Application Note

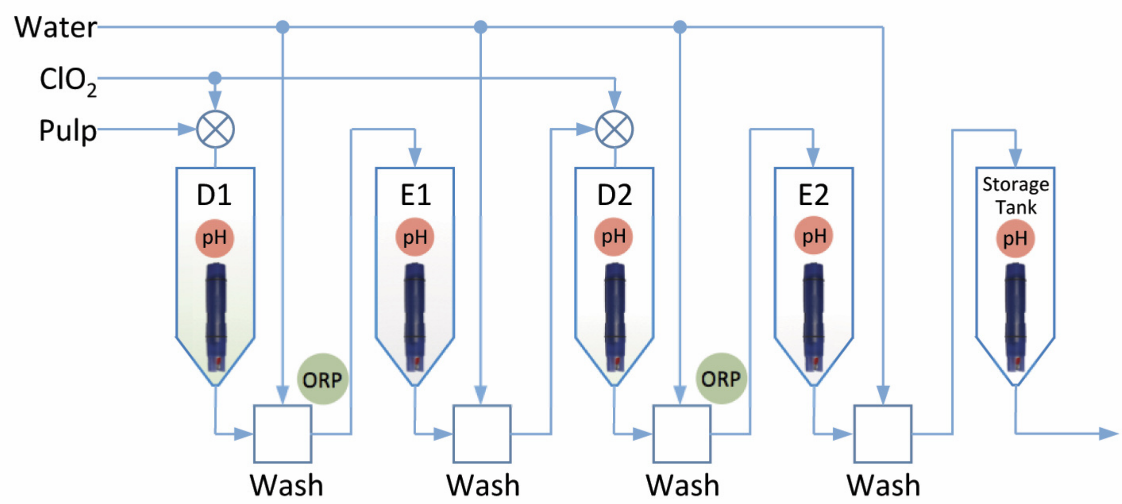
Pulp & Paper Wet End pH Measurements

Bleach Plant

Delignification of pulp is carried out to brighten the pulp and make it ready for paper manufacture. Lignin is naturally brown in color and affects the quality of the final paper product, so must be removed. Most lignin is removed by “cooking” early on in the paper making process, but it is not possible to remove 100 percent of the lignin by cooking alone as this damages the pulp fibers. Bleaching is therefore used to complete delignification of raw pulp stocks after cooking.

Bleaching is a multistage process and the number of stages used is largely dictated by the final brightness of the pulp required. The most common process is the ECF (elemental Chlorine free) method as this is more environmentally friendly than earlier Chlorine bleaching methods.

Chlorine Dioxide (commonly referred to as the “D” stage) is mixed with the pulp as it is fed into each D tower (see diagram below) where the two components react. Retention time in each D tower is typically one to three hours, although shorter and longer times can occur in some plants. The Chlorine Dioxide selectively attacks the phenolic groups of lignin without degrading cellulose fiber, allowing for both increased yield and a higher strength bleached pulp. pH in the D towers is maintained at relatively low levels (around 4) to encourage vigorous chemical reaction and reduce overall Chlorine Dioxide consumption. An overall dose rate of 5% chlorine dioxide is not uncommon.

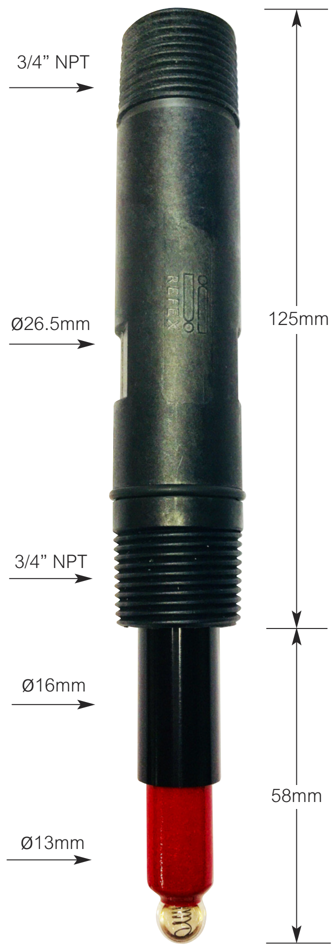


Typical Pulp Bleaching Process

Following reaction (bleaching) with Chlorine Dioxide in each D tower, the reacted pulp undergoes caustic extraction (referred to as the “E” stage) where in the lignin is removed by dissolving under high pH conditions (typically over 11). Lower pH levels will not dissolve all of the lignin. The reacted pulp is washed to reclaim chlorine dioxide and minimize acid carryover while being transferred from a D tower to an E tower (where caustic extraction is carried out).

