

## CHLORINE DIOXIDE BLEACHING OF SODA-ANTHRAQUINONE JUTE PULP TO A VERY HIGH BRIGHTNESS

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Bleaching of soda-anthraquinone jute pulp by chlorine dioxide (ClO<sub>2</sub>) was studied to reach a target brightness of above 88% for the purpose of using less bleaching chemicals. The performance of either chlorine dioxide or peroxide in the final bleaching to boost brightness was also studied. The experimental results revealed that the final brightness depended on ClO<sub>2</sub> charge in the D<sub>0</sub> and D<sub>1</sub> stages. The brightness reversion was lower when the final stage brightening was done by peroxide. The use of Mg(OH)<sub>2</sub> in the D<sub>1</sub> and D<sub>2</sub> stages improved the final brightness due to the formation of less chlorate and chlorite during the Mg(OH)<sub>2</sub>-based ClO<sub>2</sub> brightening stages. The strength properties of pulp bleached by peroxide in the final stage was slightly better than that from ClO<sub>2</sub> as the final ClO<sub>2</sub> bleaching stage.

*Keywords: Jute pulp; Chlorine dioxide bleaching; Peroxide bleaching; Magnesium hydroxide; Brightness; Brightness stability; Strength properties*

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### INTRODUCTION

In order to follow the trend to a very high brightness for wood-free paper, currently increasing amounts of optical brightening agents, OBA, are applied. However, technical limits exist for the amounts to be used. Too much OBA does not increase the brightness level (Zhang et al. 2007, 2009a; Zhang et al. 2009b). In addition, the associated cost could be prohibitive. An alternative approach would be to increase the brightness of pulp furnish by using long bleaching sequences and/or more bleaching chemicals. It is known that the OBA performance is enhanced dramatically when the pulp brightness is about 88% ISO and above. Final brightening sequences consisting of D<sub>1</sub>ED<sub>2</sub> or D<sub>1</sub>P are known to have the best response to reach a high brightness for wood-based market pulp (higher than 88% ISO) (McDonough et al. 2001).

Many studies have been undertaken on jute pulp bleaching. Li et al. (1987) bleached a jute pulp from the alkaline bisulfite process in a 2-stage hypo-process produced pulp with a final brightness of 74% ISO. A jute pulp made from the peroxyformic acid process was bleached to a brightness of maximum 82% ISO by an alkaline peroxide-based bleaching process (Jahan et al. 2007). Soda-anthraquinone (soda-AQ) jute pulp was bleached to a 85% brightness by the DE<sub>p</sub>D<sub>1</sub> sequence (Jahan et al. 2007). In the soda-additive processes, the jute pulp was bleached to a final brightness of 81–87% with a three-stage bleaching sequence (CEH) (Jahan 2001). These results may be partly related to the fact that the brownstock had a relatively high Kappa number.

Ghosh (2007) studied different ECF bleaching processes of soda-AQ jute pulps. The sequences of ODED, ODEP, and ODEpD gave brightness of about 86% ISO. The CEHH and DEpD sequences reached about 80% ISO brightness at the cost of reduced strength properties and a higher pollution load (Ghosh et al. 2006, 2007). The effects of cooking temperature, caustic soda dose, and residual alkali, on the bleached pulp brightness have been studied. The extent to which the Kappa number and viscosity of the pulp influence bleaching was also investigated (Kotte and Ghosh 2006). Reports are scarcely available in the literature on jute pulp bleaching to a brightness target of higher than 88%.

Studies have shown benefits of replacing the final  $\text{ClO}_2$  stage of a conventional ECF chemical pulp sequence with a peroxide stage (P) for the purpose of improving the final brightness (Senior et al. 1998; Van Lierop et al. 2000; Suess et al. 2000, 2004), and the brightness stability of the bleached pulp (van Lierop et al. 2000; Suess et al. 2000; McDonough et al. 2001); in addition, savings in bleaching chemical cost were reported (Suess et al. 2000, 2004; McDonough et al. 2001).

