

# Medium-consistency ozone bleaching with enzyme pretreatment

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**ABSTRACT:** *Several elemental chlorine-free bleaching sequences with ozone and low levels of chlorine dioxide were evaluated. The sequences focused on medium-consistency ozone bleaching with xylanase pretreatment. Oxygen-delignified softwood kraft pulp was bleached with either ZED or XZED sequences. Brightness, viscosity, and kappa number were determined and effluent characteristics evaluated. The use of xylanase pretreatment resulted in significant brightness gains and kappa number reduction. This reduction in kappa number can also be used to decrease the ozone charge.*

**KEYWORDS:** *Chlorine free bleaching, chlorine compounds, medium consistency, multistage process, ozone bleaching, pretreatment, xylanase.*

The paper industry today is facing a number of environmental constraints that are requiring it to re-examine its production processes to minimize environmental impact. Two matters of current concern are reducing the volume of effluent released into receiving waters and the amount of chlorinated organics produced in the bleach plant.

Elemental chlorine free (ECF) and total chlorine free (TCF) bleaching sequences have been suggested to address both of these problems. TCF bleaching permits recycle of

the bleach plant effluent to the kraft recovery cycle, thus avoiding the production of chlorinated organics and reducing the volume of effluent sent through the wastewater treatment system. ECF bleaching still allows the use of chlorine dioxide, but the amount of chlorinated organics produced is dramatically reduced.

Enzyme treatment has been proposed (1, 2) as a means to reduce the amount of chemicals used in ECF and TCF bleaching while retaining acceptable pulp properties. Other advantages of enzyme pretreatment

are minimal capital cost, improved bleachability of pulp, and a reduced amount of AOX, adsorbable organic halides, discharged to the wastewater treatment plant.

There are two ways the enzyme is proposed to work (1). First, the enzyme may degrade xylan which is in the fiber pores, thus preventing the free flow of bleach chemicals into the fiber and the transfer of lignin degradation products out of the fiber. Second, the enzyme may cleave lignin-carbohydrate bonds, releasing lignin into the bulk solution where it does not require bleach chemicals for removal.

Recent work using the EnZone (enzyme + ozone) process has shown that pulp can be bleached to 90+ brightness (3). This process utilizes a high-consistency (40%) ozone bleaching system to evaluate TCF bleaching sequences. The pulp is reported to have better brightness reversion characteristics, and the process can increase the brightness ceiling by 10 points for a softwood kraft pulp.

The objective of the research reported herein was to evaluate ECF bleach sequences using hemi-cellulase enzyme pretreatment and ozone at medium consistency (10%).

## Methods and materials

### Pulp sample

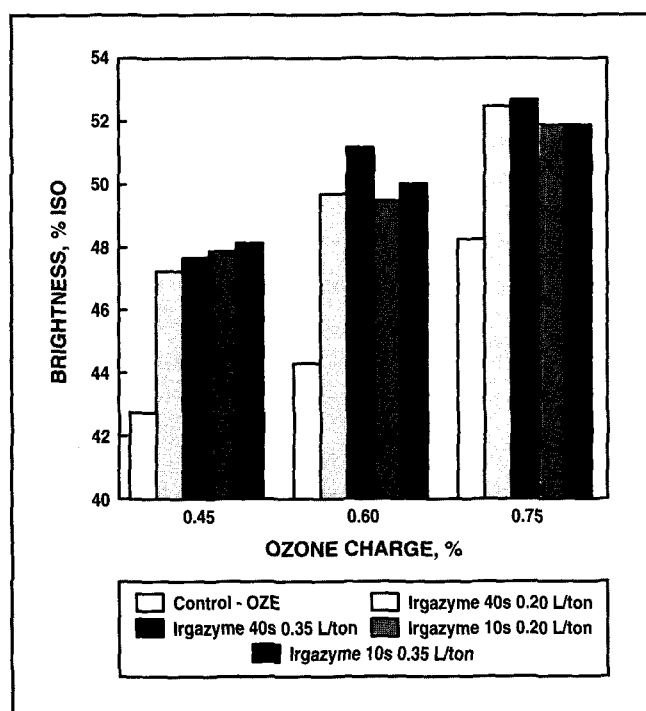
The pulp used for this experiment was an oxygen-delignified softwood

