

Xylanase treatment for the bleaching of softwood kraft pulps: the effect of chlorine dioxide substitution

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ABSTRACT: *The effectiveness of xylanase treatment of softwood pulps in bleaching to high brightness is influenced by the degree of chlorine dioxide substitution used in the bleach sequence and by the final target brightness that is to be achieved. In a standard (CD)EDED sequence, xylanase treatment reduced chlorination-stage charges at all substitution levels examined, but was particularly effective at 100% substitution (DEDED sequence). Up to 40% reduction in AOX can also be achieved. Organic halide content of pulps was only marginally improved by xylanase treatment. Xylanase treatments also raise the brightness ceiling of fully bleached pulps. Therefore, the use of xylanase in pretreatment of pulps bleached using (CD)EDED type sequences to > 91% ISO brightness becomes attractive. These brightnesses can be realized using lower chlorine multiples than the controls and with lower chlorine dioxide substitution.*

KEYWORDS: *Adsorbable organic hydrogen, brightness, chemical consumption, chlorine dioxide, kraft pulps, pretreatment, processes, sequences, softwood pulps, substitutes, xylanase.*

Enzyme use in pulp bleaching has rapidly evolved from a laboratory curiosity to an effective method of chemical reduction in pulp mills. Xylanase treatment of pulps was first demonstrated to reduce bleaching chemical requirements in comparison to untreated pulps in 1986 (1). Soon thereafter, the biobleaching effect was confirmed in pulps bleached to lower

brightnesses (2-4) and higher market pulp brightnesses (5-10). Many mill trials have been run worldwide and enzymes are now in full time use in several mills.

When cellulase-free xylanases have been applied to pulps, reductions in bleach chemical requirements have been concomitant with nominal improvements in viscosity (4, 6, 9) and

paper properties such as beatability (4, 11), tear strength and brightness (4, 7). Reduction in chlorine usage has also been shown to lower substantially AOX levels in effluents (10, 12) and the organic halide content (OX) level in hardwood pulps (10). Chlorinated dioxin levels have also been shown to be reduced in mill trials (12) after xylanase use.

Despite numerous reports describing the biobleaching effect and mill trial results, there have been comparatively few studies conducted that attempt to identify interactions of enzyme use with traditional bleaching chemistry. Recently we demonstrated that xylanase treatment raises the brightness ceilings of fully bleached hardwood (9) and softwood (10) pulps and that the percent of substitution of chlorine dioxide for chlorine has an effect on the success of the xylanase treatment (9) in hardwood pulps.

In this report, we have examined how the degree of chlorine dioxide substitution in a traditional bleaching sequence affects the overall success of xylanase treatment in softwood pulps. The importance of choosing appropriate levels of substitution and brightness targets is discussed.

