Chemical reduction of AOX and COD from hardwood kraft chlorination-stage effluent

Hiroshi Fukui, Bradford S. Barron, and Motoo Matsukura

ABSTRACT: This article examines the use of alkali [NaOH or $Ca(OH)_2$] and alum [$Al_2(SO_4)_3$] to reduce AOX (adsorbable organic halogen) and COD (chemical oxygen demand) in chlorine-stage (C-stage) effluent for hardwood kraft pulps. Tests were conducted on the whole effluent and on its molecular-weight fractions. The results indicate that 80% of the AOX in the C-stage effluent can be removed by treating the effluent with NaOH at pH 12.5 prior to conventional sedimentation with alum. Ether extraction of the hardwood C-stage effluent before and after chemical treatment suggests that these extractives are the primary source of residual AOX.

KEYWORDS: Adsorbable organic halogen, alkali treatment, chemical oxygen demand, effluent treatment, hardwood pulps, multistage process.

The pulp and paper industry produces large quantities of spent bleach liquor. These liquors contain toxic chlorinated organic compounds that are biologically inactive *(1–4)* and, therefore, accumulate in the environment *(5, 6)*. Current legislation is very strict concerning effluent quality, especially the amount of chlorinated organics. For example, in Japan, the amount of organic chlorine, measured as AOX (adsorbable organic halogen), must be reduced to 1.5 kg/ton of bleached kraft pulp by the end of 1993.

Wastewater treatment methods such as flocculation, sedimentation, and activated sludge are used to reduce COD (chemical oxygen demand) and AOX. However, these methods do not always effectively remove chlorinated organic compounds *(7)*. Low-molecular-weight compounds are particularly difficult to remove. This explains why flocculation and sedimentation are more effective at treating softwood bleach effluent, which has a larger percentage of high-molecular-weight organic compounds than hardwood bleach effluent. Consequently, low-molecular-weight chlorinated compounds in the bleach effluent from hardwood kraft pulp are usually discharged in the treated wastewater. Most of these low-molecular-weight compounds contain alkali-unstable carbon–chlorine bonds. An example is a single chlorine bonded to the α-carbon of a carbonyl group or hydroxyl group. We propose to dechlorinate such compounds with alkali treatment.

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C-stage effluent characteristics

Chlorination-stage (C-stage) effluent was taken from our Ishinomaki mill, which produces hardwood kraft pulp. The bleaching sequence was OC(EO)HD.

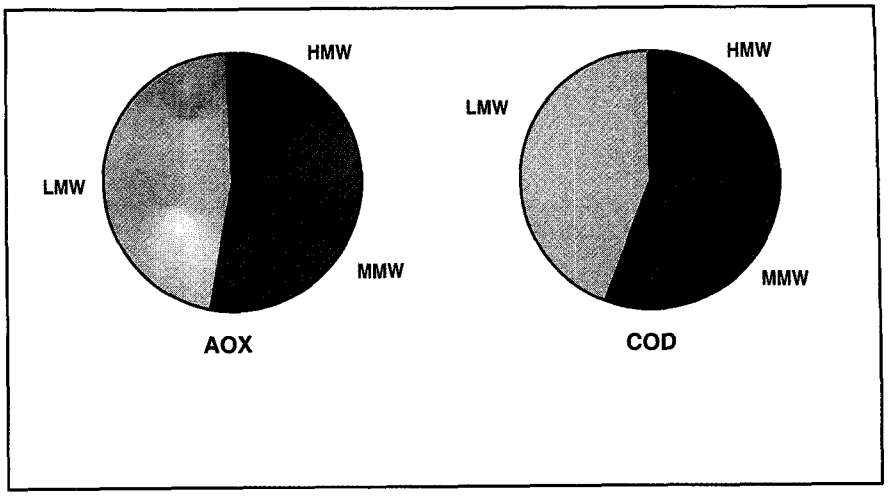
Our first objective was to determine the distribution of AOX and COD within the chlorination-stage effluent. We separated the effluent into three molecular-weight (MW) fractions by ultrafiltration: MW < 1 kDa, MW 1–10 kDa, and MW > 10 kDa. We then analyzed each fraction to determine its AOX and COD content.

