



# General pulp bleaching chemistry

PAPTAC Bleaching Committee Meeting Fall 2014

Shree Prakash Mishra

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# Purpose of pulp bleaching

- Increase Pulp brightness
- Improve brightness stability
- Suitability for end product grades
  - Printing, writing, photo, absorbent, cellulose derivatives
- Improve cleanliness of the pulp (shives, metals and dirt removal)
- Etc.

# Target components

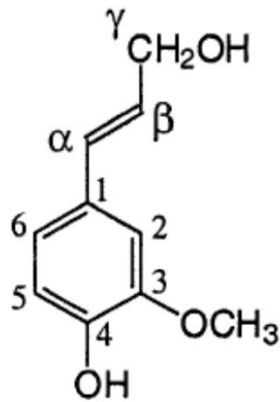
- Residual lignin (3.5-5.5% SW; 1.5-3.0% HW)
- Hexenuronic acids (0.15-0.45% SW and 0.5-0.9% HW equivalent to lignin)
- Extractives (0.1-0.3% SW and 0.5-1.0% HW)
- Shives

# Favorite Components

- Cellulose
  - Hemicellulose (some grades)
- } Naturally white; no need to bleach

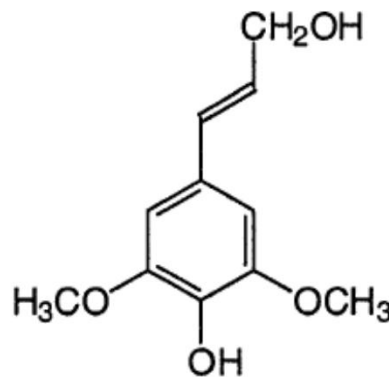
# Lignin

- Basic unit phenyl propane ( total 9 carbons)



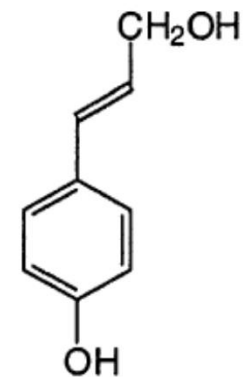
*trans*-Coniferyl alcohol

Predominantly SW; a small amount in HW



*trans*-Sinapyl alcohol

HW

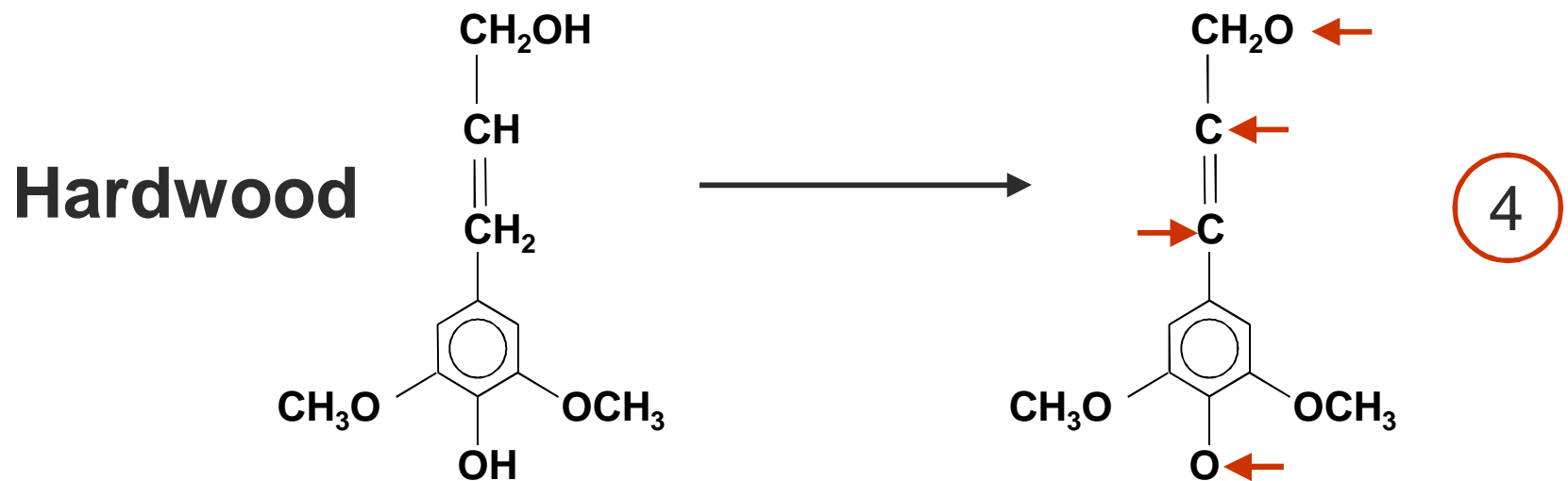
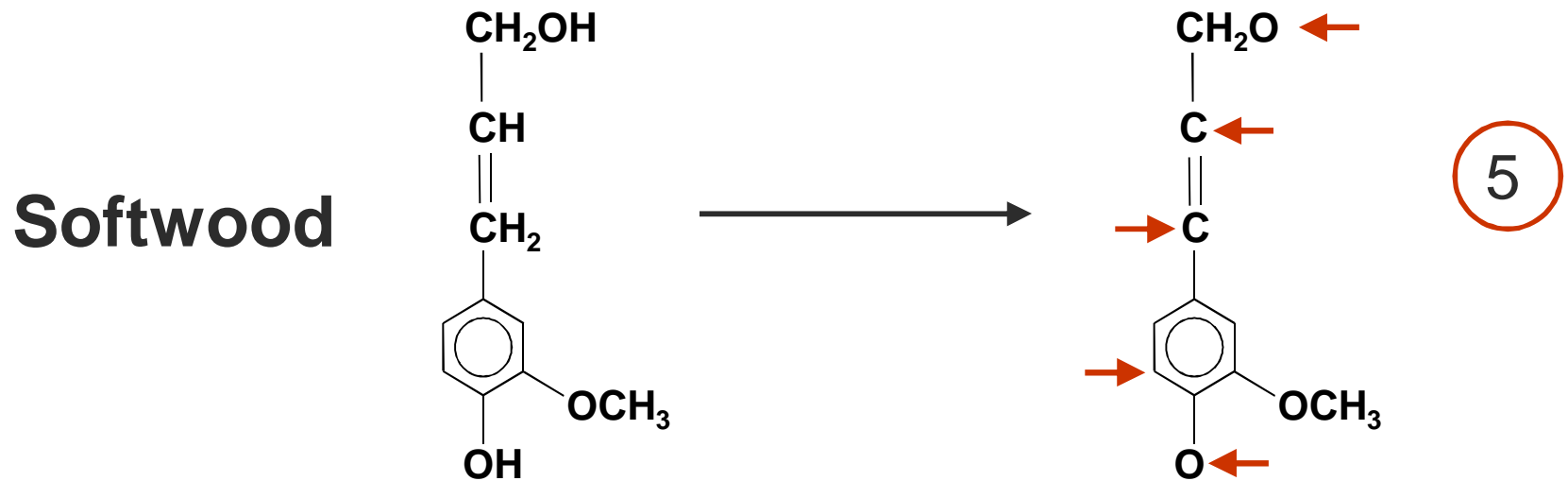