In the  $D_1$  and  $D_2$  stages of a conventional ECF sequence, sodium hydroxide is usually used to control the pH so that an optimum end pH can be obtained; the initial pH of the NaOH-based chlorine dioxide ( $\text{ClO}_2$ ) brightening stage ( $D_1$ ) can be as high as 11 to reach an end pH of 3.5 (Wattiovaara 1982; He and Ni 2009), which may cause alkaline decomposition of  $\text{ClO}_2$  to form chlorate ( $\text{ClO}_3^-$ ) and chlorite ( $\text{ClO}_2^-$ ) (Svenson et al. 2006; Ni et al. 1993; Hoige and Bader 1994), leading to the loss of oxidizing power of  $\text{ClO}_2$ . It was reported that weak alkalis, such as magnesium hydroxide, magnesium oxide, and calcium carbonate, can be used for pH control in a chlorine dioxide brightening stage (Amidon et al. 2007; He and Ni 2009; Jahan et al. 2010; Sepall 1967). It has also been shown that the  $\text{Mg}(\text{OH})_2$  or PCC-based process provided relatively stable pH in the process (He and Ni 2009), leading to improved brightening performances. The explanation for the improved chlorine dioxide performance is that less chlorate and chlorite would be formed in the  $\text{Mg}(\text{OH})_2$  or PCC-based process.

The objectives of the present study were: 1) to bleach the soda-AQ jute pulp to a brightness of higher than 88% ISO; 2) to increase the bleaching efficiency by replacing NaOH with  $\text{Mg}(\text{OH})_2$  for the pH adjustment in the  $D_1$  and  $D_2$  stages; 3) to compare the differences between bleaching sequences of  $\text{DE}_p\text{DED}$  and  $\text{DE}_p\text{DP}$ .

## EXPERIMENTAL

Soda-AQ jute pulps were made in BCSIR Laboratories, Dhaka, according to the following conditions: 16% AA; 0.1% AQ; max. temperature: 170EC; time to the max. temperature: 90 min; time at the max. temperature: 60 min. The Kappa number of the pulp was 6.1. The bleaching conditions were as follows:

- $D_0$ : The  $\text{ClO}_2$  charge was 0.42 or 0.47 or 0.52% (on oven-dried pulp). The temperature was 70°C, and the time was 60 min. The consistency was 10%, and the end pH was 2.5.
- $E_p$ : The NaOH charge was 1.5%. The temperature was 70°C, and the time was 60 min. The consistency was 10%. The  $\text{H}_2\text{O}_2$  charge was 0.25%.

- D<sub>1</sub>: The E<sub>p</sub> processed pulp was first mixed with the 0.05% of sodium hydroxide or Mg(OH)<sub>2</sub>, a thorough mixing was provided, and subsequently 0.23 or 0.38% of ClO<sub>2</sub> solution was charged. The bleaching temperature was 70°C, and the time was 120 min. The consistency was 10%.
- E<sub>2</sub>: The NaOH charge was 0.30%. The temperature was 70°C and the time was 90 min. The consistency was 10%.
- D<sub>2</sub>: The E<sub>2</sub> processed pulp was first mixed with the 0.01% of sodium hydroxide or Mg(OH)<sub>2</sub>. The ClO<sub>2</sub> charge was 0.11% and was thoroughly mixed. The conditions were 70°C, 120 min., and 10% pulp consistency.
- P: The D<sub>1</sub> processed pulp was first mixed with 0.25% of sodium hydroxide and 0.03% magnesium sulphate, subsequently 0.20% of peroxide was charged. The conditions were 70°C, 120 min., and 10% pulp consistency.

All of the bleaching experiments were carried out in plastic bags in a water bath. The pulp was washed with deionized water in a Büchner funnel after each stage. The Kappa number was determined by following TAPPI standard method T236. Pulp brightness, brightness reversion and viscosity were determined according to the TAPPI standard methods T272, T260 and T230, respectively.

