

## Nonchlorine bleaching of pulp produced by the modified continuous cooking process

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**ABSTRACT** *The modified continuous cooking (MCC) process is a process that produces pulps of high viscosity suitable for oxygen delignification. MCC, oxygen-delignified, bleached pulps were prepared using bleaching sequences with and without chlorine, using a four-stage sequence of (C+D)(EO)DD. When hydrogen peroxide was added in the EO stage, brightnesses as high as 91% ISO were obtained. At 100% substitution of chlorine dioxide for chlorine in the first stage, the extra chemical costs for D(EOP)DD bleaching are estimated to be about \$10/ton. AOX is less than 1.0 kg/ton in the effluent before external treatment, chlorinated phenols are 98% eliminated, and the dioxin content of the bleached pulp is close to the limit of detection.*

### KEYWORDS

Bleaching  
Chlorination  
Chlorine dioxide  
Environmental control  
Hydrogen peroxide  
Kraft pulp  
Oxygen delignification  
Strength properties

In recent years, numerous studies have been carried out for the purpose of reducing the use of chlorine in bleaching. A number of methods have been suggested and evaluated, like extended delignification, oxygen delignification, low-chlorine-multiple bleaching, and high substitution of chlorine dioxide for elemental chlorine (1-11).

A brightness of up to 84-86% ISO is not too difficult to achieve. However, to produce market pulp of over 90% ISO on softwood without using chlorine requires extra effort in each stage of the whole fiber line, from cooking to final bleaching.

Here, we present a method to prepare fully bleached pulp of greater than 90% brightness, using modified continuous cooking, oxygen delignification, and a four-stage bleaching sequence—D(EOP)DD.

### Modified continuous cooking

The modified continuous cooking process (MCC) has been successfully introduced in the pulp industry during the last decade. Today, the method has been applied in about ten mills in Scandinavia, North America, and Japan (12-15).

The most important feature of MCC pulp is its high viscosity, about 100 SCAN units higher than that of conventional pulp at a given kappa number. This feature allows the reduction of the kappa number by 5-6 kappa units, while still preserving the potential pulp strength.

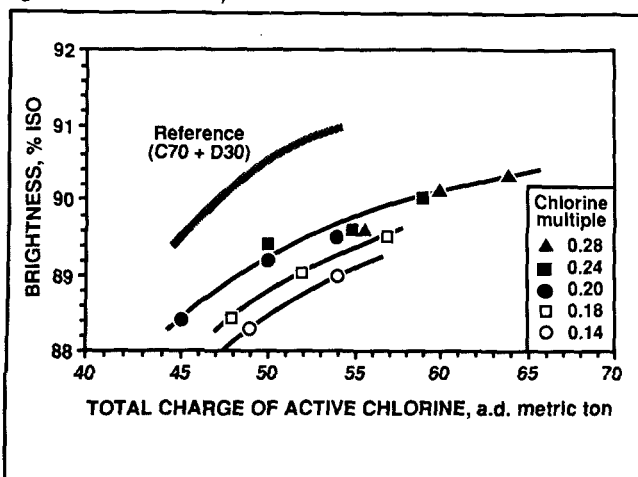
MCC pulp is therefore suitable for oxygen delignification. Oxygen pulps of kappa nos. 12-14 can be prepared using the MCC process. Using these pulps gives a better starting point for final bleaching than using a conventional oxygen-bleached pulp of kappa

nos. 18-20—or an unbleached pulp of kappa nos. 28-32.

