Elemental Chlorine Free Bleaching

A TAPPI PRESS Anthology of Published Papers

Edited by Katherine A. Kulas, Ph.D.

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About the Editor

Dr. Kulas has a B.S. in Chemical Engineering from the University of New Hampshire, and a M.S. and Ph.D. in Paper Science and Engineering from the Institute of Paper Chemistry. She worked for nine years at Champion International Corporation's Quinnesec Mill, most recently as a Senior Process Engineer covering the Bleach Plant and Chemical Preparation areas. She led the ECF conversion project for the mill in 1994. Dr. Kulas is currently self-employed.

Introduction

Elemental Chlorine Free (ECF) bleaching of kraft pulp is the new standard set by the EPA in the cluster rules. Although many mills have converted to ECF bleaching in the past decade, many mills still need to convert to this method of bleaching by the deadline set by the EPA. This anthology is intended to assist mills with their ECF conversions by collecting published papers on actual mill conversions to ECF bleaching. Mills that have already switched to ECF bleaching will find this anthology useful in their troubleshooting and optimizing efforts.

Many excellent papers on ECF bleaching have been published in the past few years. This anthology does not include all of them. Only a few articles concerning hydrogen peroxide, ozone, and enzyme prebleaching are included. They are all anthology topics in their own right.

A comprehensive review of each bleach stage can be found in "Pulp Bleaching—Principles and Practice" edited by Carlton W. Dence and Douglas W. Reeve, TAPPI PRESS, 1996.

Katherine A. Kulas, Ph.D.
November, 1998

Table of Contents

Chapter 1: Mill Experiences

Chapter 1
Mill Experiences

CHLORINE DIOXIDE DELIGNIFICATION PRACTICES IN CANADA

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ABSTRACT

The speed of implementation of complete replacement of chlorine dioxide for chlorine in the first stage of chemical pulp bleaching, i.e., chlorine dioxide delignification, has been remarkable. Beginning in 1989, the production of pulp using chlorine dioxide as the only chlorine-containing bleaching agent, often referred to as "Elemental Chlorine Free" (ECF), has grown quickly. Almost ninety percent of bleach plants in Canada will produce ECF in 1996, totaling 8.2 million tonnes of bleached pulp. ECF pulp now accounts for almost seventy percent of Canadian bleached chemical pulp production.

Chlorine dioxide delignification is rapidly becoming standard practice in the first stage of bleached chemical pulp bleach plants. Optimum conditions, (based on laboratory bleaching) are well developed for: 1) minimizing cost; 2) maximizing delignification; 3) maximizing pulp quality; and 4) minimizing environmental impact. However, the practical conditions utilized in actual mill scale production of ECF pulps are not well documented.

This paper, based on the results of a survey of operating conditions employed by Canadian bleached chemical pulp mills producing ECF grades, describes mill practice for bleaching market pulp to high brightness where chlorine dioxide is used in the first stage of bleaching. Conditions for minimizing bleaching chemical cost and consumption are identified for conventionally delignified softwood kraft pulps.

INTRODUCTION

Chemical pulp bleaching in Canada continues to evolve. In 1988, bleach plants began adopting substantial substitution of chlorine dioxide for chlorine. Today in 1996, all bleach plants in Canada use substantial substitution of chlorine dioxide in the first stage of bleaching, (i.e., ≥ 50%). On a production weighted basis, chlorine dioxide substitution now averages 87% for all bleached chemical pulp. Softwood grades average 90% and hardwood grades average 79%.

The number of mills practicing complete replacement of chlorine with chlorine dioxide, so-called Elemental Chlorine-Free (ECF) bleaching, continues to grow. Almost 90% of bleach plants in Canada will produce ECF in 1996, totaling an estimated 8.2 million tonnes of bleached pulp. ECF now accounts for 67% of Canadian bleached chemical pulp production. Almost 60% of bleach plants and over 50% of bleached chemical pulp mill sites in Canada produce ECF exclusively.

Market demand for Elemental Chlorine-Free (ECF) pulps, i.e., bleached without elemental chlorine (Cl_2), and regulations limiting the discharge of AOX are the driving forces behind this evolution.

