Chlorate Reduction in ClO₂ Prebleaching by the Addition of HClO Scavengers

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Abstract

In chlorine dioxide delignification and bleaching, the formation of chlorate is undesirable because it does not react with lignin and is harmful to the environment. Chlorate is mainly formed from the in-situ generated hypochlorus acid, which is also the main reason for AOX formation. In previous literature, scavengers of hypochlorous acid, such as sulfamic aicd, DMSO, and hydrogen peroxide have been added to bleaching stages to reduce AOX formation but less attention has been paid to chlorate reduction. This paper thus focuses on the reduction of chlorate content caused by the following additives, sulfamic aicd, DMSO, hydrogen peroxide, and oxalic acid.

The results show that only sulfamic acid and DMSO reduce chlorate formation under our chlorine dioxide prebleaching conditions. Results by UV spectroscopy and pH adjustment show that scavengers react with hypochlorous acid much faster than with chlorine. Hydrogen peroxide and oxalic acid react with HClO/Cl₂ much slower than DMSO and sulfamic acid do. The reason for the ineffectiveness of hydrogen peroxide and oxalic acid is ascribed to their slow reaction rates with HClO compared to that of chlorate formation. The fact that only 30-35% of the chlorate can be reduced by sulfamic acid and DMSO when charged in same mole ratio to chlorine dioxide, suggested that the reaction rate of DMSO and sulfamic acid with hypochlorous aicd are of the same magnitude as that of chlorate formation.

Introduction

It is known that chlorate is formed during ClO₂ delignification and bleaching. The formation of chlorate corresponds to a loss of 20-36% of the total ClO₂ charge[1]. Because chlorate does not react with lignin, the formation of chlorate decreases the reaction efficiency of ClO₂. Also chlorate is a well-known herbicide and biocide, and its discharge has been regulated[2]. Thus, it would be beneficial to find methods that can reduce the formation of chlorate during chlorine dioxide bleaching.

It has been reported[3] that chlorate is mainly formed by the following reaction (1)

$$HClO + ClO_2^- \rightarrow H^+ + Cl^- + ClO_3^- \qquad (1)$$
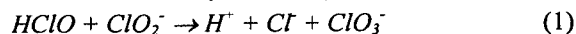
The hypochlorous acid is known to be produced in-situ during ClO₂ bleaching and it has also been reported to be the main reason for AOX formation[4]. Thus it is reasonable to think that both chlorate and AOX can be reduced by the addition of HClO scavengers to the bleaching stages. This was found to be true for AOX reduction by the use of additives such as sulfamic acid, H₂O₂, and DMSO[4-11]. However, in these papers much less attention was paid to the reduction of chlorate. As a matter of fact, AOX formed in D₀ delignification accounts only about 4% of the original chlorine dioxide charge[5]. Therefore we think the effect of the additives on chlorate reduction will be much higher than AOX reduction and the effect of the scavengers on chlorate reduction should be thoroughly checked. The scavengers tested in this study are sulfamic aicd, DMSO, hydrogen peroxide, and oxalic acid[13].

Experimental

Chlorine solution was prepared by dissolving chlorine gas directly into chilled distilled water. Crude ClO_2 solution was prepared by adding chlorine solution into acidic sodium chlorite solution. From the crude ClO_2 solution, ClO_2 gas was stripped with N_2 gas and re-dissolved into chilled water, thus pure chlorine dioxide solution was made. A portion of the Cl_2 solution was mixed into the pure ClO_2 solution again to make Cl_2/ClO_2 mixture where 5% of the oxidation power will be supplied by chlorine, and this Cl_2/ClO_2 mixture was used in the bleaching.

The unbleached kraft pulp used in this study had a kappa number of 17.6 and a brightness of 41.0% ISO. Bleaching was carried out in sealed polyethylene bags. The scavengers, added in the same molar amount as chlorine dioxide, were hand-mixed into the pulp slurry. Then chlorine dioxide solution was charged, quickly mixed, and put into a water bath with constant temperature. The D_0 pre-bleaching conditions were: pulp consistency 3%, kappa factor 0.15, temperature 60°C, reaction time 60min and 4% sulfuric acid on o.d. pulp. The end pH of D_0 bleaching was around 1.7-2.0. E_1 extraction conditions were: pulp consistency 3%, alkali addition 0.7% on o.d. pulp, temperature 70°C, and reaction time 60min. Brightness was measured with an elrepho 3300 spectrophotometer (Datacolor Interantional Co. Ltd.). Kappa number was measured according to Tappi standard T236 cm-85. The COD and chlorate contents of the D_0 effluents were measured respectively according to CPPA standard H. 3P and Tappi standard T-700 om-93 with Dionex-200 ion chromatograph.

