Chlorinated organic matter in bleached chemical pulp production

The effect of chlorination-stage variables on chlorinated organic matter in effluent

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ABSTRACT Softwood kraft pulps were chlorinated at low and medium consistency in the laboratory, covering a wide range of chlorination levels, with and without chlorine dioxide substitution. The filtrates from the chlorination and extraction stages were analyzed for organically bound chlorine (AOX) and solvent-extractable organically bound chlorine (EOX). AOX formation decreased when mixing was improved, but EOX was unchanged. Consistency had little effect. At 50% chlorine dioxide substitution in the C stage, (C+E)-stage AOX formation fell by 40%. AOX and EOX formation were proportional to the amount of elemental chlorine in the chlorine and chlorine dioxide consumed. AOX and EOX formation increased dramatically with extensive delignification. Equations were developed to estimate the amount of AOX and EOX formed, based on the elemental chlorine in the oxidant consumed by the pulp.

KEYWORDS
Bleaching
Chlorine
Delignification
Effluent
Extraction
Pulping

During the bleaching of kraft pulp, 45–90 kg of organic material is dissolved per metric ton of pulp produced (*1*). About 75–90% of this material is produced in the first two bleaching stages, chlorination and extraction (*2*). When elemental chlorine is used to bleach the pulp, some of the dissolved organic matter in the bleach plant effluent will have chlorine atoms covalently bonded to the organic molecules. An average of 5 kg of organically bound chlorine is produced for each metric ton of hardwood or softwood pulp bleached by conventional methods. Since world-wide bleached pulp production is approximately 50 million metric tons per year, approximately 250,000 metric tons of organically bound chlorine is discharged annually (*3*).

Some chlorinated organic compounds exhibit mild acute toxicity, some are persistent, some bioaccumulate, and some cause sub-lethal effects. Effluents containing these compounds are coming under increasing scrutiny and regulation around the world (*4*). Several process responses are available to decrease discharge. A lower lignin content in the pulp entering the bleach plant will decrease the chlorine demand, and biological treatment of effluents can remove some chlorinated organic matter. However, some chlorine and chlorine-containing oxidants are still essential, currently, for the economical production of clean, stable pulp of high brightness. It is therefore important to understand fully how chlorinated organic matter is formed during bleaching and to find out if chlorination-stage process variables can be altered to minimize formation of chlorinated organic matter. There have been several reports on this subject (*2, 5–9*).

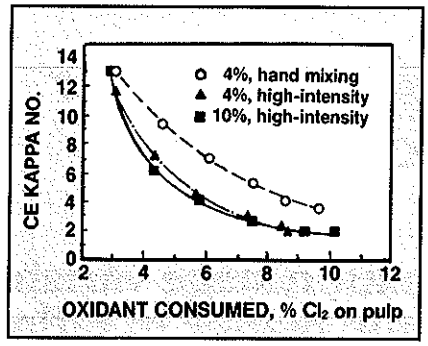
Over 200 chlorinated organic compounds have been identified in bleach plant effluent (*10*), but this only accounts for about 20% of the total organically bound chlorine. About 80% of the organically bound chlorine is in the high-molecular-weight fraction (*3*). A simple and economical method for determining organically bound chlorine is to measure AOX, or adsorbable organic halogen. However, probably only a small fraction of the AOX material is potentially hazardous to the environment. It is therefore desirable to also measure

I. EOX solvent efficiency

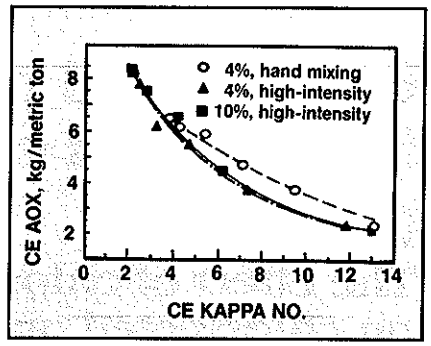
Solvent	EOX, mg/L
Heptane	2.5
Pentane	2.8
Hexane	2.8
Cyclohexane	2.9
Toluene	7.5
1-octanol	42.0

1:10 extraction of (D50C50) seal tank filtrate.

