pH IN THE BLEACH PLANT – WHY IT’S IMPORTANT AND WHAT TO DO ABOUT IT. PART 1 – ClO$_2$ STAGES.

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ABSTRACT

pH is critically important in every bleaching stage in order to obtain high pulp quality and optimum costs. It must be well-controlled if advanced controls such as Compensated Brightness, Compensated Kappa Factor, and Model Predictive Control are to perform to their full capability. This paper reviews the reasons why pH is so important, the challenges associated with its measurement and control, and strategies for overcoming those challenges in ClO$_2$ stages. It also includes a summary of the performance currently being achieved by North American mills.

INTRODUCTION

There has been a great deal of work done over the years on pH as it relates to kraft pulp bleaching. This includes application studies to determine optimum pH, research studies to understand the myriad reactions that occur in bleaching stages, advances in pH sensor design, maintenance/calibration practices for pH probes, and development of pH control strategies.

The goal of this paper is to summarize key points from all areas of this work and provide a reference to help mills optimize pH, pH measurement, and pH control in their ClO$_2$ stages. Part 2 of this series will review these topics as they relate to extraction stages.

HOW DOES pH AFFECT ClO$_2$ STAGES?

1. D0 Stage

Several studies have examined the effect of pH in the D0 stage. They found that performance deteriorates significantly for most furnishes when pH exceeds 3.5-4.0 (Figures 1 and 2). Low pH often causes a smaller decrease in performance but is not usually an issue in practice because it is difficult to drive the pH much below the optimum even with excessive amounts of acid. This can, however, cause increased NaOH usage in the Eop stage. Remember that the D0 and Eop stages work together to delignify the pulp, so Eop kappa and brightness are typical measures of the impact of D0 pH.

![Figure 1. Impact of D0 pH on delignification and brightness [1]. O$_2$ - Delignified softwood, kappa # 18.](image-url)
2. D1 Stage

The impact of pH on the D1 stage is well-documented. The classic work on this was done by Rapson and Anderson [3] in 1976 (Figure 3). They showed that maximum brightness was obtained at pH 3.5-4.0 and that it coincided with minimum chlorate and chlorite formation. They also found that the presence of salt improved bleaching efficiency. Their results were based on conventional softwood kraft pulp, and the bleach sequence started with a chlorination stage.

Fifteen years later, Basta et al. [1] showed similar results on oxygen-delignified softwood pulp using an ECF sequence (Figure 4). Additionally, they showed that ClO$_2$ application rate changes the curve, shifting the optimum pH lower as more ClO$_2$ is added.

Finally, Hart and Connell presented a series of experiments in 2005 [4] that confirmed the earlier studies and showed that ClO$_2$ application rate and wood species have a large influence on the shape and optimum of the pH-brightness curve. Higher ClO$_2$ application rates push the optimum pH lower, and softwood pulps typically have a lower optimum pH than hardwood pulps for the same amount of ClO$_2$ (Figures 5 and 6).

They also developed a graph to predict the optimum pH based on wood species and ClO$_2$ application rate (Figure 7). This can be used as a starting point for a mill to set its pH target, although the most accurate method is to perform a lab optimization study on the mill’s own pulp.
Figure 3. Impact of D1 pH on brightness [3]. Conventional chlorinated softwood, kappa #28.

Figure 4. Impact of D1 pH on brightness [1]. O2 - Delignified ECF softwood, kappa #18.
Figure 5. Impact of D1 pH on brightness – ECF hardwood [4].

Figure 6. Impact of D1 pH on brightness – ECF softwood [4].

Figure 7. Optimal D1 pH based on wood species and ClO$_2$ application [4].
3. D2 Stage

Hart and Connell showed that the D2 stage also exhibits a pH optimum and that it is often higher than the D1 optimum, at least for softwood (Figure 8).

![Figure 8](image)

Figure 8. Impact of D2 pH on brightness – ECF softwood [2].