The data were collected from 25 experiments generated by five kinds of treatments (DMSO, sulfamic acid, hydrogen peroxide, oxalic acid, and the control) and 5 replicates for each treatment. The 25 experiments were carried out in a random way. The data were analyzed using the GLM procedure of the SAS (Strategy Application System) statistical package, and the method used to compare the treatment differences were the least significant difference method (LSD method) at 5% level of significance[14].

To verify the reactivity of $HClO/Cl_2$ with the scavengers, chlorine solutions were mixed with various portions of scavengers and the reactions were carried out 5 minutes at ambient temperature, the residual oxidation equivalents of the mixtures were titrated iodometrically and expressed in units of milli mole equivalent (mmeq).

The UV spectrometer used was UVS-2100 manufactured by Sinco Co. Ltd. Korea. A micro magnetic stirrer was installed under the UV cell and the $HClO/Cl_2$ solution was stirred at 1000rpm. As soon as the scavenger solutions were added into the $HClO/Cl_2$ solution, time-interval-experiments were carried out. This is to get a spectrum ranging from 200-400 nm every 5 or 10 seconds. Because the spectrometer is a single-beamed multi channel system connected with a photo diode array detector (PAD detector), it has the characteristics of fast scanning and can do the time-interval-experiments quite well.

Results and Discussion

1. Oxidation power changes of $HClO/Cl_2$ solution when scavenges were charged

The scavengers, DMSO, sulfamic acid, hydrogen peroxide and oxalic acid, had been reported to be able to eliminate chlorine/hypochlorous acid[4-13]. The reactivity of $HClO/Cl_2$ with the scavengers was briefly checked by mixing chlorine solutions with various portions of scavenger solutions followed by checking the residual oxidation power iodiometrically. The results are summarized in Table 1.

Table 1. Residual oxidation equivalent of reacted solution by mixing 2 ml of HClO/Cl₂ solution (0.75M) with various portions of scavenger solutions (0.296M)

Scavengers (ml)		0	3.0	5.0	7.0	10.0
	DMSO	3.00	1.09	0.33	0	0
Residual OXE	Sulfamic Acid	3.02	2.99	2.98	2.98	2.97
(mmeq)	H₂O₂	3.00	1.03	0.49	1.84	4.00
	Oxalic Acid	3.05	1.15	0.31	0	0

It was found that in the case of DMSO and oxalic acid, the oxidation power dropped substantially after 5 minutes reaction. This indicated that HClO/Cl₂ were eliminated effectively.

In the case of hydrogen peroxide, the oxidation power decreased at first, but with the increasing addition of hydrogen peroxide, the oxidation power increased again. This is because, at first HClO/Cl₂ reacted with hydrogen peroxide so that the residual oxidation power decreased. With the increasing addition of hydrogen peroxide, all the HClO/Cl₂ would be consumed and then the excessive hydrogen peroxide would contribute to the residual oxidation power.

However, it is unexpected that sulfamic acid did not reduce the oxidation power after it was charged into the HClO/Cl₂ solution. This does not mean that sulfamic acid can not react with HClO/Cl₂, but rather that, the reaction product, chlorosufamic acid (HClNSO₃H), is also an oxidant, and it can oxidize KI during the iodometic titration[12].

