

Reduction in chlorine use during bleaching of kraft pulp following xylanase treatment

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ABSTRACT: *Xylanase-treated pulp bleached at 10% substitution required almost 80% less Cl_2 and 5% less ClO_2 than the control pulp to reach 90% ISO brightness. Xylanase allows the mill to bleach to 90% ISO at a Cl_2 level equivalent to 80% ClO_2 substitution but with a 33% reduction in ClO_2 . Pretreatment also allowed pulps of 92% ISO to be prepared with a chlorine multiple of 0.15, whereas the analogous pulp at a multiple of 0.25 reached less than 91% ISO.*

KEYWORDS: *Bleaching, brightness, chlorine, chlorine dioxide, kraft pulps, pretreatment, reduction, xylanase.*

Growing public concern about the environment is giving rise to dramatic technological changes in pulp bleaching. Applications of biotechnology in the bleach plant appear to offer a viable and novel means of facilitating these needed changes. The expected short-term impact of these developments will be the elimination of molecular chlorine from the bleach plant without a sacrifice of pulp quality or an increase in chemical costs. In the longer term, this new approach will be important in pulp bleaching processes that admit no chlorine-containing chemistry, that have effluents that are substantially improved in terms of acute and chronic toxicological effects, and that have process waters that are fully recyclable.

The concept of biological bleaching with xylanases emerged from efforts to selectively remove hemicellulose

from chemical pulps and prepare dissolving-grade pulp suitable for derivatization to cellulose acetate, rayon, etc. (1). It was later found that xylanase pretreatment of pulp caused reductions in lignin content and that savings in chemicals can be obtained (2-8). When cellulase-free xylanases have been applied to pulps, reductions in bleach chemical requirements have been concomitant with improvements in viscosity (6, 7) and paper properties such as beatability (7, 9), tear strength, and brightness (7, 8). Reduction in chlorine usage, in part due to xylanase treatment of pulp, has also been shown to substantially lower levels of AOX (adsorbable organic halogens) and dioxin in mill trial effluents (10).

As the pulp and paper industry moves toward technology that reduces chlorinated organic compounds in bleach plant effluents, a growing ten-

dency has been toward the use of higher percentages of ClO_2 substitution. High ClO_2 substitution has been shown to reduce dramatically the formation of chlorinated organic compounds in bleach plant wastewater (11). Chemical savings derived from xylanase treatments have been reported by various workers, using different ClO_2 substitutions. However, there have been no systematic studies on the impact of xylanase pretreatment on the chlorination stage and chlorine dioxide substitution. In this regard, there have been only limited attempts to properly quantify downstream bleaching chemical savings following xylanase use and to maximize the potential benefits. Likewise, the use of xylanase pretreatment to improve overall bleached pulp brightness has not been described.

In this report, we focus on the relationship between the effectiveness of xylanase pretreatment and the levels of ClO_2 substitution in the bleaching sequence. We also describe the merits of xylanase use from the point of view of mill operations, looking at how xylanase pretreatment facilitates the preparation of pulps of very high brightness.

