Implementation in full scale—the next step for Prenox®

Rolf Brännland
Senior research engineer, Mo och Domsjö AB, Örnsköldsvik, Sweden

Solveig Nordén
Manager, research & development, Chemical Pulping, Sunds Defibrator Industries AB, Sundsvall, Sweden

Lars-Åke Lindström
Vice president, research & development, Sunds Defibrator Industries AB, Sundsvall, Sweden

ABSTRACT *Environmental problems associated with the production of bleached chemical pulps have led to development work aimed at decreasing the lignin content of pulp prior to bleaching with chlorine chemicals. To achieve this, a new process has been developed. In this process, Prenox softwood kraft pulp is treated with nitrogen dioxide, NO_2, prior to oxygen delignification. This treatment allows for a substantial decrease in the kappa number after the oxygen stage.*

Here, we report on the results after finalizing laboratory and pilot plant trials. Results on incinerating nitrogen-containing black liquors in full-scale industrial production are also presented.

KEYWORDS
Bleaching
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Effluents
Kraft pulp
Mechanical properties
Nitrogen dioxide
Oxygen
Softwoods

The Swedish Environmental Protection Board has published an "Action plan against marine pollution." The plan calls for reducing the discharge of chlorinated organic compounds, expressed as total organic chlorine (TOCl), according to the schedule in **Table I.** This plan shows the Swedish ambition to practically eliminate the discharge of chlorinated organic substances originating from the pulp and paper industry (*1*).

Sunds Defibrator has been involved for a long time in development activities aimed at decreasing pollution from bleaching. These activities include oxygen delignification, extended delignification in cooking (*2*), and ozone delignification. The principal strategy for these developments is to decrease the lignin content of pulp prior to beaching.

In the early 1980s, Samuelson and coworkers (*3*) showed that pretreating softwood kraft pulp with NO_2 and O_2 under acidic conditions decreased cellulose degradation in an oxygen-delignification stage. Based on these experiences, a joint development project was formed in 1984 with participation from AGA, EKA-Nobel, Mo och Domsjö AB, and Sunds Defibrator AB. The aim of the project was to develop the findings of Samuelson into a commercially applicable process. This process, Prenox, would make it possible to drastically lower the kappa number of pulp prior to bleaching with chlorine chemicals. The consequence would be to decrease emissions from the bleach plant, especially the emissions of chlorinated organic material.

Here, we summarize the results achieved in laboratory and pilot plant trials. Preliminary reports have been given elsewhere (*4-6*). Our main objectives here are to discuss the environmental aspects related both to the emissions from the bleaching process and to NO_x from the recovery furnace.

The Prenox process

A simplified flowsheet of the pilot plant is shown in **Fig. 1.** The process

I. Action plan regarding discharge of chlororganic compounds from the Swedish pulp and paper industry, 1975-2010

Year	TOCl, kg/a.d. ton of bleached pulp
1975	5-6 (possibly 6-8)
1984	~3.5
1988	1.5-3.5
1992	1.5
2005	0.5
2010	0.1

II. Trials with softwood kraft pulps by mill, pilot, and laboratory segments

	Cooking	Prenox	Oxygen delignification	Bleaching
Paper strength properties	Mill	Pilot	Pilot	Lab
Chemical characterization of spent bleach liquors	Mill, lab	Pilot, lab	Pilot, lab	Lab
Biological characterization of spent bleach liquors	Mill	Pilot	Pilot	Lab

consists of a high-consistency Prenox stage followed by a medium-consistency oxygen stage. Unbleached pulp is withdrawn from the kraft mill and is stored in a separate low-consistency chest. During operation, the pilot plant has been running continuously for 3-4 days at a time and at a capacity of three metric tons per day. Countercurrent washing has been performed by adding wash liquor after the oxygen stage.

The initial laboratory trials showed that when Prenox was combined with an oxygen stage, a much lower kappa number could be reached than with an oxygen stage alone. Kappa numbers of about 9-10 were reached after the oxygen stage vs. kappa numbers of 18-20. In both cases, the pulp viscosity was about 950 dm^3/kg. By combining modified extended cooking and Prenox, kappa numbers as low as 7-8 were reached (*4*).

In the pilot plant, the laboratory results were confirmed. However, to allow for process fluctuations, a kappa number target of 10 would be appropriate (*5*).

Pulp quality

Paper strength properties of bleached pulps produced with the Prenox process have been shown to be equal to those produced in conventional systems (*4, 5*). Our study has confirmed this result.

