Peroxide Bleaching of Eucalyptus CTMP Using $Mg(OH)_2$ as the Alkali Source

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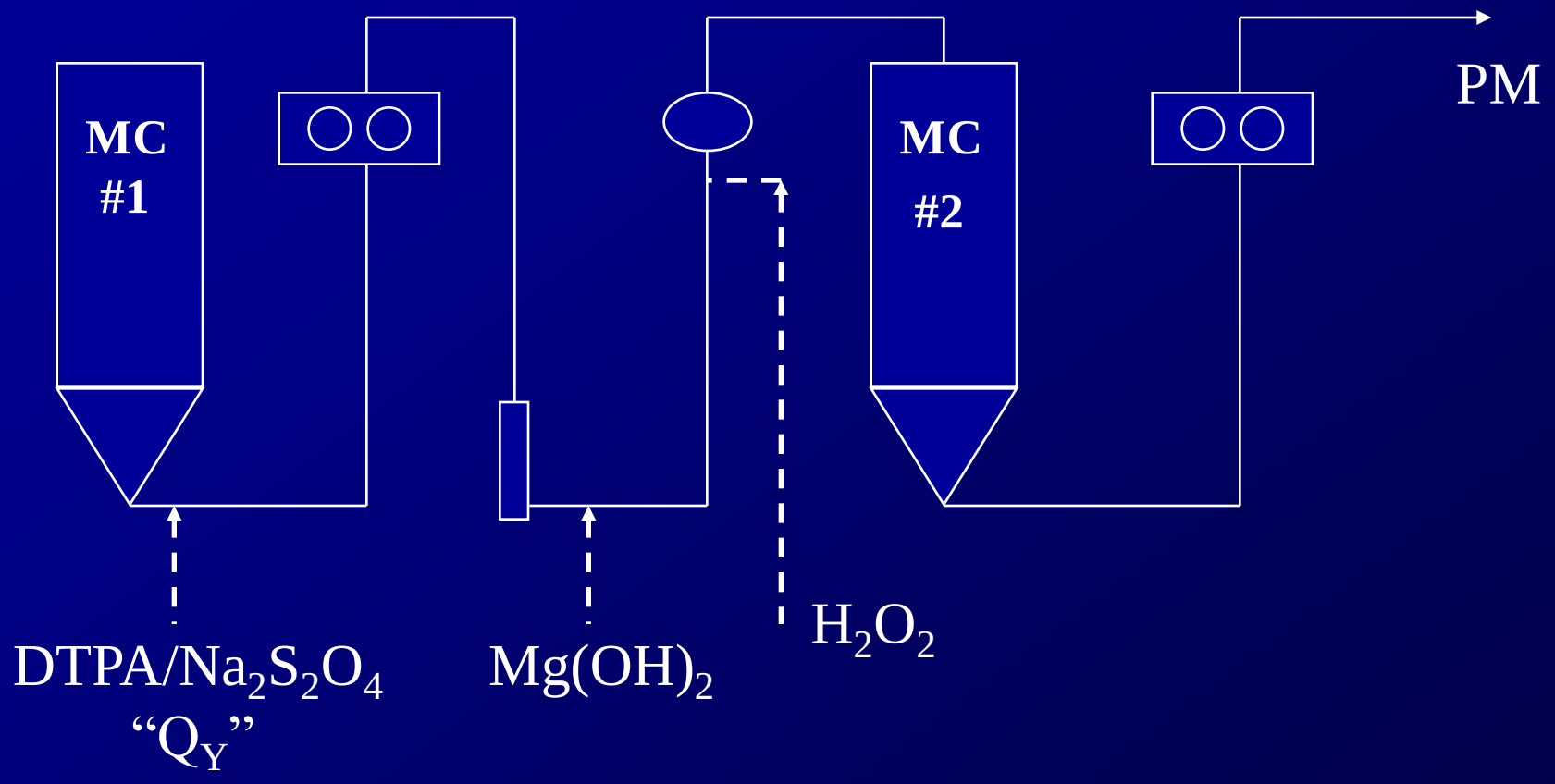
Conventional Peroxide Bleaching of Mechanical Pulp

- Use NaOH as the alkali source
- High alkalinity, especially in the initial phase
- Peroxide decomposition and darkening reactions
- High COD load of the effluent
- High anionic trash production
- Decreased light scattering coefficient
- Decreased pulp yield

$Mg(OH)_2$: An Alternative Alkali for Peroxide Bleaching

- Mild alkalinity
- Gradual release of HO^- due to low solubility
- One unit weight of $Mg(OH)_2$ equals to 1.4 NaOH in the capacity of accepting protons.