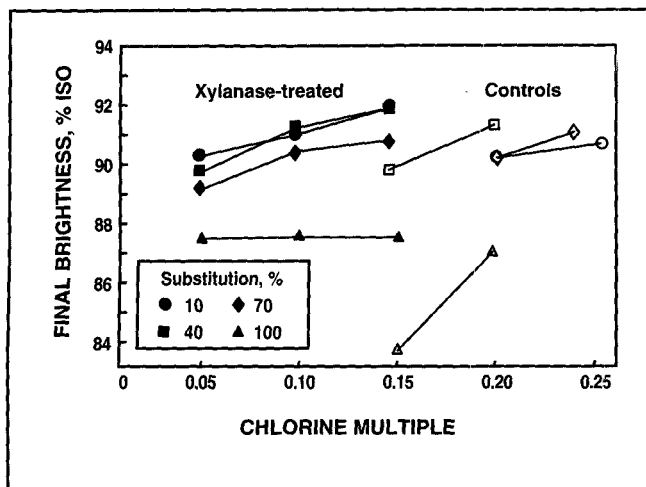
Experimental procedures

Preparation of xylanase enzyme

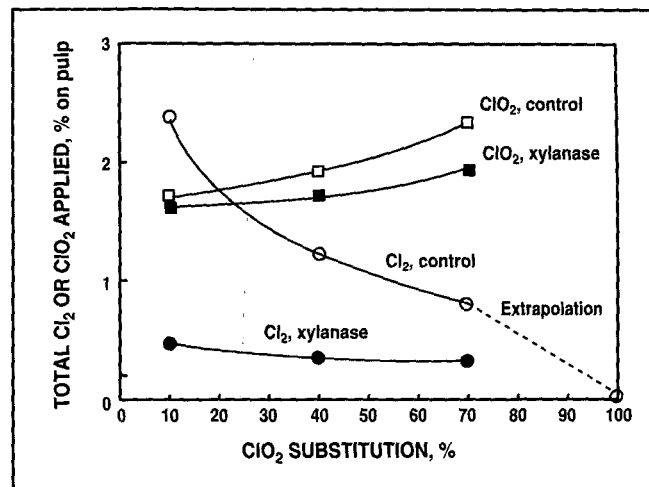
Xylanase enzyme was produced by batch fermentation of *Streptomyces lividans* [pIAF18]. This high-xylanase-producing, cellulase-negative microorganism was obtained through a generic engineering program at the Institute Armand Frappier, Montreal. The en-

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1. Effect of chlorination-stage total equivalent chlorine multiple on the final brightness of xylanase-treated and control hardwood kraft pulps



2. Charges of Cl_2 and ClO_2 combined to achieve 90% ISO brightness for control and xylanase-treated pulps, for various chlorine dioxide substitutions



zyme was prepared as described by Bertrand *et al.* (12).

The activity of the enzyme preparation was 1033 IU/mL, where an IU (international unit) is that amount of enzyme which catalyzes the formation of 1 μmol of xylose per minute from a solution containing xylan.

A stock solution of 1.5% (wt/vol) of the water-soluble fraction of oat spelt xylan was dissolved in 50mM McIlvaine's buffer, pH 6.0, and this was used as the assay substrate. Assay reaction times were 10 min. The reducing sugars produced were determined, relative to standard xylose solutions, according to the dinitrosalicylic acid method of Miller (13).

Xylanase treatment of pulp

Xylanase treatments were carried out on 200-g batches of hardwood kraft pulp of mixed furnish, as obtained from an eastern Canadian mill. The pulp was adjusted to pH 5.5–6.0 by the addition of 1M H_2SO_4 solution. Xylanase was added to the pulp, with mixing in a Mark II Quantum Reactor at a consistency of 6% (wt/wt).

The enzyme reaction was carried out while maintaining the pulp temperature at 50°C for 2 h. An enzyme charge of 0.012% on pulp was applied, which was equivalent to 85 IU/g of pulp. Following the enzyme treatment, the pulps were washed at 1% consis-

tency in water and were filtered using suction. Control pulps were prepared identically to the enzyme-treated pulps, with the enzyme being replaced with water.

Bleaching experiments

Control and xylanase-treated pulps were subjected to standard (CD)EDED bleaching. During the chlorination stage, the pulp consistency was adjusted to 3.5%, and the chlorination reaction, using 150 g o.d. pulp, was carried out in a stirred vessel at 40°C for 30 min. For xylanase-treated pulps, chlorine multiples of 0.05, 0.10, and 0.15 were applied. Control pulps were treated with higher multiples, as specified in the figures and tables.

The substitution of ClO_2 for Cl_2 was varied stepwise through percentages of 10%, 40%, 70%, and 100%. At 10% substitution, Cl_2 and ClO_2 were premixed in aqueous solution, prior to being added to the pulp. For 40% substitution, the ClO_2 was added 30 s before Cl_2 ; for 70% substitution, ClO_2 was added 60 s before Cl_2 . Following the chlorination stage, pulps were washed with stirring at 1% consistency and were filtered using suction.