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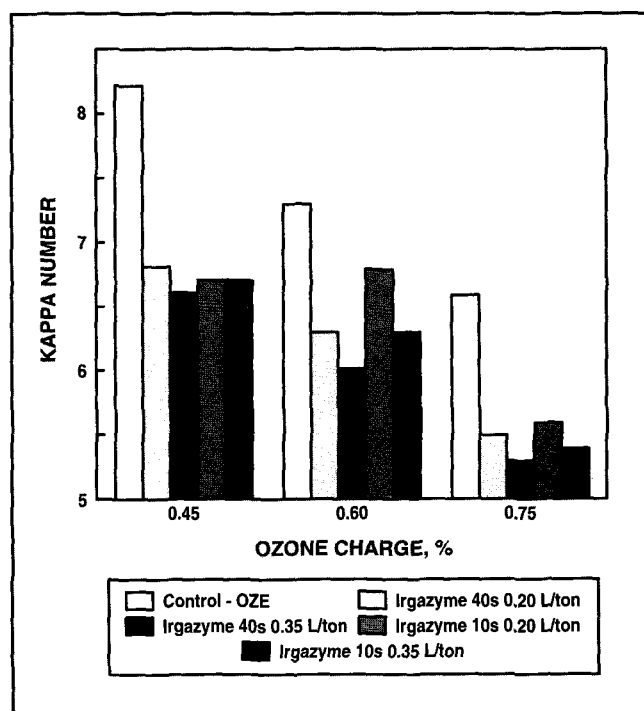
## I. Experimental conditions for bleaching stages

| Bleaching stage | Consistency, % | Temp., °C | Time, min | pH                       | Chemical addition                                                   |
|-----------------|----------------|-----------|-----------|--------------------------|---------------------------------------------------------------------|
| X               | 10             | 50        | 60        | 7.0-7.5<br>or<br>5.5-6.0 | 0.2 and 0.35 L/ton<br>H <sub>2</sub> SO <sub>4</sub>                |
| Z               | 10             | 50        | 1         | 2.0                      | 0.45%, 0.6%, or 0.75%<br>H <sub>2</sub> SO <sub>4</sub>             |
| E               | 10             | 70        | 60        | 12.0-12.5                | 1.5% NaOH                                                           |
| E <sub>OP</sub> | 10             | 70        | 60        | 11.5-12.0                | 1.5% NaOH, 1% H <sub>2</sub> O <sub>2</sub> , 20<br>min @ 30psi     |
| D               | 10             | 70        | 180       | 3.0-3.5                  | 1.0%, 1.25%, 1.5% ClO <sub>2</sub><br>0.5% NaOH of ClO <sub>2</sub> |

### 1. Effect of ozone on brightness after OXZE



### 2. Effect of ozone on kappa number after OXZE



kraft from a mill in the southeastern United States. The brownstock characteristics were kappa number 14.9, brightness 31.4% ISO, and 17.8 cP CED viscosity.

### Bleaching stages

The six bleaching stages used in this experiment were: enzyme (X), ozone

(Z), extraction (E), peroxide-reinforced extraction (E<sub>OP</sub>) and chlorine dioxide (D). The operating conditions for the stages are shown in Table I. After the extraction stage, CED viscosity, kappa number, and brightness were measured. After the chlorine dioxide stage, CED viscosity and brightness were measured.