$Mg(OH)_2$ - P_M Bleaching Process



$P_{Mg(OH)2}$ Versus P_{NaOH}

$P_{Mg(OH)2}$	P_{NaOH}
Lower pH	Higher pH
Silicate decreased or eliminated	Silicate needed
Longer time required	Less sensitive to time
Less dissolved organics	More dissolved organics
Lower COD	Higher COD
Less anionic trash	More anionic trash

Objectives

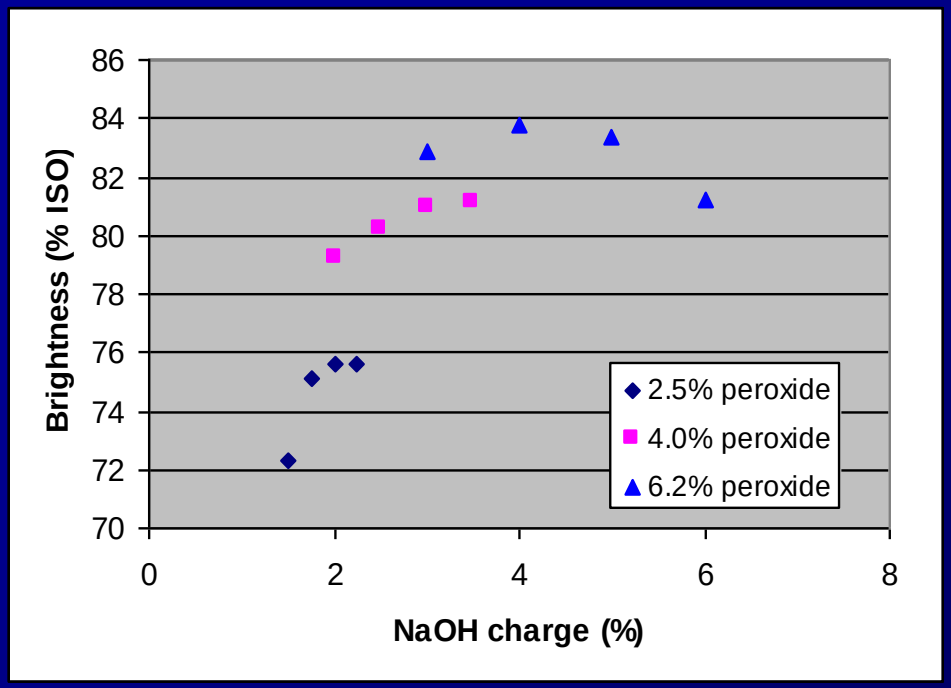
- To compare the $Mg(OH)_2$-based and NaOH-based peroxide bleaching of a eucalyptus CTMP, in terms of
  - Pulp brightness
  - COD
  - Anionic trash
  - Pulp yield

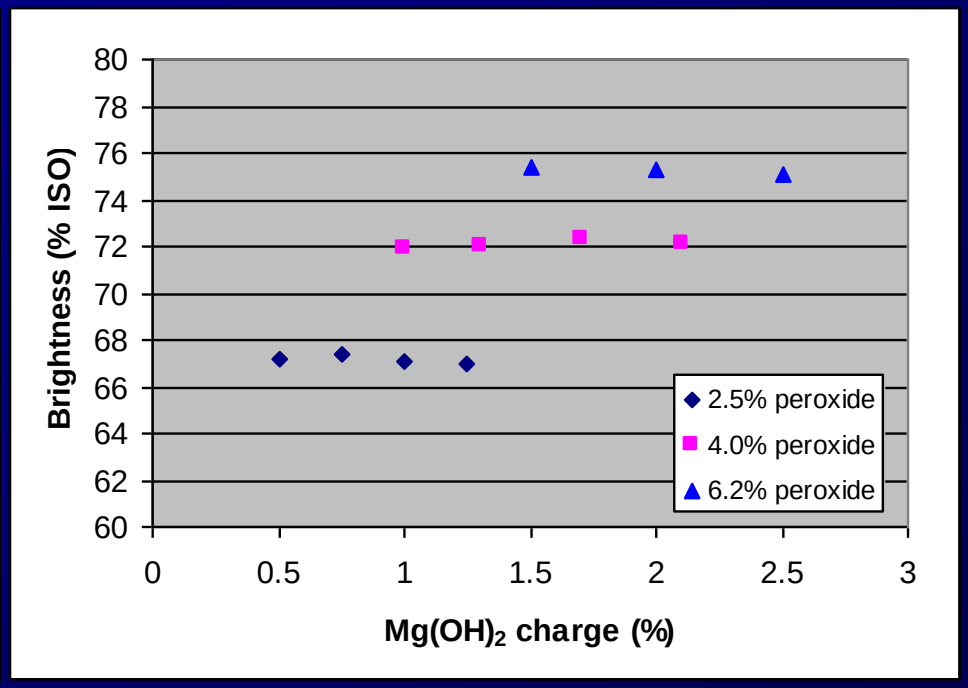
Experimental

- Eucalyptus CTMP from a Brazilian mill
- Chelation: 0.2% DTPA (as 100%), 3% consistency, pH 6.0, 70°C, 30 minutes.
- Bleaching conditions:
  - 2.5%, 4.0%, 6.2% H_2O_2;
  - 1.5%-6.0% NaOH, or 0.5%-2.5% $Mg(OH)_2$;
  - 16% (MC), 30% (HC) pulp consistency;
  - 80-90 °C, 2-6 hours.

