Reducing AOX by increasing oxidation potential in the first caustic extraction stage

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ABSTRACT *An increase in the standard oxidation potential of the reinforcing agent in the first caustic extraction stage will reduce the amount of AOX in the stage's effluent. A chlorinated brownstock pulp was treated alternatively in a basic caustic extraction (E) stage, an oxygen-reinforced caustic extraction (EO) stage, and an extraction stage reinforced with oxygen and peroxide (EOP). An AOX reduction of up to 30% was obtained in the effluent from the peroxide-reinforced extraction stage.*

In addition to the brownstock work, using two different model lignin compounds, we ran tests using oxygen, potassium permanganate, hydrogen peroxide with oxygen, and ozone with oxygen-reinforced caustic stages. In all cases, increasing the oxidation potential of the reinforcing agent decreased the amount of AOX detected in the effluent.

KEYWORDS
Bleaching
Chlorine
Environmental control
Effluents
Hydrogen peroxide
Kraft pulping
Oxygen
Ozone

The use of chlorine to delignify kraft pulps has drawn disapproval because of the formation and release of chlorinated organic compounds. The release of organic chlorides into receiving waters has become an important environmental issue. Many governments have set regulatory limits on the amount of absorbable organic halogens (AOX) that may be released (*1*, *2*). Some governments have also started placing restrictions on the amount of certain inorganic chemicals, mainly chlorate ion, that may be released into receiving waters (*3*).

Much research has been directed toward the reduction of AOX in bleaching effluent. One common means of reducing AOX is to reduce the amount of chlorine used in the bleaching sequence. **Figure 1** shows the effect that reducing chlorine has on the amount of AOX produced.

The methods of reducing chlorine requirements may be divided into pre-chlorination modifications, changes in the chlorination stage, and post-chlorination modifications. Pre-chlorination modifications include extended delignification (*4*, *5*) and oxygen bleaching (*6*). In the chlorination stage, chlorine dioxide has been substituted for chlorine (*7*). After the chlorination stage, caustic extraction stages have been reinforced with the use of oxygen and hydrogen peroxide (*8*). Split stream chlorination has also been applied as a method of reducing the formation of AOX in the chlorination stage (*9*).

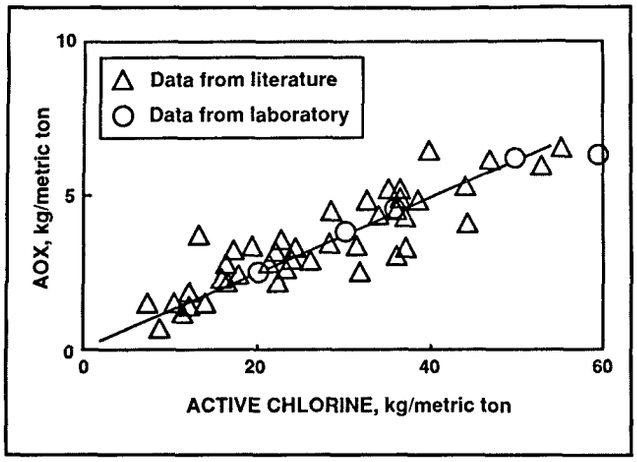
Oxidative caustic extraction

The use of oxygen-reinforced caustic extraction, designated as the EO stage, has rapidly spread throughout the bleached kraft pulp industry. The actual process changes result in the addition of approximately 4–5 kg O_2/ton of pulp and the installation of a pre-retention tube to the extraction tower. The additional chemical cost associated with the oxygen is justified by the reduction in chlorine (*10–12*).

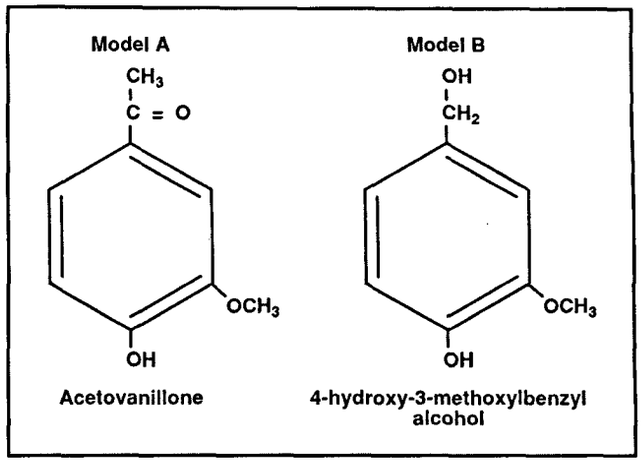
Oxidative extraction stages help reduce the chlorine demand by moving some of the delignification duty from the chlorination stage (the C stage) to the first caustic extraction stage (the E stage). Because less delignification is required in the C stage, less chlorine is needed. The process of extending delignification to the E stage is further enhanced by adding peroxide in conjunction with oxygen. The peroxide addition can reduce the chlorine demand of softwood kraft pulps by as much as 20–30% (*8*).

