

# Enhancing the pulp quality by optimization of pH of Chlorine Dioxide solution at the D-stage of bleaching process



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**Abstract:** The focus of the study is to enhance the pulp quality by optimizing the pH of the Chlorine Dioxide solution at the D-stage in the bleaching process. The bleaching sequence adopted in this study is C<sub>1</sub>E<sub>p</sub>H<sub>1</sub>D. The D-stage of the sequence has been studied in particular. Chlorine dioxide (ClO<sub>2</sub>) oxidizes lignin compounds via number of reaction pathways. Several of these pathways regenerate ClO<sub>2</sub>, thus enhancing the efficiency of ClO<sub>2</sub> bleaching. The ideal pH of the D-stage reaction tower to be maintained 3.5-4.5. To achieve the aim of study, two phases have been adopted. In the initial phase sulphuric acid along with ClO<sub>2</sub> solution, is added to the inlet of D-stage to lower the pH from Hypo stage (pH=10) to the ideal pH. In the final stage, the pH of the ClO<sub>2</sub> solution pulp was reduced from 3.7 to 1.7 by use of spent liquor before dosing to D-stage inlet while the dosing of sulphuric acid was entirely ceased. The ClO<sub>2</sub> consumption was recorded for both the phases and pulp brightness and viscosity was analysed. It was observed that by use of spent liquor the consumption of ClO<sub>2</sub> solution was found to lower by 9.45% as compared to the dosing of sulphuric acid. While the pulp attributes such as brightness was found to be maintained at 88.3°PV, viscosity of pulp enhanced by 5.26%.

**Key words:** Sulphuric acid, spent liquor, Chlorine Dioxide, Bleaching, Viscosity

## Introduction

Bleaching of wood pulp is the chemical processing of wood pulp to lighten its colour and brighten the pulp. The primary product of pulp is paper, for which brightness and whiteness are important characteristics.

Chemical pulp bleaching is accomplished with various compounds containing chlorine or chlorine dioxide and alkali extractions in several stages. As lignin is a complex molecule with different types of linkages, the use of different chemicals will break various types of bonds. For example, a large increase in brightness is achieved by using relatively small amounts of ClO<sub>2</sub> in a later stage that could only be achieved using massive amounts of additional Chlorine (Cl<sub>2</sub>) in stage 1; use of large amounts of chlorine in stage 1 would also cause much carbohydrate degradation. Bleached chemical pulps are insensitive to color reversion, but high temperatures may induce some color reversion. Lignin removal is accompanied by significant losses of pulp yield and strength of the individual fibers. Bleaching of chemical pulps involves the use of chemicals which are more specific to lignin removal than to carbohydrate degradation compared with the chemicals used in pulping. Each stage consists of a pump to mix the chemical with the pulp, a retention tower to provide time for the bleaching chemical to react with the pulp and a washer to remove the bleaching chemicals and solubilized pulp components. (Bajpayee P, 2018)

In Orient Paper and Industries Ltd (OPIL), the initial brightness of unbleached pulp is 24°PV and bleached in the sequence of CD-Ep-H-D in four stages. The final pulp brightness is maintained around 88±1°PV. The bleached pulp is stored in Bleached High Density Tower.

Present Bleaching sequence is CD-Ep-H-D with conventional drums.

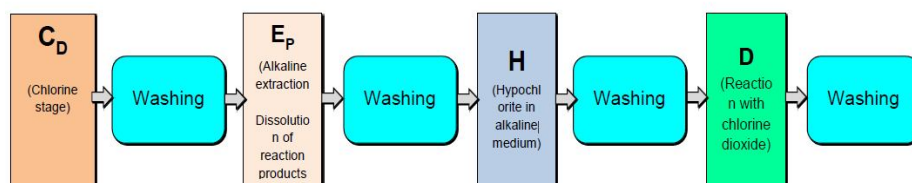


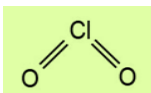
Figure 01: Bleaching section of OPIL

## Enhancing the pulp quality by optimization of pH of Chlorine Dioxide solution at the D-stage of bleaching process

The aim of this study is to understand the role of pH in Chlorine dioxide stage of the bleaching process, impact on pulp quality and further optimize the pH to improve the pulp quality.