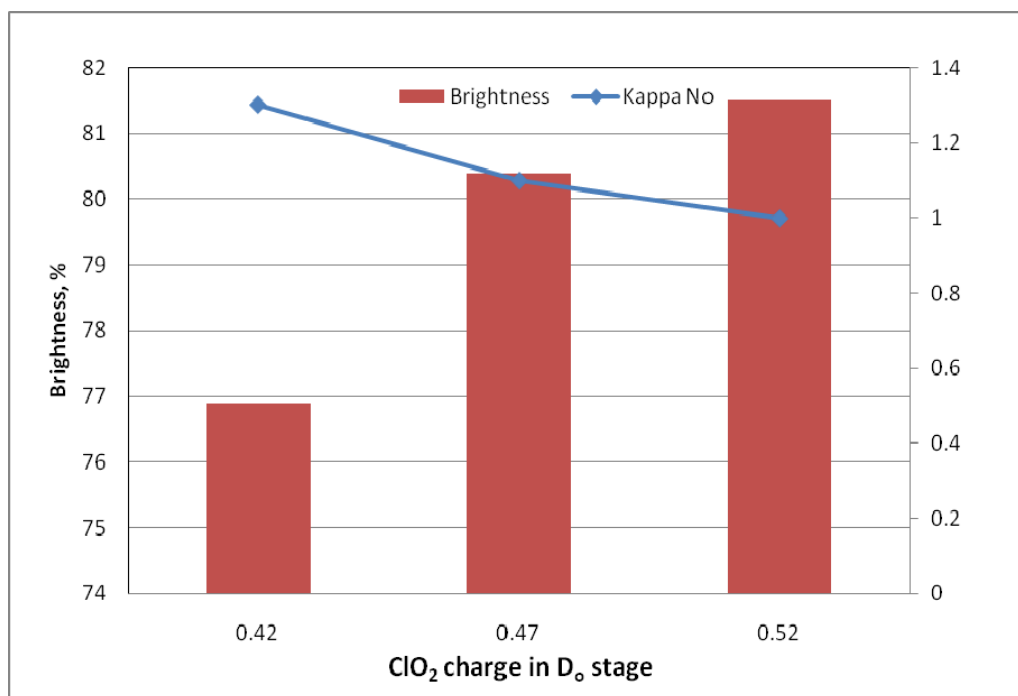
## RESULTS AND DISCUSSION

We determined the effect of ClO<sub>2</sub> charge in the D<sub>0</sub> stage on the bleaching performance. An increase of the ClO<sub>2</sub> charge can be expected to increase the delignification degree and would allow easier final pulp bleaching. In Fig. 1 the effect of ClO<sub>2</sub> charge on the Kappa number and brightness after the E<sub>p</sub> stage is shown. The Kappa number decreased and brightness increased with the increase of ClO<sub>2</sub> charge. After the application of 0.42% ClO<sub>2</sub> charge, the Kappa number decreased to 1.3 with the brightness of 76.9%. An additional charge of ClO<sub>2</sub> increased brightness above 80% with a slight decrease in the Kappa number.

The question of whether it would be easier to achieve a high brightness level if the ClO<sub>2</sub> charge in the D<sub>0</sub> stage is very high was tested with the sequence of D<sub>0</sub>E<sub>p</sub>D<sub>1</sub>ED<sub>2</sub>. The results in Table 1 indicate that there is a limited benefit on the final brightness with an increase of the ClO<sub>2</sub> charge in the D<sub>0</sub> stage. The final brightness increased from 89% to 89.7% with an increase of the ClO<sub>2</sub> charge from 0.42% to 0.52% in the D<sub>0</sub> stage and keeping the ClO<sub>2</sub> charges constant in the D<sub>1</sub> and D<sub>2</sub> stages. To accomplish the goals of getting a higher final brightness, the ClO<sub>2</sub> charge was increased in the D<sub>1</sub> stage, and the final brightness was further increased to 90.3% if the ClO<sub>2</sub> charge in the D<sub>1</sub> stage increased to 0.38% from 0.23%.

To improve the ClO<sub>2</sub> brightening efficiency, Mg(OH)<sub>2</sub> was used to control the pH in both the D<sub>1</sub> and D<sub>2</sub> stages. It should be noted that Mg(OH)<sub>2</sub> is now used in the pulp and paper industry as the alkali source during the peroxide bleaching of mechanical pulps (He et al. 2004, 2006a,b; Johnson et al. 2002; Li et al. 2005; Yu et al. 2004). The results are included in Table 1, and it can be found that the final brightness was further increased by 0.5-0.8 points when NaOH was replaced by Mg(OH)<sub>2</sub> for controlling the pH in the D<sub>1</sub>