It has been documented that the use of oxidative extraction reduces the amount of AOX released to receiving waters. One of the reasons for this reduction is that less chlorine is required in the C stage (*13*). Recently, researchers have reported that EO alone has little or no effect on the

1. AOX production as a function of applied chlorine, based on data from laboratory work and literature sources



2. Compounds used to represent lignin: acetovanillone (Model A) and 4-hydroxy-3-methoxylbenzyl alcohol (Model B)



amount of organic chlorides emitted to the receiving waters. The use of EO in conjunction with oxygen bleaching before the C stage, however, is effective in reducing the amount of AOX in both the pulp and the effluent. In the chlorination of oxygen-prebleached pulp, more oxidation and less substitution occur than in the chlorination of unbleached pulp (*13*).

The mineralization of AOX is another way of reducing AOX release. The mineralization and oxidative extraction of AOX during the E stage may reduce the amount of AOX that is released into receiving waters. Our objective was to determine the effects on AOX mineralization caused by strong oxidizing materials such as peroxide and ozone.

I. Conditions for chlorination and extraction experiments

Chlorination	
Softwood kraft brownstock, g	32
Kappa number	27.6
Active chlorine,[a] % by wt.	6.0
Consistency, %	3.5
Temperature,°C	30
Reaction time, min	30
Rotation rate, rpm	60
Extraction	
Chlorinated pulp, g	30
NaOH,[b] % by wt.	5
Consistency, %	10
Temperature, °C	70
Time, min	90
Rotation rate, rpm	60
Final pH	9.5-10

[a]Chlorine factor = 0.22.
[b]Delivered in a 10*N* solution.

II. Chlorine recovery, %

	Base level of chlorine, kg/metric ton	
Stage	*30*	*60*
Model Compound A		
CE	99.8	102.0
C(EO)	98.2	101.8
C(E+MnO_4^-)	...	102.5
C(EOP)	100.9	101.1
C(EZ)	...	100.0
Model Compound B		
CE	99.6	101.7
C(EO)	101.2	91.1
C(E+MnO_4^-)	...	99.1
C(EOP)	99.2	98.9
C(EZ)	...	100.7

Z = ozone.

Theory

Strong oxidizing chemicals can break the chemical bonds between halogens and carbon-based molecules. This oxidation of the halogen-carbon bond mineralizes the organic halogen into inorganic halide ions. Aliphatic halogens do not require reduction potentials as high as do aromatic halogens to become mineralized (*14*).

The atomic surroundings also affect the oxidation potential required to mineralize organic halogens. For this reason, one oxidizing material should reduce AOX to different extents, depending on the type and location of the halogen-carbon bond. As the standard oxidation potential of the reinforcing agent is increased, the dependance of atomic surroundings is decreased, and the extent of AOX reduction should increase.

The standard oxidation potential required to convert aromatic, organically bonded chlorine (C-Cl) into chloride ion through the addition of one electron to the chlorine atom and fracturing of the chlorine-aromatic carbon bond is 1.1 V. Thus, chemical reinforcing agents with a standard oxidation potential of greater than 1.1 V should be able to mineralize organic chloride to some extent.

The oxidation potential required to break a chlorine-chlorine bond (Cl-Cl) is 1.36 V. For this reason, all of the chlorine-based species present in a standard caustic extraction stage should start to undergo mineralization at oxidation potentials greater than 1.36 V. When this oxidation potential is reached, we should encounter a strong reduction of AOX.

The use of materials with higher standard oxidation potentials should result in a much greater efficiency in AOX reduction. The parabolic relationship between mineralization and the standard oxidation potential is the reason for improved AOX reduction efficiency at higher oxidation potentials.

Experimental procedures

In this work, we concentrated on AOX release in the caustic extraction stage. A Dohrmann DX-20A Total Organic Halogen Analyzer was used to determine the amount of AOX in the effluent. The effects of oxidative extraction on AOX formation were studied during softwood kraft bleaching. These effects were also studied using two different model lignin compounds (**Fig. 2**).

