Analytical Measurements Protect Recovery Furnace and Boiler in a Pulp and Paper Mill

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Recovery Boiler operations can be improved considerably by using continuous analytical measurements. The information they collect can be used to optimize black liquor conversion and energy extraction in the furnace without compromising safety and reliability of boiler tubes and other components. The Recovery Furnace oxidizes concentrated black liquor, thereby generating feedstock for green liquor and the rest of the Kraft process, and simultaneously producing steam for millwide use. The furnace is optimized by controlling excess combustion air levels to maximize smelt recovery, prevent corrosion, and maximize steam production. The boiler is optimized for longevity by monitoring the quality of water used to produce steam. This also protects the boiler tubes against corrosion and pitting due to harmful mineral deposits. Effective analytical measurements can assist in optimizing these operations. Additionally, accurate analysis of both combustion flue gases and boiler water can be used to prevent explosive conditions.

Furnace Operations

While traditional natural gas or oil burner arrangements may be used for boiler start-up, the black liquor reaction is exothermic, and once started, it is self-sustaining. The black liquor is viscous, and great care is exercised to maintain at least a 50-60% solids content. The liquor is injected from above through oscillating nozzles, and forms a molten bed in the bottom of the furnace. Fuel control is comparatively poor, and fuel/air ratio control is difficult. Partially pyrolyzed liquor can form

Model 320 HP provides a stable signal for pH measurement

Model 404 flow through conductivity sensor monitors condensate purity

Model 499A TrDO measures trace dissolved oxygen

localized pockets of explosive gases, so reliable gas analysis is important to not only maintain efficiency and optimize conversion, but also to prevent explosions.

In-situ zirconium oxide oxygen sensing technology works well in this application. Typically, the heated sensor is placed onto the end of a probe that is 3-9 feet long, minimizing problems involved with filter plugging, since there is no sample transport required. It should be noted that since the sensor is heated to approximately 1500° F, the sensing cell will burn any combustible components in the flue gases, and read the remaining O_2. Excursions of high CO or other combustible components will result in a depleted O_2 reading, so a low O_2 alarm should be utilized in the DCS control system for optimum control.

A passive hastelloy filter (diffuser) protects the sensing cell from particulate matter, and can endure the high temperatures and corrosive attack inside the recovery boiler. The buildup of salt cake on this in-situ filter (diffusion element) can pose a problem over time, reducing the speed of measurement response. The best way of diagnosing a plugged diffuser is a flow test with calibration gas. This can be done on-line, but the boiler operator should be notified so that any control loop can be placed into manual for safety considerations. Use bottled calibration gas with a different O_2 value than the normal operating range (for instance, 8% O_2). Once the O_2 readings have stabilized at the bottled gas value, remove the cal gas, and note the time it takes to return to the normal process value.

With a new diffuser, the reading should begin to return within 3-5 seconds ($T_{initial}$). The reading should return all the way back to the normal process value within 30 seconds or so (T_{final}). A badly plugged diffuser may take 30 seconds to reach $T_{initial,}$ and a minute or more to reach T_{final}. Besides delaying the normal speed of response, a plugged diffuser can cause a shifted reading if the probe is calibrated with a plugged diffuser. Care should be taken to prevent flowing too much cal gas to the sensor, pressurizing the cell during the calibration procedure. Set the calibration gas flow to specification only when installing a new diffuser. As the diffuser plugs, a lower flow rate will be noted, but never increase the flow rate back up as this will mask the problem.

The buildup of salt cake deposits is a unique problem associated with recovery boilers. This can be can be minimized by periodically back-purging with instrument air down the calibration gas line inside the probe. The back-purge can physically remove some material, and it also burns off any combustible components in the heated sensing cell and diffuser. Frequency and duration of this burn-off procedure is highly variable from furnace to furnace, and depends greatly on how the boiler is being operated.

SO_2 and other sulfurous components can shorten the life of a ZrO_2 sensing cell by attacking the platinum electrode that generates the O_2 measurement signal. This condition is further aggravated by furnace operation with O_2 levels below 1%. Rosemount's Oxymitter product utilizes a "calibration recommended" diagnostic which will notify technicians when the sensing cell should be recalibrated. Sulfur-resistant cells increase cell life considerably in recovery boiler service.

Boiler Operations
Protecting the boiler side of the recovery area requires verifying that the steam produced in the boiler is not contaminated by potentially corrosive chemicals, dissolved oxygen, or high levels of dissolved solids. pH, conductivity, and trace dissolved oxygen are three very common online measurements that can easily be installed for this purpose. These measurements are common to all large scale industrial boilers.

Boiler water is usually treated with chemicals to produce an optimum pH in the 8-9 range, which tends to minimize corrosion and scaling. Excursions above or below this range usually indicate a process leak in a heat exchanger tube. Continued operation in this mode can lead to widespread corrosion and expensive tube replacements. pH measurement of condensate can be problematic due to low ionic strength in the sample, but sensors designed for high purity measurement such as the model 320HP provide a stable signal by controlling both sample flow and reference flow rates.

The steam produced in the boiler is used to preheat and concentrate the black liquor in multiple effect evaporators before combustion in the furnace. The condensed steam provides an opportunity to monitor the purity of the boiler water and specifically check for black liquor leaks into the condensate. Black liquor is both highly alkaline and highly conductive, so it is easily detected by pH and/or conductivity measurements. Retractable conductivity sensors can be installed upstream and downstream of potential leak sources.

The Black Liquor Recovery Boiler Advisory Committee (BLRBAC) recommends "The installation of a conductivity sensor with alarm at an individual spout outlet or at a common point in the vacuum cooling water system can be helpful in the early detection of a spout leak, since the initial stages of a spout leak could allow small amounts of smelt to leak into the spout, slightly contaminating the purity of the cooling water prior to the leak becoming large enough to "break" the vacuum or siphon interrupting cooling water flow to the affected spout."

Conductivity is an excellent leak detection method because it can indicate the presence of any ions in the condensate. It can quickly indicate a spout leak or indicate a slow buildup of solids over time. Boiler water is reused many times and can build up contaminants from several sources that eventually cause scaling or other damage to metal surfaces. Localized scale prevents heat conduction in the boiler tubes, leading to overcompensation and localized overheating. This is a costly and potentially dangerous activity as overheating may lead to leaks. A localized area of heat stress results, which is more easily corroded from the furnace side. A hole develops, and the steam explodes. Stainless clad boiler tubes are used to reduce heat stress failures and conductivity is continuously measured to prevent the accumulation of scale.

Water treatment chemicals add to the conductivity of water, so some data interpretation may be necessary to determine if harmful levels of ions are present. A condensate monitoring system with reboiler can be used to isolate the contribution of salt ions from

the water treatment chemicals and dissolved gasses that may be present. Flow through conductivity cells can also be used separately to monitor general condensate purity.

Dissolved oxygen is also a major cause of metal corrosion and is removed using a deaerator and/or injection of an oxygen scavenger chemical. Boiler water must be treated to reduce dissolved oxygen from ambient parts per million (ppm) levels to 50 parts per billion (ppb) or lower. Measurement of trace dissolved oxygen in the ppb range specifically verifies oxygen removal. Amperometric sensors use the current generated by the diffusion of oxygen across a semi-permeable membrane as an indication of the concentration in the solution. One model uses a patented technique for eliminating background interference due to ambient oxygen that saves several hours of calibration time.

Continuous gas and liquid analyzers provide critical measurements for safely optimizing the operation of the recovery furnace and boiler.