

Focused Technologies for  
Focused Results in Bleaching.

IMPROVING  
CHLORINE DIOXIDE  
BLEACHING EFFICIENCY

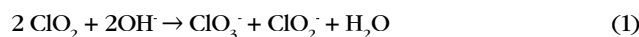
# Improving chlorine dioxide bleaching efficiency by selecting the optimum pH targets

PETER HART AND DANIEL CONNELL

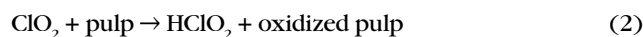
**ABSTRACT:** When operating chlorine dioxide (D) bleaching stages under mill conditions, it is important to establish reasonable operating targets and ranges. We examined the relationship between optimum pH, acceptable range for pH control, bleaching efficiency, and mill specific parameters such as wood species, pulp quality, and chemical charge. The D stages of eight separate fiber lines were simulated in the laboratory using mill pulps obtained from the various bleach plants studied. Both hardwood and softwood species were examined. We examined each simulated D stage over a range of final pH targets and chlorine dioxide charges to determine the relationship of pH to bleaching efficiency. Our work shows that, in practice, the optimum pH for a specific D stage varies with mill specific parameters. We categorized these practical relationships to draw some general conclusions. Mill data from three mill trials were used to validate the relationships.

**Application:** By fully understanding the importance and impact of pH at their specific mill, engineers and operators will be able to optimize the bleach plant and reduce operating costs. The current work shows the importance of pH in optimization and how to best examine local pulps to determine optimal conditions.

Chlorine dioxide ( $\text{ClO}_2$ ) oxidizes lignin compounds via a number of reaction pathways. Several of these pathways regenerate  $\text{ClO}_2$ , thus enhancing the efficiency of  $\text{ClO}_2$  bleaching. Beginning with early work on  $\text{ClO}_2$  stages in the 1950s, researchers have advanced our basic understanding of these intermediate reactions [1-8]. In water,  $\text{ClO}_2$  reacts with hydroxyl ions to form chlorate ( $\text{ClO}_3^-$ ) and chlorite ( $\text{ClO}_2^-$ ) ions according to Eq. 1.



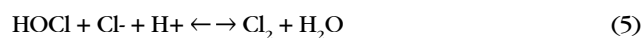
The rate of reaction 1 increases as the pH increases, but is relatively slow compared to the reactions of  $\text{ClO}_2$  with pulp. At a pH of 4, reaction 1 is slow and after 3 h, less than 10% of the  $\text{ClO}_2$  is decomposed. At pH 7, 90% of the  $\text{ClO}_2$  is converted to chlorate and chlorite ions under the same conditions. In the presence of pulp, the oxidizing equivalent made available by reduction of  $\text{ClO}_2$  to chlorous acid ( $\text{HClO}_2$ ) is consumed by the pulp instead of oxidizing another mole of  $\text{ClO}_2$  to form chlorate ion. Thus, with pulp present, the dominant reaction is that given in Eq. 2.



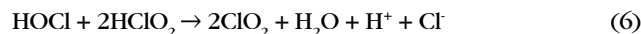
If the pH of the pulp is above 7, reaction 2 is extremely vigorous and attacks both lignin and cellulose, thereby damaging pulp strength. Chlorous acid in an aqueous solution rapidly establishes equilibrium with its dissociation products, hydrogen ion and chlorite ion, as shown in Eq. 3. Chlorous acid may also react to form chlorate ion, hypochlorous acid ( $\text{HOCl}$ ), and hydrogen ion according to Eq. 4. Therefore, depending on pH and specific ion concentrations, chlorous acid can decompose to form chlorate and hypochlorous acid or it can ionize to form chlorite.



Chlorous acid tends to be exceptionally reactive towards phenolic lignin, producing hypochlorous acid as a reduction product. In the presence of chloride ion, hypochlorous acid also establishes a pH-dependent equilibrium with chlorine according to Eq. 5. In this way, chloride ion suppresses the formation of chlorate ion.



If no chloride ion is present in the immediate reaction medium, hypochlorous acid reacts with chlorous acid to regenerate  $\text{ClO}_2$  and hydrochloric acid according to Eq. 6. This is the preferred pathway for maximum bleaching efficiency.



Not only does pH affect the intermediate reactions, but different types of lignin favor different reaction pathways. Researchers have determined that nonphenolic groups in lignin oxidized at high pH form only chlorite ion and not hypochlorous acid. Therefore, at high pH and a high amount of nonphenolic lignin there may be an excess of chlorite relative to hypochlorous acid [5]. Alone, chlorite ion is unreactive toward lignin. However, chlorite and hypochlorous acid regenerate  $\text{ClO}_2$  via reaction 6, which then further reacts with lignin via reaction 2 and forms more chlorous acid. Additionally, at a very low pH, hypochlorous acid can participate in substitution reactions with lignin, leading to the formation of organic chlorine compounds (AOX). As the reaction approaches completeness, the  $\text{ClO}_2$  is converted to chlorate,

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chlorite, or chloride ions. The final concentration of chlorate or chlorite ion greatly depends on pH.

Careful observation of the reactions listed above suggests that most of the lost oxidizing power of ClO<sub>2</sub> occurs in the reaction pathways that produce chlorate ion, an inactive species toward pulp bleaching. The result of this relationship between intermediate reactions and pH is the well established rule that the best ClO<sub>2</sub> bleaching efficiency is at the pH that minimizes the final concentration of chlorate and chlorite. Early work by Rapson [1,2] showed the effect of the final pH of the bleaching stage on the relative ratios of chlorate and chlorite ion concentration. As the pH decreases, the amount of chlorate ion increases, resulting in lost efficiency. On the other hand, as the pH increases, more chlorite is formed than can participate in regenerating active ClO<sub>2</sub>. Typically, the minimum chlorate plus chlorite ion concentration occurs at a final pH of about 3.8.