Brownstock chlorination and extraction

The experiments were initiated through a standard brownstock chlorination sequence conducted in a sealed rotary evaporator that had been converted to simulate a chlorination tower. Aqueous chlorine was added directly to 32 g (oven dry) of brownstock and was allowed to react for 30 min. The reaction conditions are listed in **Table I.**

After 30 min, the reaction mixture was diluted with 1.00 L of distilled water and was immediately filtered through a glass fritted funnel connected to an aspirator. Effluent samples were collected and were acidified to pH 1.5–2.0 with nitric acid. All effluent samples were stored in amber glass jars and were refrigerated at 5°C.

Caustic extraction experiments were conducted in a stainless steel oxygen bomb fitted with a belt-driven impeller shaft. The experimental conditions used are listed in **Table II.**

The chlorinated pulp was diluted to the proper consistency and was heated to the reaction temperature. At that time, the NaOH was injected through ports in the reaction vessel. At the end of the reaction time (90 min), the pulp was diluted with 1.00 L of distilled water and was filtered through the glass fritted funnel with aspiration. The effluent was collected and acidified to pH 2 with the concentrated nitric acid.

This caustic extraction procedure was used for all of the experiments conducted with kraft pulp. Oxygen and peroxide reinforcement was accomplished by adding 20-psi oxygen gas to the reaction vessel and by forcing 0.5% (by weight) peroxide into the reactor under 20-psi oxygen pressure. All other experimental conditions were held constant.

Model lignin compounds

The model lignin structures shown in Fig. 2 represent the guaiacyl component of softwood lignin. The guaiacyl group was chosen as representative of softwood kraft lignin because it makes up approximately 30% of the total lignin structure (*15*) in softwoods. No other single structural group makes up as large a portion of the lignin molecule as this one. Also, most of the organochlorides that have been identified in bleaching effluents consist of aromatic compounds (*16*).

Actual kraft lignin undergoes both oxidation reactions and electrophilic substitutions during treatment with chlorine. The model structures chosen lend themselves to both types of reactions, and the two organic compounds were considered representative of the lignin molecule.

In the model lignin study, we examined more than the ordinary caustic extraction sequence used for brownstock pulps and the caustic extraction sequences reinforced with oxygen and with peroxide and oxygen. In addition to these, chlorinated model lignin compounds were subjected to alkaline potassium permanganate and to alkaline ozone-enhanced oxygen conditions. These two oxidation-reinforcing chemicals were chosen because their oxidation potentials are above that of oxygen, not because we are recommending them at this time.

Model lignin chlorination was conducted in a rotary evaporator. Initial work placed the model lignin compounds onto the surface of softwood kraft fibers bleached to a brightness of 90. Kappa number tests were conducted on this model brownstock. A linear relationship was found between the amount of model compound placed onto the fiber surface and the kappa number. Next, the model lignin compounds were chlorinated and extracted without the flexible cellulose fiber supports. The same relationship was found between the amount of compound and the kappa number.

The reason the presence of fiber supports did not affect the model lignin reactions is based on the solubility of organic molecules in chlorine water. The model lignin compounds are only sparingly soluble in solutions of chlorine and water. Discrete solid organic portions exist when the model lignin is dispersed in the aqueous phase. The mass transfer associated with this type of reaction morphology is similar to the mass transfer associated with model lignin deposited on flexible fiber supports.

The reaction results indicated that no significant differences existed between using model lignin placed on fiber supports and using powdered model compounds dispersed in the reaction solution. Therefore, we used dispersed model compounds instead of model lignin on flexible fiber supports.

Model chlorination and extraction

We placed 2.5 g of powdered model lignin in the reaction flask and allowed it to react with chlorine water for 30 min at 30°C under conditions similar to those used with the brownstock. The consistency of the reaction mixture was set by the solubility of chlorine in water. Only enough liquid to supply the required amount of chlorine was used. No other consistency controls were used for the model compound studies.

