COMPOSITE TUBES AT LOWER FURNACE OF KRAFT PULPING PROCESS CHEMICAL RECOVERY BOILER– MATERIAL AND CRACKING PROCESS ANALYSIS

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Abstract. Chemical recovery boiler is an essential and critical equipment at Kraft pulping mills. Essential because it makes the Kraft process economically feasible by recovering the chemical products used for pulping, besides the steam production for process and energy generation, and critical due to the highly aggressive environment its construction materials are subjected to. An especially critical area is the lower furnace where the combustion and chemical reactions of the fuel, called black liquor, occurs resulting in a corrosive environment with a high melting point mixture of salts denominated smelt. If a crack allows the contact of the water that flows through the boiler tubes with the molten smelt, the entire furnace can explode due to instantaneous vaporization. Therefore, the boiler tubes cracking is, not only a safety and operational problem, but also a financial problem, being necessary the application of tubes especially resistant to corrosion, high temperatures and loads besides economically viable. This paper addresses the development and performance of composite tubes applied at lower furnace of chemical recovery boiler and the experience of Klabin Papéis Monte Alegre.

Key-words: composite tube, recovery boiler, cracking, kraft pulping.

1. Introduction

Brazil is the seventh largest cellulose pulp and the eleventh largest paper producing country in the world with an annual production of 9.5 and 8.2 million metric tons respectively. Since the production is intensively directed to exportation and creates directly about 100 thousand employs, the pulp and paper industry contributes greatly to the Brazilian economy (Bracelpa, 2004).

To keep the global competitiveness it is essential for pulp and paper mills to reduce costs and maximize operational resources. Therefore the application of new technologies to enhance reliability and consequently increase the overall efficiency of the mill is a key element in the global economy.

This is especially applicable to mills that use the Kraft pulping process. Among the pulping processes, the Kraft is the most used worldwide, inclusive in Brazil where 97% of the mills utilize this process (Bracelpa, 2004). The Kraft is a chemical and high demanding electricity process, facts that to comply environmental, power supply and economical conditions, require large investments in equipments.

Among all process equipments, the chemical recovery boiler is the most important and complex at a Kraft pulp mill; it is the biggest in size and in investment required (Velázquez, 2000). The economical feasibility of Kraft pulping process resides on the fact that almost all chemicals used can be regenerated. The chemical recovery boiler is then essential for the process; primarily it recovers the cooking chemicals and secondarily produces energy and process steam (Kulas, 1989).

The recovery boiler subjects its structural tubes to high temperature, pressure and corrosive environment that can cause cracking. If a crack allows water that flows through the tube to escape and come into contact with the molten mixture of salts, called smelt, formed by the combustion of the fuel, strong black liquor, inside the furnace, a large explosion can occur, since the rapid vaporization of one pound of water can release as much energy as half pound of TNT (Parrish, 1998). The damage caused by such explosions typically requires days to week to repair and endangers the personnel life. According to Howell, Silbertglitt and Norland (2002), the pulp and paper industry estimates that, on average, for each day a recovery boiler is shut down, a company loses US$ 300.000,00.

To prevent the incidence of cracks in recovery boiler tubes, the application of composite tubing of stainless steel on carbon steel at critical areas have become a common practice. Over time, operating procedures and performance improvements have been made, resulting in heat flux, temperature, pressure and corrosivity increase to a level where conventional carbon steels are no more applicable (Keiser et al, 2001). Alternate materials have been providing acceptable solutions in most recovery boilers; however in some cases the alternate materials have solved the original problem but introduced new issues.

For Parrish (1998), although much study has been done, the only known method to avoid smelt-water explosion is to prevent smelt-water contact. Therefore, the specification and behavior understanding of tubing materials under
operational conditions is a very important matter to prevent cracks and to ensure plant safety and economical performance.

This paper constantly addresses the recovery boiler of the Klabin Papéis Monte Alegre mill as a case study. The mill has one chemical recovery boiler built in 1978 and underwent modifications to increase the capacity at the years 2000 and 2003.

2. Kraft pulping process

In the cellulose pulp production by Kraft process, the wood chips that have been reduced to a manageable size are cooked in a digester with a solution composed mainly of sodium hydroxide (NaOH) and sodium sulfite (Na₂S), known as white liquor. The goal of cooking is separate lignin, the substance that holds the wood fibers together, from cellulose, that is, to allow the wood chips to be broken into individual fibers to form the cellulose pulp.

