Control of the Extraction Stage Using the True Terminal pH  
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ABSTRACT

Control of the pH of the extraction stage in a kraft bleaching sequence, has long been recognized as a means of optimizing the conditions throughout the tower, including the terminal pH of the reaction. However, in many cases, the final pH sample is taken after the influence of the low pH dilution water, for a down flow stage, from the next stage. A filtrate extractor was installed in the tower above the ring dilution zone and the pH of the filtrate sample was measured. Chemical consumption of both the extraction stage sodium hydroxide and the subsequent stage chlorine dioxide was controlled. Mill data and potential cost savings will be presented.

INTRODUCTION

Although fiberline configurations and bleaching sequences in general, have changed considerably over the past thirty years, the function and importance of the alkali extraction stage has remained the same. In the actual bleach plant, the first alkaline extraction stage following chlorine dioxide delignification is typically operated at medium consistency, 10-16%. The purpose of an alkaline extraction stage is to dissolve then remove compounds made alkali-soluble in the preceding acidic delignification treatment. Much of the delignification work accomplished in the D₀ stage is not realized until the alkali soluble lignin fragments are removed. (1) In most mills today, the alkali extraction stage has been modified by the addition of oxygen and or hydrogen peroxide. Newer designs include pressurized vessels commonly referred to a PO stages. Shown below is a typical configuration of an upflow-downflow Eop stage.

![Chemical Addition in Eop Configuration](image)

Fig. 1 Eop Stage Schematic (2)

Many literature sources and research studies cite results that deal with the importance of the terminal pH for this stage. (1) By definition, the terminal pH is the pH taken at the end of the extraction reaction, but normally this is not the same as the exit pH of a down flow tower. This due to the fact that most down flow towers utilize what is known
as a ring dilution zone to mine the pulp out of the tower. In most cases, the source of the dilution or ring dilution water is from a counter current stage normally the next D1 stage filtrate. This is a useful technique as it assists with the lowering of the pH, which is necessary for efficient control of the subsequent chlorine dioxide stage. However, the resultant pH of the stock entering the Extraction washer is not representative of the true terminal pH of the reaction due to the impact of the much lower D1 stage filtrate which by itself is often a pH of XX. Several methods are used to measure this pH and estimate the actual terminal pH. One of the most common methods is to manually take a grab sample of the stock entering the Extraction stage washer vat. Again, this sample has been influenced by the lower pH of the dilution stream. Reed and Morissette (2) showed that unless temperature compensation is used on this sample, the reading will be almost always incorrect up to 1.5 units off, and have a high degree of variability. It is important to note that this compensation is in addition to the temperature compensation built into most pH sensors used today. For process control purposes, this is the least accurate method. The other issue with manual testing that is worth consideration, is the variability that is often introduced by the manual testing itself. Shown below is a control chart showing the variability commonly present in a manual pH test.

![Individuals Chart for pH](image.png)

**Fig. 2 Control Chart of Manual Lab Tests**

If manual tests are to be used, then it is recommended that an audit of the sample collection, preparation (if any) and testing method be undertaken. This would include ensuring that fresh pH buffer standard solutions be used.

This value is however, often used to estimate the terminal pH by applying a constant bias and to make adjustments to the sodium hydroxide charge being applied to the extraction stage. The caustic which is normally charged as a ratio to the production rate on a mass to mass basis or as percent applied, can also be rationed to the first stage chlorine dioxide charge, expressed as Total Equivalent Chlorine, TEC. This is referred to as the Caustic to TEC ratio. The objective once again is to control the end pH of the extraction reaction and short-term feedback can be used by measuring the pH directly after the caustic mixer before the pulp enters the extraction tower or pre-tube if it is an Eo stage. Measurement of the pH directly in the pulp stock line has proven to be particularly challenging. The high consistency, up to 15%, and the harsh chemistries are beyond the capabilities of most pH sensors. The typical pH sensor tends to require regular cleaning and few sensor reference cells are able to withstand the strong oxidizing environment. For many installations, the pH sensor is installed directly into the process with or without a ball valve. For these installations, the probe is typically initially calibrated with a known buffer, but often is not routinely checked. This may because the removal of the probe is not easily done while the process is operating, or is in a
difficult location. Maintenance of this type of installation is often overlooked and as a result, the sensor becomes unavailable for control. For this reason, pH sensors are often not even installed directly into the process but mounted in a filtrate extraction device. An improvement over a direct probe installation, is for this measurement to be continuous and utilizing some form of filtrate extraction device. This is an inline device that on a regular basis, extracts a filtrate sample for the pulp and by using a flow through cell, a continuous pH measurement can be made.

Fig. 3 Filtrate Extractor in Down Flow Tower (BTG)    Fig. 4 pH sample pot with probe

Often the emphasis is put on controlling the post mixer pH in an attempt to have the terminal pH in the desired range. As previously mentioned, feedback from the tower exit or vat pH, is also be used for adjustment. Vat pH can prove to be misleading in the case of counter-current bleach plants due to the introduction of D1 filtrate at the bottom of the extraction tower.

In a mill study, the manual extraction washer vat pH was compared to a manual pH sample taken above the ring dilution in the extraction tower as shown in the photo below. The pH tests have no correlation to the vat pH or the tower pH. However, we can see the influence of lower pH filtrate on the washer vat pH.

Fig. 5 Example of sample Tap in Tower
In addition to manual vat pH tests, some mills do utilize an inline filtrate sampler located in the stock line leading up to the extraction stage washer vat. The advantage here over manual sampling is that the depending on the type of sampler, the signal will be at best discontinuous and this creates a lag time between the pH measurement and what is actually occurring in the process.