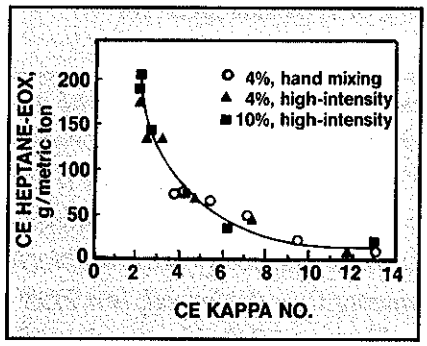
1. The effect of mixing and consistency on delignification (C100)



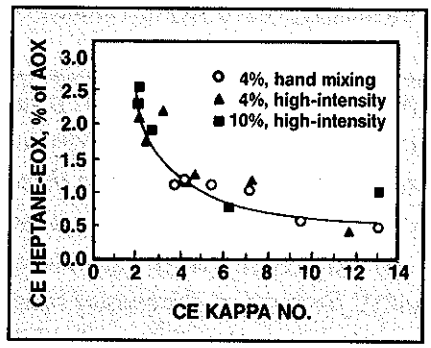
2. The effect of mixing and consistency on AOX formation (C100)



3. The effect of mixing and consistency on heptane-EOX formation (C100)



4. The effect of mixing and consistency on heptane-EOX, with EOX as a fraction of AOX (C100)



the solvent-extractable organic halogen, or EOX. The compounds in the EOX-fraction are more lipophilic, which means they are attracted to fat, and tend to bioaccumulate. Therefore, these compounds are more likely to result in environmental problems. The dispersion of EOX in sediment has also been correlated with dispersion of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2378-TCDD) and 2,3,7,8,-tetrachlorodibenzofuran (2378-TCDF) (*11*) and could be used to track these compounds and estimate their concentrations. EOX will vary, depending on the solvent used; a nonpolar solvent such as heptane or cyclohexane should extract only the more lipophilic material.

Experimental procedures

The chlorination (C) and extraction (E) stages were examined, since they are the source of most of the chlorinated organic material (*2*) and because the CE kappa number can be used to predict the chlorine dioxide needed for final bleaching (*7*). A wide range of chlorine charges was applied, significantly underbleaching and overbleaching the pulp.

The equivalent chlorine multiple ranged from 0.10 to 0.35. The chlorine multiple times the unbleached kappa number yields the percent equivalent chlorine on pulp. We studied pure chlorination, or C100 E, and 50% sequential chlorine dioxide substitution, or (D50 C50)E.

A softwood kraft pulp (kappa no. 30) from a Northern Ontario mill was studied (80% jack pine and 20% black spruce). Pulp samples were preacidified to pH 2 with HCl and chlorinated at 50°C for 30 min. When chlorine dioxide substitution was used, the chlorine dioxide was added 30 s before the chlorine. Chlorine was added as a solution to the hand-mixed pulp and as a gas to the machine-mixed pulp. Studies in our laboratory indicate that the form in which the chlorine is added has no effect on the bleaching results. The pulps were extracted with sodium hydroxide at 10% consistency and 70°C for 60 min, using an NaOH charge equal to 0.55 times the equivalent chlorine charge. The kappa number was determined by TAPPI Method T-236.

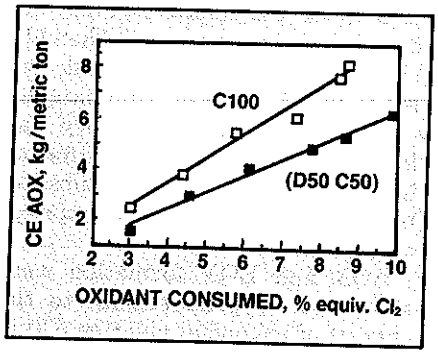
Filtrates were acidified to pH 2 with nitric acid and were stored at 5°C. Combined filtrate samples from the chlorination and extraction stages were analyzed for AOX and heptane-EOX, using a Mitsubishi TOX-10 analyzer, as described elsewhere (*12*). EOX was determined using *n*-heptane (pesticide analysis quality). Studies in our laboratory show that EOX-values are similar for pentane, hexane, cyclohexane, and heptane extraction, as presented in **Table I.** Samples were also analyzed for chlorinated phenolic compounds (phenols, catechols, and guaiacols) and for chloroform. Results of the phenolics and chloroform analyses will be presented elsewhere (*13*).