To keep abreast of the developments in bleaching practice, the CPPA Bleaching Committee issued questionnaires to mills in Canada in 1994, 1995 and 1996. The questionnaires were designed specifically to investigate the extent and impact of increased chlorine dioxide substitution and complete replacement of chlorine with chlorine dioxide in the first stage of bleaching. In 1996 the questionnaire was expanded to assess ECF bleaching practices and to determine, if possible, optimum conditions for maximizing brightness while minimizing cost.

In 1996 the questionnaire was sent to forty-two mills and thirty-eight mills responded. The authors estimated pulp production for the outstanding mills based on the 1995 survey [1]. Supplemental questionnaires for 36 ECF bleaching lines were received and analyzed. This paper summarizes the data reported in the questionnaires.

PULP BLEACHING IN CANADA

Table 1 summarizes bleached chemical pulp production in Canada. The dominant end use is market pulp. The dominant pulping process is kraft.

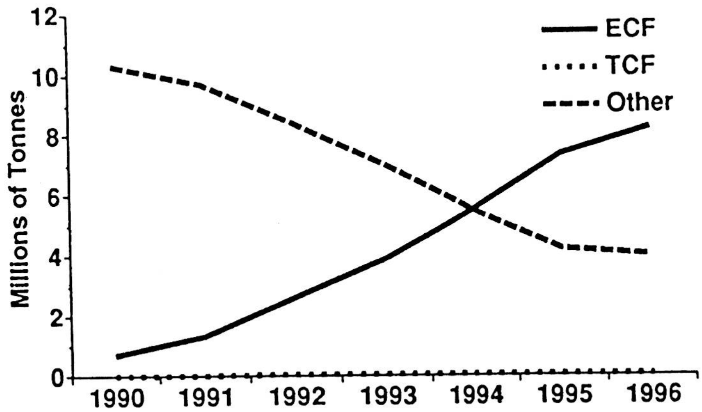
Table 1:
1996 Canadian Bleached Chemical Pulp Production (million tonnes)

	ECF	TCF	Other*	Total
HWD	1.40	0.006	1.57	2.98
SWD	6.82	0.035	2.42	9.28
Total	8.22	0.04	3.99	12.26

* Pulps bleached with substantial substitution of chlorine dioxide. Softwood and hardwood pulps average 60% ClO_2 substitution.

Figure 1 shows the changing nature of bleached chemical pulp production since 1990. ECF pulp production continues to rise, and will account for sixty-seven percent of bleached chemical pulp in 1996. In 1996, Totally Chlorine-Free (TCF) pulp is expected to be produced at only two sulfite mills.

Figure 1
Canadian Bleached Chemical Pulp Production

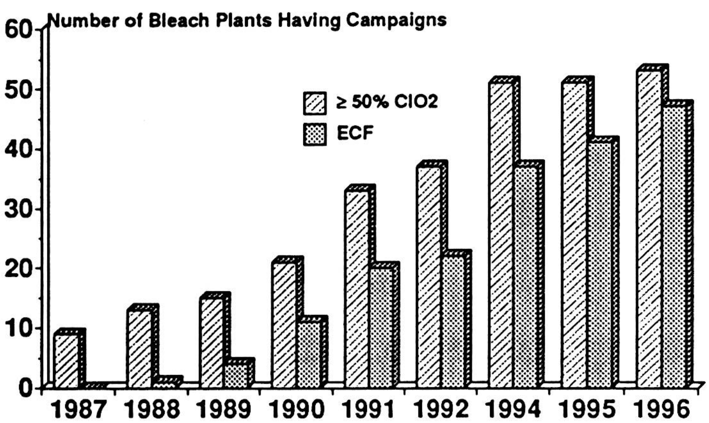


CHLORINE DIOXIDE SUBSTITUTION PRACTICE

Development of Chlorine Dioxide Substitution

In 1987 only 9 bleach plants in Canada were practicing substantial substitution of chlorine dioxide [2]. Since 1988, the number of bleach plants practicing substantial substitution has been steadily increasing as shown in Figure 2. In 1996, in Canada, fully 100% of the bleach plants practice substitution ≥ 50%. Perhaps even more dramatic is the 'growth of complete replacement of chlorine with chlorine dioxide in the first stage of bleaching. Beginning in 1989, the number of bleach plants producing ECF has grown quickly. ECF is now produced at 36 of 42 mill sites and in 47 of 53 bleach plants. Twenty-three mill sites produce only ECF grades.