A caustic extraction was carried out immediately after the washing stage. Pulp and sodium hydroxide solution (2% on pulp) were mixed in a Hobart

mixer. Caustic extraction was carried out for 1 h at 70°C in polyethylene bags. The first D stages were carried out on 20-g samples in sealed glass Mason jars using ClO_2 charges of 1.2% on pulp (except as specified otherwise) at 6% consistency and 70°C for 3 h. All first D stages were optimized with sodium hydroxide addition to achieve an exit pH of 3.5–4.0. The second extraction stage was performed using caustic charges of 0.6% on pulp with the same consistency, temperature, and time as the first extraction stage. A constant ClO_2 charge of 0.4% on pulp in the second D stage was used throughout at a temperature of 70°C for 3 h.

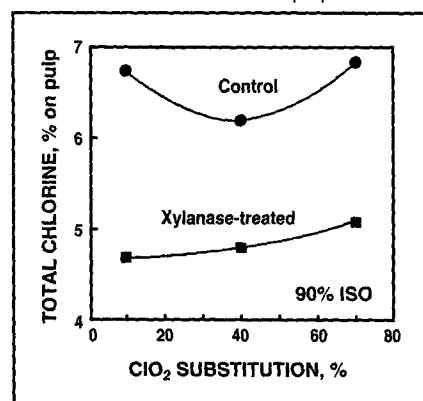
We also studied the effect of the order of addition of Cl_2 and ClO_2 on the bleachability of xylanase-treated pulps. Xylanase-treated pulp was bleached using the sequence (CD)EDED, under which the order of addition of Cl_2 and ClO_2 was varied in the (CD) stage. For 40% ClO_2 substitution and a chlorine multiple of 0.10, ClO_2 was added 30 s before Cl_2 in a (DC)EDED sequence, ClO_2 and Cl_2 were premixed before being added to the pulp in a (C+D)EDED sequence, and Cl_2 was added 30 s before ClO_2 in a (CD)EDED sequence.

The subsequent extraction stage was carried out as already described. The first D charges of ClO_2 were varied from 0.4% to 1.2% on pulp followed by

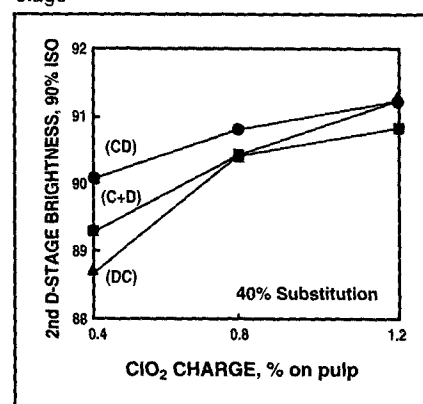
1. Properties of brownstock and xylanase-treated hardwood kraft pulp

	Brown stock	Xylanase-treated
Brightness, % ISO	31.3	33.9
Kappa number	13.2	11.2
Viscosity, mPa · s	28.8	30.9

3. Total applied equivalent chlorine charges ($\text{Cl}_2 + \text{ClO}_2$ as Cl_2) to achieve 90% ISO brightness in treated and untreated pulps



4. Effect of the order of addition of Cl_2 and ClO_2 on pulp brightness at the end of the second D stage



an extraction stage and second D stage as described. Final stage brightnesses were determined to assess the bleachability effect. The experiments were also repeated using 80% ClO_2 substitution.

All measurements of kappa number, brightness, and viscosity were performed according to TAPPI and CPPA procedures.

Results and discussion

Samples of an eastern Canadian hardwood kraft pulp were treated with our *Streptomyces lividans* xylanase preparation prior to use in bleaching experiments. This enzyme functions effectively over broad ranges of temperature and pH (up to 60°C and pH 4.5–7.0) and thus offers the mill operator the flexibility to incorporate xylanase into his system with little capital expense or retrofitting.

