Advanced Materials For the Pulp and Paper Industry

Innovative Materials and Operating Practices Save Energy in Recovery Boilers

Innovative materials and operating procedures developed with support from the U.S. Department of Energy are boosting the safety and energy efficiency of a essential manufacturing operation in the forest products industry – the pulp and paper recovery boiler. Materials innovations have substantially improved operating reliability, reducing costly unplanned shutdowns, risk of explosions, and energy use.

Background

The forest products industry consumed over 2,660 trillion Btu (TBtu) of primary (onsite) energy in 2001, approximately 11% of all the primary energy consumed in United States manufacturing. It is the third largest consumer of fossil fuels (1,070 TBtu/year) in the manufacturing sector. Only the petroleum refining and chemicals industries consume more fossil energy. Notably, the industry is the largest producer and consumer of renewable energy today, self-generating over half of its energy from biomass.

For nearly a decade, the Office of Energy Efficiency and Renewable Energy, Industrial Technologies Program (ITP) has partnered with the forest products industry, universities, and Oak Ridge National Laboratory (ORNL) to address materials problems affecting energy efficiency in pulp and paper recovery boilers. This work has been instrumental in the development of innovative materials, operational practices and understanding of corrosion and failure mechanisms in recovery boiler operations. Innovative materials and practices developed through this partnership effort can lead to an estimated 2.5% to 5% energy efficiency improvement. This is equivalent to energy savings of 65 to 130 TBtu/year.

Figure 1: Recovery Boilers are the heart of the pulp and paper making process, and the largest single structure at a mill

Roles and Challenges of Recovery Boilers

The recovery boiler is the heart of the pulp and paper mill. It makes the entire process economically practical through the generation of nearly all of the mill's steam power, 60 to 80% of the mill's electricity and the recovery of the valuable pulping chemicals. It is also the most capital-intensive (typically over $100 million) operation in the mill.

A recovery boiler acts as both a high-pressure (1,000 to 1,750 psig) steam boiler and as a chemical reactor with reductive and oxidative zones. The large fireside walls, floor and heat exchange surfaces in the boiler are subjected to high temperatures 1,200 to 1,600°F (700 to 900°C) and gaseous and molten pulping chemicals that are extremely corrosive. These conditions impose severe demands on the materials used in recovery boiler design, construction and maintenance.

The fuel for a recovery boiler is "black liquor." This energy-rich byproduct is created when cleaned wood chips are "digested" to extract the fibers (cellulose) that are the raw material for pulp and paper making. The extraction process (kraft) used by 85% of the industry utilizes an alkaline solution of sodium sulfide (Na_2S) and sodium hydroxide

(NaOH), called "white liquor." Subsequent washing steps separate the cellulose fibers from the remaining solution, "black liquor," which contains the spent digestion chemicals, and the lignin and hemicellulose fractions of the original wood chips.

Black liquor (~15% solids fraction) carries about half of the energy of the original wood chips. Black liquor is concentrated through evaporation processes until its solid fraction reaches 75% to 80% and it becomes combustible (~6,250 Btu/lb of solids). The concentrated black liquor is sprayed into and burned in large recovery boilers. The organic fraction burns to produce heat and the inorganic fraction becomes a molten smelt that builds on and then flows off the floor of the recovery boiler.

The smelt, which contains the spent pulping chemicals (Na_2S and Na_2CO_3), is dissolved in water to form "green liquor" which is reacted with lime (CaO) to convert the Na_2CO_3 back into NaOH, recreating the original "white liquor." This essentially closed recycling loop of "white to black to green to white liquor" provides significant economic and environmental benefits.

Approximately 186 recovery boilers are located in the United States. The average recovery boiler processes approximately 1,240 tons of black liquor dry solids per day resulting in an energy production of ~2.6 TBtu of steam and ~30 MW of electricity annually (total useable output of ~3.5 TBtu/yr).

