

# MECHANISM OF CHLORATE FORMATION AND REDUCTION OF *HClO* DURING CHLORINE DIOXIDE PULP BLEACHING

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## 1. INTRODUCTION

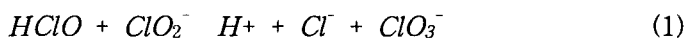
Chlorine dioxide has been used in pulp delignification and bleaching field for about half a century. It has been known that during delignification and bleaching,  $\text{ClO}_2$  decomposes and ionizes into chlorate( $\text{ClO}_3^-$ ), chlorite( $\text{ClO}_2^-$ ), and chloride( $\text{Cl}^-$ ). Hypochlorous acid is also produced, but it is rather an intermediate, which reacts very rapidly with lignin and non-selectively with cellulose. Thus hypochlorous acid is called to be produced in-situ.

Chlorate formation is unfavorable not only because it is a well-known herbicide and biocide (the discharge of chlorate has already been regulated<sup>1)</sup>, but also because it cannot react with lignin in the full bleaching pH range. Chlorate formation corresponds to a big amount (around 20-36%) of the total  $\text{ClO}_2$  charge<sup>2)</sup>. Thus it is important to understand the mechanism of chlorate formation fundamentally in order to improve the bleaching efficiency and environmental friendliness.

The formation of the chlorate, as well as other chlorine species, is very dependent on pH conditions. Although some papers<sup>2-5)</sup> reported that chlorate formation increased with the increasing of bleaching pH, the result was found only in some special cases, e.g., large amount of chlorine was used together with chlorine dioxide, low/high dual pH is carried out, and buffer solution was used to control the pH. When pure  $\text{ClO}_2$  or  $\text{ClO}_2$  solution containing small amount of chlorine was used in chlorine dioxide delignification and bleaching, chlorate formation decreased with the increase of bleaching pH<sup>6-12)</sup>.

Researchers have suggested various kinds of reaction mechanisms and

pathways<sup>6, 11,13-15)</sup> to support their results, a recent one by Ni Y. *et al*<sup>14)</sup> seemed to be most convincing. It stated that chlorate is mainly formed by the following reaction (1)



However, it is a pity that in their research no detailed information describing the above reaction was available, and the explanation on why chlorate decreased with increasing pH was not sufficient. Thus our work aimed to elucidate the mechanism of chlorate formation more clearly.

## 2. EXPERIMENTAL

### 2.1 Materials

Pure ClO<sub>2</sub> solution was prepared by stripping a crude one with N<sub>2</sub> gas and re-dissolving the ClO<sub>2</sub> gas into chilled water. The concentration of ClO<sub>2</sub> turned out to be 1.04g/L with undetectable chlorine. Here the crude ClO<sub>2</sub> solution was prepared by adding chlorine solution into acidic sodium chlorite solution.

Oxygen delignified Kraft pulp produced by DongHae Pulp Co. Ltd., Korea, was used in this study. Its kappa number was 10.7 and brightness was 41.0% ISO. Bleaching was carried out in sealed polyethylene bags. The D<sub>0</sub> stage bleaching conditions were: pulp consistency 3%, kappa factor 0.20, temperature 60°C, reaction time 60min. Various portions of 0.05M H<sub>2</sub>SO<sub>4</sub> or 0.1M NaOH were premixed into pulp slurry so that at the end of bleaching, certain ranges of end pHs could be attained. In case DMSO was used as HClO scavenger, it was also mixed with pulp slurry before ClO<sub>2</sub> charge.

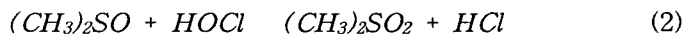
### 2.2 Ion analysis

The amount of chlorite and chlorate was determined with a DIONEX DX-500 ion chromatographer. An aliquot amount of sample was ultra-filtrated by 0.20μm membrane filter, injected into a 50μl loop, eluted with 1.8mM/1.7mM Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> solution through an AG9-GC 4mm guard column, an AS9-SC

4mm separate column and an AMMS-II 4mm suppress column at the flow rate of 2.0ml/min, and finally the ions were detected by a conductivity detector.

### 2.3 Hypochlorous acid analysis

The in-situ produced HClO was captured by DMSO according to reaction (2). The content of HOCl was the same as that of methylsulfone which was analyzed by HPLC. The HPLC system was consisted of Waters 600S Controller; Waters 616 Pump, Waters 2140 RI detector and Autochro Data Module made by Youglin Scientific Co, Ltd, Korea. The RI detector was used at sensitivity 1024, scale factor 20, filter 1, internal oven temperature 30°C, and external oven temperature 35 °C. The column used was NovaPack C18 (60Å, 4µm, 3.9×300mm). Pure water was used as eluent and the flow rate was 1.0 ml/min.



