Ozone wasn't the whole story at the 1994 International Pulp Bleaching Conference

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About two decades ago, mechanical pulpers began inventing their "alphabet-soup" lexicon of processes. Bleachers of chemical pulps are rapidly catching up. But it's a disordered state, sometimes with Z ahead of P (and sometimes not), AO transformed into I, TCF changing its middle initial to E, and other curiosities.

Bleaching technology is in a great state of flux. Environmental impact, chemical and biological reagents, economics, and marketing are all in play. The once-ubiquitous CEDED is gone forever.

How, then, to catch up on the bleaching revolution? For 560 people from around the world, attending the 1994 International Pulp Bleaching Conference last June was the answer. Gas-phase reactions took on new meaning in Vancouver as the Stanley Cup series ended that week. Atmospherically, the liquid phase was foremost. And after a solid four days of the latest in bleaching, BOZO was the last sequence on anyone's mind.

The International Pulp Bleaching Conference is a cooperative effort of the CPPA's Technical Section (this year's organizer), TAPPI, SPCI, and EUCEPA. Last held in Stockholm in 1991, it will shift to the United States in 1996, breaking the triennial pattern. Bleaching can't wait three years anymore.

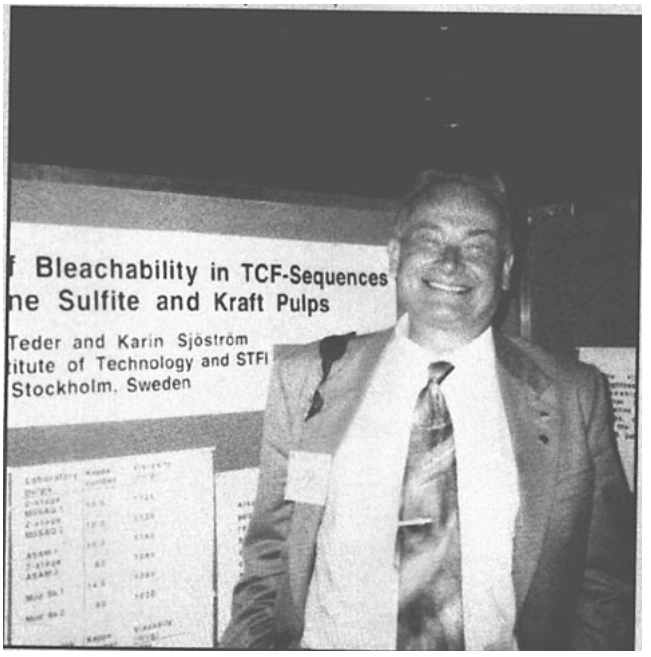
In attendance, continuing his streak since the first such conference in 1957, was Howard Rapson, godfather to the world's bleachers. Ants Teder of KTH in Stockholm, the Wallenberg Prize co-winner in 1993, was conference chairman. Doug Reeve of the University of Toronto served as program chairman. And an impressive cast of bleaching experts from seven countries—if not from Abu Dhabi to Zimbabwe, then at least from Brazil to the United States—assembled the program.

Getting a fix on ClO_2

Arguably the most scholarly offering at this conference was that by K. Solomon (U. of Guelph) and four scientific experts recently employed to assemble a definitive picture of the environmental impact of ClO_2 use vis-à-vis Cl_2 in pulp bleaching. Along with such nuggets as "dose-response characterization is what you've all done at one time or another, such as with alcohol—different organisms have different responses" and "reduced gonad size is something I'd be worried about if I were a fish," Solomon effectively summarized a massive amount of literature. In the committee's judgment, the substitution of ClO_2 for elemental Cl_2 results in:

- Reduction in the quantities of organochlorines produced.
- Reduction in the degree of Cl_2 substitution in the organochlorines produced.
- Reduction in the degree of persistence of the organochlorines produced.
- Reduction in the potential for bioaccumulation and food chain transfer.
- Reduction in adverse ecological effects, *decreasing their risk to insignificant levels.*

Ants Teder of KTH, Stockholm, was conference chairman, a main session co-author, and a poster boy.



Solomon also pointed out that much of the science to date concerns acute lethality, and he recommended that increasing attention be given to long-term chronic studies. To determine what's happening at the molecular level, he said, will require identifying the chemical structures of compounds that cause biological effects. This paper should be required reading for those associated with industrial pulp bleaching practice and everyone responsible for setting regulations.

Another paper on environmental impact came from T. J. Hall and colleagues (NCASI). He discussed chronic bioassay work in marine and freshwater settings, focusing on what happens when a kraft bleachery is converted to high ClO_2 substitution (the target mill went from <17% to 60–70%). The principal answers: moderate AOX reduction in this case, some reductions in chlorinated phenolic compounds (and increases in others), but no clear improvements in effluent bioassay responses.

Hall found that the bioassays were often at or near detection limits, so differences were hard to find. At this mill, "the overriding influence on effluent quality was the efficient functioning of the biological treatment system . . . which had more influence . . . on bioassay response than the conversion to increased ClO_2 substitution."