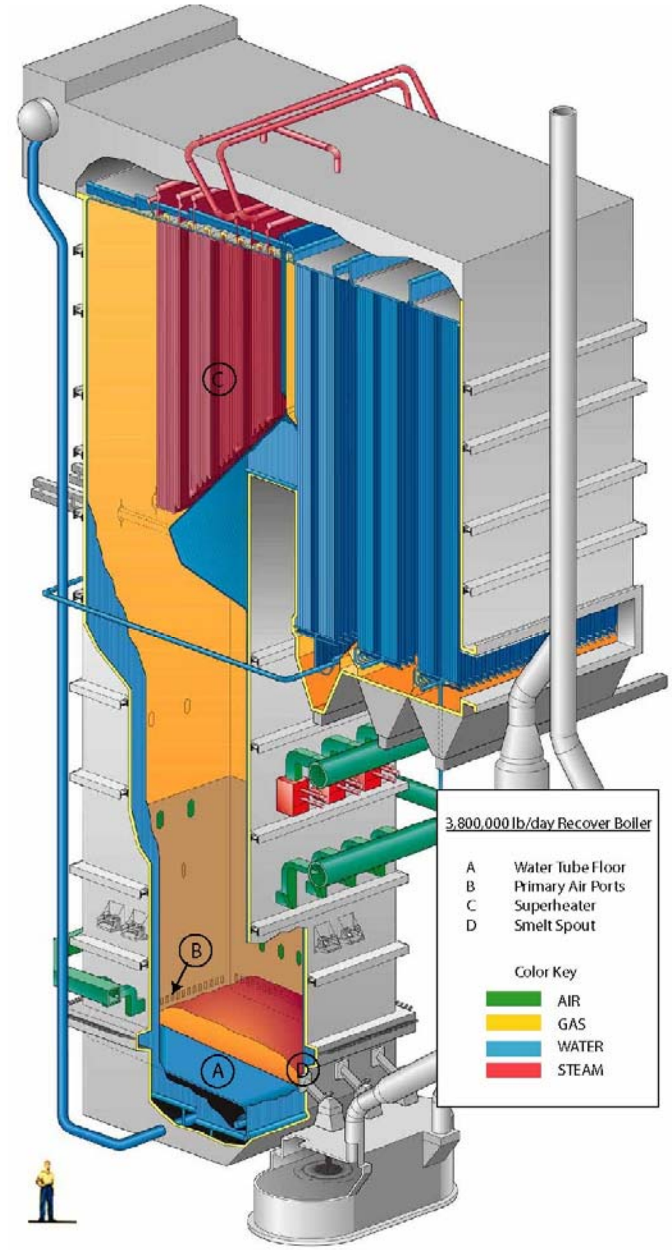

Figure 2: Kraft Recovery Boiler
(Illustration courtesy of The Babcock & Wilcox Company)

Materials for Improved Boiler Efficiency

Innovative materials for pulp and paper mill recovery boilers can increase energy efficiency by raising allowable operating temperatures and reducing shutdowns. Industrial boiler efficiency is directly related to operating temperature and equipment design. If innovative materials could allow a 30°C increase in operating temperature, then the energy efficiency would increase from 1.5% to 3%. Operating temperature energy efficiency gains will result as experience and confidence in robust innovative materials is gained by the operators and makers of recovery boilers.

Every boiler shutdown results in an energy loss. Boilers on shutdown cool and many times must be cooled sufficiently to allow internal access for maintenance and repair. At restart, the massive boiler structure and contents (which includes the water, steam drum, heat exchange tubes, floor and wall tubes, insulation, piping, etc.) must be heated up to operating temperatures, typically with natural gas. This heat-up represents lost energy.

Innovative materials can lengthen the intervals between scheduled shutdowns, decrease unscheduled shutdowns, and reduce maintenance, thus boosting energy efficiencies and productivity benefits. The estimated energy benefits for avoiding shutdowns are in the 1% to 2% range.

The shutdown of a recovery boiler greatly reduces or ceases mill production. Approximately 30% of the paper mills in the United States operate only one recovery boiler. In these mills, productivity loss due to a shutdown can be enormous, averaging $300,000 per plant per day. Plants with more than one recovery boiler do not suffer as great losses, but production capacity is still reduced.

Shutdowns Linked to Recovery Boiler Tube Cracking

A number of events can cause unplanned shutdowns of recovery boilers – one of the most extreme causes being the cracking of boiler tubes. When cracks in the boiler tubes extend deep enough to allow water and steam to leak into the recovered molten pulping chemicals (smelt) on the floor of the boiler, a large explosion can occur.