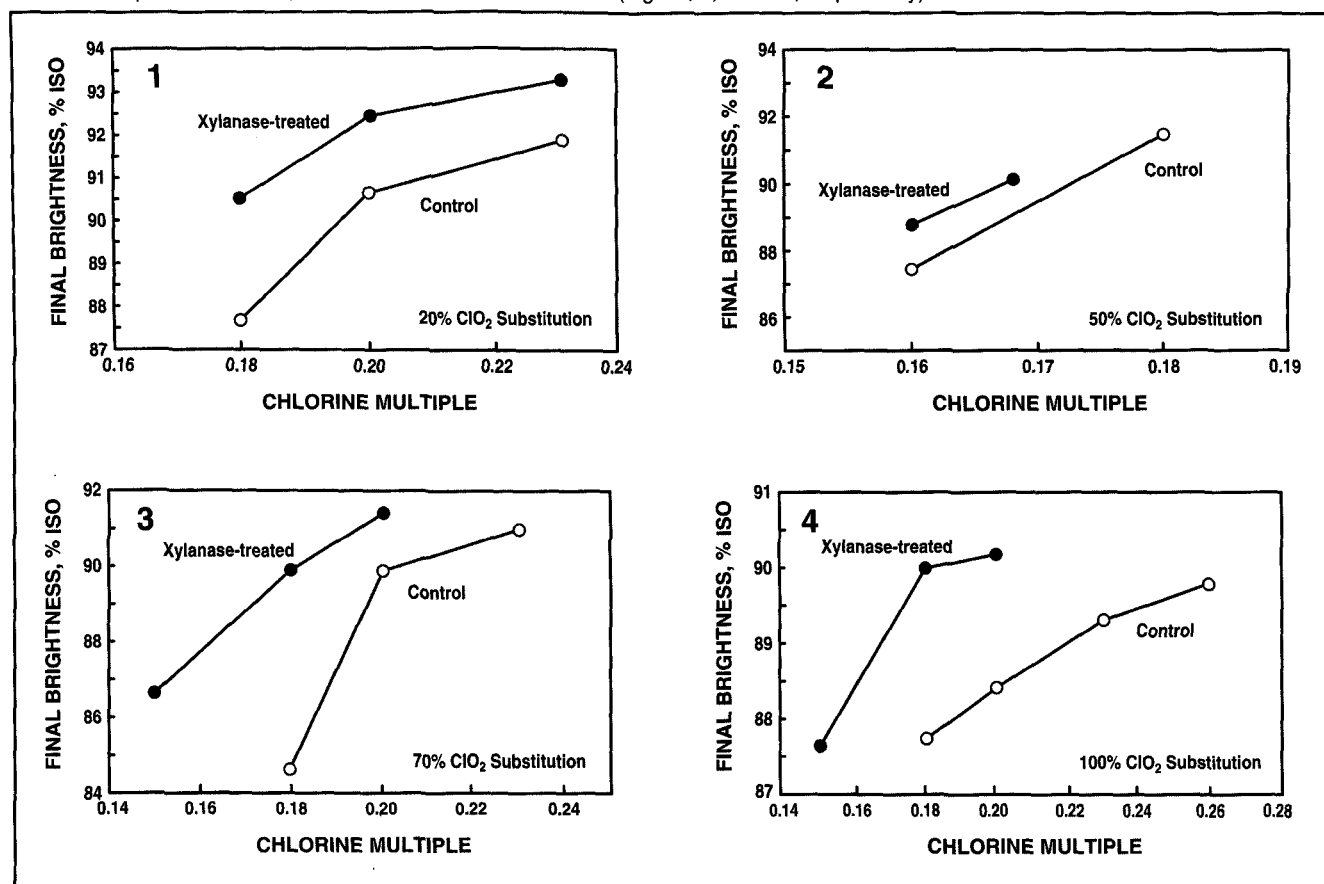
Experimental

Preparation of xylanase enzyme

Cellulase-free xylanase enzyme was supplied by R. L. Bernier, ICI BioProducts and Fine Chemicals. The microbial source was *Streptomyces lividans* [pIAF 20] and conditions for

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1-4. Effect of xylanase pretreatment on biobleaching of softwood pulps. Xylanase-treated and control pulps were bleached over a variety of chlorine multiples and at 20%, 50%, 70% and 100% substitution (Figs. 1, 2, 3 and 4, respectively).



production and assay of enzyme activity were as previously described (9).

Xylanase treatment of pulps

All xylanase treatments were carried out on 300-g batches of softwood brownstock pulp (kappa number 28.8) supplied from an Eastern Canadian mill. Treatments were conducted in a Quantum Mark II Reactor® at a consistency of 12%. Pulp was adjusted to a pH between 5.5 and 6.5 by addition of 1 N sulfuric acid. Enzyme was added at a dose of 5 international units (IU)/g (ovendry basis), pulp/enzyme mixture was mixed for 2 min. Pulp temperature was maintained at 50°C throughout the entire 2-h reaction. Following this treatment, unwashed pulps were subjected to bleaching experiments. Control pulps were similarly prepared but with enzyme solution being replaced with water. Kappa numbers of xylanase-treated and control pulps

were 27.4 and 28.3, respectively. All measurements of kappa number, brightness and residuals were performed according to TAPPI and CPPA Technical Section procedures.

Bleaching experiments

Control and xylanase-treated pulps were subjected to a standard (CD)EDED bleaching sequence in which the percent of substitution of ClO₂ for Cl₂ was varied from 20% to 100%. During the chlorination stage (C stage), pulp consistency was adjusted to 3.5% and the chlorination reaction, using 100 g (o.d.) samples, was carried out in a stirred vessel at 40°C for 30 min. Chlorine multiples were as specified in figures and tables. At 20% substitution, Cl₂ and ClO₂ were premixed in aqueous solution, prior to addition to the pulp (sequence: (C+D)EDED). For pulps bleached at 50% and 70% substitution, chlorine di-

oxide was applied 30 s and 60 s, respectively, prior to chlorine addition (sequence: (DC)EDED). For pulps bleached with 100% ClO₂ substitution, 50-g samples were treated in Mason jars and a temperature of 50°C was maintained (sequence: DEDED).