ORP/Redox measurement is often employed to monitor the efficiency of this tower transfer washing process. The amount of caustic needed to achieve lignin dissolution is proportional to the amount of chlorine dioxide added in the D stage. Once all of the lignin is removed, the raw pulp is transferred to storage where it is held in readiness for final processing and delivery to the paper machine.

Bleach plant process sequences vary from mill to mill where other chemical stages may be included to increase brightening efficiency or to suit local conditions. However, the basic D-E-D-E stage sequence is quite common. Pulp consistency (% solids) is typically maintained at a high level (up to 10%, sometimes 15%) to minimize water use and temperature is typically controlled at around 60°C / 140°F.



Pulp Stock Preparation

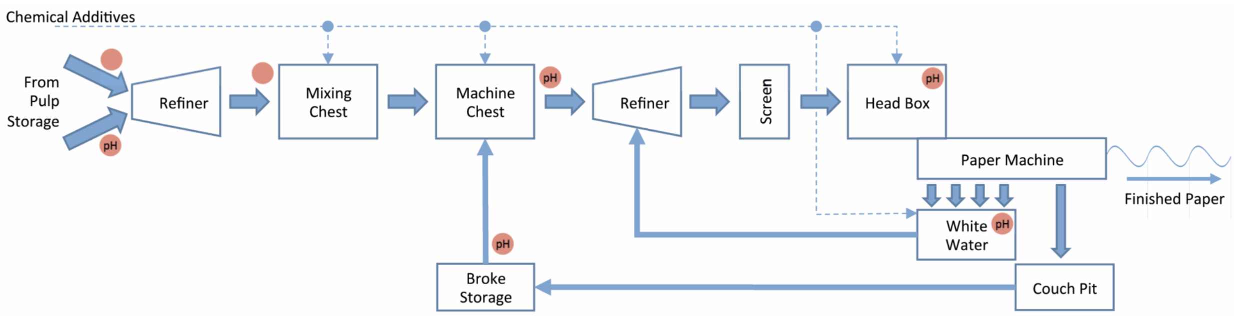
The monitoring and control of pulp stock pH is critical to manufacturing efficiency and the final quality of the product in the paper making process. pH **must** be maintained to very tight limits throughout all steps of production.

While delignification and bleaching of wood fiber creates the raw pulp for the paper making process, this raw pulp is not ready for paper manufacturing until it has been further processed and refined. Improvements in fiber binding, strength, smoothness, color, and opacity are achieved through both mechanical processing and the addition of additives such as resin, dye, filler and sizers. The efficiency of many of these chemicals can be impacted by pH, underlining the need for pH to be carefully controlled for optimum results.

A typical first stage after basic raw pulp dilution is to pass it through a refiner which shreds and flattens the pulp to improve its bonding characteristics. pH has an effect on the tensile strength (bonding) of the pulp fibers. Higher pH levels (> 8pH) improve the ability to shred the pulp and can contribute to energy savings when running the refiner. The pulp is then passed to a mixing chest, where chemical additives are introduced. pH measurement is made upstream of the mixing chest to allow feed forward control of acids/bases into the mixing chest. Maintaining pH levels close to neutral aids in the proper chemical reaction of additives and the retention of fillers. Residence time and agitation within the mixing chest provides for complete blending of these additives with the pulp. Common pulp stock additives include the following:

- Acids and bases: pH control
- Sizing agents: repels water
- Starch: dry strength and stiffness
- Polymers: links fibers for wet strength
- Kaolin, TiO_2: fillers for gloss, brightness and opacity
- Surfactants: control foaming tendencies in the process and reduce entrained air

From the mixing tank, the pulp flows to the machine chest where pulp consistency is set by thickening/dilution in preparation for feed to the paper machine. Recycled "broke" pulp stock is often blended in with the new pulp at this point. pH measurement of the incoming recycle stream allows for pH control in the machine chest while pH measurement downstream of the machine chest ensures that enough retention time has been allowed for the proper reaction of added chemicals to occur. From the machine chest, pulp is further refined, de-aerated and passed through screens to remove any remaining "lumps and bumps" that could affect paper quality before arriving at the paper machine headbox. In the headbox, pH is once again measured with final chemical additions and pH corrections made to the pulp stock before it is applied to the wire mesh of the paper machine for drying and rolling.