*trans-p*-Coumaryl alcohol

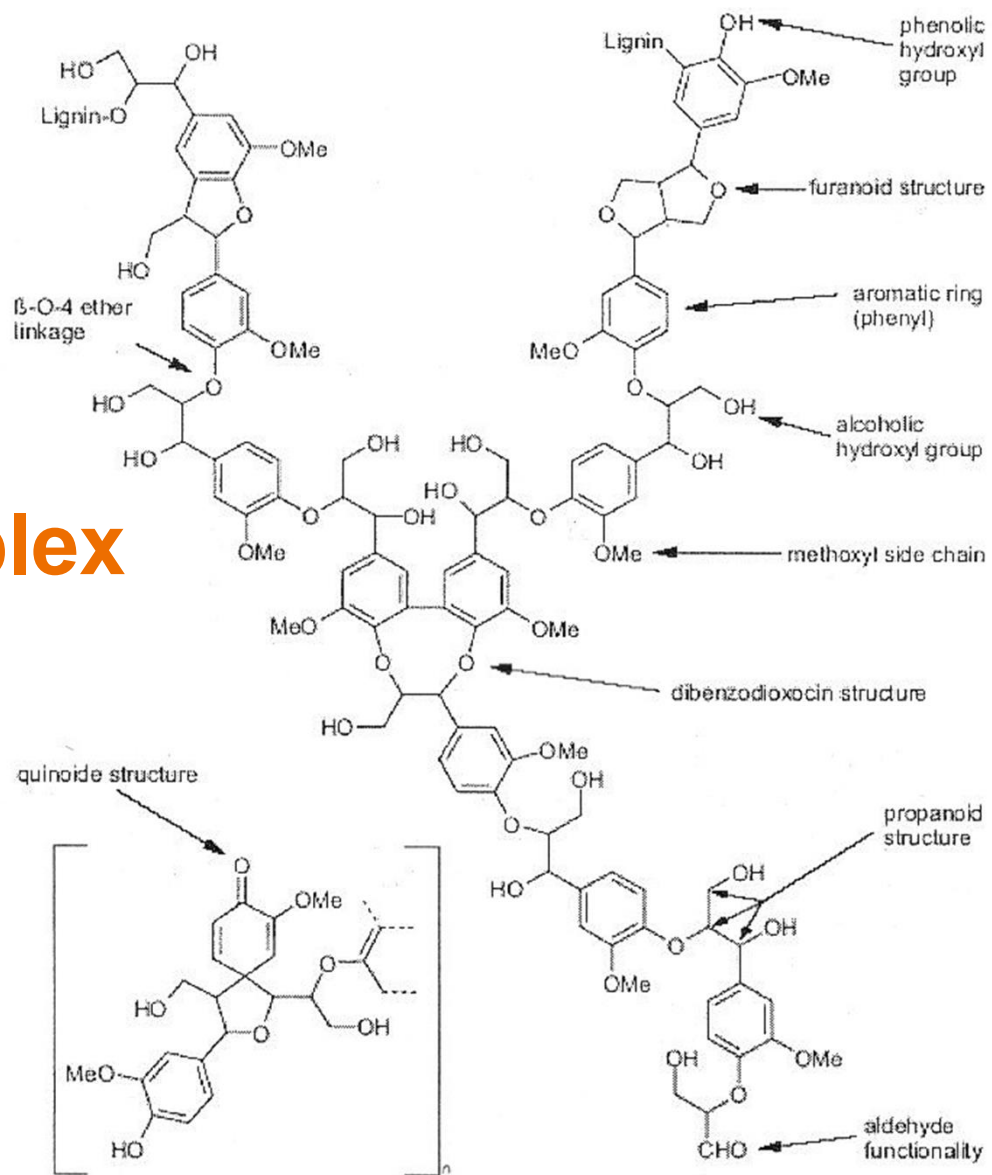
Compression wood

Ref.: Alen, R., In: *Forest products chemistry*, (Stenius, P., ed.), Fapet Oy, Finland Book-3, p.11-57 (2000)

# Softwood vs. Hardwood Lignins



# Lignin is a Complex Macromolecule



Softwood lignin from Brunow et al., 2001

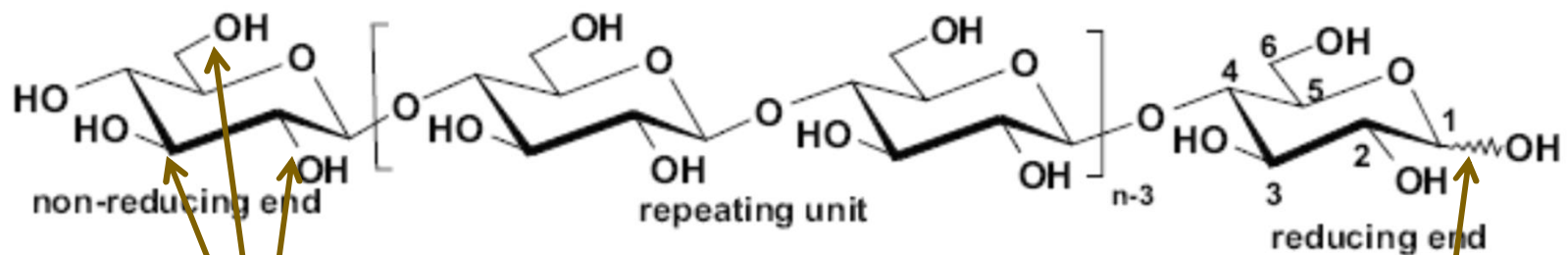
# Phenolic hydroxyl groups in different lignin fractions

Lignin type	OH-groups/100 C9
Wood	13
Residual	27
Dissolved	50-60

Ref.: Gellerstedt, G., and Lindfors, E., *Svensk. Papperstidn.* (1984)

# Cellulose

- Cellulose is a **linear polymer** ( $\beta$ -(1 $\rightarrow$ 4) link)
- DP 10,000 in wood
- DP 1000-2000 in paper making pulps