and D<sub>2</sub> stages. By using Mg(OH)<sub>2</sub>, about 1 kg/t of ClO<sub>2</sub> charge (from 0.52% to 0.42% ClO<sub>2</sub> charge) can be saved to reach a same final brightness of 90%. The better ClO<sub>2</sub> bleaching performance in the Mg(OH)<sub>2</sub>-based system is due to the better pH profile of the bleaching system, i.e. the buffering effect of Mg(OH)<sub>2</sub> (He and Ni 2009). The initial pH of the NaOH system was very high as compared to the Mg(OH)<sub>2</sub> system (11 for the NaOH-based system vs 7 for the Mg(OH)<sub>2</sub>-based system) (He and Ni 2009). The pH of the NaOH-based process dropped rapidly within the first 10 min., while it was quite stable for the Mg(OH)<sub>2</sub>-based process. It is known (Svenson et al. 2006; Ni et al. 1993; Hoige and Bader 1994) that under an alkaline condition, chlorine dioxide will be decomposed to form chlorate; therefore, the milder pH profile of the Mg(OH)<sub>2</sub>-based system resulted in less chlorine dioxide decomposition, thus less chlorate formation. The minimization of the chlorate formation by controlling pH can improve the efficiency of the chlorine dioxide bleaching process (Strumila and Rapson 1979).



**Fig. 1.** Effects of ClO<sub>2</sub> charge in the D<sub>0</sub> stage on the D<sub>0</sub>E<sub>p</sub> Kappa number and brightness.

Also, under the conditions of ClO<sub>2</sub> brightening, the presence of chlorite represents the waste of chlorine dioxide (Kolar et al. 1983; Ni et al. 1992). More chlorite is formed in the NaOH-based process, which also contributed to the decreased ClO<sub>2</sub> brightening efficiency. It was reported that a higher pH of the chlorine dioxide stage would lead to the formation of more chlorite: at a pH of 8, around 50% of the initial ClO<sub>2</sub> was converted to chlorite, while at a pH of 2 about 3% of the initial ClO<sub>2</sub> is in the form of chlorite (Svenson et al. 2002; Strumila and Rapson 1979).

The application of hydrogen peroxide (P) in the final stage is an answer to the concept of shortening the bleaching process so that a four-stage (D<sub>0</sub>E<sub>p</sub>D<sub>1</sub>P) sequence instead of a five-stage (D<sub>0</sub>E<sub>p</sub>D<sub>1</sub>E<sub>2</sub>D<sub>2</sub>) sequence can be used. The savings in capital for a

shortened bleaching sequence are attractive to the industry. Hence the final stage bleaching of jute pulp was also evaluated by using a peroxide stage, and the results are given in Table 1. The final brightness in the shorter sequence (with a P as the final bleaching stage) was slightly inferior to the D<sub>2</sub> stage bleaching.

**Table 1.** ClO<sub>2</sub> Bleaching of Soda-AQ Jute Pulp

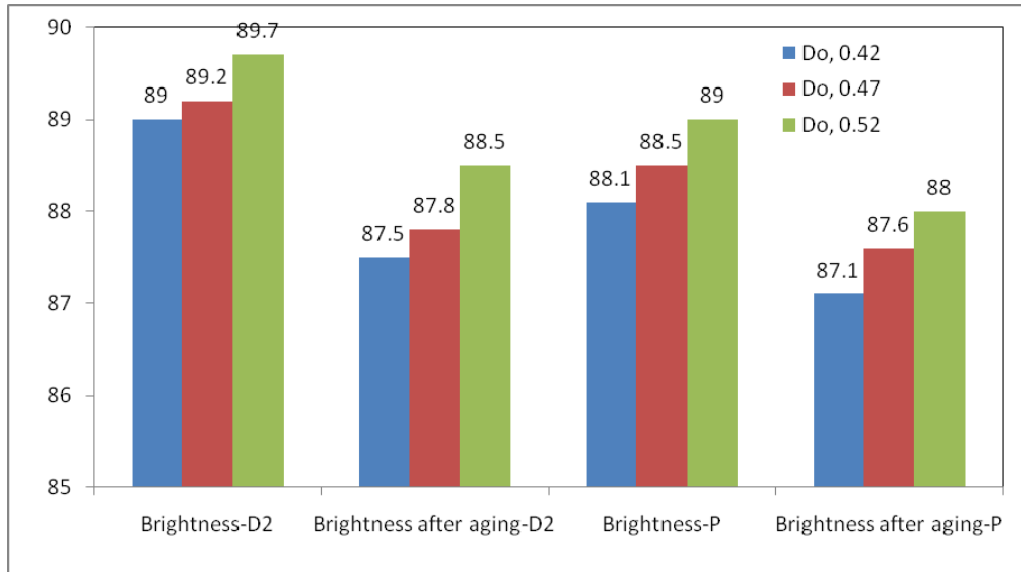
Alkali source in D <sub>1</sub> & D <sub>2</sub>	D <sub>0</sub> ClO <sub>2</sub> charge %	D <sub>1</sub> stage			D <sub>2</sub> stage			P-stage
		ClO <sub>2</sub> charge %	pH	Bright-ness % ISO	ClO <sub>2</sub> Charge %	pH	Bright-ness % ISO	Bright-ness % ISO
NaOH	0.42	0.23	3.7	87.4	0.11	4.8	89.0	88.1
		0.38	3.5	87.7	0.11	4.8	89.5	88.8
	0.47	0.23	3.6	87.9	0.11	4.7	89.2	88.5
		0.38	3.5	88.1	0.11	4.9	89.4	89.2
	0.52	0.23	3.7	88.0	0.11	4.6	89.7	89.0
		0.38	3.4	88.5	0.11	4.8	90.3	89.4
Mg(OH) <sub>2</sub>	0.42	0.23	3.5	88.1	0.11	4.5	89.6	89.1
		0.38	3.3	88.5	0.11	4.3	90.1	89.5
	0.47	0.23	3.6	88.4	0.11	4.7	89.8	89.3
		0.38	3.4	88.5	0.11	4.3	90.2	89.8
	0.52	0.23	3.5	88.8	0.11	4.5	90.3	89.7
		0.38	3.3	88.9	0.11	4.3	90.8	89.8

