Reduction of AOX formation during chlorine dioxide bleaching

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ABSTRACT

The principal source of the organically bound chlorine (AOX) that is formed during ClO_2 bleaching is hypochlorous acid (HOCl), which is generated when ClO_2 reacts with lignin. At low pH, this HOCl can be converted to Cl_2, which contributes to AOX formation. Laboratory studies show that AOX formation can be almost totally suppressed by adding dimethylsulfoxide (DMSO), which reacts with HOCl to give dimethylsulfone ($DMSO_2$). The quantity of HOCl captured by DMSO represents roughly 75% of the initial ClO_2 charge (on a mole basis). However, this translates to a one-third loss of delignification efficiency. Consequently, any reduction of AOX by adding DMSO would require an increase in the ClO_2 charge to maintain delignification efficiency. Another approach based on the same HOCl-scavenging mechanism was also studied. In this case, HOCl is captured by the chlorite ions that are formed when ClO_2 reacts with lignin. The results show that AOX formation can be reduced significantly by splitting the ClO_2 charge and adding alkali to raise the pH to neutral when each ClO_2 split is applied. This approach shows promise because it did not reduce delignification.

Application:

Two methods of lowering AOX formation during ClO_2 bleaching are examined. One involves addition of DMSO to the first bleaching stage, and the other involves splitting the initial ClO_2 charge while manipulating pH.

FORMATION OF CHLORINATED ORganic compounds during the bleaching of chemical pulps has been an environmental issue for several years. A CEDED sequence typically produces 4–6 kg of organically bound chlorine (expressed as AOX, i.e., adsorbable organic halogen) per metric ton of pulp. Some of this chlorinated organic matter is toxic, especially the highly chlorinated aromatic fraction of low molecular weight. Regulations limiting the discharge of AOX at levels 5–10 times lower than these values are in place or are under preparation.

Substitution of chlorine dioxide (ClO_2) for elemental chlorine (Cl_2) is expected to reduce the formation of AOX by 80%. Therefore, in some cases, using ClO_2 instead of Cl_2 will satisfy the regulatory limits. However, in other cases, further reduction will be needed to meet these requirements.

It is now well established that the reaction of residual lignin with ClO_2 produces chlorite (ClO_2^-) and hypochlorous acid (HOCl) simultaneously *(1)*. When the pH is low enough, HOCl can be converted to Cl_2 via the reaction in Eq. 1.

$$HOCl + Cl^- + H^+ \leftrightarrow Cl_2 + H_2O \quad (1)$$

A pH lower than 1.5 is required to move the equilibrium far to the right. In most cases, HOCl or mixtures of HOCl and Cl_2 are present and are responsible for the chlorination reactions.

HOCl and Cl_2 are also involved in other reactions. They both react with chlorite to give the intermediate Cl_2O_2, as seen in Eq. 2. The Cl_2O_2 reacts further to regenerate ClO_2 or form chlorate (ClO_3^-) via reactions depicted in Eqs. 3 and 4, respectively *(2)*.

$$HOCl(Cl_2) + ClO_2^- \rightarrow Cl_2O_2 + OH^-(Cl^-) \quad (2)$$

$$Cl_2O_2 + ClO_2^- \rightarrow 2ClO_2 + Cl^- \quad (3)$$

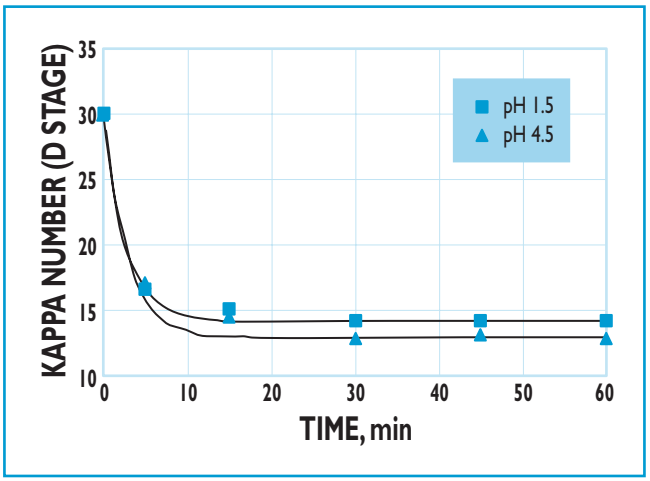
$$Cl_2O_2 + H_2O \rightarrow ClO_3^- + Cl^- + 2H^+ \quad (4)$$

The reactions in Eqs. 2 and 3 are the basis of ClO_2 generation in some laboratory and pilot-scale equipment. The reaction in Eq. 2 proceeds rapidly under acidic conditions and is slow at pH higher than 5 *(1)*. Low pH also favors the formation of ClO_2 (Eq. 3) relative to that of ClO_3^- (Eq. 4). The chlorite anion ClO_2^- can also disappear via acid-catalyzed decomposition. Several mechanisms have been proposed *(3)*. The most recent findings *(2)* are that ClO_2^- generates HOCl in a first step and then reacts with it according to the reactions in Eqs. 2–4.

