Recent advances in bleached chemical pulp manufacturing technology

Part 1: Extended delignification, oxygen delignification, enzyme applications, and ECF and TCF bleaching

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The technology of extending the kraft cook to lower residual lignin contents continues to advance by research and experience gained in the operation of new commercial installations.

The technology of bleached chemical pulp manufacture has entered a period of extremely rapid change driven by growing concern for the environment. Many conference reports appearing in the past year are evidence of the feverish level of research and development activity in the design and implementation of new environmentally benign processes for bleached chemical pulp manufacture. Environmental consciousness is evident not only in the marketplace but also in increasingly stringent government regulation of the industry's waste streams, processes, and products. The resulting changes are occurring so rapidly that they may be considered revolutionary.

One example is the demise of chlorine bleaching in Sweden where Cl_2 use went from 150,000 metric tons per year in 1987 to zero in 1993 *(1)*. The virtual eradication of dioxins in North American mill effluents following their discovery in 1985 is a second example *(2)*. Another example is the rapid growth in the market for pulp bleached in elemental chlorine-free (ECF) and totally chlorine-free (TCF) processes *(3)*. ECF increased from 3.5 million metric tons in 1990 to 23.5 million metric tons in 1994. TCF increased from zero in 1990 to 4.4 million metric tons in 1994. A further example is the sudden appearance of seven commercial ozone bleach plants in 1993 compared to none in 1992 *(4)*.

This paper will review the status of newly introduced or rapidly evolving technologies for bleached chemical pulp production. The recent completion of a series of relevant conferences culminating with the 1994 International Pulp Bleaching Conference in Vancouver in June affords a timely opportunity to take a "snapshot" view of the situation.

Bleached chemical pulp production and market

The enormous size of the world bleached chemical pulp market guarantees that changes in production methods will have extensive consequences. Production was 28.3 million metric tons in the United States *(5)* in 1992. Worldwide production was 72 million metric tons of which 9.8 million metric tons were in Canada *(3)*.

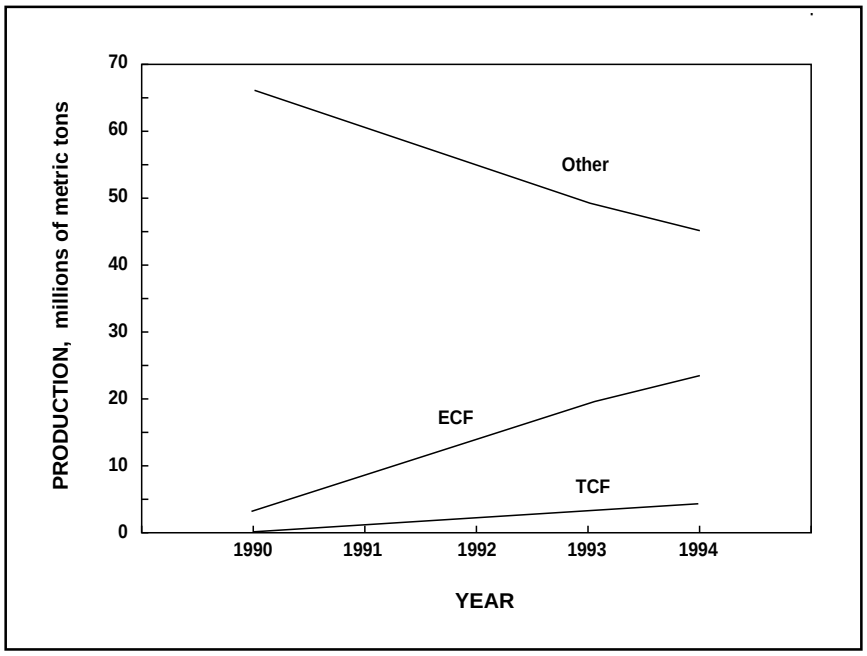
The combined market share of ECF and TCF pulps has grown rapidly since 1990 from 4.3 to 27.9 million metric tons. Figure 1 shows that 85% or 20 million metric tons is in ECF *(3)*. Despite the attention TCF receives, it remains a small factor in the world pulp market. Virtually all TCF production is in Europe. North American producers doubt the market's willingness to pay the substantial premium necessary to offset the increased costs of TCF production. The sole U.S. producer, Louisiana Pacific at Samoa, CA, has experienced weak demand.

Environmental issues and regulations

Apart from market forces, the main driving force for much of the technological change currently underway is industry regulation by government agencies. In the United States, the recent publication of proposed guidelines for regulation of pulp mill emissions by the U.S. Environmental Protection Agency (EPA) has highlighted this issue. Because the regulation includes both air and water standards in a single set of rules, it has the designation "Cluster Rule." Public comments received since publication will be reviewed before the final version is promulgated in late 1995. Mills must comply within three years of promulgation.