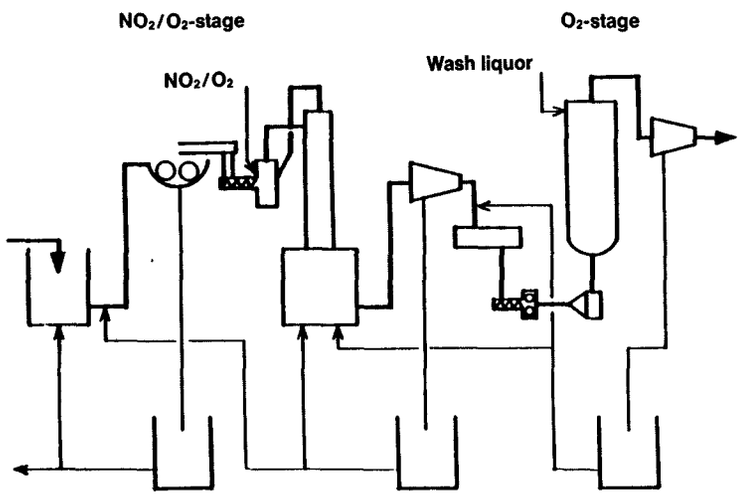
Figure 2 shows tear index vs. tensile index, and **Fig. 3** shows tensile index vs. beating, for dried bleached pulps. Bleaching has been performed in the laboratory, whereas unbleached, oxygen-delignified, and Prenox pulps have been produced in

III. Bleaching conditions

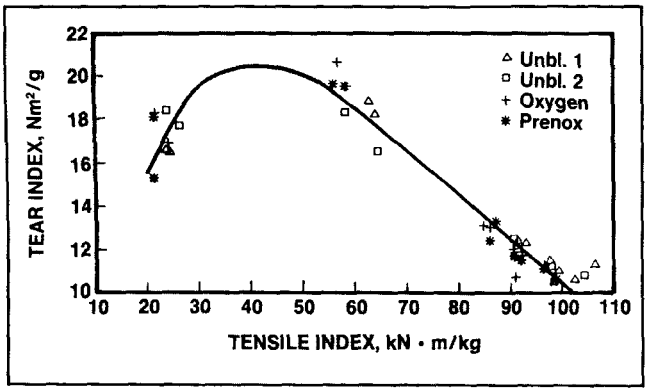
	Unbleached	Oxygen-delignified	Prenox®
Kappa number	28	18	10
Sequence	(C+D) (EO)DED	(DC) (EO)DED	DC(EO)D
ClO_2 in first stage, %	10	40	50
Cl_2, kg/o.d. ton of unbl. pulp	54	18	10
Total consumption, kg active Cl/o.d. ton of unbl. pulp	82	45	31
Brightness, % ISO	91	90	89

Carryover of 10 kg COD/o.d. ton of unbleached pulp

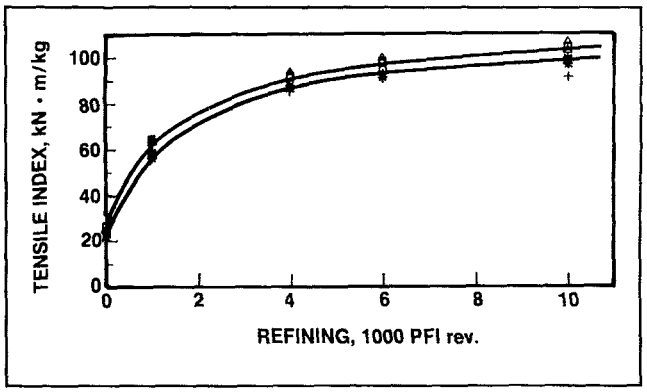
1. Principal flow sheet of Prenox pilot plant



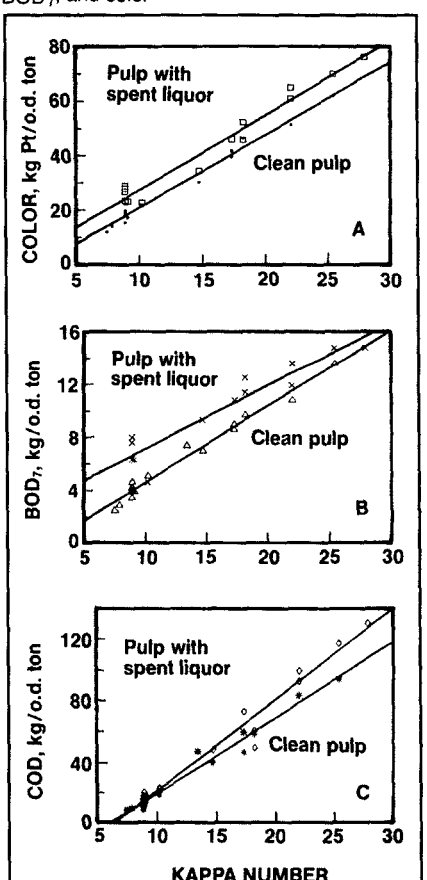
2. Tear vs. tensile for dried bleached pulps