Figure 2
ClO2 Substitution Practise



ECF BLEACHING PRACTICE

As previously discussed expanded questionnaires were issued to those bleach plants producing ECF to assess bleaching practices. The questionnaires requested information on unbleached pulp, process conditions, chemical consumption, mixing, control strategy etc. Responses were received covering 36 bleach plants, 29 softwood and 7 hardwood. This paper summarizes the bleaching practices from the softwood bleach plants within two categories, oxygen-delignified and conventionally delignified softwood. As shown in Table 2, these two categories were further subdivided into "low" and "high" relative sequence chemical consumption.

The hardwood data base was not sufficient to characterize practices. The questionnaires and the full data analysis for both softwood and hardwood can be obtained from the CPPA Bleaching Committee.

For ECF grades, the dominant sequence is DEopDED (Figure 3). Most grades are bleached to high brightness, typically 88-90% ISO as shown in Figure 4.

Figure 3
ECF Bleaching Sequences

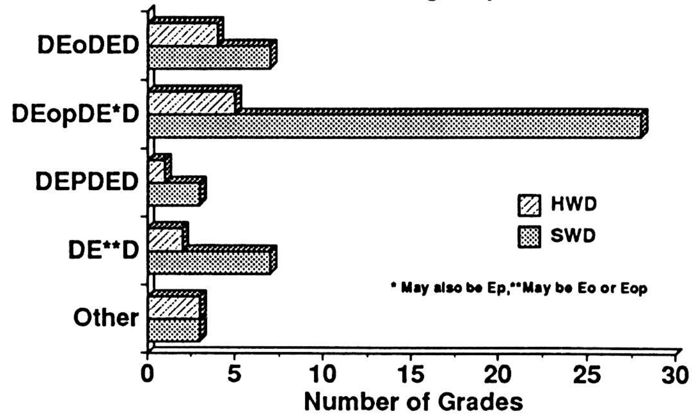
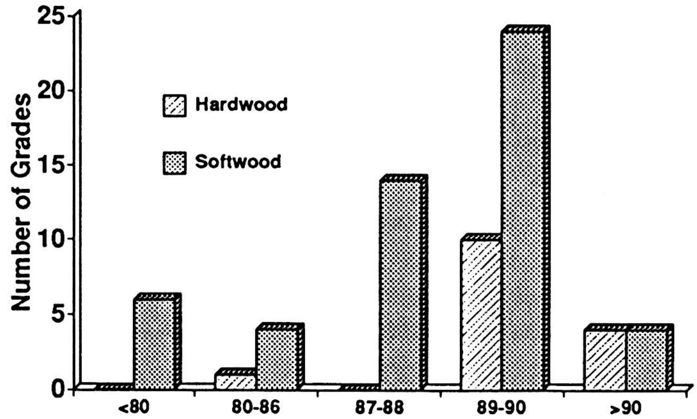


Figure 4
Final Brightness, % ISO



UNBLEACHED PULP

Kappa Number

The softwood kappa number to the bleach plant for conventionally delignified pulps averages 28.7 and for oxygen-delignified pulps, 17.5. Some softwood is now being produced with kappa numbers less than 20 indicating the growing significance of oxygen delignification and modified cooking (Figure 5). Twenty-eight percent of kraft pulp is now oxygen-delignified in Canada at 11 sites, representing 3.5 million tonnes of production.