The part of the proposed rules most pertinent to this discussion concerns effluents from mills producing paper grade bleached kraft pulp. Table I shows limitations on the levels of specific compounds in bleach plant effluents *(6)*. The list includes dioxins—specifically 2, 3, 7, 8-tetrachlorodibenzodioxin (TCDD) and 2, 3, 7, 8—tetrachlorodibenzofuran (TCDF). The requirements are for TCDD to be nondetectable and TCDF to be present at a daily average level no greater than 359 ng/ton. This is equivalent to approximately 7 parts per quadrillion (ppq) in the effluent from a typical bleach plant. The lowest level of either of these two compounds that is reliably detectable is approximately 10 ppq. The remaining compounds singled out for specific regulation are two halocarbons, two ketones, and nine chlorophenols.

1. Production growth of ECF and TCF bleached chemical pulp from 1990 to 1994



Besides these limitations on specific compounds in the effluent from the bleach plant, proposed new limits apply to the whole mill effluent at the final discharge point. They govern the levels of adsorbable organic halide (AOX), biochemical oxygen demand (BOD), total suspended solids (TSS), chemical oxygen demand (COD), and color. Table II provides these levels compared with the corresponding limitations proposed by four Canadian provinces *(7)*. The proposed EPA limits, especially those on AOX and COD, are very demanding. Compliance would require not only the elimination of elemental chlorine but also extended delignification, oxygen delignification, and perhaps both with an efficient secondary biological treatment system.

Other countries have enacted legislation, or regulations are pending. As an example, Table III shows approximate limits on discharges from mills in Sweden *(8)*. There may be more exact values for individual mills on a case-by-case basis.

Clearly, stringent regulation of chlorinated and difficultly biodegradable unchlorinated organic compounds in mill effluents is quickly becoming the universal rule. Augmented by parallel market forces, this has set the stage for extensive change in the processes used to produce bleached chemical pulp. The remainder of this review examines in detail some specific developments that comprise the growing body of technology that has arisen in response to the demands imposed by these regulatory and market pressures.

Extended delignification

Perhaps the most attractive route to reduced bleach plant discharges is modification of the pulping process to allow reduction of the residual lignin content of the unbleached pulp. The past 15 years have seen introduction of a variety of approaches. These include extension of the kraft cook in existing equipment by using anthraquinone (AQ), polysulfide (PS), adjustment of pulping conditions, or some combination of these; batch system modifications including black liquor preimpregnation, liquor displacement, and cold blow; and continuous digester modifications including multiple white liquor addition points, introduction of a countercurrent cooking zone, and isothermal cooking. Other suggestions are more far-reaching modifications. An example is conversion to alkaline sulfite processes such as the one based on addition of both AQ and methanol.

AQ addition to kraft digesters and simple extension of the cook by manipulating pulping variables are suggestions from 1980 for achieving lower unbleached residual lignin content *(9)*. More recently, both ideas have resurfaced because they offer the possibility of significant reductions in unbleached kappa number without the substantial capital cost of digester replacement or retrofitting. At 25% sulfidity, addition of 0.1% AQ reduces the unbleached kappa number of softwood kraft pulps by 18%. There is no loss in yield and therefore no increase in loading to the recovery furnace *(10)*. The reduction increases with decreasing sulfidity and is smaller for hardwoods. Recent work has shown that extended cooking to kappa no. 20 in conventional digesters without AQ will not incur a strength penalty *(11)*.

Another idea proposed in the early 1980s was the combined use of PS and AQ to lower the unbleached kappa number *(12)*. This has also attracted renewed interest*(13, 14)*. It is possible to reduce unbleached kappa number from 30 to approximately 18 without yield loss by conversion of part of the sulfur in 30% sulfidity white liquor to PS sulfur. The required extent of conversion corresponds to a sulfidity reduction to 12%. The resulting PS sulfur charge is greater than 1% (o.d. wood basis).

I. U.S. EPA proposed bleach plant effluent limitations for paper grade kraft mills

Parameter	*Maximum daily average, g/ton*	*Maximum monthly average, g/ton*
TCDD	ND	NA
TCDF	359×10^{-9}	NA
Chloroform	5.06	2.01
Acetone	43	21.9
Methyl ethyl ketone	3.81	1.75
Methylene chloride	1.33	0.518
Trichlorosyringol	0.218	NA
Trichlorocatechols	ND	NA
Trichloroguaiacols	ND	NA
2,4,5–trichlorophenol	ND	NA
2,4,6–trichlorophenol	0.0786	NA
Tetrachlorocatechol	ND	NA
Tetroachlorguaiacol	ND	NA
2,3,4,6–tetrachlorophenol	ND	NA
Pentachlorophenol	ND	NA

ND = nondetectable
NA = not applicable

In extended modified continuous cooking, the combined use of PS and AQ can decrease the kappa number from 20 to 12 with no yield loss but with a slight loss in tear strength. The strength loss is the same as that by cooking to kappa no. 12 with neither PS nor AQ.