ICI xylanase can be readily applied in the mill's brownstock storage chest, where process conditions are highly compatible with the optimum conditions for xylanase action. Using xylanase charges identical to those in this work, we have found that substantial effects can be gained with enzyme-stage treatment times as short as 30 min, while retention times of 16 h or longer present no problems to pulp viscosity, because of the cellulase-free nature of this enzyme (unpublished results).

The brownstock and xylanase-treated pulps used for the chlorine bleaching had characteristics as described in Table I. After xylanase treatment, we observed an increase in brightness of 8% and a reduction in kappa number of 16%, which showed that xylanase can delignify pulp to a limited extent. The improvement in viscosity confirms that there is an enrichment of the high-molecular-weight cellulose fraction, which occurs when xylan is selectively removed (14, 15).

Reduction in bleaching chemical requirements

One of our objectives was to quantify the reduction in first-stage bleaching chemicals that can be achieved by pre-treating the pulp with xylanase. Xylanase-treated pulps were subjected to bleaching using first-stage total equivalent chlorine multiples from 0.05 to 0.15 over four levels of chlorine dioxide substitution. The bleaching sequences used at the various levels of chlorine dioxide substitution were:

- 10% ClO_2 : (C+D)EDED

- 40% ClO_2 : (DC)EDED
- 70% ClO_2 : (DC)EDED
- 100% ClO_2 : DEDED.

At substitution levels of 40% and 70%, chlorine was added to the pulps after chlorine dioxide and after a slight delay (as specified). Subsequent to the first-stage bleaches, all EDED stages were performed using constant chemical charges. Exit conditions and brightness data for the bleached pulps are found in Table II. Nonxylanase-treated pulps prepared as controls were bleached with chlorine multiples in the range of 0.15–0.25, unless indicated otherwise.

Several differences between fully bleached, xylanase-treated and untreated pulps were immediately apparent. At 10%, 40%, and 70% ClO_2 substitution, a brightness of 90% ISO was readily achieved for the xylanase-treated pulps with a substantial reduction in chlorination-stage charge (Fig. 1). Brightnesses of the xylanase pulps bleached with 10% and 40% substitution were nearly identical and were substantially higher than for all other treatments. Brightnesses of 91% and 92% ISO could be readily achieved with chlorine multiples of 0.10 and 0.15, respectively, when xylanase-treated pulp and low- to medium- ClO_2 substitution were used.

The brightness curve of xylanase-treated pulp bleached at 10% ClO_2 substitution is virtually linear and did not show signs of reaching a brightness ceiling even when the highest chlorine multiple (0.15) was used. This outcome indicates that pulps of +92% ISO brightness could be easily achieved while maintaining a lower chlorine multiple than with the nonxylanase-treated control pulp. The control pulp bleached at 10% ClO_2 substitution reached an apparent brightness ceiling below 91% ISO. Bleaching this control pulp at 10% ClO_2 substitution with a chlorine multiple of 0.25 yielded only 90.7% ISO brightness. At 70% ClO_2 substitution, the xylanase-treated pulp easily reached 90% ISO brightness, with less chemical charge than the con-

trol pulp required.

Impact of chlorine reduction on chlorine dioxide substitution

The requirements for bleach chemicals for control and xylanase-treated pulps, bleached at various ClO_2 substitution levels, indicate the potential chemical savings available when xylanase is employed. With constant chemical charges maintained in the first and second D stages, the chemical savings could be realized in the chlorination stage.

Figure 2 shows the charges of Cl_2 and ClO_2 required to reach 90% ISO brightness for control and xylanase-treated pulps at each level of ClO_2 substitution. The xylanase-treated pulp bleached at 10% substitution required almost 80% less Cl_2 and 5% less ClO_2 than the control at 10% substitution to reach the target brightness. This amount of Cl_2 is equivalent to that required to bleach the control using 80% substitution (taking the point at 80% on the extrapolated line).