3. Tensile vs. beating (PFI rev.), dried bleached pulps



4. Conventional effluent parameters for COD, BOD_7, and color



mill and pilot plant trials, as shown in **Table II**. The bleaching conditions are given in **Table III**.

Bleaching trials

Bleaching effluents were produced in the laboratory from pulps made in the laboratory and pulps made in the pilot plant under well-controlled conditions. We bleached both well-washed pulps and pulps to which spent liquors produced in the pilot plant had been added to simulate a carryover corresponding to 10 kg COD/o.d. ton. In this way, we simulated the bleaching of mill-washed pulps.

The bleaching was carried out in three or five stages to a final brightness of 85–91% ISO.

Bleach plant effluents

Conventional parameters

The conventional effluents parameters, COD, BOD_7, and color were all reduced in proportion to the kappa number of the pulp to be bleached, as **Figs. 4A–C** show.

A reduction of the kappa number from 28 to 18 means that the COD value is reduced from 75 kg/o.d. ton, for example, to 45 kg/o.d. ton. A reduction in kappa number from 28 to 10, by the same token, causes a decrease in the COD value from 75 kg/o.d. ton to 25 kg/o.d. ton.

Chlorinated organic material

The amount of TOCl formed during bleaching was linearly proportional to the amount of elemental chlorine, in Cl_2 and ClO_2. **Figure 5** shows this result. Similar results have been published by Germgård (*7*) and Axegård (*8*).

Based on this linear relationship, we calculated the influence of kappa number and ClO_2 substitution on TOCl formation. The result is presented in **Fig. 6**. For this calculation, we also estimated that the total consumption of active chlorine for 15%, 50%, and 90% ClO_2 substitution in the chlorination stage is 2.9, 2.9, and 3.3 kg/ton per kappa number, respectively. The charge of active chlorine in the chlorination stage, as percent on pulp, has been set to (0.18 × kappa no.).

The new regulations in Sweden allow a maximum of 1.5 kg TOCl/a.d. ton of bleached pulp. This limit corresponds to about 1.6 kg TOCl/a.d. ton of unbleached pulp. According to Fig. 6, this level can be reached with the following combinations:

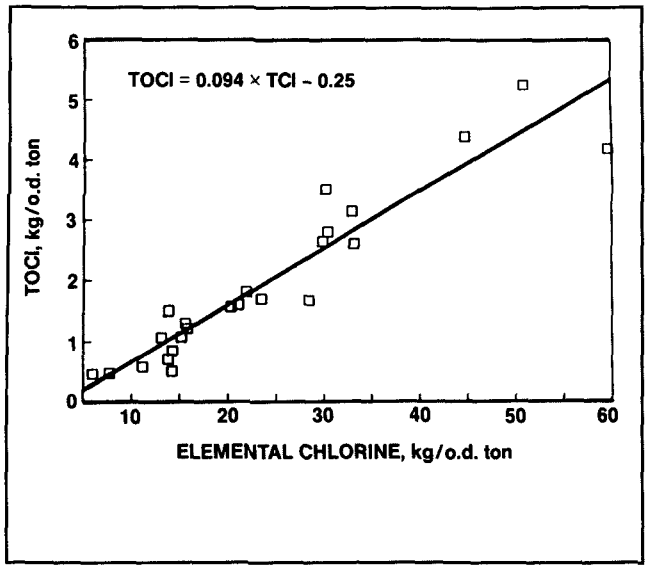
- Kappa no. 11, 15% ClO_2 substitution
- Kappa no. 15, 50% ClO_2 substitution
- Kappa no. 24, 90% ClO_2 substitution.

As mentioned, the TOCl limit in Sweden is likely to be decreased further. At 0.5 kg/a.d. ton of bleached pulp, corresponding to about 0.55 kg/a.d. ton of unbleached pulp, both a low kappa number prior to bleaching and a high chlorine dioxide substitution will be required—e.g., kappa no. 10 and a 90% ClO_2 substitution.