Digester modifications for extended delignification are based on four principles:

- A hydroxide ion concentration that is as low as possible, especially at the beginning of the cook, and as nearly constant as possible throughout the cook
- A hydrosulfide ion concentration that is as high as possible, especially in the early stages of the cook
- A dissolved lignin concentration that is as low as possible, especially in the later stages of the cook
- A temperature that is as low as possible throughout the cook

It is necessary to follow each of these as closely as possible subject to constraints imposed by practicality and the need to accomplish the desired extent of delignification within a reasonable time. An additional requirement for batch systems is provision of some method for gently discharging the digester to preserve pulp strength. Such measures include "cold blow" (displacing the contents of the cooled digester by compressed air or steam) and pumped discharge. "Strength delivery" (the ratio of the strength of the discharged pulp to that of a corresponding laboratory cook or basket cook) measures their success *(15)*. Both batch and continuous extended delignification systems exist that incorporate some or all these principles.

Modifications of batch digester systems for extended delignification are available under several trade names—Rapid Displacement Heating (RDH), SuperBatch, and Enerbatch. A review describes the first two *(11)*, and a recent conference presentation describes the last *(16)*. All incorporate multiple liquor accumulators and a series of liquor changes within each cook by which a liquor of different composition and temperature displaces the liquor in the digester to one accumulator. The RDH system employs a warm black liquor preimpregnation of the uncooked chips, displacement of this liquor by hot white and black liquors, heating, cooking, and displacement of the black liquor in two stages by washer filtrate. The SuperBatch system primarily differs in the conditions of the black liquor preimpregnation. It uses more severe conditions to achieve improved selectivity. The Enerbatch system sacrifices the black liquor preimpregnation in favor of low-temperature white liquor preimpregnation for improved uniformity.

A recent paper describes the results obtained during the initial months of operation of the first two mill-scale SuperBatch units *(17)*. One unit at Enocell Oy in Finland has achieved routine production of softwood pulp at kappa no. 15 with 90% strength delivery compared to 75% from conventional systems. The other at SEPAP Štětí, Czech Republic, has had similar experience. The Enocell mill has produced softwood pulp of kappa no. 10 with good quality. Laboratory bleaching of this pulp has shown that it can be fully bleached in a chlorine dioxide based sequence. There is very low chemical consumption and pulp quality is equivalent to that of the corresponding fully bleached conventional pulp *(18)*. The same studies showed that the SuperBatch-bleached pulps reach 90 brightness in a TCF sequence, with strength equivalent to that of the fully bleached conventional pulp.

The well–known modification of continuous digesters to "modified continuous cooking" (MCC) provides for multiple white liquor addition points to decrease the maximum alkali concentration and smooth out the concentration profile. There is also countercurrent flow of liquor in the latter part of the cooking zone to decrease the dissolved lignin concentration at the end of the cook. More recent stages of evolution have led to "extended modified cooking" (EMCC) in which there is an additional countercurrent zone, and "isothermal cooking" (ITC), in which the temperature of the concurrent and first countercurrent cooking zones decreases and that of the second countercurrent zone (formerly the wash zone) increases to the same value. This gives a uniformly low temperature throughout the cook. Benefits include higher strength at low kappa numbers and lower rejects. An even more recent modification is the inclusion of a black liquor preimpregnation step in the preimpregnation vessel. This provides better selectivity and increased tear strength at low kappa numbers *(19)*.

Mills prepared to take a bolder step toward lower unbleached kappa numbers and easy bleaching may wish to consider the uncommercialized alkaline sulfite–AQ–methanol (ASAM) process. The pulping liquor, as the name suggests, contains about 15% sodium sulfite, 5% sodium hydroxide (both as Na_2O, o.d. wood basis), and 0.1% AQ (o.d. wood basis) dissolved in a mixture of 80% water and 20% methanol by volume. Compared to kraft MCC, ASAM requires higher temperature, comparable total cooking times, and lower alkali charges. The ASAM process requires a smaller causticizing plant, a methanol recovery system, a sulfide–sulfite conversion process, digesters rated for higher pressure, and more washing capacity to compensate for the loss of the washing that occurs in the MCC digester. Such equipment changes may be worth considering, because the ASAM process applied to southern U.S. softwood over the kappa number range 15 to 25 has several advantages *(20)*. These include 3% higher yield over the entire kappa number range, 20% higher tear strength at a given tensile strength, a significant ultimate tensile strength advantage, and easy bleaching in both chlorine dioxide based and TCF sequences.