Simplified Wet End Stock Preparation Process

The pH of the applied pulp stock is critical for printability. Most paper produced will be printed when used. If the paper is too acidic, it will affect printability. Pulp stock pH also affects the distribution of paper fibers in the final product. At low or high pH levels, paper fibers tend to form clumps which in turn affect paper surface smoothness. It can be seen that the impact of out of spec pH at the headbox can create a considerable expense to the mill in terms of off-spec or scrap product.

Water is recovered from the pulp (white water) and after pH adjustment, is recycled to the process. Pulp carried over from the paper machine (broke pulp) is also collected and returned back into the process.

Measurement Challenges

It can be clearly seen that pH must be measured in the D and E towers to allow control of reaction conditions during bleaching. Note that this highly important measurement of pH in the D and E towers has historically been among the most difficult measurement applications in a pulp mill. pH must also be reliably measured throughout all stages of pulp preparation to ensure the material applied to the paper machine is in the best possible condition.

The high pulp densities and harsh chemistries in the process are beyond the capabilities of most common pH sensors and while there have been many pH probes especially “designed” to perform under these very difficult process conditions, they all suffer from the same fundamental weakness – a porous reference junction.

- The E_0 diffusion potential found across reference porous junctions creates an error of at least 0.3pH. This error contributes to process inefficiencies that can affect the quality of the pulp.
- Traditional electrodes require frequent cleaning to remove coating and build up that block porous junction paths, creating sluggish and non-responsive measurement.
- The strongly oxidizing environment of the process has free rein to enter the measurement reference cell through these porous junctions, diluting the electrolyte within to cause drift in the measurement. The process fluid also attacks the AG/AgCl electrode, leading to the rapid demise of the sensor itself.

A common strategy to combat some of the problems above has been to mount pH probes behind sample extraction valves rather than directly in the process. While this can extend the life of traditional probes in the application and apart from the cost and maintenance of the additional equipment required, this creates an undesirable time lag between pH measurement and what is actually occurring in the process. This time lag affects efficiency and can result in prolonged reaction times and additional chemical consumption.

Measurement Solution

The real solution to these problems is a pH probe with a non-porous junction between process and reference cell. REFEX pH and ORP sensors feature an electrochemically active, ionically conductive interface that forms an impenetrable barrier between the process fluid and the Ag/AgCl reference electrode. Non-porous REFEX sensors are immune to electrolyte dilution, fouling and poisoning and provide drift free, accurate measurement in the most extreme of conditions. Note that some maintenance is still required. Probes must be extracted and cleaned from time to time to remove pulp buildup. Exner automated and manual hot tap systems are recommended to ensure probes are maintained in good condition and will provide trouble free measurement throughout their life.

SFI OCM44X

Exner electrode holder

REFEX Sensor Advantages:

- Protected Ag/AgCl reference half-cell - REFEX barrier/interface prevents all liquid contact/exchange
- Resistance to fouling and poisoning
- Suitable for temperatures between 0…100°C
- Operate in pressures between full vacuum and 20 bar / 290 psi
- Instantaneous response to pH change
- Constant E_0 zero - almost maintenance free
- Long electrode life - many times longer than all others
- Compatibility with all modern pH instruments featuring dual high impedance inputs for pH and reference electrodes.
- No electrolyte refilling - sealed for life

EC-1"-CA-2001-Pt1000-LE	EC-3/4"-CA-2001-Pt1000-LE	S8-CA-2001-120mm	YG-CA-2001-120mm	EC-FT-CA-2001-Pt1000 - 120mm EC-FT-CA-2001-Pt1000 - 225mm
1" NPT mount insertion/submersion sensor with fixed cable (1, 3, 5, 10m)	3/4" NPT mount insertion/submersion sensor with fixed cable (1, 3, 5, 10m)	Ø12mm, Pg13.5 mount sensor with S8 connector	Ø12mm Yokogawa Y-cap connection Sensor	Ø12mm, Pg13.5 mount sensor with fixed cable (1, 3, 5, 10m)

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