# Chlorine-free bleaching: ozone and enzymes to the rescue?

Martin MacLeod

EF70—Environmentally Friendly 70% brightness pulp: Is this the market kraft pulp of the future? Will your mill get to 0.5 kg of effluent AOX per ton of pulp, only to see AOX measurements abandoned in favor of 10 or 20 tests for specific chlorinated compounds? Is it time to learn a new lexicon of bleaching-oxidation equivalents, toxicity equivalents, Gonad Somatic Indexes?

Welcome to the 1990s, the Environmental Decade, in which the stress of pulp bleaching mounts to new heights. And welcome to Sweden, host country for the 1991 International Pulp Bleaching Conference, June 11–14, the first of these triennial gatherings to take place outside North America.

The 640 delegates who journeyed to Stockholm were treated to a wide-ranging program of eight sessions, 40 papers, a trade exhibition, social events, and a marathon mill tour.

Industrial in tone and content, this bleaching conference dealt with the serious business of making pulp whiter while rendering effluents clean, or more nearly so. Technologies employing such agents as ozone and enzymes were touted as almost mill-worthy right now. Scholarly offerings were less prominent than in the past.

And always at the forefront, environmental concerns.

## Environmental assessment the Swedish way

The technology of bleaching has an ever-changing character. So, too, does the science of environmental impact assessment, a specialized field in which Sweden has demonstrated a long-term commitment. The comprehensive and continuing Swedish Forest Industries Water and Air Pollution Research Foundation (SSVL) studies, which started in 1977, attest to this.

The now commonplace notions of $O_2$ delignification before bleaching, high $ClO_2$ substitution in C-stages, $O_2$ and $H_2O_2$ reinforcement of caustic extraction, and low "chlorine" multiples in the first bleaching stage are process modifications closely associated with this work. An evolutionary development was environmental testing in model ecosystems, still a little-used technique elsewhere in the pulp and paper industry.

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Front and center, as always, was **Howard Rapson**, the international dean of pulp bleaching. No International Pulp Bleaching Conference would be complete without him. This was his 12th in a row.

On Day 1, Stockholmsmassan was ready and waiting for action. The temperature was low, but the conference kinetics were impressive anyway.


A fourth SSVL study is under way, with a particular focus on Södra Skogsägarna's 350,000 tons/year Mönsterås mill on Sweden's Baltic Coast, conceivably the most environmentally assessed kraft pulp mill in the world. (At the project's conclusion, the total bill for the SSVL examinations will have exceeded US$ 30 million.)

So what's the latest news? As described by Roland Lövblad of Södra, effluents from this softwood/hardwood swing mill, currently with O(CD)(EOP)D(EP)D bleaching, have been characterized in almost every way imaginable. This has led to specific strategies for decreasing such things as chlorate release, dioxins, and polychlorinated phenolics and resin acids.

That, Lövblad admitted, still leaves the "fine tuning" to be done: further acute and chronic toxicity concerns, and work towards a model ecosystem simulating Baltic coastal waters. A further tier of research entails field studies in the receiving waters adjacent to the Mönsterås mill.

Remarkably (at least from a North American perspective), this work now includes data on effluent characteristics following secondary treatment in an aeration lagoon, a standard part of most kraft mills in the United States and Canada.

The systematic, long-term, thorough nature of the SSVL work is well presented in Lövblad's paper. A few of the conclusions bear repeating:

- "With regard to chemical characterization, sum parameters such as COD, BOD, and AOX have been drastically decreased in the Swedish mills.

- "There has been a drastic decrease in the formation and discharge of polychlorinated compounds, but this change is not adequately mirrored by the change in AOX.

- "Using modern bleaching technology, the degree of chlorination of the high molecular weight material in the effluents has been shown to be low. Therefore, it is most improbable that the 'chlorolignin' material could break down in the environment into polychlorinated fragments that could be of any importance with regard to biological effects."

One can only hope, after all of this, that the author's description of the Mönsterås mill's technology as "last generation" will in fact turn out to be only the "latest." Permits are being sought to double the mill's capacity, even though it's a lightning rod for Swedish environmental groups.