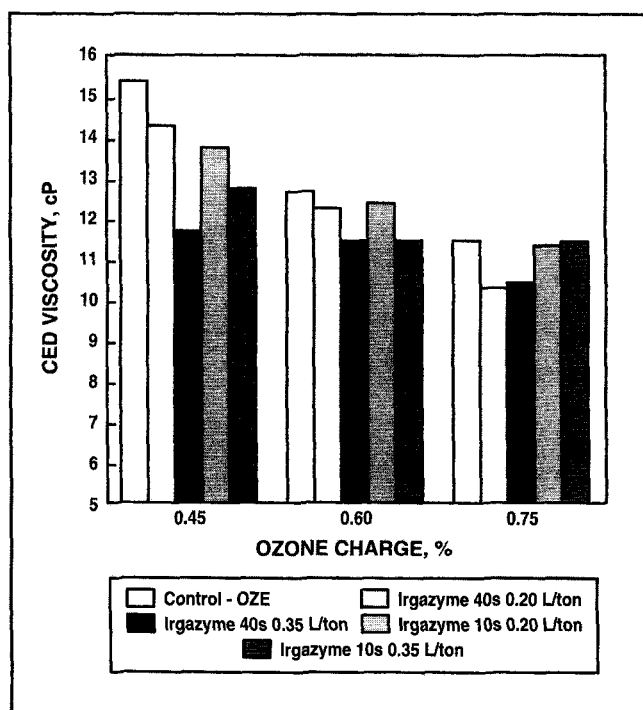
### Enzyme pretreatment

Enzyme pretreatment was done with two enzymes, Irgazyme 40s and Irgazyme 10s, on oxygen-delignified softwood kraft pulp. The Irgazyme 40s is derived from the fungus *Trichoderma longibrachiatum*. The xylanase activity was determined with RBB blue xylan-AZO-birchwood to be approximately 4000

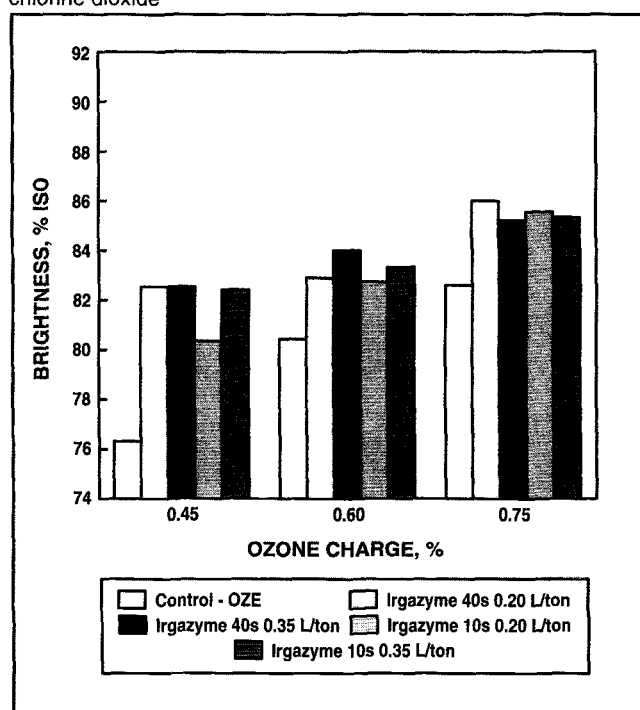
## II. Bleaching results from OZE<sub>OP</sub> and OXZE<sub>OP</sub> sequences

| Sequence           | Ozone charge, % | Enzyme charge, L/ton | Brightness, %ISO | CED viscosity, cP | Kappa no. |
|--------------------|-----------------|----------------------|------------------|-------------------|-----------|
| OZE <sub>op</sub>  | 0.45            | 0                    | 50.7             | 9.0               | 7.2       |
| OXZE <sub>op</sub> | 0.45            | 0.2                  | 54.5             | 9.0               | 6.0       |

3. Effect of ozone on viscosity measured after OXZE



4. Effect of ozone on brightness after OXZED, 1.5% charge of chlorine dioxide



X.A.U./mL. The pH was controlled with sulfuric acid to 7.0 to 7.5 (Irgazyme 40s) or 5.5 to 6.0 (Irgazyme 10s). After each bleach stage, effluent was collected and the pulp was thoroughly washed. The enzyme was charged at levels of 0.2 and 0.35 L/ton of o.d. pulp. Treatment took place at 50°C for 1 h.