Early studies of ClO<sub>2</sub> bleaching (D<sub>1</sub> and D<sub>2</sub> stages) found that the maximum brightness was generally achieved when bleaching was carried out at a constant pH of around 6 [1] with the aid of a buffer. The use of a buffer was impractical and cost prohibitive in the mill environment, so the general practice is to allow the pH to fall during the reaction time. For instance, for a given reaction with a specific stock, the initial pH after ClO<sub>2</sub> addition may be 7.0. The pH will rapidly fall as the reaction proceeds so that the final pH may be 3.5. Without a buffer to hold the pH constant, a mill must target a final pH that will create the best pH conditions over the entire retention time. Under this strategy, maximum brightness is typically achieved at a final pH between 3.5 and 5.0. For most D<sub>1</sub> or D<sub>2</sub> stages, this requires addition of caustic at the beginning of the stage. The 2003 PAPTAC bleaching survey of Canadian mills found that 50% of the D<sub>1</sub> stages op-

erate with caustic for pH control while 20% operate with acid addition [7].

Since promulgation of integrated air and water emission standards for the pulp and paper industry (the Cluster Rule) in the late 1990s, many U.S. (and Canadian) kraft bleach plants have converted the first stage of bleaching from chlorine to chlorine dioxide. This stage is typically referred to as the D<sub>0</sub> stage. The optimum pH for a D<sub>0</sub> stage is considerably lower than for the D<sub>1</sub> or D<sub>2</sub> stages. The main reason for this difference is that the objective of the D<sub>0</sub> stage is different from the objective of the D<sub>1</sub> and D<sub>2</sub> stages. The purpose of the D<sub>0</sub> stage is to react with lignin so that it may be removed in the subsequent caustic extraction stage. In contrast, the D<sub>1</sub> and D<sub>2</sub> stages are primarily used to brighten the pulp. The PAPTAC Canadian survey reports 30% of conventional fiber lines and 80% of O<sub>2</sub>-delignified fiber lines operate with acid in the D<sub>0</sub> stage.

## METHOD

We simulated the ClO<sub>2</sub> stages at a series of North American mills via laboratory bleaching. First, pulp samples were collected at the various mills from the decker, E stage washer, or D<sub>1</sub> stage washer. Those samples were then bleached in a constant temperature water bath in the laboratory. For each stage simulated, the ClO<sub>2</sub> charge and the final pH were varied. For the D<sub>0</sub> stage simulation, the pulp was carried through a subsequent EP or EOP stage to fully evaluate the delignification across the front end of the bleach plant. Bleaching conditions are described in **Table I**.

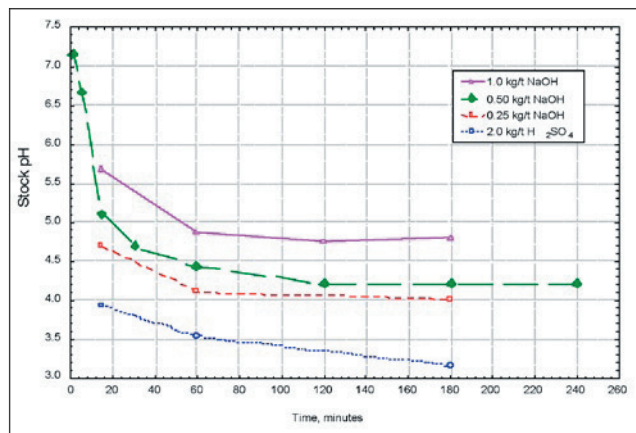
## CONTROL OF D STAGE pH

### Effect of time

As seen in the reaction pathways discussed above, many of

Furnish ID	Species	Stage	Initial Kappa	Initial Brightness % ISO	Time min	Temperature °F	ClO <sub>2</sub> lb/ton	pH Range
1	Hardwood	D <sub>0</sub>	13	---	20	135	18, 34	2.3 - 6.6
2	Hardwood	D <sub>0</sub>	17	---	45	127	24, 31	2.4 - 9.3
3	Softwood	D <sub>0</sub>	19	---	45	127	31, 43	2.3 - 7.7
7	Softwood	D <sub>0</sub>	27	---	20	140	38, 50	2.2 - 6.0
8	Hardwood	D <sub>0</sub>	16	---	45	140	23 - 42	2.1 - 7.8
1	Hardwood	D <sub>1</sub>	3.1	79	210	165	4 - 8	2.8 - 10.7
2	Hardwood	D <sub>1</sub>	4.8	65	140	170	7 - 24	2.3 - 8.5
4	Hardwood	D <sub>1</sub>	4.8	59	120	170	7 - 28	3.0 - 10.0
6	Hardwood	D <sub>1</sub>	2.5	76	180	170	8 - 20	2.2 - 6.5
3	Softwood	D <sub>1</sub>	4.1	62	180	160	6 - 36	2.2 - 10.2
5	Softwood	D <sub>1</sub>	4.0	52	120	157	10 - 35	1.9 - 10
7	Softwood	D <sub>1</sub>	2.6	69	240	165	9 - 27	2.0 - 9.9
2	Hardwood	D <sub>2</sub>	1.1	80	300	175	4 - 16	1.7 - 11.5
6	Hardwood	D <sub>2</sub>	1.4	86	180	170	2 - 6	2.9 - 5.8
3	Softwood	D <sub>2</sub>	1.6	83	310	180	6 - 12	2.2 - 9.7

**I. Bleaching conditions for the D<sub>0</sub>, D<sub>1</sub>, and D<sub>2</sub> stages.**



1. pH of chlorine dioxide treated stock over the course of the reaction (hardwood  $D_1$  stage, 20 lb/ton  $ClO_2$ , 155°F).

the dominant  $ClO_2$  reactions with lignin produce substantial amounts of acid products. As these reactions proceed, the stock becomes more acidic as  $ClO_2$  is converted into acidic intermediates or reaction products. **Figure 1** illustrates the effect of reaction time on the pH of the stock with different amounts of caustic or sulfuric acid added.