Medium-Consistency (MC) System

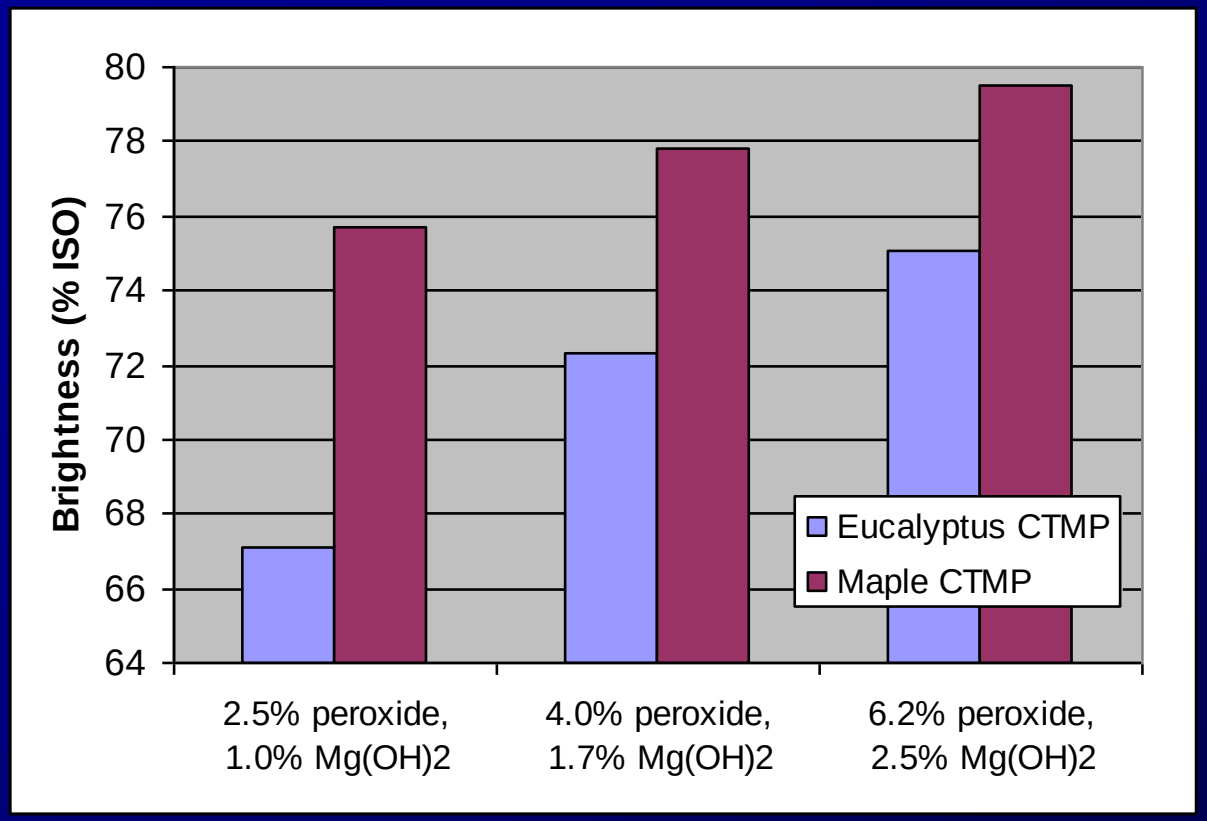
Effect of Peroxide and Alkali Charge on Brightness (MC System)





Other bleaching conditions: 2.6% silicate, 0.13% Epsom salt (NaOH-based process), 16% pulp consistency, 80°C, 3 hours

Eucalyptus CTMP vs. Maple CTMP: $Mg(OH)_2$-based Peroxide Bleaching



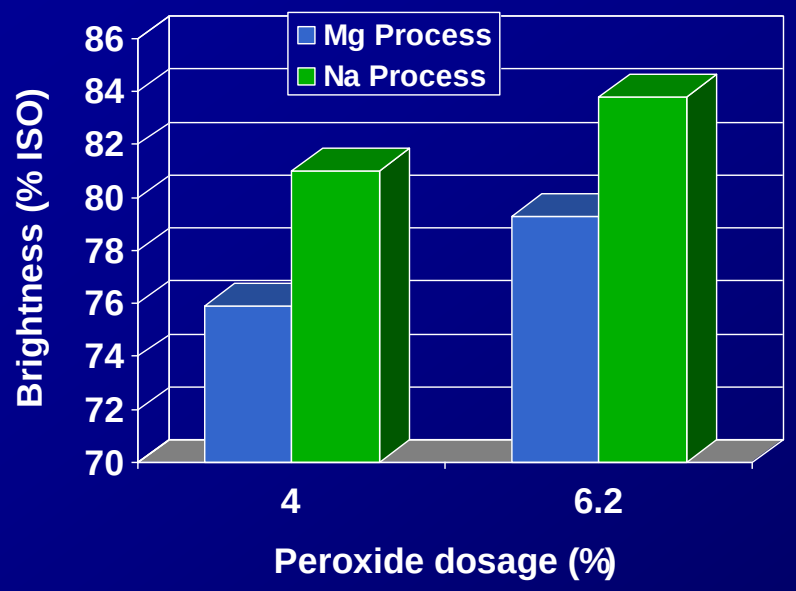
- The eucalyptus CTMP is less bleachable in the $Mg(OH)_2$-based process, compared with the maple CTMP.

Why Is the Eucalyptus CTMP Less Bleachable in the $Mg(OH)_2$-based Process?

