Chlorine dioxide bleaching

Chlorine dioxide as a bleaching agent

- $\text{ClO}_2$ is a radical bleaching agent
- $\text{ClO}_2$ is manufactured by several methods:
  - Mathiesson process
  - R3/SPV generator
  - Etc.
- $\text{ClO}_2$ is an unstable gas and therefore it must be stored in solution.
  - 7-10 g/l solution water
- Less AOX load than in chlorine bleaching, although there is chlorine present also in chlorine dioxide bleaching.

Process conditions:

- pH
  - Pre-bleaching stage pH 3-4
  - Non-phenolic lignin
  - Final bleaching stage pH 9-10
  - Phenolic lignin
- Temperature
  - (40-85 °C, often 70 °C)
- Time
  - (Long reaction time, 3-5 hours)
- Dosage
- Consistency

Chemistry of chlorine dioxide bleaching is complex since due to the reduction there are several intermediates present during the process:

- Chlorate $\text{ClO}_3^-$ (+5)
- Chlorine dioxide $\text{ClO}_2$ (+4)
- Chlorite $\text{ClO}_2^-$ (+3)
- Hypochlorous acid $\text{HClO}$ (+1)
- Chlorine $\text{Cl}_2$ (0)
- Chloride $\text{Cl}^-$ (-1)
Reactions with wood compounds

I Lignin
- Reacts with phenolic and non-phenolic lignin structures
II Carbohydrates
- Not particularly reactive with carbohydrates
III Hexenuronic acid groups
IV Extractives
- Reacts and removes wood extractives especially during the pre-bleaching (low pH)

Reactions with lignin

- As chlorine dioxide oxidizes lignin it is reduced to chlorite. Depending on pH chlorite (ClO$_2^-$) is partly converted to chlorous acid (HClO$_2$) (pK$_1$~2).

\[ K_1 = \frac{[\text{ClO}_2^-][\text{H}_3\text{O}^+]}{[\text{HClO}_2]} \]

Conversion of chlorite ion to chlorine and hypochlorous acid

\[
\begin{align*}
\text{Log Reaction rate) } \\
\text{Low pH} & \quad \text{High pH} \\
\text{HClO}_2 & \quad \text{ClO}_2 \\
\downarrow & \quad \downarrow \\
\text{Cl}_2 & \quad \text{HClO} \\
\end{align*}
\]

ClO$_2$ and lignin

- ClO$_2$ reacts readily with non-phenolic lignin structures.
- Chlorine dioxide reacts even more easily with phenolic lignin and ionized lignin structures.
- Neither chlorite nor chlorous acid are reactive toward lignin.

\[
\frac{d[\text{ClO}_2]}{dt} = -k_1[\text{Lign}_{\text{non-phenolic}}] - (k_2 + k_3K_2[H_3O^+]) \cdot \frac{[\text{Lign}_{\text{phenolic}}]}{1 + K_2[H_3O^+]}
\]
Reactions with lignin

ClO$_2$ and lignin

- In acidic conditions chlorite is decomposed via formation of chlorous acid. Reaction is partly catalyzed by chloride ions.

\[
\frac{d[\text{ClO}_2]}{dt} = -k_1[\text{HClO}_2]^2 - k_2[\text{HClO}_2][\text{Cl}^-]
\]  

(1)

- The reaction is followed by several other reactions

Formation hypochlorous acid, chlorine dioxide, chlorate, chloride, etc. Hypochlorous acid is in balance with hypochlorite (pK4 ~ 7.5) and chlorine.

ClO$_2$ and lignin

- Both electrophiles (HOCl, Cl$_2$) and nucleophiles (ClO$^-$) are formed during the chlorine dioxide bleaching stages.

- The final pH of D$_0$ stage is typically 2-3 and ClO$_2$ exists mainly as chlorine. During other D stages the final pH is so high (4-5) that the proportion of chlorine is low.
ClO$_2$ and lignin
Chlorination and hydroxylation

- Reactions of chlorine with lignin lead to chlorination, whereas hypochlorous acid increases the amount of (phenolic) hydroxyl groups in lignin.

ClO$_2$ and HexA

- ClO$_2$ is a very selective lignin oxidant.
- Reactions with carbohydrates are limited.
- Chlorine dioxide is able to react with hexenuronic acid groups of xylan.
- Degradation products of HexA are chlorinated and hydroxylated dicarboxylic acids.
Reactions of hexenuronic acid groups

- Chlorine or chlorous acid reacts first with electrophilic carbon-carbon double bonds.
- Chlorine dioxide does not oxidize hexenuronic acid groups.
- In a normal chlorine dioxide stage both lignin and HexA contents decrease in a same way. If the final pH is above 6, HexA doesn’t react because under these conditions chlorite is not able to degrade into hypochlorous acid and chlorine.

ClO$_2$ and extractives

- Chlorine dioxide reacts with unsaturated lipophilic extractive (i.e. resin) components.
- CIo$_2$ favours oxidation reactions. The reaction products of resin comprise a mixture of oxidized products containing hydroxyl, carboxyl or carbonyl groups.
- The reaction products are more hydrophilic than the original compounds and therefore they are easier to wash out of the pulp.