In most laboratory bleaching methods, the final stock pH after the full retention time is recorded. It is this final pH that most researchers refer to when recommending a pH target for bleaching. Many mills have online pH measurements in an upflow tube or immediately after the  $ClO_2$  mixer. As is evident from Fig. 1, the pH measured online at the upflow tube location will be higher than the final pH. If the instrumentation is reliable and the control loop tuned properly, it is possible to control the final stage pH by controlling the upflow tube pH. However, it must be emphasized that the pH target to establish is the final pH with upflow pH control simply being a means to that end.

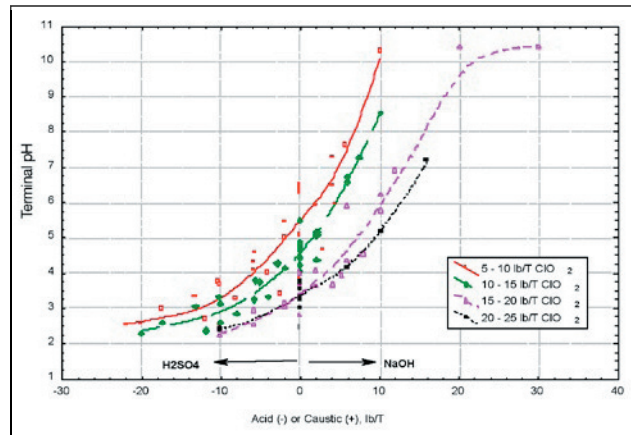
As shown in Fig. 1, even with an initial charge of caustic or acid, the pH of the reaction mixture rapidly drops and after the first 60 min the reaction pH tends to be relatively stable. Thus, for bleaching stages that routinely last several hours, most of the reaction proceeds at nearly constant pH. Even after only 40 min of reaction time, only relatively small variations in pH occur.

#### Controlling stage pH with caustic or acid

The relationship of caustic, acid and  $ClO_2$  dosages to the final pH is plotted in **Fig. 2** for a typical hardwood  $D_1$  stage. However, the curves shown in Fig. 2 are typical of other furnishes as well. High charges of  $ClO_2$  lead to a pH lower than typical optimum conditions for the D stages engaged in brightening. Therefore, caustic addition at the beginning of the stage is required to control the final pH to the desired target for many  $D_1$  and  $D_2$  stages. For the  $D_0$  stage, acid addition may be required at the beginning of the stage to obtain the desired final pH target.

#### Contribution of $ClO_2$ charge

Both  $ClO_2$  solution acidity and the acidic reaction products of



2. Effect of acid or caustic on  $D_1$  stage pH (hardwood furnishes).

$ClO_2$  bleaching lead to acidic final stock pH at normal  $ClO_2$  charges. The pH with no acid or caustic added is referred to as the natural pH of the bleaching stage. The natural pH is plotted against  $ClO_2$  charge in **Fig. 3**. Of the furnishes examined in this study, the hardwood furnishes show slightly higher final pH at the same  $ClO_2$  charges compared to the softwood furnishes. This trend is exhibited in  $D_0$ ,  $D_1$ , and  $D_2$  stages and indicates that different types of lignin may lead to different reactions with  $ClO_2$ . As noted in the introduction, nonphenolic lignin structures tended to result in chlorite ion formation and slightly higher pH values.

### OPTIMUM pH FOR $D_0$ (EOP) DELIGNIFICATION

#### Optimum pH for delignification

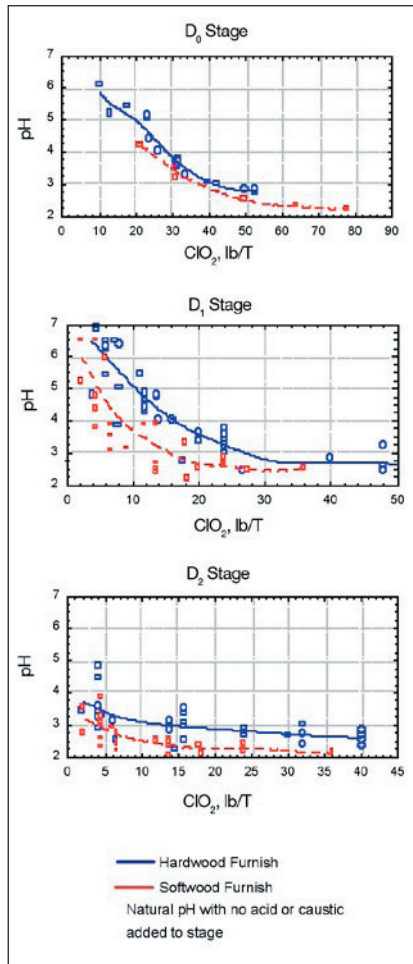
When determining the optimum operating conditions for the  $D_0$  stage, it is important to compare the results after the completion of the following extraction stage. Much of the delignification work accomplished in the  $D_0$  stage is not realized until the alkali soluble lignin fragments are removed. Therefore, an evaluation of the effect of final pH in the  $D_0$  stage requires that each  $D_0$  stage condition be followed by some form of caustic extraction stage.

Many researchers report that efficient delignification in a  $D_0$  stage is achieved at a final pH between 3 and 4 [9-11] while other work recommends a pH as low as 2 [9,12]. Some work suggests that for delignification, a pH of around 3 would be sufficient, but it is desirable to operate at lower pH to mitigate the effect of nonprocess elements on subsequent bleaching stages [13,14]. It is clear from the literature that the optimum pH is dependent on the furnish and the operating strategies of the  $D_0$  stage.

Examination of four separate furnishes indicates that an optimum pH does exist for maximum delignification measured through the EOP stage. At a pH of about 3, minimum lignin levels are obtained for most of the furnishes studied. **Figure 4** shows the effect of  $D_0$  stage final pH on kappa.