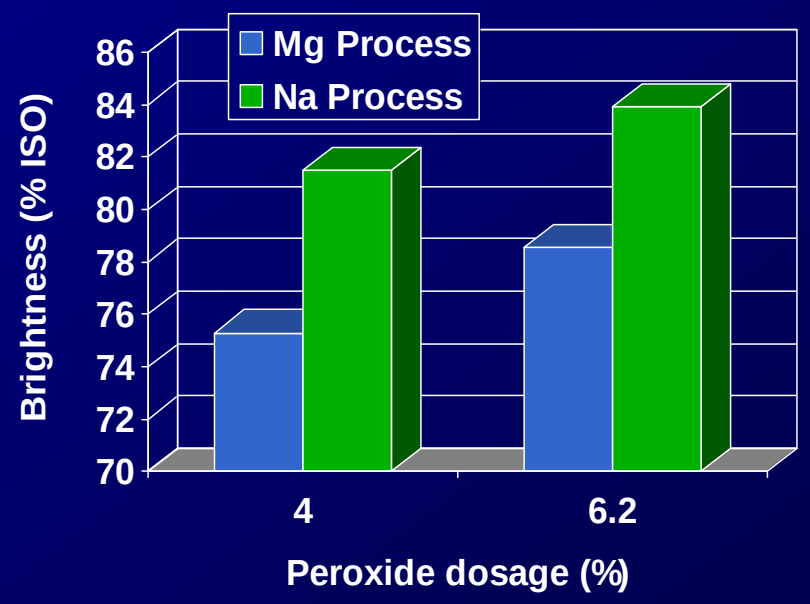
- Wood properties
  - Extractives
  - Lignin
- Pulping process
  - Chemical pretreatment (alkali dosage)

Effect of Acetone Extraction

Without acetone extraction



With acetone extraction

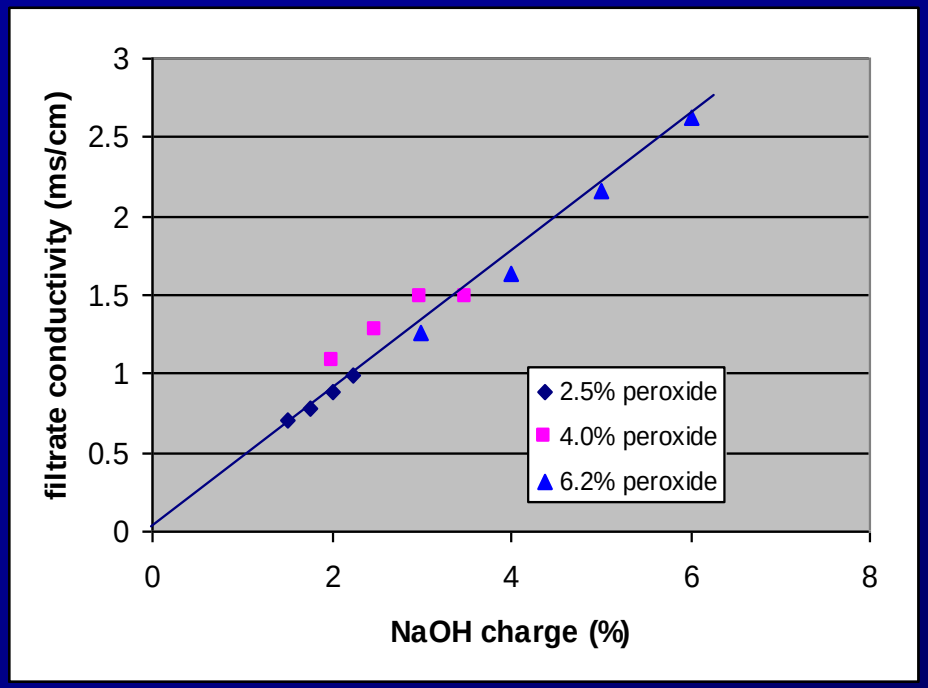


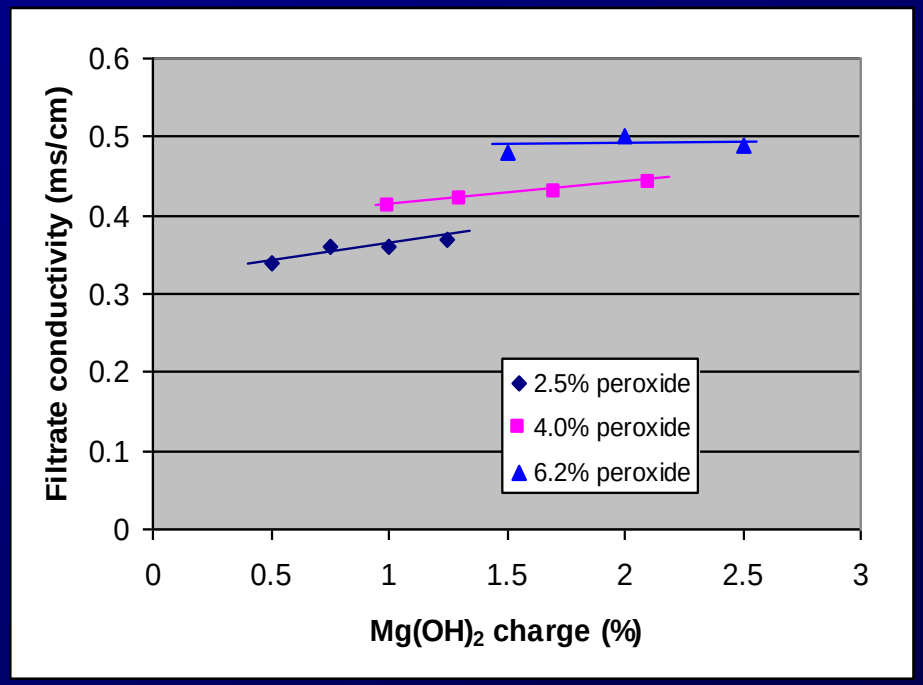
Other bleaching conditions: 2.6% silicate, 0.13% Epsom salt (Na process), 16% pulp consistency, 80°C, 3 hours (6 hours for the Mg process).