Even more important, however, is the substantial savings in ClO_2 that can be realized. A mill operating at 80% ClO_2 substitution would require a total ClO_2 charge of at least 2.4% on pulp for this brownstock pulp, whereas only 1.6% ClO_2 would be required under xylanase pretreatment. Xylanase use would allow the mill to bleach to 90% ISO brightness at a Cl_2 level equivalent to 80% ClO_2 substitution for untreated pulp, gaining at least a 33% reduction in ClO_2 requirement. Also, the chlorine multiple (0.05) required to obtain +90% ISO brightness with xylanase-treated pulp using 10% substitution is well below the threshold of 0.15–0.17 for chlorinated dioxin and furan formation in softwoods (16).

Chlorine and chlorine dioxide act synergistically in pulp bleaching when used at a ratio of approximately 1:1 (17). This effect explains why the minimum requirement for bleaching chemicals for our control sequence pulps occurs at about 40% substitution (Fig. 3). Surprisingly, the xylanase-treated pulp was found to require less total

II. Effects of xylanase pretreatment on (C+D)EDED bleachability of hardwood kraft pulp using 10% chlorine dioxide substitution

	(C+D)E ^a		First D stage ^b		Second D stage ^c		
	Chlorine multiple	Total available chlorine, % on pulp	Exit pH	Residual, % on pulp	Exit pH	Residual % on pulp	Brightness, % ISO
10% Substitution							
Control	0.20	2.64	3.6	0.15	4.2	0.22	90.2
	0.25	3.30	3.7	0.25	4.5	0.10	90.7
Xylanase	0.03	0.34	4.5	0.01	3.9	0.09	86.1
	0.05	0.55	4.2	0.04	3.9	0.30	90.3
	0.10	1.11	3.7	0.42	4.2	0.31	91.3
	0.15	1.67	3.8	0.52	4.3	0.31	92.0
40% Substitution							
Control	0.15	1.98	3.6	0.17	4.4	0.19	89.8
	0.20	2.68	3.7	0.19	3.8	0.25	91.3
Xylanase	0.05	0.56	4.1	0.03	4.0	0.17	89.8
	0.10	1.12	3.9	0.08	3.7	0.26	91.4
	0.15	1.69	3.8	0.20	3.7	0.34	91.9
70% Substitution							
Control	0.20	2.63	3.7	0.25	3.9	0.21	90.2
	0.23	3.04	3.6	0.42	4.0	0.24	91.0
Xylanase	0.05	0.56	4.1	0.05	4.0	0.08	89.2
	0.10	1.09	3.6	0.22	3.7	0.09	90.5
	0.15	1.66	3.7	0.30	3.8	0.25	90.8
100% Substitution							
Control	0.15	1.98	4.5	0.07	4.1	0.06	83.6
	0.20	2.64	3.5	0.04	4.0	0.15	87.0
Xylanase	0.05	0.58	4.7	0.06	3.9	0.15	87.5
	0.10	1.16	4.2	0.03	4.0	0.23	87.5
	0.15	1.73	4.0	0.03	4.2	0.26	87.5

^a First E charge: 2% on pulp.

^b ClO_2 charge: 1.2% on pulp.

Second E charge: 0.6% on pulp.

^c ClO_2 charge: 0.4% on pulp.

chlorine charge at 10% substitution than at other substitutions. For hardwood basestocks, xylanase-pretreated pulp is more easily bleached at low chlorine dioxide substitution than at high substitution.

Effect of the order of addition of chlorine and chlorine dioxide

Samples of xylanase-treated pulp were bleached using sequences in which ClO_2 was added 30 s before Cl_2 [(DC)EDED], simultaneously with Cl_2 [(C+D)EDED],

and 30 s after Cl_2 [(CD)EDED]. The degrees of substitution chosen for these experiments were 40% and 80%, and a chlorine multiple of 0.10 was applied to the first stage.

