Reduced AOX and biological effects by modification of a mill ClO_2 stage

STEN LJUNGGREN, ELISABETH BERGNOR GIDNERT AND FILIPE DE SOUSA

ABSTRACT

The first ClO_2 stage in a modern OD(EPO)DD sequence for bleaching softwood kraft pulp at the Iggesund paperboard mill has been modified by lowering the ClO_2 charge, raising the pH level, and introducing a more effective reinforced EPO stage. The ClO_2 charge in the last D-stage was, however, raised slightly to maintain the same high pulp brightness of 90%. The mixed D and EPO effluents obtained before and after this modification were compared.

The chemical analyses included AOX, EOX, COD, TOC, BOD_7, chloroform, and chlorinated phenolics and extractives. The bioassays consisted of acute toxicity (Microtox), growth inhibition [green algae (S. carpicornutum)], survival and reproduction (C. dubia), and embryo-larval toxicity with zebrafish (B. rerio) tests. Effluents were also tested in a minimodel ecosystem.

The chemical characterization study clearly showed that the process modifications resulted in a reduction in the amount of chlorinated matter in the bleach plant effluent. An AOX reduction of 20% was observed, while chlorinated acetic acids and chlorinated phenolic compounds were reduced by 55% and 35%, respectively. With some of the test methods used in the bioassay study, an improvement in effluent quality was observed.

Application:

By using this process modification, it is possible for a mill to reduce organic chlorine material such as AOX. From the presented results of the chemical and biological analysis of the bleaching effluent, no apparent significant disturbance of an ecosystem will occur.

MUCH EFFORT HAS BEEN devoted in recent years to reducing the content of chlorine-containing material in the effluents and pulps from ECF sequences in pulp and paper mills (1). The use of adsorbable organic halides (AOX) is an accepted method for quickly screening this material (2). However, for more reliable effects on the environment, different biological assay methods must be used (3).

In this paper, results of analyses of effluents and pulps from a modified OD(EPO)DD bleaching sequence producing softwood kraft pulp at the Iggesund paperboard mill in Sweden are presented, including biological tests.

RESULTS

Process modifications

The aim of this study was to optimize the distribution of chlorine dioxide in the different D-stages, especially to minimize the amount in the first D-stage, and to reduce the influence of the effluent on the environment *(4)*. As a host mill for these trials, the Iggesund paperboard mill was chosen. This mill runs a modern ECF (elemental chlorine-free) bleaching sequence, including a prolonged delignified cooking mode [MCC (modified continuous cooking)] with a subsequent oxygen delignification stage. Several alternative process changes were evaluated from the results of laboratory experiments. One interesting alternative was to select a pH profile in the first ClO_2 stage. This meant using in principle a pH profile of a low-acid pH (2–3) for a short time (0.5 min) and then a high-alkaline pH (10) for the remaining time in the first D-stage (60 min). It has been shown *(5)* that this method can be used to lower the AOX by 40% (from 0.33 to 0.13 kg/ton in laboratory experiments) and still reach a high brightness.

For practical and economical reasons, we found it better to simply lower the ClO_2 multiple in the D1 stage of the mill, including other changes. The ClO_2 multiple was thus lowered from 0.16 (used in 1993) to 0.10. However, it was necessary to compensate for this reduction by slightly increasing the ClO_2 charge in the remaining final D2 and D3 bleaching stages. The total ClO_2 charge, however, was lower. Modifications were also made in the EPO stage. The peroxide was increased and fed via a mixer. The temperature was raised by heat exchange approximately 9°C in the EPO and 8°C in the D1 stage. Acid addition to the D1 stage was omitted to avoid acid hydrolysis of the pulp, which would have lowered the strength properties. These process changes are summarized in **Table I,** where the conditions in June 1993 are regarded as a reference period and the conditions in April 19 represent the test point after the process change. As can be seen in this table, although the total charge of ClO_2 was lowered, the brightness remained the same, i.e., 90% ISO. The viscosity decreased slightly, however, but no impact on the strength could be observed.

