



REDUCING CHLORINATED ORGANICS, AOX, IN THE BLEACHERY EFFLUENTS OF A TURKISH PULP AND PAPER PLANT

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ABSTRACT

The possibility for reducing the chlorinated organic compounds in the bleachery effluents of the Turkish pulp and paper industry has been studied. Within the experimental work of this study, three different chlorine dioxide substitutions and three different total chlorine application rates were examined and nine experiments were performed. The AOX formation has been shown to be proportional to the amount of molecular chlorine consumed during delignification, regardless of whether it is from chlorine or chlorine dioxide. However, molecular chlorine contributes to AOX formation to a much greater extent. The lowest AOX concentrations were achieved when the total available chlorine dosage was lowest (10 kg/ton) and ClO₂ substitution level was highest. An increase in the percentage of chlorine dioxide leads to a substantial reduction in the AOX concentration in the bleachery effluents. A chlorine dioxide substitution of 90%, when the chlorine charge was 40 kg/ton, causes a 77% decrease in the DC-AOX, and a 82% decrease in the EO-AOX. However, as the chlorine dioxide substitution reduced to 10%, the decrease in the the AOX concentration became less and only 51% and 41% reductions in DC-AOX and EO-AOX could have been achieved respectively. Copyright © 1996 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

AOX; bleachery effluents; chlorinated organics; pulp and paper industry.

INTRODUCTION

SEKA Dalaman Pulp and Paper Plant, which is located on the Aegean coast of Turkey, is the largest mill in Turkey with a pulping capacity of over 100,000 tons/annum. Dalaman mill mainly produces kraft pulp from soft wood and linter cellulose. One of the most urgent problems faced by the plant management, as with other pulping plants in Turkey, is the high pollution load coming from the bleachery effluents.

A general concern of the pulping industry is the chlorinated organic compounds in the bleachery effluents (Heimbürger *et al.*, 1988; Reeve *et al.*, 1989) which tend to be toxic, carcinogenic or mutagenic to the environment. Serious efforts are now being spent to limit discharges of organic halides to receiving basins. For example, discharging of AOX, a generic name used to describe organic chlorine compounds, is completely banned in U.S.A.

In Canada, The MISA Expert Committee in 1993 set the limits as <1.5 kg AOX / a.d.t.(air dried ton) pulp; furthermore suggested minimization of AOX rather than end-of-pipe treatment for AOX reduction.

Similarly, the National Environmental Protection Board of Sweden has established the limit for organic chlorine compounds as 1.5-2.0 kg TOCl (total organic chlorine)/ ton of pulp produced, starting from 1989. Germany stipulated 1.0 kg AOX/ton of pulp produced as the discharge limit for organically-bound chlorine since 1990, and an AOX limit of 1.5 kg/ton of pulp produced has been adopted by the European Community for bleachery effluents (Reeve *et al.*, 1989).

At present there is no limit set for AOX discharges by the Turkish Water Pollution Control Regulation. Nevertheless, the State Enterprise SEKA, which is the main pulp producer in Turkey, has initiated a research towards reducing its AOX discharges considering the global trends and this study is largely based on this effort.

PULP BLEACHING PROCESSES AND BLEACHERY EFFLUENTS

Bleaching of kraft pulp is a lignin removal process applied to the cooked pulp to remove any residual lignin in order to brighten the finished paper. Chlorine has historically been used as the primary agent in kraft pulp bleaching as it is selective towards lignin and economical compared to other bleaching processes. It completes the process of lignin removal and renders pulp fibers responsive to final brightening treatment. Alkaline extraction, following chlorination, completes solubilization of chlorine-treated lignin fragments. Therefore effluents from chlorination, alkaline extraction and hypochlorite brightening processes are all characterized by their high AOX contents and these collectively make the bleachery effluents. The AOX contents of the bleachery effluents are greatly affected by the operating conditions in chlorination and alkaline extraction stages (Allison *et al.*, 1990).