C100 E bleaching

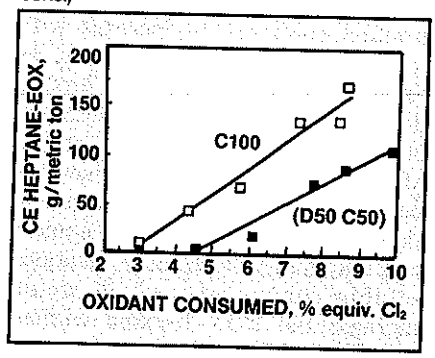
Figure 1 illustrates the effects of mixing and consistency in the chlorination stage on CE delignification. As has been previously reported, improved mixing significantly improves delignification efficiency (*14, 15*), while increased consistency improves delignification efficiency slightly (*15, 16*). Extremely low CE kappa numbers can be attained with high-intensity mixing, with delignification to CE kappa no. 2-3. Extensive delignification such as this, combined with oxygen enrichment of the E stage, could allow high-brightness bleaching in only three stages.

Improved delignification efficiency, however, means that more delignification takes place for a given charge of chlorine. Since dissolved chlorinated organic matter is a direct result of delignification with chlorine, improved delignification efficiency should also result in increased AOX,

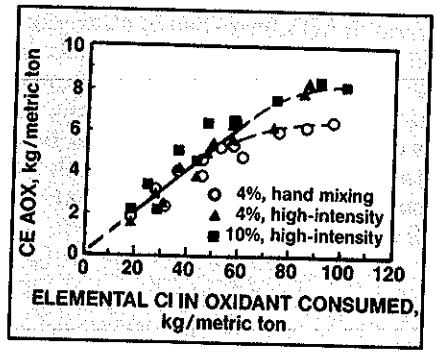
5. The effect of chlorine dioxide substitution on AOX formation (chlorinated at 4% cons.)



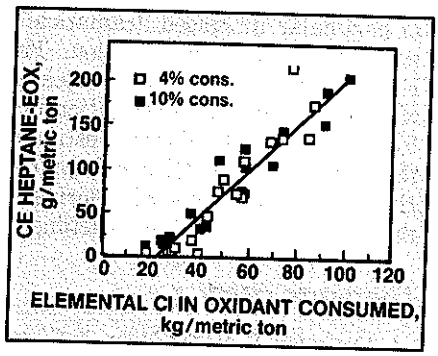
6. The effect of chlorine dioxide substitution on heptane-EOX formation (chlorinated at 4% cons.)



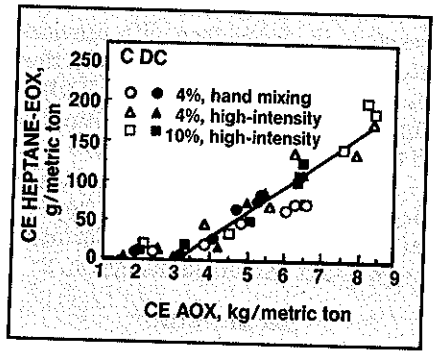
7. AOX formation (C100,D50 C50)



8. Heptane-EOX formation (C100,D50 C50)



9. Heptane-EOX formation



for a constant chlorine charge. This is in fact the case.

It is therefore more appropriate to compare AOX formation at a given level of delignification, as shown in **Fig. 2**. These results show that high-intensity mixing can decrease AOX formation for delignification to a given CE kappa number, compared to laboratory hand mixing. However, with extensive delignification (i.e., below CE kappa no. 4), this difference disappears. There is no effect of consistency on AOX formation. Note also that the AOX curve is not linear with delignification. Each additional kappa unit of delignification results in more additional AOX than the last; that is, incremental AOX increases as delignification continues.

A similar curve for heptane-EOX formation is shown in **Fig. 3**. No effects of mixing or consistency could be discerned. As in Fig. 2, the curve is not linear. When delignification proceeds below CE kappa no. 6, EOX formation increases dramatically. **Figure 4** shows EOX formation as a fraction of AOX. As delignification continues, the heptane-extractable portion of the AOX increases, from less than 1% at CE kappa no. 6 to 2% at CE kappa no. 2. If the solvent extract does in fact contain the more hazardous compounds, then extensive delignification with chlorine could result in a more hazardous effluent.