At many kraft mills, bleaching renovations encompass a hard struggle of decisions, money, and implementation. Harmac Pacific is one of these, having recently gone through a major makeover of three bleach plants designed many years ago. Despite different parentages, all three are now fraternal triplets—DEEoDED—with elimination of hypo and minimization of caustic via Papricycle. AOX has declined from about 6 kg/ton pulp to less than 1 kg/ton. D. McKenzie's paper bears examination for how they did it.

Also of interest is their new mini-O_2 delignification system ahead of B Bleach. It's a 30-min tube reactor made of Type 2205 duplex stainless steel, operated at 90 psig, blowing pulp into a high-density tower. Washing comes six hours later; about 25% delignification is the target. By installing a second tube, they can double the system's capacity.

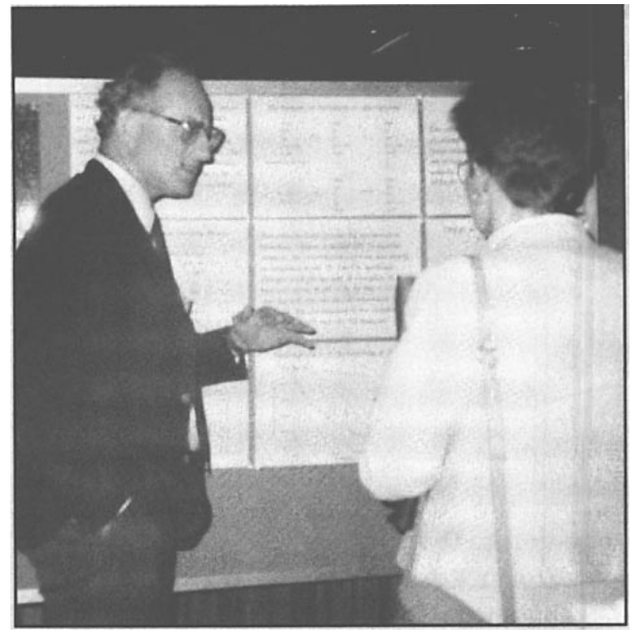
And now hear this from a Swedish speaker: "When proper conditions are chosen, chlorine-containing chlorine dioxide can be used with as good a result, with regard to the formation of chlorinated organics, as pure chlorine dioxide." So said A. Törngren (KTH, Stockholm), after working on O_2-delignified kraft softwood pulps. He found that certain conditions—including rapid consumption of small amounts of Cl_2, as others have noted—produce no increases in levels of AOX, chlorinated organics, or chlorinated dioxins.

Sequence worthy of Liberace

A stream of scientific news continues to emerge from lab studies of the current hot topic, ozone bleaching:

- U. Germgård (Sunds Defibrator): The sequence O(QZ)Q(PO), incorporating high-consistency ozone and pressurized peroxide/O_2, and using only wash presses, can produce strong hardwood and softwood TCF pulps at 90% ISO brightness. A low kappa number after O_2 is essential. PO at 110°C is far better than P at 90°C.
- D. Lazar *et al.* (Union Camp and Riocell): Using Riocell's eucalyptus chips, pulp at kappa no. 12.5 was made in the lab, O_2 delignified to kappa no. 9 at medium consistency, and then subjected to a variety of sequences using O_3, H_2O_2, and chelation. ZQP could reach 90% brightness at a cost comparable to D(EO)DED (no O_2). Simulated filtrate carryover was part of the experimental work, a technique worthy of consideration by more researchers.
- R. Malinen *et al.* (KCL, Helsinki): Using a specially designed flow-through O_3 reactor, they studied how best to use ozone in TCF bleaching. Their main conclusion: both ozone and peroxide are required to reach market brightness at acceptable cost, with perhaps small sacrifices in strength and light-scattering ability. The overriding factor is how low the kappa number is before bleaching. Malinen emphasized that "O_2 delignification is the workhorse of a TCF line, having much more potential than is usually being realized."

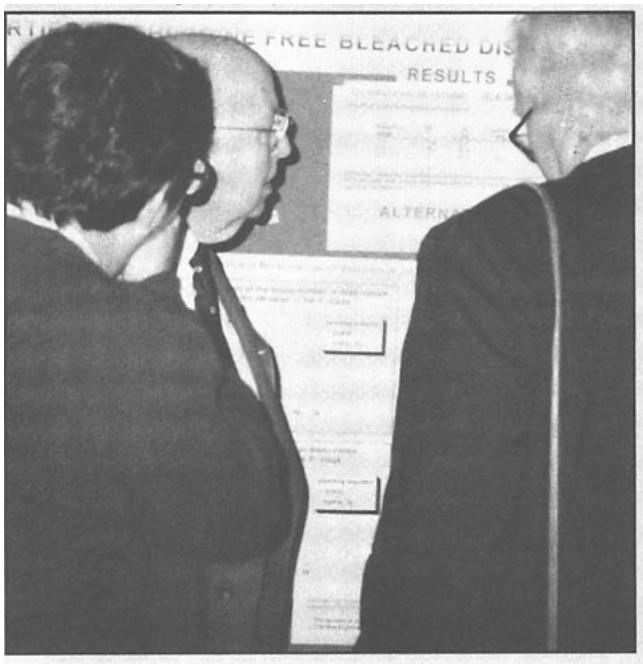
Adrian Wallis (left) of CSIRO, Australia, explains the nuances of eucalyptus pulping to **Anna Tigerström** of AGA, Sweden.