We diluted the fractionated effluent threefold. Although too much dilution of bleach effluent can cause failure of fractionation when using ultrafiltration filters *(8)*, our experiment showed the clear character of fractionated effluent. We believe ultrafil-

tration is a convenient method for this type of experiment as long as dilution is not too high and filtration is conducted at least twice *(3)*.

Figure 1 shows the AOX and COD distributions for the untreated effluent. Most AOX was located in the low-molecular-weight (LMW) fraction. The high-molecular-weight (HMW) fraction contained only about 14% AOX. Effluent COD showed the same trend, with the LMW portion containing the largest amount of COD and the HMW fraction the lowest, approximately 23% of the total COD.

1. AOX and COD distribution in hardwood kraft pulp C-stage effluent



Chemical treatment of effluent

We treated the whole effluent—as well as the three molecular-weight fractions—with alkali [NaOH or $Ca(OH)_2$] and alum [$Al_2(SO_4)_3$]. The added amounts were in excess of those required in the pulp mill. The large doses were necessary to elucidate the effects of these chemicals on the effluent.

Figure 2 shows the effects of chemical treatment on AOX. For the treated lower-molecular-weight fractions, the one treated with $Al_2(SO_4)_3$ clearly contained the greatest portion of AOX. All three treatments reduced AOX to varying degrees for the whole effluent as well as for the three MW fractions. The alkali $Ca(OH)_2$ was the most successful in lowering the level of AOX. NaOH and $Al_2(SO_4)_3$ had varying degrees of success, depending on the molecular-weight range being treated. NaOH was better than $Al_2(SO_4)_3$ when the molecular weight was less than 10 kDa (i.e., the LMW and MMW fractions). In the HMW fraction, both were equally effective. NaOH was slightly more effective when treating the whole effluent.

Figure 3 details the effect of the treatments on COD. As with AOX, the LMW fraction consistently contained the most COD. In this case, however, the most effective of the three treatments was $Al_2(SO_4)_3$, which precipitates and flocculates many compounds contributing to COD. $Ca(OH)_2$ also can precipitate some compounds and thus is useful in reducing COD. NaOH has no precipitating ability and thus cannot reduce COD very well. Some difficulties were experienced in controlling the fractionated effluents at exactly pH 12.5, since the samples were almost three times as diluted as the original effluent. This may have affected the results shown in Fig. 3.

I. AOX reduction in sequential effluent treatment

Step	AOX Reduction, %	Step	AOX Reduction, %
1. NaOH	62	1. $Al_2(SO_4)_3$	33
2. $Al_2(SO_4)_2$	19	2. NaOH	46
Residual	19	Residual	21

Multistage treatment of effluent

Alkali, particularly $Ca(OH)_2$, is best for reducing AOX (Fig. 2), while $Al_2(SO_4)_3$ is best for treating COD (Fig. 3). $Ca(OH)_2$ aids in precipitation and dechlorinates the effluent, while $Al_2(SO_4)_3$ precipitates COD-causing compounds. Because NaOH and $Al_2(SO_4)_3$ follow different mechanisms, a combination of the two may be the best method for AOX and COD removal. In a separate set of experiments, we investigated the sequential addition of NaOH and $Al_2(SO_4)_3$.