II. Proposed regulatory legislation

Year	Regulatory body	kg/ton	AOX, kg/ton	BOD, kg/ton	TSS, kg/ton	COD, kg/ton	Color,
1993	British Columbia		2.5	7.5	11.55		
	Alberta		1.3	3.0	5.0		
	Alberta		0.3[1]				
	Ontario		2.5	5.0	4.6		
	Quebec		1.5[2]	5.0	8.0		
	Quebec		2.5[3]	5.0	8.0		
1995	British Columbia		1.5				
	Ontario		1.5				
	Quebec		1.0[2]	5.0	8.0		
	Quebec		2.0[3]				
1998	U.S. EPA:						
	Max. daily		0.267	4.26	8.75	35.7	120
	Min. monthly		0.156	2.19	3.89	25.4	76.3
1999	Ontario		0.8				
2002	British Columbia		0				
	Ontario		0				
	Quebec		0.8				

1 = applicable to a specific, recently constructed mill
2 = hardwood
3 = softwood

Oxygen delignification

Oxygen delignification is a well-known and well-established technology for removing a substantial portion of the residual lignin in unbleached pulp. The dissolved lignin can then go to the recovery furnace instead of to the bleach plant where it would become a potential source of environmental problems.

Despite the maturity of oxygen delignification technology, research and development efforts continue to result in improvements and new applications. Recent reports have dealt with two-stage oxygen delignification, the use of magnesium oxide as base, an open oxygen stage to permit low AOX bleaching, and application of a static mixer for oxygen addition.

To maximize environmental benefits and cost savings, it is normally desirable to remove as much lignin in the oxygen stage as possible without adversely affecting pulp quality. This is usually 40–60%. Achieving these levels in practice is often difficult, however, in medium-consistency systems. There may be limitations on the degree to which all of the oxygen added can disperse as sufficiently small bubbles. Coalescence of bubbles may contribute to a slowing of the reaction as the pulp progresses upward through the reactor. Attempts to increase delignification by increasing the oxygen charge may be counterproductive. The gas dispersing ability of the mixer decreases and channeling becomes more likely as the volumetric fraction of gas in the pulp suspension increases.

These considerations led to the development of two-stage medium-consistency systems *(21)*. They differed from their single-stage predecessors only by the addition of a mixer and a second reactor between the first reactor and the blow tank. More recently, the two-stage concept has been extended to include alkali and oxygen addition between stages with optional interstage washing. Without interstage washing, two successive oxygen stages each using 3% NaOH give a total delignification of 70%. This compares to 53% in a single stage for softwood kraft. When using interstage washing, the extent of delignification decreases but selectivity improves. One way to use such a system would be as part of a strategy for extended delignification. Here the kraft cook would terminate at a high kappa number, and oxygen would extensively delignify the pulp. Compared to the conventional route of 50% delignification of kappa no. 30 pulp in a single oxygen stage, terminating the kraft cook at kappa no. 40 and subsequently delignifying to kappa no. 13 in two oxygen stages would increase yield, decrease cost, decrease the solids load on the recovery furnace, decrease AOX generation in the bleach plant, and slightly decrease pulp strength *(22)*. A similar system is now operating in a mill at Moss, Norway *(23)*. The medium consistency sequence consists of a refiner used as a mixer, a 13 m^3 first stage reactor, another mixer, and a 46 m^3 reactor

without interstage washing. The brownstock is kappa no. 60 PS pulp. The first and second stage oxygen charges are 2.5% and 1.25%. The process uses 5–6% alkali in the first stage only. The process incorporates another interesting innovation—pretreatment of the brownstock with sulfite liquor to improve the selectivity of the oxygen stages. Delignification as high as 66% is possible.

Hardwood prehydrolysis kraft dissolving pulps delignify more selectively in two oxygen stages than in one. Two-stage oxygen delignification to kappa no. 3 of eucalyptus pulp having an unbleached kappa no. 9 resulted in a viscosity of 915 mL/g compared to 840 mL/g when the same degree of delignification occurred in only one stage *(24)*. In these experiments, the approximate retention times were 15 min in the first stage and 60 min in the second. Addition of most of the alkali was to the first stage, and there was no interstage washing. Inclusion of interstage washing gave slight improvements in both selectivity and extent of delignification.

A recent mill installation is another interesting application of oxygen delignification *(25)*. It has a "no moving parts" medium consistency system in which a static mixer disperses oxygen in the pulp. The reactor has a static distributor at the bottom and a static discharger at the top. The system reduces the kappa number of unbleached pulp from 16 to 10 and allows the chlorine dioxide substitution level in the next stage to increase from 30% to 80% with a reduction in total chlorine dioxide usage. Pulp production was increased by unloading the downstream diffusion bleach plant.

Most mills installing oxygen stages justify the cost on the basis of environmental benefits resulting from recycling the oxygen stage dissolved solids to the recovery system. Another recent mill installation shows that this is not always the case, however *(26)*. The mill had to produce an extremely low AOX grade that demanded very low unbleached kappa number. Extending the kraft cook could achieve this, but the resulting recovery boiler and causticizing system overloads caused costly decreases in production. The solution to the problem was a medium-consistency oxygen stage from which the dissolved solids were discharged instead of recycling them to recovery. This gave the required kappa number decrease with no increase in the load on the recovery system.