## Getting the bug

Chemistry isn't the only way to get more chlorine out of bleach plants. Think biochemistry!

Biotechnology for the pulp and paper industry has been incubating for quite some time, and the use of xylanases prior to bleaching looks like a break-out point. Unfortunately, the terminology itself isn't a great starting point—these enzymes don't bleach anything. They do go to work on the residual lignin in kraft pulps, but produce only marginal reductions in kappa numbers. Once $Cl_2/ClO_2/NaOH$ chemistry is applied, though, the enzyme effect becomes readily apparent: considerable savings in bleaching chemicals without sacrificing final pulp brightness.

Three speakers described their wares in the session on "biobleaching": Paul Skerker of Biogen Sandoz, Lars Pedersen of Novo Nordisk, and John du Manoir of ICI Canada. Their ß-endo-xylanases had a range of pedigrees (not all are created equal, either by the parent organisms or by the culturing).

The speakers all agreed that realistic treatment conditions for kraft pulp might be 50°C and 2–3 hours at 5–10% consistency. More optimistically, they'd all like to get the time down to 30 minutes.

The ICI work takes the prize for best-described experimental details, and also for the biggest apparent effect. For example, du Manoir contrasted a case of enzyme treatment, a chlorine multiple of 0.15, and about 92% brightness with no xylanase, a multiple of 0.25, and a final brightness below 91%.

Xylanase treatments tend to result in pulps of higher viscosity at a given kappa number, presumably the result of selective removal of some of the xylan, thereby "enriching" the cellulose content of the pulp. In some cases, the beating energy required to reach a given freeness or tensile strength can increase, although tear-tensile performance is not affected, at least in the lab pulps.

The animated discussion produced many questions and responses, such as the following:

**Q.** *Is it logical to do the enzyme treatment in brown stock high-density towers?*

**A.** Yes, provided that the pH of the stock is adjusted to be appropriate for the particular enzyme. No special post-enzyme wash or extraction procedure is needed.

**Q.** *Do you need $O_2$ delignification first to see the effect?*

**A.** No, regular unbleached pulps also respond well, although the relative effect is less because there's more residual lignin in such pulps.

**Q.** *How about enzyme treatment of sulfite pulps?*

**A.** Little work appears to have been done on them.

**Q.** *Okay, what about cost?*

**A.** "About US$ 5–7 per ton of pulp," said Skerker, with general head-nodding and murmurs of agreement from the other speakers.

## Inner secrets of residual lignin

Residual lignin—the fuel of pulping and bleaching research—is also the big challenge for pulp producers because it causes so many bleaching headaches and environmental woes. Göran Gellerstedt of the Royal Institute of Technology (KTH), Stockholm, gave a keynote talk on residual lignin: what it is, what it's doing still lurking there in the pulp, and what's known in detail about lignin removal chemistries.

Gellerstedt made the case, for example, that efficient cleavage of ß-alkyl-aryl-ether linkages in macromolecular lignin is essential in liberating phenolic hydroxyl groups which will then render lignin fragments soluble in alkali. He suggested that an additional factor is at work in "modified" kraft pulping—more extensive cleavage of the alkyl-aryl-ether bonds, producing dissolved lignin with a lower overall molecular weight distribution, hence greater solubility for that reason alone.

Switching to bleaching, Gellerstedt zeroed in on the oxidation of aromatic rings in residual lignin. This results in the formation of carboxylic acid groups, making the lignin products water-soluble. He noted that there's still a lot to learn about how residual lignin and carbohydrates may be linked, and how the linkages can be taken apart.

Gellerstedt's paper concludes with this intriguing statement: "Considering the fact that the residual lignin (in kraft pulp) has a molecular weight distribution which is similar to dissolved kraft lignin, it is surprising that such large chemical changes have to be introduced in order to get the remaining fiber lignin into solution. Again, restrictions to dissolution caused by the presence of lignin-carbohydrate linkages may be of major importance."