For delignification there does not appear to be any benefit to pushing the final pH lower than 3. The optimum pH

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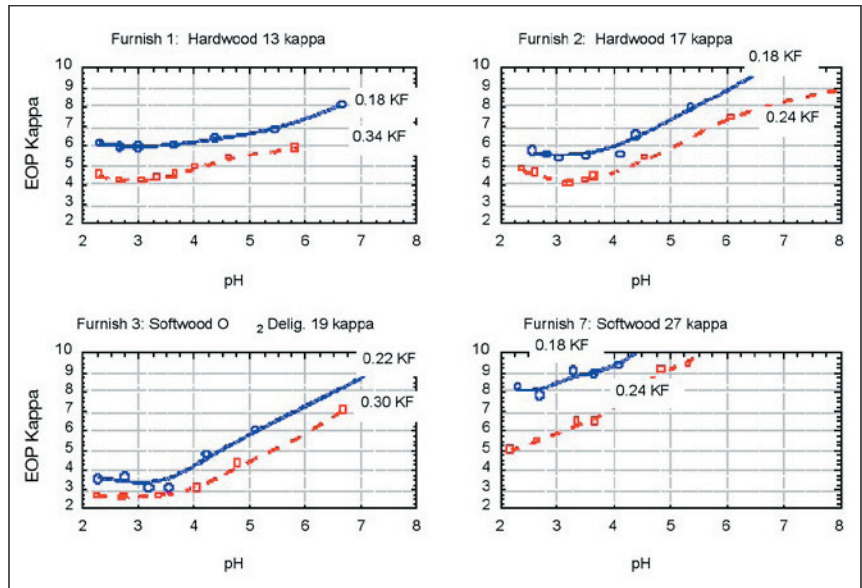


### 3. Impact of stock furnish on the natural pH of chlorine dioxide stages.

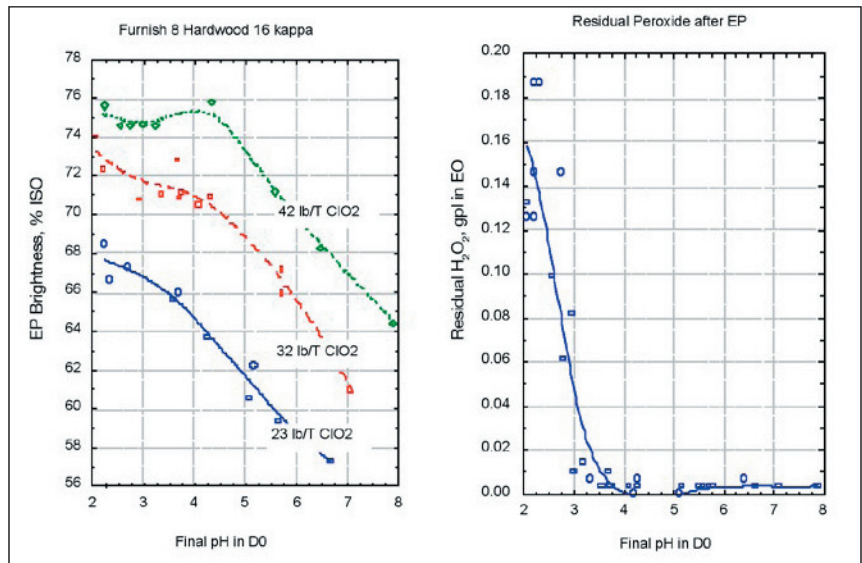
for the two hardwood furnishes is between 2.8 and 3.5. Small but significant decreases in delignification efficiency were observed when the final pH was below 2.5. The softwood furnishes operated most efficiently across a wider pH range of 2.0 to 3.8.

#### Subsequent peroxide stages

In some cases, the optimal pH for D<sub>0</sub> stage operation may depend on factors other than ClO<sub>2</sub> chemistry. The final pH of the D<sub>0</sub> stage can have a significant effect on the amount of nonprocess elements that carry forward into subsequent bleaching stages [13,14, 17,18]. A lower than optimal pH for delignification in the D<sub>0</sub> stage can provide an environment in which some metal ions stay in solution and are therefore more likely to be removed by washing in the D<sub>0</sub> stage washer. Careful observa-



### 4. Effect of D<sub>0</sub> pH on EOP kappa and D<sub>0</sub> residual.



### 5. Effect of D<sub>0</sub> pH on EP brightness and EP peroxide residual.

tion of the bleaching response of a hardwood furnish indicates that a slight positive effect on D<sub>0</sub> (EP) brightness occurs as the pH is pushed below 3.0.

By observing the peroxide residual of the EP stage and brightness response shown in **Fig. 5** in the EP stage, we find the residual peroxide increases dramatically at a D<sub>0</sub> stage pH below 3. The most probable explanation for this behavior is an improved removal of transition metals at the lower D<sub>0</sub> final pH. At a D<sub>0</sub> final pH less than 3, metals are maintained in solution and removed at the washer between the D<sub>0</sub> and EP stage,

which in turn decreases the amount of transition metals available in the EP stage to decompose the peroxide in the EP stage.

#### Scale formation

Another variable to consider when selecting the optimum D<sub>0</sub> pH is scale formation in the D<sub>0</sub> and EOP stages. While troubleshooting scale formation can be quite complex, we can make two statements about the contribution of acid:

1. Sulfate contained in sulfuric acid can contribute to barium sulfate scale, provided there is barium in

the stock [15].

- Acid conditions below 2.5 pH in the D<sub>0</sub> stage can assist in removing metals sorbed to the stock (with calcium being the most relevant), provided there is adequate purge of D<sub>0</sub> filtrate [16].

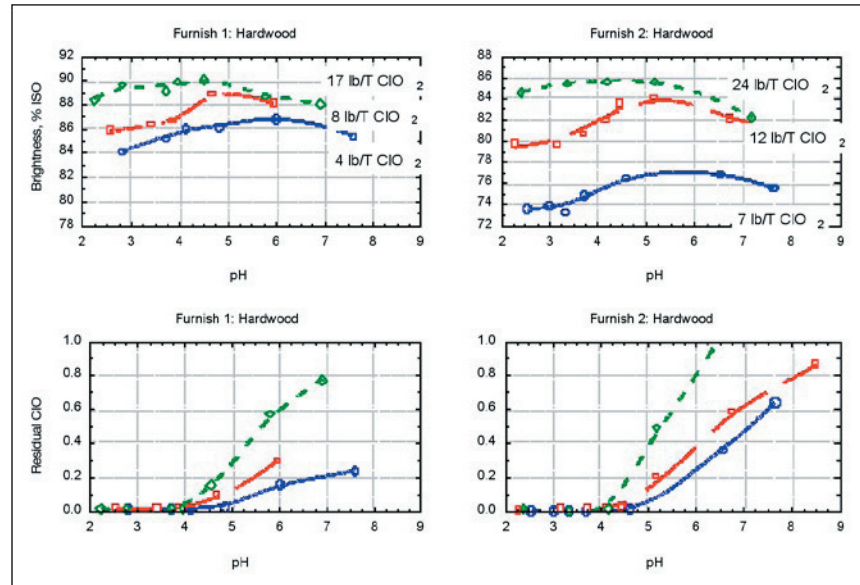
These two statements lead to the following recommendations:

- To eliminate barium sulfate scale, operate the D<sub>0</sub> stage toward the high side of the optimal delignification range (3.5 for the three furnishes examined).
- To eliminate calcium-based scales (oxalate and carbonate), operate at a pH below 2.5.

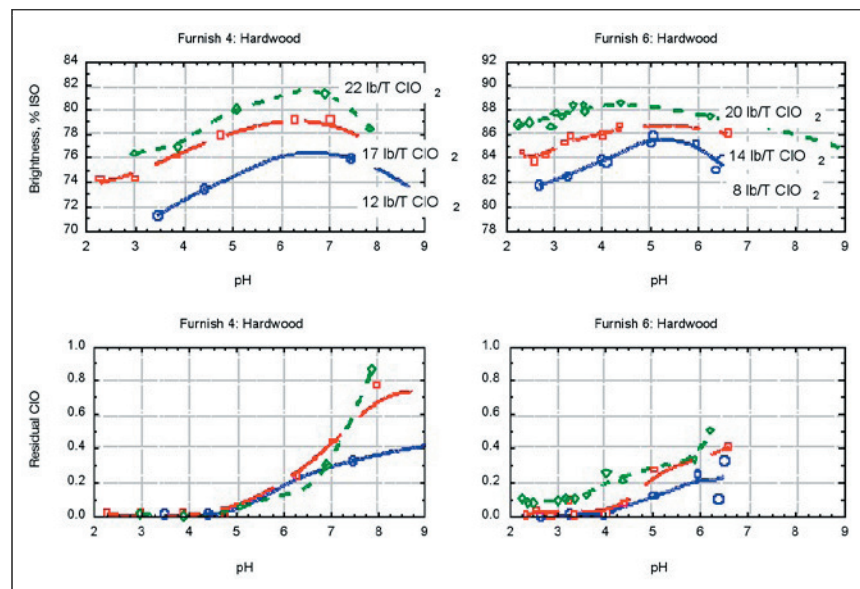
These two solutions tend to preclude each other and using the low pH solution to eliminate oxalate or carbonate scale may lead to the formation of barium scale. In practice, operating the D<sub>0</sub> stage at a final pH range of 2.5–2.8 is typically sufficient to balance the removal of calcium ions with a small enough increase in sulfate ions to avoid the formation of both calcium and barium scale [13,14,17]. Recently, successful advances have been made in predicting operating conditions that strongly favor scale formation and determining changes in operating conditions to avoid scale formation. These advances have been reported elsewhere [18,19].

## OPTIMUM pH FOR BRIGHTENING IN D1 AND D2 STAGES

It is well documented in other studies and supported by the data shown in **Figs. 6-9** that while the optimum pH for D<sub>0</sub> delignification is typically below 3.5 (see Fig. 4), the optimum pH for the D<sub>1</sub> and D<sub>2</sub> stages is higher [3,10,20-22]. This is not surprising because the objective of the D<sub>1</sub> and D<sub>2</sub> stages is to brighten the pulp, while the objective of the D<sub>0</sub> stage is delignification. It is desirable for the ClO<sub>2</sub> reactions to follow different pathways to obtain these very different outcomes. Chlorine dioxide bleaching is highly dependent upon pH to determine which set of reaction pathways



6. Effect of pH on D<sub>1</sub> stage brightness and residual for hardwood furnishes 1 and 2.



7. Effect of pH on D<sub>1</sub> stage brightness and residual for hardwood furnishes 4 and 6.

are followed in a given reaction. As a result, the typical optimal pH for the D<sub>1</sub> and D<sub>2</sub> stages is higher than for the D<sub>0</sub> stage.

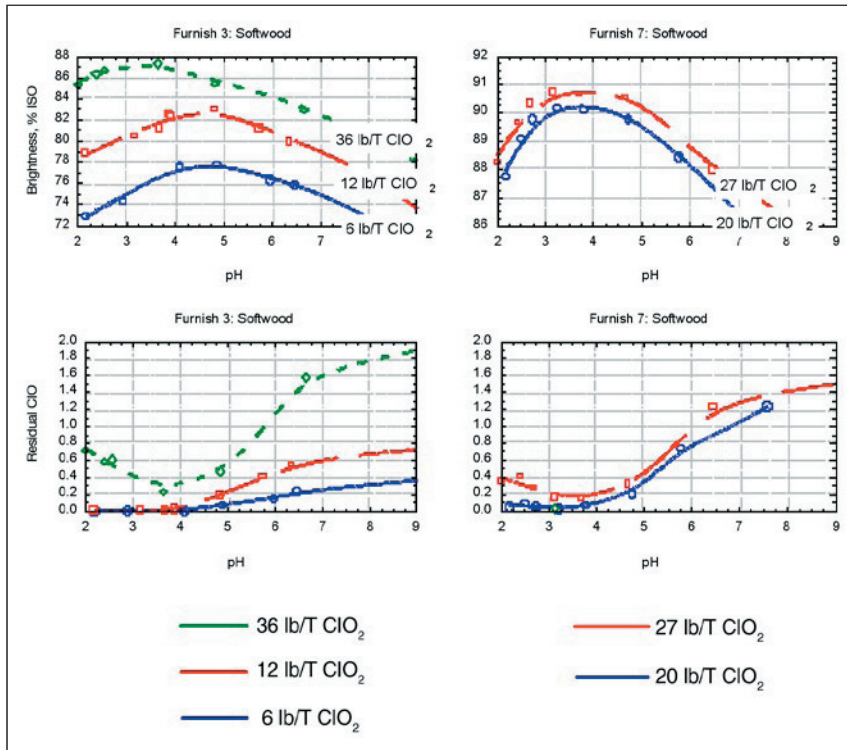
In all cases studied, the optimum pH occurred in the presence of some amount of measured ClO<sub>2</sub> residual and at a final pH between 3.5 and 5.5. It has been well documented [8] that the amount of chlorite residual starts to increase rapidly above a final pH of around 3.5 and the chlorate plus chlorite residual concentration is at a minimum at a pH of about 3.8. The standard