Following the C stage, pulps were washed with stirring at 1% consistency and suction filtered. A caustic extraction was carried out immediately following the wash. Pulp and sodium hydroxide (3% on pulp) were mixed in a Hobart mixer at 10% consistency. Extraction was conducted for 1 h at 70°C in polyethylene bags and a filtration and washing stage (as above) was done immediately after extraction.

A D₁ stage was conducted on 20-g pulp samples in sealed glass Mason jars. Chlorine dioxide, at specified charges, was injected into the pulp sample with a large bore syringe. Typically, caustic soda was also added to

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maintain a pH of 3.8–4.3. Temperature of the D_1 stage was held at 70°C for 3 h and a pulp consistency of 6% was used. Pulps were then filtered and washed, as above. A second extraction stage (E_2), followed by another chlorine dioxide stage (D_2), was performed using a caustic charge of 0.4% and chlorine dioxide charge of 0.2%. Pulps were filtered, washed and brightness sheets were made.

In addition, samples of the same xylanase-treated and control pulps were also bleached, as above, at 20% ClO_2 substitution. However, 0.3% H_2O_2 was included in the E_1 stage.

Effluent AOX and OX analysis

Samples of filtrates from all stages of pulp treatment were collected and mixed in appropriate volumes that reflected the contribution of each stage to the full sequence effluent. Adsorbable organic halogen contents (AOX) were determined using a Mitsubishi TOX-10 analyzer, following directions of the manufacturer. The aqueous samples were acidified to pH 2 with nitric acid prior to analysis. Samples of control and xylanase-treated pulps bleached to 90% ISO brightness were air dried, ground using a Wiley mill fitted with a No. 40 screen, and analyzed for organic halogen content following Papiertechnische Stiftung method PTS-RH 012/90.

Results and discussion

In our previous work, we examined the enhanced bleaching properties of xylanase-treated hardwood pulps (9, 10). This report is an extension of our earlier work where we now concentrate on the biobleaching effect in softwood kraft pulp. The intention of these studies is to optimize the conditions of enzyme treatment with the traditional chemistries used in the bleach plant.

The degree of ClO_2 substitution, used in the C stage, has been shown to have a significant effect on the final brightnesses of xylanase-treated hardwood pulps (9). In this work, we bleached xylanase-treated softwood

I. Pulps bleached at 20% ClO_2 substitution

(C+D)E		D_1				D_2		
Chlorine multiple	(C+D) Exit pH	D_1 ClO_2 charge, % on pulp	D_1 Exit pH	D_1 Residual, % on pulp	D_1 Brightness, % ISO	D_2 Exit pH	D_2 Residual, % on pulp	D_2 Brightness, % ISO
Control pulps								
0.18	1.9	1.2	3.4	0.01	74.6	3.9	0.04	87.6
		0.4	4.2	...	61.6	3.6	...	80.5
0.20	1.9	0.8	3.7	0.02	74.0	3.7	0.02	88.6
		1.2	3.6	0.04	83.4	3.9	0.04	90.6
0.23	1.9	0.4	3.8	0.01	67.5	3.5	0.02	86.7
		0.8	3.4	0.03	79.5	3.7	0.04	90.5
		1.2	3.8	0.08	85.8	3.8	0.08	91.8
Xylanase pretreated pulp								
0.18	2.0	0.4	3.9	...	56.6	3.5	...	72.9
		0.8	3.5	...	66.0	3.5	0.02	86.2
		1.2	3.6	0.01	78.2	3.7	0.04	90.4
0.20	2.1	0.4	3.4	...	66.7	3.5	0.02	88.2
		0.8	3.4	0.03	80.9	3.5	0.03	91.6
		1.2	3.5	0.14	87.3	3.6	0.06	92.4
0.23	1.9	0.4	3.4	0.01	71.1	3.5	0.07	90.2
		0.8	3.5	0.05	85.7	3.6	0.10	92.9
		1.2	3.4	0.15	89.2	3.7	0.17	93.2