## The story on ozone

Bjorn Dillner of Kamyr AB described ozone treatment of MCC-made, $O_2$-delignified softwood kraft pulp (kappa 13.5) in the sequence (DZ)(EOP)D(ED). He estimated that the relative costs of (DZ) were a little lower than those of D100, but that both cases were significantly more expensive than a conventional D50C50 front-end (all costs included).

Dillner added this: "If a mill is planning to eliminate chlorine, and excess $ClO_2$ capacity is available, there is no economical incentive to invest in ozone generation and bleaching. On the other hand, if the $ClO_2$ generation capacity must be expanded, ozone appears to be an interesting alternative. However, the main reason for applying ozone is the significant effects on environmental parameters such as AOX and chlorinated phenols."

Two slots earlier in the program, Dominique Lachenal of CTP, Grenoble, had also advocated (DZ) without washing as the first stage in a bleaching sequence for low environmental impact.

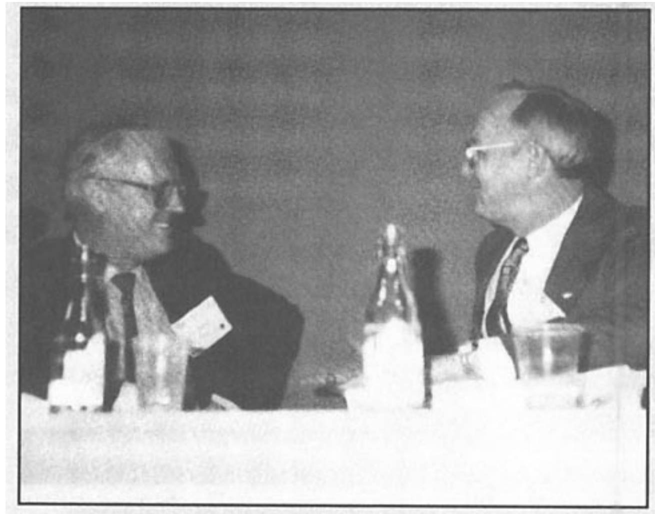
"Ozone, with its high oxidation potential, is a logical candidate to replace chlorine," Lachenal stated, "as neither oxygen nor oxygen plus hydrogen peroxide can do as good a job of lignin removal." (For more on ozone treatment, see B&T Special Report, p. 22.)

Nils Hartler of KTH added more on high-consistency ozone work: ozone-treated pulp has more leachable lignin than its oxygen-treated counterpart. And a cautionary note: Falsely low pulp viscosities result when ozonization is followed by alkaline extraction, or even dissolution in cupriethylenediamine. A borohydride pretreatment will stabilize the polysaccharides to cuene effects.

Carl-Anders Lindholm (KCL) began the ozone session with a thorough and scholarly summary of the science of $O_3$ bleaching at low and high consistencies: chemical theory, homogeneity considerations, reactions of ozone with lignin, and so forth.

Despite all the research work that's been done at low and high consistencies, there now seems to be a bias toward medium consistency for compatibility with most bleach plant operations. But it's not a foregone conclusion that MC is the only way to go. Further, with ever more agreement on what constitutes suitable process conditions for ozone bleaching, $O_3$ generation itself becomes the crucial factor in the bargain.

Conference Chairman **Jurgen Kramer** (left) chats with **Wells Nutt** of Union Camp Technologies, the first keynote speaker.



## Assembling an overall perspective

Peter Axegård (STFI) did an elegant job of coupling modern process alternatives (including effluent treatment options) with their effects on effluent parameters and pulp quality. Oxygen delignification has broad positive effects across the range of factors normally measured. It's second only to advanced biological treatment, which is strongly positive in its overall influence.

None of these technological options generally confers similar blessings on pulp quality (e.g., brightness, strength, beatability, cleanliness). It's rare just to find positive effects. In some cases, the results are quite negative: pulp cleanliness may decline when less chlorine is used, for instance.

Axegård made a particularly good point about consistent quality: "By stretching internal process measures to the asymptotic limit, the safety margins are extremely small. These margins are needed to compensate for the normal process variations that occur. One solution to this dilemma is sophisticated process control combined with very good process knowledge."