4. An Example

Examination of the graphs in the previous sections shows that operating away from the optimum pH can significantly reduce brightness (or increase kappa number in the case of the D0/E1 stage). If the pH is not corrected, then ClO$_2$ application must be increased to compensate.

As an example, Figure 5 is reproduced below in Figure 9. The scale has been changed to make the example easier to see. If the mill normally runs at point A under optimum conditions but lets the pH drift to point B, then the brightness will drop by 1.3% ISO. By interpolation, the controls or the operator will have to add an additional 2.5 kg/t ClO$_2$ to regain brightness (point C). If the pH is subsequently corrected, then the brightness will increase to point D and the controls or operator will have to decrease ClO$_2$ to maintain the correct brightness. The net result is that brightness exiting the D1 stage varies by 2.3% ISO from its minimum at point B to its maximum at point D and the mill uses more ClO$_2$ than it should solely because of poor pH control within the stage.

![Figure 9](image)

Figure 9. Example of how a pH upset affects brightness in a D1 stage. Hardwood pulp. Curves taken from [4].
WHY DOES pH AFFECT ClO₂ STAGES?

ClO₂ chemistry is complex and a detailed discussion is beyond the scope of this paper. Many papers have been written on this topic, and the reader is referred to them for additional information (reference [6] has an excellent section on this). The main point to recognize is that multiple reactions occur in a ClO₂ stage. ClO₂ reacts with lignin/chromophores and produces byproducts that still have oxidizing potential. These byproducts can react again with lignin/chromophores or with other byproducts to form useful species such as ClO₂ or useless species such as chlorate, or they can participate in equilibrium and decomposition reactions that result in a variety of useful or useless species. Which reactions occur, and the relative speed of those reactions, depends on a variety of factors such as pH, temperature, the nature of the lignin/chromophores, and the concentration of species present. This is why the curves shown earlier in this paper vary depending on the stage, ClO₂ application, and furnish.

A partial list of reactions is included below [5], [6], [7]:

Lignin reactions:
- ClO₂ + Lignin → Oxidized lignin + HClO₂
- HClO₂ + Lignin → Oxidized lignin + HOCl
- HOCl + Lignin → Chlorinated lignin + Cl-
- Cl₂ + Lignin → Chlorinated lignin + Cl-

Equilibrium reactions:
- HClO₂ ↔ ClO₂⁻ + H⁺ (higher pH favors ClO₂⁻)
- Cl₂ ↔ HOCl (higher pH favors HOCl)
- HOCl ↔ ClO⁻ (higher pH favors ClO⁻)

Regenerate ClO₂:
- HOCI + 2HClO₂ → 2ClO₂ + H₂O + HCl

Decomposition reactions:
- 2HClO₂ → HOCl + ClO₃⁻ + H⁺
- ClO₂ + OH⁻ → ClO₃⁻ + ClO₂⁻ + H₂O (slow at pH 4, fast at pH 7)
- HClO₂ + ClO₂⁻ → HOCl + ClO₃⁻

Figure 10 shows how these various reactions can interact. For example, starting in the top left corner ClO₂ reacts with lignin and produces HClO₂ which then reacts with lignin to form HOCl. Additionally, some of the HClO₂ and HOCl can react with each other to regenerate ClO₂, setting up a cycle of ClO₂ consumption and regeneration as long as both species (HClO₂ and HOCl) are present simultaneously. On the other hand, high pH converts HClO₂ to chlorite in a pH-dependent equilibrium reaction and also leads to the reaction at the top of the figure in which ClO₂ is converted to chlorite and chlorate. Chlorate is essentially “lost forever” while chlorite can become useful again if the pH drops and it converts back to HClO₂.

Note that Figure 10 is simplified; lignin is a complex substance made up of many different components and each one reacts to a different extent with each of the oxidizing species. The figure also does not contain every possible reaction, information on reaction rates, the impact of process conditions, etc.
HOW IS pH MEASURED?