ClO<sub>2</sub> residual test actually measures both chlorite and ClO<sub>2</sub>. The potassium iodide reagent reduces both ClO<sub>2</sub> and chlorite under the acid conditions of the test. For this reason, it is reasonable to assume that the maximum brightness occurs in a pH range that leaves some small amount of chlorite residual in the final stock.

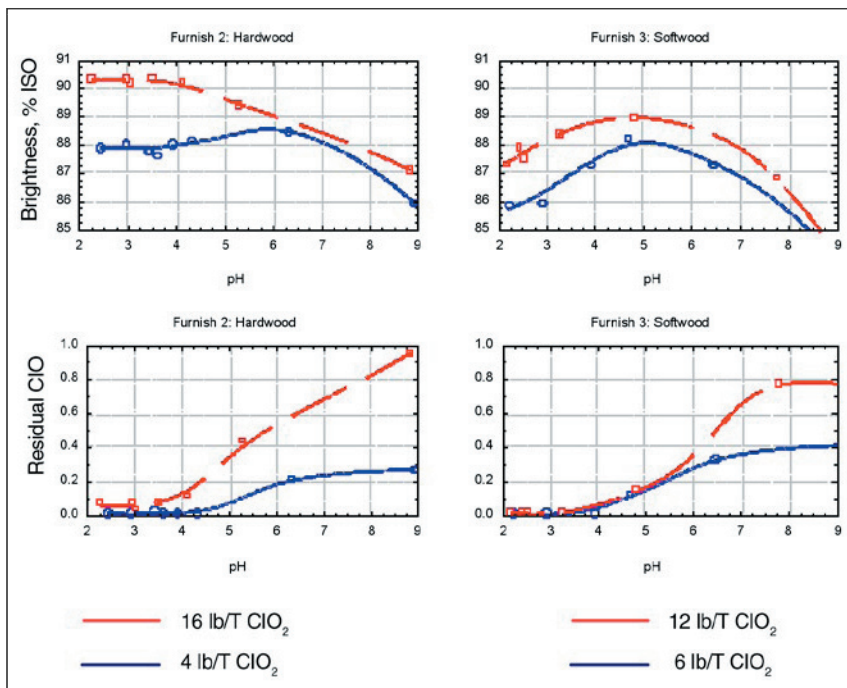
### Hardwood furnishes in the D<sub>1</sub> stage

The first observation we can make from a review of the hardwood D<sub>1</sub> stag-

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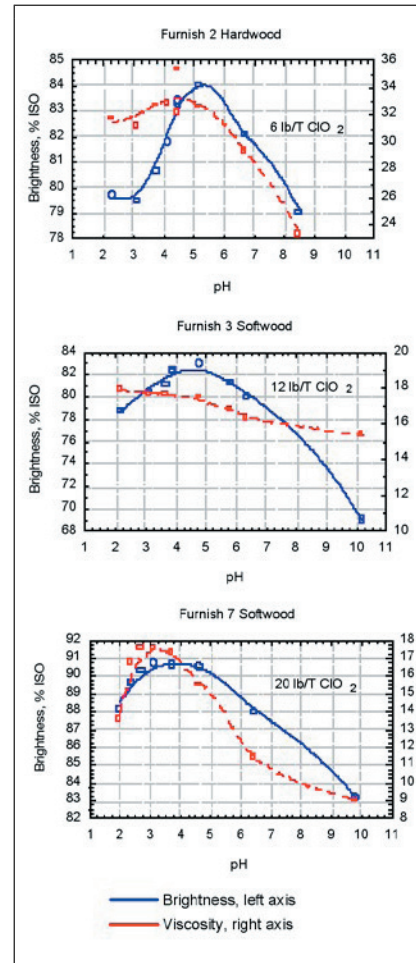
8. Effect of pH on  $D_1$  stage brightness and residual for softwood furnishes.



9. Effect of pH on brightness and residual in  $D_2$  stages.

es (Figs. 6 and 7) is that the optimum pH for brightening can vary from mill to mill and by  $\text{ClO}_2$  charge within the same mill. Determined graphically, the optimal pH appears to vary from 4 to as high as 6. For a specific curve, the pH

range over which the maximum brightness is achieved (to within 0.25% ISO) appears to be about 0.5 pH units higher or lower than the exact optimal pH. Some curves seem to have a broader maximum brightness range than oth-



10. Effect of pH on viscosity.

ers and this tends to be the higher dosage curves. The high dosage curves also exhibit a lower optimum pH than the low dosage curves. From these observations we can conclude that the higher the  $\text{ClO}_2$  dosage, the lower the optimum pH and the more forgiving the brightness penalty for not operating at that optimal pH.

Another important observation is the effect of pH on the measured residual present in the final pulp. Note in Figs. 6 and 7 that the optimal pH in every case occurs at a point at which measurable residual is present. In all of the hardwood cases, the maximum brightness was obtained at a point with about 0.1–0.2 g/L residual, as measured by the laboratory test described above. In every furnish except furnish 6, a pulp bleached at a pH below 4 contained no residual. This suggests that less efficient reaction pathways oc-

curred at pH below 4 and that the more efficient reaction pathways were those that lead to some minimum of chlorite residual.