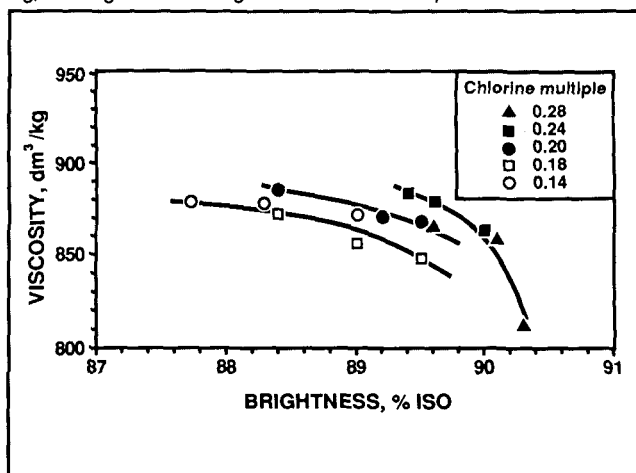
### Conventional bleaching of MCC pulp

We conducted a laboratory study to show the bleachability of MCC pulp. Oxygen-delignified pulp was bleached with a sequence of (C+D)(EO)DD using normal and low-multiple charges in the first stage and varying degrees of ClO<sub>2</sub> substitution. This first stage was carried out at medium consistency with a high-intensity mixer (16, 17). Chlorination at medium consistency is substantially more efficient than traditional low-consistency systems, reducing the chemical consumption by 15-20%. This is especially the case with a high degree of ClO<sub>2</sub> substitution in combination with sequential application (16).

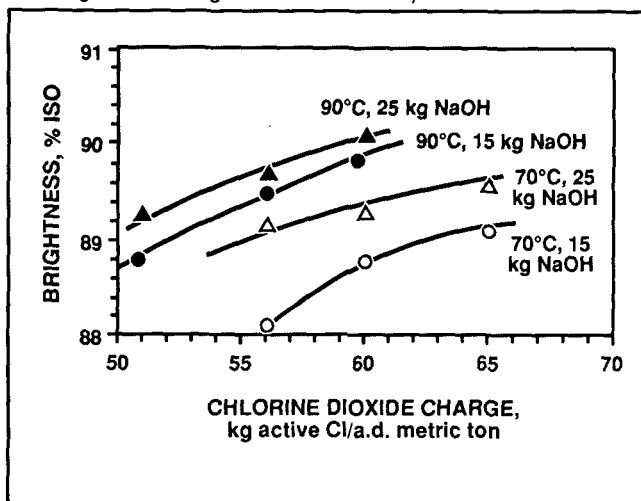
1. D(EO)DD bleaching: brightness development with varying charges in the first stage (Oxygen pulp. Kappa no. 13.3, washing losses of 9 kg COD/a.d. metric ton.)



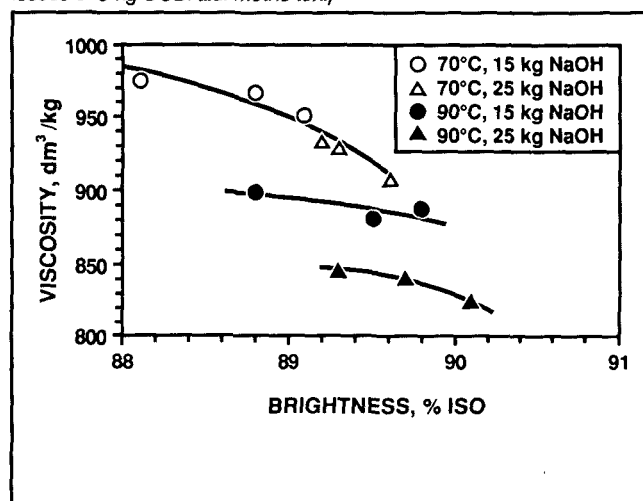
2. D(EO)DD bleaching: viscosity of bleached pulp with varying charges in the first stage (Oxygen pulp. Kappa no. 13.3, viscosity of 966 dm<sup>3</sup>/kg, washing losses of 9 kg COD/a.d. metric ton.)