Effluent characterization

Effluent handling. The effluent from the acid D1-stage was mixed in known proportions with the alkaline EPO-stage effluent before the chemical and biological analyses. The efflu-

Stage	Parameter	TRIAL PERIOD Reference (June 93)	Test (April 94)
Kraft pulping (MCC)	Kappa number	20.5	20.5
	Viscosity, mL/g	1120	1020
Oxygen delignification	Kappa number	12.0	11.5
	Viscosity, mL/g	1020	920
Production rate, t90/h*		20	20
COD in, kg/t90	-	4.4	5.9
D1	Charge ClO_2, a Cl_KK, %	0.16	0.10
	Charge ClO_2, kg a Cl/t90	19.3	11.8
	Temp., °C	60	68
	Retention time, h	1	1
	Acid add., m^3/t90	0.05	0.01
	pH	2.8	-
EPO	Charge O_2 kg/t90	7	6
	Charge H_2O_2, kg/t90	2	6
	Charge NaOH kg/t90	21	21
	Retention time, h	1	1
	Temp, °C	75	84
	Kappa no.	3.1	4.3
D2	Charge ClO_2, kg a Cl/t90	15.5	20.6
	Charge NaOH 1 kg/t90	-	-
	Temp., °C	68	69
	Retention time, h	3	3
	ISO brightness, %	85.9	84.4
D3	Charge ClO_2, kg a Cl/t90	7.5	7.1
	Charge NaOH 1,9 kg/t90	-	-
	Temp., °C	78	79
	Retention time, h	3	3
Total charge, kg a Cl/t90		**42.3**	**39.5**
ISO brightness, %		**90**	**89.9**
Viscosity, mL/g		**880**	**790**

*t90 indicates weight of pulp at 90% dryness.

I. Process conditions at Iggesund paperboard mill before and after modification. Pulp consistency was 10% in all stages.

ents were continuously withdrawn during a 4-hour period with stable process conditions. Pulp samples were withdrawn once per hour after the oxygen stage and after the final stage. One day before the withdrawal, the ClO_2 multiple in D1 was set to 0.16 for the reference effluent and to 0.10 for the test effluent. All samples withdrawn were filtered and frozen before analysis. The analyses performed on both the effluents and the pulps are shown in **Fig. 1.** Note that the content in these mixed effluents may be regarded mainly as the material of the total effluent from the bleach plant, since the mixed effluent also contains effluent originating from the oxygen stage and recirculated water from the last D-stages.

Chemical analysis of effluents. The values of suspended material, color, biological and chemical oxygen demand (BOD and COD), and total organic carbon (TOC) content are shown in **Table II.** The pH values of the mixed acid and alkaline effluent (which is nearly neutral) are given for both the reference and test waters. Clearly, the values of all these parameters are lower in the test water effluent. Furthermore, AOX, EOX, and chlorate all show lower values after the process modification. The AOX value of 0.2 kg/ton pulp is well below typical mill effluent averages in North America; it is comparable with that of other Swedish mills that use an oxygen prebleaching stage *(6)*. This AOX value, however, was measured *before* the secondary effluent pond treatment, which normally further reduces AOX by more than a half. This means that a final AOX value below 0.1 kg/ton pulp could be expected *after* the secondary treatment; this is below the proposed U.S. EPA cluster rule maximum of 0.156 kg/ton *(7)*. The COD value also meets the EPA's proposed discharge limit, which is less than 25.4 kg/ton pulp.

Tables III and IV present levels of chlorinated compounds in the D(EPO) effluents. Note that the amounts of chlorinated acetic acids have decreased by more than 50% as a result of the process change but that the amount of chlorinated sulfones are almost unchanged, although they are very low. Chloroform could not be detected in any of the effluents. Of chlorinated phenolic compounds, only monochlorinated and dichlorinated phenols were detected (Table IV), of which the monochlorinated phenols are clearly dominating. The total amounts were decreased by half to 0.28 g/ton pulp in the test water.

Wood extractives, sterols, and triterpene alcohol were also examined, as shown in **Table V,** and the levels were likewise greatly reduced by the process change. However, fatty

and resin acids (**Table VI**) were at the same total level in the two effluents, at about 20 g/ton pulp.

We also measured the effects of both high- and low-molecular-weight effluent material *(8)*, since low-molecular-weight material is suspected to penetrate membranes in living organisms. However, the distributions of high- and low-molecular- weight material (separated by ultrafiltration—nominal molecular weight cutoff of 1.000 DA) according to the AOX, COD, and TOC were approximately the same in both effluents.

