Pulp & Paper Industry Solutions
Accurate and Reliable Liquid Analysis

ROSEMOUNT®
Analytical

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Process Management
Papermaking is a highly sophisticated process involving several processing steps to turn wood logs into paper products. In addition to the actual papermaking process, there are also supporting areas such as waste water treatment, recovery boiler operation, steam production, and cooling towers that benefit from on-line analytical measurements.

You need a partner that can deliver the best in knowledge and systems, and do it quickly, thoroughly and cost-effectively. Emerson Process Management’s Rosemount Analytical brand of products provide measurements of pH, ORP, conductivity and dissolved oxygen that are specially designed for long life and reliable results in the demanding environment of the pulp mill. These measurements provide substantial control benefits that can reduce costs with a typical payback time of less than one year. Read on and discover how the liquid analysis professionals from Emerson can help you improve your bottom line.

Although not present at all mills, there are five major steps to the papermaking process: mechanical preparation of the wood into wood chips, wood digestion (pulping) to form pulp, pulp whitening (bleaching), pulp stock preparation, and finally paper formation.

The first of these steps uses strictly mechanical processes to form small chips from the logs supplied to the mill. Byproducts such as bark and even some of the chips themselves are used as fuel to produce electricity and steam for mill use. Although some water may be used for lubrication purposes, this is primarily a dry process and proceeds with a minimum of process instrumentation.

The pulping process has many variations. Most common is chemical pulping using either caustic (Kraft sulfate process) or acidic (sulfite process) chemicals.

The chemicals are used and regenerated in a recovery process that reduces chemical costs and minimizes waste disposal costs. Process conductivity measurements optimize both the pulp yield and the recovery of chemicals in this stage. Other pulping techniques such as groundwood or semichemical use pH measurements to optimize yields or improve the properties of the pulp.

Pulp stock leaving the digester is a brownish liquid that is usually bleached to make more acceptable white paper. This process uses large quantities of expensive bleaching chemicals (usually ClO₂) and represents raw material and waste disposal challenges. pH measurement in this area optimizes the efficiency of the bleaching process, lowering bleach consumption, discharge and associated costs.

Prior to running in the paper machine, different batches of pulp may be blended to produce paper of various required properties. Starches and retention aids are added to improve the wetting properties of the paper. The pH measurement standardizes this process, helping to produce the same quality paper day in and day out.

The paper machine is usually considered the last place to get conditions right for the final product. A reliable pH signal at this location can prevent large runs of off spec product. These locations can represent difficult applications for sensors, but recent advances in sensor technology have vastly improved the performance and reliability of online sensors.
On-line electrochemical measurements such as pH, electrical conductivity, and dissolved oxygen provide real improvements in process control, quality, efficiency and profitability in Pulp and Paper operations. Mill effluent, especially from bleaching operations, is increasingly the target of environmental regulations such as the Cluster Rule and must be monitored closely.

There are many different processes that can be used to make paper and each process involves several steps. Chemical pulping, the most common process of producing a pulp slurry from wood chips, involves strong chemicals that are typically regenerated and reused. Dosage of these chemicals and control of the recovery process is monitored using electrical conductivity measurement. The pulp slurry is treated using bleach, sizing agents and other furnish before being run in the paper machine. These pulp additives can be very ineffective if the pH of the pulp slurry is not controlled. Common measurement locations are bleach towers, machine chest, headbox, and white water chest.
Kraft Pulping

Kraft pulping produces strong pulp but typically needs further processing such as bleaching to provide acceptable brightness for average users. Cost effectiveness comes from reuse of the pulping chemicals in the recovery process (see page 7). Pulping is conducted in a digester and the process can be operated in either batch or continuous mode. There are many kinds of pulping processes, but generally the most cost effective one is the chemical process called Kraft pulping.

In the Kraft process, wood chips are cooked in a strong alkali solution called white liquor. The white liquor is basically a solution of sodium hydroxide and sodium sulfide with an effective concentration of about 100 grams per liter. Measuring white liquor alkali concentration allows optimization of cooking time and product pulp properties. Direct measurement of the alkali concentration is possible using automatic titrators. However, due to the difficulty of extractive sampling many mills opt to use electrical conductivity to provide real-time control feedback.

The clarified white liquor feed to the digester is the optimum location to install the retractable Model 228 Toroidal Conductivity Sensor. This sensor has a unique lead screw design that allows for safe retraction at up to 295 psig for cleaning purposes.

Measuring the alkali concentration entering into the digester allows fine control of the liquor flow rate to match the wood loading, improving throughput and minimizing variability.