In most cases, the specific mill would benefit from the addition of caustic to raise the pH from its natural level. However, for a few curves (most notably all the furnish 4 curves), either the natural pH falls within the optimal range or acid might be warranted to lower the pH. A probable explanation for the unusually high natural pH of the furnish 4 curves is poor washing from the previous stage. The quality of washing in the preceding caustic extraction stage is an important contributor to the amount of caustic or acid required to obtain the optimal pH for brightening in the D<sub>1</sub> stage.

### *Softwood furnishes in the D<sub>1</sub> stage*

The D<sub>1</sub> stage softwood furnishes (Fig. 8) exhibit a trend similar to the hardwood furnishes. A broad optimum pH range exists that is slightly higher than the optimum pH for the D<sub>0</sub> stage. High ClO<sub>2</sub> charges have a lower optimal pH than smaller charges of ClO<sub>2</sub> and just as with the hardwood, bleaching at the optimal pH leads to a small measured residual in all cases. For the high dosage, a condition under which active residual is possible regardless of pH, the residual is moderately high at low pH. As the pH increases, the residual curve goes through a minimum before increasing again, due mainly to measured chlorite, as discussed previously. For these curves, the optimal pH for brightening occurs at this minimum residual point. For lower ClO<sub>2</sub> dosages, no measured ClO<sub>2</sub> residual, or only trace amounts, is present at the lower pH operation. As the pH increases, so does the amount of measured residual. Maximum brightness tends to occur at the pH that supplies a measured ClO<sub>2</sub> residual of about 0.1–0.2 g/L. As with hardwood, most of the optimum pH bleaching conditions require some amount of caustic addition.

The most notable difference between the hardwood D<sub>1</sub> curves and the

softwood D<sub>1</sub> curves is the lower range of observed optimum pH between 3 and 5. Again, this result is expected because higher ClO<sub>2</sub> charges are used in softwood brightening than in hardwood brightening and the softwood lignin generally contains more phenolic end groups. Thus, for softwood, more HCl is generated in the bleaching reactions resulting in a lower final pH.

### *D<sub>2</sub> stages*

Second D stages were simulated for one hardwood furnish and one softwood furnish. Multiple chemical charges were examined for the D<sub>2</sub> stage. The brightness and measured residual are plotted in Fig. 9. The D<sub>2</sub> stage brightness typically exhibits a flatter relationship against pH than the D<sub>1</sub> stage. Brightness gains of 1% to 2% are possible, however, by adjusting from the natural pH of 3 to the optimal pH of 4.5 or higher (note furnish 3). As in the D<sub>1</sub> stages, we observed an optimal brightness at measured residual concentrations in the 0.1–0.2 g/L range. The optimum pH to obtain these residuals tends to be higher than for the D<sub>1</sub> cases. In all cases studied, the addition of caustic would be required to obtain the desired optimum pH range.

### **OPTIMUM pH TO PRESERVE PULP STRENGTH**

The optimum pH for preservation of pulp viscosity tends to match the optimal pH for brightening, as observed from the selected curves in **Fig. 10**. The significant drops in pulp viscosity that occur at high pH confirm that more vigorous nonselective reactions occur at neutral and slightly alkaline pH. On the acid side, hypochlorous acid may be participating in more nonselective reactions. The degrees to which these reactions occur and to what degree pulp viscosity is affected vary widely from furnish to furnish. That the optimal set of reactions for pulp brightening typically coincide with the optimal set of reactions for viscosity preservation is true for high charge bleaching as in furnish 7 and milder charge bleaching as in furnish

3. In general, the reaction pathways that favor the use of ClO<sub>2</sub> in brightening reactions prevent the ClO<sub>2</sub> from degrading cellulose.

### **NON-OPTIMAL pH OPERATION DUE TO SHIVES**

Sometimes mills are forced to operate the D<sub>1</sub> and D<sub>2</sub> stages at a pH that is lower than optimum. If a mill is experiencing significant difficulties with shives in the final bleached product, it may be advisable to lower the pH of the D<sub>1</sub> stage. As the pH of the D<sub>1</sub> stage rises above 4.0, the tendency for shive removal decreases sharply [23]. Drawbacks with lowering the pH of the D<sub>1</sub> stage to control shives include a decrease in pulp strength and an increase in bleaching chemical consumption to obtain a target brightness. Other methods of enhancing shive reduction are to decrease the temperature of the D<sub>1</sub> stage [24] and to increase the concentration of ClO<sub>2</sub> in the D<sub>1</sub> stage [25]. Generally, the use of temperature to control shive reduction is the first line of defense in mill operations.

### **MILL RESULTS**

Trials conducted at three different commercial kraft mills confirm the benefits of controlling the pH in the D<sub>1</sub> stage. In each trial, the mill began with no caustic addition for pH control. The pH in the vat simply varied with D<sub>1</sub> chlorine dioxide charge and prior stage washing efficiency. During the trials, caustic was added before the medium consistency (MC) pump standpipe to raise and control the D<sub>1</sub> washer vat pH. In each case, either the D<sub>1</sub> washer vat residual or the Kajaani Cormec chlorite residual increased during the pH control period, confirming the importance of the intermediate reactions in ClO<sub>2</sub> chemistry.

In all three trials, higher D<sub>1</sub> brightness was achieved with the same or lower total charge of ClO<sub>2</sub> throughout the sequence. **Table II** shows the mill results. Each trial represents at least a month of operating data split evenly between the baseline and trial periods.