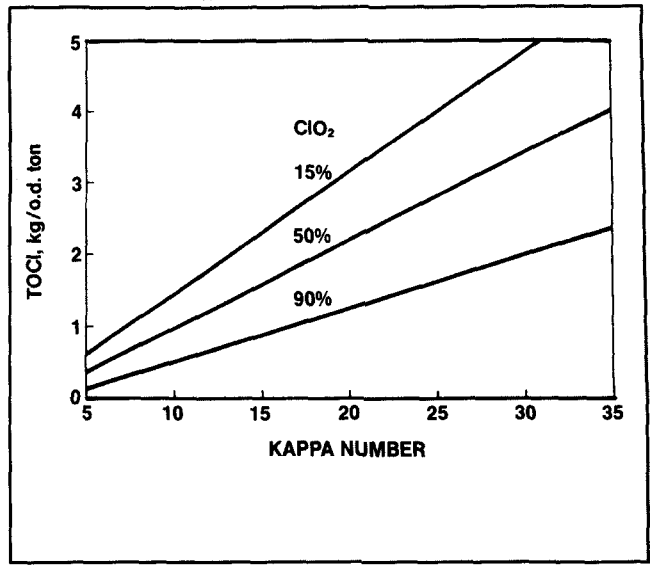
TOCl may be too coarse a measure of the environmental hazards of spent bleach liquors, especially at lower discharge levels (*9*). At lower discharges, the focus should be on highly chlorinated organic compounds, which could be considered priority pollutants.

Low-molecular-weight, trichlorinated and tetrachlorinated phenolic

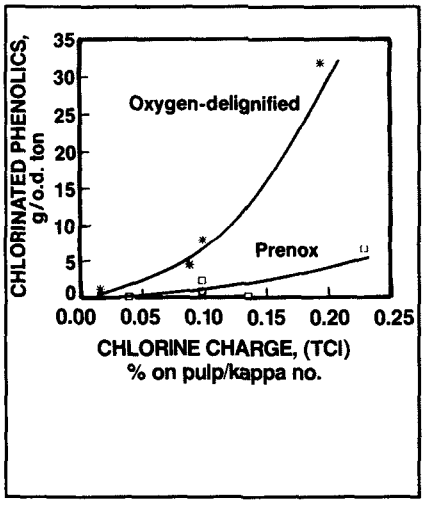
5. The amount of TOCl formed during bleaching is linearly proportional to the amount of total chlorine.



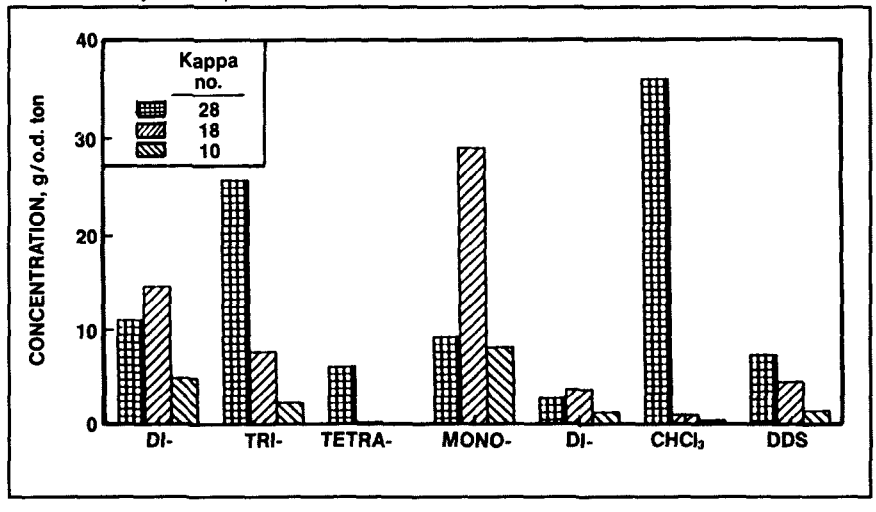
6. The influence of kappa number and ClO_2 substitution on the formation of TOCl [using a (C+D)(EO)DED sequence]



7. Trichlorinated and tetrachlorinated chlorophenols, guaiacols, and catechols vs. total elemental chlorine



8. Concentrations of chlorinated organic compounds after bleaching for kappa numbers of 27.9, 18.2, and 10.2 (DI-, TRI-, and TETRA = di-, tri-, and tetrachloroguaiacols, -phenols, and -catechols. MONO- = monochlorovanillin. DI- = dichlorovanillin. $CHCl_3$ × 0.1 = chloroform × 101 DDS = dichlorodimethylsulfone.)



compounds are considered toxic. It has been reported that, with the exception of catechols, they have a high potential for bioaccumulation (*10, 11*).