After cooking stage, the cellulose pulp is separated from the cooking solution in water washers, and the leftover substance, denominated weak black liquor at this part of the process, is sent to the recovery unity. The weak black liquor contains chemicals and organic components (wood impurities consisting of mostly lignin) with an average 15% solid concentration.

At the recovery unit, the weak black liquor is concentrated in multiple evaporators to over 58% of solids, denominated then strong black liquor, and sent to the chemical recovery boiler. At the recovery boiler, the strong liquor is combusted to recover feedstock. As the black liquor is burned, a substance composed mainly of sodium carbonate (Na₂CO₃) and sodium sulfide (Na₂S) called smelt forms at the bottom of boiler furnace and, after reaching a certain depth, flows out of the boiler through smelt spouts and is sent to the chemical recovery process.

The smelt is then separated in small clusters by a series of shatter jets, which sprays steam onto the smelt at a high speed, and solubilized with water forming a substance called green liquor. The green liquor is treated with hydrated lime, which turns the sodium carbonate (Na₂CO₃) into sodium hydroxide (NaOH). The completion of this process converts green liquor into white liquor that is then fed back into the digester to continue through the pulping process again.

2.1 Chemical recovery boiler

The chemical recovery boiler is a chemical reactor and a steam generator. The pulp production capacity of a mill determines the size of the recovery boiler. For each ton of pulp, about 1.36 ton of dry solids are generated (Parrish, 1998). A contemporary recovery boiler is similar to a large industrial watertube boiler and may be either two drum design or single drum. The single drum design has the advantage of removing the drum from the corrosive flue gases formed by the combustion of the black liquor and eliminating potential leakages from rolled tubes joints.

A modern recovery boiler is normally composed of four main parts: furnace, superheaters, boiler bank and economizers. The furnace is generally taller than a utility or industrial watertube boiler of similar steam generating capacity, due to the sticky nature of the combustion gases (Parrish, 1998).

The furnace is the most critical area for the boiler tubes because it is where the combustion, pyrolysis, drying and salts reduction of the black liquor take place. These complex reactions and processes are contained within a completely water-cooled furnace composed of walls of tubes linked by fins. Especially critical is the lower part of the furnace where the melting salts undergo the most part of the chemical reactions at high temperature and the partially combusted liquor accumulates. Black liquor is burned in oxygen deficient environment and the gaseous and molten inorganic combustion products are extremely corrosive (Clement and Blue, 1996).

The black liquor is sprayed into the lower furnace, being dried and occurring pyrolysis of the organic fraction as it falls toward the furnace hearth. The inorganic fraction is reduced in the char bed to regenerate the pulping chemicals. The fuel is sprayed, not atomized, to minimize the quantity of particles dragged by combustion gases out of the furnace that can cause deposits at the superheater and boiler bank.

Black liquor recovery boilers have auxiliary fuel burners located near the floor to raise the temperature for initiating combustion of the black liquor an to stabilize combustion if upsets occur. Auxiliary burners may also be provided higher in the furnace to supplement heat input during times of limited liquor availability or other reasons (Parrish, 1998). The auxiliary fuel burners are located at the furnace walls as well as the black liquor sprayers and the air supply ports.

The recovery boiler at Klabin Papéis Monte Alegre mill has air ports distributed in three (primary, secondary and tertiary) levels, six black liquor sprayers and seven auxiliary burners (heavy oil as auxiliary fuel) located at the same level of the secondary air ports. At the mill, the black liquor is concentrated to 72-80% of solids with a calorific power range of 2900 to 3200 cal/g depending on the wood characteristics and cooking conditions. The burning capacity of the boiler is 2200 tons of dry solids per day, 50 to 55 bar of steam pressure at the drum and temperature of 400 °C at the primary superheater outlet.

3. Characterization of lower furnace environment
The fireside of the recovery boiler lower furnace is exposed to very high temperatures and a complex chemical environment. The black liquor burned at the case study boiler contains 60-75% of dissolved organic elements and the remaining inorganic constituents are mainly Na$_2$CO$_3$, Na$_2$SO$_4$, NaOH, Na$_2$S, Na$_2$S$_2$O$_3$ with minor quantities of NaCl, potassium salts and transition metal ions, besides 28-20% of water.

The remaining char contains 5 to 10% carbon in addition to the inorganic salts. In the char bed, the carbon is oxidized to CO and CO$_2$, and Na$_2$SO$_4$ is reduced to Na$_2$S. The inorganic salts melt and flow out of the boiler through smelt spouts (Kulas, 1989).