### Characteristics of Chlorine Dioxide as bleaching agent:

- Chlorine dioxide is an oxidizing agent for pulp bleaching.
- It is a yellowish-green gas, pungent odour and stable upto 11°C.
- It is highly soluble in water, particularly in chilled water.



### Effect of sulphuric acid pre-treatment in D-stage bleaching:

The sulphuric acid pre-treatment conditions, while conducive to the removal of lignin, also initiate acid hydrolysis of cellulose, resulting in yield and viscosity losses of pulp. If the purpose of pre-acidification is to activate the lignocellulosic structures to enhance the delignification of pulp, then the acid used is critical since it would have an impact not only on the delignification of pulps but also on cellulose degradation and its removal. (Ikeda et.al; 1999)

### Impact of pH on Pulp quality:

- In a study conducted by Hart P. it has been found that there is a significant drop in pulp viscosity when  $\text{ClO}_2$  bleaching is conducted at high pH. This

occurrence at high pH confirms that more vigorous non-selective reactions occur at alkaline pH. Further, he added that the degrees to which these reactions occur and to what degree pulp viscosity is affected vary widely from furnish to furnish.

- Further, if there is significant difficulty with shives in the final bleached product, it may be advisable to lower the pH of the D-stage. As the pH of the D-stage rises above 4.0, the tendency for shives removal decreases sharply.
- The control of the pH may produce significant cost savings and improved bleach plant operation.

### Method and Methodology

#### Material:

In this study, the pH of the  $\text{ClO}_2$  solution added in the D-stage of bleaching process was optimised maintaining the targeted pulp brightness i.e.  $88 \pm 0.5$  °PV and viscosity  $6.5 \pm 0.5$  cps. This was achieved by ceasing the dosage of concentrated sulphuric acid at D-stage inlet and lowering the pH of  $\text{ClO}_2$  solution by addition of spent liquor (consisting of 400 gpl  $\text{H}_2\text{SO}_4$  and 12.5 gpl chlorate) to  $\text{ClO}_2$  solution.

Sr. No.	Parameters	C <sub>D</sub> E <sub>P</sub> H <sub>D</sub>			
		C <sub>D</sub> (Chlorine)	E <sub>P</sub> (Extraction)		D (ClO <sub>2</sub> stage)
1.	Bleach Chemicals	Chlorine	NaOH	H <sub>2</sub> O <sub>2</sub>	Chlorine as Hypo
2.	Strength (gpl)	5.80	>80	>60	>22
3.	Dosage (Kg/ton)	28	25	9.0	30
4.	pH	<2	>10		>8
5.	Temperature (°C)	Ambient	70-75		42-45
6.	Retention Time (mins)	45-50	60-90		180
7.	Brightness (°PV)	>50	>55		82-84

Table 01: Pulp bleaching conditions for different stages of C<sub>D</sub>E<sub>P</sub>H<sub>D</sub> sequence

### Methodology:

After Hypo stage (H) having pH of 10.5, the most favourable pH of vat pulp, for reaction to occur in D-stage reaction tower, is 3.5-4.5. To attain this pH, concentrated  $\text{H}_2\text{SO}_4$  was dosed along with  $\text{ClO}_2$  solution (having pH of 3.7 on an average) at the D-stage inlet.

The  $\text{ClO}_2$  solution pH, and consumption was recorded. Alongside the essential pulp properties such as pulp brightness and viscosity were investigated according to and recorded for analysis.

In the second phase of the experimental study, spent liquor consisting of 400 gpl  $\text{H}_2\text{SO}_4$  and 12.5 gpl chlorate was added to  $\text{ClO}_2$  solution, during chemical preparation to lower the pH of  $\text{ClO}_2$  solution from 3.7 to 1.7. This  $\text{ClO}_2$  solution of pH 1.3 was then dosed to the D-stage inlet to maintain the pH of D-stage vat pulp as 3.5-4.5. The addition of sulphuric acid at D-stage inlet was completely stopped.