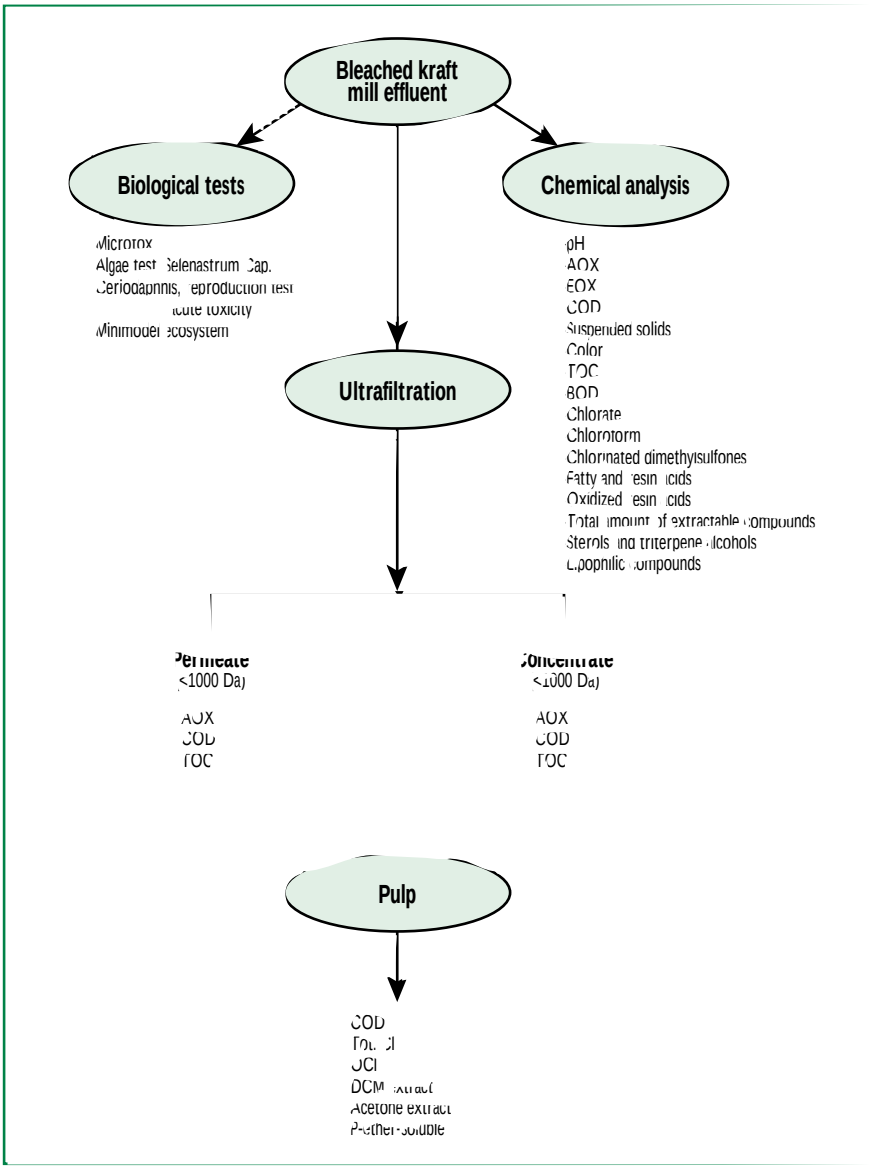
Chemical analysis of pulp samples. Four pulp samples, unbleached and fully bleached before and after the process change, were examined with regard to their contents of chlorinated material and extractives (see **Tables VII and VIII**).

In unbleached oxygen-predelignified pulp, no organic-bound chlorine material (OCl) could be detected (as expected). The level in the test bleached samples was very low, at 66 mg/kg. A level of 30 mg/kg could be taken as an assurance of chlorine-free bleaching *(9)*. The level of total chlorine (probably including chloride, etc.), however, was higher in the test pulp samples. Extractives (fatty acids, alcohols, and sterols) were very low and decreased to one-half as a result of the process change. Resins could not be detected in the acetone extracts from any of the samples.

Biological tests of effluents. Bioassay tests were made on the effluents by studying the effect concentrations (EC) at which organisms were toxified or dead after exposure to the effluent (expressed as vol/vol, %).

The EC_{50} value indicates the amount of effluent that affects half of the organism population or decreases some effect by 50%.

