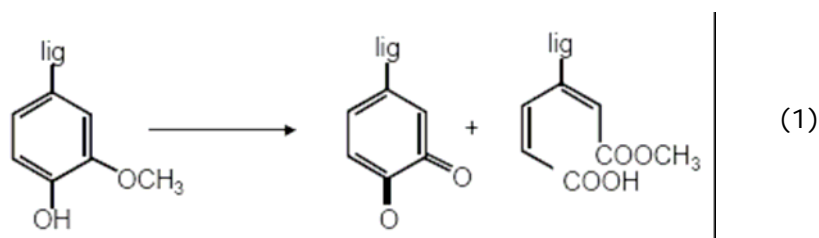


## Reactions of chlorine dioxide with pulp

Chlorine dioxide reacts predominantly with free phenolic structures in lignin. The primary reaction mechanism leads to oxidation of the aromatic rings with subsequent formation of quinones (1<sup>st</sup> product of reaction) and hydrophilic muconic acids (2<sup>nd</sup> product of reaction) as shown in Figure 1.



**Figure 1 Reaction of softwood lignin with chlorine dioxide**

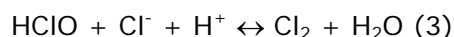
Source: [NCASI, 2002].

The reaction of ClO<sub>2</sub> with lignin (reaction 1) leads to the formation of chlorous acid (HClO<sub>2</sub>), which very rapidly establishes equilibrium with its dissociation products, chlorite ion and hydrogen ion:



This equilibrium is pH-dependent. The higher the pH (i.e. lower concentration of H<sup>+</sup>), the more HClO<sub>2</sub> is dissociated, and viceversa.

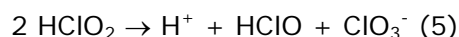
Chlorite ion is unreactive toward lignin, but HClO<sub>2</sub> is very reactive. It oxidises lignin and is thereby reduced to hypochlorous acid (HClO) which in the presence of chloride ion (Cl<sup>-</sup>) enters into the following pH-dependent equilibrium:



In the absence of Cl<sup>-</sup>, HClO reacts with HClO<sub>2</sub> to form ClO<sub>2</sub> and hydrochloric acid (HCl):



Simultaneously HClO<sub>2</sub> reacts with itself to form chlorate, HClO and H<sup>+</sup>:



The HClO from reaction (5) is then available to form ClO<sub>2</sub> by reaction (4), which is then available to react with lignin to form more HClO<sub>2</sub> by reaction (1).

Moreover, ClO<sub>2</sub> reacts with hydroxyl ions in water to form chlorate and chlorite ions:



Eventually, ClO<sub>2</sub> is converted to chlorate, chlorite and chloride, the proportions of which are highly dependent on the pH of the solution and the lignin concentration in pulp [TAPPI Press, 1979].

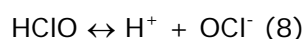
## The chlorine-water system

When  $\text{Cl}_2$  dissolves in water, it undergoes a reversible hydrolysis, in which both  $\text{HClO}$  and  $\text{HCl}$  are formed:



This is the equilibrium shown as reaction (3) in the previous section.

Hydrochloric acid ( $\text{HCl}$ ) is completely dissociated in dilute aqueous solutions for all practical considerations, whereas at the pH of  $\text{Cl}_2$  water,  $\text{HClO}$  is dissociated only slightly according to the equilibrium:

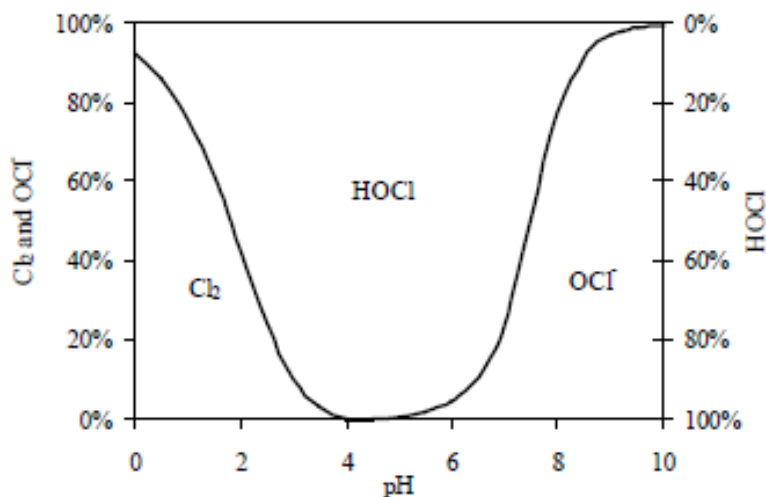


Because these reactions are equilibrium processes, the composition of the  $\text{Cl}_2$ -water system is sensitive to process variables which cause displacement of the equilibria in one direction or the other.

For example:

- Higher dilution (more  $\text{H}_2\text{O}$ ) causes a shift of reaction (7) to the right (forward direction), increasing the concentrations of  $\text{HCl}$  and  $\text{HClO}$ .
- Higher temperature also causes a shift of reaction (7) to the right.
- Higher pH causes first  $\text{HClO}$  and then hypochlorite ion ( $\text{OCl}^-$ ) to become the dominant chlorine species.
- Lower pH causes a shift to the left (reverse direction) of both reactions and  $\text{Cl}_2$  becomes the dominant species. An example of this effect is the addition of  $\text{HCl}$  in the absorber/ stripper of a low- $\text{Cl}_2$  integrated  $\text{ClO}_2$  plant aimed at generating a  $\text{ClO}_2$  solution with low contamination of  $\text{Cl}_2$  (see Section 2.10.1.1 – “Integrated chlorine dioxide plants” in the report).