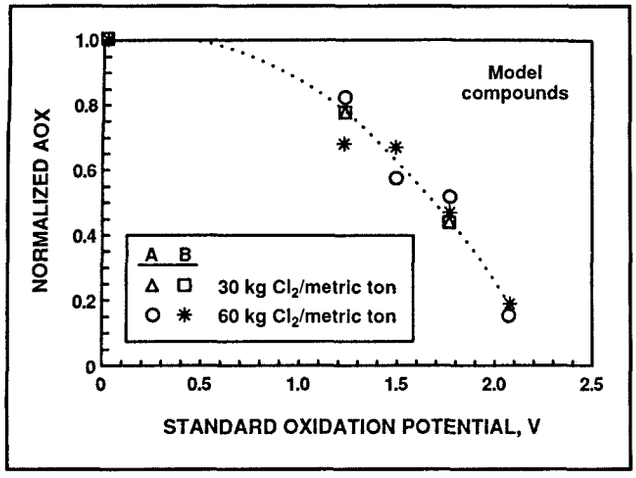
Next, the chlorinated mixture was neutralized to pH 6.5–7.0 with the addition of small amounts of NaOH. Finally, the resulting mixture was transferred to the bomb reactor and was subjected to the caustic extraction conditions. In addition to the oxygen and peroxide reinforcement, 0.5% (by weight) of permanganate (based on the theoretical weight of brownstock pulp) and ozone (approximately 20 mg/L in 20-psi oxygen) were used as well. At the end of the reaction time, the mixture was acidified to pH 2 with concentrated nitric acid and was refrigerated in amber glass jars.

To determine the appropriate amount of chlorine to use in the model lignin studies (6% by weight based on pulp, chlorine factor = 0.22), we had to determine some method of correlating the 2.5 g of model lignin to the theoretical amount of pulp. To accomplish this, we used the relationship between the lignin content of kraft pulp and the kappa number:

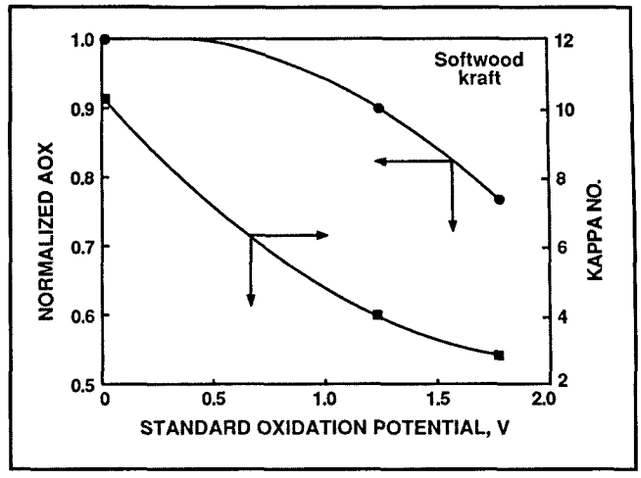
$$\text{lignin, wt. \%} = 0.147 \times \text{kappa no.} \quad (1)$$

Therefore, a softwood pulp of kappa no. 27.6 would contain 4.057% by weight of lignin. Taking this percentage, we determined that the 2.5 g of model lignin compound represented 4.057% of 61.62 o.d. g of unbleached softwood kraft. Therefore, we used 6% of 61.62 g, or 3.697 g, of active chlorine

3. Model study: the effect of increasing the oxidation potential of the caustic reinforcing agent on the amount of AOX produced



4. Softwood kraft study: the effect of increasing the oxidation potential of the caustic reinforcing agent on the amount of AOX produced and on the kappa number of the pulp



in a saturated water solution to react with the model lignin.

AOX and chloride ion analysis

Once the samples had been collected, we analyzed the AOX content with a Dohrmann DX-20A Total Organic Halide Analyzer. Standard analytical procedures were used to determine the amount of AOX present in both the pulp and in the resulting bleach plant effluent. All data collected have been converted into kilograms of AOX per metric ton of pulp.

The Dohrmann DX-20A unit was also used to determine the amount of inorganic chloride ion in the bleaching effluent. Chloride ion determinations were conducted by potentiometrically titrating 50-mL samples of acidified bleaching effluent to silver chloride. Standard analytical methods were used for this determination also.

Results

As shown in **Figs. 3 and 4**, increasing the oxidation potential of the E stage effectively lowered the amount of AOX released in the effluent. The model compound studies indicated that as much as 80% of the AOX formed in the chlorination stage could be destroyed through the judicious use of chemicals with high oxidation potential in the caustic extraction stage. Presented in Fig. 3, these results were obtained with the caustic stage reinforced with oxygen, potassium permanganate, hydrogen peroxide, and ozone.