Inside the digester, at temperatures near 180°C and pressures around 250 psig, the following reaction occurs:

\[ \text{Na}_2\text{S} + \text{NaOH} + \text{wood chips} \rightarrow \text{Na}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 + \text{pulp} \]

As this reaction proceeds, the Kappa number decreases until the “cook” is completed in about 2 to 4 hours. Kappa Number is difficult to measure, so many mills monitor the digester by measuring the concentration of chemicals in the cooking liquor using three chemical titrations called “ABC tests”. Results of the ABC tests are used to establish NaOH, Na₂S, and Na₂CO₃ levels in the liquor. As the cook progresses, NaOH is consumed and Na₂CO₃ is produced. When the NaOH level has dropped to the appropriate level, the cook is complete and the product (called brownstock) is released from the digester and further processed. This technique still requires that samples be extracted and processed by a lab every 2-4 hours.

Although the application inside the digester is significantly different from the application in base white liquor, electrical conductivity measurement is valuable here also. Conductivity can be correlated to the A and B tests since the active NaOH has much higher conductivity than the product. As the cook continues, conductivity steadily decreases. Conductivity is best measured in the upper recirculation zone for rapid response to process changes, but the high solids concentration at this location tends to plug most conductivity sensors.

Process measurements in heavy slurries such as cooking liquor require robust flow-through sensors like the Model 242 Toroidal Conductivity Sensor. This sensor consists of a replaceable ceramic liner and externally mounted toroid measurement coils. The toroidal conductivity method is resistant to the effects of coating, and the Model 242’s external mounting protects the toroids from the high temperature and pressures in the digester. The Model 242 is recommended for lines up to 4” in diameter.
Bleaching and the Wet-End

Bleaching is the process of purifying and whitening pulp by chemical treatment. Several stages are typically used to generate pulp with the desired brightness. To meet environmental regulations, nearly all pulp mills use elemental chlorine free bleaching (i.e. chlorine dioxide). Some mills have gone to totally chlorine free bleaching via peroxide or ozone.

A typical bleach sequence consists of a pair of bleaching stages each followed by an extraction stage. Chlorine dioxide bleaching allows efficient bleaching at lower pH (3.5 to 4) without degrading the cellulose component of the pulp. The extraction stages are conducted at elevated pH (10-11) to maximize color removal. pH measurement is very cost effective here because the chemicals used to manufacture chlorine dioxide represent a significant operating cost. Stable pH control increases net bleaching efficiency and lowers cleanup costs since less bleach is required.

A pH sensor consists of a pH sensitive measurement electrode (traditionally made of glass) and a reference electrode that is designed to remain unchanged over the lifetime of the sensor. Both electrodes must remain in working order with an electrical path (provided by a small flow of electrolyte through a junction) linking the two electrodes through the process. Application concerns occur when either electrode is attacked by the process or when the link between them is broken.

Conditions inside the bleach tower are harsh on all parts of the pH sensor. Consistency can be up to 10% solids, which can coat a standard pH sensor very quickly, plugging the reference junction.

The bleaching chemicals are aggressive and incompatible with many sensor materials. The 70°C temperature accelerates the rate of chemical attack.

Emerson’s TUph™ sensor technology minimizes the effects of coating by using a patented composite junction with over 400 times the surface area of standard junction membranes. The abundance of .02 micron pores preserves a minimum flow of KCl electrolyte, and thus a stable reading in the presence of solids.

Our TUph sensors resist the effects of process coating, reducing costly maintenance and downtime.

The Model 398R TUph Sensor, with Tefzel® body and Kalrez seals, is specifically designed for severe duty in harsh bleaching chemicals. ACCU-GLASS™, the product of a two year study, incorporates the most temperature resistant formulations possible for a long-life pH sensor at elevated temperatures.
After bleaching, there may be several pulp stock preparation steps in the wet-end of the paper machine. Pulp from different sources is mixed as needed for various products and mechanically refined prior to delivery to the headbox. Sizing agents, dyes, and additives (furnish) are typically added at the mixing chest(s) to promote desired paper characteristics. These chemicals are more effective under controlled pH conditions, and each may require different conditions for optimum results.

Superior pH control is achieved by monitoring upstream of the mixing chest for feed-forward control. Pulp from the storage tanks will be mixed with the plant water based on a consistency setpoint. This water can change the pH significantly and requires constant pH monitoring to prevent product waste. As mills strive to conserve and reuse precious water resources, there is an increased need to monitor and control the pH in the recycle loops. At this stage, the TUph Model 396R, with polypropylene junction and EPDM seals, is a fine low-maintenance sensor for the job.