In these tests, chlorination at 10% consistency produced the same amounts of AOX and EOX as at 4% consistency. However, these pulps were chlorinated in the laboratory, using water for dilution. In many low-consistency chlorination stages, the pulp is diluted from medium consistency in the brownstock storage tower to 3–4% consistency in the chlorination stage using recycled chlorination filtrate. This filtrate contains dissolved organic substances, which may add to the AOX produced. Medium-consistency stock can be pumped and chlorinated without dilution, however, so that there is no recycled chlorination-stage filtrate. Thus, in practice AOX from medium-consistency chlorination may be lower. Studies are presently being conducted to test this hypothesis.

D50 C50E bleaching

Substitution of chlorine dioxide for 50% of the molecular chlorine produced results similar to those of the (C100 E) experiments. The trends were similar to those shown in Figs. 1-4, but the curves were shifted down and to the left. The decrease in AOX and EOX formation due to high-intensity mixing was more apparent in the (DC) results. In comparison to Figs. 1-4, 50% chlorine dioxide substitution:

1. Decreased first E-stage kappa number for a given equivalent chlorine consumption (Fig. 1)
2. Decreased AOX for a given first E-stage kappa number (Fig. 2)
3. Decreased EOX for a given first E-stage kappa number (Fig. 3)
4. Decreased the EOX fraction of AOX for a given first E-stage kappa number (Fig. 4).

These results arise because of the superior delignification efficiency (*17*) of 50% chlorine dioxide substitution. Furthermore, chlorine dioxide provides five oxidizing equivalents with only one chlorine atom (*18*).

Results showed that 50% ClO_2 substitution combined with high-intensity mixing can be used to delignify to (DC)E kappa no. 3 with an equivalent chlorine multiple of 0.22 (6.6% equivalent chlorine on pulp of kappa no. 30). **Figures 5 and 6** compare the AOX and EOX results of (C100 E) and (D50 C50,E) bleaching at 4% consistency in the mixer. For a typical chlorination (pulp of kappa no. 30) using 6.6% Cl_2 on pulp, 6.6 kg AOX/metric ton of pulp will be formed. A 50% chlorine dioxide substitution decreases AOX formation

proportionally, by approximately 31% in this case. For all data studied, 50% chlorine dioxide substitution decreased AOX formation by an average of 40%. Both AOX curves extend back to the origin. Heptane-EOX formation is decreased proportionally as well, but there also appears to be a threshold value, below which no solvent-extractable material is formed.

Elemental chlorine

The formation of AOX is proportional to the amount of the elemental chlorine (Cl) consumed, regardless of its form (*8, 9*). This is also true of the heptane-EOX fraction, as **Figs. 7 and** 8 show. In Fig. 7, AOX increases proportionally with the amount of Cl consumed in bleaching, regardless of whether it originates from Cl_2 or from ClO_2. At approximately 60 kg of Cl/metric ton of pulp, the curve begins to level out. This result is consistent with knowledge of the mechanisms of chlorination. As the charge is increased, a larger fraction of the chlorine is consumed in oxidation than in substitution reactions (*19*)—with some being consumed in oxidation of carbohydrates. Consequently, the amount of organically bound chlorine will not increase further in that stage.

AOX may be estimated from the elemental chlorine in the oxidant consumed, using the following equation:

$$AOX = 0.10\,(Cl_2 + 0.526\,ClO_2) \qquad (1)$$

with a 95% confidence interval of ±6%, where AOX has units of kg Cl/metric ton of pulp, and Cl_2 and ClO_2 have units of kg of chemical/metric ton. Equation 1 is similar in form to the so-called "Germgard Equation" for estimating the Swedish parameter TOCl (*20*).

In Fig. 7, the formation of AOX from hand-mixed chlorination appears to level off at a lower value than the AOX from chlorination with high-intensity mixing. This result is probably due to the poor delignification efficiency of hand-mixed chlorination. Less delignification takes place for an equal amount of oxidant, especially at high chemical charges. This means that less AOX is formed for an equal amount of elemental chlorine. However, with poor mixing, much of the elemental chlorine is wasted, either not reacting at all or reacting with the cellulose and decreasing viscosity.