However, filtrate extractors are designed to give a "semi-continuous flow" of filtrate to an off-line pH sample pot. The pH probe sits in the pot that receives the continuous flow. The pH measurement is interrupted intermittently when the extractor initiates a cleaning cycle. Typically, the cleaning takes under 10 seconds. During this time, the pH reading to the DCS is held at the last value and resumes updating after the cleaning cycle has completed. Air is used during this cycle so the filtrate is not altered. The length of time between cleaning cycles is dependent on species and process conditions. Software species usually give high filtrate flows from the extractor and can have longer sampling periods. Hardwood species require shorter sampling times with more frequent cleaning cycles due to the short fiber length which plugs the filtrate extractor tip. The choice of pH probe is also very important. Common failure issues have been plugging of the reference cell junction and what is referred to as caustic poisoning of the glass tip.

Many different technologies do exist on the markets that have attempted to overcome these known issues. One such design is known as Axial Ion Path (A.I.P), reference and is supplied by Honeywell and Bartens. Like other rugged semi-solid state references, the reference is formed by a series of wood segments impregnated with KCL The difference with this technology is where others utilize an epoxy or impermeable barrier between each of the wood segments; the A.I.P. uses a pair of formed discs. When the two formed disc faces are positioned adjacent to one another they form an axial ion path (filled with electrolyte) between each of the segments. This provides a more complete transition of KCl ions between the wood segments forward and creates a difficult and longer distance for poisons traveling back into the reference from the specimen fluid.
This is a porous surface, which passes ions between the reference and measurement fluid. The primary function is to allow very small amounts of KCl to leach from the reference and provide the millivolts necessary for pH measurement. The secondary function is to maintain a barrier between the measurement fluid and the reference so that the measurement fluid does not rapidly poison or foul the reference. In order to be effective, temperature compensation must also be available.

**The Use of Advanced Control**

In the previous section, we mentioned the use of the TEC ratio in controlling caustic addition to the extraction stage. In an advanced control scenario, the Do stage and Extraction stage comprise the “Delignification Controller”. The controller has disturbance variables (DV), which is the incoming kappa, manipulating variables (MV), and control variables (CV). Without advanced control, the caustic for the extraction stage is usually being manipulated by one of the following:
- Pound per ton basis
- Maintaining a specific pH into the extraction tower
- Running to a specific extraction washer vat pH

The Advanced Process Control objective is to control final tower pH to ensure proper extraction, using intermediate process parameters, such as up flow tube pH, (if available) for short term control. True terminal pH in the downflow tower to tightly control the caustic addition improves the overall control. A manual lab pH test can be substituted, but does not give the rapid update to the controller that would yield maximum savings. In addition, the controls will allow the NaOH/TEC ratio to be dropped closer to its stoichiometric optimum, from high ratios of around 0.48 to 005 higher or lower. Below are examples of high NaOH/TEC ratios, where the bleaching operation uses kappa factor control and one of the 3 methods:

![Fig. 9 Examples of Caustic Ratio Control](image)

The correlation is quite poor due to the regulatory nature of the control.

The Delignification Controller looks at the Do and Extraction stages as one unit controlling to an end stage extraction kappa or post extraction washer brightness. Below is an example when using advanced control:

<table>
<thead>
<tr>
<th></th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incoming Kappa</td>
<td>9.90</td>
<td>9.95</td>
</tr>
<tr>
<td>D0 % ClO2 Charge</td>
<td>0.947</td>
<td>0.950</td>
</tr>
<tr>
<td>Incoming Eo pH</td>
<td>10.75</td>
<td>10.77</td>
</tr>
<tr>
<td>Eo Caustic Charge</td>
<td>1.196</td>
<td>1.055</td>
</tr>
<tr>
<td>% D1 ClO2 Charge</td>
<td>0.86</td>
<td>0.82</td>
</tr>
<tr>
<td>D1 Brightness</td>
<td>86.58</td>
<td>87.60</td>
</tr>
</tbody>
</table>
Conclusions:

The alkaline extraction stage remains a critical part of the bleaching process even though bleaching sequences have changed over the years. Literature cites the importance of measuring terminal pH of the extraction stage but in practice pH is measured by taking a manual sample from the extraction washer vat. This can lead to misleading results since the extraction washer is using lower pH D1 filtrate. A mill study comparing extraction washer vat pH versus a filtrate sample above the ring dilution in the extraction tower showed no correlation but did demonstrate the influence of the lower pH D1 filtrate used for vat dilution.

Filtrate extractors offer another method of obtaining filtrate for a semi-continuous pH signal to the DCS. Extractors can be installed in the process pipe or directly in the tower to obtain the true terminal pH of the extraction stage. The choice of pH probe is also very important. Common failure issues have been plugging of the reference cell junction and what is referred to as caustic poisoning of the glass tip. It is important to select the best technology for your operation that is available from a variety of suppliers.

In closing, the use of advanced control can greatly improve the results from the extraction stage. Without advanced control, the caustic for the extraction stage is dosed based on a pound per ton basis, maintaining a specific pH into the extraction tower or running to a specific extraction washer vat pH. Advanced Process Control will control the final tower pH to ensure proper extraction, using intermediate process parameters, such as up flow tube pH, (if available) for short term control. The true terminal pH in the downflow tower to tightly control the caustic addition will improve the overall control.

References