Table III shows that the effectiveness of bleaching by Cl_2 and ClO_2 depends on the order in which they are added when xylanase-treated pulp is used at 40% ClO_2 substitution. Using 40% substitution, the addition of Cl_2 before ClO_2 in the chlorination stage was more effective than when the reagents were pre-mixed or when ClO_2

III. Effect of the order of addition of Cl_2 and ClO_2 on the bleaching efficiency of xylanase-treated pulps using 40% ClO_2 substitution

	Kappa no.	Bright- ness, % ISO	Charge, % on pulp	Bright- ness, % ISO	Bright- ness, % ISO	Viscosity, mPa*s
40% Substitution						
(DC)EDED	5.0	48.3	0.4	74.9	88.7	...
			0.8	83.3	90.4	...
			1.2	85.6	91.2	23.0
(C+D)EDED	2.9	51.4	0.4	81.2	89.3	25.7
			0.8	86.3	90.4	23.1
			1.2	87.4	90.8	23.2
(CD)EDED	3.2	52.6	0.4	82.1	90.1	25.2
			0.8	86.6	90.8	24.0
			1.2	87.4	91.2	22.2
80% Substitution						
(DC)EDED	5.6	49.4	0.4	74.0	86.9	...
			0.8	83.4	87.2	...
			1.2	85.2	88.7	...
(C+D)EDED	5.4	47.4	0.4	71.9	86.4	...
			0.8	82.1	87.9	...
			1.2	85.1	88.8	...
(CD)EDED	5.1	51.7	0.4	74.4	87.3	...
			0.8	81.6	88.7	...
			1.2	85.5	89.9	...

(DC): Cl₂ was added 60 s after ClO₂.
(C+D): Cl₂ and ClO₂ were added simultaneously.
(CD): Cl₂ was added 60 s before ClO₂.

was added first. This result was evidenced by a substantially lower kappa number and the higher brightness of the extraction-stage pulp.

Three charges in the first D-stage (0.4%, 0.8%, and 1.2% on pulp) were then applied to samples of each pulp from the three different chlorination-stage sequences. In Table III, comparing the brightnesses at each charge for all three sequences, we see that, again, the pre-mixing of Cl_2 and ClO_2 or the pre-adding of Cl_2 gave higher brightnesses than when ClO_2 was

added first. This effect was more obvious at the lowest charge (0.4%). The effect of the mode of addition was less apparent, however, at the second D stage because the pulp brightnesses were at the brightness ceiling or were approaching it (Fig. 4). Nonetheless, for pulps bleached with the lowest first D ClO_2 charge (0.4%), a trend in second D-stage brightness was observed, with brightness increasing according to: (DC) < (C+D) < (CD). These results are unexpected in light of our conventional understanding of the effects of

chlorine dioxide substitution on chemical pulp bleaching (18, 19) and viscosity protection (20).

With 80% substitution, the order of additions had minor effects on increasing the second D-stage brightnesses, when Cl_2 was added one minute ahead of ClO_2 or simultaneous with ClO_2 (Table III).

The correct order of addition of Cl_2 and ClO_2 after xylanase pretreatment indicates potential for further reduction of ClO_2 charges in the first and second D stages. Also, the addition of the chlorine ahead of chlorine dioxide is preferred in order to minimize or eliminate chlorinated dioxin and furan formation in softwoods (16). Xylanase pretreatment appears to facilitate this option.

The improvement in bleaching of xylanase-treated pulp at low ClO_2 substitution was found to arise following the chlorination stage. Figure 5 shows that the greatest delignification (as measured by kappa number at the end of (CD)E) was obtained with xylanase-treated pulps bleached at low ClO_2 substitutions. As the ClO_2 levels were increased, progressive reductions in delignification were observed. Control pulps treated at constant charges, however, retained maximal delignification at 40% substitution.

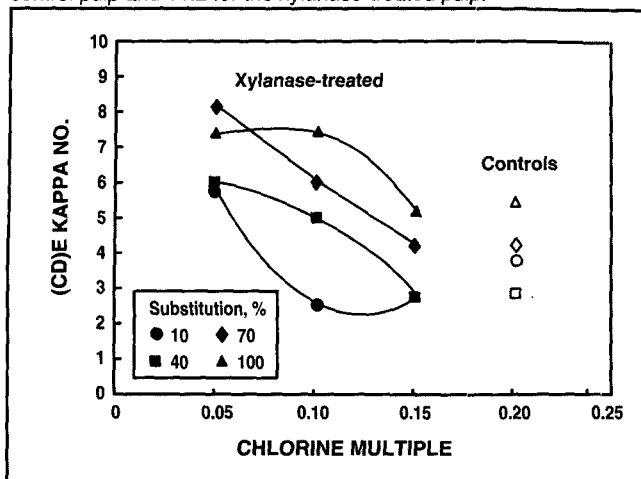
Effect of xylanase pretreatment on pulp viscosity