2. Effect of scavengers on the chlorate reduction
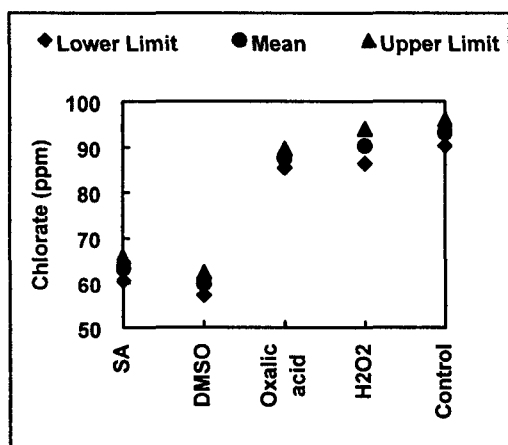

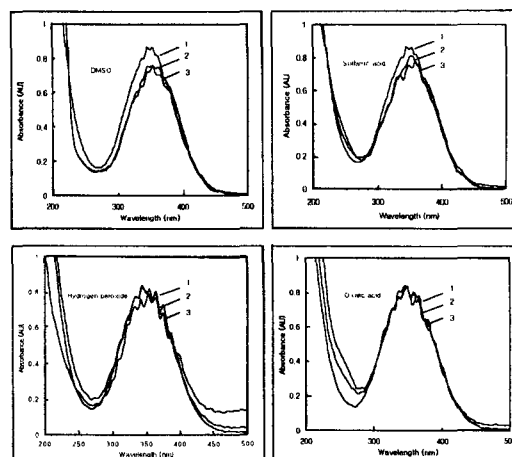Fig. 1 Effect of additives on chlorate formation in ClO₂ prebleaching

Fig. 2. Time interval experiments by UV spectrometer (1. 10mM Cl₂ in 3ml 10N H₂SO₄; 2. 0.2ml scavenger solutions (0.296M) added to Cl₂ solution 3. spectrum after 300 seconds reaction)
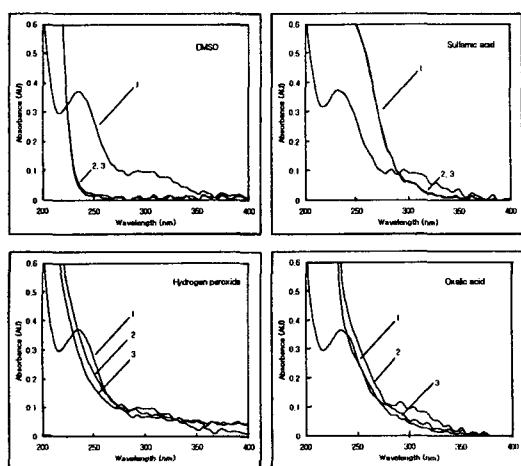
Fig. 3 Time Interval Experiments by UV Spectrometer (1. 4.43mM HClO/Cl₂ in 3ml pH 1.98 H₃PO₄/NaH₂PO₄ Buffer Solution; 2. 0.1ml Scavenger Solutions (0.296M) Added to HClO/Cl₂ Solution; 3.
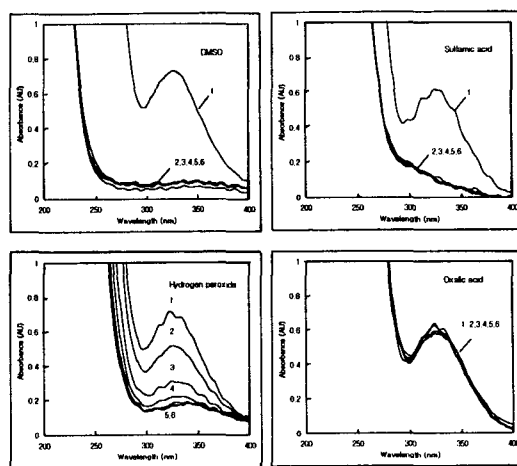
Fig. 4 Time Interval Experiments by UV Spectrometer (1. 7.76mM HClO/Cl₂ in 3ml 3M HCl solution; 2. 0.2ml scavenger solutions (0.296M) added to HClO/Cl₂ solution; 3-6. Spectra Scanned after 10,

Fig. 1 shows the result of additives on chlorate reduction during D_0 prebleaching. Unexpectedly, only DMSO and sulfamic acid decrease the chlorate formation. Hydrogen peroxide and oxalic acid show no significant change of chlorate contents compared to the control.

The above results indicate that hydrogen peroxide and oxalic acid do not scavenge HClO/Cl₂ effectively during ClO₂ bleaching. This discovery is evidently contrary to the fact discussed in the above section, where oxalic acid and hydrogen peroxide eliminated HClO/Cl₂ efficiently.