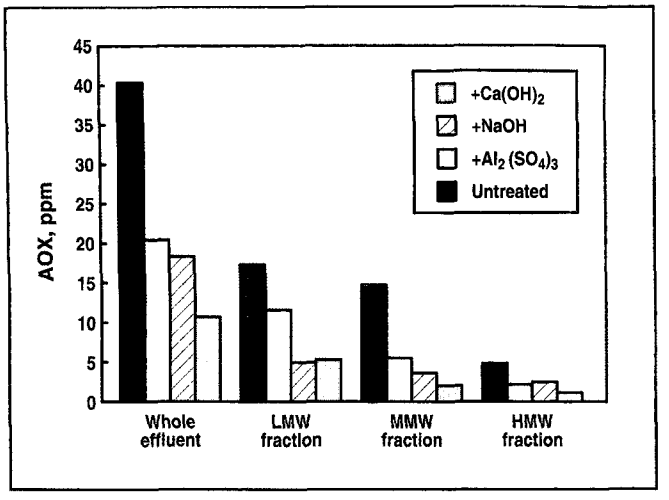
Table I details the effect on AOX. The results demonstrate that the overall reduction of AOX is essentially the same, regardless of the order of chemical addition. Thus, NaOH and $Al_2(SO_4)_3$ react with different types of compounds: NaOH dechlorinates, while $Al_2(SO_4)_3$ precipitates and flocculates.

From this experiment, we can infer the response of the C-stage effluent to various treatments. **Figure 4** shows that about 62% of the AOX is alkali unstable. Approximately three-quarters of the alkali-unstable region is nonprecipitable and therefore could not have been removed with $Al_2(SO_4)_3$. Because of this, use of the alkali allows a much greater reduction in AOX than $Al_2(SO_4)_3$ alone.

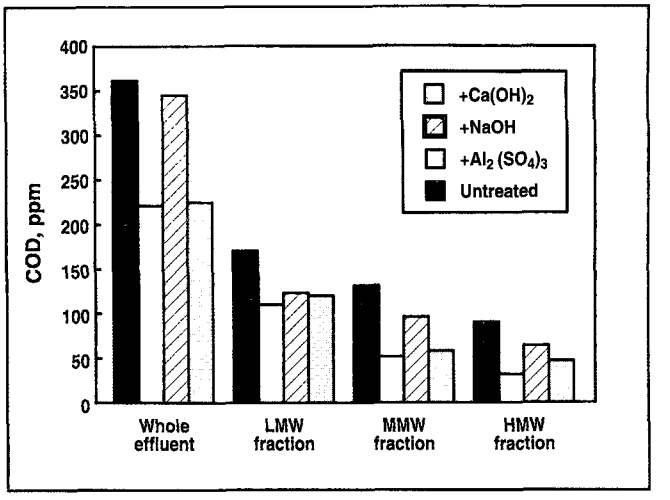
Of the 38% that is alkali stable, half can be removed by precipitation and flocculation with $Al_2(SO_4)_3$. Therefore, by combining alkali and precipitation/flocculation treatment, we can remove approximately 80% of the AOX from the chlorination effluent. Because $Al_2(SO_4)_3$ is acidic and acts as a buffer, the alkali should be added first to prevent excess addition, thus facilitating neutralization of the treated effluent.

$Ca(OH)_2$ was also effective in reducing AOX. However, its precipitation mechanism may be different from that associated with $Al_2(SO_4)_3$.

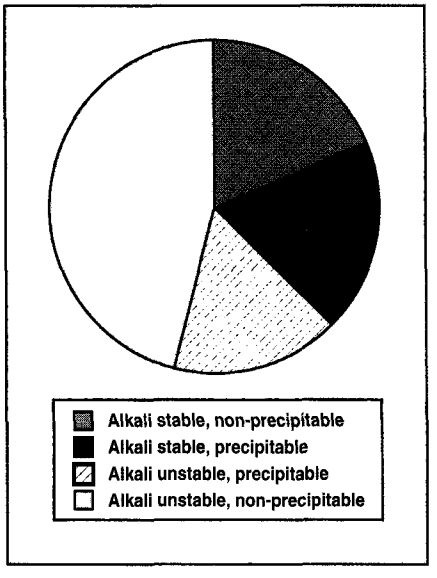
2. Response of AOX to chemical treatment