II. Pulps bleached at 50% substitution

DC)E		D_1				D_2		
Chlorine multiple	DC Exit pH	D_1 ClO_2 charge, % on pulp	D_1 Exit pH	D_1 Residual, % on pulp	D_1 Brightness, % ISO	D_2 Exit pH	D_2 Residual, % on pulp	D_2 Brightness % ISO
Control pulps								
0.16	2.0	0.8	3.8	...	67.8	3.6	...	83.0
		1.2	3.7	...	75.6	3.6	...	87.4
0.18	1.9	0.8	3.5	0.01	81.6	3.6	0.02	90.3
		1.2	3.6	0.09	87.4	3.9	0.08	91.5
Xylanase pretreated pulps								
0.160	2.2	0.8	3.8	...	66.9	3.5	...	85.2
		1.2	3.6	...	76.4	3.5	0.02	88.7
0.168	2.2	0.8	3.8	0.008	69.6	3.5	0.02	86.4
		1.2	3.5	0.03	78.3	3.4	0.05	90.1

III. Pulps bleached at 70% ClO₂ substitution

(DC)E		D ₁				D ₂		
Chlorine multiple	DC Exit pH	D ₁ ClO ₂ charge, % on pulp	D ₁ Exit pH	D ₁ Residual, % on pulp	D ₁ Brightness, % ISO	D ₂ Exit pH	D ₂ Residual, % on pulp	D ₂ Brightness, % ISO
Control pulps								
0.18	2.0	0.4	4.3	0.06	51.9	4.6	0.02	68.3
		0.8	4.3	0.08	63.4	3.6	...	78.8
		1.2	4.4	0.08	72.1	4.2	...	84.6
0.20	2.0	0.4	4.3	0.04	66.0	3.8	...	83.2
		0.8	4.0	0.08	74.8	3.5	0.01	88.3
		1.2	4.1	0.08	81.7	3.6	0.02	89.9
0.23	1.6	0.4	4.3	0.03	74.8	3.6	0.02	87.6
		0.8	4.2	...	84.3	3.7	0.05	90.4
		1.2	4.0	0.15	86.8	4.1	0.05	91.0
Xylanase pretreated pulps								
0.15	2.4	0.4	4.5	...	57.2	4.3	<0.0001	73.2
		0.8	3.8	0.02	66.4	3.7	0.01	82.5
		1.2	3.9	0.12	75.1	3.8	0.02	86.6
0.18	2.1	0.4	4.3	0.03	62.7	3.8	...	79.1
		0.8	3.6	0.06	72.6	3.7	0.02	86.8
		1.2	3.7	0.16	80.2	3.6	0.03	89.9
0.20	2.0	0.4	4.2	...	71.4	3.5	...	85.2
		0.8	3.5	0.02	80.1	3.1	0.02	90.0
		1.2	3.6	0.03	85.7	3.3	0.07	91.4

pulps using a traditional (CD)EDED-type sequence to determine if the degree of ClO₂ substitution has an impact on the final brightness.

A comparison of xylanase-treated and control pulps bleached over a variety of chlorine multiples and at 20% substitution is shown in Fig. 1. Final brightness shown is determined after full sequence bleaching using the chemical charges previously stated. All figures reporting substitution data are plotted using a D₁ charge of 1.2% on pulp, in the bleaching sequence. Bleaching data are found in Tables I-IV.

As can be seen in Fig. 1, a reduction in C-stage charge of about 10% was achieved for full sequence bleaching of xylanase-treated pulp to 90% ISO brightness. More outstanding is an increase in the brightness ceiling of the xylanase-treated pulp of about 1.5 brightness units. This confirms our previous observations in hardwoods (9) and softwoods (10). The C-stage

chemical reductions for xylanase-treated softwood pulps at 20% ClO₂ substitution becomes more pronounced at higher brightnesses. Xylanase-treated pulp bleached, with 50% ClO₂ substitution to 90% ISO brightness, showed almost no difference in C-stage chemical requirements in comparison to the control (Fig. 2). The xylanase-treated pulp did have a slightly higher brightness at higher chlorine multiples than the control.

Xylanase-treated pulp, bleached using 70% ClO₂ substitution, was seen to have similar chemical savings, compared to the control, as pulp bleached at 20% substitution (Fig. 3). As was also the case for 20% substitution, the xylanase-treated pulp bleached at 70% substitution has greater chemical savings at higher chlorine multiples and indications of improved brightness ceilings were evident.