Sulfite mills have also joined the trend toward oxygen delignification. A German magnefite mill has successfully started a single-stage bleaching process using a combination of oxygen and hydrogen peroxide with magnesium oxide from the recovery system as base *(27)*. Spruce magnesium base sulfite pulp delignifies from kappa no. 18 to kappa no. 5 with a corresponding brightness increase to 82. Although the conditions required are severe (6 h at 95°C when using 1% MgO), the equipment for the previous three-stage sequence can easily accommodate them. A similar system in an Austrian mill has a 2 h retention time and can delignify magnesium base sulfite pulp from kappa no. 24 to kappa no. 14 with no increase in brightness *(28)*.

Addition of hydrogen peroxide to oxygen delignification stages is also under examination for kraft pulp applications *(29)*. Selectivity and extent of delignification improve with addition of hydrogen peroxide and cyanamide. The latter compound activates the peroxide toward delignification and stabilizes it toward decomposition.Repeated PO stages can be combined for even more extensive and selective delignification.

Enzyme applications

The beneficial effects of treating pulp with hemicellulose-degrading enzymes before bleaching are well known *(30)*. When applied to kraft pulp at pH and temperature values that are appropriate for the particular enzyme being used under conditions of very good mixing, xylanases can reduce total active chlorine requirements in both chlorine based and chlorine dioxide based sequences. The savings typically amount to 10–15% for softwood pulps and 20–25% for hardwood pulps. The greater effect with hardwoods is presumably due to their higher xylan content. Unfortunately, this may also cause a small but significant yield loss in hardwood applications. The mechanism of bleaching enhancement may involve removal of reprecipitated xylan from the fiber surface, enlargement of the intrafiber pore structure, and release of lignin fragments that are chemically bonded to lignin. A recent study employed fiber staining techniques to measure the accessibility of the fiber wall interior before and after enzyme treatment *(31)*. The results showed that the enzyme treatment increased pore size. This reinforces the hypothesis that the mechanism involves removal of a physical barrier to the diffusion of lignin fragments from the fiber wall. Accessibility of the fiber wall to the enzyme may also be an important factor. Another study showed that replacing sodium and other metal ions in the pulp with hydrogen ions before enzyme treatment makes the enzyme ineffective *(32)*. Presumably the well-known decrease in swelling that accompanies replacement of metal ions with hydrogen ions makes the fiber wall less accessible to the enzyme. This effect has practical implications for using enzymes in TCF bleaching. Acid washing or chelation should not precede enzyme treatment in TCF sequences.

Movement in the industry toward chlorine dioxide based ECF and TCF bleaching has not reduced interest in enzymes. Mill trials have shown the effectiveness of enzymes in TCF bleaching *(33)*. The kappa factor (ratio of active chlorine charge to kappa number) in the first stage of a softwood D(EO)D(EP)D sequence was decreased from 0.165 to 0.125 with no loss in brightness and good strength properties. A laboratory investigation *(34)* showed that the kappa factor could be decreased from 0.13 to 0.08 by xylanase pretreatment. The total chlorine dioxide saving was 0.5% (as ClO_2, o.d. pulp basis). More significantly, perhaps, the pretreatment allowed use of a kappa factor as low as 0.08 without significant increases in the total requirement for chlorine dioxide. This gave significant reductions in AOX output.

A study of TCF applications showed that addition of an enzyme stage to a hardwood OQPZP sequence gave a 20% reduction in ozone requirement and an 11% increase in viscosity at 89 brightness *(35)*. Similar results occurred at the 91

brightness level. Another interesting observation was that brightness and viscosity were virtually independent of the position of the enzyme stage in the sequence. Moving the enzyme stage closer to the ozone stage, however, did significantly decrease the required ozone charge. Another investigation showed that, at a given level of ozone consumption, enzyme treatment before TCF bleaching of kraft pulps increased the final brightness by 6 points for eucalyptus and 4–5 points for softwood *(36)*. The strengths of the TCF pulps were lower than those of the ECF controls.

Besides using the xylanases to enhance delignification during bleaching, more specialized preparations and applications have appeared. These include one specifically targeted at elimination of dioxin formation during the chlorine bleaching of kraft pulp *(37)* and one designed to enhance shive removal *(38)*.

The xylanases have no direct delignifying effect. The kappa number after enzyme treatment is equal to or only slightly smaller than before treatment. Lignin-degrading fungal systems will secrete enzymes that function by direct fragmentation of the lignin structure. These systems will delignify pulp as a recent investigation reports *(39)*. The kappa number of hardwood kraft pulp decreased from 15 to less than 6 by a three-day fungal treatment followed by washing. The long treatment time is an obvious drawback of this approach.

