over an inner pressure-bearing layer of carbon steel, were introduced to the industry as a result of this research. They have generally performed very well in recovery boilers. Composite wall tubes and floor tubes were first installed in Swedish and Finnish boilers in the 1970's. About 100 North American recovery boilers now have composite water wall tubes installed in the lower furnace. Although composite tubes are generally maintenance-free, they have specific vulnerabilities to fireside cracking in floor tubes and to localized corrosion in air port tubes that will be discussed later.

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

Floor tubes corrode less than wall tubes, because they are normally covered by a thick layer of smelt that 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.

Fireside cracking of composite floor tubes

About 65 of the approximately 340 recovery boilers in North America have composite floor tubes. Note that composite tubes are unnecessary and problematic in floor tubes at smelt runs. Although fireside cracking 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 appeared in composite spout opening tubes and in membranes between composite floor tubes 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 in composite floor tubes reach the stainless steel-carbon steel interface, they either end in a corrosion pit in the carbon steel or turn 90° and propagate along the interface.

There is increasing evidence that floor tube cracking is initiated during shut downs and water washes rather than during operation [16, 17]. 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 range 160-200ºC (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.

The stress-corrosion cracking only occurs when tensile stresses are present. Finite element analysis has shown that the difference between the thermal expansion coefficients of the two layers of composite tubes produces compressive stresses in these tubes when the boiler is at its operating temperature. However, temperature monitoring has shown that the floor tubes can experience brief temperature spikes of several hundred degrees. These temperature spikes develop tensile stresses in the stainless surface layer that remain when the boiler cools to room temperature in a shutdown. Stress modeling 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 Alloy 825 or 625 should be used as replacements in boilers with floor tube cracking problems.

The temperature spikes in floor tubes that develop tensile stresses in the surface of composite tubes also propagate stress-corrosion 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.

Thermal fatigue cracking of wall tubes surrounding 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 previously 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.

Work by Tran and others [18] shows that improved firing practices can reduce the fireside cracking of composite tubes by reducing the occurrence of thermal spikes. In cases where the cracking cannot be eliminated by improved operational control, cracked wall tubes should be replaced with Alloy 825-clad or Alloy 625-clad composite tubes.

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 [19]. Localized wastage on the furnace side of air port tubes is caused by high temperatures produced by the exothermic combustion of unburned 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) can be 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 (0.25 – 1.25 mm per year) on the stainless steel layer but only 0.03 - 0.08" per year (0.75 – 2.0 mm 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” should be weld-repaired with Alloy 625 before serious damage is done.

Molten smelt environments

Researchers at IPST documented corrosion rates on carbon steel up to the equivalent of 50" per year (1.25 m per year) when the metal temperature was allowed to rise to the smelt temperature, simulating the case where tubes have boiled dry. The flow of smelt across a 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 (4.5°C) can increase spout life four times. However, the temperature of spout cooling water must be kept above 140°F (60°C) to avoid dew point condensation that could risk smelt-water explosions.

Like smelt spouts, wall tubes depend on the cooling effect of the water that flows through them to freeze the smelt on their fireside surface and to insulate them from the corrosive effects of molten smelt. Smelt that freezes across air ports, or across 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 a boiler wall produces similar thermal cycles in the wall tubes. Because the outer stainless layer of composite tubing is restrained by the inner carbon steel layer, composite tubes are more vulnerable than solid carbon steel tubes to thermal fatigue cracking, particularly at fireside attachment welds. When waterwall panels are being replaced, attachments should be welded to the membrane rather than to the tubes.

Because composite tubes are softer than carbon steel lances, rods should be made from stainless steel or nickel to avoid to avoid mechanical damage.

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 these reasons, 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 before an extended outage). Laboratory measurements showed that moist tube deposits corrode carbon steel at about 0.001" per day (0.025 mm 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 [20]. 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 [21] 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 [22]. Fatigue cracking is aggravated by locally severe restraint, sharp corners on vibration bars, and local external wear from worn vibration bars.