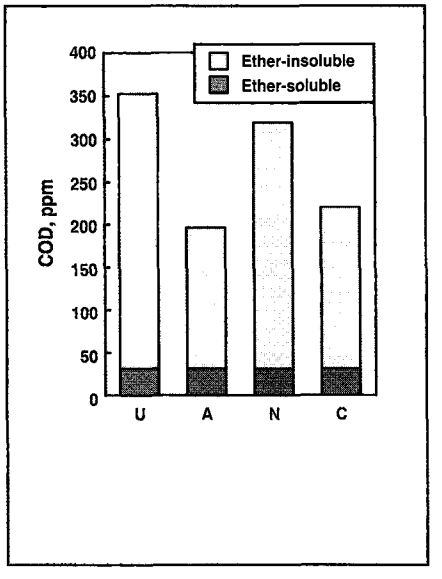
3. Response of COD to chemical treatment



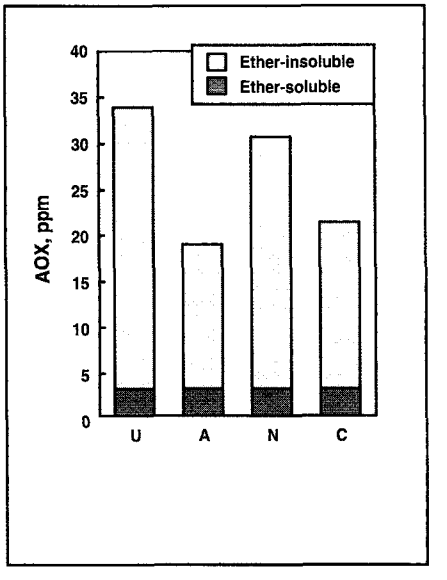
4. Character of AOX in effluent



5. Ether solubility of COD. *U* =untreated; *A* =$Al_2(SO_4)_3$; *N* =NaOH; *C* =$Ca(OH)_2$.



6. Ether solubility of AOX. *U* =untreated; *A* =$Al_2(SO_4)_3$; *N* =NaOH; *C* =$Ca(OH)_2$.



Ether extraction of effluent

After removing 80% of the AOX with a two-stage treatment, we were curious about the 20% that could not be removed by our methods. Over 50% of this residual AOX lies in the LMW fraction. By performing an ether extraction (which normally extracts toxic and low-molecular-weight hydrophobic compounds) on the treated and untreated effluent, we were able to examine a subset of the LMW portion. This subset is considered hard to remove and includes compounds that are largely hydrophobic and nonpolar.

Figures 5 and 6 show the results of this experiment for COD and AOX, respectively. From Fig. 5, it is clear that the ether-extractable compounds make essentially no contribution to COD. However, the situation is very different for AOX. Figure 6 shows that the ether-soluble compounds account for approximately 30% of the total AOX. Only about 35% of these compounds can be treated by the methods investigated. The rest of them will still remain after treatment.

Treatment of model compounds

To determine what types of LMW compounds are treatable by precipitation/flocculation or by alkali addition, we chose several chlorinated organic compounds to serve as models of the hardwood kraft chlorination effluent. **Figure 7** presents the results of the treatments on the models. All of these model compounds are typically found in the chlorination effluent, some in quite high quantities *(2)*. We treated dilute solutions of *o*-chlorophenol, trichloroacetic acid, 1,3-dichloro-2-

propanol, and *o*-chlorobenzoic acid. Because of their low molecular weights, all resisted treatment with $Al_2(SO_4)_3$. Only 1,3-dichloro-2-propanol could be decomposed with alkali. The rest were alkali stable.