Cracked tubes can take days to weeks to repair and result in significant production losses from downtime. In the worst reported incidents, where explosions have occurred, damage was so extensive that injury or death of operating personnel occurred and months of repair work were required.

The floors, walls, overhead structure and heat exchange surfaces of a recovery boiler are built with water- and steam-filled tubes. The structures are made by welding conventional tubes together using a small "web" to facilitate the weld.

Carbon steel tubes are the predominant construction material in conventional fossil fuel-fired boilers. The black liquor solids that are fired in recovery boilers create a unique fireside environment (high temperature atmosphere rich in sulfur-containing species). This environment promotes sulfidation, which produces iron-sulfur compounds. The iron-sulfur compounds form on or beneath the surface of the tube and lead to thinning and eventual failure of carbon steel tubes. As a result, co-extruded

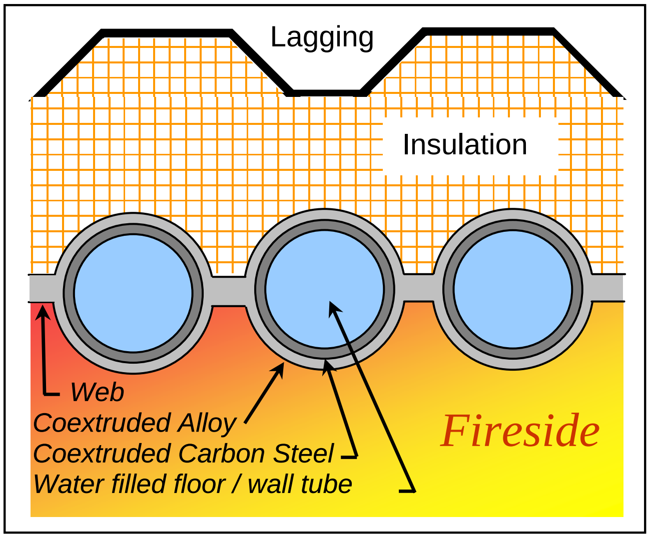

Figure 3: Water tube panel with web

composite boiler tubes with 304L stainless steel and carbon steel (SA-210 Gd Al) were introduced during the 1970s. The tubes were made of stainless steel on the outside fireside surface and carbon steel on the inner water surface. Each surface is exposed to a different service environment. By the mid-1980s, the forest products industry in North America had switched to composite tubes in the recovery boiler floor and lower wall areas to mitigate high-temperature sulfidation of the carbon steel tubes.

Unfortunately, the outer stainless steel layer was affected by the fireside service environment. The first cracking problems with co-extruded tubes were reported in North America in 1992. By 1995, the industry had determined that stainless steel composite tubes had not fully solved the tube cracking problem and the cracking mechanism was indefinite.

R&D Collaboration Approach

In 1995, ITP began to sponsor R&D work with the forest products industry to explore innovative materials that could reduce boiler tube cracking and improve energy efficiency. Research and development in this area were driven by the ITP's commitment to research, design, develop, engineer, and test new and innovative materials. The ITP project work created a collaboration partnership consisting of ten pulp and paper companies, five recovery boiler manufacturers, one composite tube fabricator and Oak Ridge National Laboratory (ORNL). The members of this partnership create a unique and wide-perspective problem solving team by combining the experience and knowledge of the end-users, original equipment manufacturers (OEM) and the OEM suppliers with the expertise and world-class analytical facilities of ORNL.

The collaborative partnership began by detailing tube failure experiences and postulating potential mechanisms that might lead to failures. The recovery boiler floor tubes were initially focused on because end-users found that even though floor tubes represent a small fraction of the exposed fireside tube area, they posed the most immediate and severe problem. The risk of a smelt-water explosion increases as the amount of water or the proximity of the leak to the smelt bed increases. An advisory committee found that almost 23% of tube leaks that caused an explosion were caused by leaks in floor tubes.