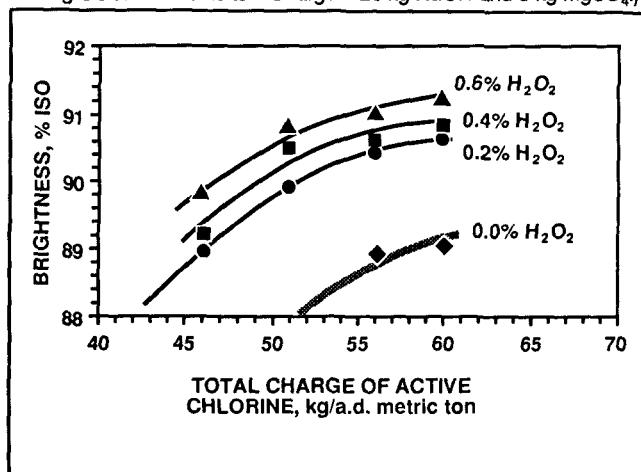
3. D(EO)DD bleaching: influence of temperature in the EO stage on the brightness development (Kappa no. 13.3, viscosity of 1049 dm<sup>3</sup>/kg, washing losses of 9 kg COD/a.d. metric ton.)



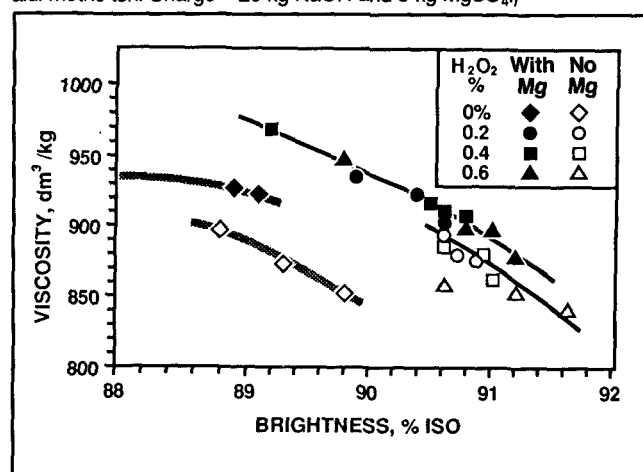
4. D(EO)DD bleaching: influence of temperature in the EO stage on viscosity (Oxygen pulp. Kappa no. 13.3, viscosity of 1049 dm<sup>3</sup>/kg, washing losses of 9 kg COD/a.d. metric ton.)



5. D(EOP)DD bleaching: influence of peroxide charge on the brightness development (Kappa no. 13.3, viscosity of 1049 dm<sup>3</sup>/kg, washing losses of 9 kg COD/a.d. metric ton. Charge = 20 kg NaOH and 5 kg MgSO<sub>4</sub>.)



6. D(EOP)DD bleaching: magnesium addition to the EO or EOP stage (Kappa no. 13.3, viscosity of 1049 dm<sup>3</sup>/kg, washing losses of 9 kg COD/a.d. metric ton. Charge = 20 kg NaOH and 5 kg MgSO<sub>4</sub>.)



When bleaching oxygen-delignified softwood pulp with a four-stage (C+D)(EO)DD sequence using normal 0.20 multiple and low  $\text{ClO}_2$  substitution, the total demand of active chlorine was about 62 kg/a.d. metric ton, of which 28 kg/a.d. metric ton was elemental chlorine. The calculated quantity of AOX (adsorbable organic halogens) is estimated to be about 3.0 kg/a.d. ton (3). Low-multiple chlorination in combination with 50%  $\text{ClO}_2$  substitution reduces the AOX quantity to some extent—to about 2.5 kg/a.d. ton. The positive effect of reducing  $\text{Cl}_2$  is slightly offset by a lower bleaching efficiency, leading to a larger consumption of total active chlorine.

## Chlorine-free bleaching

Everything mentioned so far represents results that can be obtained using today's technology. If elemental chlorine were totally excluded, what would be the impact on pulp quality and the environment?

### Pulp and procedure

We carried out a laboratory study using a mill MCC pulp on softwood of kappa no. 22.3, which was further oxygen delignified at medium consistency on a laboratory scale.