In principle, it should be possible to isolate the delignifying enzymes and use them to delignify pulp. Considerable research effort has gone toward this goal. Its progress has been the subject of a recent review *(40)*. There are three relevant enzyme activities: laccase, manganese peroxidase, and lignin peroxidase. A fungus that delignifies pulp produces the first two but not the third. Neither is commercially available. Manganese peroxidase applications have not reached the point of commercial viability. Isolated laccase is ineffective as a delignifying agent. A recent report *(41)* claims addition of another compound or "mediator" can overcome its inactivity. The enzyme oxidizes the mediator that oxidizes the lignin in turn. Softwood kraft pulp was delignified by as much as 67% in a single stage in the presence of enzyme (0.25–2 kg/ton), mediator (5–20 kg/ton), and oxygen (1–14 atm). The identity of the mediator is unknown, but it may be a low-cost, commercially available heterocyclic compound.

ECF bleaching

Forces concerned for the environment have caused a strong movement away from bleaching with chlorine in its elemental form. The easiest alternative is to replace all the chlorine with chlorine dioxide. This alternative is ECF bleaching. Its technology is developing rapidly.

Much of the impetus for this movement comes from the lower amounts of chlorinated organic byproducts formed by chlorine dioxide. The results of a study of the amounts and characteristics of the materials dissolved in the effluents from chlorine dioxide and chlorine bleaching of both unbleached and oxygen delignified softwood kraft pulps illustrates this *(42)*. The chlorine to carbon ratio (Cl/C) of each of several fractions of each effluent type provided a predictor of environmental effect. Substitution of chlorine dioxide for chlorine sharply reduced the AOX and Cl/C of the whole effluents. More significant were the observations that the reductions were larger in the ether soluble fraction and its phenolic subfraction. These fractions were also less in size. The results show that replacement of chlorine with chlorine dioxide is more beneficial than the reduction in whole effluent AOX would suggest.

III. Regulatory limits for Swedish pulp mills

	Discharge limit, kg/ton		
Item	*1991*	*1995*	*1999*
BOD	10–20		
COD	10–20		
TSS	40–70		
TOCl, softwood	2.0	1.0	0.5
TOCl, hardwood	1.0	0.5	0.3
AOX, softwood	2.5		
AOX, hardwood	1.3		
Nitrogen	0.3		
Phosphorus	0.1		

There has been considerable research aimed at finding conditions for the chlorine dioxide delignification stage that will maximize the benefits accruing from its substitution for chlorination. One parameter of interest in this regard is the pH of the stage. This affects the extent of delignification achieved, the amount of AOX formed, and the characteristics of that AOX. Studies have shown that delignification becomes less effective, less substitution of chlorine onto organic material occurs, and less AOX forms as the pH increases. Despite these general observations, a study has shown that increasing the pH from 2 to 4 at the point of chlorine dioxide addition and then allowing it to fall gives more extensive delignification. There is no additional AOX formation. The AOX that forms is more benign in character as indicated by ether soluble and phenolic Cl/C *(43)*.

A similar observation was part of the results of a study of the combined effects of pH and chloride ion addition *(44)*. In that study, increasing the D stage pH from 2 to 4 decreased both the kappa number and the amount of AOX produced. An unexpected observation was that addition of chloride ions to the pH 4 stage caused further decreases in both kappa number and AOX. A practical implication of this is that chlorine-containing chlorine dioxide (such as that produced by many existing chlorine dioxide generators) forms less AOX than pure chlorine dioxide provided application is at pH 4 in the presence of added chloride ion. In other research aimed at minimizing D stage AOX formation, AOX formation increased with chloride addition at low pH and with increased consistency *(45)*.

Another important variable is reaction time. In an investigation of the effect of D stage reaction time on D(EO) bleaching

of oxygen delignified softwood kraft pulp, a D stage of only 3 s duration resulted in 67% of the delignification of a 30-min stage *(46)*. It also produced only 26% of the AOX and 34% of the Cl/C. A 1-min D stage achieved 84% of the delignification while generating only 42% of the AOX and 51% of the Cl/C of the 30-min stage. The Cl/C of all effluent fractions except the neutral fraction was much lower at short reaction times. The size of the ether soluble fraction reached a minimum at a reaction time of 1 min.

Beneficial effects on effluent characteristics will also arise from limiting the amount of chemical applied in the first chlorine dioxide stage. The reason is that the proportion of the chlorine atoms applied that appears as AOX is much lower for the first chlorine dioxide stage than for succeeding ones. Considerable bleach sequence development work has exploited this phenomenon and evaluated the resulting cost in terms of the increase in total chemical charge required for fully bleached final brightness. Regarding the latter point, the kappa factor that minimizes total ClO_2 consumption by softwood kraft pulp in a five-stage ECF sequence (following oxygen delignification) is surprisingly low—approximately 0.12 *(34)*. Another important finding was that xylanase pretreatment allowed the kappa factor to be decreased to 0.08 for AOX reduction with only a slight (3 FIM) increase in total bleaching chemical cost.