Recovery Boiler Floor Tube Cracking

The research team designed a program to identify and confirm which one or combination of the potential failure mechanisms was responsible for floor tube cracking. Five tasks were designed to identify failure mechanisms and characterize the material properties needed to reduce or eliminate failures:

1) Examine the microscopic characteristics of new and cracked tubes to determine cracking mechanisms (i.e., thermal fatigue, mechanical fatigue, stress-corrosion, …)
2) Measure and model the forces (stresses) on the surface of the tubes to determine failure mechanisms through a regime of experimental measurements, theoretical calculations, and computer simulations
3) Define the characteristics of the service environment (e.g., temperature, pressure, chemical environment, ...)
4) Identify the cause of the cracking
5) Identify more ideal processes, materials, or material properties.

The project team determined that co-extruded floor tubes cracked in as little as six months of operation and that these cracks were independent of the boiler floor design. These surface cracks were frequently visible using dye penetrants (Figure 4).

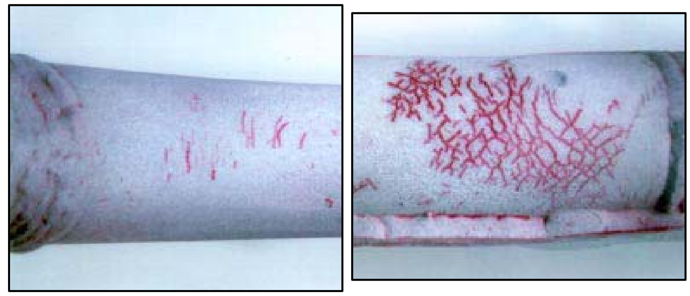

Figure 4: Dye-marked circumferential and crazed tube cracking

Microscopic examination showed the surface cracks to have minimal branching and typically did not extend beyond the carbon steel interface (Figure 5). In some instances, the crack would turn and follow the interface allowing direct corrosion of the carbon steel.

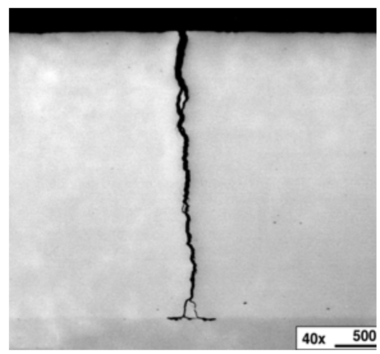

Figure 5: Boiler tube crack following the stainless/carbon interface

Differences in the thermal expansion and mechanical properties of stainless steel and carbon steel can create stresses in the co-extruded tubes. Large temperature changes occurring during startup and shutdown or localized operating temperature fluctuations cause the tubes to undergo alternating compressive and tensile forces; however, based on the examination and the modeling of tube stress profiles, no conclusive evidence was drawn that the cracking was due to thermal fatigue alone.

Hydrated green liquor salts ($Na_2S \bullet H_2O$) were known to cause rapid stress corrosion cracking (SCC) in 304L stainless steel. Although these hydrated salts do not exist in the recovery boiler under normal operation, smelt salts are routinely washed out of the recovery boiler during shutdowns and cleaning. The water remaining on the walls and floors of the recovery boiler contains these dissolved salts, which become concentrated as the water is evaporated during dry-out and restart. The research team concluded that these concentrated wet salts lead to 304L cracking when the boiler was shut down for maintenance and the tubes were washed with water – not during normal plant operations. They noted that the growth of cracks initiated by the SCC mechanism is accelerated during thermal cycling of the recovery boiler.

Solutions for Floor Tube Cracking

The team's findings resulted in a significant advancement in the understanding of recovery boiler corrosion and cracking mechanisms, and two major recommendations for recovery boiler floor tubes. The first recommendation called for a modification of shutdown maintenance procedures, particularly the water-wash and dry-out cycle, to reduce the occurrence of conditions that might promote SCC on the surface of boiler floor tubes. These procedures and their benefits have been widely published and most operating facilities are aware of and have adopted these modifications.