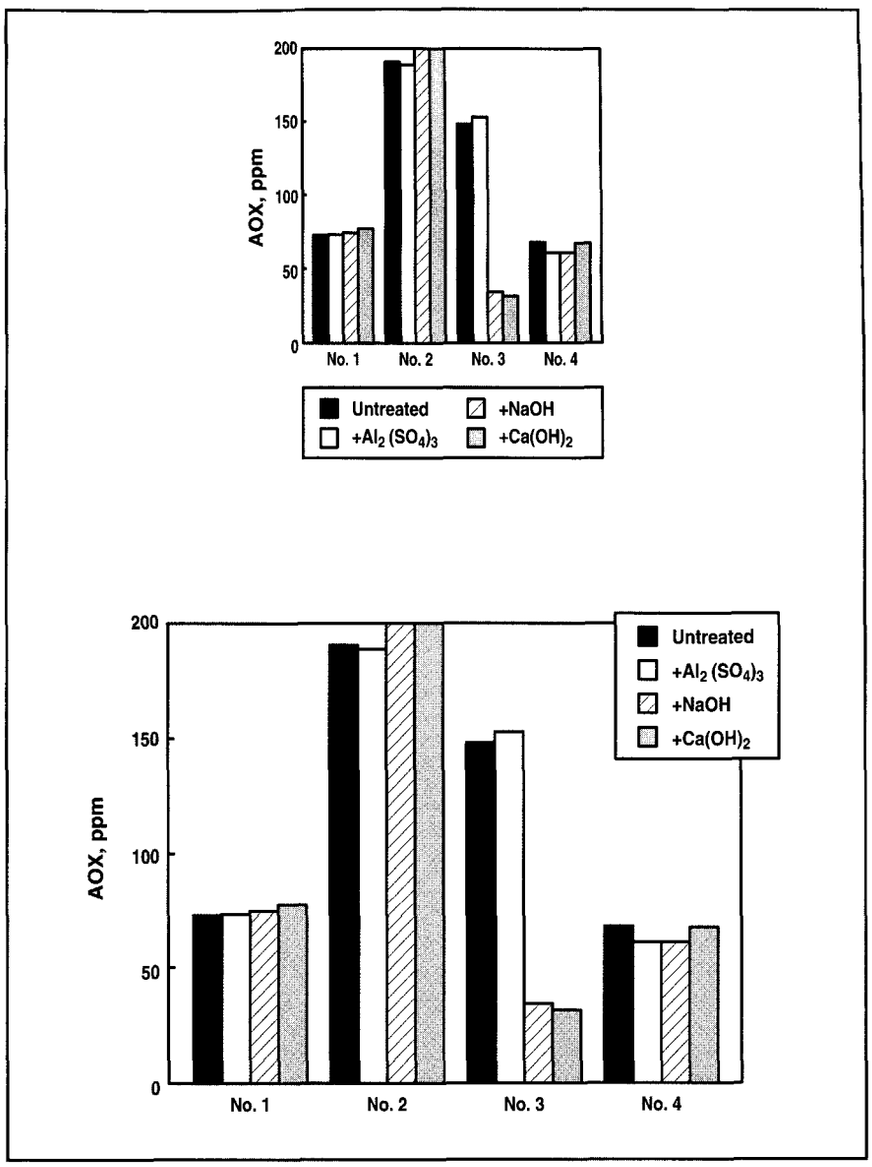
In addition to AOX analysis, we mixed 10 mL of 10m*M* model compounds (dioxane was used as solvent) with 10 mL of 1*N* NaOH. Each sample was stored overnight to investigate the alkali stability. Gas chromatography was used to examine the decomposition of several model compounds. This analysis identified the structures that are unstable in alkali. We analyzed *o*-chlorobenzoic acid, *m*-chlorobenzyl alcohol, dichloromaleic anhydride, and 1,3-dichloro-2-propanol. The carbon–chlorine bonds in the first three structures were alkali stable. However, as in the AOX analysis, 1,3-dichloro-2-propanol was alkali unstable. This result is similar to that achieved by Taneda *et al.*, who showed that a single chlorine bonded to the α-carbon of an alcohol group is alkali unstable *(9)*.

Conclusions

A significant reduction of AOX and COD in hardwood kraft C-stage effluent is possible by chemical means. Simply increasing the pH to more than 12.5 can reduce AOX by 62%. (Even when pH was close to 11.0, reduction of AOX was still about 60%.) Precipitation and flocculation with alum alone reduced COD up to 45%. A combination of precipitation and flocculation with alkali treatment removed 80% of the AOX from hardwood kraft chlorination effluent. The $Al_2(SO_4)_3$ precipitates large organic compounds, while alkali serves to dechlorinate the effluent.