The oxygen pulp for the bleaching studies had a kappa number as low as 13, while its viscosity was maintained at more than 1000  $\text{dm}^3/\text{kg}$  (measured according to SCAN - C15:62).

The bleaching sequence was D(EO)DD, and we paid special attention to the conditions in the first two stages. As an alternative, peroxide was also added to the extraction stage (EOP).

### First stage

In normal chlorination, one way to reduce AOX is to use a low chlorine multiple. However, if no Cl is available for the first stage, there is basically no reason for this modification. Therefore, we studied the effect of varying the chemical charge on the overall efficiency of bleaching. This is expressed as the consumption of active chlorine in the whole sequence for obtaining a certain brightness.

Figure 1 shows the development of final brightness for bleachings using various charges in the first stage,

from a chlorination multiple of 0.14 (about 18 kg/a.d. metric ton) to 0.28  $\times$  kappa no. (about 36 kg/a.d. metric ton). The charges in the chlorine dioxide (D) stages were adjusted to aim at a final brightness of 90% ISO. The EO conditions were kept constant ( $90^\circ\text{C}$ , 20 kg NaOH/a.d. metric ton, and pressure = 5 bar). The low-multiple bleachings gave poorer results, and it was even difficult to achieve the brightness target of 90% ISO. An increased multiple, above 0.20  $\times$  kappa no., resulted in more satisfactory results, and 90% brightness was obtained. Still, (C+D) was more efficient than only D in the first stage.

High multiples also gave better viscosities, as Fig. 2 shows. About 860 SCAN units at 90% ISO was obtained, corresponding to a total viscosity reduction of about 100 SCAN units in the entire bleaching process.

Thus, for optimal use of chlorine dioxide, the charge in the first stage should be higher than normal. Low multiples on kappa number will give poorer results.

### The EO stage

The extraction stage must be especially reinforced to compensate for the absence of chlorine. In our study, it was actually modified to a medium-consistency oxygen stage with a pressure of 5 bar in gauge. This corresponds to the average pressure in a normal medium-consistency oxygen delignification system.

Some process parameters were studied, and the results are shown in Fig. 3. To obtain 90% ISO brightness, a temperature of  $70^\circ\text{C}$  and a hydrostatic pressure of 1.5 bar was not sufficient even with an excessive alkali charge of 25 kg. However, increasing the temperature to  $90^\circ\text{C}$  and the pressure to 5 bar improved the brightness.

Unfortunately, this brightness improvement results in an extra viscosity drop, as Fig. 4 shows, especially at a high alkali charge.

### The EOP stage

Peroxide gives a significant boost to the extraction stage (18, 19), even with small additions, as shown in Fig. 5. Brightnesses as high as 91% ISO were obtained in this way.

When comparing the chemical requirements for obtaining a certain

brightness, such as 89% ISO, it appears that EOP with only 0.2% peroxide requires about 12 kg less active chlorine, a remarkable effect. The high reduction is essentially explained by the flat slope of the curves in this brightness range.

### Adding magnesium to the EO or EOP stage

As mentioned, the viscosity drop in the reinforced extraction stage was unacceptably large. Addition of magnesium ions improves viscosity significantly, by 40–60 units as shown in Fig. 6.

The effect is approximately the same both for EO and EOP stages. A consequence of adding  $\text{MgSO}_4$  is that some extra alkali is required for precipitating  $\text{Mg}(\text{OH})_2$ . To some extent, this explains why the delignification appears to be retarded by magnesium.

### Chemical costs

Based on laboratory tests, we prepared bleached MCC pulps using bleaching sequences with and without chlorine. As a reference, a conventional pulp was also bleached. The pulps were used for evaluating quality, whereas the effluent waters were characterized according to their environmental impact.