There are a number of process options to reduce the generation of AOX in kraft mill bleachery effluents (Heimburger *et al.*, 1988; Du Manoir *et al.*, 1989). All of these primarily rely on reducing the amount of elemental chlorine used in the initial chlorination stage since the vast majority of organically bound chlorine is produced through the electrophilic addition of chlorine to the aromatic ring of the residual lignin in the pulp (Singh, 1979). Use of molecular chlorine in the bleaching process can be reduced by replacing it, at least in part, with chlorine dioxide in the first stage. Chlorine dioxide, too, produces organically bound chlorine, but only one-fifth of the same amount of the elemental chlorine when compared on an active chlorine basis (Germgard *et al.*, 1982; Axegard, 1989). Therefore, substitution of chlorine with chlorine dioxide (DC) appears as a promising option for reducing AOX emissions. However, the final brightness reached by chlorine dioxide bleaching is normally unacceptable should a post-reinforced extraction not follow the chlorine dioxide treatment (Allison *et al.*, 1990).

Table 1. Bleaching conditions for the CEHDED sequence; softwood kraft pulp

Operational variable	C	E	H	D	E	D
Pulp consistency	3%	10%	10%	10%	10%	10%
Reaction time, (h)	1	1.5	4	4	1.5	4
Temperature, °C	20	70	40	75	70	75
Chemical dosage, kg/ton	60-70 (Cl ₂)	50-60 (NaOH)	30-40 (NaOCl)	12 (ClO ₂)	50-60 (NaOH)	6 (ClO ₂)
Effluent AOX, mg/l	42.90	92.00	66.20	17.22	4.28	2.92

This way, it becomes possible to shift delignification from the chlorination stage to the first extraction stage and thereby decrease the total active chlorine charge (Basta *et al.*, 1990).

In SEKA Dalaman Pulp and Paper mill, softwood kraft pulp is normally bleached by a CEHDED (chlorination, extraction, hypochlorite, chlorine dioxide, extraction, chlorine dioxide) bleaching sequence. Bleaching conditions and the AOX discharges for all the stages of this sequence are given in Table 1.

The mill is now considering to use chlorine dioxide together with molecular chlorine in the chlorination stage with an aim to reduce the discharge levels of AOX in its bleachery effluents, and to adopt an oxidative extraction alkali stage to follow up, to maintain the target permanganate number in the pulp. The new process train is denoted by "DC(EOP)DED"; where, DC:sequential chlorine dioxide and chlorine application; EOP: oxygen and hydrogen peroxide reinforced extraction bleaching sequence.

The present research aims to formulate and determine the operation conditions for chlorine/chlorine dioxide options at SEKA Dalaman Pulp and Paper Plant with an aim to reduce its discharge AOX levels in the near future. This paper therefore discusses process research carried out in the laboratory to determine the operational parameters of chlorination and extraction stages on pulp quality and AOX emissions.

EXPERIMENTAL

Source pulp

Kraft pulp, direct from the cooking plant, with 17.6 permanganate number, 7.8 cp. viscosity and with a dry matter content of 19.52% was supplied by SEKA Dalaman Pulp and Paper Mill.

Chlorination

The DC treatments were performed on 75 g air dried pulps in sealed plastic bags. Desired quantities of bleaching chemicals were added sequentially under the following standard conditions: 3% pulp consistency, 30°C reaction temperature and 60 min reaction time. Constant temperature was provided by placing plastic bags in a water bath. Pulp samples were pre-acidified to pH 1.6 with 4N sulfuric acid before adding bleach chemicals.

After treatment, pulps were drained and washed with 1.0 l of tap water. Collected wash waters were analyzed for residual available chlorine, final pH, and AOX. Half of the washed pulps were analyzed for permanganate number and pulp viscosity, while the other half was subjected to oxidative extraction treatment.