Alkaline Pre-treatment on Peroxide Bleaching of A TMP

NaOH %	$Mg(OH)_2$ %	Silicate %	DTPA (40%) %	End pH	Residual H_2O_2, %	Bright. % ISO
Without alkali pre-treatment						
1.85	0	2.0	0	7.97	1.24	71.5
1.85	0	0	0.4	7.65	1.24	71.6
0	1.0	0	0.4	7.81	1.70	71.2
With alkali pre-treatment						
1.0	0	2.0	0	9.20	1.43	67.6
1.0	0	0	0.4	9.39	1.22	67.3
0	1.0	0	0.4	8.90	1.83	62.7

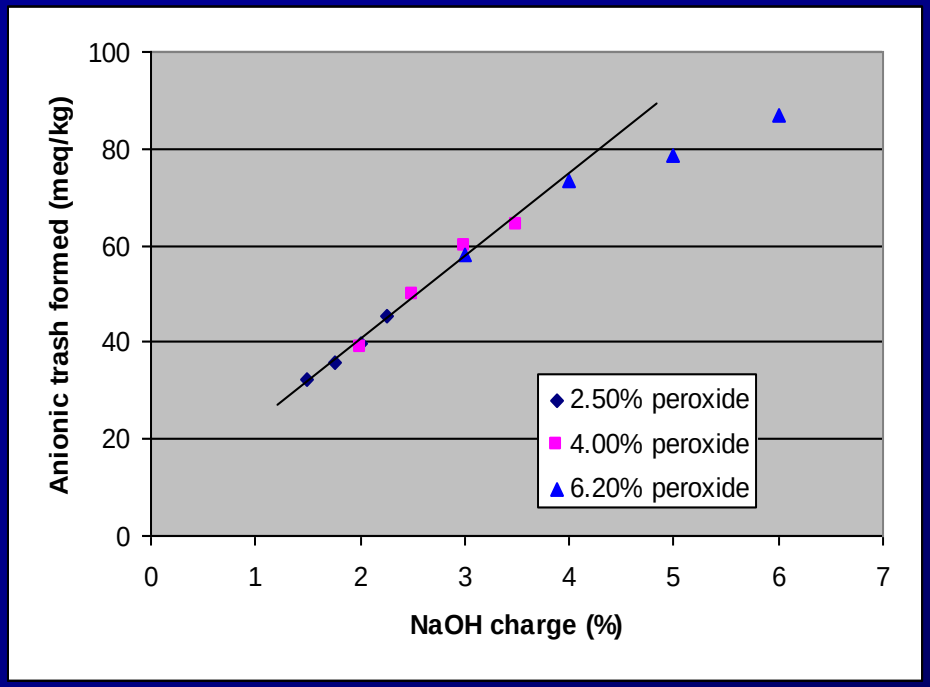
Conductivity of Bleach Filtrate (MC System)

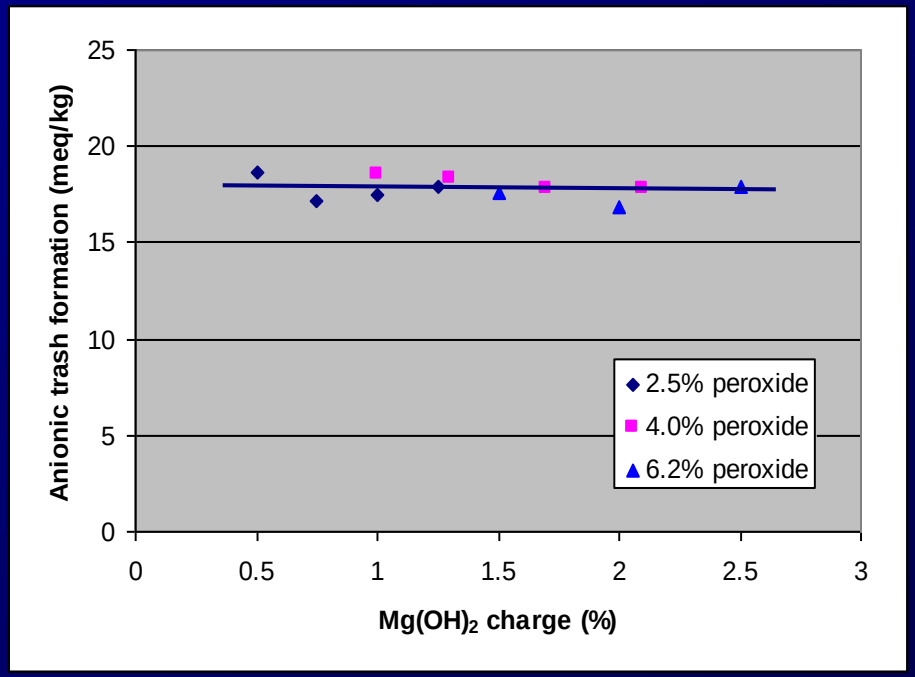




Other bleaching conditions: 2.6% silicate, 0.13% Epsom salt (NaOH-based process), 16% pulp consistency, 80°C, 3 hours