The chemical charges and costs for various bleaching alternatives are given in Table I. For "conventional bleaching" of MCC pulp with 30% substitution, the total chemical cost is about \$21/ton (in U.S. dollars), or \$6.6/ton less than that of the conventional pulp. As expected, increasing the substitution to 100% is a more expensive alternative, with a cost of \$31/ton, an increase of about \$10/ton. However, compared with the conventional alternative, the extra cost is only \$3.4/ton. Thus, nonchlorine bleaching results in a significant but still reasonable increase in cost.

The extra heating cost for the elevated temperature in the EOP stage has to be included in the nonchlorine alternative. Of course, this energy requirement should be utilized for heat recovery.

### Pulp quality

The bleached pulps were PFI beaten and tested for strength. Table II shows strength data for the pulps. Because the viscosities, yields, and

carbohydrate compositions of the pulps were the same, no significant difference in physical strength was observed.

#### Effluent characteristics

The combined effluents from bleaching the different sequences were analyzed at STFI by Gellerstedt and coworkers. They determined chlorate, AOX, and various chlorinated phenols, guaiacols, and catechols.

Table III also contains data for conventional pulps. Most of the data would be self-explanatory. As expected, the amount of chlorate increases with higher chlorine dioxide substitution, but a DC stage at 50% substitution actually yields less  $\text{ClO}_3$  than the normal (C+D) alternative with 30% substitution.

The total amount of chlorinated organic compounds AOX is substantially reduced to below 1.0 kg/ton in the nonchlorine alternative, which is quite an accomplishment, considering the latest rules for mills, particularly in Sweden.

The most toxic part of the chlorinated compounds in bleach plant effluent is the chlorinated phenols. Using the nonchlorine alternative reduces the phenols from 22–42 g/ton in the conventional alternative to 0.5 g/ton or more than 98%, a quite spectacular achievement.

The content of dioxins in the pulps was also analyzed at STFI by de Sousa and coworkers (Table IV). The results were recalculated to TCDD (tetrachlorinated dibenzo-*p*-dioxins) equivalents using Eadon, Nordic, and U.S. EPA conversion factors. The differences between the factors are not significant. Very low levels were obtained, especially for the alternative with 100% substitution, which was almost at the detection level.

Thus it appears that the nonchlorine bleaching alternative would meet even severe environmental requirements for effluents and products.

#### A nonchlorine fiber line

Figure 7 presents a simplified flow-sheet of a fiber line that has been commissioned in a Scandinavian mill. It consists of a digester for medium-consistency cooking and a medium-consistency, oxygen-delignification stage, followed by an efficient post-oxygen washing stage with pressure

#### I. Chemical charges and costs for different bleaching processes

|                                               | Conventional<br>kraft plus<br>oxygen<br>delignification | MCC plus oxygen delignification |            |            |            |
|-----------------------------------------------|---------------------------------------------------------|---------------------------------|------------|------------|------------|
|                                               | (C+D) (EO)<br>DD                                        | (C+D) (EO) DD                   | DC (EO) DD | D (EOP) DD | D (EOP) DD |
| Kappa number                                  | 18.4                                                    | 13.2                            | 13.2       | 13.2       | 13.2       |
| D substitution, %                             | 30                                                      | 30                              | 50         | 100        | 100        |
| Brightness, % ISO                             | 90                                                      | 90                              | 89.9       | 89.9       | 89.9       |
| Viscosity, $\text{dm}^3/\text{kg}$            | 900                                                     | 965                             | 950        | 930        | 930        |
| Chemical, kg/a.d.<br>metric ton               |                                                         |                                 |            |            |            |
| $\text{Cl}_2$ active Cl                       | 29                                                      | 18                              | 10         | ...        | ...        |
| $\text{ClO}_2$ active Cl                      | 34                                                      | 29                              | 44         | 51         | 51         |
| Sum of active Cl                              | 63                                                      | 47                              | 54         | 51         | 51         |
| NaOH                                          | 23                                                      | 16                              | 16         | 21         | 21         |
| $\text{O}_2$                                  | 3                                                       | 3                               | 4          | 6          | 6          |
| $\text{H}_2\text{O}_2$                        | ...                                                     | ...                             | ...        | 2          | 2          |
| $\text{MgSO}_4$                               | ...                                                     | ...                             | ...        | 3          | 3          |
| Chemical costs, \$U.S.<br>per a.d. metric ton | 27.7                                                    | 21.1                            | 25.7       | 31.1       | 31.1       |