Site for oxidation;  
carbonyl and  
carboxyl formation

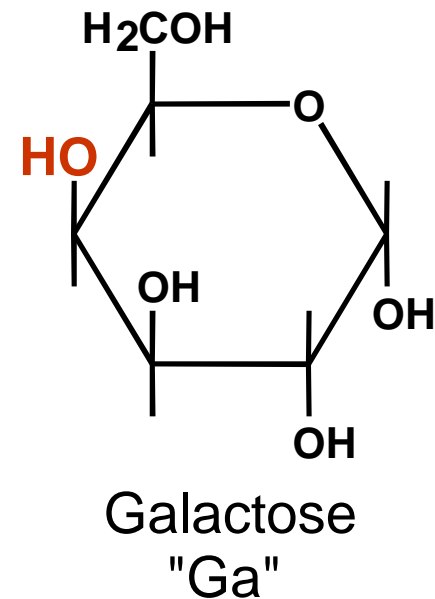
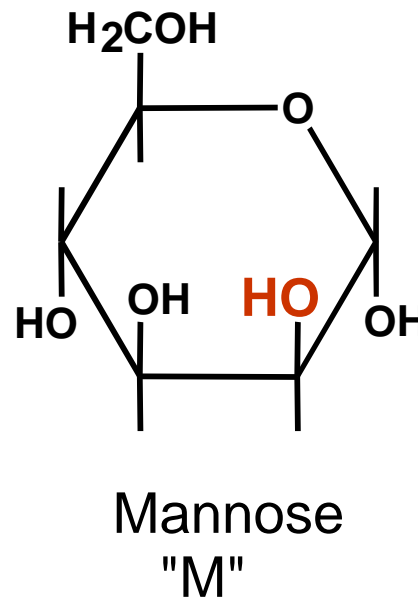
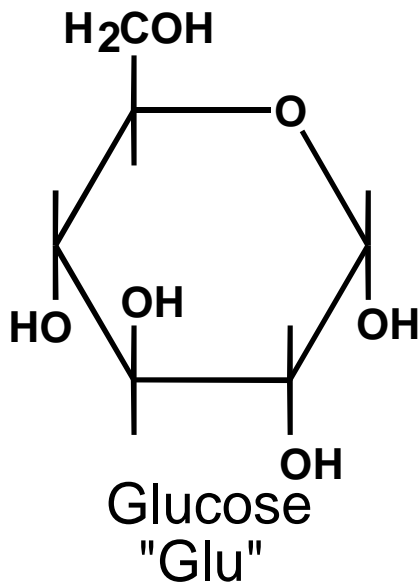
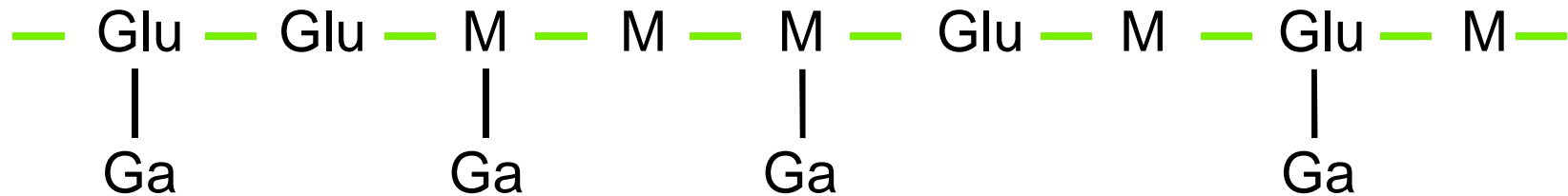
Site for the peeling  
reaction

Ref.: Koch, G., *Handbook of pulp* (Sixta H. ed.), (2006)

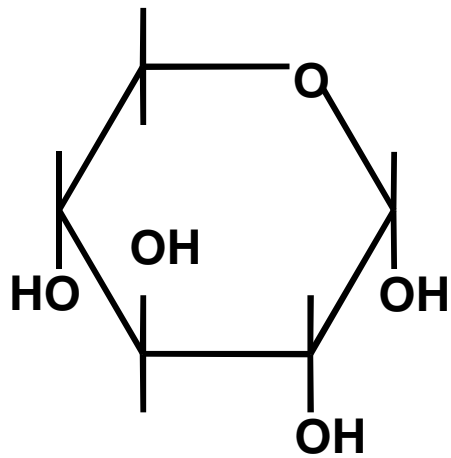
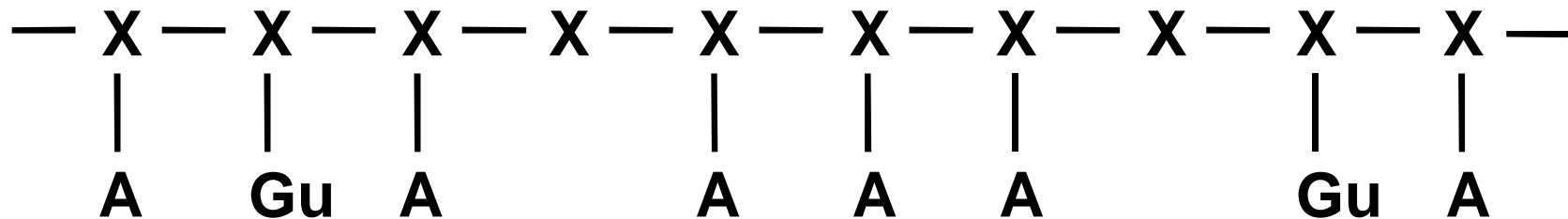
# Hemicelluloses

- Hemicelluloses are chemically and physically different than cellulose :
  - Heteropolymer (different types of sugars)
  - Shorter chain (DP 100-200)
  - Open structure
  - Presence of carboxylic acid groups
  - Presence of acetyl group
  - Generates hexenuronic acid during pulping

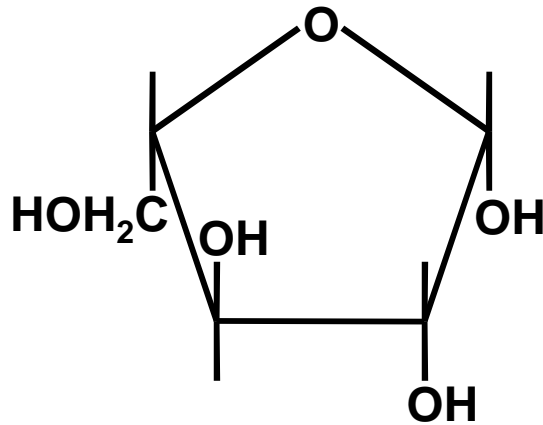
# The Main Hemicellulose in Softwoods: Galactoglucomannan



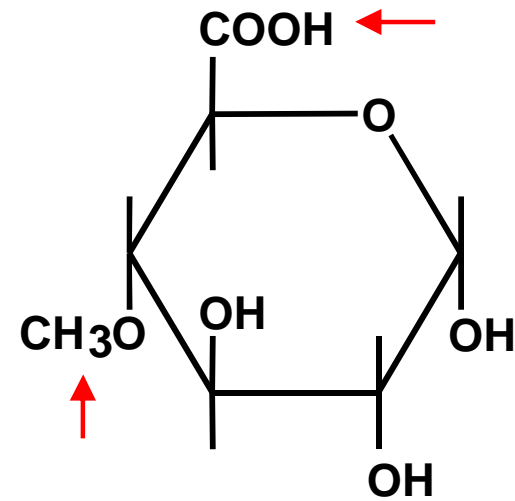
# The Main Hemicellulose in Hardwoods: Xylans



D- xylose  
" X "

