CHEMICAL RECOVERY IN WOOD PULPING

INTRODUCTION

Two major processes for chemically pulping wood are the acid-sulfite process, which involves red liquor, and the Kraft (or sulfate) process, which involves black liquor. Recovery boilers burn the organic portion of these liquors, producing steam to heat process equipment and generate electric power. The unburned portion of nonsodium-based red liquor exits with the boiler flue gases. The unburned portion of either black liquor or sodium-based red liquor collects in the boiler bed as smelt, which the mill processes and uses to pulp more wood.

The acid-sulfite process uses one of four chemical bases: ammonia; calcium; magnesium; or sodium. This process is suitable for hard woods only. The primary hazard associated with the acid-sulfite process is uncontrolled ignition of unburned fuel in the recovery boiler. Sodium-based red liquor recovery boilers are also subject to smelt-water explosions.

The Kraft process, which is suitable for both hard and soft woods, is much more common than the acid-sulfite process. The hazards associated with this process include both uncontrolled ignition of unburned fuel and smelt-water explosions. (See GAP.17.5.0 for a flow diagram of the Kraft process.)

Chemical recovery enables the pulp mill to meet strict environmental laws and maximize production, but it is also hazardous. Losses in recovery boilers can result in significant property damage and long downtimes. Properly protecting recovery operations is therefore very important. This GAP Guideline describes how to protect chemical recovery operations in pulp mills.

POSITION

Because they do not have smelt beds, nonsodium-based red liquor recovery boilers are not subject to smelt-water explosions. The key protection features for these boilers are:

- A boiler design that meets Section I of the ASME Boiler and Pressure Vessel Code;
- Combustion safeguards in accordance with NFPA 85 and GAP.4.0.1 on the auxiliary fuel systems;
- A control system to monitor red liquor firing;
- Thorough preventive maintenance programs on all boiler components.

Recovery boilers with smelt beds are subject to smelt-water explosions. Black Liquor Recovery Boilers (BLRBs) have long been the most common source of large losses in the pulp and paper industry. The Black Liquor Recovery Boiler Advisory Committee (BLRBAC) was formed to address these losses and develop guidance for safer operation of BLRBs. BLRBAC has published six recommended good practices, one guideline and one advisory concerning operation of BLRBs.

Global Asset Protection Services (GAPS) recommends following BLRBAC guidance for BLRBs. Also, protective features comparable to those advocated by BLRBAC should be provided for sodium-based red liquor recovery boilers. The following sections summarize BLRBAC and GAPS guidance.
Construction

Building Construction

Consider the forces that may result from a smelt-water explosion in the building structural design. Design the wall panels to relieve the explosion pressure and the building frame to resist collapse. If the recovery boiler exposes any equipment (other than its auxiliary equipment), separate the boiler from this equipment with explosion-resistant walls.

Securely anchor the roof and floor decking of the recovery boiler building. Use solid, leak-resistant flooring, and provide curbs to contain liquids where spills are possible. Provide adequate stairways, platforms and ladders to permit proper inspection, operation and maintenance of the boiler and accessory equipment.

Totally enclose, and provide explosion-resistant walls for, normally occupied areas such as control rooms, motor control centers, break rooms, laboratories and maintenance and supervisory offices. Also protect elevator shafts and stairwells.

Locate the control room a reasonable distance from the recovery boiler based on the room’s explosion resistance. Do not place the control room on a line connecting the diagonal corners of the boiler, and do not put it under the boiler. Provide nonlockable, self-closing, explosion-resistant doors and arrange them to open into the recovery boiler area to prevent blowing open during an explosion. Use the smallest and fewest windows possible, and do not put them in any walls facing the boiler. Install windows in gasketed steel frames and use only tempered, bulletproof or shatterproof glass.

Supply control room air from a source independent of the BLRB area. Keep the control room under positive pressure and equip it with air locks. Use either high-pressure tubing or pressure transducers to transmit signals into the control room. Do not permit piping in the control room. Provide emergency lighting for critical control areas and for all emergency escape routes.