Unlike AOX, the heptane-EOX fraction continues to increase with increasing elemental chlorine, as shown in Fig. 8. Even if no further delignification takes place, additional chlorine can still chlorinate material already dissolved, which will increase both AOX and EOX. Chlorine oxidation of large, heptane-insoluble material may also yield smaller, heptane-soluble compounds, which would increase the EOX fraction without changing the amount of AOX.

Note also that the heptane-EOX curve does not pass through the origin. Apparently, a minimum amount of elemental chlorine is needed to form heptane-extractable compounds. This result is in accordance with previous studies which show, for example, that essentially no dioxin (2378-TCDD) is formed below a chlorine multiple of 0.15 (*21*).

Heptane-extractable chlorinated organic compounds may also be estimated from the elemental chlorine in the oxidant consumed, using Eq. 2:

$$\text{Heptane-EOX} = 2.6\,(Cl_2 + 0.526\,ClO_2) - 60 \qquad (2)$$

with a 95% confidence interval of ±13%, where EOX has units of g Cl/metric ton and Cl_2 and ClO_2 have units of kg of chemical/metric ton.

AOX and the heptane-EOX fraction also have a straight-line relationship, as shown in **Fig. 9**. Heptane-EOX can be estimated from AOX using Eq. 3:

$$\text{Heptane-EOX} = 33\,AOX - 100 \qquad (3)$$

with a 95% confidence interval of ±16%, where EOX has units of g Cl/metric ton and AOX has units of kg Cl/metric ton.

The linear relationship of AOX and EOX with elemental chlorine and the concept of the asymptotic limit of delignification explain the results of Figs. 2 and 3 and the similar results of the (D50 C50,E) experiments. Each additional kilogram of bleaching agent does progressively less delignifying work but still forms the same amount of AOX and EOX. AOX and EOX must therefore increase exponentially as delignification continues.

Summary

AOX formation from delignification to a given CE kappa number was decreased when mixing in the chlorination stage was improved, but heptane-EOX was unchanged. Chlorination-stage consistency had little effect on AOX and EOX formation. A 50% chlorine dioxide substitution decreased CE AOX by approximately 40%.

AOX and EOX formation were shown to be proportional to the amount of elemental chlorine (Cl) in oxidants consumed during delignification, regardless of whether it was from Cl_2 or ClO_2. AOX and EOX formation increased exponentially with delignification. EOX formation in particular increased dramatically with extensive delignification. The EOX fraction of AOX also increased with the extent of delignification. Equations were developed to estimate the formation of AOX and heptane-EOX from the elemental chlorine in the oxidant consumed in bleaching.□

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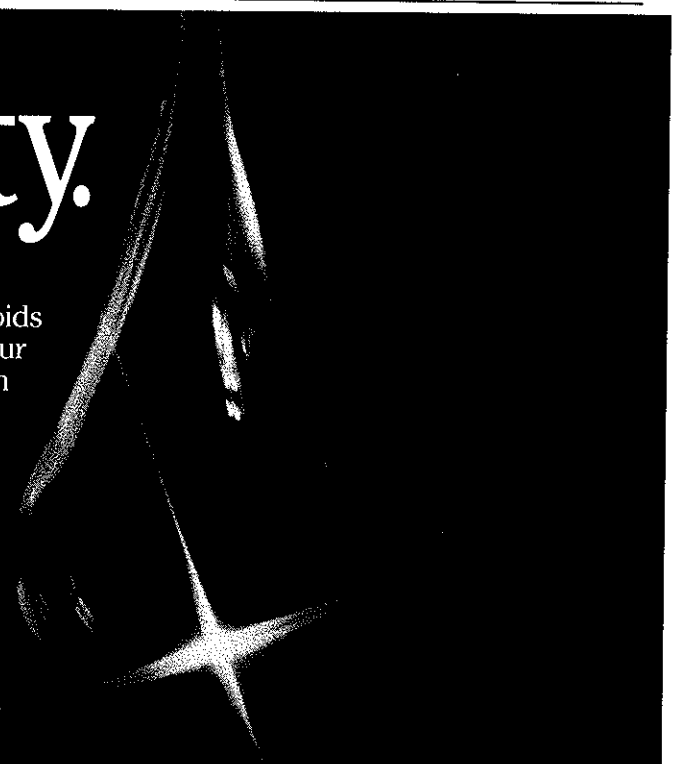
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