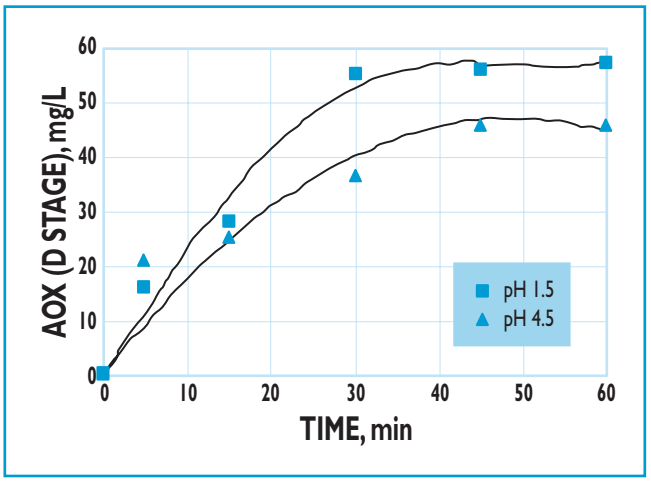
$$ClO_2^- + Cl^- + 2H^+ \rightarrow 2HOCl \rightarrow Cl_2O_2 \ldots$$

Whatever the mechanism, the decomposition of ClO_2^- is significant only at pH lower than 5.

Several attempts have been made to reduce the formation of AOX during ClO_2 bleaching. Lower AOX can be achieved by decreasing the pulp consistency and increasing the pH *(4)*. However the lower AOX is generally obtained at the expense of delignification. A recent study proposed combining the addition of chloride ions with an increase in pH *(5)*. The use of additives, such as sulfamic acid, to reduce AOX formation is another possibility *(6)*.



1. Evolution of kappa number with time during ClO_2 bleaching (D stage only, conditions given in Table I)



2. Formation of AOX during ClO_2 bleaching (D stage only, conditions given in Table I)

FORMATION OF AOX DURING ClO_2 BLEACHING

A softwood kraft pulp of kappa no. 30 was treated with ClO_2 (at a kappa factor of 0.2) at 70°C for 60 min. Kappa number and AOX were measured after 5, 15, 30, 45, and 60 min. Two pH levels (initial pH 1.5 and 4.5) were used. **Figure 1** shows the extent of delignification with time, and **Fig. 2** shows the quantity of AOX liberated in the D-stage effluent. The two apparent kinetics were roughly similar. Most of the delignification was achieved within 10 min. A slight delay was observed in the formation of AOX, which continued to increase significantly after delignification had stopped. This means that the formation of AOX globally paralleled the delignification but that very likely some chlorination also took place in solution and produced AOX.

Formation of AOX was significantly higher at low pH (initial pH 1.5). The pH had no significant effect on lignin dissolved during the D stage.

Initial pH	DMSO, % on pulp	DE AOX,[b] kg/metric ton	DE kappa number	Final pH
1.5	0.0	1.35	6.2	1.5
1.5	0.1	1.17	7.3	1.6
1.5	0.5	1.06	7.7	1.6
1.5	1.0	0.70	8.4	1.6
1.5	7.0	0.25	14.1	1.5
4.0	0.0	1.15	7.4	1.9
4.0	0.1	1.10	7.8	2.0
4.0	0.5	0.90	9.7	1.9
4.0	1.0	0.70	11.0	1.8
4.0	7.0	0.24	13.0	2.5

[a] Softwood kraft pulp, initial kappa no. 37; D-stage conditions: 5% consistency, 70°C, 60 min, kappa factor 0.2, ClO_2 applied = 22mM; E-stage conditions: 5% consistency, 70°C, 60 min, NaOH = active chlorine/2
[b] AOX is the sum of AOX in the D and E stages