D<sub>0</sub>: Temperature 60 min at 70°C; E<sub>p</sub>: 1.5% NaOH, 0.25% H<sub>2</sub>O<sub>2</sub>, 90 min at 70°C; D<sub>1</sub>: 0.05% NaOH or Mg(OH)<sub>2</sub>, 60 min at 70°C; E<sub>2</sub>: 0.3% NaOH, 120 min at 70°C; D<sub>2</sub>: 0.01% NaOH or Mg(OH)<sub>2</sub>, 120 min at 70°C; P: 0.25% NaOH, 0.2% H<sub>2</sub>O<sub>2</sub>

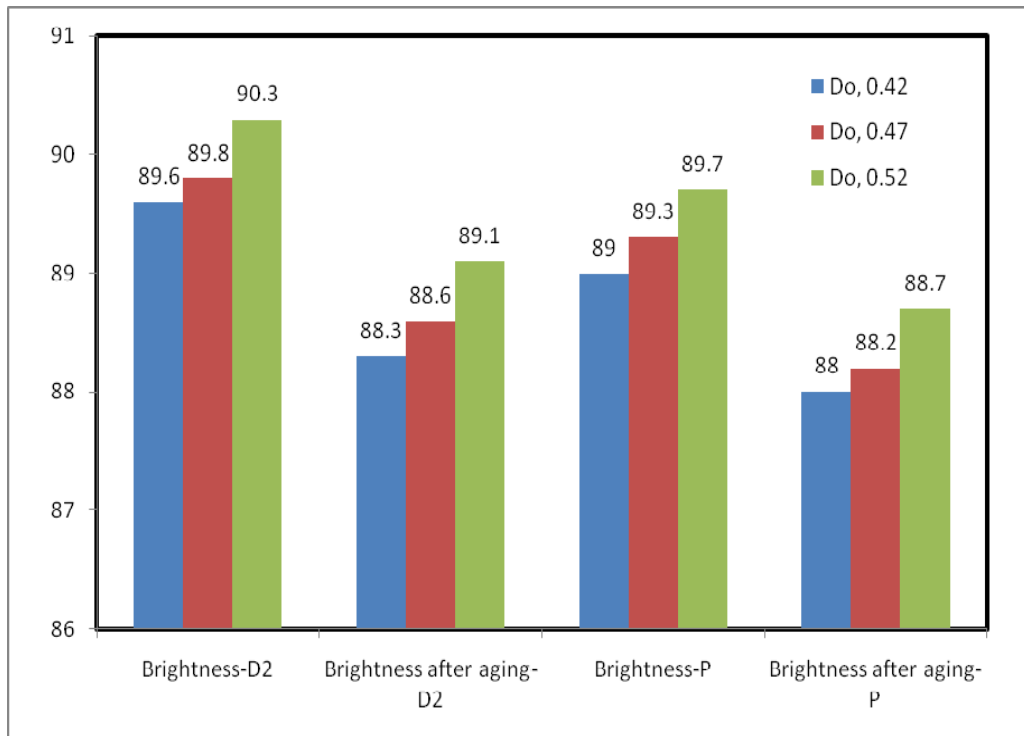
A good brightness stability is desirable for bleached chemical pulps, particularly for market pulp producers. In Figs. 2 and 3, the effect of ClO<sub>2</sub> charge in the D<sub>0</sub> stage on the final brightness and the brightness stability of the fully bleached pulps obtained from both the NaOH- and Mg(OH)<sub>2</sub>-based processes was presented. The results showed that the brightness after reversion increased with increasing ClO<sub>2</sub> charge in the D<sub>0</sub> stage, which is consistent with the Kappa number after D<sub>0</sub>E<sub>p</sub> stage (Fig. 1). It was reported (Shackford et al. 2009) that sequences using more chlorine dioxide produced pulps of lower brightness reversion because of the complete oxidation of chromophore. The insufficient removal of hexenuronic acids in pulp due to incomplete oxidation is known to contribute to the brightness reversion of fully bleached chemical pulps (Bjorklund et al. 2005). The type of raw materials has also been cited as a source of pulp brightness instability (Colodette et al. 2004; Foresail 2000; Gomide et al. 2005).