Anionic Trash Formation (MC System)





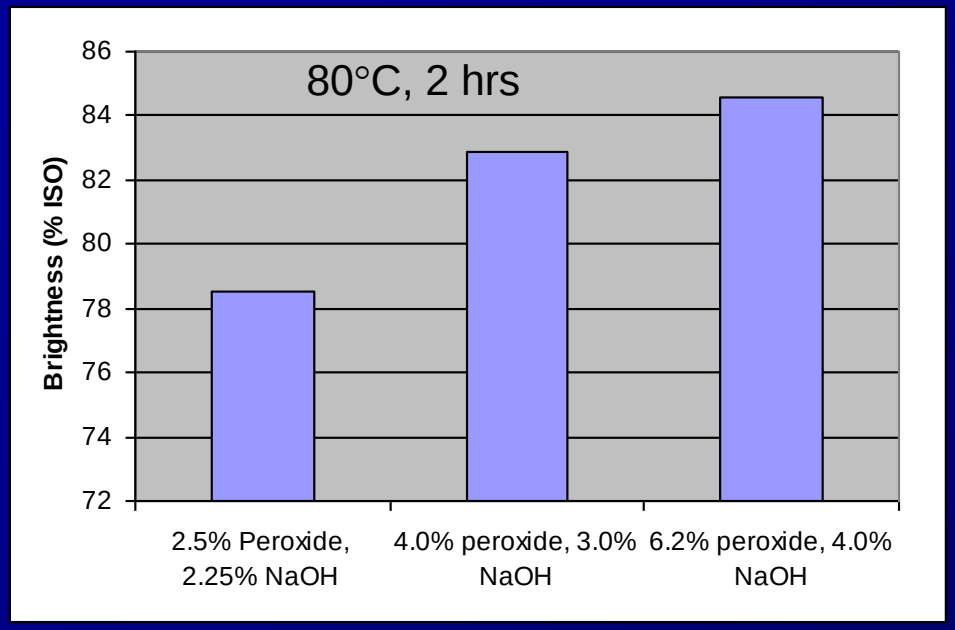
Other bleaching conditions: 2.6% silicate, 0.13% Epsom salt (NaOH-based process), 16% pulp consistency, 80°C, 3 hours

Summary

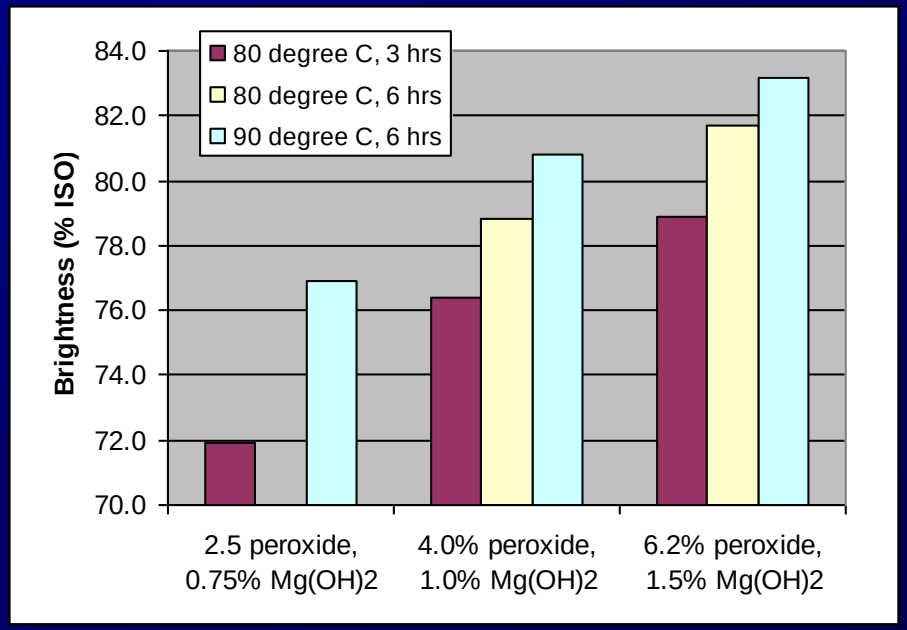
- In the MC system
  - The Na process was effective
  - The Mg process gave ~ 5 units lower brightness than the Na process at the same peroxide dosage.
  - But the Mg process produced less anionic trash and conductivity

High-Consistency (HC) System

Effect of Temperature and Time on Brightness (HC System)



NaOH-based Process



$Mg(OH)_2$-based process

- Other bleaching conditions: 2.6% silicate, 0.13% Epsom salt (NaOH-based process), 30% pulp consistency.