We found that control pulps bleached using 100% ClO₂ substitu-

tion required a substantially higher chlorine multiple to achieve a 90% ISO final brightness than control pulps bleached at lower substitution (Fig. 4). A multiple of about 0.26 was necessary and this is a typical charge used in a mill running at 100% substitution. Interestingly, a xylanase pretreatment allowed bleaching to 90% ISO brightness to be obtained with a significantly reduced chlorine multiple of 0.18. The brightness ceiling of the xylanase-treated pulp was also improved in comparison to the control. However, the highest brightness ceiling improvements caused by xylanase treatment were observed at lower substitution levels.

A comparison of requirements of chlorine-based bleaching chemicals for xylanase-treated and control pulps, bleached with 20% to 100% chlorine dioxide substitution, is shown in Fig. 5. Control pulps and xylanase-treated required a minimum of bleaching chemicals at 50% substitution, and this reflects the synergistic effect of Cl₂ and ClO₂ at this level of substitution, first reported by Rapson and Anderson in 1966 (13). A higher C-stage total applied chlorine charge (TAC) was needed to bleach to 90% ISO using 100% substitution. Using 90% ISO brightness as a target, the difference in TAC charges between the xylanase-treated and control pulps bleached at 20%, 50%, and 70% substitution was marginal. This was somewhat surprising as our previous work on hardwoods suggested that significant savings in TAC charges could be achieved and that xylanase-treated hardwood pulp was more easily bleached at low rather than high substitution (Fig. 6).

Very little difference in bleach chemical requirements was observed between xylanase-treated and control pulps bleached with 50% ClO₂ substitution to 90% ISO brightness. Conversely, a significant reduction in C-stage charge was observed for xylanase-treated pulp bleached with 100% substitution. The chlorine multiples required to bleach xylanase-treated and control softwood pulp to 90% ISO brightness (Fig. 4) and the

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net chemical reduction (Fig. 5) are identical to those recently reported in a mill trial at Canadian Forest Products Limited (Canfor) (14). These data suggest that use of xylanase for the bleaching of softwoods to 90% ISO brightness will be most advantageous at 100% ClO_2 substitution.

A reduction in chlorine-based bleaching chemicals, resulting from xylanase treatment, was expected to bring about reductions in AOX in effluents. AOX levels in full bleach sequence effluents were determined for control and xylanase-treated pulps bleached to 90% ISO. In Fig. 7, it is seen that AOX levels are directly proportional to the level of ClO_2 substitution. Xylanase-treated pulps bleached at 20% and 70% ClO_2 substitution have slightly lower AOX levels than their controls, and this small reduction appears to parallel the reduction of chlorine multiple that was observed. At 100% ClO_2 substitution, the extent of AOX reduction in effluent for xylanase pretreated pulp is about 40%. The absolute levels of AOX for xylanase-treated and control pulps (0.62 and 1.04 kg/metric ton of pulp, respectively) agree well with the levels of AOX reported in the Canfor mill trial that was conducted under similar bleaching conditions (14).

Levels of organic halogens (OX) bound to the pulp were also determined. As is seen in Fig. 8, OX content drops with increasing substitution of chlorine dioxide for chlorine during bleaching. Xylanase-treated pulps had only slightly reduced OX contents in comparison to the controls. Our previous work has shown that greater reductions in OX content in hardwood pulps could be achieved with xylanase treatment (10).

When bleaching with 20% ClO_2 substitution, we have seen that marginal chemical savings can be achieved for xylanase-treated pulps, when 90% ISO brightness is the target. However, the improvements in the brightness ceilings of xylanase-treated pulp mean that the chemical reductions become more substantial at higher brightness targets. These reductions would be expected to result in greater reduction in AOX in effluents.