The model compound studies showed a parabolic type of relationship between the effluent AOX reduction and the reinforcement of oxidizing potential in the caustic extraction stage. Oxygen reinforcement reduced the model AOX by about 22%. Peroxide decreased model AOX releases by as much as 55%.

Mass balances were conducted on chlorine to ensure that the oxidizing chemicals were not simply breaking chlorinated aromatic ring structures into either chlorinated, low-molecular-weight, volatile compounds or carboxylic acid fragments that were still chlorinated. If chlorinated volatile products were being formed, the result would be a net loss of recoverable chlorine. Chlorocarboxylic acids may not be quantitatively recovered either, because AOX measurements depend on the AOX materials being hydrophobic and the nonaromatic chlorocarboxylic acids are soluble in water.

All of the experiments conducted with model compounds were subjected to chlorine balances. Recoveries ranged from 91.7% to 102.5%, with most of the recoveries being near 100%. The results of these chlorine mass balances are shown in Table II. Therefore, the oxidizing chemicals were not simply breaking down the aromatic rings into chlorinated volatile compounds or carboxylic acid fragments.

The results obtained from actual brownstock studies, showed a marked reduction in the amount of AOX released in both the effluent and the pulp. Presented in Fig. 4, these results were obtained using oxygen and hydrogen peroxide as the reinforcing agents. The results were not as favorable as the results obtained in the model studies. The best AOX reduction, about 23%, was obtained with the use of peroxide, the strongest oxidizing agent used in the brownstock study.

Reasons for lower AOX reduction in the brownstock

There are four major reasons for the lower levels of AOX reduction in the brownstock study.

The first reason is that the kappa number of the extracted pulp was not constant. Oxygen reinforcement lowered the kappa number of the pulp by about 60% over the basic caustic extraction sequence. Hydrogen peroxide treatment lowered the kappa number by 72%. By lowering the kappa number, oxidative reinforcement brought AOX out of the pulp matrix and into the resulting effluent (*13*).

The oxidizing agent had to overcome this additional load of AOX before a reduction of AOX could be detected. For this reason, lower values of AOX reduction were expected in the brownstock work.

Second, the AOX in the brownstock E stage consists mainly of organochlorides that are not water soluble. Many of these materials are lignin fragments of high molecular weight. On the other hand, the model lignin compounds are low-molecular-weight

materials, which form alkali and water-soluble fragments upon being chlorinated.

Most of the water-soluble AOX formed during the chlorination of kraft brownstock is removed by the washing step between the C and E stages. No washing step was used for the model compounds because the model lignin starts as a low-molecular-weight material and becomes somewhat water soluble upon chlorination. If we had used a washing step for the model compounds, most of the material, whether solubilized or not, would have passed into and through the glass fritted funnel. Recovery would have been low, and measurements of AOX reduction would have been of little value.

Third, mass transfer also represents a significant difference between the model studies and the work done with actual brownstock. Much of the AOX in the brownstock caustic stage is intricately woven throughout the three-dimensional fiber network. Interior lignin is slow to react because of the diffusion problems associated with transferring chemicals to the reaction site and the possible formation of chlorolignin blocking groups that prevent total delignification (*17*).

As the caustic stage is continued, some of the internal lignin is solubilized into the bulk liquid phase. In the model studies, all of the chlorinated model material is readily available to the reaction chemicals through the entire reaction time. The better transfer of oxidizing chemicals to the AOX in the model studies is a factor contributing to the more extensive reduction of AOX in the model studies.

Fourth, the concentration of AOX in the brownstock reaction mixture was lower than the AOX concentrations used in the model studies. Brownstock chlorination takes place at 3.5% consistency. To reach this consistency, a considerable amount of dilution water has to be added to the reaction system. For the model compounds, we used only the amount of water required to achieve the chlorine levels desired for the reaction. Hence, the amount of water in the model studies was set by the solubility of chlorine in water.

The higher AOX concentration was chosen to help the reaction kinetics. It could have been that the kinetics associated with the reduction of AOX were more favorable toward the model studies, thus reducing AOX to a greater degree.

Conclusions

Increasing the oxidation potential of the reinforcing agent used in the caustic extraction stage is an effective way to reduce the amount of AOX released in the bleaching effluent coming from that stage.

The ability of the caustic extraction stage to mineralize AOX depends on the oxidation potential of the reinforcing agent used. The caustic reinforcing agents of higher oxidation potential mineralize a greater amount of AOX, thus releasing less AOX into bleaching effluent streams.□

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