Oxidative extraction

Oxidative extraction was performed in a specially designed pressurized laboratory reactor equipped with a stirring mechanism. The experimental conditions were: 6% NaOH; 3 atm oxygen pressure; 10% pulp consistency; 0.05% MgSO₄; 70°C; 60 min. Following the treatment, pulps were drained and washed with 1.5 l of tap water. Effluent filtrates for each pulp were analyzed for residual alkaline, final pH, and AOX. Washed pulps were analyzed for extracted permanganate number and pulp viscosity.

Hydrogen-peroxide reinforced oxidative extraction

To observe the effects of hydrogen peroxide addition to pulp quality and AOX discharges, H₂O₂ charges of 0.4 and 0.5% (on dry basis) were tested in the EO-stage. Only the pulp chlorinated under 90% chlorine dioxide substitution with a total available chlorine charge of 40 kg/ton was used in this experiment.

Analytical methods

Effluent filtrates from chlorinations and extractions were analyzed for AOX using Euroglass Analytical Instrument according to DIN norm 34809. Pulp consistency was measured in terms of permanganate number according to the method "TAPPI 214m-50".

RESULTS AND DISCUSSION

Base-line study

The base-line conditions summarized in Table 2, which are currently being employed in the plant, were simulated in the lab. A 60 kg/ton (total available) was used as chlorine charge for the C-stage. The sample pulp was initially chlorinated at a constant temperature, and then treated with NaOH at atmospheric pressure to simulate the existing (E-stage) extraction. The average AOX concentrations for the effluents of the simulated base-line experiments are also given in Table 2.

Table 2. The experimental conditions and the effluent quality in the simulated base-line experiment

Operational variables	CE
% Cl ₂	100
Total available chlorine, kg/ton	60
Temperature, °C	30
% NaOH	4
C-AOX, mg/l	49.40
E-AOX, mg/l	47.49

Chlorine dioxide substitution and oxidative extraction

In the second part of the experimental work, three different chlorine dioxide substitutions and three different total chlorine application rates were examined and nine (total of 18 with parallels) experiments were performed. Pulp samples were initially bleached under the conditions shown in Table 3. Then, the bleached pulps were sent to extraction stage where oxidative extraction was employed. The measured AOX concentrations in the wash waters of the chlorination (DC-AOX) and extraction stages (EO-AOX) at different ClO₂ substitution levels and at different total available chlorine charges are also given in Table 3. As can be seen from this table, the lowest AOX concentrations were achieved when the total available chlorine dosage was lowest (10 kg/ton) and ClO₂ substitution level was highest. As the applied chlorine dose increases, DC-AOX and EO-AOX also increases, despite the high proportion of chlorine dioxide used. This was not unexpected as chlorine charge employed to lower permanganate number of the pulp is known to be an important variable affecting AOX production.

Table 3. The conditions and the effluent quality in the (DC)(EPO) tests

Tot. Av. chlorine kg/ton	10	10	10	25	25	25	40	40	40
% ClO ₂	90	50	10	90	50	10	90	50	10
% Cl ₂	10	50	90	10	50	90	10	50	90
DC-AOX, mg/l	2.7	2.2	5.2	4.76	8.76	11.2	11.5	10.27	24.3
EO-AOX, mg/l	6.7	5.5	8.3	2.40	2.48	20.9	8.61	22.04	27.9

The Figures 1 and 2 depict DC-AOX and EO-AOX decreases obtained when relative amounts of chlorine dioxide were increased. As can be seen from both figures, an increase in the percentage of chlorine dioxide leads to a substantial reduction in the AOX concentration in the bleachery effluents. A chlorine dioxide substitution of 90%, when the chlorine charge was 40 kg/ton, causes a 77% decrease in the DC-AOX, and an 82% decrease in the EO-AOX. However, as the chlorine dioxide substitution reduced to 10%, the decrease in the the AOX concentration became less and only 51% and 41% reductions in DC-AOX and EO-AOX could have been achieved respectively.