Table IX shows that there is a low acute toxicity, according to the Microtox method, but that none of the effluents show an acute toxicity to crayfish, at least not after 24 hours of



1. Chemical and biological characterization of bleached kraft mill effluent and pulp

Effluent	Susp., kg/tp[a]	Color, kg/tp	BOD, kg/tp	COD, kg/tp	TOC, kg/tp	pH	AOX, kg/tp	EOX, g/tp[b]	$NaClO_3$ kg/tp
Reference (June 93)	2.63	22.4	8.1	25.0	10.9	7.25	0.24	3.0	5.9
Test (April 94)	2.43	18.8	7.5	22.5	10.1	8.90	0.19	2.6	4.4

[a]kg/ton pulp
[b]g/ton pulp

II. Chemical analysis of bleaching effluent at Iggesund. All analyses were measured on bleaching effluents that had not been subjected to secondary treatment, i.e., an aerated pond.

Substance	Ref. (June 93)	Test (April 94)
Monochloro-acetic acid	20.0	12.0
Dichloro-acetic acid	5.7	0.5
Trichloro-acetic acid	2.7	0.3
Total	**28.4**	**12.8**
1,1-Dichloromethyl sulfone	4.2	3.2
1,1,3-Trichloromethyl sulfone	0.06	0.06
Chloroform	ND*	ND

*Not detected

III. Chlorinated acetic acids and sulfones in bleaching effluent. Units in g/ton pulp.

exposure (EC_{50}>100). The reproduction of crayfishes is affected, but much less by the test water than by the reference.

Table X shows the EC_{50} values (and EC_{20} values) for growth inhibition of green algae together with the lowest and no-effect concentration levels, LOEC and NOEC, respectively. Surprisingly, all these values were lower for the test water. This means that this effluent affects the green algae slightly more than the reference effluent, although the chlorate content is lower (see Table II).

Bioassays were also made on zebrafish *(10)* (see **Table XI**). The reference effluent had significant effects in an undiluted condition (i.e., at 100%) on the reproduction and survival time of embryo-larvae but no effect at 90% mixing. In the case of the test effluent, no significant effects on embryo-larvae of zebra-fish could be detected.

KEYWORDS
Alkaline pulps, analysis, biological tests, bleaching, chemical analysis, chemical pulps, chemical tests, chemical treatment, chlorine dioxide, ecosystems, kraft pulps, multistage process, oxides, pollution, processes, pulps, softwood pulps, test methods.

Minimodel ecosystem Sampling and testing..

When the interaction of specific compounds (or mixtures of these compounds) on structure and function of a natural ecosystem is studied, it is preferable to use a complex system with a high degree of realism. However, smaller test systems (minimodels) are easier to reproduce because of their smaller structure and less biotic and abiotic interactions. A minimodel cannot, therefore, be an exact copy of a natural ecosystem. The benefits of using a minimodel include a high test capacity, many concentration levels, the possibility to replicate, lower cost, and shorter time required. For the studies of the bleach effluents in this work, we have used a minimodel ecosystem that was developed by and performed at the Institute for Water and Air Pollution Research (IVL), Stockholm, Sweden (11).

The test organisms that participate in this multispecies model system are

Compound	Ref. (June 93)	Test (April 94)
Chlorinated phenols		
2,4-Dichlorophenol	0.037	0.008
2,4,6-Trichlorophenol	<0.0003	<0.0003
2,3,4,6-Tetrachlorophenol	<0.0003	<0.0003
Pentachlorophenol	<0.0003	<0.0003
Chlorinated guaiacols		
5-Monochloroguaiacol	0.050	0.026
4,6-Dichloroguaiacol	0.0003	0.0003
4,5-Dichloroguaiacol	0.100	0.051
3,4,5-Trichloroguaiacol	<0.0003	<0.0003
4,5,6-Trichloroguaiacol	<0.0003	<0.0003
Tetrachloroguaiacol	<0.0003	<0.0003
Chlorinated catechols		
4,5-Dichlorocatechol	<0.0003	<0.0003
3,4-Dichlorocatechol	<0.0003	<0.0003
3,4,5-Trichlorocatechol	<0.0003	<0.0003
Tetrachlorocatechol	<0.0003	<0.0003
Chlorinated syringols		
3-Monchlorosyringol	<0.0003	<0.0003
3,5-Dichlorosyringol	<0.0003	<0.0003
3,4,5-Trichlorosyringol	<0.0003	<0.0003
Chlorinated vanillins		
5-Monochlorovanillin	<0.0003	<0.0003
6-Monochlorovanillin	0.23	0.19
5,6-Dichlorovanillin	<0.0003	<0.0003
Chlorinated syringaldehydes		
2-Monochlorosyringaldehyde	<0.0003	<0.0003
2,6-Dichlorosyringaldehyde	<0.0003	<0.0003
Total amount of compounds	**0.42**	**0.28**
Summary		
Monochlorinated phenolic compounds	0.28	0.22
Dichlorinated phenolic compounds	0.14	0.06
Trichlorinated phenolic compounds	ND*	ND
Tetrachlorinated phenolic compounds	ND	ND
Total amount of compounds	**0.42**	**0.28**