Hand sheet was prepared for determination of brightness and viscosity.

### Determination of bleached pulp brightness:

The pulp brightness was measured using the standard method of TAPPI T452 om-18.

### Determination of bleached pulp viscosity:

The viscosity of the pulp was estimated by capillary viscometer method using 1.0 M cupriethylenediamine (CED) solution using the standard method of TAPPI 230 om-08.

### Results and Discussion:

The aim of the experimental study was achieved in two phases.

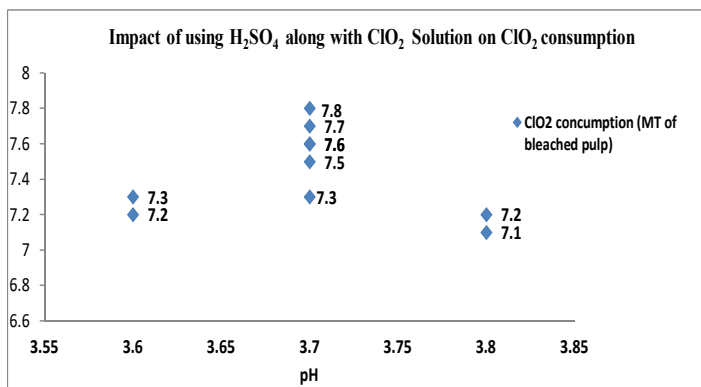
S.No	ClO <sub>2</sub> sol. consumption (Kg/MT of bleached pulp)	ClO <sub>2</sub> sol. pH	Brightness (°PV)	Viscosity(cps)
1	7.5	3.7	88.4	6.1
2	7.3	3.6	88.3	6.3
3	7.2	3.8	88.0	6.2
4	7.7	3.7	88.4	6.3
5	7.6	3.7	88.1	6.0
6	7.8	3.7	88.2	6.1
7	7.3	3.7	88.6	6.2
8	7.1	3.8	88.6	6.5
9	7.6	3.7	88.6	6.6
10	7.2	3.6	88.6	6.4
Avg	7.4	3.7	88.3	6.27

Table 02: Impact of  $\text{H}_2\text{SO}_4$  dosage at D-stage inlet along with  $\text{ClO}_2$  solution on  $\text{ClO}_2$  bleaching

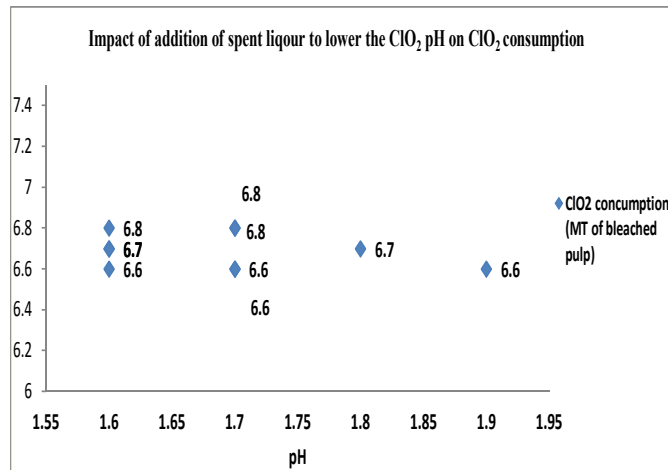
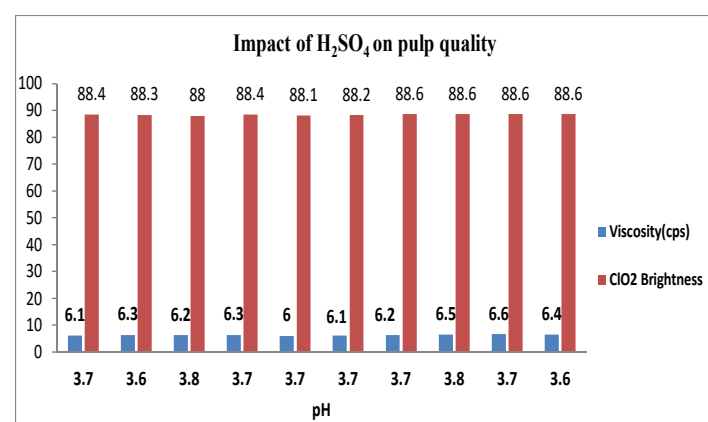
### Phase I:

In the initial phase, the sulphuric acid was dosed along with  $\text{ClO}_2$  solution at the D-stage inlet.  $\text{ClO}_2$  solution pH, consumption along with pulp parameters were investigated and analysed.

The above table records the  $\text{ClO}_2$  pH, respective consumption and essential pulp attributes such as brightness and viscosity. It has been observed that on an average pH of 3.7, 7.4 MT/ Ton of  $\text{ClO}_2$  solution was consumed maintaining the brightness to 88.3 °PV and pulp viscosity 6.27 cps.

Fig 02: Impact of using H<sub>2</sub>SO<sub>4</sub> along with ClO<sub>2</sub> solution on ClO<sub>2</sub> consumption

The ClO<sub>2</sub> consumption and impact on pulp quality with respect to use of H<sub>2</sub>SO<sub>4</sub> along with ClO<sub>2</sub> Solution at D-stage inlet has been depicted in Figure 01 and Figure 02 respectively.

Fig 04: Impact of addition of spent liquor to lower the ClO<sub>2</sub> pH on ClO<sub>2</sub> consumptionFig 03: Impact of H<sub>2</sub>SO<sub>4</sub> on pulp quality

### Phase II:

In the final phase of the study, the pH of the ClO<sub>2</sub> solution was lowered before addition to the D-stage inlet. This was done by the addition of spent liquor. The ClO<sub>2</sub> solution consumed in this phase was recorded along with ClO<sub>2</sub> solution pH, along with pulp brightness and viscosity.

S.No	ClO <sub>2</sub> sol. consumption (Kg/MT of bleached pulp)	ClO <sub>2</sub> sol. pH	Brightness (°PV)	Viscosity(cps)
1	6.7	1.6	87.9	6.1
2	6.6	1.7	88.5	6.7
3	6.8	1.6	88.4	6.7
4	6.7	1.8	88.3	7.0
5	6.6	1.6	87.9	6.3
6	6.8	1.7	88.0	6.0
7	6.6	1.7	87.9	6.2
8	6.8	1.9	88.6	7.2
9	6.8	1.7	88.4	6.5
10	6.7	1.6	88.8	6.9
Avg	6.7	1.7	88.3	6.6

Table 03: Impact of spent liquor addition along with ClO<sub>2</sub> solution

When the pH of ClO<sub>2</sub> solution was lowered by addition of spent liquor, the consumption of ClO<sub>2</sub> solution was also lowered to 6.7 (Kg /MT of bleached pulp) on an average. The brightness of pulp was maintained to targeted value (88.3°PV). While the viscosity was observed to be enhanced to 6.6 cps. This has been recorded in table no. 03 and figuratively in Figure 03.

The ClO<sub>2</sub> solution consumption while addition of sulphuric acid to the D-stage inlet was compared to the Consumption while pulp bleaching without the use of H<sub>2</sub>SO<sub>4</sub> i.e. ClO<sub>2</sub> pH lowered by addition of spent liquor was compared and analysed.