Costs are based on the following rates per kg:  
 \$0.23 for chlorine  
 \$0.42 for chlorine dioxide as active chlorine  
 \$0.28 for NaOH  
 \$0.11 for oxygen  
 \$1.0 for hydrogen peroxide as active  
 \$0.39 for magnesium sulfate.

#### II. Physical properties of MCC pulps bleached with different sequences

| Bleaching sequence                  | (C+D)<br>(EO)DD | (DC)<br>(EO)DD | D(EO)<br>DD | D(EOP)<br>DD | D(EOP)<br>DD <sup>a</sup> |
|-------------------------------------|-----------------|----------------|-------------|--------------|---------------------------|
| D substitution, %                   | 30              | 50             | 100         | 100          | 100                       |
| Brightness, % ISO                   | 90.0            | 89.9           | 90.1        | 89.9         | 89.9                      |
| Viscosity, $\text{dm}^3/\text{kg}$  | 964             | 948            | 867         | 865          | 931                       |
| Beating, PFI rev.                   | 1600            | 1500           | 1800        | 1700         | 2200                      |
| Freeness, °SR                       | 17.5            | 17.0           | 18.0        | 17.5         | 19.0                      |
| Density, $\text{kg}/\text{m}^3$     | 695             | 700            | 710         | 715          | 725                       |
| Burst index, $\text{mN}/\text{kg}$  | 7.0             | 7.2            | 7.0         | 7.3          | 7.2                       |
| Tear index, $\text{Nm}^2/\text{kg}$ | 13.2            | 14.2           | 13.7        | 13.5         | 13.9                      |

Data interpolated at tensile index = 80 MN/kg.  
<sup>a</sup>Mg in EOP stage. <sup>b</sup>Chlorine dioxide substitution in the first stage.

diffuser and a wash press. Bleaching is carried out with the sequence (C+D)(EOP)DD with a pressurized extraction stage and a pressure diffuser for efficient washing. If required, the first stage can be carried out without chlorine.

This fiber line can be regarded as one of the most advanced in the world today, meeting current and future requirements for the environment while still producing fully competitive pulp.

#### Conclusions

It is possible to produce bleached pulp without the use of chlorine, achieving brightnesses even above 90% ISO, the level required for the most demanding market pulps. However, the absence of chlorine requires extra efforts in all process stages from cooking to final bleaching.

The combination of modified continuous cooking and oxygen delignification can result in a pulp of low kappa number, with pulp quality

### III. Effluent characteristics from bleaching reference and MCC pulps

| Pulp                       | Sequence     | Kappa no. | COD carry-over, kg/ton | D substitution,* % | ClO <sub>2</sub> , kg/ton | AOX, kg/ton | Cl <sub>x</sub> phenols, g/ton | Cl <sub>x</sub> guaiacols, g/ton | Cl <sub>x</sub> catechols, g/ton | Total chlorinated phenols, g/ton |
|----------------------------|--------------|-----------|------------------------|--------------------|---------------------------|-------------|--------------------------------|----------------------------------|----------------------------------|----------------------------------|
| Conventional kraft         |              |           |                        |                    |                           |             |                                |                                  |                                  |                                  |
| Unbleached                 | (C+D)(EO)DED | 27.9      | 10                     | 10                 | 4.0                       | 5.3         | 4.04                           | 13.6                             | 25.20                            | 42.8                             |
| O <sub>2</sub> delignified | (DC)(EO)DED  | 18.2      | 10                     | 38                 | 3.4                       | 2.3         | 3.45                           | 12.4                             | 6.59                             | 22.4                             |
| MCC                        |              |           |                        |                    |                           |             |                                |                                  |                                  |                                  |
| O <sub>2</sub> delignified | (C+D)(EO)DD  | 13.2      | 9                      | 30                 | 3.1                       | 2.0         | 1.08                           | 3.91                             | 3.78                             | 8.8                              |
| O <sub>2</sub> delignified | (DC)(EO)DD   | 13.2      | 9                      | 50                 | 2.3                       | 1.5         | 1.21                           | 1.26                             | 1.15                             | 3.6                              |
| O <sub>2</sub> delignified | D(EOP)DD     | 13.2      | 9                      | 100                | 6.1                       | 0.9         | 0.30                           | 0.08                             | 0.07                             | 0.5                              |