Comparison of the Bleaching Performance at Optimized Conditions (HC)

Process	NaOH-based (2.6% silicate, 0.13% Epsom salt, 80 °C, 3 hrs)				$Mg(OH)_2$-based (2.6% silicate, 90 °C, 6 hrs)			
H_2O_2, %	2.5	4.0	6.2	8.0	2.5	4.0	6.2	8.0
NaOH, %	2.0	2.5	4.0	4.0	0	0	0	0
$Mg(OH)_2$, %	0	0	0	0	0.75	1.0	1.5	2.0
Resid. H_2O_2, %	0.60	1.08	1.53	2.30	0.67	1.53	2.05	2.97
Bright., % ISO	78.5	82.9	85.8	86.9	76.9	80.8	83.2	85.0

For a very high-brightness CTMP

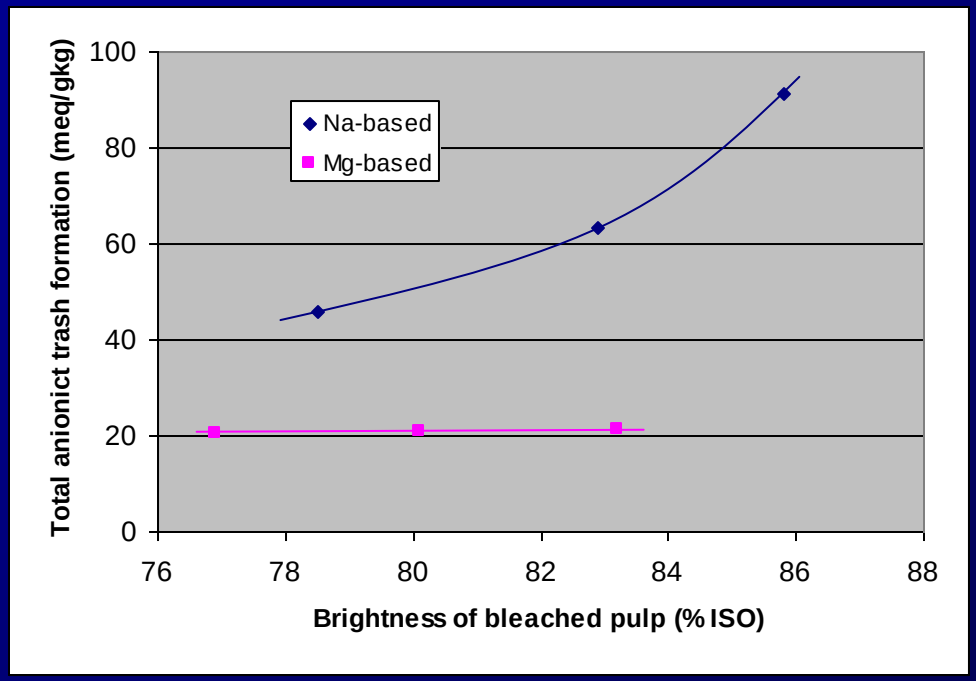
- Peroxide bleaching first
- Followed by the addition of OBA/FWA

Addition of Fluorescent Whitening Agent to Pulps from the $Mg(OH)_2$-based Process

FWA (Tinopal UP), %	0	0.2	0.4	0.8
Brightness, % ISO	83.2	85.5	87.2	87.8
Flu. comp., % ISO	0	2.76	4.00	5.17
CIE whiteness, %	59.0	66.9	71.5	72.9
L*	97.1	97.2	97.3	97.3
a*	-2.12	-1.51	-1.21	-1.04
b*	7.41	5.71	4.77	4.46

Other bleaching conditions: 6.2 % H_2O_2, 2.6% silicate, 30% pulp consistency, 90°C, 6 hours.