Brightness reversion is caused by the impurities, which in turn, are affected by the bleaching conditions. Among these, oxidised structures such as carbonyl groups are important contributors (Adorjan et al. 2006). The results in Figs. 2 and 3 indicated that the final peroxide stage improved the brightness stability slightly. This fact has been recognized by other researchers (Anderson and Amini 1996; Eiras and Colodette 2005; Foresail 2000; Lachenal and Nguyen 1993) and attributed to the oxidation of carbonyl groups in pulp by peroxide (Anderson and Amini 1996; Foresail 2000; Lachenal and Nguyen 1993) and to alkali-induced dissolution of colored substances. The chemical

structures of the last remaining chromophores present in the pulp are more prone to react with hydrogen peroxide than with  $\text{ClO}_2$  (Graç et al. 2008).



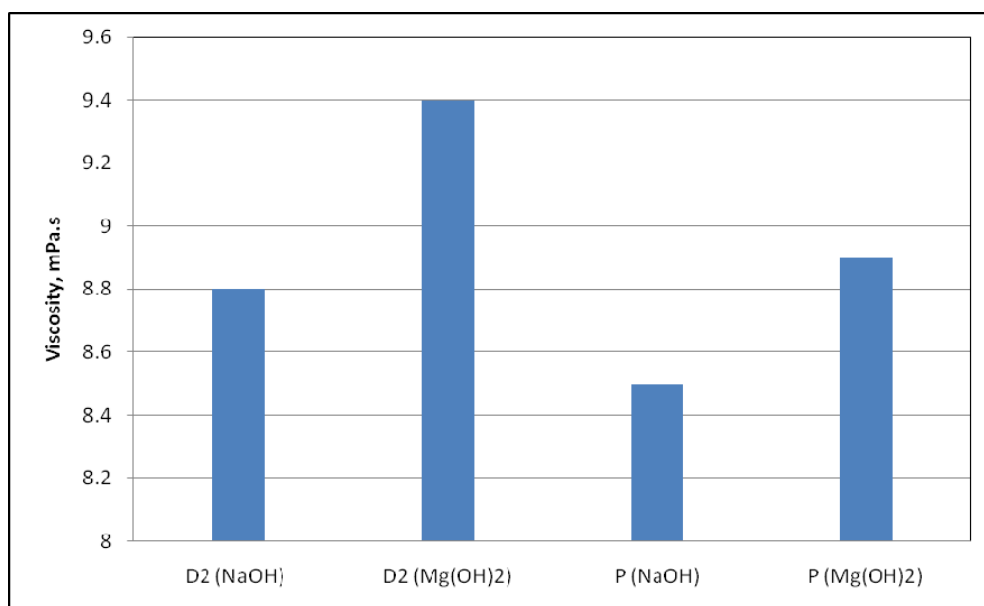
**Fig. 2** Effect of final brightening agent on the final brightness and brightness stability of NaOH-based brightening (bleaching conditions for each stage same as those in Table 1).