*Not detected

IV. Chlorinated phenolic compounds in bleaching effluent. Units in g/ton pulp.

of ecological relevance for Swedish seawaters and are also well characterized. The test organisms used in our system were larvae of mosquitos *(Chrionomus riparius),* blue mussels *(Mutilus edulis),* and stickleback fishes *(Gasterosteus aculeatus),* all common species in the Baltic Sea at Scandinavia.

The two effluents (named *Ref.* and *Test*) were mixed with sea brackish water (containing 0.5% salt) at three different concentrations (0.1, 0.5, and 1.7%) in 80-L aquariums. The water flow was 200 mL/min *(12).* All exposures to the effluents were made in duplicate, in addition to a control replicate aquarium. This resulted in using a total of 15 aquariums for these experiments. The exposure time was 70 days. Each aquarium also contained natural sediments from the sea together with the studied organisms: 75 mosquitos larvae, 20 juvenile sticklebacks, and 20 blue mussels.

The latter were placed in separate aquariums due to problems with their excrements. At the end of the trial period, all fishes were weighed and measured, and some were dissected for morphological and immunohistochemical studies. These studies included determining the liversomatic index (LSI) (i.e., liverweight/total weight) and EROD activity, i.e., the ability of the liver to metabolize toxic compounds.

The mussels were examined with respect to their respiration and ammonium excretion (O/N ratio). The mosquitos were counted, and their sizes were determined. Statistical methods, such as the Mann-Whitney U-test, were used.

Results of the ecosystem studies

The biomass of the mosquito larva is depicted in **Fig. 2.** In relation to the control group, there is a tendency toward a decrease in weight as the concentration of effluent is increased. This tendency is not, however, statistically supported.

No significant effects were found with regard to the growth rate and mortality of blue mussels with either of the effluents. No effect was found for the O/N ratio (**Fig. 3**).

The growth rate of the stickleback fish in all aquariums was 15–20%, but in the exposed water (the reference effluent), the growth rate was higher, at 30%. The mortality varied between 15 and 35% in the aquariums. No significant effect was found. The LSI varied between 2 and 2.5%. As **Fig. 4** shows, there was a large scatter in the LSI values, but there is a tendency for higher LSI values at all concentrations of reference effluents (but not with the test effluent).

The EROD activity was also measured for the case of the stickleback. **Figure 5** shows that there is no significant difference at the studied concentrations of effluents.

In summary, at these concentrations of effluents, which are higher than those normally used when studying effects on ecosystems (0.05–0.25%), no significant effects on the organisms were found with either the reference effluent or the test effluents.

Compound	Reference (June 93) Filter	Water	Total	Test (April 94) Filter	Water	Total
Cholesterol	0.03	ND*	0.03	ND	0.57	0.57
Campesterol	0.25	ND	0.25	ND	ND	ND
Campestanol	0.16	ND	0.16	ND	ND	ND
Sitosterol	1.50	0.68	2.18	1.49	0.02	1.51
Sitostanol	1.46	0.52	1.98	0.14	0.57	0.71
Lupeol	ND	ND	ND	ND	ND	ND
Cycloartanol	ND	ND	ND	ND	ND	ND
7-Betula prenol	ND	ND	ND	ND	ND	ND
2,4-Methylene cycloartanol	ND	ND	ND	ND	ND	ND
Citrostadienol	ND	ND	ND	ND	ND	ND
Betulinol	ND	ND	ND	ND	ND	ND
Methyl betulinate	ND	ND	ND	ND	ND	ND
8-Betula prenol	ND	ND	ND	ND	ND	ND
Total	**4.60**	**2.79**	**7.39**	**1.63**	**1.16**	**2.79**