S.No	ClO <sub>2</sub> sol. consumption (Kg/MT of bleached pulp)		Viscosity (cps)	
	Phase I (With dosing of H <sub>2</sub> SO <sub>4</sub> )	Phase II (Without dosing of H <sub>2</sub> SO <sub>4</sub> )	Phase I (With dosing of H <sub>2</sub> SO <sub>4</sub> )	Phase II (Without dosing of H <sub>2</sub> SO <sub>4</sub> )
1	7.5	6.7	6.1	6.1
2	7.3	6.6	6.3	6.7
3	7.2	6.8	6.2	6.7
4	7.7	6.7	6.3	7.0
5	7.6	6.6	6.0	6.3
6	7.8	6.8	6.1	6.0
7	7.3	6.6	6.2	6.2
8	7.1	6.8	6.5	7.2
9	7.6	6.8	6.6	6.5
10	7.2	6.7	6.4	6.9
Avg	7.4	6.7	6.27	6.6

Table 4: Comparative chart representing the variation in ClO<sub>2</sub> consumption and pulp viscosity with and without dosage of H<sub>2</sub>SO<sub>4</sub>

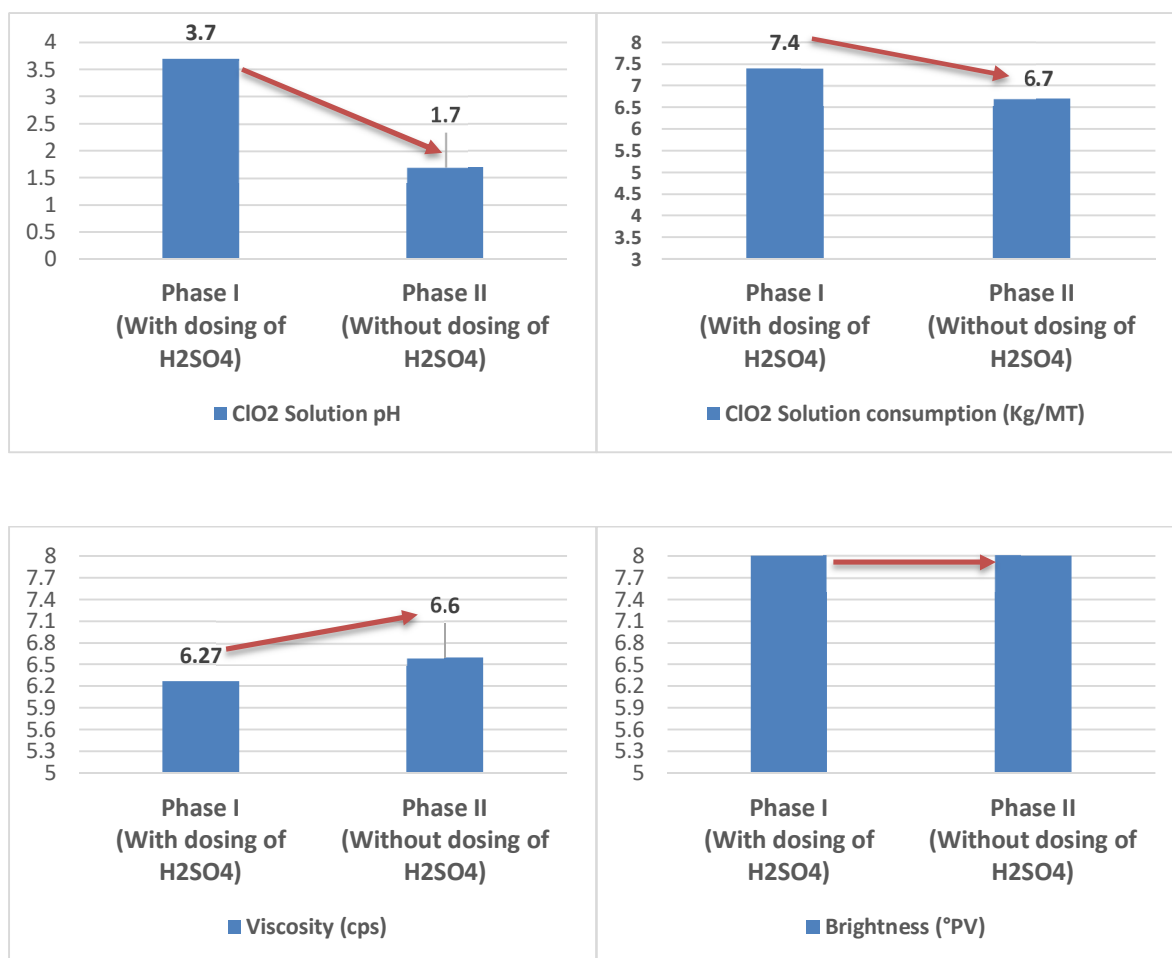
The above comparative table clearly highlights that the consumption of ClO<sub>2</sub> solution was found to be 7.4 Kg/MT of bleached pulp when H<sub>2</sub>SO<sub>4</sub> was dosed at the inlet of D-stage while it reduced to 6.7 Kg/MT of bleached pulp when the pH of ClO<sub>2</sub> was lowered with spent liquor before dosing (i.e. in the absence of H<sub>2</sub>SO<sub>4</sub>). The viscosity of pulp also enhanced from 6.1 cps to 6.6 cps when spent liquor was dosed in bleaching system eliminating the dosage H<sub>2</sub>SO<sub>4</sub>.