The first commercially successful pH meter was introduced in 1934 by Arnold Beckman [8]. Due to this long history, they are sometimes overlooked in mills as more attention is given to new analyzers such as kappa analyzers and online brightness meters. These new analyzers are outstanding and make it possible to implement control strategies that could only be imagined previously, however, they are designed to build on basic controls such as pH, not to replace them.

A pH probe is essentially a very weak battery [9] whose voltage changes depending on the pH of the liquid it is immersed in. The two electrodes of the “battery” (probe) are connected at one end by the liquid being measured and at the other end by a voltmeter (the pH meter) which converts the measured voltage to pH (Figure 11). The voltage produced is very low (maximum of approximately 400 mV [9]), as is the current (on the order of nanoamps [10]).

Since the probe is a battery, it is made of two half-cells. These are:

1. The measurement electrode. This electrode uses a special gel-covered glass tip, and the potential across the tip (between the outside and inside of the glass) changes depending on the difference in H⁺ concentration between the two sides of the glass. The inside is filled with electrolyte (a known buffer solution) and the outside is exposed to the liquid being measured. The H⁺ concentration inside the tip is known, so the concentration outside (and hence the pH of the solution being measured) can be calculated. Current flows through the glass.
2. The reference electrode. This electrode is designed to have the same potential regardless of the solution being measured. It is intended to be a constant reference used for comparison to the other electrode. It is made of an impervious shell filled with an electrolyte (usually KCl and a small amount of AgCl). In order to complete the circuit and allow current to flow, the electrolyte must contact the liquid being measured so it can form a “salt bridge.” This is done through a junction that has the task of allowing contact but without losing the electrolyte or allowing the measured liquid into the probe. In practice, it is impossible to completely achieve all three of these objectives, so manufacturers do their best to minimize the rate of electrolyte loss into the measured liquid and the amount of measured liquid that finds its way into the electrode. Approaches include:
a. Use a gel or solid electrolyte instead of a liquid. For example, ABB’s widely used TB(X)5 probes and their forerunner, the Bailey TBI probes, use a solid electrolyte.
b. Use multiple chambers (with multiple junctions) to slow the flow of electrolyte and measured liquid
c. Use different materials for the junction such as kynar, teflon, fiber, or porous ceramic [9].
d. Use very small holes for the junction (although this makes it subject to plugging, which stops current flow)
e. Pressurize the electrolyte reservoir [9]

There are other designs for the electrodes using different materials (especially for the reference electrode), but the above description covers most pH probes.

Figure 11 shows the components of a pH meter. Current follows the path shown in Figure 12. Modern pH probes have the glass measurement electrode (aka “pH electrode”), reference electrode, and temperature element built into one housing (Figure 13).

Note that the relationship between pH and voltage changes with temperature so the measurement will be incorrect whenever the temperature changes. Fortunately, this effect is reproducible and can be calculated using the Nernst equation. This correction is built into all pH meters and is either applied automatically or via a knob that the user sets to the sample temperature. This does not correct for changes in actual pH of the liquid being measured due to temperature. These changes are different for every liquid and therefore cannot be programmed in advance without knowing the liquid being measured. See Figure 18 later in this paper for an example of how D1 and D2 stage filtrates are affected by temperature.

![Figure 11. Components of a pH meter [10].](image-url)
** Figure 12. ** Current flow in a pH meter.

** Figure 13. ** pH probe with both electrodes in one housing [11]. (Reference junction is another name for the liquid junction)

** pH MEASUREMENT CHALLENGES **

All pH meters must receive regular attention to operate correctly. They should be checked regularly against a lab test (more about this in the next section) and, if necessary, cleaned and recalibrated. If this is not sufficient, then additional diagnostics may need to be performed and/or the probe may need to be replaced. Some potential problems and diagnostic procedures are summarized below. Additional information can be found in operating/troubleshooting guides from various instrument manufacturers (many of them for free on their websites) or in books such as reference [23]. Many pH meters now contain built-in diagnostics to assist with troubleshooting and routine checks.

