Chlorine dioxide bleaching

Chlorine dioxide as a bleaching agent

- ClO_2 is a radical bleaching agent
- ClO_2 is manufactured by several methods:
  - Mathiesson process
  - R3/SPV generator
  - Etc.
- 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 ºC, often 70 ºC)
- Time
  - (long reaction time, 3-5 hours)
- Dosage
- Consistency

Chlorine dioxide as a bleaching agent

- ClO_2 is an oxidant and it is reduced during bleaching reactions.
- Chemistry of chlorine dioxide bleaching is complex since due to the reduction there are several intermediates present during the process:

Chlorate	ClO_3^-	(+5)
chlorine dioxide	ClO_2	(+4)
Chlorite	ClO_2^-	(+3)
Hypochlorous acid	HClO	(+1)
Chlorine	Cl_2	(0)
Chloride	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

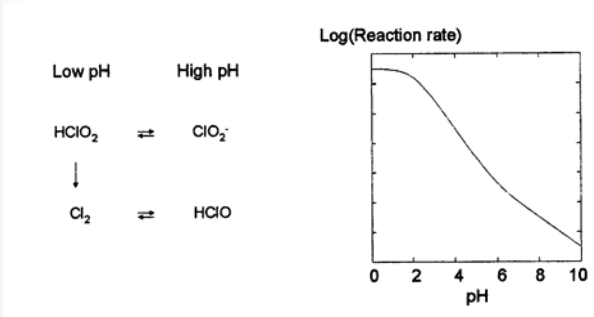
IV Extractives
- Reacts and removes wood extractives especially during the pre-bleaching (low pH)

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).

$$K_1 = \frac{[ClO_2^-]\cdot[H_3O^+]}{[HClO_2]}$$

Conversion of chlorite ion to chlorine and hypochlorous acid

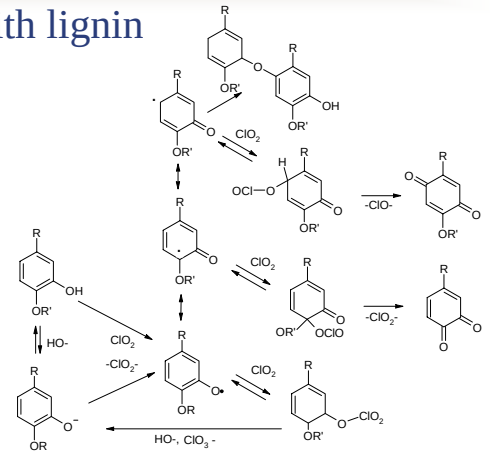


ClO_2 and lignin

- ClO2 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.

$$\frac{d[ClO_2]}{dt} = -k_1[Lign_{non-phenolic}] - (k_2 + k_3K_2/[H_3O^+])\cdot\frac{[Lign_{phenolic}]}{1+K_2/[H_3O^+]}$$

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.

$$\frac{d[ClO_2^-]}{dt} = -k_4[HClO_2]^2 - k_5[HClO_2]\cdot[Cl^-] \quad (1)$$

- 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

$Cl_2 + 2H_2O \leftrightarrows HOCl + H_3O^+ + Cl^-$ (2)

$$K_3 = \frac{[HOCl]\cdot[H_3O^+]\cdot[Cl^-]}{[Cl_2]} \quad (3)$$

$HOCl + H_2O \leftrightarrows ClO^- + H_3O^+$ (4)

$$K_4 = \frac{[ClO^-]\cdot[H_3O^+]}{[HOCl]} \quad (5)$$

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

hypochlorous acid=alikloorihapoke

ClO_2 and lignin
Chlorination and hydroxylation

$$\frac{d[Lign_{Cl}]}{dt} = k_6[Lign]\cdot[Cl_2] \qquad (6)$$

$$\frac{d[Lign_{OH}]}{dt} = k_7[Lign]\cdot[HOCl] \qquad (7)$$

(6)+(7) ⇒

$$\frac{d[Lign_{Cl}]}{d[Lign_{OH}]} = \frac{k_6[Cl_2]}{k_7[HOCl]} \qquad (8)$$

Or also

$$\frac{d[Lign_{Cl}]}{d[Lign_{OH}]} = \frac{k_6[H_3O^+]\cdot[Cl^-]}{k_7 K_3} \qquad (9)$$

ClO_2 and lignin
Chlorination and hydroxylation

- The degree of lignin chlorination is linearly dependent on the hydrogen and chloride ion concentrations
- Increasing chemical dosage increases the amount of chloride present in the chlorine dioxide stage.

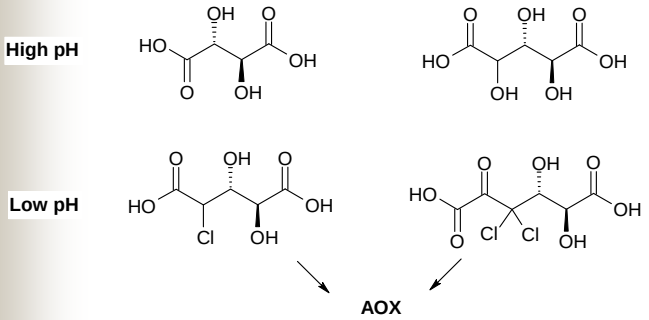
⇒ Degree of chlorination increases.

⇒ AOX load increases

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



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.
- ClO_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.