The waterwall tubes in the lower furnace can be exposed to three different phases: lower furnace gases, molten smelt and frozen smelt. Major constituents of lower furnace gases are N$_2$, H$_2$O, H$_2$, O$_2$, CO and CO$_2$ with smaller quantities of H$_2$S and SO$_2$. Kulas (1989) study reveals that the elements H$_2$S and O$_2$ have the biggest effect on corrosion rate.

At boiler operation, the wall tubes in lower furnace are covered with a layer of flowing smelt with a thin layer of molten smelt flowing down the outside of the frozen layer because smelt melting point is considerably above the surface temperature of the tubes. Occasionally the frozen smelt layer falls off exposing the tube surface to molten smelt, corrosive gases or both.

During normal operating conditions, a solid bed of salts (primarily Na$_2$S and Na$_2$CO$_3$) forms on the floor of the recovery boiler. These salts have a melting point of at least 500°C, barring large temperature fluctuations. During water-wash (process with purpose to remove deposits from tubes to facilitate maintenance and inspection), boiler start-up and dry-out (process to remove moisture remaining from water wash), the environment consists mainly of Na$_2$S, Na$_2$SO$_4$ and Na$_2$CO$_4$. Na$_2$S is known to absorb and retain water at temperatures up to 180°C and the presence of NaOH, which can form when water is introduced to the boiler, tends to increase its ability to retain a liquid phase at even higher temperatures (Howell, Silbergiltt and Norland, 2002).

4. Characterization of boiler tubes

4.1. Introduction of composite tubes

Composite tubes consist of an external layer of stainless steel, metallurgically bonded to an internal load carrying layer of carbon steel tube. They are typically made by hot co-extrusion followed by cold rolling, annealing and straightening. In recovery boilers, they were first used in the early 1970’s with the outer layer of stainless steel providing corrosion protection and the inner layer providing mechanical strength. Besides, the inner layer is carbon steel because stainless steel in contact with the boiler water is susceptible to stress corrosion cracking (Kulas, 1989).

Before the introduction of composite tubes, carbon steel tubes with studs on the outer surface were used in the Kraft recovery boilers. They were chosen for their low price, ease of welding and capability to withstand very high pressures. The studs on the outer tube surface were intended to promote insulation from the high temperatures inside the boiler through solidification of the smelt, as shown in Fig. 1. However, according to Howell, Silbergiltt and Norland (2002), at high temperatures, the carbon steel exhibits an especially high sulfidation rate, which sometimes led to failure of the tube.

![Figure 1. Schematic of studs insulation](image-url)

The first composite tube installed in recovery boilers was with stainless steel type AISI 304L at the outer surface due to its resistance to sulfidation at high temperatures. The industry main objective of introducing this kind of tubing was a maintenance free furnace, but by the early 1980’s, it became apparent that composite tubing could develop cracks (Barna and Rivers, 1999).

At the case study recovery boiler, the floor is made of SA 210 A1 studded carbon steel tubes with 63,5mm outer diameter and 6,3mm wall thickness. There are 116 tubes in the floor. The tube walls at the lower furnace are still fabricated using SA 210 A1/AISI 304L composite tubes with the same dimensions of the floor tubes and welded in panels with AISI 304L fins. Figure 2 is the schematic cross section of the walls tubes at lower furnace.
4.2. Characterization of cracking and tube materials

The potentially devastating consequences associated with tube failure require the understanding of the mechanisms responsible for tube cracking. Inspections, nondestructive and metallographic examinations of cracked tubes have allowed the opportunity to improve this understanding and great debate continues as to the root cause of cracking in composite tubing, but some issues are generally agreed upon.

Cracks initiate in the stainless steel cladding and penetrate transgranularly the cladding with little branching to the interface with the carbon steel inner layer. At the inner layer cracks normally end with a corrosion pit or grow along the interface not penetrating the carbon steel layer (Barna and Rivers, 1999).

Hänninen et al. (2001) remark that when the propagation along the interface occurs, the heat transfer is limited producing a crevice where corrosion can be enhanced and in worst cases delamination and spalling of the stainless steel can occur exposing the carbon steel layer to the aggressive furnace environment. Yet, in some cases, cracks may continue past the interface and penetrate the carbon steel layer.

Barna and Rivers (1999) relate that if cracks exist in the form of a crazed pattern, they will typically not penetrate beyond the stainless cladding and into the carbon steel pressure bearing tube and if cracks develop in a circumferential pattern, there is a likelihood that cracking has or will penetrate into the carbon steel layer. Metallographic examination of cracked tubes retired from the case study boiler revealed that the characteristics cracking patterns were followed. Figures 2 shows the lower portion of a smelt spout opening taken off operation in 2004 showing a crazed pattern cracking and Fig. 3 shows the cross section indicated with crack ending at the composite tube interface.