Solutions to Recovery Boiler Floor Tube Failures:

- *Modify maintenance procedures to reduce the conditions identified that promote stress corrosion cracking of the floor tubes*
- *Change the co-extruded exterior to an alloy 825 material which will provide better corrosion resistance properties and is a better thermomechanical match to the carbon steel interior surface.*

The second recommendation advised a change in the material making up the outer layer of the co-extruded tube: from stainless steel to a more SCC-resistant alloy with thermal and mechanical properties more similar to the inner carbon steel layer. Alloy 825, a nickel-iron-chromium material with additions of molybdenum and copper was suggested. It has excellent resistance to SCC, to both reducing and oxidizing acids, and to localized pitting and crevice corrosion. The alloy is especially resistant to sulfuric and phosphoric acids, and is widely used for chemical processing, pollution-control, oil and gas well piping, nuclear fuel reprocessing, acid production, and pickling equipment.

Figure 6: Interior view of recovery boiler during tube maintenance and replacement

Estimated Energy Benefits

The two recommendations for avoiding floor tube cracking have different costs and benefits, but are not mutually exclusive. Mills can easily adopt the recommended maintenance procedures at no cost and use the 825 type alloy materials whenever boiler tubes are slated for replacement. While alloy substitution will greatly increase tube resistance to cracking, the use of the modified maintenance procedures is still strongly recommended. Although 825 type alloy tube cracking still occurs, widespread adherence to both the proposed recommendations has vastly improved current practices and norms in industry.

Recovery boilers are normally scheduled to shutdown once per year for maintenance. Based on experience, the collaborative partners estimate that 1/7 of all recovery boilers experience at least two shutdowns per year and approximately, 1/14 of all recovery boilers have at least 3 shutdowns per year. These additional or unscheduled boiler shutdowns waste energy.

A recovery boiler shutdown in mills with one boiler results in the complete stoppage of production. For mills with more than one boiler, the single boiler shutdown does not necessarily lead to the complete stoppage of production. The mill can be kept operating, albeit inefficiently, by a) transferring black liquor to other sites for processing, b) purchasing additional electricity for utilities, and c) burning natural gas or petroleum fuels to produce steam energy used in various unit operations. The estimated energy benefits from avoiding unscheduled shutdowns are in the 1% to 2% range.

An analysis of industry maintenance requirements and boiler tube replacement rates suggests that combining improved maintenance procedures to avoid cracking with accelerated tube replacement (e.g., at a rate of 5% per year instead of the historical 1.5% per year) could provide cumulative industry-wide savings of 66 TBtu with a net present value in energy and productivity savings of nearly $1.5 billion (2005 dollars with a 5% discount rate) over the next 30 years. These estimates assume that one-half of the industry adopts the 825 type alloy tubes by 2035 – reducing days shut down for maintenance by an average of two days – and that one-half of these plants save an additional average 1.5% of their energy use. In addition, these energy savings translate directly into cumulative reductions of 8,700 tons of nitrogen oxides, 17,200 tons of sulfur dioxide, and 843,000 tons of carbon equivalent greenhouse gas emissions.

By the end of 2004, about ten U.S. mills have installed partial or complete floor panels using 825 type alloy. Field evaluations of these new panels will require time; however, the clear benefits of 825 type alloy should bring widespread adoption as recovery boilers are maintained and rebuilt.

Recovery Boiler Air Port Cracking

The successful identification and recommendations from the recovery boiler floor tube investigation has encouraged the continuation of collaboration to explore tube cracking in other critical areas of the recovery boiler.

The operating conditions, tube geometry and environment on the floor of a recovery boiler differ greatly from the other recovery boiler surfaces. Combustion air ports are constructed in tube walls by bending the co-extruded tubes back and removing the web. This creates an opening in the boiler wall from which air can be supplied to support the combustion of the black liquor solids. The "primary" air ports are located closest to the boiler floor. These air ports experience cracks similar to those on boiler floor tubes, but the research partnership found that the cracks in primary air port tubes sometimes penetrate beyond the outer layer and into the carbon steel base material (Figure 7). This difference can make air port tube failures a more urgent concern than the resolved floor tubes. Although no explosions have resulted from air port tube failures, emergency shutdowns have occurred.