In **Fig. 7**, we have plotted the total amount of trichlorinated and tetrachlorinated phenols, guaiacols, and catechols found in spent bleach liquors against the elemental chlorine in Cl_2 and ClO_2 charged in the chlorination stage. This charge has been expressed as % Cl on pulp divided by the kappa number, where the total chlorine, *TCl*, is:

$$TCl = Cl_2 + (0.2 \times ClO_2) \quad (1)$$

The diagram shows that the bleaching of Prenox pulps produces much less trichlorinated and tetrachlorinated phenolic compounds than the bleaching of oxygen-delignified pulps. Similar results have been presented by Axegård (*12*).

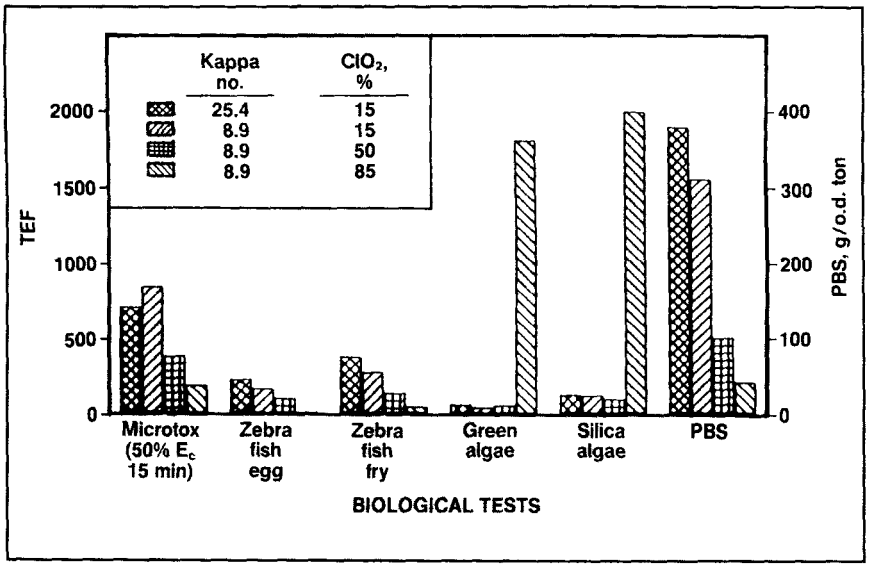
From these results, we conclude that the discharge of highly chlorinated organic material can be decreased to low levels by reducing the kappa number prior to bleaching. A further reduction can be achieved by replacing Cl_2 with ClO_2 in the chlorination stage or by decreasing the charge in the chlorination stage.

Figure 8 further confirms the importance of reaching a low kappa number before bleaching in order to decrease the discharge of low-molecular-weight, chlorinated organic material. Especially notable is the large decrease of the neutral components chloroform and DDS (dichlorodimethylsulfone). Chloroform has been decreased from about 360 g/o.d. ton to only 10 g/o.d. ton and 4 g/o.d. ton, respectively, for oxygen delignification and Prenox treatment prior to bleaching.

Biological tests

Besides performing chemical analyses on bleach plant effluents, we also

9. Biological effects of bleaching liquors from oxygen-delignified pulps with kappa numbers of 25.4 and 8.9



tested them for biological effects. One important reason was to find out if new toxic compounds are produced when Prenox pulp is bleached.

Two series of tests were performed. The acute toxicity tests applied were Microtox®, the hatching frequency of zebra fish eggs, the survival of zebra fish fry, and tests with *Daphnia magna* and with green and silica algae.

The amounts of PBS, substances with high bioaccumulation potential, were also analyzed. [PBS is a lipophilic material with a $P_{ow} > 5 \times 10^4$, according to Renberg *et al.* (*15*).]

Figures 9 and 10 show the results from these two test series. In both series, oxygen-stage spent liquor, corresponding to a wash loss of 10 kg COD/o.d. ton of unbleached pulp, was added to the pulp prior to bleaching.

In Fig. 9, effluent analyses from the bleaching of oxygen-delignified pulp of kappa no. 25.4 bleached with 15% ClO_2 substitution are compared with effluent analysis from Prenox pulps, with kappa number 8.9, bleached with 15%, 50%, and 85% ClO_2 substitution.