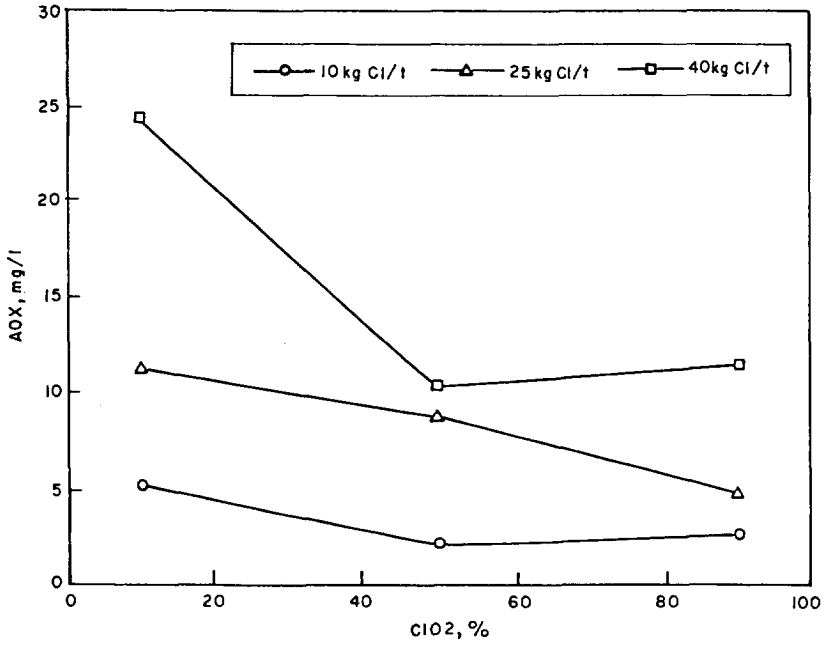


Figure 1. DC-stage AOX vs. ClO₂ substitution level.

Unfortunately conditions producing minimal AOX displayed only limited bleaching capability and produced pulps with high permanganate numbers. Therefore, when assessing the effects of chlorination conditions on effluent properties the major constraint is the bleaching of pulp.

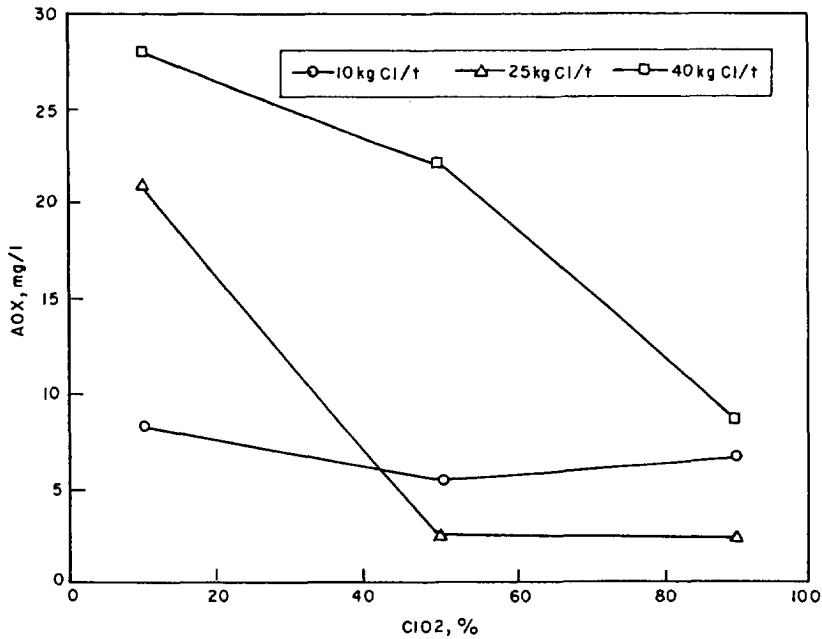


Figure 2. EO-stage AOX vs. ClO₂ substitution level.