It's gatherings such as the International Pulp Bleaching Conference, of course, which foster advances in process knowledge and help identify areas where information is still lacking.

## New C-stage: chelation

When contemplating a $Cl_2$-free (but not necessarily $ClO_2$-free) future, bleaching options are gradually expanding. Depending on what criteria are acceptable in the finished pulp, a few unusual possibilities are already close to industrial acceptability; ozone use and enzyme treatments are prominent examples from Stockholm.

Add Lignox to the list—EDTA treatment to strip metal ions from the pulp, then alkaline peroxide bleaching. These stages are sandwiched between $O_2$ delignification and $ClO_2$ bleaching.

This work, fostered by Eka Nobel and under development at Aspa Bruk in Sweden, is meant to provide a relatively low-cost, nonchlorine alternative that's compatible with existing equipment.

Jiri Basta of Eka Nobel described the interplay of EDTA and $H_2O_2$ process conditions on the bleachability of softwood kraft pulp in the lab. He went on to talk about implementation trials at the Aspa mill. Two scenarios have been pursued: high-brightness pulp in an EDTA(EP)D(EP)D sequence to about 89% brightness and an effluent AOX value of 0.3 kg/ton, and "special" pulp via EDTA(EP)(EP) to 71% brightness and zero AOX. Both of these start with $O_2$-delignified softwood pulp, kappa no. about 19, and use 2 kg/ton of EDTA in the "chlorination" stage (no $Cl_2$, of course).

The high-brightness route required 25 kg/ton of peroxide (most of it in the first extraction) plus 42 kg/ton of $ClO_2$ in the D stages. With the special pulp, 26 kg/ton $H_2O_2$ all went in at E1, and the D stages were bypassed.

Pulp quality? Good, according to Basta, both in strength and cleanliness.

The work has inspired Aspa (or at least its marketing people) to invent a special moniker for their new grade: EF70, for "Environmentally Friendly 70% ISO" pulp. Next, EF80? (Lab work is under way!)

Lignox trials have been run in other Swedish mills too, and more are planned soon.

## My kappa is lower than yours

Despite an ever-widening range of bleaching options, the guts of substantial extra delignification still rest mainly with pulping. And there's promising news of kraft pulps with much lower kappa numbers—how about 10 on softwood *before* $O_2$ delignification? (How about at steady-state too?)

Beloit, Kamyr, and Sunds—the Big Three who bring you new pulping systems—provided information on recent advances:

• Solveig Nordén (Sunds): A "novel extraction technology" labeled ($E_{OX}$D) to finish a bleaching sequence, using $O_2$ and/or $H_2O_2$ reinforcement, gives brighter pulp than just a $D_N$D approach. Also, Super-Batch softwood pulps $O_2$-delignified to as low as 10 kappa are fine for bleaching, with effluent AOX values below 0.5 kg/ton in $Cl_2$-free sequences. She revealed that recent mill trial work has produced unbleached softwood pulps of 10–12 kappa.

• Andy Andrews (Beloit): Lab simulations of RDH pulping of hardwoods can routinely go to 10 kappa without problems in bleachability. In fact, "RDH pulps are as easy or easier to bleach relative to conventional ones, regardless of kappa level," Andrews asserted. He also noted that in lab pulping, RDH and conventional runs gave comparable results in pulp yield at a given kappa number.

• Brian Greenwood (Kamyr): Lab-simulated conventional, MCC, and EMCC softwood kraft pulps at kappa nos. of 32, 23, and 18, respectively, were bleached using chelation, double $O_2$ delignification, and ozone combinations, but no $Cl_2$. An example: TOOZRPZRP. Yes, you should read the paper to interpret this.

Greenwood offered an observation always worth repeating when one changes delignification chemistries: "... casual comparison of pulp viscosities among different pulps should be done with caution. The relationship between pulp strength and viscosity may be dependent both on the kraft cooking process and the bleaching sequence used."