Equipment Construction

Design the boiler in accordance with Section I of the ASME Boiler and Pressure Vessel Code. Consider increasing corrosion allowances on parts whose leakage presents higher risk of damage to the boiler. Arrange the boiler to allow access to all areas subject to erosion or corrosion. Nondestructively test all field butt welds with radiography or ultrasonics.

Design all process equipment and BLRB components to prevent water from entering the smelt bed. Minimize welded attachments to boiler tubes. Weld attachments to tubes with adequate wall thickness, using only circumferential or longitudinal welds. Tangential welds are inadequate either inside or outside the boiler, and should be prohibited. Slot long stubs and large filler plates to accommodate differential expansion of tubes and attachments.

Properly pitch and trap steam connections to the boiler, such as sootblower or liquor line blow-out connections, to prevent condensate from entering the boiler. Provide sufficient condensate removal to prevent water hammer in all steam lines. Also provide steam lines with double valve and bleeder arrangements to ensure positive shutoff and drainage. Pipe bleed lines to open funnel type drains away from the boiler.

Minimize use of water connections for black liquor dilution and flushing of black liquor lines. Provide double valve and bleeder arrangements for water lines, and close and drain the lines when they are not being used. If double valve and bleeder arrangements are not provided, disconnect the lines when they are not being used. Do not use water-cooled doors on a BLRB.

Provide a rapid drain system for the BLRB, including the economizer, capable of draining water to the 8 ft (2.4 m) level in 20 min or less. Permit only the boiler manufacturer to design this system. Install only one automatic drain valve on each drain line. Install a manual valve downstream of each automatic drain valve to permit testing of the automatic valves without shutting down the boiler. Terminate the drains at grade.

Do not permit either permanent connections downstream of or bypasses around refractometers or mass flow meters. GAPS does not recommend burning waste streams in a Black Liquor Recovery
Boiler. Recognizing the incineration of waste streams in a recovery boiler adds complexity and potential hazards to the operation, BLRBAC does not encourage this practice. However, where this practice is conducted, BLRBAC recommends following the Waste Stream Guideline to minimize the risk. See BLRBAC’s “Recommended Good Practice – Thermal Oxidation of Waste Streams in Black Liquor Recovery Boilers”.

Make provisions for washing and drying the boiler prior to internal inspection. Provisions should include a warm water supply and adequate access doors on the boiler. BLRBs may be dried by circulating hot feedwater or using electric blowers.

**Protection**

Arrange the auxiliary fuel system in accordance with NFPA 85, GAP.4.0.1 and BLRBAC’s “Recommended Good Practice for Safe Firing of Auxiliary Fuel in Black Liquor Recovery Boilers.” This publication includes startup and tripping logic and piping schematics for the auxiliary fuel system. BLRBAC recommends automatically tripping the auxiliary fuel system under the following conditions:

- Evaporator outlet temperature more than 200°F (111°C) above design temperature;
- Precipitator outlet temperature more than 200°F (111°C) above design temperature;
- Loss of forced or induced draft fan;
- Furnace pressure more than 80% design pressure;
- Air flow below liquor nozzles less than 30% normal air flow;
- Flame failure;
- Low water level;
- Loss of atomization means (for oil);
- Unsafe fuel temperature or pressure (depending on fuel);
- Initiation of emergency shutdown procedure.

GAPS recommends the following additional trip conditions:

- Furnace pressure below -16 in. (-41 mm) W.C.;
- Steam pressure exceeding the maximum allowable working pressure.

Also include timed trial for ignition during lightoff, the standard double valve and vent (or bleeder) arrangement for fuel lines and manual trip capability in auxiliary fuel systems.

Arrange the black liquor system in accordance with BLRBAC’s “Recommended Good Practice for Safe Firing of Black Liquor in Black Liquor Recovery Boilers.” This publication includes startup and tripping logic and piping schematics for the black liquor system. BLRBAC recommends automatically diverting black liquor upon the following conditions:

- Evaporator outlet temperature more than 200°F (111°C) above design temperature;
- Precipitator outlet temperature more than 200°F (111°C) above design temperature;
- Loss of forced or induced draft fans;
- Furnace air pressure more than 80% design pressure;
- Low water level;
- Black liquor solids below 58%;
- Black liquor temperature below 78°F (26°C);
- Black liquor pressure less than 5 psi (0.4 bar) below minimum operating pressure;
- Initiation of emergency shutdown procedure.