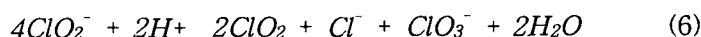
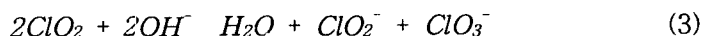
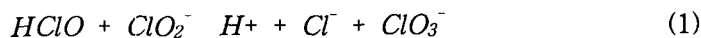
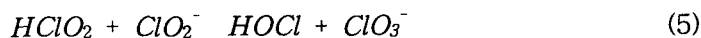
## 3. RESULTS AND DISCUSSION

It is known that when pure ClO<sub>2</sub> or ClO<sub>2</sub> solution containing small amount of chlorine is used in chlorine dioxide delignification and bleaching, chlorate formation decreases with increasing bleaching pH while chlorite formation increases with increasing pH<sup>6-12</sup>.

One thing can be ascertained from the above result is that the decomposition of chlorine dioxide, reaction (3), can not be the main reason of chlorite and chlorate formation, or else both chlorate and chlorite would increase with increasing pH and almost same mole ratio of chlorite to chlorate would be observed. Ni Y. *et al.* also concluded this by a different method<sup>14</sup> where full bleached pulp was used. Germgård *et al.*<sup>6</sup> concluded that the disproportion reaction only account for 2% of the total chlorate formation during ClO<sub>2</sub> bleaching.



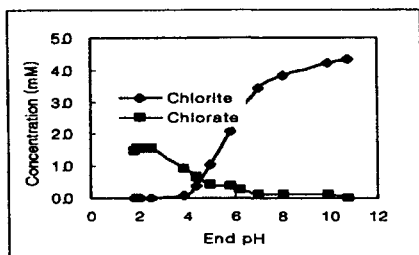
Rapson *et al.*<sup>7)</sup> tried to explain that during delignification and bleaching, the main reason for chlorate formation was due to the acidic decomposition of chlorous acid according to reaction (4) and (5). While this seemed to be able to explain the fact that chlorate formation decreases with increasing pH since according to reaction (4) and (5), at lower pH, the concentration of HClO<sub>2</sub> is higher, and chlorate formation is speeded up; as pH is increased, HClO<sub>2</sub> is accumulated into un-reactive chlorite, slowing up reactions (4) and (5), and chlorate formation is decreased. However, this explanation was proved to be incorrect by Ni. Y<sup>14)</sup> and Germgård's<sup>6)</sup> works that chlorate formation from the decomposition of HClO<sub>2</sub> only contributes to a very small portion of the total chlorate formation during delignification and bleaching.



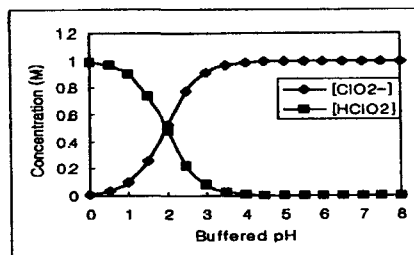
Ni Y. *et al.*<sup>14)</sup> investigated the mechanism of chlorate formation considering reactions (1), (3) and (6) which had been reported to be the most possible source of chlorate formation<sup>16)</sup>. They stated that in chlorine dioxide delignification and bleaching, reaction (1) is the main reason for the chlorate formation, while the other two reactions, (3) and (6), are negligible. Ni Y. *et al.* explained that in chlorine dioxide bleaching, an increasing amount of chlorite remains with increasing pH is the reason for the phenomenon that chlorate decreases with increasing pH; if all the chlorite had been consumed, then the chlorate formation would have been higher with increasing pH.

However, that HClO favors the formation of chlorate while Cl<sub>2</sub> favors the regeneration of chlorine dioxide is a well-accepted mechanism suggested by Taube and Dodgen.<sup>17)</sup> and later modified by Emmemegger and Gorden<sup>18)</sup>. According to this

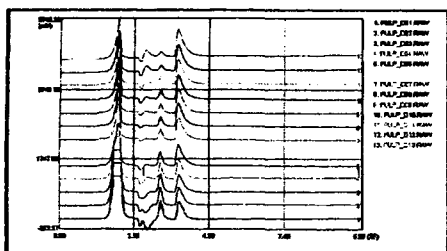
mechanism (hereafter called Taube-Dodgen-Emmemegger-Gordens mechanism), increasing the acidity will convert more in-situ produced hypochlorous acid into molecular chlorine (reaction 7), thus regeneration of chlorine dioxide (reaction 8) is favored over the formation of chlorate (reaction 1). This means that increasing pH should increase chlorate formation, which is contrary to the result that chlorate formation decreases with increasing pH. Apparently till now the understanding on chlorate formation has not been sufficient.