In previous work, we have observed that xylanase pretreatment leads to improvements in pulp viscosity. In this work also, we found xylanase-pretreated pulps bleached to 90% ISO brightness at 10%, 40%, and 70% ClO_2 substitution to have higher viscosities than untreated controls (Fig. 6).

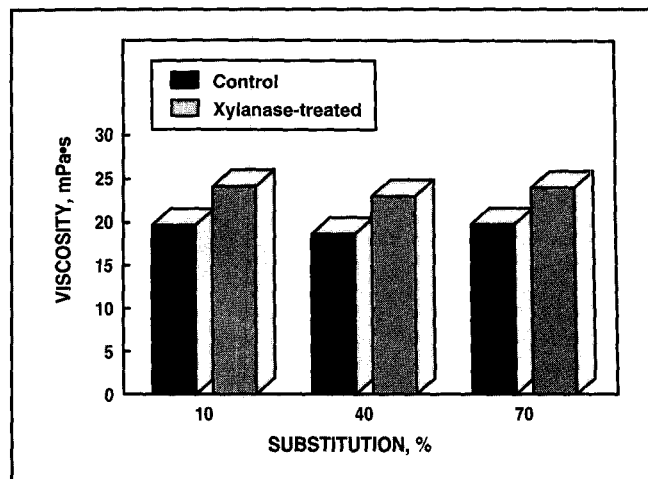
Conclusions

Xylanase-pretreated hardwood kraft pulps that were bleached using a standard (CD)EDED sequence were found most susceptible to bleaching when low chlorine dioxide substitution was applied. A large reduction in Cl_2 requirement was observed, and the treat-

5. Effect of xylanase action on the reduction of kappa number (taken after the (CD)E stage). The starting kappa number was 13.2 for the control pulp and 11.2 for the xylanase-treated pulp.



6. Effect of xylanase pretreatment on the viscosity of (CD)EDED-bleached pulp



ment permitted bleaching to high brightness (90% ISO) at Cl_2 levels equivalent to 80% ClO_2 substitution without xylanase pretreatment. In addition, the ClO_2 level needed to obtain the target brightness was even less than if 10% ClO_2 substitution was in place.

The results suggest that mills using xylanase could operate under conditions equivalent to 80% ClO_2 substitution while employing at least 33% less ClO_2 . This valuable reduction in bleach chemical requirement would also have a major impact on AOX and dioxin reductions and would help improve the cost efficiency of mill operations. Xylanase use would therefore allow hardwood bleach plants currently producing ClO_2 for 10% substitution to reduce chlorine requirements by 80% or more without creating any additional need for major capital investment in facilities to generate chlorine dioxide or other oxidizing chemicals.

The order of addition of Cl_2 and ClO_2 during the first bleaching stage was found to be important when bleaching xylanase-treated pulps. With respect to total bleach chemical requirements, the addition of Cl_2 prior to or simultaneously with ClO_2 in the chlorination stage using 40% ClO_2 substitution was more effective than when ClO_2 was added before Cl_2 .

Xylanase pretreatment permitted pulps of very high brightness of 91–

92% ISO to be prepared using the conventional bleach sequence (CD)EDED. The chlorine multiple could be reduced to 0.10 for pulp bleached to 91% ISO and to 0.15 for pulp bleached to 92% ISO. Xylanase-treated pulps bleached to 92% ISO brightness using 10% ClO_2 substitution showed no indication of a brightness ceiling when bleached at 0.15 chlorine multiple. The resulting pulps had better viscosities than the nonxylanase-treated control pulps. ▮

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