To explain the contradiction, it was thought that although oxalic acid and peroxide reacted with chlorine in water solution where no pulp was used, the situation in bleaching where pulp existed might be very different. During bleaching, as the HClO is in-situ produced, chlorine is also formed in equilibrium with HClO according to reaction (2).

$$HCl + HClO \leftrightarrow Cl_2 + H_2O \qquad (2)$$

Afterwards HClO/Cl₂ has three pathways to go:

1) HClO/Cl₂ continues to react with lignin structures.
2) HClO/Cl₂ reacts with ClO₂⁻ to form chlorate according to reaction (1).

$$HClO + ClO_2^- \rightarrow H^+ + Cl^- + ClO_3^- \qquad (1)$$
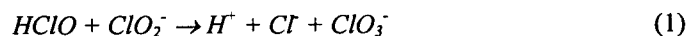
3) HClO/Cl₂ reacts with the scavengers according to reactions (3-6);

$$(CH_3)_2SO + HOCl \rightarrow (CH_3)_2SO_2 + HCl \qquad (3)$$
$$NH_2SO_3H + HOCl \rightarrow NHClSO_3H + H_2O \qquad (4)$$
$$H_2O_2 + HClO \rightarrow HCl + O_2 + H_2O \qquad (5)$$
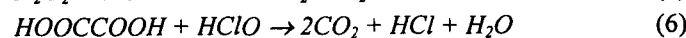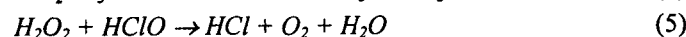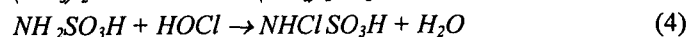$$HOOCCOOH + HClO \rightarrow 2CO_2 + HCl + H_2O \qquad (6)$$

Fig. 1 showed that only 30-35% of the chlorate was reduced by the addition of scavengers based on the

same mole ratio to the original charged chlorine dioxide. This indicates that the rates of reaction (3) and (4) are of the same magnitude as reaction (1). On the other hand, since hydrogen peroxide and oxalic acid had no significant effect on chlorate formation, reactions (5) and (6) are slower than reaction (1). In addition, it might be interesting to point out that only 10-40% of AOX could be reduced by the addition of DMSO and sulfamic acid in literatures [7-9, 11].

The reactions (1-6) are very fast. It is difficult to obtain direct kinetic data to compare these reactions. However, by UV spectroscopy and pH adjustment, it could be demonstrated that reactions (3) and (4) are much faster than reactions (5) and (6).

In Fig. 2, chlorine was dissolved in 10N H_2SO_4. In this extremely acidic condition, the amount of HClO is very low. Thus Fig. 2 showed that chlorine reacted with the scavengers very slightly.

In Fig. 3 chlorine was dissolved in a NaH_2PO_4/H_3PO_4 buffer solution of pH 1.98. At this condition chlorine and hypochlorous acid coexist in equilibrium as shown in reaction (2). The results in Fig. 3 indicate that all four scavengers react very fast with $HClO/Cl_2$ solution, but it is hypochlorous acid that reacts with the scavengers first, and chlorine is consumed after it is changed into the HClO form. The higher reactivity of HClO than Cl_2 is due to the higher oxidation potential of HClO than Cl_2 as expressed in equation (7) and (8) [15].

$$HOCl + H^+ + 2e \leftrightarrow Cl^- + H_2O \qquad \varphi^o = 1.49 \ V \qquad (7)$$
$$Cl_2 + 2e \leftrightarrow 2Cl^- \qquad \varphi^o = 1.36 \ V \qquad (8)$$

In Fig. 4, by further adjusting the pH, that is, dissolving chlorine into 3M HCl solution, the reactivity differences of scavengers with $HClO/Cl_2$ can be seen clearly to be in the order of DMSO > sulfamic acid >> hydrogen Peroxide > oxalic acid. This might explain why hydrogen peroxide and oxalic acid showed no significant effect on chlorate reduction.

3. Other supporting evidence

Data on effluent end pH, effluent COD load, and D_0E kappa number, E stage removable chromophore contents are summarized in Table 2. All these suggest that DMSO and sulfamic acid have significant effect when charged into bleaching stage, while the effect of hydrogen peroxide and oxalic acid are not significant. This is stated in more detail in the following subsections.