Empirical studies have concluded that generating bank vibration bars cause more problems than they solve unless the drum-to-drum distance exceeds 31’ (9.5m) [23]. Where vibration bars are required, making them from an oxidation-resistant alloy such as Type 304L stainless steel extends their life.

Fatigue cracking can also 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 initially reacts much faster than iron, chromium oxides are much more protective 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)

A more complete review of corrosion in recovery boiler superheaters may be found in References 24 and 25.

Because some of the most corrosion-resistant superheater alloys (the austenitic stainless steels like Type 347HFG and 310) would be vulnerable to waterside stress-corrosion cracking if water contaminated by chlorides entered the superheater, some mills have instead installed 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.

Unburned 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 [24, 25]. For example, a 5°F (2.8°C) increase in tube temperature (beyond the deposit melting point) can increase corrosion rates four- or five-fold.

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 temperature acidic sulfate deposits and by erosion-corrosion caused by water droplets entrained in the sootblower steam.

Generating bank tubes often suffer "near drum thinning" [26]. This is localized fireside thinning within about 0.5"(13mm) of the outer surface of the mud drum. It typically 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 [27].

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 in the remaining liquid. 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 300°F (149°C). Such 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 [28], 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 all 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 tube temperatures are far below the melting temperatures of economizer deposits. However, corrosion can be caused by dew point condensation. If surface metal temperatures in an economizer, precipitator or stack fall below the dew point temperature (typically 155-170°F; 68 to 77°C), moisture will condense out of the flue gases onto these surfaces. This moisture will readily dissolve furnace gases (e.g. CO_2, NO_x, SO_x) producing acidic solutions with pH as low as 3.0 or 2.5. Such acidic condensates will dissolve carbon steel. Dew point condensation generally occurs in the winter, during low-load operation and where the flue gases are coolest. In precipitators it tends to occur first where shell heating or insulation are inadequate. In most boilers 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 and thus increasing 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, and the type of cleaning chemicals that would be useful.

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 [29]. 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 [30], 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 [31] 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 [32]. The locations most vulnerable to stress-assisted cracking are floor-to-sidewall seals and attachment welds at air ports and smelt spouts. Similar cracking has been documented in recovery boiler superheater tubes. The mechanism is probably the same – cycles of cracking of the steam-side deposit under tensile stress followed by oxide formation on the exposed metal surface. Specialized radiographic techniques have been developed to detect these cracks and estimate their severity [33].

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.

Flow-assisted corrosion (FAC, sometimes called flow-accelerated corrosion) caused more than one-third of tube failures in utility boilers between 1998 and 2008 [34] but has received little attention in the pulp and paper industry. FAC is not the same as erosion-corrosion. Erosion-corrosion involves impingement by particles or cavitation by bubbles that produce mechanical wear. In FAC, fast-flowing water dissolves a waterside oxide that would normally be rather insoluble, exposing the metal substrate which then corrodes to re-form more oxide in continuous cycles of metal loss.

Although Reference [34] offers a list of the most vulnerable sites to FAC in conventional fossil plants and a flow chart of recommended steps to address it, the selection of inspection sites to determine whether or not FAC is present presents a major challenge. Utility companies typically use CHECWORKS software developed by EPRI to predict the most likely locations based on models of flow and water chemistry. In contrast, pulp and paper mills select a few representative sites that are expected to be vulnerable to FAC, e.g. unalloyed carbon steel experiencing water velocities >2.4 to 3 m/s (particularly at changes in geometry like elbows and reducers that can produce turbulence), pH 7 to 9.5, oxygen concentrations <20 ppb and temperatures 100 to 250°C [35]. Where significant FAC damage is found, the inspection is expanded to include additional potential sites.

Thickness measurements to detect FAC should use a three-dimensional method, like phased array ultrasonic testing, that interrogate a large volume of material rather than grid measurements that can miss the thinnest spots in a scalloped surface. To measure thinning rates, inspection locations must be very carefully documented to allow the exact overlay of subsequent thickness profiles.

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