### Conclusion:

The pH is a significant factor for chlorine dioxide bleaching. A fraction of chlorine dioxide is converted to chlorite, chlorate or chloride. The overall reaction mechanisms are quite complex. The formation of chlorite increases with increasing of pH value whereas the formation of chlorate increases with decreasing the pH value, and the chloride ion is increased at a pH value below 3-4.

The chlorite (ClO<sub>2</sub><sup>-</sup>) exists as inert at above the pH 7. On the other hand, this compound is very active below pH 7.

**Comparative trend between Phase I and Phase II of the experimental study:**



The study conducted aiming to eliminate sulphuric acid dosage in pulp bleaching system has significant benefits. Sulphuric acid is highly viscous and corrosive chemical. The use of H<sub>2</sub>SO<sub>4</sub> in the pulp bleaching system has several cons. Owing to its high acidity and corrosive nature, it corrodes the machinery parts such as MC pump those are involved in the pulp bleaching system. Thus, reducing the life of machinery. Moreover, the spent liquor passing out with effluent from ClO<sub>2</sub> plant is reused in the process flow, thus, making the process environmentally sustainable. Use of spent liquor instead of sulphuric acid has also aided in maintaining consistent ClO<sub>2</sub> pH.

The consumption of ClO<sub>2</sub> solution was found to lower when spent liquor was used in bleaching system instead of dosing H<sub>2</sub>SO<sub>4</sub> in the D-stage inlet. It was observed that the consumption reduced by 9.45%. The reduction of ClO<sub>2</sub> consumption is due to the higher generation of chlorate at low pH added to the chlorate present in the spent liquor which enhances the efficacy of bleaching at lower dose of ClO<sub>2</sub>. The pulp brightness was found to be maintained at 88.3°PV. The viscosity of pulp which denotes the pulp strength also enhanced from 6.1 cps to 6.6 cps i.e., by 5.26 %. The enhancement in pulp strength which is denoted by the pulp viscosity is owing to the fact that due to direct dosing of H<sub>2</sub>SO<sub>4</sub>, owing to its corrosive nature, the fibres might have undergone cellulose degradation. This would further fetch multiple advantages such improvement in machine runnability, speed, productivity, and end product quality as well. Hence, it can be concluded that the use of spent liquor D-stage pulp bleaching system and elimination of sulphuric acid dosage to lower the pH can be potential methodology with multifold advantages. By adoption of this bleaching technology, one can not only improve the machinery life but also reduce chemical consumption successfully.

Presently, Hypo bleaching sequence is being used in OPIL, which will be converted into ECF bleaching very shortly, project is already under process. The new sequence of bleaching in post ECF project will be D<sub>0</sub>E<sub>p</sub>D<sub>1</sub>D<sub>2</sub>. Henceforth, ClO<sub>2</sub> solution consumption will be optimised further.

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