A similar study of the corresponding three-stage sequence following oxygen delignification showed that the total bleaching chemical cost was a minimum at kappa factor 0.20 *(47)*. The combined use of an enzyme pretreatment and peroxide addition to the extraction stage allowed the kappa factor to decrease to 0.10 with a concomitant 10% increase in total bleaching chemical cost. Mills with no oxygen delignification stage may also consider low kappa factor ECF bleaching as a route to low AOX emissions. The sequence D(EOP)PDP, for example, can fully bleach softwood kraft pulp with the production of only 0.4 kg AOX per ton of pulp *(48)*. A review of laboratory studies of low kappa factor bleaching of softwood and hardwood kraft pulps with and without oxygen delignification *(49)* is in agreement with the conclusions of the work described above. It suggests the additional possibility of "zero kappa factor bleaching." This involves replacing the D stage preceding the EOP stage with a chelation or acid wash. This could provide AOX reductions of 57–85% depending on the type of pulp.

There have been investigations of a variety of ECF sequences both in the laboratory and in the mill. Conversion of a (C+D)(EOP)D sequence to ECF is technically feasible for full bleaching of both softwood and hardwood pulps *(50)*. There are potentially large increases in bleaching chemical cost, however. Certain changes could minimize the cost increase: increase the first stage consistency from 3% to 12%, increase the extraction stage temperature from 75°C to 95°C, operate the final D stage at high temperature, and add a peroxide stage at the end of the sequence. Another short sequence, OD(EP)P, can bleach softwood kraft pulp to a brightness of 89 if chelants are added at several stages and the peroxide stage operates under severe conditions (2% H_2O_2, 30% consistency, and 4 h at 90°C) *(51)*. A similar, forcing, final peroxide stage can allow full bleaching of softwood kraft pulp in the OQPDP sequence (Q = chelation stage) *(52)*. This is one step further along the road to TCF bleaching than the OQPD(EP)D sequence that has the same performance. A western Canadian mill uses the sequences DE(EO)DED and OD(EP)(EOP)DED *(53)*. In another mill, using ozone in the OAZ(EOP)D(EP)D sequence has given fully bleached pulp with properties similar of the ECF reference sequence without the ozone stage *(54)*. Cost is similar.

Conclusions

Research and commercial experience in new installations are advancing the technology of extending the kraft cook to lower residual lignin contents. Oxygen delignification is not a mature technology. It has undergone considerable recent advances. The most notable of these are the new two-stage systems and stages enhanced by the addition of hydrogen peroxide and activators. Biotechnological applications appear poised for a breakthrough in mediated lignin-degrading enzyme systems. Hemicellulase pretreatments continue to gain recognition as a technique to simplify bleaching. They are appearing in more specialized forms. Studies directed toward increasing understanding and optimization of the chlorine dioxide delignification stage, toward methods of minimizing the kappa factors employed, and toward development of new sequences are advancing ECF bleaching. Part 2 of this article will discuss TCF bleaching and related topics. ■

Literature cited

1. Lagergren, S., *1994 International Nonchlorine Bleaching Conference Proceedings*, Miller Freeman, San Francisco.
2. McDonough, T. J., *Proceedings of the Fourth China Paper Technical Conference*, TAPPI PRESS, Atlanta.
3. Pryke, D.C., Trends in World Bleached Chemical Pulp Production: 1990-1994, *Alliance for Environmental Technology*, Erin, ON, 1994.
4. Govers, T. R., *1994 International Nonchlorine Bleaching Conference Proceedings*, Miller Freeman, San Francisco.
5. Anon., *Statistics of Paper, Paperboard, and Wood Pulp 1993*, AFPA, Washington, p. 54.
6. McCubbin, N., *80th Annual Meeting Preprints*, CPPA, Montreal, 1994, p.B247.
7. Evans, T., Manolescu, D., Mason, J., *et al., 1994 International Nonchlorine Bleaching Conference Proceedings*, Miller Freeman, San Francisco.
8. Shrinath, S. A. and Brown, I. J., *TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 1.
9. McDonough, T. J. and Van Drunen, V. J., *Tappi* 63(11): 83(1980).
10. Sturgeoff, L. G. and Pitl, Y., *TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 423.
11. Tikka, P. O., *TAPPI 1992 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 699.
12. Pekkala, O., *Paperi ja Puu* 64(11): 735(1982).
13. Katz, G., *TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 323.
14. Jiang, J. E., *TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 313.
15. MacLeod, J. M., Cyr, M., Embley, D. F., *et al., J. Pulp Paper Sci.* 13(3): J87(1987).
16. Kubelka, V., Wizani, W., Neubauer, G., *et al., 1994 International Nonchlorine Bleaching Conference Proceedings*, Miller Freeman, San Francisco.