The headbox location is a critical pH measurement since an upset condition here will immediately result in offspec product. Alum (Al₂(SO₄)₃) or sulfuric acid is added to regulate the pH prior to the headbox. It is preferable to use sulfuric acid for this purpose since alum is primarily used as a retention aid and can lead to a buildup of solids in the white-water. Using inexpensive sulfuric acid for pH control allows tighter control of water retention and prevents unnecessary cleaning of pH sensors.

Convenient mounting options for pH sensors such as the PASVE Rotary Valve can be used to automate cleaning routines, taking the guesswork out of how and when to maintain the sensor. The rotary design requires little force to insert the sensor and includes flushing ports for internal cleaning.

A cleaned pH sensor should respond quickly when reintroduced into the process. Monitoring the recovery time of a pH sensor can verify the cleanliness of the sensor and is an excellent tool to minimize maintenance costs on the wet-end measurements.
Monitoring the concentration of active chemical (referred to as active alkali or effective alkali in the Kraft process) is best achieved by using online conductivity measurement throughout the process.

This loop begins with the spent white liquor that was used in the digester. The first regeneration step separates the chemicals from the pulp in the brownstock washers. The flow of washwater to each stage is set to maximize the removal of chemical without diluting the black liquor too much. This weak black liquor consists of a mixture of sodium compounds and lignin organics. At this point, the black liquor is quite viscous and is best measured using a toroidal conductivity sensor such as the large bore Model 226.

After oxidation in the furnace, the smelt is redissolved in a weak liquor to form a stronger greenish liquor consisting of mostly sodium carbonate (Na\(_2\)CO\(_3\)) and sodium sulfide (Na\(_2\)S). The causticizing process that takes place in the slaker and causticizer converts the carbonate to active hydroxide by chemical reaction with lime:

\[
\text{Ca(OH)}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaOH}
\]

Causticizing efficiency measures what percentage of the sodium carbonate is converted to sodium hydroxide. An excellent online method of determining the causticizing efficiency compares the conductivity of the white liquor with the conductivity of the incoming green liquor. This requires two conductivity sensors, one in the green liquor line and another in the slaker or causticizer.

The causticizing reaction is an equilibrium process, so several large tanks are used in series to maximize the efficiency of the reaction. The byproduct CaCO\(_3\) (lime mud) has a low solubility, and is removed at each tank.

Ideally, the best response time would be obtained from measuring the conductivity in the initial reaction zone (slaker), but the slurry is full of solids and very frothy. In practice, most mills measure conductivity in the relative stability of the first causticizer using a retractable toroidal conductivity sensor.

Lime sources have varying characteristics. Monitoring efficiency at the first and third causticizers and the downstream clarifier is very common. The lime itself is regenerated in a lime kiln in a separate cycle.

The lime mud washer optimizes removal of white liquor from the lime mud. The weak liquor obtained from the lime mud is used to dissolve the smelt from the recovery furnace. Conductivity measurement is used to control flow rates in the washer.
The recovery boiler is an integral part of the Kraft process and provides steam and electrical power for the pulp mill. Water used to make steam must be of sufficient purity to prevent scaling and corrosion inside the boiler tubes. The water is recirculated many times, so there is ample opportunity for impurities to enter the steam plant. These impurities can come from black liquor leaks, makeup water, or internal gas leaks. Expensive water treatment chemicals such as ammonia or hydrazine will be added when necessary to keep the water chemistry under control.

The first step in protecting the boiler tubes is to monitor the conductivity of the condensate. Most recovery boilers will target conductivity in the 1-10 mS/cm range. When the conductivity exceeds this value, some of the circulating water will be removed (blowdown) and some pure makeup water will be added. The method for preparing the makeup water will differ from mill to mill but may involve reverse osmosis and/or ion exchange columns.

Condensate conductivity measurements are taken using contacting conductivity sensors such as the Model 402 sensor. Temperature compensation is especially important for condensate conductivity, so each sensor has an integral RTD, which the analyzer will use to correct the measured conductivity value to 25°C.

Ion exchange columns contain resins that slowly saturate with ions and need to be regenerated.

When the column is no longer performing, it will be switched out of line and purged with acid (for cation columns) or caustic (for anion columns). These acid and caustic solutions have much higher conductivity values and are measured using toroidal conductivity sensors such as the Model 228.

Boiler pH control is usually targeted between 7.5 and 8.5 due to the sharp increase in corrosion below pH 7. Operating at pH over 8.5 tends to increase the formation of solids on metal surfaces that can degrade the efficiency of heat exchanger tubes.

Measuring pH at low conductivity can be problematic due to the high impedance of the glass measuring electrode. A well-grounded metallic flow cell is recommended to prevent excessive noise and a low, constant flow rate is recommended to prevent excessive dilution of the reference electrolyte. The Model 320HP sensor has been well accepted by pulp and paper mills in steam plant operations.