The Figure 3 shows EO-AOX concentrations with 10 to 90% chlorine dioxide substitutions, producing 5 to 13 extracted permanganate numbers. As can be seen from Figure 3, EO-AOX was clearly reduced by a decrease in the extent of bleaching (i.e., higher extracted permanganate number with higher AOX) and by an increase in the proportion of chlorine dioxide in the applied chlorine charge. However, at 90% chlorine dioxide substitution, bleaching to a low extracted permanganate number produced as high AOX amount as bleaching with 50% substitution. This effect was evidently due to a sharp decrease in bleaching effectiveness at high substitutions. Therefore, in agreement with Allison *et al.* 1990, for higher degrees of chlorine dioxide substitution the total available chlorine charge in the chlorination stage must be substantially increased, or the subsequent extraction stage must be reinforced in order to produce a pulp with an acceptable extracted permanganate number.

In Figure 4, the influence of total available chlorine charge on the extracted permanganate number was shown for varying degrees of chlorine dioxide substitution. This plot confirms that 90% substitution requires high chemical charges especially when bleaching to low extracted permanganate numbers.

Hydrogen-peroxide reinforced oxidative extraction

In the second phase of the experimental work, hydrogen peroxide reinforced oxidative extraction sequence was adopted as post-treatment to follow the DC bleaching sequence. The pulp used in this phase of the study was the one bleached with a total chlorine charge of 40 kg/ton and a chlorine dioxide substitution of 90%. In these experiments two different hydrogen-peroxide doses, namely 0.4 and 0.5% (on dry pulp basis), were employed. The results obtained are presented in Table 4.

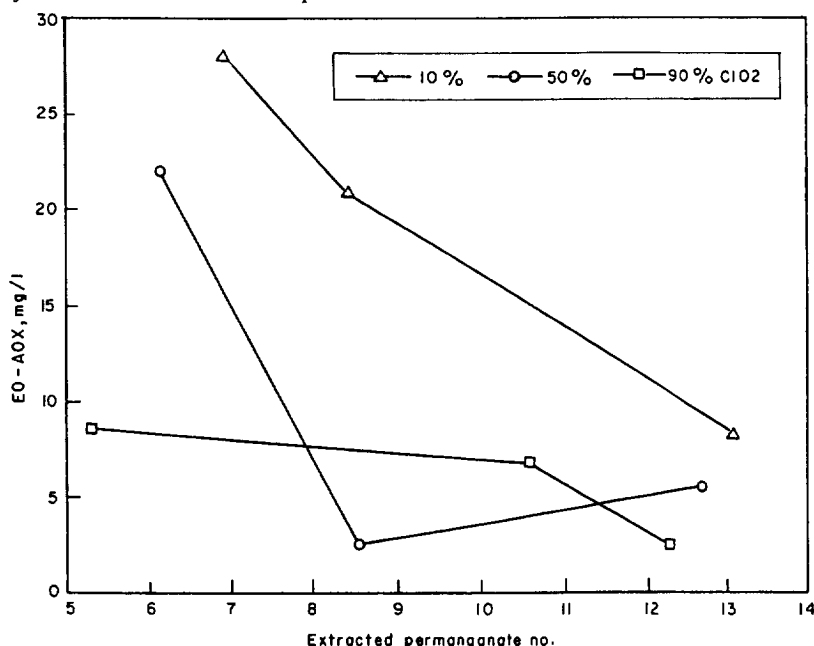


Figure 3. The relationship between EO-stage AOX production on extracted permanganate number at different chlorine dioxide substitution levels.