Industrial-strength ozone

Ozone, of course, has already escaped from the lab, finding a home in several kraft mills since the 1991 conference. At Stora's Skoghall mill, for example, a medium-consistency O_3 system was installed in September 1992 at the front end of a switchable softwood line that can be ECF or TCF. Final products are MG paper and board for liquid packaging. In R. Helander's paper, there's information on how they chose the ozone-generating and mixing equipment and the position for Z. Only minor changes in pulp properties were found. The

As always, **Howard Rapson** (center) immersed himself in the goings-on, here examining a poster presentation.



Hector Audette of Dow Chemical presents a classy poster on how metal ions affect bleaching.



TCF version of this line achieves 86% brightness, and effluent quality has been improved significantly, but they're not recovering the O_3 filtrate yet.

Another advance toward closed bleach plants is unfolding on the 300,000-tpa birch kraft line at MoDo's Husum mill. MoDo previously pioneered bleach plant closure at its Domsjö sulfite mill in the late 1980s.

As can be predicted at mills elsewhere, the closure scenario at Husum has been a stepwise progression, including a major rebuild in 1992 and the addition of a medium-consistency O_3 system in 1993. The hardwood line runs in an ECF mode (OQPDD) or a TCF one (OQPZP). Filtrate flow is countercurrent. First-stage filtrate is used to wash O_2-bleached pulp, thereby entering the recovery cycle. Much attention has been paid to maximizing the efficiency of the drum washers. Also, extra filtrate tank capacity was added throughout the line, and still more is needed. Other considerations (metals management, extractives control, and pulp quality) are addressed in E. Vikberg's interesting paper, which amply demonstrates why full closure is not an overnight achievement.

Here are some take-home lessons if you're contemplating a Z stage in a TCF line: get the kappa number as low as possible after both pulping and O_2; manage the dissolved metals balance rigorously; and use peroxide efficiently, preferably in the (PO) mode.

Champion's bleach filtrate recycle (BFR™) process is another approach to closure. In an OD(EOP)D lineup, the D_{100} and EOP filtrates would be used to wash post-O_2 pulp, and the extra chloride loading in the recovery loop would be removed from the electrostatic precipitator dust. To date, this is lab-scale work.

Maximizing metals management

Chelation prior to peroxide bleaching of kraft pulps—is it the only way to go, or just the most expensive? The answer, according to J. Bouchard *et al.* (Paprican), is that appropriate acid treatment is preferable. It is just as effective for metal ion removal, it needn't decrease pulp viscosity, and the effluent can be recycled many times without affecting brightness. Time, temperature, and pH have to be matched to the pulp being treated, and Mg^{2+} must be added before the P stage.

Several speakers tackled the subject of metal ion removal and control, an essential consideration in TCF bleaching and also in the TEF era predicted to follow. J. Basta *et al.* (Eka Nobel) noted that the metals profile in a pulp must be known accurately if one is to have any hope of controlling it properly. Maintaining appropriate pH conditions may be a better technique than trying to restore a suitable balance after metals have been stripped via an acid wash.

A broad perspective, in both the range of metal ions and in suitable locations to deal with them in kraft mills, was advocated by H. Lindberg and colleagues (Kamyr/Ahlstrom). They recommended adding a precipitation system for acidic bleach plant filtrates, especially to concentrate Mn and Fe in a small purge stream. Reusing this stream with weak wash allows green liquor filtration to be the outlet for the metal ions. The fate of other nonprocess elements—Ba, Ca, Al, and Si—is also discussed in Lindberg's paper.

On the enzyme front, the initial flurry surrounding the use of xylanase has settled down to routine practice in a modest number of mills. The search is now on for enzymes with true delignifying power. Lignolytic enzymes from some fungi ap-

pear promising, but they remain lab curiosities so far—too slow, and unavailable commercially. Watch for news at the 1996 conference.

So what's the mid-1994 review in the sci-tech theater of chemical pulp bleaching? For now, the leading actor is ECF; TCF plays a supporting role, and sometimes has the lead in Northern European productions. After a very long wait in the wings, ozone has appeared on center stage, but the more experienced actors (especially ClO_2) still have most of the good lines. Ticket prices to enter the newest shows are up (the actors and stage equipment aren't cheap).

Will the market support this trend? You could wait and see, but probably not for very long—customers stop going to old shows.