\*Chlorine dioxide substitution in the first stage.

### IV. Dioxin quantities in bleached pulps from various processes

| Pulp                       | Sequence     | Kappa no. | D substitution, <sup>a</sup> % | TCDD, µg/ton <sup>b</sup> |        |          |
|----------------------------|--------------|-----------|--------------------------------|---------------------------|--------|----------|
|                            |              |           |                                | Eadon                     | Nordic | U.S. EPA |
| Conventional kraft         |              |           |                                |                           |        |          |
| Unbleached                 | CEHDED       | 30        | ...                            | 10-30                     | ...    | ...      |
| O <sub>2</sub> delignified | (C+D)(EO)DED | 18.5      | 30                             | ...                       | 2.2    | 1.5      |
| MCC                        |              |           |                                |                           |        |          |
| O <sub>2</sub> delignified | (C+D)(EO)DD  | 13.2      | 30                             | 0.11                      | 0.08   | 0.04     |
| O <sub>2</sub> delignified | DC(EO)DD     | 13.2      | 50                             | 0.03                      | 0.06   | 0.03     |
| O <sub>2</sub> delignified | D(EOP)DD     | 13.2      | 100                            | 0.02                      | 0.03   | 0.02     |

<sup>a</sup>Chlorine dioxide substitution in the first stage.

<sup>b</sup>1 µg/ton = 1 ppt (part per trillion).

maintained. For final bleaching, the sequence D(EOP)DD is suitable, with some modifications of normal practice. In the first stage, the chemical charge should be generous. Low-multiple alternatives are not relevant when chlorine is absent. Also, in the enforced extraction stage, both temperature and oxygen pressure should be high. Magnesium is a good viscosity protector in such an EOP stage and when the hydrogen peroxide is absent.

The extra chemical costs for D(EOP)DD bleaching are about \$10/ton or less, a reasonable cost when compared with conventional alternatives.

Compared with conventional bleaching, a nonchlorine alternative has some significant effects on the environment. AOX is less than 1.0 kg/ton in the effluent before external treatment. Chlorinated phenols are 98% eliminated. Finally, the dioxin content of the bleached pulp is ex-

tremely low, close to the limit of detection.

### Experimental procedures

All bleaching stages, including chlorination, were carried out in medium consistency (10%). An oxygen liquor carryover of 9 kg COD/ton of pulp was included in the pulp, and the pH was adjusted to pH 4.0 prior to chlorination.