As can be seen from Table 4, the addition of hydrogen peroxide has provided an acceptable pulp quality with low AOX concentrations in both chlorination and extraction effluents, compared with the reference CE bleaching sequence. The C-stage AOX concentration has decreased from its earlier value of 49.40 mg/l to 10.40 mg/l while the pulp quality -in terms of extracted permanganate number- remains almost unchanged. Similarly, E-stage AOX concentration has also decreased from 47.49 mg/l down to 13.82 mg/l.

A comparison of the permanganate numbers measured after (DC)(EO) and (DC)(EPO) sequences reveal that H_2O_2 addition to oxygen-reinforced extraction improves delignification, however, this effect has not appeared for the H_2O_2 dose of 0.4%, indicating that 0.4% H_2O_2 was not sufficient for extended delignification.

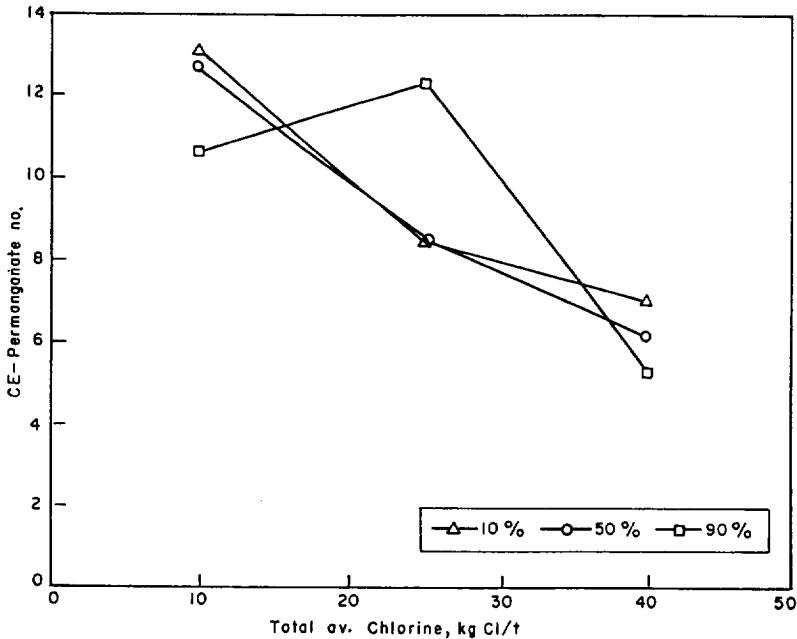


Figure 4. Extracted Permanganate number versus total available chlorine.

Table 4. Comparison between (DC) (EPO) pre-bleaching and CE pre-bleaching sequences

Operational variables	CE	(DC) (EO)	(DC) (EPO)	
			% 0.4 H_2O_2	% 0.5 H_2O_2
% Cl_2	100	10	10	10
% ClO_2	-	90	90	90
Tot. Av. chlorine, kg/ton	60	40	40	40
% NaOH	4	6	6	6
Extracted permanganate No.	4.3	5.5	5.6	4.2
C stage AOX, mg/l	49.4	12.13	11.48	10.40
E stage AOX, mg/l	47.49	10.41	13.37	13.81

CONCLUSIONS

The following conclusions can be drawn from this study:

1. The AOX formation has been shown to be proportional to the amount of molecular chlorine consumed during delignification, regardless of whether it is from chlorine or chlorine dioxide. However, molecular chlorine contributes to AOX formation to a much greater extent.

2. Partial substitution of chlorine dioxide for chlorine and post-oxygen reinforced alkali extraction could reduce AOX emissions substantially and produce acceptably bleached softwood kraft pulp. The lowest AOX concentrations are obtained with the highest chlorine dioxide substitution. However, the target pulp quality cannot be reached with high substitution levels of chlorine dioxide without post-alkali extraction with hydrogen peroxide.
3. The (DC)(EPO) bleaching technology seems to be a convenient process alternative for SEKA-Dalaman pulp and paper plant.
4. To implement the proposed process modifications described herein, further efforts on the pilot-plant scale are needed.

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