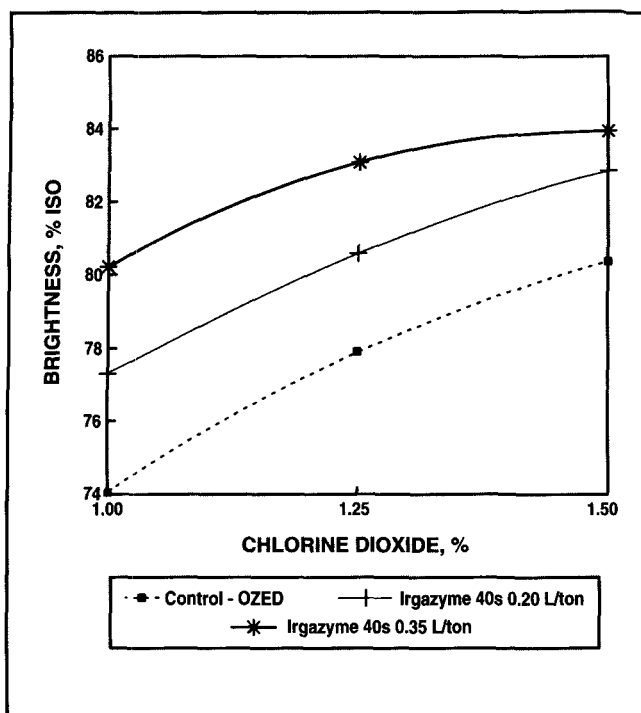
### Ozone bleaching

The ozone bleach stage was performed in a Quantum high shear mixer. Ozone gas was produced with a Polymetrics Laboratory Ozonator (Model T-816) from pure, dry oxygen. The ozone concentration was monitored with a PCI control system (Model HC-NEMA12). The gas

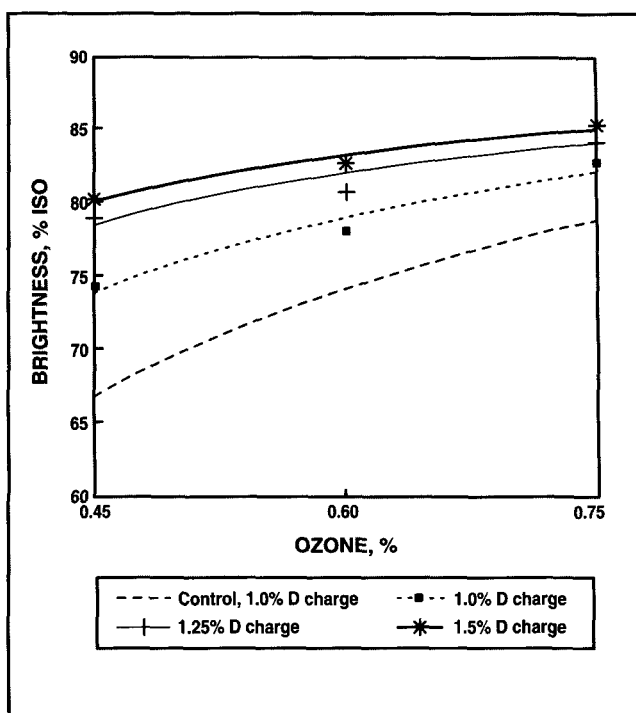
was compressed to 125 psi and charged to the mixer. Mixing was carried out for 15 s and a 1 min reaction time was allowed. The gas was then released into a potassium iodide solution to measure the residual concentration of ozone. This procedure was done 3 or 4 times to achieve the desired ozone charge.

## ECF Bleaching

5. Effect of enzymes on brightness after OXZED, 0.6% charge of ozone



6. Effect of ozone on brightness after OXZED, xylanase charge at 0.2 L/ton, no enzyme charge in control



### Characterization of pulp properties

Kappa number and viscosity were both determined. The viscosity was measured following the capillary viscometer method, TAPPI T 230 om-89. The kappa number test was done by the microprocedure TAPPI T 236 cm-85. The only optical property measured was brightness, which was measured on all pulps after the extraction and chlorine dioxide bleach stages. The brightness procedure followed was TAPPI T 535 om-86.

### Effluent characterization

The effluent from the bleaching stages was monitored. For the chlorine dioxide bleaching stage, all effluent samples were tested for residual chemical and pH. Color was monitored with the spectrophotometric determination recommended by NCASI (Bulletin No. 253). The chemical oxygen demand (COD) (4), was also measured.