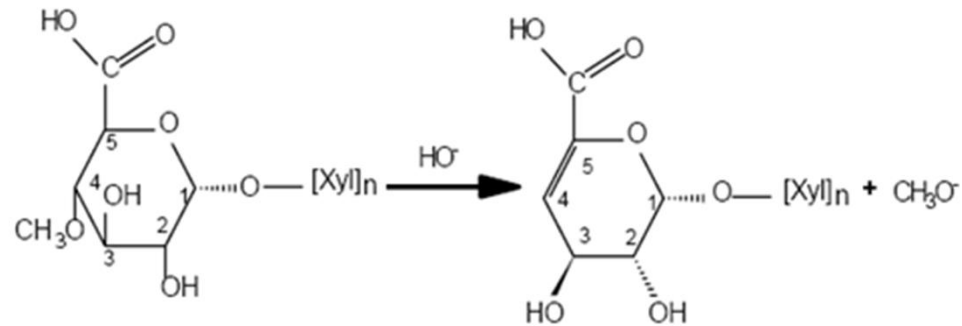


L- arabinose  
" A "



4-O-methyl  
glucuronic acid  
" Gu "

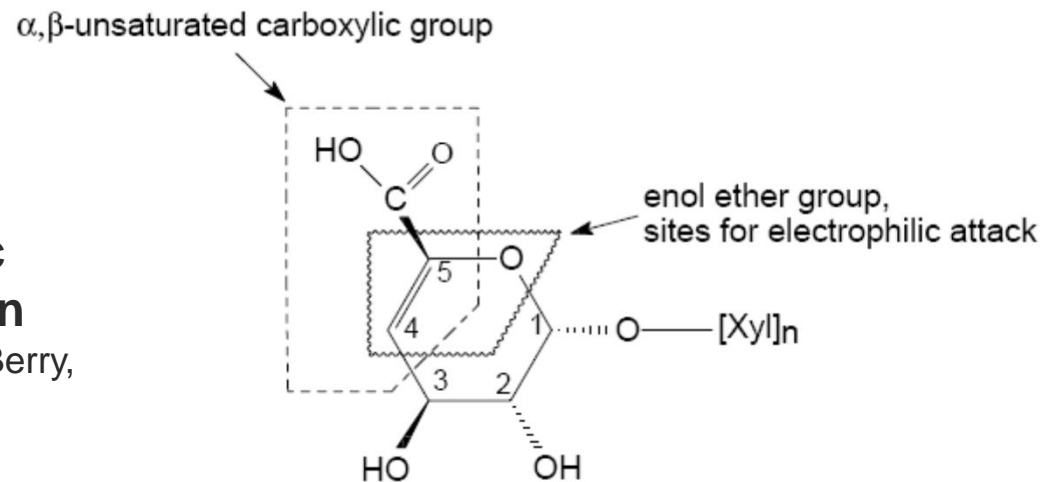
# Hexenuronic acid



**The conversion of 4-O-methylglucuronoxylan to hexenuronoxylan during kraft pulping** (Ref.: Clayton, D.W., *Svensk Papperstidn.*, 66, 115-124 (1963))

## Functionality of hexenuronic acid groups attached to xylan

(Ref.: Jiang, Z.-H., Van Lierop, B. and Berry, R., *Tappi J.*, 83(1), 167-175 (2000))



# Extractives

- Families of compounds
  - Terpenes and terpenoids
  - Resin Acids (Softwood)
  - Fatty Acids
  - Polyphenols
- May be problematic (deposit, pitch)
- Softwood kraft: Tall oil and turpentine
- HW: Large amount of neutral components (difficult to remove during pulping)

# Classification of bleaching chemicals with regard to their reactivity towards lignin and carbohydrate structures.

Parameters	Category		
	I	II	III
Bleaching chemicals			
Chlorine containing	Cl <sub>2</sub>	ClO <sub>2</sub>	NaOCl, ClO <sub>2</sub> <sup>-</sup>
Chlorine free	O <sub>3</sub>	O <sub>2</sub>	HOO <sup>-</sup> , H <sub>2</sub> O <sub>2</sub>
Type of reaction	Electrophilic	electrophilic	nucleophilic
pH level	acid	Acid/alkaline	alkaline
Reaction sites in lignin structures	Olefinic and aromatic	Free phenolic groups and double bonds	Carbonyl groups, conjugated double bonds
Reaction sites in Carbohydrate structures	Hexenuronic acids	Hexenuronic acids only ClO <sub>2</sub>	

Ref.: Lachenal, D. and Muguet, M., *Nord. Pulp Pap. Res. J.*, 6(1), 25-29 (1992).

# Standard reduction potential of common bleaching chemicals

- Ozone is a very strong oxidizing agent and a powerful bleaching agent for lignocelluloses (Rice, R.C., handbook 1982)

Chemicals	Oxidation reaction	Std. red. potentials (eV)
O <sub>3</sub>	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	+2.07
H <sub>2</sub> O <sub>2</sub>	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	+1.78
HClO <sub>2</sub>	$HClO_2 + 3H^+ + 4e^- \rightarrow Cl^- + 2H_2O$	+1.56
HOCl	$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O$	+1.49
Cl <sub>2</sub>	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
ClO <sub>2</sub>	$ClO_2 + H^+ + e^- \rightarrow HClO_2$	+1.15
O <sub>2</sub>	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.40

# How to Measure Bleaching Efficiency

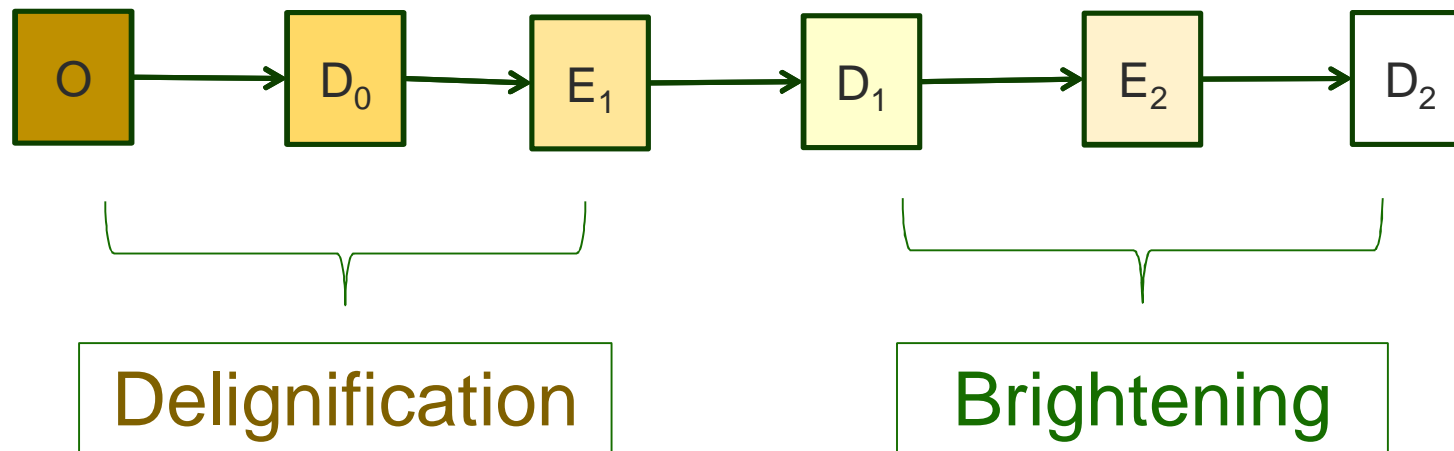
We measure:

- **Kappa Number** (Residual lignin)
- **Viscosity** (Cellulose chain length)
- **Brightness** (reflectance of visible blue light centered at 457 nm)

**Selectivity:** 
$$\frac{\text{Kappa}}{\text{Viscosity}}$$

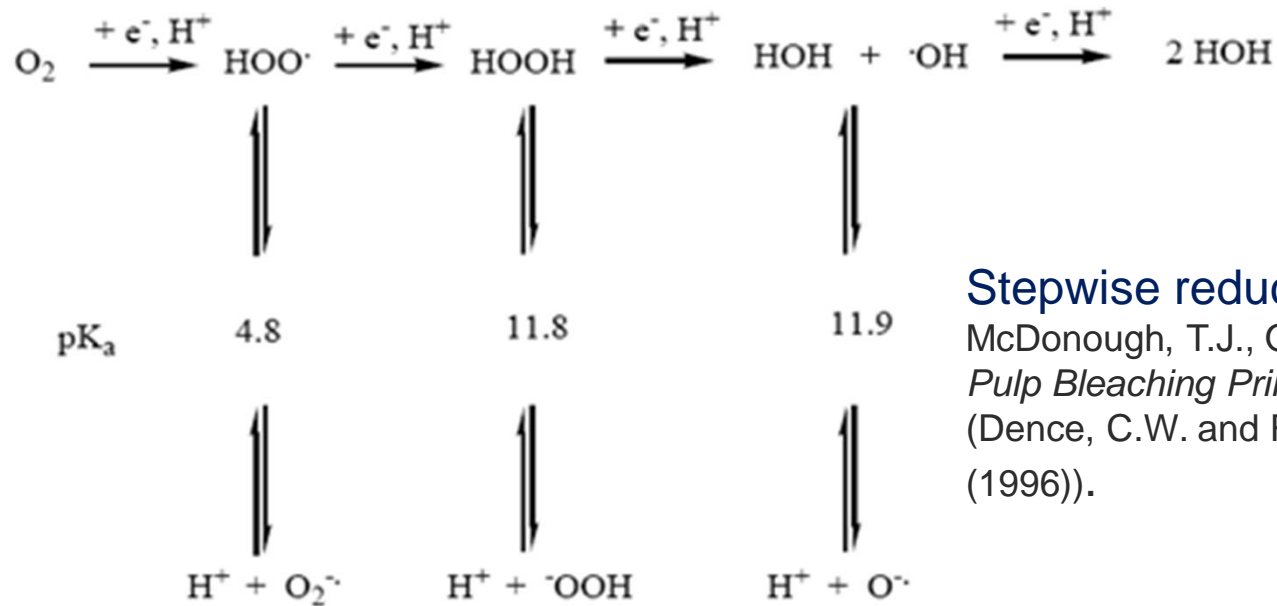
# Bleaching chemistry through stages

- Multi-stage ECF bleaching sequence



# Oxygen delignification

- Oxygen - abundant, cheaper
- O-stage filtrate is part of the recovery process (Environment friendly)

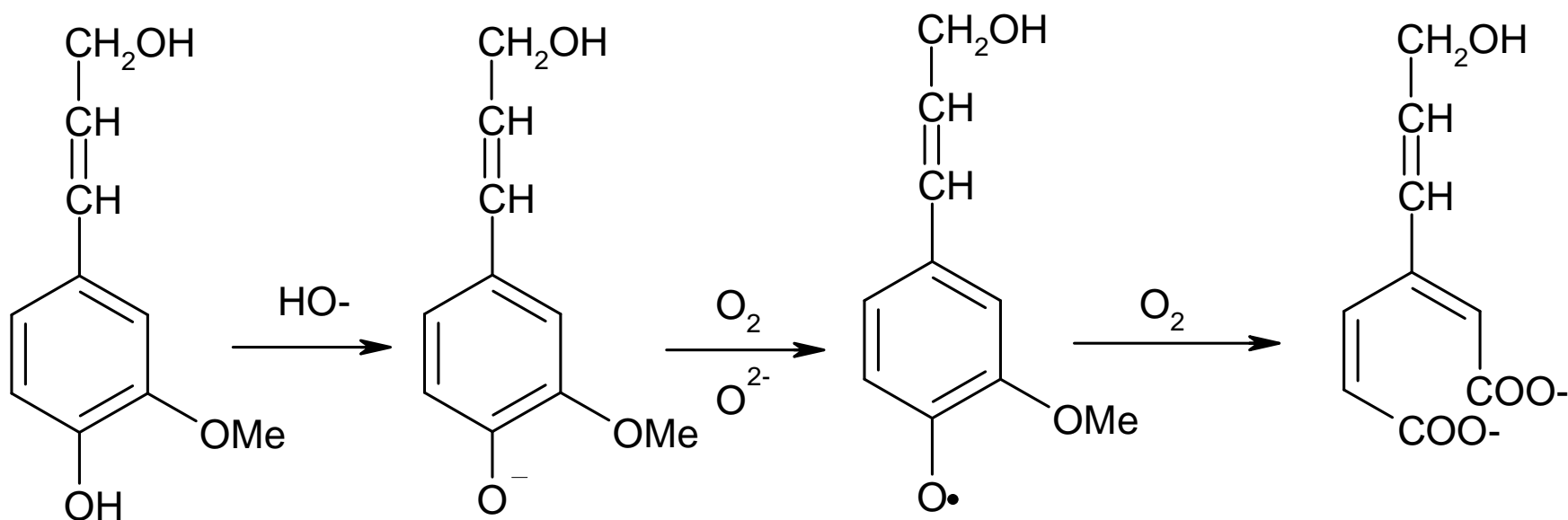


Stepwise reduction of oxygen (Ref.: McDonough, T.J., *Oxygen delignification, Pulp Bleaching Principles and Practice*, (Dence, C.W. and Reeve, D.W., eds.), (1996)).

Both the  $\text{HOO}\cdot$  and  $\text{HO}\cdot$  radicals (or their corresponding bases) have higher oxidation potential than their parent oxygen

# Steps in the mechanism of oxygen bleaching

- Oxidation proceeds via several intermediates, e.g., peroxides, organic radicals and hydroxyl radicals.
- These intermediates are non specific oxidative agents, and hence oxygen is not as selective for lignin removal as the chlorine-containing compounds



(Ref.: McDonough, T.J., Oxygen delignification, *Pulp Bleaching Principles and Practice*, (Dence, C.W. and Reeve, D.W., eds.), (1996)).