17. McDonald, S., Uusitalo, P., and Hiljanen, S., *TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 415.
18. Nordán, S. and Boman, R., *TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 711.
19. Hjort, A., *1994 International Nonchlorine Bleaching Conference Proceedings*, Miller Freeman, San Francisco.
20. Borgards, A., Patt, R., Kordsachia, O., *et al., TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 629.
21. Greenwood, B. F., *TAPPI 1990 Bleach Plant Operations Short Course Notes*, TAPPI PRESS, Atlanta, p. 63.
22. Parsad, B., Gratzl, J., Kirkman, A., *et al., TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 297.
23. Kleppe, P. J., *1994 International Nonchlorine Bleaching Conference Proceedings*, Miller Freeman, San Francisco.
24. Sixta, H., Schuster, J., Mayrhofer, C., *et al., 1994 International Nonchlorine Bleaching Conference Proceedings*, Miller Freeman, San Francisco.
25. Busnardo, C. A., Haywood, S. T., Pita, P. M., *et al., 1994 International Nonchlorine Bleaching Conference Proceedings*, Miller Freeman, San Francisco.
26. McKenzie, D. J., *1994 International Pulp Bleaching Conference Papers*, CPPA, Montreal, p. 163.
27. Nimmerfroh, N., Süss, H. W., Böttcher, H. -P., *et al., 1994 International Pulp Bleaching Conference Papers*, CPPA, Montreal, p. 247.
28. Merzeder, K., Bargfrieder, E., and Stockinger, H., *1994 International Nonchlorine Bleaching Conference Proceedings*, Miller Freeman, San Francisco.
29. Odermatt, J., Patt, R., Kordsachia, O., *et al., CPPA 1994 International Pulp Bleaching Conference Papers*, CPPA, Montreal, p. 77.
30. Dunlop-Jones, N. and Gronberg, V., *CPPA 80th Annual Meeting Preprints*, CPPA, Montreal, p. A191.
31. Yu, X., Minor, J. L., Atalla, R. H., *et al., CPPA 1994 International Pulp Bleaching Conference Papers*, CPPA, Montreal, p. 63.
32. Buchert, J. and Viikari, L., *CPPA 1994 International Pulp Bleaching Conference Papers*, CPPA, Montreal, p. 59.
33. Jean, P., Hamilton, J., and Senior, D., *CPPA 80th Annual Meeting Preprints*, CPPA, Montreal, p. A229.
34. Malinen, R., Rantanen, T., and Rasimus, R., *TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 925.
35. Ledoux, P., Detroz, R., deBuyl, E., *et al., TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 1057.
36. Yang, J. L., Cates, D., Sacon, V. M., *et al., TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 1033.
37. Tolan, J. S. and Foody, B. E., *CPPA 1994 International Pulp Bleaching Conference Papers*, CPPA, Montreal, p. 263.
38. Tolan, J. S. and Guenette, M., *CPPA 80th Annual Meeting Preprints*, CPPA, Montreal, p. B41.
39. Kakezawa, M., *CPPA 1994 International Pulp Bleaching Conference Papers*, CPPA, Montreal, p. 183.
40. Paice, M. G., Bourbonnais, R., Reid, I. D., *et al., CPPA 1994 International Pulp Bleaching Conference Papers*, CPPA, Montreal, p. 211.
41. Call, H. P. and Mücke, I., *1994 International Nonchlorine Bleaching Conference Proceedings*, Miller Freeman, San Francisco.
42. Schwantes, T. A. and McDonough, T. J., *TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 17.
43. Schwantes, T. A. and McDonough, T. J., *CPPA 80th Annual Meeting Preprints*, CPPA, Montreal, p. A95.
44. Teder, A. and Törngren, A., *CPPA 1994 International Pulp Bleaching Conference Papers*, CPPA, Montreal, p. 177.
45. Reeve, D. W., Weishar, K. M., and Li, L., *CPPA 1994 International Pulp Bleaching Conference Papers*, CPPA, Montreal, p. 281.
46. Schwantes, T. A. and McDonough, T. J., *CPPA 1994 International Pulp Bleaching Conference Papers*, CPPA, Montreal, p. 217.
47. Vegega, A. M., Strunk, W. G., Elm, D.D., *et al., TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 1049.
48. van Lierop, B., Liebergott, N., and Faubert, M., *1994 International Nonchlorine Bleaching Conference Proceedings*, Miller Freeman, San Francisco.
49. Klein, R., Strunk, W. G., and Vegega, A. M., *1994 International Nonchlorine Bleaching Conference Proceedings*, Miller Freeman, San Francisco.
50. Parthasarathy, V. R., Rudie, G. F., and Detty, A. E., *TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 933.
51. Desprez, F., Devenyns, J., and Troughton, N., *TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 443.
52. Devenyns, J., Desprez, F., and Troughton, N., *TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 341.
53. McKenzie, D. J., *CPPA 1994 International Pulp Bleaching Conference Papers*, CPPA, Montreal, p. 163.
54. Helander, R., Nilsson, B., and Bohman, G., *CPPA 1994 International Pulp Bleaching Conference Papers*, CPPA, Montreal, p. 289.

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