It can be surprisingly difficult to tell when a pH probe needs to be replaced. A bad probe will usually still respond to changes in pH and can still be calibrated to match at least one point. It may, however, have a non-linear response and therefore be inaccurate in certain ranges.

Most pH sensor failures (>80%) [10] are related to the reference electrode so this is the first place to look when problems arise and is the part of the meter that should receive the most routine maintenance/checks. This is not too surprising considering that the reference electrode contains the liquid junction, which has the near impossible task of
allowing the electrolyte and measured liquid to contact each other without flowing into each other. Typical problems include:

1. Partial plugging of the reference junction introduces junction potentials that cause inaccurate measurements while complete plugging stops the measurement altogether [9]. A sensor that has scaled up will usually have high reference impedance (> 20 kohm) [10].
2. Electrolyte gets pumped out of the reference electrode through the junction and replaced with the measured liquid. Since electrolyte concentration affects the reference potential, this will change the indicated pH. If the measured liquid reacts with the electrolyte then the effect will be even more severe. Moderate poisoning can be overcome by recalibration, but at a certain point the probe will have to be replaced. This is most common with inline probes that are subjected to temperature and pressure swings [9]. An offset greater than ±30 mV usually indicates a serious problem with the reference electrode due to poisoning. Check this by measuring the voltage when the probe is immersed in pH 7 buffer – it should be between -30 mV and +30 mV. In theory, the instrument should read 0 mV when the probe is immersed in pH 7 buffer at 25°C [16]. Some other manufacturers suggest that an offset greater than ±25 mV indicates a problem [15].

The glass measuring electrode can also cause problems:

1. The glass electrode will not respond properly if it is installed with the tip facing up. Even a tip-down installation of less than 15° from horizontal is problematic in many cases. Most electrodes contain a bubble to prevent the glass from breaking due to thermal expansion and contraction of the electrolyte. This bubble interferes with the measurement if it gets into the tip because it prevents the electrolyte inside the electrode from contacting that part of the glass. It can also dry out the gel inside the electrode on that section of glass. The gel can sometimes be “rejuvenated” if it didn’t dry out for too long but if not then the probe must be replaced. For this reason, most inline probes should be installed with the tip facing down, and all pH probes should be stored with the tip facing down. Figure 14 shows installation recommendations from manufacturers whose instruments are often used in bleach plants.
2. The glass electrode can be cracked or otherwise damaged if the probe is dropped or if an inline probe is hit by something flowing past it in the process. Even a small crack will negatively affect performance. This can usually be identified by low glass electrode impedance (< 10 Mohm) [10].
3. The glass measuring tip may have deteriorated. Common causes include age of the probe and improper cleaning (such as with a brush). Slope < 49 mV/pH indicates that the glass is bad and the probe should be replaced [14]. Check this by measuring both the pH and voltage in two different buffers and calculating the slope. Theoretical slope for a pH meter @25°C is 59.16 mV/pH.
4. The glass electrode will not respond properly if it becomes coated with scale, pitch, or anything else.
5. The glass tip can dry out if the probe is not kept wet before being installed, or when removed during maintenance, or if the liquid level drops below the probe during a shutdown. As described earlier, the gel can sometimes be “rejuvenated” if it didn’t dry out for too long but if not then the probe must be replaced.

As mentioned earlier, scale, pitch, and other deposits will cause problems with both the reference and measuring electrode. Depending on the nature of the deposit, the probe can be cleaned by immersing the tip in weak acid (i.e., 5% HCl), weak caustic (i.e., <4% NaOH), or a detergent or organic solvent that is compatible with the probe materials [10]. Avoid wiping the tip of the probe and using brushes or abrasive powders because they can damage the gel layer on the glass measuring probe.