All three speakers made it clear that kraft pulping of both softwoods and hardwoods can now be taken to very low kappa levels by choosing appropriate conditions. This usually implies extra alkali, more time, and sometimes higher temperatures (in batch systems).

More documentation of the dynamics of a "modified" kraft mill's operations at times of pulp sampling should rate a higher level of consideration, though, and *definitive* information on lab simulations is overdue. Loads on recovery boilers got little attention in Stockholm—maybe it's time to consider linking the bleaching and chemical recovery conferences.

Even so, developments in low-kappa pulping auger well for significantly decreasing the residual lignin entering downstream operations.

## On to a brighter (?) future

As the bleaching conference expands, it becomes ever harder for an attendee to cover it all—impossible, in fact, with this year's simultaneous sessions. As with any top-notch conference, you have to read the papers, even if you were there! You'll find plenty of information on sulfite pulp bleaching and on chlorine replacement, for instance, and a session on mill experiences with low-kappa pulping and with high $ClO_2$ substitution.

If the jam-packed technical program wasn't sufficient for the delegates, additional features included a trade show with 25 exhibitors, a reception at Stockholm's impressive City Hall (courtesy of the city), a conference dinner at the Wintergarden of the Grand Hotel, and a monumental mill excursion on Day 4 to experience first-class hospitality at the Iggesund bleached paperboard mill 300 km north of Stockholm. Those who experienced the last of these events—three busloads of them—could be deemed the true survivors of the 1991 International Pulp Bleaching Conference.

One can conclude from the conference in Stockholm that while not already dead, chlorine bleaching is certainly in rapidly failing health, and "new" bleaching chemicals are on the rise, especially ozone. Chlorine dioxide probably has a long life still ahead of it, based on widening environmental knowledge and on its sheer efficiency in lignin removal and pulp brightening. Enzyme pretreatments are getting a workout in industrial bleach plants. There'll be a lot more use of hydrogen peroxide at many points along new bleach lines.

And less environmental pressure several years hence? No, that would be wildly optimistic. Instead, pulp bleaching will become an even more demanding race, with $ClO_2$ and $O_3$ perhaps leading the way. Ladies and gentlemen, start your generators. □

*The 1991 International Pulp Bleaching Conference, June 11–14, was cosponsored by the CPPA Technical Section, EuCePa, and TAPPI. It was organized and run by The Swedish Association of Pulp and Paper Engineers (SPCI), led by Bengt Jacobsson. Its theme: "Production of Bleached Chemical Pulp in the Future." The three conference books are available by contacting SPCI at Villagatan 1, S-114 32, Stockholm, Sweden; fax: (08)11 54 19.*

*Conference Chairman: Jurgen Kramer of Simons, Brazil. Program Chairman: Ants Teder (Swedish Pulp and Paper Research Institute—STFI), ably assisted by 15 prominent bleachers from six countries.*

# "Best Picks" of the conference

No official awards are given at the International Pulp Bleaching Conference, so here are a few suggestions from a panel of one:

• Most mind-boggling new sequences: A tie between TOOZRPZRP (Brian Greenwood, Kamyr Inc.) and (PFA)OZ(EB)PPP (Kristiina Poppius-Levlin, Finnish Pulp & Paper Research Institute). Soon to come: UDSERVABRAK2DA?

• Best slides: Another tie, this one between John du Manoir (ICI Canada) and Jiri Basta (Eka Nobel).

• Best support for why anyone, especially operating companies, ought to do bleaching R&D: From Wells Nutt (Union Camp Corp.) in his keynote address on the opening day.

• Most impressive technical terms: "Mesocosm" (a model ecosystem), and "Gonad So--matic Index," both in a paper by Lövblad *et al.* (Södra Skogsägarna).

• Terminology-of-the-future (?): "Oxidation Equivalents" (OXE) to put the chemical power of bleaching reagents on a new, nonchlorine base (Roland Grundelius, Stora).

• Most pressure diffusers along one kraft mill fiber line: Iggesund Paperboard, with three, including one after the pressurized first extraction stage in the bleach plant.

*—Martin MacLeod*