*Not detected

V. Wood extractive compounds (sterols, etc.) in bleaching effluents. Units in g/ton pulp.

Acid	Reference (June 93) Filter	Water	Total	Test (April 94) Filter	Water	Total
Saturated fatty acids	1.7	16.7	18.4	3.73	3.88	7.61
Linked fatty acids	0.17	0.50	0.67	1.22	1.00	1.22
Unsaturated fatty acids	ND*	0.03	0.30	6.87	0.25	7.12
Resin acids	0.22	0.42	0.64	1.25	0.23	1.48
Oxidized resin acids	0.03	0.00	0.03	1.45	0.05	1.50
Chlorined fatty acids	ND	0.04	0.04	0.55	0.30	0.85
Total	**2.12**	**17.3**	**19.42**	**15.07**	**5.71**	**20.78**

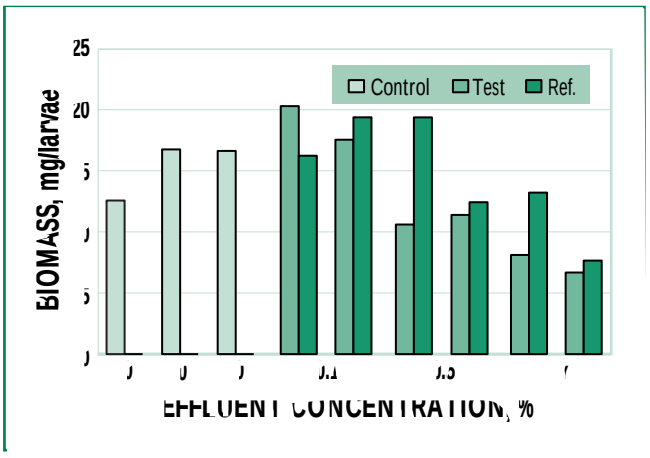
*Not detected

VI. Fatty and resin acids in bleaching effluents. Units in g/ton pulp.

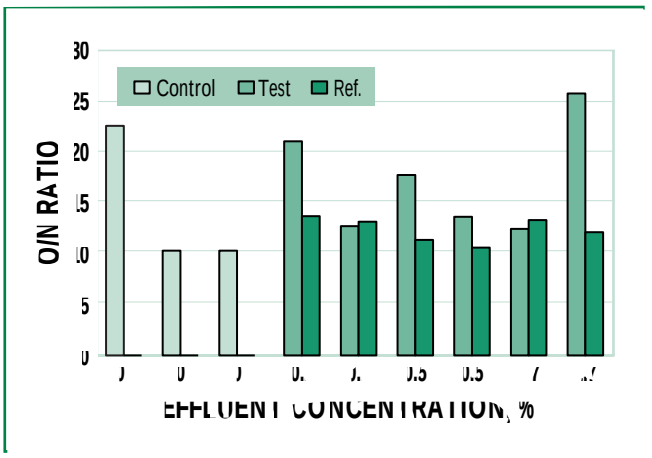
Effluent	TotCl	OCl
Unbleached reference	19.5	ND*<5)
Unbleached test	48	ND (<5)
Bleached reference	144	93
Bleached test	288	66

*Not detected

VII. Chlorinated material in pulp samples. Units in mg/kg pulp.



2. Biomass of mosquito larvae at different concentrations of effluents (in percent after dilution)



3. O/N ratio of blue mussels at different concentrations of effluents (in percent after dilution)

Effluent	Acetone, %	DKM, %	p-ether-, soluble, %
Unbleached reference	0.05	0.05	0.04
Unbleached test	0.035	0.02	0.016
Bleached reference	0.04	0.03	0.02
Bleached test	0.026	0.012	0.008

VIII. Extractives in pulp samples (dried)

Effluent	EC_{50}	EC_{20}	LOEC	NOEC
Ref. (June 93)	55.0	35.1	28.2	26.0
Test (April 94)	43.3	27.2	22.9	19.9

X. Growth inhibition of green algae **(S. Capricornutum)** *by effluents*

	ACUTE TOXICITY				Reproduction
	Microtox		Crayfish *(C. Dubia)*		of crayfish
Effluent	5 min	15 min	24 h	48 h	48 h
Ref. (June 93)	13.8	14.4	100	97	32
Test (April 94)	29.8	29.1	100	41	71

IX. Bioassays, EC_{50} (vol %) of effluents

	REPRODUCTION				SURVIVAL		DEFORMATION	
	Frequency		Time		TIME		TIME	
Effluent	LOEC	NOEC	LOEC	NOEC	LOEC	NOEC	LOEC	NOEC
Ref. (June 93)	<100	-	100	90	100	90	>100	-
Test (April 94)	>100	-	>100	-	>100	-	>100	-

XI. Bioassays, EC (vol %). No (NO) and low (LO) embryo-larvae toxicity of zebrafish **(B. Rerio)** *of effluents*

CONCLUSIONS

The process modification in the first ClO_2 stage, including the subsequent E-stage, resulted in lower emissions of chlorinated organic material and extractives in the effluents. AOX was reduced by 20%, and the EOX, BOD, COD, and TOC were also reduced. The biotests were negative (i.e., had no effects), except for the growth rate of green algae, which was slightly inhibited by the results of the process modification. No negative effects could be observed on zebra-fish from any of the effluents.