Figure 5
Kappa Number to D_0 Stage

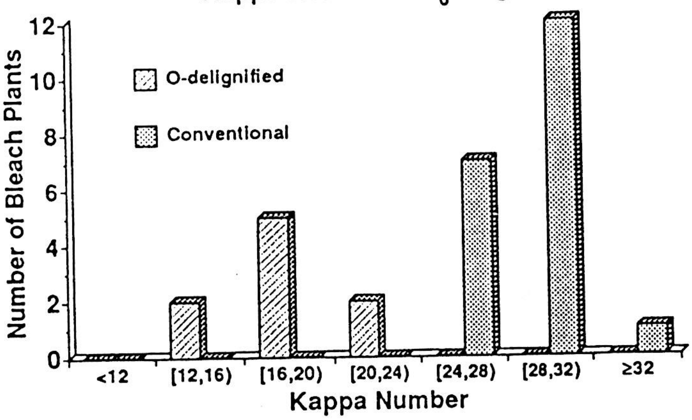
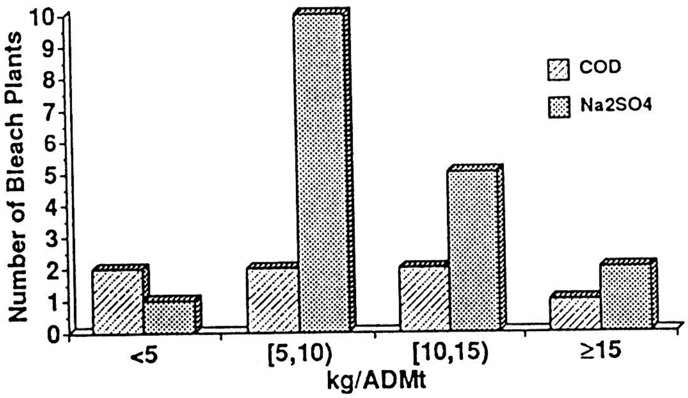


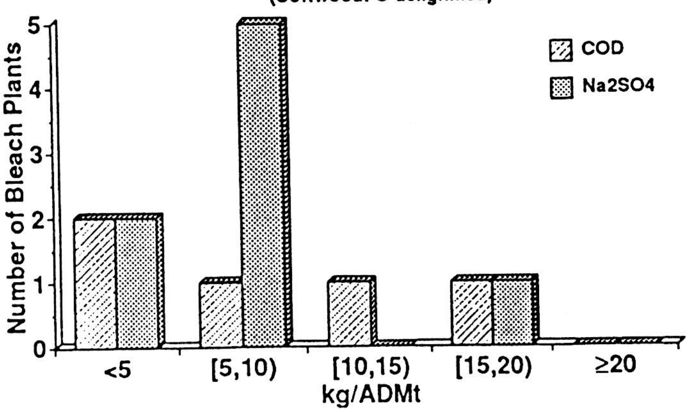
Figure 7
Carryover to Bleach Plant
(Softwood: Conventional delignification)



Carryover to the Bleach Plant

Carryover to the bleach plant (i.e., the first chlorine dioxide stage) is determined by measuring the sodium concentration in the liquor associated with the unbleached pulp or oxygen-delignified pulp and expressed as kg Na_2SO_4 per ADMt. More recently, mills are beginning to use Chemical Oxygen Demand (COD) to measure carryover of chemicals that will consume chlorine dioxide in the first stage of bleaching. As shown in Figures 6 and 7, the carryover typically ranges from 5-20 kg/ADMt for either Na_2SO_4 or COD. The average value of both Na_2SO_4 and COD carryover, for both conventional and oxygen-delignified pulps, is ~ 8 kg/ADMt.

Figure 6
Carryover to Bleach Plant
(Softwood: O-delignified)



FIRST CHLORINE DIOXIDE (D_0) STAGE

Operating Conditions

Typically the first chlorine dioxide stage, D_0, is operated at low consistency, reflecting the transition from chlorine to chlorine dioxide. Eighty per cent of the bleach plants operate at low consistency and twenty per cent at medium consistency. Furthermore, 87% are upflow towers and only 13% upflow-downflow. Retention time is 36 minutes with a range of 6-120. Temperature averages 54°C ranging from 35 to 65°C. Residual chlorine dioxide is typically zero. Approximately 80% of oxygen delignification bleach plants and 65% of conventional lines control the end pH at 2.5 with addition of H_2SO_4.

Process control in the first stage is dominated by optical and residual sensors before the tower, 80% controlling to a compensated brightness set point. About 30% use a post tower optical sensor as well. Approximately 30% control to an extracted kappa number. Thirty-five per cent of the conventional lines have kappa number analyzers.