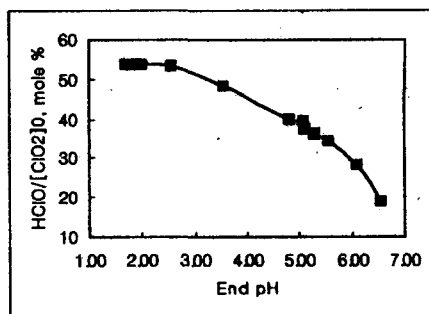
**Fig. 1.** Effect of pH on  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$  formation in  $\text{ClO}_2$  prebleaching of oxygen delignified kraft pulp (kappa no. 10.7, kappa factor 0.20, pulp consistency 3.5%, 60°C, 60 min)



**Fig. 2.** Behavior of chlorite and chlorous acid concentrations according to pH (Start  $[\text{HClO}_2]=1 \text{ M}$ , 25°C.



**Fig. 4.** HPLC chromatograms of bleaching effluents produced from  $\text{ClO}_2$  prebleaching of oxygen delignified kraft pulp (kappa no. 10.7, kappa factor 0.20, pulp consistency 3.5%, DMSO is 1.5 folds of  $\text{ClO}_2$  charge on mole ratio, end pH values were 1.69, 1.81, 2.00, 2.57, 3.56, 4.80, 5.07, 5.10, 5.28, 5.40, 5.56, 6.10, 6.55, for curves 1-13 in the figure). Peaks at retention time 3.36 and 3.97 minutes were DMSO<sub>2</sub> and DMSO respectively.



**Fig. 5.** Effect of pH on the content of in-situ produced HClO in  $\text{ClO}_2$  prebleaching of oxygen delignified kraft pulp. Conditions same as those in Fig. 4.

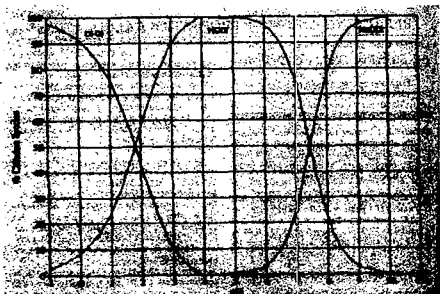
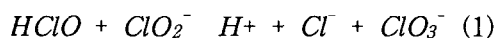
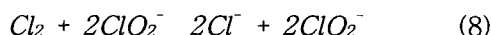
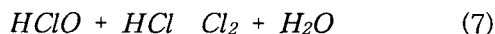


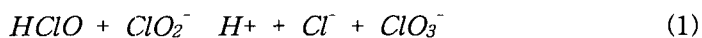
Fig. 3. Chlorine species as a function of pH in saturated chlorine water (0.05 M  $\text{Cl}_2$ ) at 25°C.



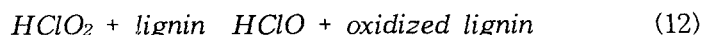
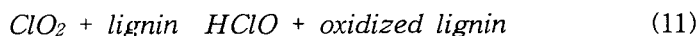
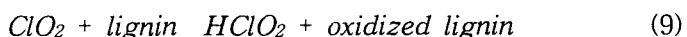
#### 4. Our Understanding and Explanation

In this study the bleaching experiments according to pH variations were repeated, but the pulp used was an oxygen-delignified kraft pulp (kappa number 10.7) instead of conventional kraft pulps (kappa number much higher) used in literature<sup>6-12</sup>. Our result in Fig. 1 showed that chlorate formation decreased with increasing end pH. However, different to the cases of conventional kraft pulp, at the lower part of pH, there was a small peak of maximum chlorate formation at around pH 2.5.

First of all, our explanation is based on the belief that chlorate is mainly formed through the reaction of hypochlorous acid with chlorite as reaction 1 shows.



During bleaching it can be thought that reaction (9) and (10) are mainly responsible for the generation of  $\text{HClO}_2$  ( $\text{ClO}_2^-$ ) and reaction (11) and (12) are mainly responsible for the generation of  $\text{HClO}^{21}$ .