The pH meter may not be calibrated correctly. Inline probes are often calibrated by removing them from the process and immersing them in buffer solution(s). When using this approach:

1. Follow the standard calibration procedure recommended by the manufacturer. This is straightforward and easy to find so will not be covered here.
2. Use fresh buffer solutions for calibration. Buffer 10 is particularly age-sensitive because it absorbs CO₂ from the air, which changes its pH.
3. Ideally, use buffer solutions that bracket the expected pH range
4. pH of the buffer solutions used for calibration change with temperature, so ensure that the meter is calibrated to the correct values

Note that this method works much of the time but not always. The probe becomes acclimated to the process that it “lives in” which means that equilibrium is eventually obtained at the liquid junction between the electrolyte in the reference electrode and the process liquid. That equilibrium is upset when it is removed from the process and
immersed in a clean buffer solution, causing unstable junction potentials to form. It sometimes takes a long time for the reference electrode to come to equilibrium with the buffer so the calibration may be performed before equilibrium is actually reached. In these cases, it is better to calibrate the meter to a process sample of known pH since the probe is already in equilibrium with that environment [9]. The sample pH is determined using a lab pH meter that has been calibrated in the normal way using buffers. Reference [9] provides an excellent discussion on calibrating new and used process pH probes.

**Figure 14.** Installation guidelines for various pH probes used in bleach plants [12], [13], [10].
Incorrect installation can cause issues with performance. Here are some general guidelines, but always follow the manufacturer’s instructions for the specific probe, process conditions, and location since they may necessitate different or additional requirements:

1. As described earlier, probes must never be installed with the tip facing up and many probes must have the tip facing down at least 15 degrees from horizontal (Figure 14).
2. Some probes (usually those with flat glass electrodes) must be installed 90° to the process flow in order to be “self-cleaning” while others may perform better if they point slightly into the process flow.
3. The probe must be inserted to the correct depth. It should protrude far enough into the process to get past the laminar flow layer at the edge of the pipe [17] but not so far that it will get sheared off.

The built-in thermocouple may have failed. The relationship between voltage and pH is temperature dependent, so modern pH meters include a thermocouple and use that measurement to correct the pH reading. A small error of a few degrees has negligible impact, but I have been to a few mills where the thermocouple was indicating 400-700°F when the actual temperature was 160°F.

Ground loops can cause erratic pH readings from a process sensor or readings that are significantly different from lab readings. To check for a ground loop, note the reading of the process sensor and grab a sample of the process in a glass or plastic container. Remove the sensor from the process and place it in the “non-conductive” container. If the reading differs significantly, a ground loop is suspected. To confirm this suspicion, ground the solution in the container to the process with a wire. If the pH reading becomes unstable or changes back to where it was when the sensor was installed, a ground loop is confirmed [9]. Ground loops are usually caused by high current motors when they or another component in the system (such as piping or the pH meter) are improperly grounded or grounded to different locations [18].

The correct probe must be specified. Manufacturers offer a large range of models and options designed to deal with a variety of real-world challenges. This offers great flexibility when dealing with a difficult application but can also make the selection process daunting. For example, one manufacturer offers 10 models for industrial applications. Each model then has the following options:

- Up to five types of measuring electrode
- Up to eight types of liquid junction
- Up to five types of internal thermocouple
- Optional built-in diagnostic hardware with choice of three metallurgies and five O-ring materials
- Up to fourteen body styles (length and material of construction)
- Up to seventeen mounting options (including different metallurgy choices)

The critical choices are model, type of measuring electrode, and type of liquid junction (the others are relatively straightforward), however, this still gives 400 different combinations and the possibility of making a wrong choice. I visited one mill that installed new pH meters throughout the bleach plant only to find out that the probes were all designed for low temperature operation (even though they had provided their process conditions to the vendor) and therefore never operated correctly under normal process conditions.