I. Effect of DMSO on AOX formation during ClO_2 bleaching [a]

Initial pH (D stage)	DMSO, % on pulp	DMSO applied, mM	DMSO in D-stage effluent, mM	$DMSO_2$ in D-stage effluent, mM
1.5	1	6.7	0	6.8
1.5	7	47.0	35	11.4
4.0	1	6.7	0	6.5
4.0	7	47.0	35	13.1

* Same conditions as in Table I

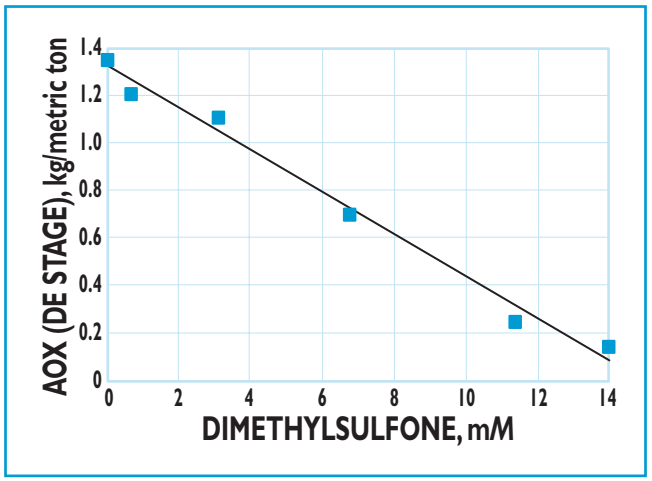
*II. Formation of $DMSO_2$ from DMSO applied during ClO_2 bleaching**

REDUCTION OF AOX BY ADDITION OF DMSO

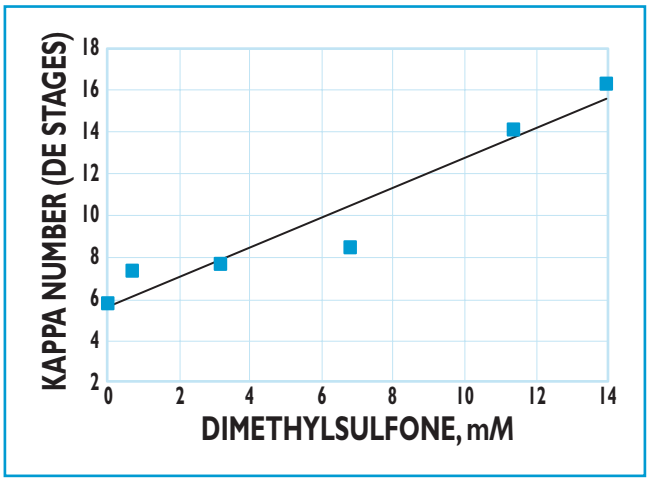
ClO_2 can be iodometrically titrated in the presence of Cl_2 if dimethylsulfoxide (DMSO) is added in excess *(7)*. The DMSO reacts with Cl_2 to give dimethylsulfone ($DMSO_2$), which does not oxidize I^-. The same procedure can be used when ClO_2 is measured by spectrophotometry. This reaction takes place within a wide range of pH (up to alkaline conditions), which means that DMSO reacts with HOCl too via the reaction in Eq. 5:

$$(CH_3)_2SO + HOCl \rightarrow (CH_3)_2SO_2 + H^+ + Cl^- \quad (5)$$

Other reactions can also occur, but the reaction in Eq. 5 seems to be the most important one. The resultant di-



3. Relationship between AOX and dimethylsulfone formed in ClO_2 bleaching with DMSO (conditions given in Table I)



4. Relationship between kappa number and dimethylsulfone formed in ClO_2 bleaching with DMSO (conditions given in Table I)

methylsulfone can be easily measured by high-pressure liquid chromatography (HPLC).

Thus addition of DMSO in chlorine dioxide bleaching should reduce AOX formation by reacting with both Cl_2 and HOCl. Indeed, this is demonstrated by the results in **Table I** for a softwood kraft pulp of kappa no. 37, after treatment in a D stage and extraction in an E stage. The D-stage treatment was carried out at two levels of initial pH (1.5 and 4.0).