IV. Pulps bleached at 100% ClO_2 substitution

DE		D ₁				D ₂		
Chlorine multiple	D Exit pH	D ₁ ClO ₂ charge, % on pulp	D ₁ Exit pH	D ₁ Residual, % on pulp	D ₁ Brightness, % ISO	D ₂ Exit pH	D ₂ Residual, % on pulp	D ₂ Brightness, % ISO
Control pulps								
0.18	2.5	0.4	4.7	0.04	62.2	4.1	...	79.4
		0.8	4.3	0.08	74.3	4.2	0.01	85.4
		1.2	4.3	0.26	78.4	3.6	0.01	87.7
0.20	2.4	0.4	4.8	0.08	65.3	3.7	0.02	81.5
		0.8	3.9	0.08	76.4	3.6	0.02	87.1
		1.2	3.9	0.11	79.0	3.5	0.05	88.4
0.23	2.3	0.4	4.6	0.08	67.8	3.7	0.02	83.6
		0.8	4.1	0.07	78.7	3.6	0.03	88.4
		1.2	4.0	0.12	82.4	3.8	0.05	89.3
0.26	2.7	0.4	4.3	0.05	73.4	3.5	...	85.6
		0.8	3.7	0.06	80.6	3.7	...	89.2
		1.2	3.8	0.08	82.4	3.4	0.02	89.8
Xylanase pretreated pulp								
0.15	2.9	0.4	4.9	...	61.2	3.7	...	71.3
		0.8	4.1	0.01	74.1	3.6	...	86.2
		1.2	4.4	0.19	77.1	3.7	0.02	87.6
0.18	2.7	0.4	4.3	0.10	70.4	4.1	...	83.0
		0.8	3.8	0.08	78.7	3.5	0.01	87.8
		1.2	4.3	0.10	82.8	3.4	0.03	90.0
0.20	2.6	0.4	4.3	0.06	73.1	3.5	...	84.6
		0.8	3.8	0.04	80.4	3.6	0.04	89.1
		1.2	4.3	0.12	84.4	3.4	0.07	90.2

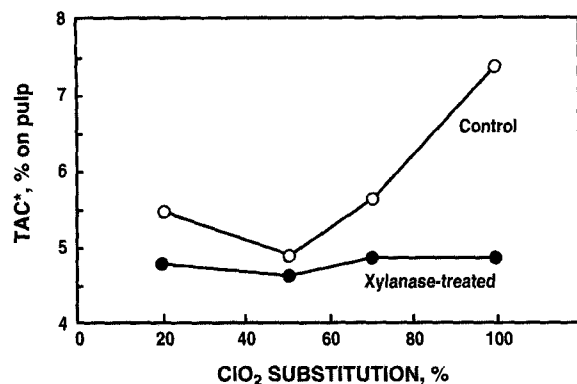
A sample of pulp was bleached as described above, at 20% ClO_2 substitution using the sequence (C+D)EpDED. Samples of effluents were collected and mixed after the full bleaching sequence and AOX levels were determined. The levels of AOX are shown in Fig. 9 for xylanase-treated and control pulps. To achieve 91% ISO brightness in the control, a high chlorination stage charge of 6.3% (chlorine multiple 0.22) was needed, in comparison to 5.2% (chlorine multiple 0.18) for the xylanase-treated pulp. Levels of AOX for these two pulps were 6.1 and 3.8 kg/te pulp, respectively. This 38% reduction in AOX suggests that xylanase use, with low chlorine dioxide substitution, provides a benefit during bleaching when higher brightnesses are targeted.

Summary

The degree of substitution of chlorine dioxide for chlorine and the final target brightnesses are major factors affecting the success of xylanase treatment in softwood pulp bleaching. Ultimately the successful use of xylanase will be mill specific and these factors must be considered.

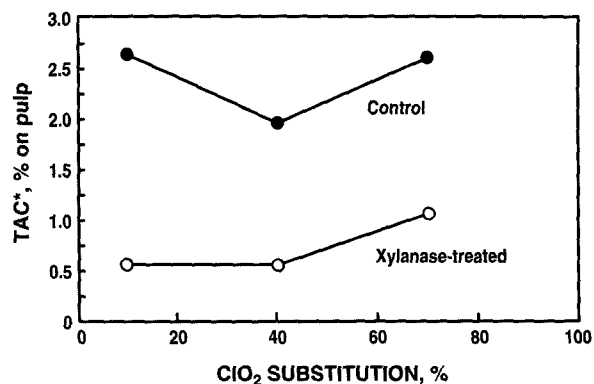
When 90% ISO brightness is the goal, bleaching of xylanase-treated softwood pulp using 20%, 50% or 70% ClO_2 substitution results in marginal reductions in chemicals, in comparison to controls. However, a significant reduction in bleaching chemicals was achieved for xylanase-treated pulp bleached at 100% substitution. In a similar manner, reductions in AOX in effluents of xylanase-treated pulps bleached with 20–70% ClO_2 substitu-

5. Effect of ClO_2 substitution on xylanase-treated softwood pulps. The effect of ClO_2 substitution on C-stage total applied chlorine requirements (TAC) is summarized for bleaching of xylanase-treated and control softwood pulps to 90% ISO brightness.