Muconic acid derivatives

# How MgSO<sub>4</sub> helps improve selectivity

## Hypothesis:

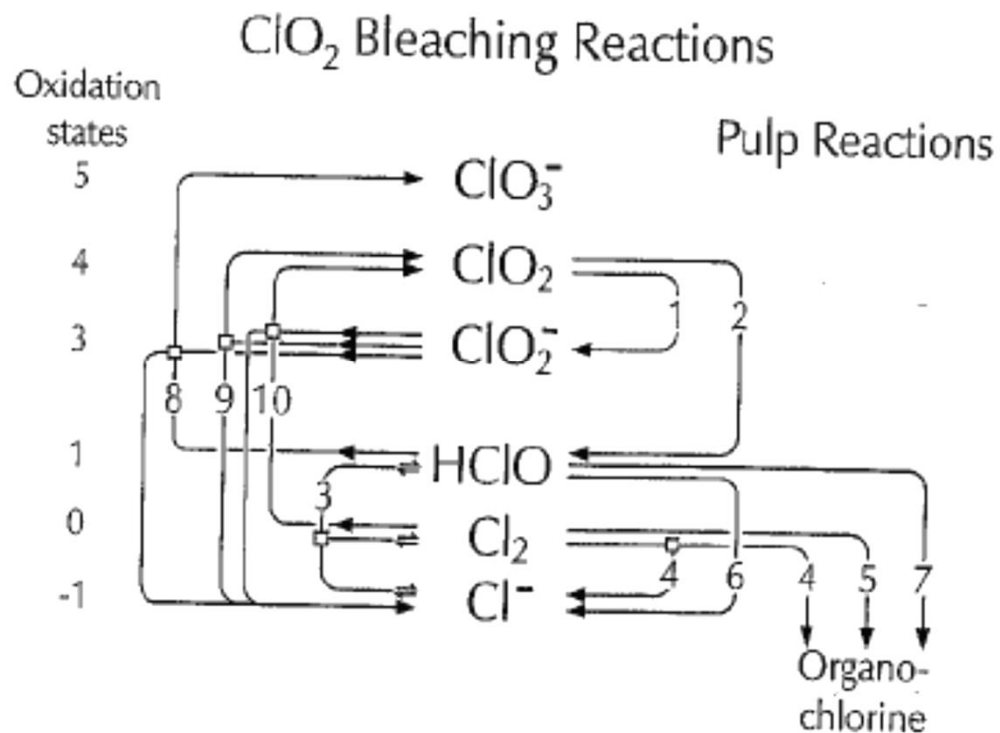
- Formation of Mg<sup>2+</sup> carbohydrate complex which stabilizes oxidized glucose units and inhibits chain scission by alkaline - elimination
- Less likely . Inactivation of transition metals by co-precipitation with Magnesium hydroxide (metals catalyze the formation of hydroxyl and oxyl anion radicals from hydrogen peroxide)

# Chlorine dioxide bleaching

- Chlorine dioxide selectively reacts with lignin and hexenuronic acids; Does not react to any significant extent with carbohydrates
- Can be used to achieve high brightness and is also extremely effective in bleaching particles.
- Considered essential to the manufacture of strong, stable, clean, high-brightness kraft pulp

# Reactions of chlorine dioxide with pulp during delignification and bleaching

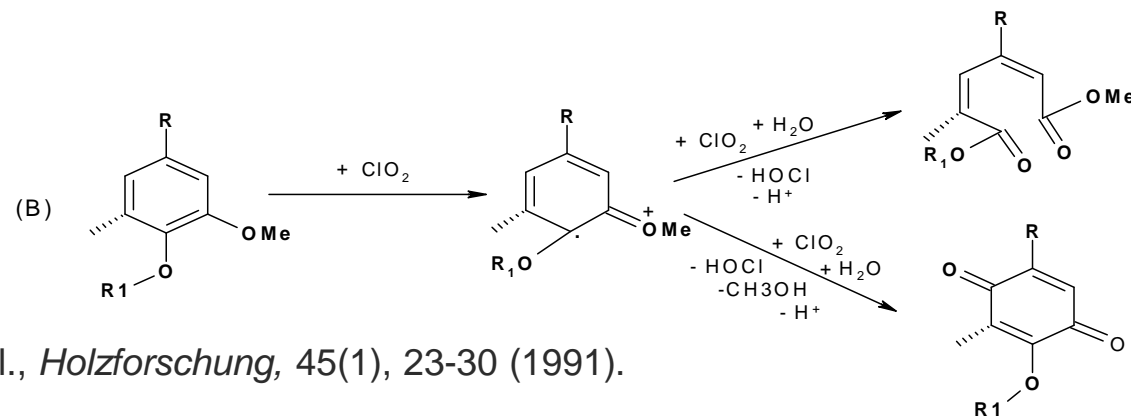
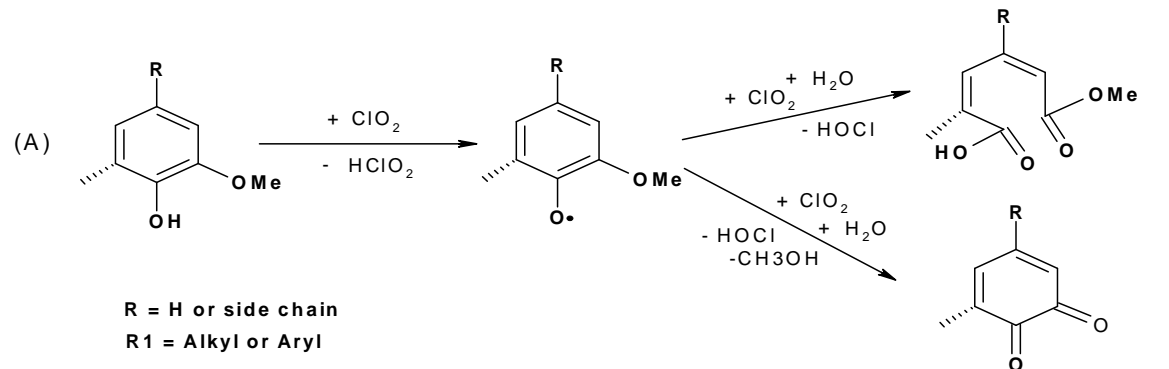
- $\text{ClO}_2$  accepts 5 electrons to completely reduce to chloride ion  
$$\text{ClO}_2 + 4\text{H}^+ + 5\text{e}^- \rightarrow \text{Cl}^- + 2\text{H}_2\text{O}$$
- Chlorine dioxide is reduced through a series of steps involving several intermediates before chloride ion is produced



Ref.: Kolar, et.al., *Wood Sci. Technol.*, 17, 117-128 (1983).