Pulp with a high kappa number was selected to increase the formation of AOX, thereby enhancing the extent of any positive effect. As seen in Table I, the AOX level decreased dramatically when DMSO was increased. For 1% DMSO on pulp, the corresponding AOX reduction was 40–50%. Since we have established that DMSO does not react with either ClO_2 or ClO_2^-, it is concluded that the AOX reduction was due to the reaction depicted in Eq. 5. Residual DMSO and $DMSO_2$ were measured in D-stage effluents, and the results are presented in **Table II**. In the experiments where DMSO was totally consumed, the corresponding $DMSO_2$ was quantitatively formed. When DMSO was added in large excess, part of the DMSO remained in the effluent, while the other part was converted to $DMSO_2$.

Figures 3 and 4 show the variation of AOX and kappa number, respectively, as a function of the $DMSO_2$ formed. Extrapolation of the trend in Fig. 3 shows that 15m*M* $DMSO_2$ is formed when there is no generation of AOX. In this case, one can assume that all of the HOCl that normally reacts with lignin has been consumed by DMSO. Given that 22m*M* of ClO_2 was used in these experiments, the quantity of HOCl captured by DMSO represented roughly 75% of ClO_2 on a mole basis. Indeed, the reaction of ClO_2 with lignin can be summarized as follows:

$$\text{lignin} + 2ClO_2 \rightarrow \text{oxidized lignin} + HOCl + ClO_2H$$

If the reactions in Eqs. 2 and 3 are taken into account, the overall ClO_2 reaction can be written as:

$$\text{lignin} + 2ClO_2 \rightarrow \text{oxidized lignin} + HOCl + HCl + H_2O$$

This indicates that 50% of ClO_2 is ending up as HOCl, which is available to react with lignin *(6)*. The fact that the HOCl captured was higher than 50% of ClO_2 means that DMSO also captured some of the HOCl that normally reacts with ClO_2^-.

At the same time, Fig. 4 shows that kappa number (at pH 1.5) increased from 6 (when HOCl was available) to about 17 when HOCl was fully captured by the added DMSO. This illustrates the strong contribution of HOCl to delignification.

These results show that AOX formation could be reduced significantly by capturing the HOCl generated during chlorine dioxide bleaching. However, destruction of HOCl (converted by DMSO into Cl^-) also inhibited the delignification reactions considerably. Several mechanistic explanations can be proposed for the decrease in delignification with decreasing levels of HOCl:

- Direct participation of HOCl in delignification
- Role of HOCl in regeneration of ClO_2
- Formation of new free phenolic groups on residual lignin by HOCl.

Clearly, the reaction of HOCl with DMSO (or any other reaction of this type) constitutes a waste of the oxidative power of ClO_2. Implementation of this approach to reduce AOX formation would increase mill operating costs, since more chlorine dioxide would be required to achieve the desired delignification.

		SPLIT ClO_2 CHARGE					
		No pH adjustment			pH adjustment [b]		
ClO_2 charge, %	2.4	0.8	0.8	0.8	0.8	0.8	0.8
ClO_2 consumed %	2.4		2.4			2.4	
Initial pH	7.0	7.0	3.2	3.1	7.0	7.1	6.8
Final pH	3.0	3.6	3.2	3.1	3.5	3.5	3.5
DE kappa number	4.0		3.9			4.3	
Viscosity, mPa·s	28.5		27.8			26.7	
AOX, kg/metric ton [c]	1.21		1.26			0.7	

[a] Softwood kraft pulp, kappa no. 30, initial viscosity 29 mPa·s; D-stage conditions: 3.5% consistency, 70°C, 60 min, with the three ClO_2 splits lasting for 15, 15, and 30 min; E-stage conditions: 5% consistency, 70°C, 60 min, 3% NaOH. In experiments where pH was adjusted to neutral before ClO_2 application, NaOH charge in the E stage was reduced to maintain 3% total NaOH charge.
[b] pH was readjusted to 7 with NaOH before each addition of ClO_2
[c] AOX was measured after mixing of D- and E-stage effluents

III. Reduction of AOX during ClO_2 bleaching by splitting ClO_2 charge and controlling the pH profile at neutral before each ClO_2 addition [a]

REDUCTION OF AOX BY SEQUENTIAL ADDITION OF ClO_2

Another way to reduce the formation of chlorinated organics is to promote consumption of HOCl by the reaction described in Eq. 2, which actually competes with chlorination of lignin. One possibility is to increase the concentration of ClO_2^- to react with HOCl. This approach has already been tested successfully by Ni *et al. (8)*, where ClO_2^- was partly substituted for ClO_2. Manipulation of the operating conditions to induce high concentrations of ClO_2^- to react with HOCl (Cl_2) is an interesting alternative that was investigated in this work.