The introduction of Prenox resulted in a small decrease in toxicity in all cases except the Microtox test, which showed an increase. An increase of the ClO_2 substitution resulted in a decrease of all parameters except for toxicity against algae. This effect can be explained by the increased chlorate formation when using a high ClO_2 substitution.

In Fig. 10, the biological effects are shown for the effluents produced according to the conditions in Table III. The biological tests showed an advantage for the oxygen delignification and Prenox with the exception of Microtox.

To further study the character of Microtox toxicity, we treated effluents with sludge and aerated them for three days. After this treatment, Microtox toxicity was reduced for all effluents, as shown in **Fig. 11**. This drop was especially pronounced for the effluent from the bleaching of Prenox pulp, which after the treatment exhibited the lowest toxicity. For the Prenox effluent, we also observed that toxicity dropped immediately after the addition of sludge.

Apparently, the components giving rise to Microtox toxicity are unstable and are easily degradable by the biological treatment. PBS and AOX (absorbable organic halogens) were also determined after the aeration of sludge-treated effluents, as **Figs. 12 and 13** show. The reduction in PBS was largest for the Prenox effluent, while the reduction of AOX was of the same order for all three effluents.

Emissions of NO_x

The quantities of nitrogen added as nitrogen dioxide or nitric acid in a Prenox process correspond to 3–10 kg/metric ton of pulp. Primarily, the nitrogen compounds end up in the black liquor as nitrate.

It has been feared that the nitrogen in the black liquor would be transformed into NO_x in the recovery boiler. **Figure 14** shows the results from full-scale trials, simulating 1% and 2% charges of NO_2 on pulp. A significant increase of NO_x emissions was observed, but less than 5% of the added nitrate was found as NO_x in the flue gases, and there was little N_2O. Evidently, most of the nitrate was reduced to nitrogen gas in the recovery boiler.

Concluding remarks

These trials have shown several important results:

- A kappa number between 8 and 10 can be reached.
- Papermaking properties are maintained at the same quality as that of oxygen-delignified pulps.
- Emissions to water are considerably decreased, even compared with the bleaching of oxygen-delignified pulps.
- Less than 5% of added nitrogen is found as NO_x in the flue gases from the recovery boiler.

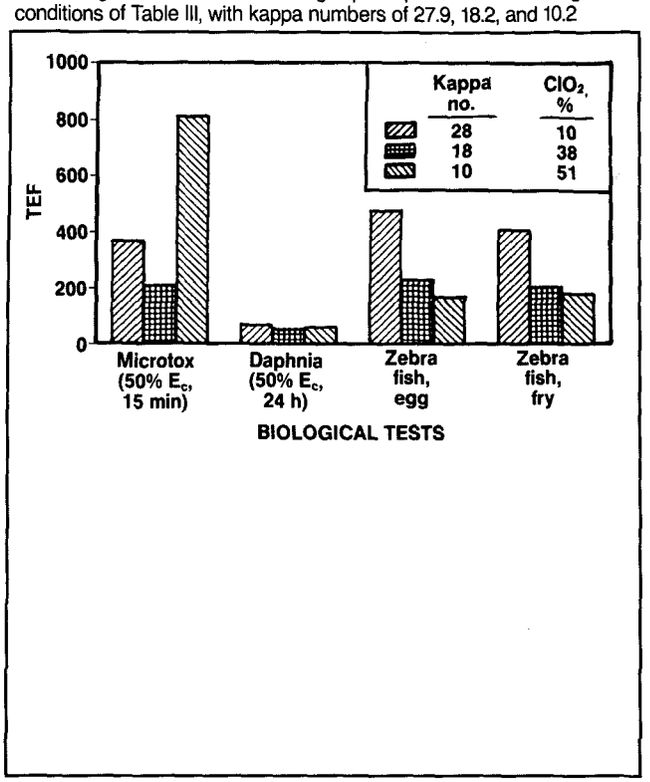
The next step in the development of the Prenox process is a full-scale prototype installation. Its purpose would be to verify the results achieved in laboratory, pilot plant, and full-scale trials.