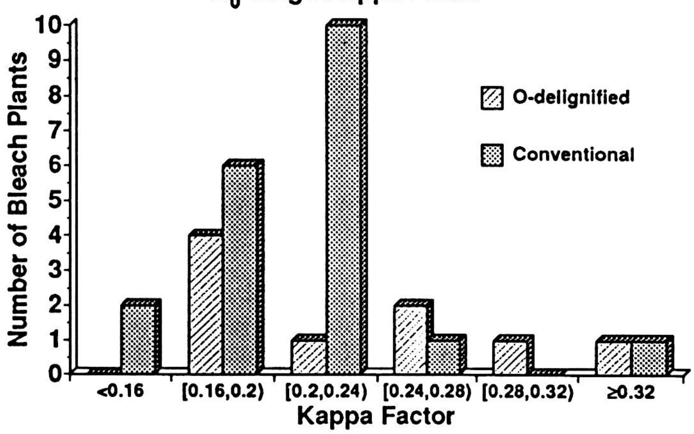
Both mechanical and static mixers are used in widely varying combinations and with widely varying distribution of chlorine dioxide among mixers. This is likely a reflection of mixing strategies implemented for substantial substitution of chlorine dioxide designs and associated hydraulic limitations. No deliberate distribution pattern for chlorine dioxide addition or mixing strategy is evident.

D_0 Kappa Factor

The kappa factor is higher for oxygen-delignified pulps, averaging 0.23, while conventionally delignified pulps average 0.20 as shown in Figure 8. Kappa factor equals percent equivalent chlorine on pulp divided by the incoming kappa number, (per cent equivalent chlorine on pulp in the D_0 stage equals 2.63 times per cent chlorine dioxide on pulp). Oxygen-delignified pulps are relatively more difficult to further delignify with chlorine dioxide. This is reflected in the higher D_0 kappa factor.

Figure 8

D_0 Stage Kappa Factor



FIRST EXTRACTION STAGE, Eop

Operating Conditions

The Eop stage retention time is 75 minutes with a range of 50-134, operating at 75°C with a range of 55-85°C. Approximately 10% of oxygen delignification bleach plants and 25% of conventional lines utilize Papricycle® to minimize sodium hydroxide consumption. The NaOH:Equivalent Cl_2 ratio averages 0.45-0.48 without Papricycle® and 0.25-0.36 with. This represents a saving of approximately 7 - 9 kg NaOH/ADMt.

Essentially all stages are controlled to an end pH of 10.5-10.8 with 50% of oxygen delignification lines and 30% of conventional lines controlling to an Eop brightness target. Eop kappa number control is more popular in conventional lines with 40% using this parameter, compared to only one oxygen delignification line.

Eop Kappa Number and Kappa Factor

Both hydrogen peroxide and oxygen are used in the extraction stage in 90% of the bleach plants. Oxygen is applied typically at 5.5 kg/ADMt and hydrogen peroxide at 3.4 kg/ADMt. The Eop kappa number for oxygen-delignified pulps averages 3.6 compared to 5 for conventional pulps.

The kappa factor for the D_0 plus the Eop stage (which includes the chlorine dioxide in D_0 plus the hydrogen peroxide and oxygen all expressed as equivalent chlorine) is higher for oxygen-delignified pulps averaging 0.39, while conventionally delignified pulps average 0.30 as shown in Figure 9. Delignification is typically 80% in both cases but with oxygen delignified pulps it takes more oxidizing chemical equivalents per unit of kappa number decrease. For oxygen delignified pulps it takes 0.47% equivalent chlorine per unit kappa decrease compared to 0.35 for conventional pulps.