GAPS recommends the following additional trip conditions:

- Furnace pressure below -16 in. (-41 mm) W.C.;
- Steam pressure exceeding the maximum allowable working pressure.
Also provide manual black liquor diversion capability at strategic locations that are safe to enter during a boiler emergency.

Monitor the quality of boiler feedwater and condensate. Monitor the flow, temperature and quality of smelt spout cooling water. Transmit an alarm to the control room when any of these parameters are outside acceptable ranges.

Provide at least two independent systems for measuring steam drum water level, both of which are visible to operators. Transmit an alarm to the control room upon unsafe water level in the steam drum.

Install two refractometers, vertically and in series, to continuously monitor black liquor solids content. Transmit an alarm to the control room if either refractometer reads below 60% solids or if they disagree by more than 2% solids content. Divert black liquor if either refractometer reads below 58% solids. Refractometers reliably measure solids content up to about 65%. For higher-solids firing, use mass flow meters to measure solids, and set higher alarm and trip points commensurate with the operation. If the trip point is less than 65%, install a refractometer in addition to the mass flow meters.

Protect instrument and control lines and all system devices against freezing.

Locate fuel lines, steam lines and main shutoff valves where they will be protected from rupture in the event of an explosion. Locate main shutoff valves where they will be safely accessible in the event of an explosion. Locate valves controlling auxiliary fuel outside the BLRB building. Do not locate any controls under the BLRB.

Provide steam from a source other than the BLRB for steam turbine-driven fans.

Loss Prevention and Control

Identify all piping systems and control valves by color coding or other suitable means. Maintain accurate and up-to-date drawings of piping and control systems. Develop and maintain written preventive maintenance procedures and schedules, written shutdown procedures for maintenance outages, pre-firing checklists and startup procedures, and emergency plans with evacuation routes. Implement written lockout/tagout procedures for all work done on recovery boiler systems.

Prepare operator training manuals tailored for each BLRB in the facility. Implement operator training and retraining programs that include the following procedures:

- Minimize all potential sources of water to the BLRB, including water or steam used in black liquor lines, sootblowers, area washdown systems and the salt cake conveying system.
- Investigate and correct all alarm conditions, and, as appropriate, divert liquor or shut down the BLRB before it becomes unsafe.
- Initiate an emergency shutdown if water is known or suspected to be entering the boiler in any amount and cannot be stopped immediately, or, if any leak develops in a pressure part inside the boiler.
- Do not introduce black liquor into a BLRB on hot restart until stable operating conditions are achieved. In recent years, several BLRBs experienced combustible gas explosions during hot restarts.
- Monitor the smelt bed with bed cameras. Also visually monitor flame stability.
- Operate direct contact evaporators in accordance with BLRBAC’s “Fire Protection in Direct Contact Evaporators and Associated Equipment.” This involves monitoring flue gas temperature and black liquor flow through the evaporator.

Separately treat boiler makeup water, condensate and smelt spout cooling water to minimize corrosion and scale formation. Continuously monitor and record water quality.

Check refractometer and mass flow meter readings against laboratory measurements of solids content at least daily. Recalibrate the refractometers and mass flow meters as necessary based on these readings. Keep records of test results and recalibrations.
Maintain proper alignment and operation of sootblowers to avoid tube erosion by steam jets.

At least once a year, conduct radiographic or ultrasonic examinations of boiler tubes in accordance with Section V of the ASME Boiler and Pressure Vessel Code. Include the superheater, boiler bank, economizer, downcomers, risers and supply tubes. Consider using more sophisticated nondestructive testing techniques on parts whose leakage presents higher risk of damage to the boiler. Maintain tube thickness maps and determine rates of erosion and corrosion. Hydrostatically test the tubes to identify small leaks and repair all leaks.

Qualify nondestructive testing personnel in accordance with ASNT-TC-1A “Recommended Practice for Nondestructive Testing Personnel Qualification and Certification.” Qualify welders in accordance with Section IX of the ASME Boiler and Pressure Vessel Code. Make all tube repairs in accordance with the National Board Inspection Code. Ascertain that repair welds do not restrict water passages, which may cause overheating. Keep records of all repairs as required by the National Board Inspection Code and by local codes.