Experimental procedures

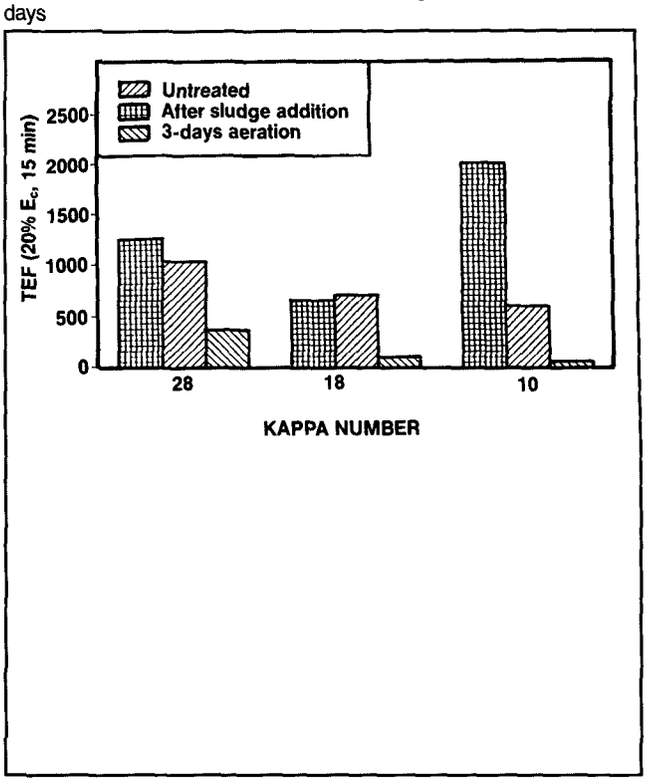
Results presented here refer to laboratory, mill, and pilot plant trials with Scandinavian softwood kraft pulps, according to Table II. Bleaching conditions relevant for results presented in Figs. 2, 3, 8, 9, and 11–13 are given in Table III. Experimental procedures are given in other publications (*2–4*).

NO_x emissions from the recovery boiler were analyzed with a Bendix chemiluminescence instrument at Norrsundet Bruks AB in Sweden. The design capacity of the boiler is about 24 metric tons of dry solids/day. The actual load was about 35 metric tons of dry solids/day. To simulate the incineration of "Prenox spent liquors," we added $NaNO_3$ to the mixing tank for Na_2SO_4 before introducing the thick black liquor to the recovery boiler. The amounts of $NaNO_3$ corres-

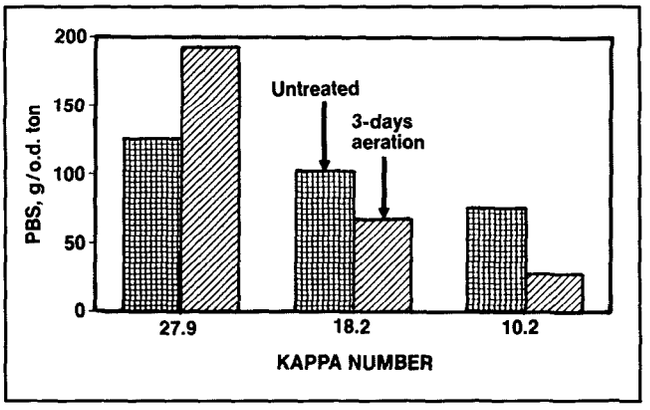
10. Biological effects of bleaching liquors produced according to the conditions of Table III, with kappa numbers of 27.9, 18.2, and 10.2



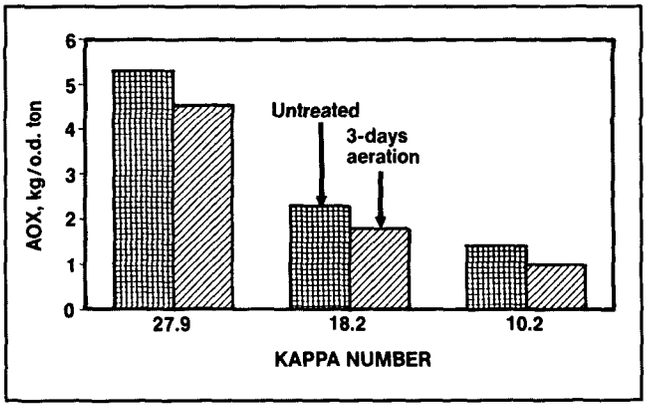
11. Microtox tests for effluents treated with sludge and aeration for three days



12. AOX concentrations after the aeration of sludge-treated effluents



13. PBS concentrations after the aeration of sludge-treated effluents



pond to 1% and 2% of NO_2 on pulp, respectively. The analyses were performed by the Institutet för Vatten- och Luftvårdsforskning.