COMPARING ONLINE AND LAB pH MEASUREMENTS

Checking the online probe with a lab test is not as straightforward as it may sound since the lab measurement is susceptible to many of the same problems plus a few extras of its own. Do not assume that the lab measurement is always correct. Potential problems include:

- The lab meter’s probe may be fouled, poisoned, or otherwise damaged
  - The diagnostic tests described in the previous section can be used to troubleshoot lab pH probes. For example, the tester could occasionally check the offset (should be between -30 mV and +30 mV when immersed in buffer 7) and slope (should be >49 mV/pH). On the other hand, lab probes are relatively inexpensive compared to the time required to perform diagnostics and the amount of chemical that can be wasted in a single day due to incorrect measurements so it may be more efficient to just replace them on a regular schedule. A probe that is only used to measure D stage filtrates could last 6-12 months while one that is used to measure E stage filtrates may need to be replaced in as little as 1-3 months. These time periods are just suggested starting points – mills can extend them if experience shows that their probes last longer.
- The probe may be stored in water instead of buffer between rounds. This can cause two problems:
In fresh deionized water, the ions in the electrode will move out of the probe and into the solution in an attempt to establish equilibrium. Over time, most of the ions will leave the electrode, rendering it useless. The glass will also degrade much faster, leading to shorter electrode lifespans [16].

- After a number of tests have been performed, the water becomes contaminated by the measured filtrates which can cause the probe to become fouled or poisoned

- **The lab meter may not be calibrated correctly.** See the previous section for potential issues.
- **The automatic temperature compensation feature may be turned off or the tester may not be adjusting the temperature compensation knob to match the sample temperature**
- **There may be issues with the test procedure such as not gently stirring the sample**
- **The mill may be using one meter to measure high and low pH samples (for example, D and E stage filtrates).** More accurate results can usually be obtained by using two meters with one calibrated to a low pH range for D filtrates and one calibrated to a high pH range for E filtrates.
- **The sample may be significantly cooler than process temperature when its pH is measured**
  - The actual pH of the sample changes as it cools – this is an additional change that the meter’s built-in temperature compensation does not account for. This is usually a fairly small change for neutral and acidic filtrates but it is important to be aware of it. See Figure 18 later in the paper.
- **The sample may not be representative of the conditions seen by the probe**
  - Make sure that the sample valve is close to the online probe
  - Make sure that the online probe reading is recorded when the sample is taken, not when the test is complete

**INSERTION VS. FILTRATE EXTRACTOR**

There is some debate over which is better, a probe inserted directly into the process or a filtrate extractor feeding a probe in a sample pot. I have seen both types work and I have seen both types not work. I think that if they are properly specified, installed, and maintained then it comes down to personal preference. The main challenge for each type is:

- **Insertion probes can be difficult to remove and reinstall for routine maintenance.** Manufacturers provide specialized valve assemblies, safety clamps or cables, and other solutions to help with this.
- **Filtrate extractors sometimes plug or provide an erratic sample that may not be representative of the process** (although newer extractors seem to be much better than the ones that were available twenty or thirty years ago). The sample will cool, sometimes by a varying amount, making full temperature compensation more important than it is for an insertion probe.

**INSTALL pH METER BEFORE OR AFTER ClO₂ ADDITION?**

pH drops throughout ClO₂ stages. Figures 15 to 17 show that the drop is especially rapid at the beginning of the

![Figure 15. pH drop over time in a D1 stage [6]. Original data from [21].](image)
Figure 16. pH vs. time in D0 and D1 stages [19].

Figure 17. pH vs. time in D2 stages [19].
stage. Therefore, production rate changes will change the pH seen by a probe installed shortly after ClO\textsubscript{2} addition. This will change the inlet pH that must be maintained in order to hit the target pH at the end of the stage. Mills can avoid this issue by:

- Installing the pH meter further downstream of the ClO\textsubscript{2} addition (i.e., partway up the J-tube), although dead zones in the J-tube can sometimes make it difficult to obtain a representative measurement from this location.
- Installing the pH meter before ClO\textsubscript{2} addition. This can work well if the mill layout permits it, although changes in ClO\textsubscript{2} addition (which will change the amount of caustic or acid required) are not accounted for. It may be possible to program an advanced control to compensate for the change in observed pH due to production rate, but no-one to my knowledge has done this.