Figure 2. Crazed pattern cracking
Figure 3. Cross section 2

Figure 4 shows a circumferential pattern crack indication after liquid penetrant test of a smelt spout opening tube taken off operation in 2003 and Fig. 5 shows the cross section indicated with crack penetrating the carbon steel layer.

Figure 4. Circumferential pattern cracking

Figure 5. Cross section 1c

Two factors determine the likely severity of a leak: the amount of water coming in contact with the smelt and proximity to the smelt bed (Howell, Silberglit and Norland, 2002). Since the floor tubes are closer to the smelt bed, they are considered more critical regarding tube leak. However, at the case study boiler, inspections of the floor tubes did not reveal major signal of studs wear or tube affecting along the operation time. Due to the proximity to the smelt bed, the main sources of risks are the primary air ports (Fig. 6) and smelt spout openings (Fig. 7).
Keiser et al. (2001) report that the smelt spout openings tubes and the tubes adjacent revealed cracking fairly soon after composite tubes were first used in wall panels. The environment around smelt spouts is expected to be especially severe because of the intermittent splashing that occurs as the smelt drains through the spout. At the tubes panels forming the side walls near the floor, there is also a fluctuating temperature due to level variation of the smelt bed.

As noted at Keiser et al. (2001) work where in addition to the conventional composite tubes with AISI 304L outer layer, composite tubes with modified 625 and 825 alloys were examined and all samples presented cracks and sign of corrosion, the smelt spout openings tubes of the case study boiler also presented frequently cracks.

At smelt spout openings tubes of the case study boiler it was applied composite tubes with stainless steel layer of AISI 304L and Sanicro 38 over a carbon steel tube type SA 210 A1 and both types of composite tubes presented cracks. Sanicro 38 is a Sandvik trade mark alloy similar to 825. They are alloyed with 38% nickel compared with 10.5% for 304L providing a substantially resistance to induced NaOH corrosion. In terms of reliability in operation both 304L and Sanicro 38 presented similar behavior when applied at the same time but in different openings or at the same opening in different occasions.

Some inspections of the openings tubes revealed shallow crack removable by grinding but others revealed severe both circumferential and crazed pattern cracking resulting in smelt spout opening tubes replacement. Most of severe cracking were related to operations procedures. Since the case study boiler operates high loaded, the operations procedures are not easy to control, reducing the safe operation margins of the materials. High loaded boilers operate with high heat flux at the boiler bottom that may result in high smelt temperature. High smelt temperature has direct impact on the thickness of the protective frozen layer. The smaller the layer is the lesser are the margins into the failure. Minor variations in the smelt temperature can result in larger temperature difference on the tube surface and can also easier dissolve the layer totally or partially.

As reported at Keiser et al. (2001) and Wensley and Woit (2002) works, primary air ports tubes of the case study boiler also presented both circumferential and crazed pattern cracking at the lower portion of the air port and in all four boiler walls. The cause of cracking is probably thermal fluctuations at the bottom of air ports where the temperature gradients, as indicated at Keiser et al. (2001) study, were greater. Many cracks nucleated at the lower port crotch plates due to stresses at weld toe caused by thermal loads (Fig. 8).
Regarding cracking mechanism, thermal fatigue has been considered as one reason for cracking of recovery boiler tubes. Thermal fatigue is a damage mechanism that occurs at stresses over the strength of a material. These stresses are developed when the free expansion or contraction by cyclic heating or cooling is restricted (Hänninen et al., 2001). As composite tubes are made of two different materials with different thermal expansion rates joined together, a stress can arise at the tube surfaces when the tube is cooled or heated.

Table 1 shows the thermal expansion rates of the most used stainless steels applied as outer layer of composite tubes: AISI 304L, alloy 625, alloy 825 and Sanicro 38. This indicates that when the 304L, Sanicro 38 and 825 composite tubes are heated to operation temperature the stainless steel layer will try to expand at a higher rate than the inner rate. An effective compressive stress is created when the stainless steel faster expansion is hindered by the slower expansion of the carbon steel. As the tube is cooled, the same occurs but in opposite direction.