### III. Effluent characteristics\*

| Sequence | Enzyme charge, L/ton | Color, Pt-Co units | COD, kg/o.d.ton |
|----------|----------------------|--------------------|-----------------|
| OZE      | 0                    | 1615               | 2.4             |
| OX*ZE    | 0.20                 | 1500               | 2.6             |
| OXZE     | 0.35                 | 1500               | 2.4             |
| OZED     | 0                    | 170                | 2.3             |
| OXZED    | 0.20                 | 150                | 2.2             |
| OXZED    | 0.35                 | 150                | 2.1             |

\*Irgazyme 40s used throughout these experiments

### Results

#### Effects of xylanase treatment and O<sub>3</sub> on O<sub>2</sub>-delignified kraft pulp

Enzyme pretreatment was done on the oxygen-delignified pulp. The treatment resulted in increased kappa number reduction and higher brightnesses. The lower kappa number after the extraction stage can also be used to decrease the ozone charge without sacrificing brightness.

Figures 1 and 2 show the effect of ozone charge on brightness and

kappa number after OXZE bleaching at different charges of enzyme. The values are compared to a control pulp after an OZE bleaching sequence. The data show that enzyme treatment can increase brightness by 4-6 points at the ozone charges studied. A decrease in kappa number was also measured with the xylanase pretreatment. On average, the kappa number decreased 15% with 0.20 L/ton enzyme addition and almost 20% with 0.35 L/ton addition. The reduction in kappa number can be attributed to better delignification through enzyme treatment.

The effect of the two enzymes at dosages of 0.2 L/ton and 0.35 L/ton on brightness after the E stage were studied (Fig. 1). Comparison of the Z(E<sub>op</sub>) and XZ(E<sub>op</sub>) showed similar benefits for brightness increase and kappa number reduction with the enzyme pretreatment (Table II). Overall results show that the treatment of pulp with enzyme improved the bleachability of the pulp, allowing subsequent bleaching chemicals to perform more effectively.

Figure 3 indicates the effect of ozone charge on viscosity at different levels of enzyme addition. The viscosities of the enzyme-treated pulps are compared to a control bleached with OZE. The viscosity loss is less than 10% for all enzyme-treated pulps, with some samples showing almost no loss at all. The viscosity decreased with increasing ozone charge (5) at all levels of enzyme application.

The brightness gains obtained with xylanase pretreatment were maintained after a chlorine dioxide bleaching stage (Fig. 4, OZED vs OXZED). A brightness increase of 3 points was measured at the low xylanase dosage (0.2 L/ton). Increasing the dosage to 0.35 L/ton increased the brightness by 6 points as compared to the controls. Maximum brightness of 86% ISO was reached. Figure 5 compares the gains in brightness that can be achieved at two different xylanase dosages. Thus, the enzyme pretreatment can result in higher brightness levels after subsequent bleaching stages.

Chemical savings can be realized in either the ozone stage or the chlorine dioxide stage (Fig. 6). The data show that enzyme treatment can allow reductions in ozone charge up to 0.3% on o.d. pulp while maintaining the same brightness. This is equivalent to a 40% reduction in chemical charge which will result in a higher viscosity, due to the decrease in the ozone charge.

The results of the effluent analysis indicate generally that the color of the effluent samples is lower with enzyme pretreatment than without it (Table III). After the extraction stage, which has the highest color load, there are decreases in color of from 2% to 11% in the enzyme-pretreated pulp. Considering that the coefficient of variation in the COD test may be up to 10% (4), the control (OZE and OZED) effluent CODs are generally comparable with enzyme treated pulp effluents.

## Summary

There are a number of benefits that are obtainable with enzyme pretreatment. The results from the three different enzyme bleaching sequences show that the treatment follows the same trends. There is an increase in brightness ceiling and a

reduction in kappa number with some loss in viscosity. By comparing results of the different bleaching sequences, a large reduction in chemical consumption when enzyme pretreatment is employed could be realized in all of the sequences. ■

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Received for review Nov. 3, 1993.

Accepted March 28, 1994.