The minimodel ecosystem showed no significant disturbance when exposed to the effluents. According to this studied model system, the test results for three living organisms show that modifying the ClO_2 charge in the bleaching process had no effect. The process modification thus had no significant value for lowering the impact on the ecosystem. This may be due to the fact that the interaction was already on a very low level before the modification was made. For this reason, the Iggesund mill judged that it is not nessecary to achieve even lower levels than before the modification. (Today, the total AOX level is 0.2 kg/ton pulp *after* the secondary plant treatment).

The Iggesund mill has adopted this modification only to a certain extent today due to expected higher bleaching costs (i.e., increased peroxide consumption). However, the knowledge

from this modification trial gives the mill an opportunity to develop the control of the process to a greater extent in the future. TJ

Ljunggren is a project leader and associate professor in wood chemistry, Gidnert is a research engineer, and de Sousa is a research engineer at STFI, The Swedish Pulp and Paper Research Institute, Box 5604, S-114 86 Stockholm, Sweden.

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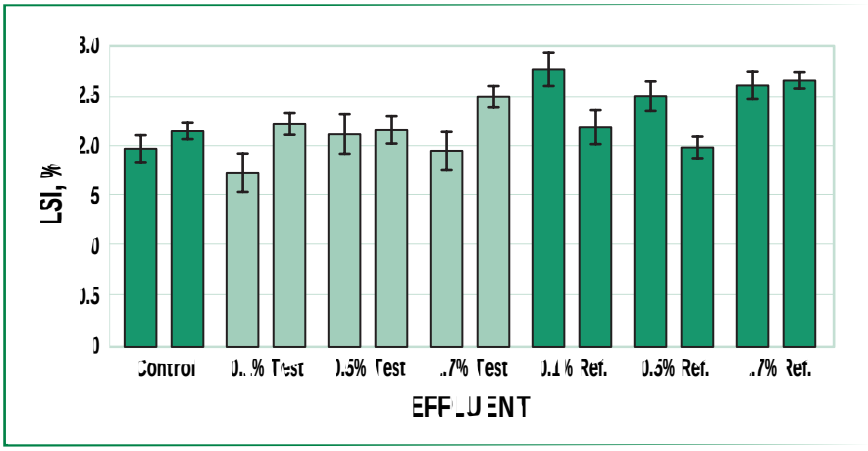
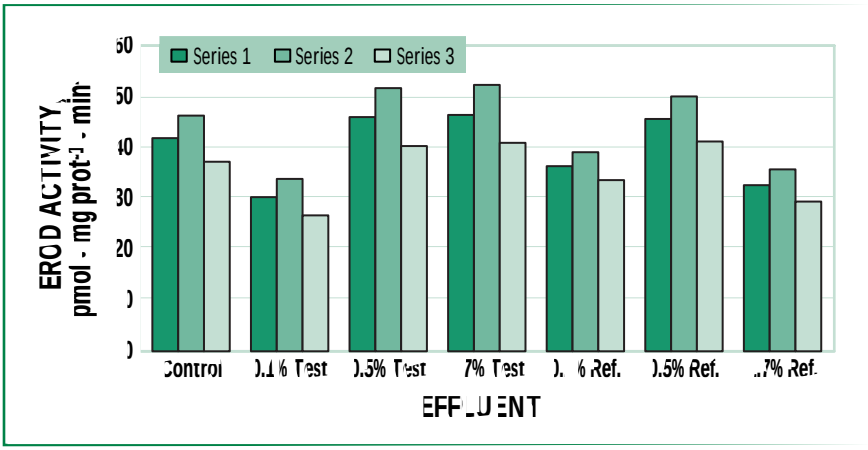


4. Liversomatic index (LSI) for stickleback fish at different concentrations of effluents



5. EROD activity for stickleback fish at different concentrations of effluents

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