**IMPACT OF TEMPERATURE ON D STAGE FILTRATE pH**

Spriggs has presented data (Figure 18) showing that temperature has an impact on the pH of D stage filtrates [20]. This is an actual change in pH that the meter’s built-in temperature compensation does not account for. The effect is much smaller than seen for extraction stage filtrates and is the reverse of what is seen for extraction stage filtrates. That is, pH decreases as a D stage sample cools while pH increases as an E stage sample cools. No mills that I’m aware of have built a chart to compensate their D stage lab or process measurements. Further work to expand on these findings would be interesting.

![Figure 18. pH change with temperature for D1 & D2 filtrates (hardwood) [20.]](image-url)
**pH CONTROL STRATEGIES IN ClO₂ STAGES**

The ultimate pH target is the pH at the end of the bleaching reaction ("terminal pH"). For a typical upflow/downflow tower this is located at the bottom of the downflow tower just before (i.e., above) the dilution zone. Ideally, the mill extracts a filtrate sample at this location and measures the pH with a lab test or a continuous analyzer. If a sample cannot be collected there, then the next best location is the washer vat (assuming a vacuum washer). This works well enough although the large amount of recirculated dilution filtrate can dampen process variation. Any washwater that breaks through the sheet and into the filtrate tank will also affect the measured pH. Most North American mills measure final pH in the washer vat but some measure it at the ideal location (some have been doing it for decades). Mills should test terminal pH every 1-2 hours unless they have an online terminal pH meter that they are confident in.

Terminal pH cannot be used to directly control caustic or acid due to the long retention time in ClO₂ stages. Most mills have a pH meter installed at the beginning of the stage, either just before or just after ClO₂ addition, and have closed loop control to maintain a constant inlet pH. The operator adjusts the inlet pH setpoint as necessary to keep the terminal pH in its target range. A few mills are attempting to use an online terminal pH measurement in a slow feedback loop to adjust the inlet pH setpoint.

Some mills that are not able to maintain a reliable inlet pH measurement have resorted to ratioing the caustic or acid to the ClO₂ and adjusting the ratio based on the terminal pH measurement. This strategy is reported to work fairly well [22] although its proponents state that “it is always preferred to measure the inlet pH with a pH sensor and use simple PID control when possible.”

**INDUSTRY EXPERIENCE – WHAT DOES GOOD pH CONTROL LOOK LIKE?**

Based on Nouryon’s experience, the best mills can achieve a long-term (up to 12 months) standard deviation of 0.20 – 0.25 for terminal pH in the ClO₂ stages (see Table I). A typical mill has 50-100% higher variation and some mills are much higher than that.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Typical Standard Deviation</th>
<th>Best Mills Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>D0</td>
<td>0.30</td>
<td>0.20</td>
</tr>
<tr>
<td>D1</td>
<td>0.45</td>
<td>0.25</td>
</tr>
<tr>
<td>D2</td>
<td>0.40</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Figure 19 shows how increased variation in D1 stage pH affects the brightness variation exiting the stage. The average pH is 4.5 in all cases and a normal distribution is assumed. The brightness curve is taken from Figure 5 [4] and the scale has been adjusted to make it easier to see. For this example, the best-controlled mills will see a maximum 0.3% ISO decrease due to pH variation while a typical mill will see a maximum 1.2% ISO decrease and a poorly controlled mill will see a maximum 2.6% ISO decrease solely due to pH variation. I have observed operating mills that fit into all three categories.
Figure 19. Impact of D1 stage pH variation on pulp brightness. Brightness curve from Hart and Connell [4].
CONCLUSIONS

The effectiveness of pH control in ClO$_2$ stages across North America varies widely. The best controlled mills see little change in brightness due to pH variation while poorly controlled mills see large changes. Mills can easily determine which category they fall into by calculating the standard deviation of their terminal pH in each stage and comparing it to Table I. If a mill’s pH measurement or control is lacking, then the information in this paper can be used to begin the troubleshooting process.

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