Continuous dissolved oxygen levels above 7 ppb have been implicated in premature failures due to pitting and metal fatigue. Oxygen scavengers are typically employed to reduce the concentration in boiler water. However, even a small leak can cause an expensive failure. Insurance against this kind of failure can be easily obtained by measuring trace dissolved oxygen following the deaeration stage.

The Model 499A TrDO Trace Dissolved Oxygen Sensor (see diagram on next page) is a membrane covered pair of electrodes that produces a current signal directly proportional to the concentration of oxygen in the water. Emerson uses a unique self-depleting design to provide fast comedown times following air calibration and maintenance.

Online measurement systems are also available for silica, hydrazine, phosphate, ammonia, sodium, chlorine, and refractive index.
Waste Treatment

The pulping processes tend to generate the bulk of the waste from a combined pulp and paper mill. The debarking process mixes fine wood shavings with water. Spent pulping liquors, collected spills, washings from dregs and lime mud, and bleach residue are by-products of the pulping process that must be collected and treated before discharging into the environment. Other mill areas such as stock preparation, finishing and converting, and gas scrubbers also produce effluents for cleanup.

Color removal is especially important and may require multiple stages of clarification using lime, alum, and/or ferric chloride. These chemicals capture contaminants by forming a solid floc that can be separated from the effluent stream. The flocculation chemicals are most efficient at controlled pH levels, but pH measurements at these locations can be costly to maintain. The TUpH sensor design has an excellent performance history for applications with heavy solids and is strongly recommended for use in clarifiers.

Pulping waste generally contains high levels of organic materials and high BOD (Biological Oxidant Demand) and may require additional treatment steps. Typical treatment methods include anaerobic digestion, controlled aeration, and sand filters. Common processes such as clarification and sludge removal, aeration basins, gas strippers, heavy metal removal, chlorination, and dechlorination are then used to prepare the wastewater for release. The exact treatment methods depend on the kind of pulping and on the local environmental regulations.

To ensure adequate treatment several electrochemical measurements are made throughout the process, including pH, ORP, electrical conductivity, and amperometric measurements such as chlorine residual, ozone, and dissolved oxygen.

Residual chlorine measurement is especially important in ensuring final disinfection of the water per environmental guidelines. Chlorine activity is largely determined by pH level, so Emerson has combined pH and chlorine measurement to provide the most accurate control possible.

An amperometric sensor completes the measurement by consuming (i.e. reducing) the specie of interest at the cathode to produce a current which is proportional to the concentration. Therefore, these sensors must be installed in a region of continuous process flow to insure a fresh sample is provided. The flow also helps prevent coating and scale on the membrane. Nonetheless, for maintenance intensive processes such as activated sludge or where large amounts of fines are expected, it is recommended to use an automatic jet spray cleaner to prevent buildup.
The optimum solution for the process relies most heavily on selecting the right sensor to match the process needs. In most cases the instrument is simple to select and depends on the power, control, and communication requirements, in addition to other desired features, such as HART®, FOUNDATION fieldbus®, preventative diagnostics, and more. Choose the one that meets your needs.

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* Not available for Turbidity
PlantWeb® Brings It All Together

Rosemount Analytical’s instruments are part of Emerson Process Management’s PlantWeb® field-based architecture: a scalable way to use open and interoperable devices and systems to build process solutions. The PlantWeb architecture consists of intelligent field devices, scalable platforms and standards, and integrated modular software, all working together to create, capture, use, and distribute information and process control data.

This architecture can reduce your capital and engineering costs, reduce operations and maintenance costs, increase process availability, reduce process variability, and streamline regulatory reporting.

To see what PlantWeb can do for your operation, call or visit us at PlantWeb.com/RunSafe.

Emerson Process Management supplies proven, robust Rosemount Analytical on-line electrochemical sensors and instrumentation. With over 60 years experience in process control, wastewater treatment and drinking water treatment, users around the world trust Emerson. In recognition of our dedication to customer service, product excellence, and quality we have received the #1 Readers Choice Award from Control Magazine for the tenth consecutive year.

Measurements in Pulp and Paper can be challenging due to the presence of suspended solids and harsh chemicals. The sensors from Rosemount Analytical are designed to continuously meet these challenges, resulting in minimized downtime and lower maintenance costs.

Accurate on-line process measurement of pH, conductivity, ORP, chlorine residual, dissolved oxygen and ozone plays a critical role in achieving a plant’s objective and meeting regulatory compliance at the local and federal level. Count on Emerson for the systems and solutions you need in an ever-changing, dynamic world. See us on the web at RAIhome.com.