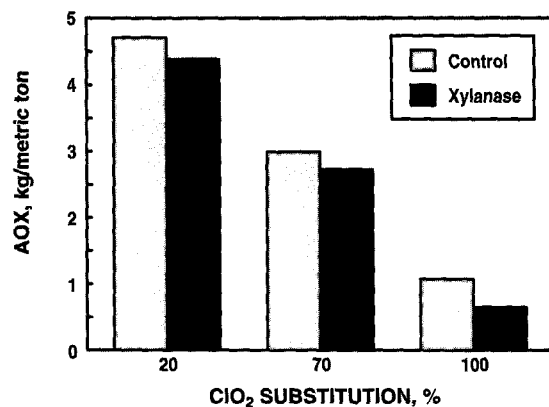
*TAC charges as chlorine equivalents in C-stage

6. Effect of ClO_2 substitution on xylanase-treated hardwood pulps. Target brightness 90% ISO (9).

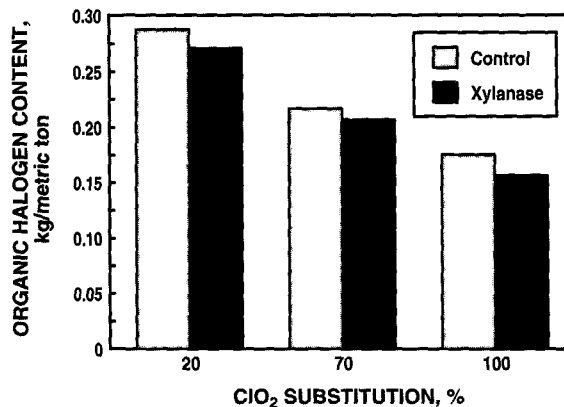


*TAC charges as chlorine equivalents in C-stage

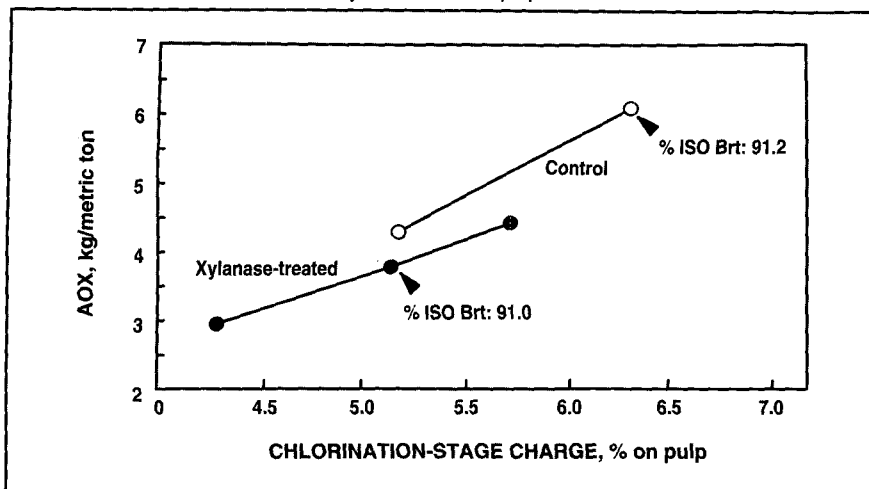
7. AOX in effluents of xylanase-treated pulps bleached to 90% ISO brightness.



8. Organic halide contents (OX) of xylanase-treated pulp bleached to 90% ISO brightness.



9. Reduction in AOX in effluents of xylanase-treated pulp



tion were only slightly reduced, whereas a 40% reduction in AOX was achieved when 100% substitution was used. Organic halide contents of the pulps were only slightly reduced.

The use of xylanase treatments in bleaching of softwood pulps is not necessarily limited to high ClO_2 substitution. The ability of xylanase treatment to increase brightness ceilings also has a positive effect on the success of the treatments, when lower levels of ClO_2 substitution are being used. For brightness targets greater than 91% ISO, the bleaching chemical charge

reductions for xylanase-treated pulp become much more pronounced. Similarly, AOX levels in xylanase-treated pulps are substantially lowered. **[7]**

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The authors would like to thank Janine Gayton for her skillful preparation of this manuscript and Jennie Kirby for AOX/OX analyses.

Received for review July 20, 1992.

Accepted Nov. 16, 1992.

Presented at the TAPPI 1992 Pulping Conference.