Molybdate activated peroxide delignification

Delignified Pulp

Peroxomolybdate

Molybdate

H₂O₂

H₂O
Reactions of molybdate-activated peroxide with pulp components

- Reaction with lignin components:
- Main reaction mechanisms of peroxomolybdate with lignin involve demethoxylation and the formation of quinoid structures, though the peroxomolybdate is not a strong enough oxidant to facilitate ring rupture in most cases, and both the side-chain in apocynol and the olefinic bonds are attacked.

Proposed reaction of HexA with molybdate-catalyzed peroxide.
Hexene uronic acid

Kraft cooking

Hexene uronic acid contents of oxygen delignified kraft pulps:

- Hardwood 30 - 50% of kappa number
- Softwood 10 - 20% of kappa number
Kappa number vs. HexA content

10 mmol/kg HexA = 1 kappa unit
Hexenuronic Acids: Importance in ECF-Bleaching

- Peroxomolybdate reacts primarily with HexA, but also with lignin.
- ClO₂ reacts first with lignin and secondarily with HexA.
- Oxygen and alkaline peroxide react with lignin, but not with HexA.
- ClO₂ consumption is decreased, if HexA has been removed.
- Lignin is activated, because savings have been observed with even oxygen-based chemicals.
Removal of lignin and HexA in mP and acid hydrolysis stages

Oxygen delignified HW Kraft pulp (Birch), kappa 17
Molybdate-activated peroxide (mP)

- **Reaction conditions**
  - Temperature: 75 - 90°C
  - Reaction time 120-180 minutes
  - Start-pH ~ 5, end-pH 4-4.5
  - Consistency 8-12% (MC)

- **Chemicals**
  - Activator: 0.2-0.4 kg/ADt (as 100% Mo)
  - H₂O₂ -consumption 1-2 kg/kappa/ADt (dosage usually ca 8 kg)
  - Sulfuric acid for pH adjustment
  - Recommended to use some chelating agent if harmful metal ions are abundant (ex. 0.5 kg DTPA, present pH range is suitable)

- **Equipment needed:**
  - A pump and a storage tank for the activator solution
  - Some piping for H₂O₂, acid, SiMo (circulation if needed)
Mill Experiences:

◆ Background:
  – High bleaching costs
  – Bleachability problems with brightness ceiling
  – High cost to campaign TCF ⇔ ECF
◆ Advantages of mP application:
  – Lower bleaching cost (-20% TCF)
  – Higher brightness, lower kappanumber
  – More economic campaigning due to lower kappa and -variation
Reaction conditions:

pH, temperature, time. SW: kappa 14

(180 min, 90°C)

(90°C)

(180 min)
Consumption of peroxide

![Graph showing the consumption of peroxide](image)

**HW**

**SW**

Trend (HW) Slope = 1.3

Trend (SW) Slope = 1.9

H2O2 consumption, kg/ton pulp

Kappa reduction (kappa units)
Bleaching Cost and Advantages

<table>
<thead>
<tr>
<th>Relative bleaching cost*</th>
<th>Reference</th>
<th>mP</th>
<th>Cooking kappa</th>
<th>Oxygen-kappa</th>
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* Normal ECF = 100

**Additional advantages:**
- Increased cooking kappa → increased yield
- Lower final kappa number → Lower PC number (yellowing)
- Lower HexA content → better drainage in drying machine
- Increase in capacity of bleaching plant → higher bleachability / production rate
- Hexa removed → less oxalate → less deposit
- Hexa removal improves also the management of harmful metal ions
Environmental Impact
of Molybdate

Activator solution
Composition (weight-%)

Na$_2$MoO$_4$ 30%
NaOH 5%
Water 60%
Other 5%

Ecotoxicity of sodium molybdate

- **Freshwater fish**
  - Fathead minnow: 7630 mg/l
  - Bluegill: 6790 mg/l
  - Rainbow trout: 7340 mg/l
  - Channel catfish: > 10 000 mg/l

- **Daphnia**
  - LC$_{50}$ (96 h): 3040 mg/l

- **Saltwater species**
  - Mysid scrimp: 3997 mg/l
  - Sheepshead minnow: 6590 mg/l
  - Pink shrimp: 3997 mg/l

- **Mammals**
  - LD$_{50}$ Oral, Rat: 4460 mg/kg
  - No effect level: > 2522 mg/l

- **Activated sludge**
  - No effect level: > 2522 mg/l

- **Anaerobic sludge**
  - No effect level: > 2522 mg/l
If catalysts are used for delignification in a pulp mill, always some catalyst is lost.

The lost catalyst can end up to:

- **Waste water treatment**
  - Biological waste water treatment removes molybdate quite efficiently and thus it is bound to the sludge

- **End product**
  - Mill experiences show that no molybdate is found in bleached pulp

- **Chemical recovery system**
  - Molybdate does not precipitate in evaporation of black liquor
  - It is also quite soluble in green and white liquor and thus the Mo content will increase during continuous use
  - However, Mo has no adverse effects in cooking, etc.