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 4-8
    - Phenolic lignin
- Temperature
  - (40-85 ºC, often 70 ºC)
- Time
  - (long reaction time, 3-5 hours)
- Dosage
- Consistency

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)

Classification of bleaching agents

RADICALS	ELECTROPHILES	NUCLEOPHILES
O_2	**Cl_2**	HO_2^- (H_2O_2)
ClO_2	**HOCl**	**ClO^-**
	O_3	Peroxyacids
	Peroxyacids	

Reactions involve a transfer of an unpaired electron (i.e radical) and these radicals are oxidants

Reactions involve a transfer of a pair of electrons

- electrophiles accept a pair of electrons (oxidants)
- nucleophiles donate a pair of electrons (reductants)

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 lignin

- ClO_2 reacts slowly with ***non-phenolic lignin*** structures.
- Chlorine dioxide reacts more easily with ***phenolic lignin*** and ***ionized lignin*** structures.

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

ClO_2 and lignin

- As chlorine dioxide oxidizes lignin it is reduced to chlorite.

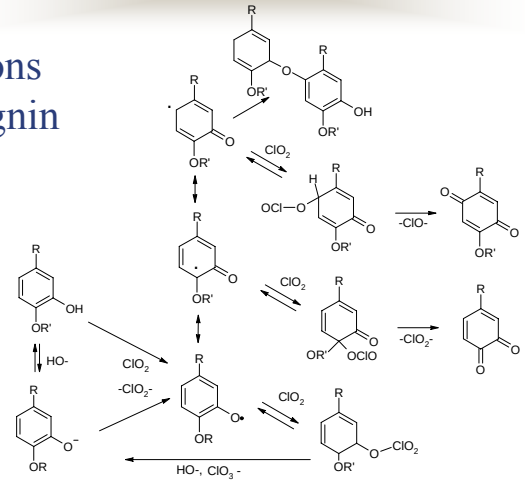
$$ClO_2\cdot + Lign \rightarrow ClO_2^- + Lign\cdot$$

- Depending on pH, chlorite (ClO_2^-) is partly converted to chlorous acid ($HClO_2$) (pK_1~2).

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

- Neither chlorite nor chlorous acid are reactive toward lignin.

Reactions with lignin



ClO_2^- decomposition

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

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

- Maximum rate at pH 2-3
- The reaction is followed by several other reactions

⇒ Formation of hypochlorous acid, chlorine dioxide, chlorate, chloride, etc.

Hypochlorous acid and chlorine

- Hypochlorous acid is in equilibrium with hypochlorite and chlorine.

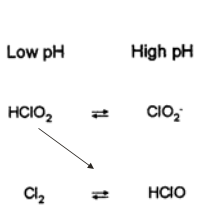
$Cl_2 + 2H_2O \leftrightarrows HOCl + H_3O^+ + Cl^-$ (2) $pK_3 \sim 3.2$

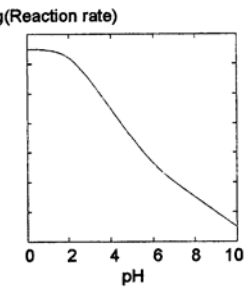
$$K_3 = \frac{[HOCl]\cdot[H_3O^+]\cdot[Cl^-]}{[Cl_2]} \quad (3)$$

$HOCl + H_2O \leftrightarrows ClO^- + H_3O^+$ (4) $pK_4 \sim 7.5$

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

Conversion of chlorite ion to chlorine and hypochlorous acid





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.

Classification of bleaching agents

RADICALS	ELECTROPHILES	NUCLEOPHILES
O_2	**Cl_2**	HO_2^- (H_2O_2)
ClO_2	**HOCl**	**ClO^-**
	O_3	Peroxyacids
	Peroxyacids	

Reactions involve a transfer of an unpaired electron (i.e radical) and these radicals are oxidants

Reactions involve a transfer of a pair of electrons
- electrophiles accept a pair of electrons (oxidants)
- nucleophiles donate a pair of electrons (reductants)

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=aliklоorihapoke

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

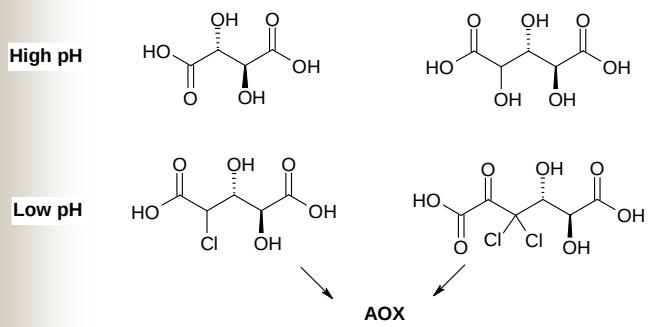
ClO_2 and lignin
Chlorination and hydroxylation

- High final pH → better bleachability
- The degradation of chlorite sets the limit for pH, if the final pH is >5, part of the oxidizing potential remains unused.

ClO_2 and HexA

- ClO_2 is a very selective lignin oxidant.
- Reactions with carbohydrates are limited.
- Hypochlorous acid and chlorine oxidize hexenuronic acid groups of xylan.
- Degradation products of HexA are chlorinated and hydroxylated dicarboxylic acids.

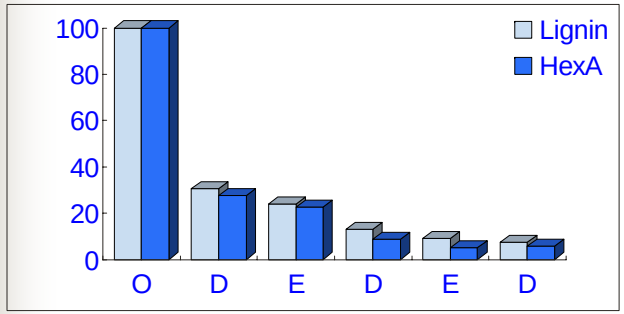
Reactions of hexenuronic acid groups



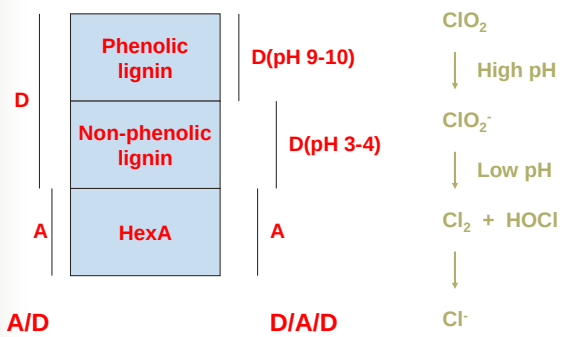
Reactions of hexenuronic acid groups

- Chlorine and hypochlorous acid react 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.

REMOVAL OF LIGNIN AND HEXENURONIC ACID IN AN ECF BLEACHING STAGE



PRINCIPLE OF A/D AND D/A/D PREBLEACHING



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.

Reactions in ClO_2 bleaching