However, 20% of the AOX cannot be eliminated by these means. Most of these stable chlorinated compounds are ether extractable, and some of them are small, hydrophobic, and nonpolar. Because of these stable chlorinated organic compounds, some residual AOX will always remain. Despite this restriction, alkali treatment followed by precipitation and flocculation is a simple method for reducing AOX in hardwood C-stage effluent.

7. Treatment of model compounds. *1* =*o*-chlorophenol; *2* =trichloroacetic acid; *3* =1,3-dichloro-2-propanol; *4* =*o*-chlorobenzoic acid.



In our opinion, treating softwood C-stage effluent by precipitation and flocculation in a clarifier would be effective for reducing both AOX and COD, since this effluent contains relatively high-molecular-weight organic compounds that can be easily sedimented. On the other hand, hardwood C-stage effluent is difficult to treat by this method because it contains relatively lower-molecular-weight compounds than that of softwood effluent.

For a mill with both a hardwood and a softwood bleaching line, our work suggests that AOX and COD can be reduced by segregating the hardwood and softwood C-stage effluents. The segregated hardwood effluent can then be treated with alkali prior to sedimentation. Lime treatment of hardwood C-stage effluent also is an effective and economical method for removing AOX and COD, especially for mills producing mainly hardwood bleached kraft pulp.

Experimental

We used effluent from the chlorination stage of the hardwood fiber line at the Ishinomaki mill (Nippon Paper Industries). It was fractionated by ultrafiltration under nitrogen with an Amicon stir cell using cutoff membranes at 1 kDa and 10 kDa. We fractionated the effluent twice with each membrane to ensure adequate molecular-weight separation. Fractionation was performed before treatment.

To test AOX reduction, we prepared solutions of 0.09 g/L for each model compound. These solutions were treated in the same manner as the mill effluent. In addition to AOX measurements, we analyzed the alkali stability of the model compounds with a GC-14A (Shimadzu) gas chromatograph equipped with an OV-1 capillary column. For this analysis, 10m*M* of the compounds was used. The samples were diluted in 10 mL of dioxane before adding 10 mL of 1*N* NaOH. The sample was thoroughly mixed, left overnight, and then analyzed. The results of this analysis were compared with a blank of 10 mL dioxane mixed with 10 mL water.

For alkali treatment, we added aqueous NaOH or a suspension of $Ca(OH)_2$ (about 800 ppm) to the effluent and model compounds until the pH was more than 12.5. For treatment with $Al_2(SO_4)_3$, we added 600 ppm and adjusted the pH from 6.5 to 7.0 with NaOH. For both $Ca(OH)_2$ and $Al_2(SO_4)_3$ treatment, the supernatant liquid was decanted after 24 h to obtain a clear supernatant. Precipitates were discarded. The supernatant was then tested for AOX and COD. We observed complete sedimentation after 2–3 h when using $Ca(OH)_2$ and $Al_2(SO_4)_3$. We did not see any differences between 3-h and 24-h decantation.

Extractions were carried out with diethyl ether in a Soxhlet extractor for a minimum of 24 h. The pH was first brought to below 2.5. The ether-soluble portion was totally evaporated at 40°C using a rotary vacuum evaporator. We then reconstituted the extractives to 200X strength using diethyl ether. For the AOX samples, we diluted a portion of these extractives to full strength in water. For COD, because diethyl ether interferes with the test, we first evaporated all the ether and then dissolved the extractives in water.

AOX was measured with an MCI TOX-10 organic halogen analyzer. A dilute effluent sample was passed in series through two glass tubes containing granular activated carbon. The inorganic chloride ions were washed from the carbon with KNO_3. The carbon was then burned, and the resulting HCl was titrated with an MCI microcoulometer. TJ

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CORRECTION

This product review originally appeared in the October 1993 issue of *Tappi Journal* and contained errors within its text. The corrected version follows:

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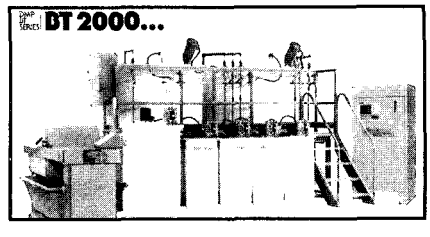

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