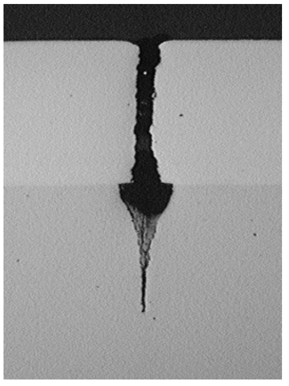

Figure 7: Air port tube crack extending into the carbon composite

A multi-faceted analytical approach similar to the floor tube analyses was used to understand and solve the problem of air port tube failures. This approach examined before and after failures of air port samples and then investigated alternate air port materials, designs, fabrication methods, and operating parameters.

To better understand local operating conditions and the causes of air port cracking, surface temperature measurements were taken on the air port tubes of an operating recovery boiler using strategically placed thermocouples. Recorded data indicated that air port tube openings with a history of cracking experienced temperature fluctuations of much greater amplitude (±500°F) and frequency than air port tubes with no cracking history. Studies using a specialized camera showed that the temperature fluctuations were a result of black liquor spray hitting, accumulating and burning directly around the air ports. These temperature fluctuations have not been considered sufficient to conclude that thermal fatigue was the only cracking mechanism, but they are believed to play a role.

Air port geometry and design were examined to determine if tube bending during air port manufacturing contributed to stresses that led to cracking. Air ports with larger radius bends (25 to 30 cm) appeared to be less prone to cracking than those constructed with smaller radius bends (12 to 15 cm). Measurement and modeling of stresses in air port tubes revealed that the bending operation affects the tube's internal stresses. In addition, the stress profiles change when the tube is subjected to temperature changes. These changing profiles along the stainless/carbon steel interface could contribute to cracks extending into the carbon steel layer.

Solutions for Air Port Cracking

The research work confirmed that the corrosive pulping compounds, localized thermal fluctuation and construction bending stresses combine to create the fatigue mechanisms responsible for air port cracking. Once local operating conditions and potential failure mechanisms were identified, solutions were sought through changes in air port materials, design, fabrication methods, and operating parameters.

The research team determined that tube temperature fluctuations can be reduced by making changes in boiler operating parameters. Primarily, a shift from burning liquor on the walls to burning liquor in suspension and on the boiler floor was recommended. Studies have also shown that changes in liquor characteristics, spray parameters, as well as secondary air patterns, can change the frequency and magnitude of temperature fluctuations. Air port designs using longer radius bends will result in lower internal tube stress and reduce crack propagation. Changes to alloy 825 tubes will also lower tube stress levels.

The results of the collaborative air port analyses have been widely published. Facilities are changing their operating procedures to avoid thermal fluctuation and are adopting new alloys and different air port designs as recovery boilers are maintained and rebuilt.

Solutions to Air Port Tube Failures:

- *Modify black liquor spray gun patterns so that spray droplets do not impinge and accumulate on the walls and air ports of the boiler.*
- *Change air port geometry to take advantage of lower stress longer radius bends.*
- *Change the co-extruded exterior to an alloy 825 material which will provide better corrosion resistance properties and is a better thermomechanical match to the carbon steel interior surface.*

NEXT STEPS – Materials for Mid-Boiler and Superheater Tubes to Provide Additional Energy Savings

The success of the recovery boiler floor and air port tube projects can be measured by the continued strong commitment of the participating partners to improve the operation of recovery boilers through additional R&D work. Today the ITP program continues with a larger consortium that now includes 16 paper companies, 4 recovery boiler manufacturers, 2 tube fabricators, Oak Ridge National Laboratory, and United States and Canadian paper institutes.

Mid-boiler and superheater tube corrosion and failure mechanisms remain industrial problems. A better understanding of the local conditions throughout the recovery boiler is evolving from this collaborative research. This understanding will contribute significantly to developing practices and materials that enhance the performance and safety of recovery boilers. In addition, the knowledge gained through these projects is applicable to many industrial heating challenges.

Innovative materials with superior corrosion tolerance in the recovery boiler mid-section and superheater would allow more energy efficient operation at higher temperatures. Higher temperature operations in recovery boilers could reduce maintenance requirements by allowing better control of ash and combustion products that affect the heat transfer characteristic in the superheater section. It is estimated that innovative materials that would allow superheater tubes to increase operating temperature by 30°C would provide an additional energy efficiency increase from 1.5% to 3%.

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