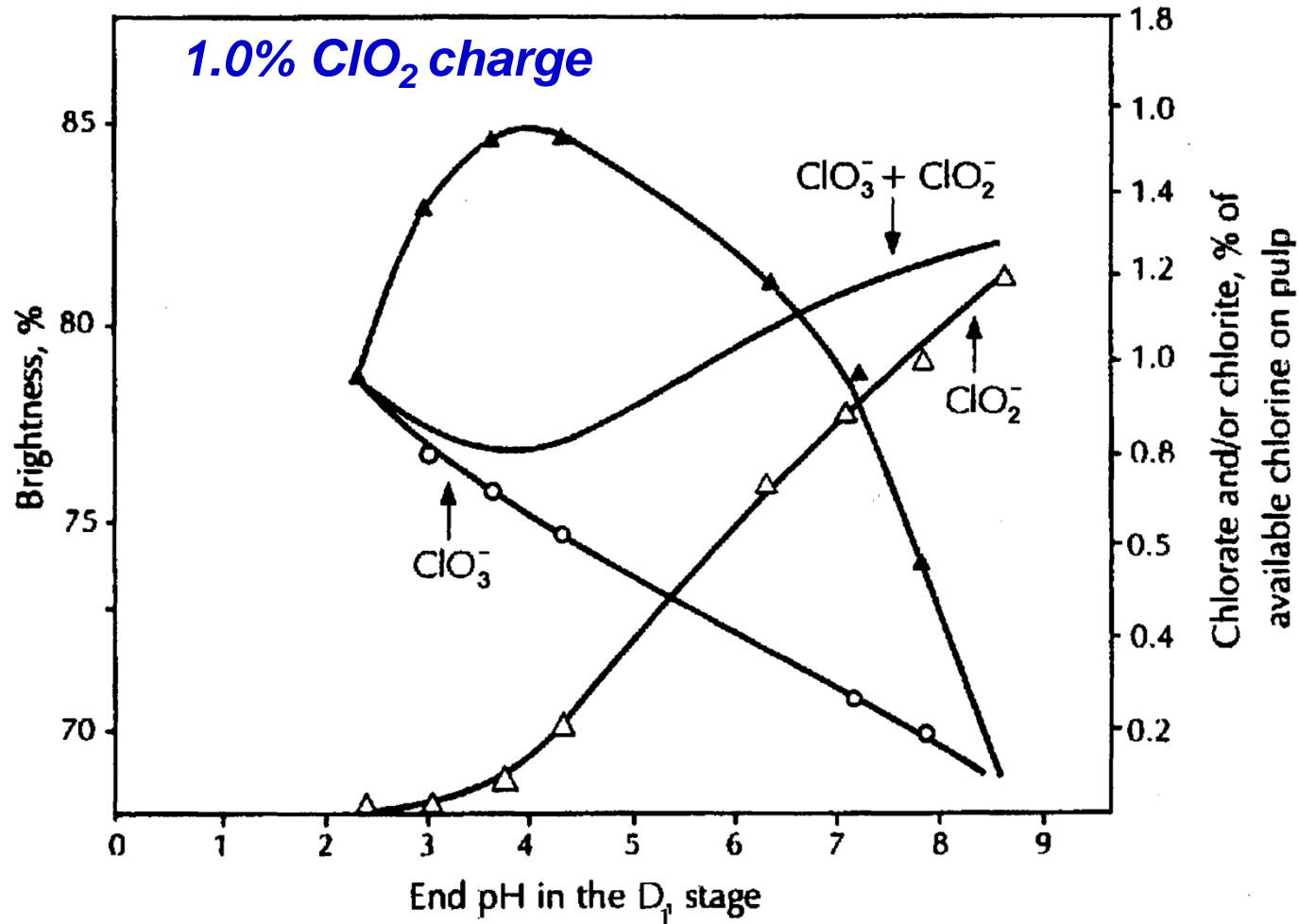
# Sequences for the reaction of chlorine dioxide with phenolic and non-phenolic rings in lignin

- Chlorine dioxide is an electrophile and as such preferentially attacks electron-rich lignin sites e.g. phenolic and non-phenolic rings and ring conjugated ethylenic groups
- End products are the same; However,
- Reaction with phenolic lignin is much faster than non-phenolic lignin



Ref: Brage, C. et al., *Holzforschung*, 45(1), 23-30 (1991).

# Change in active $\text{ClO}_2$ species with pH



Rapson and Anderson, CPPA Trans. Tech. Sect., 3(2): TR52 (1977)

# Near neutral final chlorine dioxide brightening (NNB)

- Optimum pH is dependent upon the amount of chlorine dioxide applied and pulp species (Hart, Tappi fall conf., 2006)
- Final pH should be close to neutral when a typical chlorine dioxide charge is applied and that chlorite is the key brightening agent under near neutral conditions (Jiang and Berry, CA 2643093 A1. 2007)

# Hydrogen peroxide

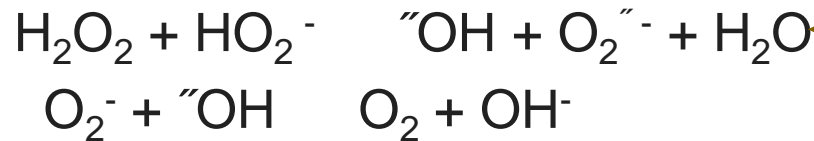
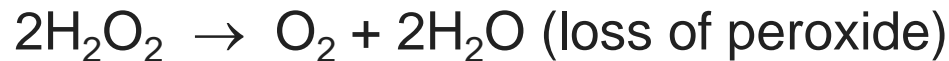
- $\text{H}_2\text{O}_2$  is used in both mechanical and chemical pulp bleaching under alkaline conditions
- Able to react with various coloured carbonyl-containing structures in lignin and carbohydrates
- May function as both de-lignifying (MINOX, LIGNOX and Peroxide reinforced oxygen) and bleaching agent (Lachenal, D. et.al., *Tappi J.*, 63(4), 119-122 (1980))
- As a bleaching agent hydrogen peroxide is normally applied in the final bleaching stages to achieve higher brightness (>92% ISO) and improved brightness stability

# Reactive species in hydrogen peroxide bleaching

- $\text{HOO}^-$  anion is a strong nucleophile and is primarily responsible for the bleaching effect of alkaline hydrogen peroxide

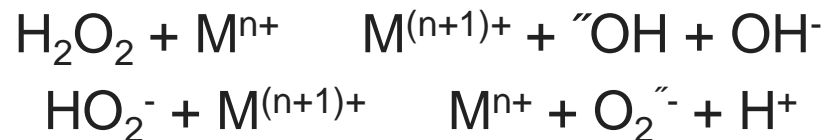


- Decomposition products



Lignin oxidation and degradation;  
Cellulose degradation

- Formation of unselective hydroxyl radicals is also catalysed by transition metal ions



Ref.: Agnemo, R. and Gellersted, G., *Acta Chem. Scand.*, B33(5), 337-342 (1979)

# How to prevent peroxide decomposition

- Decomposition of hydrogen peroxide can be controlled by:

Using mild alkaline bleaching conditions,

Stabilizing the hydrogen peroxide by magnesium sulphate and sodium silicate addition

Removing transition metals from the pulp by chelation etc.