**Fig. 3** Effect of final brightening agent on the final brightness and brightness stability of  $\text{Mg}(\text{OH})_2$ -based brightening (bleaching conditions for each stage are the same as those in Table 1).

Figure 4 shows that the viscosity of pulp bleached by  $\text{ClO}_2$  in the final stage was slightly better than that of the peroxide bleached pulp, due to the fact that chlorine dioxide is more selective than peroxide. Using  $\text{Mg}(\text{OH})_2$  to replace  $\text{NaOH}$  in the  $\text{D}_1$  and  $\text{D}_2$  stages also resulted in a higher pulp viscosity. This is because of the higher pH (particularly at the beginning) of the  $\text{NaOH}$ -based process. These results are consistent with those reported recently (Hart and Connell 2008), that at a pH of above 7 during chlorine dioxide brightening, more carbohydrate degradation occurred, thus damaging pulp strength. Non-selective species can be formed from chlorine dioxide at a high pH in the  $\text{NaOH}$ -based process (He and Ni 2009).

The physical properties of the bleached jute pulps are presented in Table 2. It is shown that a final bleaching with peroxide enables better tensile and tear indexes in comparison with that with a final  $\text{D}_2$  brightening. It is also seen from Table 2 that the use of  $\text{Mg}(\text{OH})_2$  in the  $\text{D}_1$  stage had a slightly better tensile index and burst index than the  $\text{NaOH}$ -based bleaching. This is because of the lower initial pH of the  $\text{Mg}(\text{OH})_2$  process than the  $\text{NaOH}$ -based process, resulting in less carbohydrate degradation, and preservation of pulp strength. These results are consistent with the viscosity data (Fig. 4).



**Fig. 4** Comparison of the pulp viscosity of bleached jute pulp (bleaching conditions are the same as those in Table 2).

**Table 2.** Effect of Using Chlorine Dioxide or Peroxide as the Final Stage on the Strength Properties of Jute Pulp (PFI Rev 3000)

Final Stage	$\text{D}_1$ with $\text{Mg}(\text{OH})_2$		$\text{D}_1$ with $\text{NaOH}$	
	$\text{D}_1\text{ED}_2$	$\text{D}_1\text{P}$	$\text{D}_1\text{ED}_2$	$\text{D}_1\text{P}$
CSF ml	330	370	350	360
Burst Index, $\text{kPa}\cdot\text{m}^2/\text{g}$	2.3	2.8	2.0	2.6
Tear Index, $\text{mN}\cdot\text{m}^2/\text{g}$	4.8	5.8	5.4	5.8
Breaking Length, Km	4.88	4.98	4.36	4.65
Tappi Opacity, %	77.30	77.10	77.01	77.23

$\text{D}_0$ : 0.42%  $\text{ClO}_2$ ;  $\text{D}_1$ : 0.38%  $\text{ClO}_2$ ;  $\text{D}_2$ : 0.11%  $\text{ClO}_2$ ; P: 0.2%  $\text{H}_2\text{O}_2$

The opacity in all pulps was similar. Opacity is the measure of the ability to obstruct the passage of light (Vaarasalo 1999). For this reason opacity increases with the number of air interfaces in the fiber web, which is responsible for the higher light scattering.

## CONCLUSIONS

1. A soda-AQ jute pulp was bleached to a brightness target of 88-89% ISO by using only 7.6 kg/ ton  $\text{ClO}_2$ . The performance of peroxide or chlorine dioxide as a final brightening agent depends on the  $\text{ClO}_2$  charge in the  $D_0$  stage or the  $D_0E$  brightness.
2. The use of  $\text{Mg}(\text{OH})_2$  to replace  $\text{NaOH}$  in the  $D_1$  and  $D_2$  stages for controlling the final pH improved the final pulp brightness.
3. The final brightness of the pulp bleached by peroxide as the final stage was slightly lower than that by  $\text{ClO}_2$  as the final stage. However, the pulp brightness after reversion was similar between the two cases.
4. The pulp viscosity from the  $\text{Mg}(\text{OH})_2$ -based process was better than that of the  $\text{NaOH}$ -based process, consequently improving the pulp physical properties.
5. The physical properties of the bleached pulp also improved when  $\text{ClO}_2$  was replaced with peroxide in the final brightening stage.

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