The most important method of controlling the composition of the  $\text{Cl}_2$ -water system is by adjustment of pH. The pH-controlled changes in composition are illustrated in Figure 2.



## Figure 2 Chlorine species as a function of pH for saturated chlorine solution (0.05M Cl<sub>2</sub>) at 25°C

Source: [Dence, 1996].

When the pH is between 2 and 7.5, the equilibrium is in favour of HClO. As the pH falls below 2, Cl<sub>2</sub> is the dominant species. At a pH of 7.5, HClO and OCl<sup>-</sup> are about equal, and as the pH goes above 7.5, increasing proportions of OCl<sup>-</sup> are present.

Modern D stages typically operate at a pH range of 3 to 4 and a temperature range of 60 to 80°C, hence, the dominant species is HClO and any Cl<sub>2</sub> that may be formed from ClO<sub>2</sub> when it reacts with pulp or may be present in the ClO<sub>2</sub> solution<sup>1</sup> is converted to HClO.

## Chlorinated organic compounds

Hypochlorous acid generates small amounts of substituted chlorinated organic compounds and chloroform when reacting with lignin.

With a combination of modified cooking, oxygen delignification and bleaching with ClO<sub>2</sub> as the only chlorine-containing chemical, the formation of chlorinated organic substances is low [Beca AMEC, 2004]:

- The content of AOX in bleach plant effluents from ECF bleaching is usually in the range 0.2-1.0 kg/ADt.
- The content of OX in ECF bleached pulp is usually in the range 30-120 g/ADt.

## Dioxins and furans

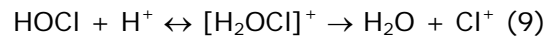
Electrophilic substitution reactions that form PCDD and PCDF from their precursors require positively-charged chlorine species such as chloronium ion, Cl<sup>+</sup> [Berry, 1989].

Both Cl<sub>2</sub> and HClO can function as electrophiles, although HClO does so to a much lesser degree than Cl<sub>2</sub> [NCASI, 2002].

The initial reacting electrophile is Cl<sup>+</sup>, formed from Cl<sub>2</sub> by cleavage of the Cl-Cl bond and from HClO by cleavage of the O-Cl bond in its conjugate acid [Dence, 1996], as shown in reaction (9).

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<sup>1</sup> Depending on the generation method used, up to 0.22 kg Cl<sub>2</sub>/kg ClO<sub>2</sub> may be present in the chlorine dioxide solution, corresponding to a substitution of 91.6%.



Chlorination of lignin and PCDD and PCDF precursors follows the mechanistic principles of electrophilic aromatic substitution, and thus proceeds in a stepwise manner. The initial chlorine substitution on an aromatic structure may occur readily, but the introduction of the second and subsequent chlorine atoms is more difficult because the aromatic ring is deactivated by an order of magnitude with each successive chlorine substitution [Ni, 1995]. Thus, formation of highly chlorinated PCDD and PCDF by electrophilic substitution is not thermodynamically favored [NCASI, 2002].

Because of the above, the probability of formation of PCDD and PCDF in ECF bleaching is extremely low, as demonstrated by the following excerpts from UNEP documents:

“Increasing the ClO<sub>2</sub> substitution decreases the formation of chlorinated aromatic substances and eliminates the formation of PCDD/PCDF” [UNEP PCDD & PCDF, 2005].

“When the ClO<sub>2</sub> substitution level is higher than 85%<sup>2</sup> in Cl<sub>2</sub> bleaching, or if ECF bleaching<sup>3</sup> is used, emissions of 2,3,7,8-TCDD and 2,3,7,8-TCDF to water are lower than the limit of quantitation (US EPA Method 1613<sup>4</sup>)” [UNEP, 2006].

In spite of this, highly chlorinated congeners do sometimes appear in bleached pulps and filtrates. The presence of significant amounts of hexa- and hepta-chlorinated CDD at some Canadian west coast mills was attributed to the use of sawmill chips made from polychlorinated phenol-treated wood as a furnish in kraft pulping [Luthe, 1993]. In these mills, the PCDD were formed in the pulping process, not in the bleach plant. Another study showed that highly chlorinated dioxins, especially octachlorodibenzo-p-dioxin (OCDD), are found in common, everyday materials and in all of the 19 unbleached pulp samples that were tested [Berry, 1993]. Filter media from house furnaces and car air intakes had the highest levels, suggesting that these compounds are widely dispersed in inhabited areas. Testing of soils in the State of Washington revealed the presence of dioxins even in remote wilderness areas (WDOE 1998). It is known that PCDD and PCDF are emitted as a consequence of combusting a wide variety of materials including fossil fuels, wood, and municipal solid wastes [Thomas, 1994], so their broad distribution in the environment is not surprising. The ubiquitous presence of these compounds could explain their detection in bleached pulp and filtrate samples through contamination of the raw materials and/or product samples [NCASI, 2002].

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<sup>2</sup> This corresponds to a ratio of 0.395 kg Cl<sub>2</sub>/kg ClO<sub>2</sub>.

<sup>3</sup> In this case the ClO<sub>2</sub> substitution level depends on the “purity” of the ClO<sub>2</sub> solution. The methanol- and peroxide-based ClO<sub>2</sub> processes (AMT) can produce a ClO<sub>2</sub> solution containing 0.02 kg Cl<sub>2</sub>/kg ClO<sub>2</sub>, equivalent to 99.2% substitution. It is claimed that the low-Cl<sub>2</sub> integrated dioxide process (an emerging technology) is able to produce a ClO<sub>2</sub> solution of the same purity.

<sup>4</sup> US EPA Method 1613 for Analysis of Dioxins and Furans in Wastewater, which has a minimum level of 10 pg/L for 2,3,7,8-TCDD and 2,3,7,8-TCDF.