3.1 Effect of additives on effluent end pH

DMSO and sulfamic acid decreased the end pH values. This is because, according to equation (3), hydrochloric acid is formed after the reaction of DMSO with HClO. In the case of sulfamic acid according to equation (4), hydrochloric acid is not produced, but sulfamic acid itself is also a strong acid and the chlorinated sulfamic acid might be even a stronger acid. No significant pH decreases were observed in the cases of hydrogen peroxide and oxalic acid, which supports that hydrogen peroxide and oxalic acid are not effective in scavenging HClO in the pH range of our experiments.

3.2 Effect of additives on effluent COD load

As can be seen in Table 2, addition of DMSO and sulfamic acid decreased the effluent COD loads, while no significant changes could be observed for hydrogen peroxide and oxalic acid. In the case of DMSO, the decrease of COD was caused by less delignification due to the elimination of hypochlorous acid (see also data on D_0E kappa number); in the case of sulfamic acid, the reason for the lower COD might be ascribed to the effect of chlorinated sulfamic acid which can react with some of the organic components[4] that contribute to COD load.

It is interesting to mention that in a recent paper by A .R. P. Van Heiningen, *et al.*[16], addition of formic acid to chlorine dioxide bleaching also showed no significant effect on delignification, AOX formation, COD load, etc. This provides further support to our results obtained with oxalic acid since formic acid and oxalic acid have very similar structure characteristics.

3.3 Effect of additives on D₀E kappa number

Table 2 showed that while addition of DMSO decreased the delignification ability of chlorine dioxide due to the elimination of active hypochlorous acid, other additives, sulfamic acid, hydrogen peroxide and oxalic acid showed no significant difference compared with the control. This is not surprising since as mentioned above, hydrogen peroxide and oxalic acid did not eliminate hypochlorous acid, and sulfamic acid maintained the oxidation power of hypochlorous acid due to the production of active chlorosulfamic acid.

3.4 Effect of additives on chromophore content removed during the E stage

The chromphore content removed by the E stage extraction were calculated from the data of D₀ brightness and D₀E brightness according to equation (9):

$$\Delta(K/S) = [\frac{(1-R_\infty)^2}{2R_\infty}]_{DoE} - [\frac{(1-R_\infty)^2}{2R_\infty}]_{Do} \qquad (9)$$

In equation (9), K and S are respectively the light absorption and light scattering coefficient, and R_∞ is the reflectance of a stack of papersheets measured at 457nm, which can be substituted by brightness data. It is known that K is proportional to the concentration of chromopores while S does not change much by bleaching if the basis weights of handsheets used in measuring are fixed[17]. Thus the value of K/S is also proportional to the concentration of chromophores, and the $\Delta(K/S)$ in equation (9) expresses the content of chromophores removed by the E extraction stage.

Table 2 showed that the chromophores removed in the E stage were higher in the case of oxalic acid, hydrogen peroxide and control than those of sulfamic acid and DMSO. As was pointed out by R. W. Allison *et al.*, and Maria Boman *et al.*[18-19], pulps delignified by chlorine have higher light absorption coefficient than those delignified by chlorine dioxide. This indicates that the in-situ produced hypochlorous acid is better in delignifing than in eliminating chromophore structures or brightening. The in-situ produced hypochlorous acid continues to react with lignin, forming chlorinated organic compounds or even chlorinated chromophores which can be mostly removed in E₁ extraction. Thus in the cases of DMSO and sulfamic acid, less E stage removable chromophores will be formed since HClO is scavenged effectively.

Conclusions

Although DMSO, sulfamic acid, hydrogen peroxide, and oxalic acid can all react with a $HClO/Cl_2$ solution, only sulfamic acid and DMSO were efficient in reducing chlorate formation when they were added to a chlorine dioxide prebleaching stage. Results by UV spectroscopy and pH adjustment illustrate that the scavengers react with chlorine much more slowly than with hypochlorous acid, and hydrogen peroxide and oxalic acid react with $HClO/Cl_2$ much slower than DMSO and sulfamic acid do. Thus the reason for the ineffectiveness of hydrogen peroxide and oxalic acid is due to their slower reaction rates with HClO compared with that of chlorate formation, i.e., reaction between hypochlorous acid and

chlorite. Based on the fact that only 30-35% of the chlorate can be reduced by sulfamic acid and DMSO when charged in equimolar amount to chlorine dioxide, the reaction rates of DMSO and sulfamic acid with hypochlorous aicd are thought to be in the same magnitude with the reaction rate of chlorate formation.

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