# Alkaline extraction

- Generally follows oxidizing stages conducted under acidic conditions and is most commonly performed with NaOH
- Neutralization of the partially degraded acidic fragments resulting in increased solubility of the lignin fragments
- Reactivates the pulp to allow for further oxidation stages.  
Chlorinated pulp + NaOH = Na<sub>2</sub>CO<sub>3</sub> + NaCl + activated lignin  
(Berry, R.M., *Holzforschung* 41(3),:177(1987))
- Removal of chlorine from lignin by nucleophilic displacement reaction in which a chlorine atom is replaced by a hydroxyl group

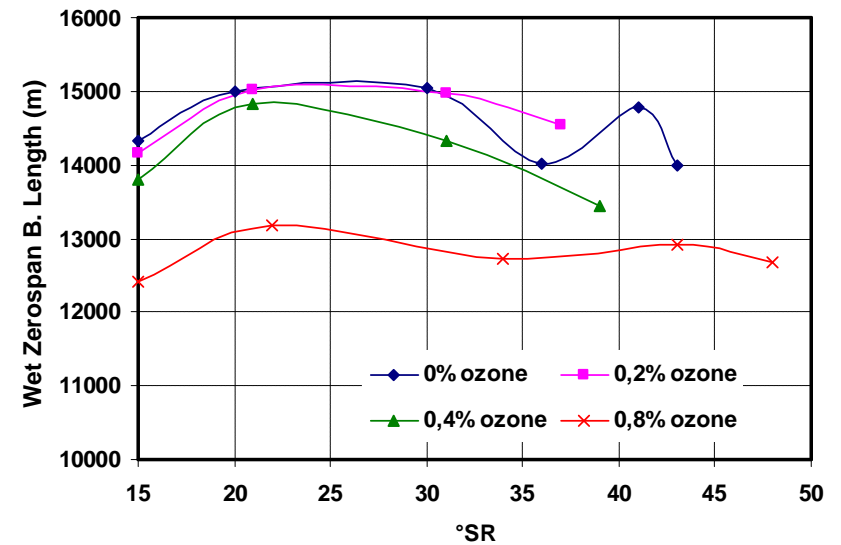
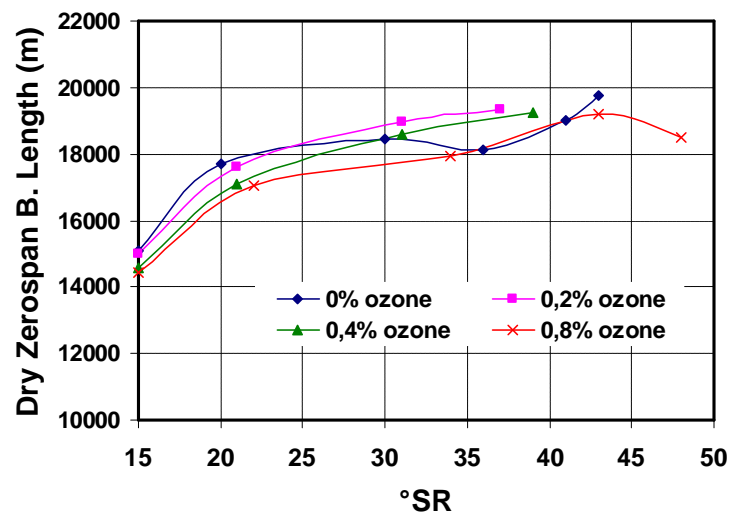
# Bleachability with ozone

Parameter	DEDD*	ZDED		
Ozone charge (%)	0	0.2	0.4	0.8
ClO <sub>2</sub> charge (%)	2.40	1.73	1.00	0.24
NaOH charge (%)	1.65	1.65	1.65	1.50
Z stage				
Brightness (%ISO)	49.0	59.4	67.5	81.8
Final pulp				
Brightness (%ISO)	90.6	90.2	90.9	91.5
Viscosity (mPa.s)	25.0	21.6	19.6	12.1

\*O stage eucalyptus pulp

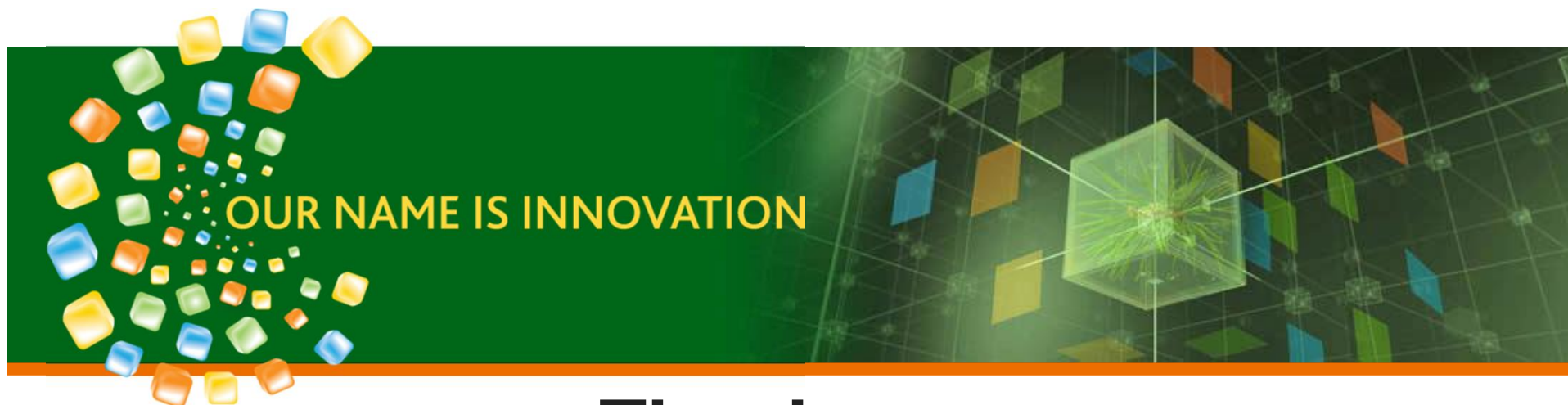
Ref: Lachenal, D. IPBC 2011

# Dry and Wet zerospan tensile strength vs °SR of fully bleached O-eucalyptus pulp



Wet zerospan tensile strength correlates with the low viscosity pulps

Ref: Lachenal, D. IPBC 2011



# Thank you

Shree Prakash Mishra, Ph.D.; Scientist / Chercher,  
Chemical Pulping / Mise en pâte chimique  
Market pulp / Pâte Commercial

570, boul. Saint-Jean, Pointe-Claire (QC) H9R 3J9

Phone: 514 782-4494 Fax: 514 630-4134

Email: [shree-prakash.mishra@fpinnovations.ca](mailto:shree-prakash.mishra@fpinnovations.ca)

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