To understand reaction (1) better, it is necessary to study the behaviors of  $\text{HClO}_2$  ( $\text{ClO}_2^-$ ) and  $\text{HClO}$  according to pH conditions.

Fig 2 shows the behavior of  $\text{HClO}_2$  and  $\text{ClO}_2^-$  according to pH variations. Above pH 4, almost all of the chlorous acid is dissociated into chlorite. Under lower pH, say pH 2-4, sufficient chlorite would be available for the reaction (1). Even under very low pH, say under pH 2, because  $\text{HClO}_2$  is a medium strong acid, still enough chlorite can be produced from reaction 10. This indicates to say, chlorite is available for chlorate formation in the whole pH range.

As to hypochlorous acid, Fig. 3 shows the well-known fact<sup>19-20</sup> that in water solution,  $\text{HOCl}$  arises to its maximum concentration at about pH 4, it shifts to the formation of chlorine when the pH is less than 4 and to the formation of hypochlorite when the pH is higher than 4.

$\text{ClO}^-$  is inactive to react with chlorite to form chlorate<sup>15,22</sup>. Thus it can be clearly seen that when the pH is increased from 4 to the higher end, the  $\text{HClO}$  decreases into inactive  $\text{ClO}^-$ , thus the chlorate formation will decrease. Another self-evident fact is that at high pH, less  $\text{HClO}$  will be produced from reaction (11) and (12) which also indicates that chlorate formation will decrease with increasing pH.

Now, lets considering the acidic side, that is, pH less than 4. In this pH range, when the acidity is decreased, hypochlorous acid is gradually changed into chlorine. According to the Taube-Dodgen-Emmenegger-Gordons mechanism<sup>16,17</sup>,  $\text{Cl}_2$  favors chlorine dioxide regeneration while hypochlorous acid favors the formation of chlorate (see reaction 1 and 8). This is to say, lowering the pH should also decrease the formation of chlorate. This is apparently opposite to the experiment results reported in literature<sup>6-12</sup>, however, it seems to be in consistency with the lower pH side in Fig. 1.

To explain more clearly, first from Fig. 2 it can be seen that lowering the pH from 4 to acidic end increases the concentration of  $\text{HClO}_2$  greatly. Thus after  $\text{HClO}_2$  reacts with lignin according to reaction 12, more  $\text{HClO}$  will be produced. This is

equal to mean that HClO produced in-situ increases with decreasing pH in bleaching. Although a part of the in-situ produced HClO will be converted into Cl<sub>2</sub>, higher concentration of HClO evidently increases the formation of chlorate.

That the in-situ produced HClO increases with decreasing end pH is clearly seen in Fig 4 where the formation of DMSO<sub>2</sub> decreases with increasing end pH while DMSO increases with increasing pH. The contents of in-situ produced HClO according to pH were calculated and shown in Fig. 5.

Thus, when the pH is lowered from 4 to the more acidic pH side, the Emmenegger and Gordons mechanism predicates that chlorate formation will decrease, but the higher HClO<sub>2</sub> leads to higher in-situ produced HClO which improves the formation of chlorate, the net work seems that the Emmenegger and Gordons effect is a little more stronger than the higher HClO effect, because from Fig. 1 one can see there is a small peak of chlorate formation at the end pH 2.5.

## 5. CONCLUSION

In this study chlorine dioxide bleaching of an oxygen prebleached kraft pulp was carried out and it was found that chlorate formation increased slightly when the bleaching end pH is increased from 1.8 to 2.5 but decreased greatly when the pH continued to increase.

A theoretical discussion on the behaviors of HClO, Cl<sub>2</sub>, ClO<sup>-</sup>, HClO<sub>2</sub> and ClO<sub>2</sub><sup>-</sup> according to pH variation shows that chlorite is available throughout the whole pH ranges, while hypochlorous acid analysis by DMSO scavenging and HPLC detection shows that the in-situ formation of hypochlorous acid decreases with the increasing pH. This gives strong support that chlorate is mainly formed through the reaction of in-situ produced hypochlorous acid with chlorite. However, as predicated by the Taube-Dodgen-Emmenegger-Gordons mechanism, chlorine favors the regeneration of chlorine dioxide while HClO favors chlorate formation, thus lowering the pH from 4 to the acidic end should decrease chlorate formation. These two opposite effects led to the maximum formation of chlorate at around end pH 2.5.



The study suggested that a better understanding of chlorate formation should combine the mechanism of hypochlorous acid-chlorite reaction with that of Taube-Dodgen-Emmenegger-Gordens.

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