Figure 9
Kappa Factor for D_0 and Eo(p) Stage

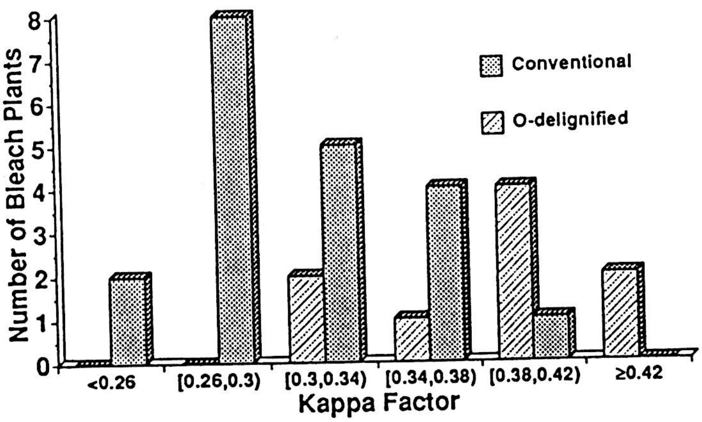
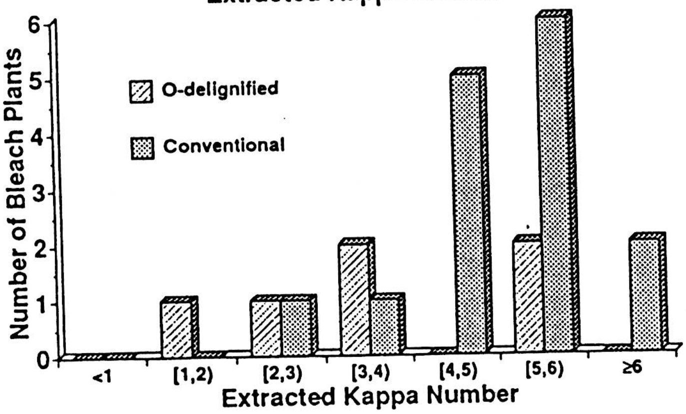


Figure 10
Extracted Kappa Number



CHLORINE DIOXIDE BRIGHTENING: (D_1) STAGE

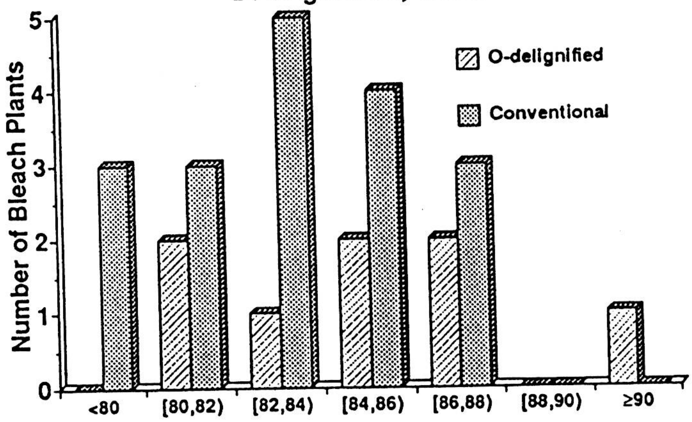
Operating Conditions

The D_1 stage retention time is 160 minutes with a range of 60-240 operating at 72°C with a range of 68-81°C. Approximately 40% of oxygen delignification bleach plants and 85% of conventional lines add NaOH to control pH. The upflow pH averages 3.8-3.9 and end pH 3.3-3.8.

Most stages are controlled using pre-tower optical and residual sensors to a compensated brightness target and end-of-tower pulp brightness. A positive chlorine dioxide residual is retained at the end of the stage, typically in the range of trace to 40 mg/L measured in the D_1 washer vat.

D_1 stage brightness is widely distributed and averages 84% ISO for oxygen-delignified pulps and 83% ISO for conventional pulps as shown in Figure 11. Chlorine dioxide is applied at 9 kg/ADMt for oxygen-delignified pulps compared to 11.3 kg/ADMt for conventional pulps, reflecting the difference in post-extraction kappa no. The application rate for both pulps is approximately 2.3 kg ClO_2/ADMt per unit Eop kappa compared to 2.0 for laboratory-generated values [3].

Figure 11
D_1 Brightness, % ISO



SECOND EXTRACTION STAGE, E_2

Operating Conditions

Recently, a number of mills have incorporated so-called short extraction stages for the E_2 stage. In some configurations, NaOH is added directly to the ring dilution at the bottom of the D_1 tower and the short residence time before the pulp is pumped to the D_1 washer is used for extraction. The pulp is then washed and forwarded to the D_2 stage. In other configurations, NaOH is added