The methods of analysis are listed in **Table IV**. The mechanical properties of bleached pulps were determined according to ISO methods after beating in a PFI mill.

The toxicity emission factor, *TEF*, was calculated according to the following formula:

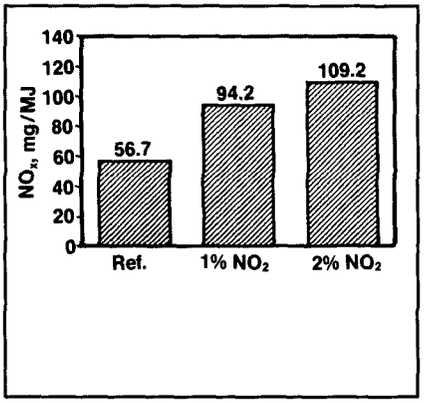
$$TEF = V(100/E_c) \qquad (2)$$

where

V = bleach plant effluent volume, m^3/o.d. ton of unbleached pulp

E_c = concentration of spent bleach liquor at which a certain predetermined effect is measured, % of total volume.□

14. NOx emissions from the recovery boiler during Prenox trials at Norrsundet



IV. Methods of analysis

Test	*Method*
Kappa number	SCAN C 1:77
Intrinsic viscosity	SCAN C 15-16:62
Brightness	SCAN C 11:75
COD	Swedish standard SS 028141
BOD_7	Swedish standard SS 028143
TOCl	Method described in Ref. 13
AOX	SCAN W 9:89
Color	Determined spectrophotometrically at pH 7 after an initial rapid stabilization at pH 10
Chlorinated phenolic compounds	Method described in Ref. 14
PBS*	Lipophilic material with $P_{OW} > 5\times 10^4$ according to Renberg *et al.* (*15*)
P_{OW}	Partition coefficient in an Octanol/Washer system
Microtox	(Photobacterium phosphoreum)
Daphnia magna	Swedish standard SS 028180
Zebra fish egg (*Brachydaniorerio*)	Method described in Ref. 16 and fry
Green algae (*Scenedesmus sp.*)	According to OECD guidelines for testing chemicals, Method 201: Alga, growth inhibition test, Paris, 1983
Silica algae (*Nitzschia sp.*)	

*Potentially bio accumulating substances

Literature cited

1. Aktionsplan mot havsföroreningar, The Swedish National Environmental Protection Board, May 1987.
2. Pursiainen, S., Hiljanen, S., Uusitala, P., Kovasin, K., and Saukkonen, M., 1989 Pulping Conference Proceedings, TAPPI PRESS, Atlanta, p. 287.
3. Abrahamsson, K., Löwendahl, L., and Samuelson, O., Svensk Papperstid. 84(18): R152(1981).
4. Lindqvist, B., Marklund, A., Lindström, L. A., and Nordén, S., J. Pulp Paper Sci. 12(6): J161(1986).
5. Simonson, O., Lindström, L. A., and Marklund, A., Tappi J. 70(8): 73(1987).
6. Brännland, R., Lindström, L. A., Nordén, S., and Simonson, O., proceedings of the 1986 EUCEPA Symposium (May 19), EUCEPA, Helsinki, suppl., p. 103.
7. Germgård, U. and Larsson, S., Paperi Puu, 65(4): 287(1983).
8. Axegård, P., 1988 Intl. Pulp Bleaching Conference Proceedings, TAPPI PRESS, Atlanta, p. 69.
9. Annergren, G., Svensk Papperstid. 91(18): 31(1988).
10. Voss, R. H., Wearing, J. T., Mortimer, R. D., Kovacs, T., and Wong, A., Paperi Puu, 62(12): 809(1980).
11. Landner, L., Lindström, K., Karlsson, M., Nordin, J., and Sörensen, L., Bull. of Env. Contamination and Toxicology 18(6): 663(1977).
12. Axegård, P., 1988 Pulping Conference Proceedings, TAPPI PRESS, Atlanta, p. 307.
13. Sjöström, L., Rådeström, R., and Lindström, K., Svensk Papperstid. 85(3): R7(1982).
14. Renberg, L. and Lindström, K. J., Chromatography 214: 327(1981).
15. Renberg, L., Sundström, G., and Rosén-Olofsson, A., Toxicol. and Chem. 10: 333(1985).
16. Landner, L., Nielson, A. H., Sörensen, L., Tärnholm, A., and Viktor, T., Ecotox. and Environ. Safety 9: 282(1985).

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