Table 1. Material thermal expansion rate chart mean to 370°C

<table>
<thead>
<tr>
<th>Property</th>
<th>Carbon Steel</th>
<th>AISI 304L</th>
<th>Alloy 825</th>
<th>Alloy 625</th>
<th>Sanicro 38</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expansion Coefficient</td>
<td>13.59</td>
<td>17.34</td>
<td>14.86</td>
<td>13.42</td>
<td>15.03</td>
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</tbody>
</table>

If the yield strength of the material is not high enough to withstand the stresses from thermal expansion difference, plastic deformation will occur. The stress state severity at composite tubes can be enhanced as they have built-in residual stresses from manufacturing and by the additional stresses due internal tube pressure. At operation of recovery boilers, will always exist thermal fluctuations, so materials with a closer match to the thermal expansion rate of carbon steel and higher yield strengths are more resistant.

But Hänninen et al. (2001) remark that thermal fatigue is not considered the sole case of cracking. The high corrosive boiler environment contributes greatly to tubes cracking. Stress corrosion cracking takes place when certain aggressive environment exists above a critical temperature at the same time with sufficiently high tensile stress in material. Howell, Silberglitt and Norland (2002) study revealed that the environment created when the boiler is washed with water and subsequently heated to remove any moisture present is ideal for stress corrosion cracking at floor tubes.

At Keiser et al. (2000) work, in almost case studies, cracks in composite floor tubes were initiated by stress corrosion and once a crack has initiated in a tube surface, it continued to grow by thermal fatigue, stress corrosion cracking or a combination of both. For composite floor tube with outer layer of 304L, as the boiler initially heats up from ambient to operating temperatures compressive stress arise at the outer layer surface and this stress remain during the normal operation of the boiler. When the boiler is cooled from operating temperatures, the surface stress become from compressive to tensile and will reach the 304L yield stress after a temperature drop of 90°C below operating temperature. Yet according to Keiser et al. (2000) study, the stress corrosion cracking becomes possible only as floor tubes cool below 250-270°C, depending on the operating pressure.

Water washing a recovery boiler subjects the hot floor tubes to a chemical environment rich in sulfide, carbonate, hydroxide, sulfate and oxidized sulfur compounds. Keiser et al. (2000) experiments demonstrated that stress corrosion cracking will occur over a temperature range of about 160°C to more than 220°C in hydrated mixture of mainly Na₂S, Na₂SO₄ and Na₂CO₃. The presence of sulfide was found to be essential for stress corrosion cracking and cracking was more severe as the content of hydroxide in the salt increased.

As the case study boiler floor is made of studded carbon steel tubes they are much more susceptible to thermal fatigue than to stress corrosion cracking. Thermal fluctuations may be result of the contact of molten smelt with the
tubes due to melt or crack of the protective solidified smelt. This creates thermal gradient and if temperature spikes are high enough and repeated many times a thermal fatigue crack can form. The crack or melt of the protective layer still subject the floor studded carbon tubes to loss of metal wall through contact with a flow of molten smelt. Clement and Blue (1996) report a study that concluded that tubes failure or loss metal were due to corrosion as a result of liquid smelt contact with the tube at a high metal temperature.

5. Conclusions

Cracking mechanisms of composite tubes at lower furnace of recovery boiler is an important issue for safety and economical reasons. Patterns and severity of cracking vary very much from one region to another at the lower furnace and the tubes must have physical characteristics to meet environment requirements.

The boiler composite tubes physical characteristics to be matched are the thermal expansion rate of the materials, the yield strength and the resistance to corrosion. The first characteristic determines the stress on the tube surface when the boiler is cooled or heated. The second characteristic determines how well the material will be able to resist the forces applied from the first characteristic and the third characteristic determines how effectively a corrosive substance can attack the material.

Basically, thermal fatigue and stress corrosion cracking are the main reasons for composite tubes cracking. Beside tube materials, these causes are directly related to operations. Tube temperature fluctuation can be reduced by making certain changes in boiler operating parameters to shift from burning liquor on the walls to burning in suspension and on the boiler floor (Keiser et al. 2001). Another important operational issue is to avoid conditions under which stress corrosion cracking is likely to occur, in particular while the boiler is being cooled, being water washed and dried.

Material improvements are a potential solution for composite tube cracking. Alloy 625, 825 and Sanicro 38 have been deployed as improvements from AISI 304L as stainless steel outer layer of composite tube. These new materials present higher yield strength, closer matches to the thermal expansion rate of the carbon steel and lower susceptibility to Na2S stress corrosion, but as remarked by Keiser et al. (2001) none of the alternative materials represent a universal solution to tube cracking experienced in the lower furnace of Kraft recovery boiler. There is not yet a unique material for every boiler and furnace area. Each boiler case and each furnace area must be considered taking in consideration the operational environment to specify the more ideal suite of material properties.

6. References


7. Responsibility notice

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