Consider installing an ultrasonic leak detection system in the boiler.

Equip the boiler with an emergency shutdown system and adopt an emergency shutdown procedure in accordance with BLRBAC’s “Recommended Emergency Shutdown Procedure For Black Liquor Recovery Boilers.” Provide controls to initiate shutdown from strategic locations that are safe to enter during a boiler emergency. Initiation of emergency shutdown should require only one operation, either pushing one button or holding two buttons simultaneously. The shutdown sequence is:

1. Activate audible and visual alarms.
2. Divert black liquor.
3. Stop firing auxiliary fuel.
4. Shut off feedwater and steam sources, except smelt shatter steam.
5. Shut off smelt spout cooling water only if it is believed to be entering the furnace.
6. Shut down air to the primary air ports and maintain balanced draft in the boiler.
7. Rapid drain the boiler and economizer to the 8 ft (2.4 m) level.
8. Reduce steam pressure as rapidly as possible.

Test the emergency shutdown system at initial startup in accordance with BLRBAC’s “Recommended Procedure for Testing ESP System for Black Liquor Recovery Boilers.” The test procedure is:

1. Make sure the smelt bed is completely burned down and clean.
2. Check the ESP logic electrically to ensure each component is wired to operate as intended.
3. Bring the boiler to normal operating pressure firing auxiliary fuel.
4. Stop firing auxiliary fuel.
5. Close the manual valves downstream of the motor-operated rapid drain valves and open the motor-operated valves.
6. Flow each drain line with the manual valve, and reclose each valve.
7. Close the motor-operated valves and open the manual valves.
8. Put the boiler back on auxiliary fuel.
9. Initiate a complete emergency shutdown by pressing the emergency shutdown button.
10. Open the drum and superheater vent valves to relieve pressure and facilitate cooling.
11. Hydrostatically test the boiler before putting it back on line.
Test the rapid drain valves monthly. Test the entire emergency shutdown system twice a year, except for draining the boiler. Keep the manual valves on rapid drain lines locked open except during tests. Entrust keys only to personnel responsible for testing or maintenance.

**DISCUSSION**

In the Kraft process, wood chips cook under pressure in digesters. Sodium hydroxide and sodium sulfide in the cooking solution dissolve the wood’s lignin matrix and release the cellulose fibers. The spent cooking solution, called weak black liquor, has approximately 15% dissolved solids.

Multiple-effect evaporators, which are steam heated, concentrate the weak liquor to strong liquor. Direct contact evaporators, which are heated by boiler flue gases, further concentrate the strong liquor to heavy liquor having 60% to 70% dissolved solids. Newer BLRBs use only multiple-effect evaporators, and some of these boilers can burn black liquor with a solids content of up to 80%.

Sodium sulfate is added to the heavy liquor, then the liquor is preheated and sent to the liquor guns in the BLRB. Burners firing auxiliary fuel, usually gas or oil, dehydrate and ignite the black liquor. Once stable burning of the liquor is established, the auxiliary burners are turned off. As the organic portion of the liquor burns, water in the boiler tubes absorb the heat to make steam. The unburned portion of the liquor falls to the smelt bed. The smelt flows through spouts into the dissolving tank, where steam shatter jets break up the smelt and enable it to dissolve in water. The solution is then treated with lime and returned to the digesters.

Black liquor recovery boilers are the heart of the Kraft recovery process. Operating BLRBs safely requires good construction and design, appropriate protection, thorough operator training, and adherence to effective preventive maintenance schedules. BLRBAC’s specific guidance in these areas is based on years of operating experience.

Smelt-water explosions are the most common and most expensive losses occurring in BLRBs. Strict control of all water sources can greatly reduce the potential for these losses. Finding every small leak during routine maintenance is also important. Such leaks are easier to find if the boiler is dried prior to internal inspection.

Mills often enhance smelt bed cooling with CO₂, nitrogen-propelled sodium bicarbonate, dry steam, or water mist. Using water mist for this purpose is not acceptable; only dry materials should be chosen. Water should never be introduced until the smelt bed is completely solidified.