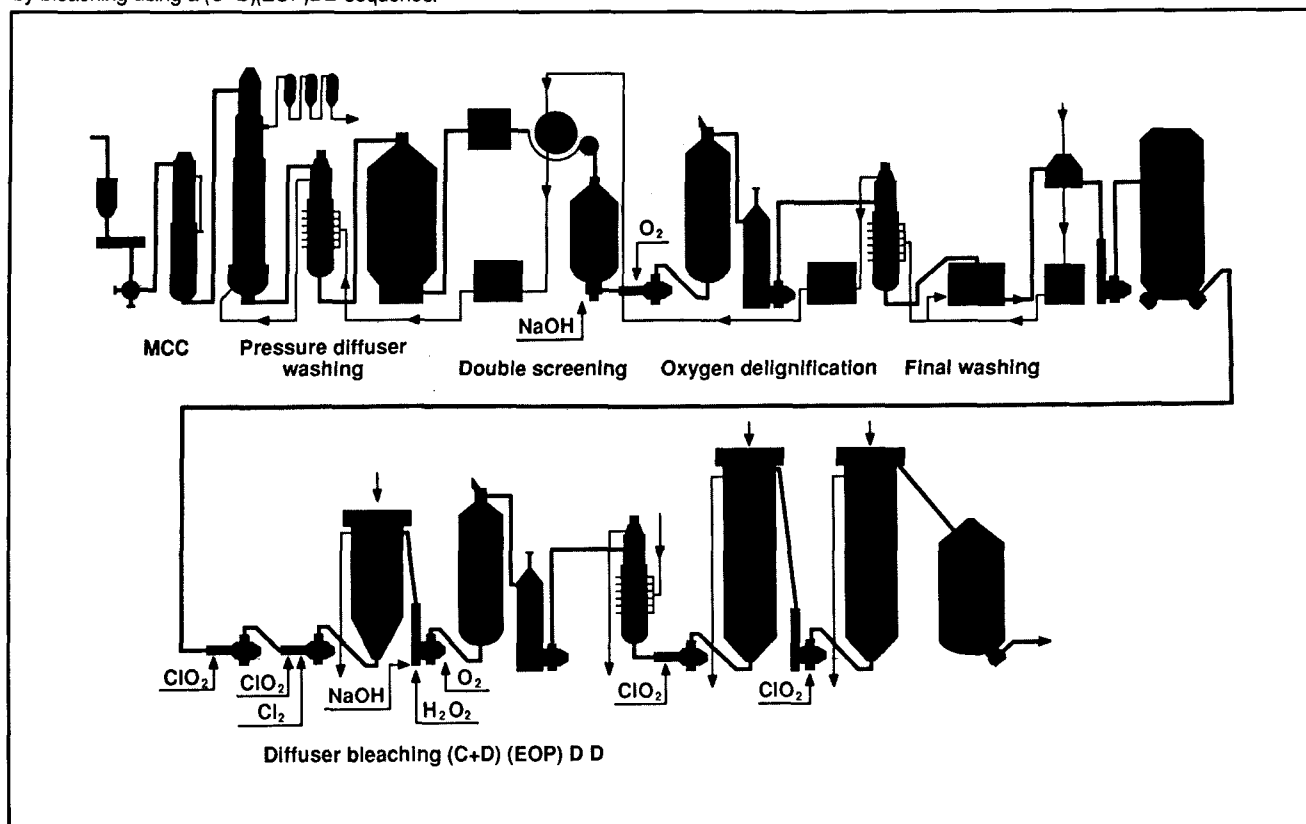
Medium-consistency chlorination was performed in a laboratory high-intensity mixer. For mixed (C70+D30) and sequential (D50 C50) chlorination, the reaction time was 15 min at 50°C.

Chlorine dioxide treatment in the first stage was performed for 60 min at 60°C. Unless otherwise stated, all (EO) and (EOP) stages were carried out in autoclaves for 1 h.

In the reference sequence (C70+D30)(EO)DD, pressurized reaction operation at 5 bar and 70°C was simulated. In all tests with 100% ClO<sub>2</sub> in the first stage, (EO) and (EOP) stages were performed at 5 bar and 90°C, unless otherwise stated.

In the second and third D stages, a temperature of 70°C was maintained

7. The newly commissioned fiber line consists of a digester for MCC cooking and a medium-consistency, oxygen-delignification stage, followed by bleaching using a (C+D)(EOP)DD sequence.



for 180 min. After the second D stage and washing, 0.2% NaOH was added for a slight pH adjustment prior to adding 0.8% active chlorine in the third chlorine dioxide stage.

After bleaching, the pulp samples were washed with SO<sub>2</sub> and water at 5 kg/ton of pulp. □

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