At neutral pH, ClO_2 readily reacts with lignin to produce ClO_2^-, which—contrary to its behavior under acidic conditions—is rather stable. The first explanation for this stability is that the reaction of ClO_2^- with HOCl (which is also formed when ClO_2 reacts with lignin) is very slow at pH 6 or above *(1)*. The second explanation is that there is no acid-catalyzed decomposition of ClO_2^- at neutral pH. If the neutral pH is lowered to acidic conditions, then the reaction in Eq. 2 proceeds swiftly. Indeed, the reaction at the acidic pH is faster than it would have been without the passage in neutral conditions, where ClO_2^- is produced in large quantities. Thus HOCl should disappear quickly by the reaction in Eq. 2 and react less with lignin.

One way to implement this scheme is to apply ClO_2 in neutral conditions (pH 6–8) to generate ClO_2^- and then let the pH naturally decrease, which regenerates ClO_2. The end of the process is therefore close to standard conditions. To keep the pH from staying at standard (acidic) conditions for too long, one can split the ClO_2 charge, with each split applied at neutral pH. A similar approach was described by Seger *et al. (9)*, although the pH profile was not the same and the results were different (no effect on a pulp of kappa no. higher than 10). The idea developed here is also similar to an approach described by Hise *(10)* for chlorination.

The benefit of splitting the ClO_2 charge and applying the ClO_2 at neutral pH is clearly apparent in **Table III**. This technique significantly reduced AOX formation while only slightly reducing delignification efficiency. Note that ClO_2 splitting alone—without adjusting pH to neutral when each split was applied—had no effect on AOX formation or delignification efficiency. AOX decreased only when pH was neutralized at the beginning of the ClO_2 phases.

CONCLUSION

The formation of organically bound chlorine (AOX) during ClO_2 bleaching can be reduced by using an additive that selectively reacts with the hypochlorous acid (HOCl) generated during ClO_2 reactions with lignin. Dimethylsulfoxide (DMSO) was found to be a particularly effective additive. Laboratory results showed that this approach can reduce AOX formation during ClO_2 bleaching. The study also provided a better understanding of the role of HOCl in ClO_2 bleaching, showing that HOCl is responsible for at least one-third of the delignification achieved in a D stage. However, this approach also would increase mill operating costs, since more ClO_2 would be required to achieve delignification targets.

A more straightforward way to reduce the formation of AOX is to increase the level of the chlorite anion so that it can capture HOCl more efficiently than it does in conventional ClO_2 bleaching conditions. Splitting the ClO_2 charge and adjusting the pH to neutral when the splits are applied appears to be a promising approach. However, further investigation is needed to optimize the practical conditions for implementing this concept.

EXPERIMENTAL

Softwood kraft pulp of Scandinavian origin was bleached with chlorine dioxide (D stage) in plastic bags. For the DMSO experiments, the brownstock had an initial kappa no. 37 and was bleached at 5% consistency at 70°C for 60 min with a kappa factor of 0.2 (ClO_2 applied = 22m*M*). The D-stage treatment was carried out at two levels of pH (1.5 and 4.0). For the experiments involving split charges of ClO_2, the brownstock had an initial kappa no. 30 and was bleached at 3.5% consistency at 70°C for 60 min. The total ClO_2 charge applied was 2.4%, with 0.8% applied in

each of three splits. Alkali was added to raise the pH to neutral when each ClO_2 split was applied. The first two ClO_2 splits were applied for 15 min each, and the final split was applied for 30 min. ClO_2 for all experiments was produced by reaction of a concentrated solution of sodium chlorite with sulfuric acid, and the resultant ClO_2 did not contain any chlorine.

After bleaching, the pulps were washed with distilled water and extracted with caustic soda (E stage) in plastic bags. For the DMSO experiments, the extraction was carried out at 5% consistency at 70°C for 60 min. The NaOH charge was 0.5 × active chlorine applied in the D stage. For the experiments involving split charges of ClO_2, extraction was carried out at 5% consistency at 70°C for 60 min using a total NaOH charge of 3%.

The AOX content in the bleach liquors from the D and E stages was measured separately with a Dohrmann analyzer. However, in some cases (indicated in the text), the two liquors were mixed before measurement. Pulp kappa number and viscosity were determined according to the appropriate TAPPI test methods (T 236 and T 230, respectively). Residual DMSO and formation of dimethylsulfone were measured by high-pressure liquid chromatography (HPLC). **TJ**

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