# BLEACHING

Mill		No pH Control	With pH Control
HWD Mill #1 D(EP)D 1400 h of data	D <sub>1</sub> Vat pH	3.2 (+/- 0.1)	4.0 (+/-0.1)
	Total ClO <sub>2</sub> , lb/ton	61.1 (+/-1.2)	60.5 (+/-1.4)
	Final Brightness, % ISO	90.5 (+/-0.1)	91.0 (+/-0.1)
SWD Mill #7 D(EP)D 700 h of data	D <sub>1</sub> Vat pH	3.1 (+/-0.1)	3.7 (+/-0.1)
	Total ClO <sub>2</sub> , lb/ton	77.8 (+/-1.6)	71.8 (+/-1.0)
	Final Brightness, % ISO	88.6 (+/-0.1)	89.8 (+/-0.1)
HWD Mill #8 D(EOP)D 4000 h of data	D <sub>1</sub> Vat pH	2.1 (+/-0.1)	2.8 (+/-0.1)
	Total ClO <sub>2</sub> , lb/ton	43.7 (+/-1.5)	43.5 (+/-1.9)
	Final Brightness, % ISO	87.8 (+/-0.1)	88.3 (+/-0.1)

**II. Effects of controlling D<sub>1</sub> stage pH on final stage pH, final brightness, and total ClO<sub>2</sub> application – three mill trials (parentheses indicate the 95% confidence interval of the mean, approximately twice the standard error of the mean).**

Evaluations via t-test statistics (at 95% confidence) indicate that the improvement in final brightness for each trial was statistically significant. Only the trial at mill #7 clearly indicated a significant decrease in ClO<sub>2</sub>. A mill gaining extra brightness can choose to reduce the ClO<sub>2</sub> charge in D<sub>1</sub> or throughout the sequence to take advantage of the improved efficiency of the D<sub>1</sub> stage.

## CONCLUSIONS

The final pH of a ClO<sub>2</sub> bleaching stage significantly affects the performance of that stage. We found that D<sub>0</sub>, D<sub>1</sub>, and D<sub>2</sub> stages exhibit optimum pH ranges and that the optimum range varies depending on furnish, stage, and ClO<sub>2</sub> dosage. For most cases studied, acid or caustic was required to adjust the final pH to the optimum pH range.

The desired results from ClO<sub>2</sub> bleaching stages are different depending upon the location of the stage in the bleaching sequence. In the D<sub>0</sub> stage, where delignification is the primary goal, an optimum final pH of 2.8–3.5 was determined to provide the best performance. Lower final pH of less than 2.5 in the D<sub>0</sub> stage resulted in a slight loss in delignification efficiency, but may result in a substantial removal of nonprocess metals. This improved metals removal may either reduce scale formation or reduce subsequent EP stage

peroxide decomposition.

The last two ClO<sub>2</sub> bleaching stages are mainly used to brighten the pulp, not to delignify it. As such, they both require a higher final pH to maximize pulp brightness. The optimum pH appears to be dependent on furnish and ClO<sub>2</sub> dosage. Hardwood D stages exhibited a higher optimum pH than softwood D stages. At lower ClO<sub>2</sub> dosages, for all furnishes, the optimum pH occurs when the ClO<sub>2</sub> plus chlorite residual is in the 0.1–0.2 g/L concentration in the final reaction mixture. As the charge of ClO<sub>2</sub> increases, this optimum pH occurs at lower pH values. For softwood D<sub>1</sub> stages using high charges of ClO<sub>2</sub>, the laboratory-measured residual goes through a minimum value (typically higher than the 0.1–0.2 g/L residual mentioned above). Maximum brightness occurs at the final pH that corresponds with this minimum residual concentration. For D<sub>1</sub> stage ClO<sub>2</sub> bleaching, this minimum typically occurs at a final pH between 3.5 and 5.5.

The optimum pH for the D<sub>2</sub> stage brightening exhibits a similar response as the D<sub>1</sub> stage. However, the brightness response is slightly less pH dependent than that of the D<sub>1</sub> stage, making for a more forgiving bleaching stage. As with the D<sub>1</sub> stage, the optimum pH tends to occur when small concentrations of residual (about 0.1–0.2 g/L) are

present in the final stock. As with the D<sub>1</sub> stage, caustic addition is typically required to obtain an optimal final pH for the D<sub>2</sub> bleaching stage.

We evaluated mill trials during which caustic was added to the standpipe of the MC pump going into the D<sub>1</sub> stage. In all cases, controlling the final pH of the D<sub>1</sub> stage to near optimum conditions has resulted in increased final pulp brightness with less ClO<sub>2</sub> addition. The amount of caustic added and the total benefit obtained tend to vary from location to location and from fiber line to fiber line within a given mill. Thus, laboratory bleaching similar to that performed in the current work needs to be performed to determine the optimum final pH for each mill stage being studied. If the mill is operating outside of optimum final pH conditions, control of the pH may produce significant cost savings and improved bleach plant operation. **TJ**

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## INSIGHTS FROM THE AUTHORS

Lowering cost and improving pulp quality are major concerns of pulp mill managers. Bleaching costs are highly visible and often offer an easy area to make improvements. Much of this research began in the early 1990s when mills were converting to elemental chlorine free (ECF) bleaching. Higher bleaching costs compared to chlorine bleaching made optimization more attractive to mills. In many cases, we knew the mill operated outside a textbook recommendation for pH. The work began as an exploration of the response for specific mill pulps to chlorine dioxide (ClO<sub>2</sub>).

This research compliments the very thorough understanding of ClO<sub>2</sub> bleaching that has developed over the past few decades. This understanding of bleaching chemistry is verified by our experiments over a wide variety of mill pulps. Most previous research has focused on understanding the fundamentals of bleaching a particular pulp. The result of our research is to answer how efficiency is maximized for a wide variety of mill pulps. We noted the similarities and differences across this range of pulps.

Before this research we were unaware of the extent to which the true optimum pH for ClO<sub>2</sub> bleaching would vary with pulp composition and ClO<sub>2</sub> dosage. We had some sense that the optimum pH varied by mill, but

were surprised to find that some pulps might operate best at a pH as high as 5, while other mills might find a pH as low as 3 to be best.

If mills want to optimize ClO<sub>2</sub> bleaching, they need to understand the best conditions for their specific pulp and bleaching parameters. They also need to evaluate the specific bleaching stage at a variety of ClO<sub>2</sub> dosages.

We found that the optimal pH tends to fall at the point at which a slight chlorite residual is measured. The next step in this research is to completely characterize the chlorine containing byproducts (chlorite, chlorate and chloride) and compare these relationships across a few specific mill pulps.

*Hart is with MeadWestvaco, Raleigh, North Carolina, and Connell is with Eka Chemicals, Marietta, Georgia. Email Hart at pwh3@meadwestvaco.com.*



**Hart**



**Connell**