Total Anionic Trash Formation in the HC System

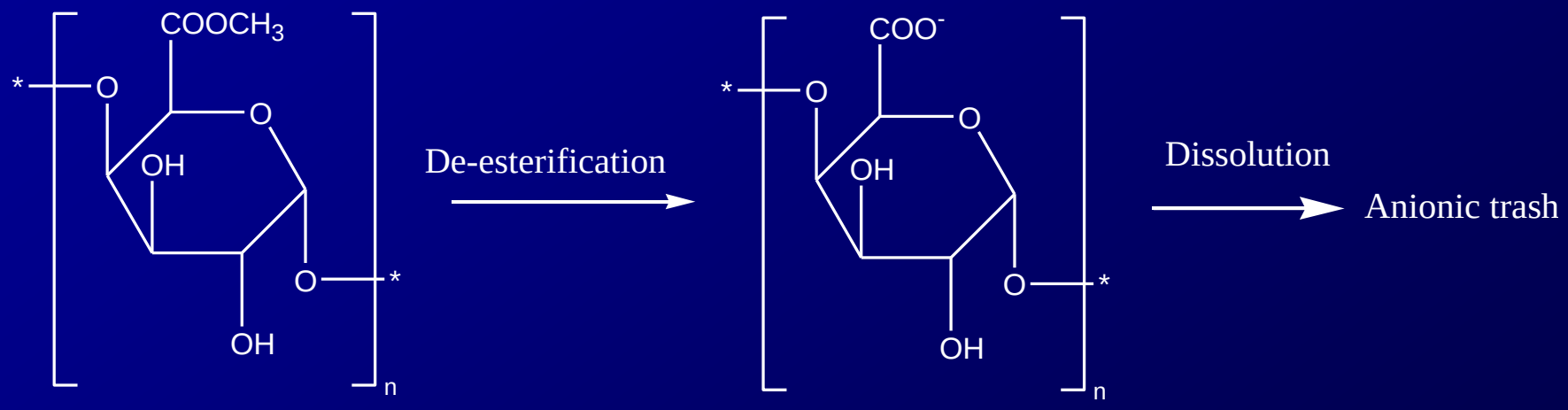


Cationic demand of filtrate measured at pH 7.0

Sources of Anionic Trash

- Polygalacturonic acids (pectic acids): polymer with uronic type of carboxylic groups (pKa= ~3.4).
- Oxidized lignin: macromolecule with lignin-bound carboxylic groups (pKa= ~5.4).
- Colloidal particles of extractive: aliphatic type of carboxylic groups (pKa= ~5.5-6.4).

De-methylation and Dissolution of Pectins

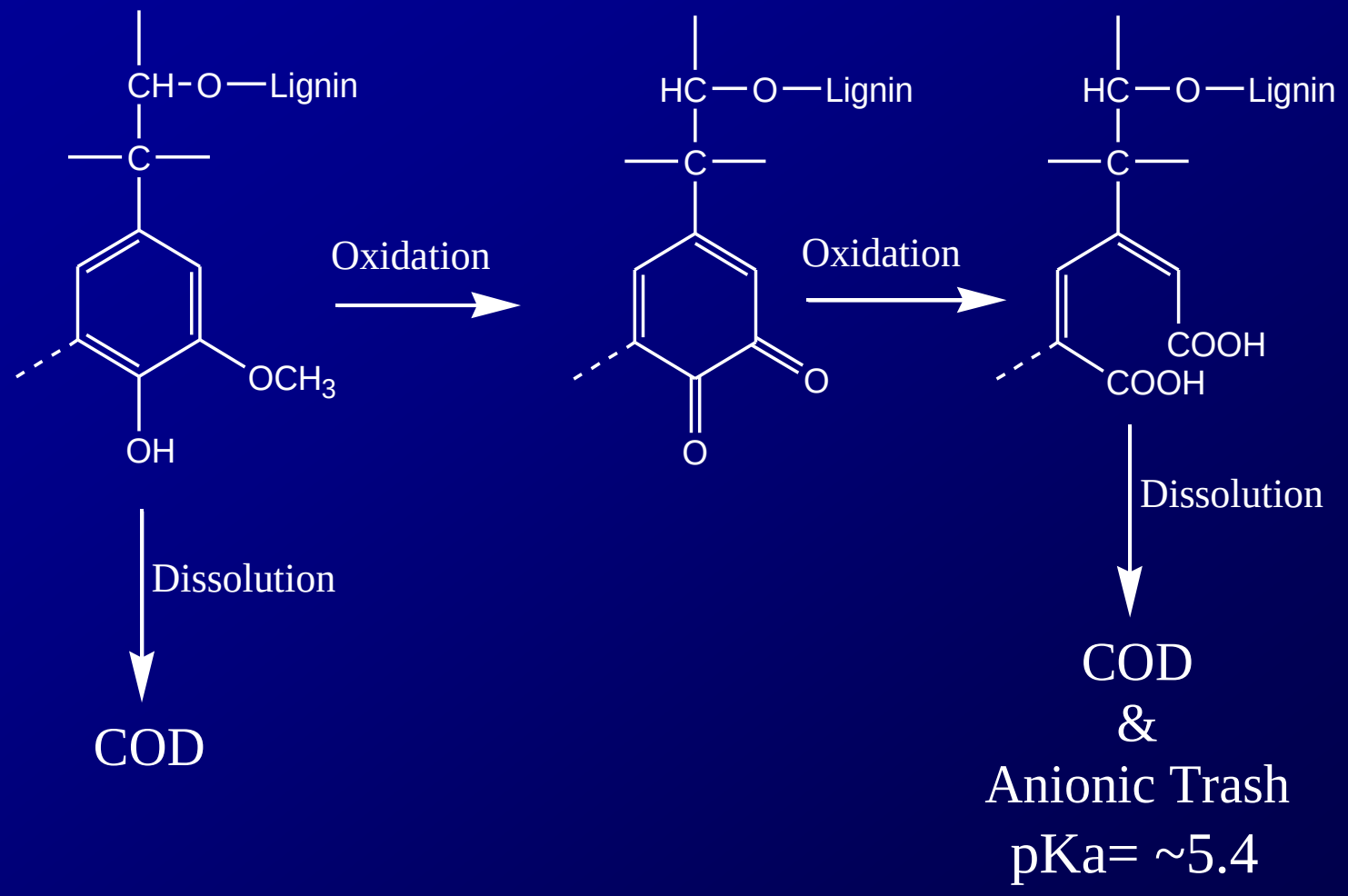


Pectin

Pectic acids

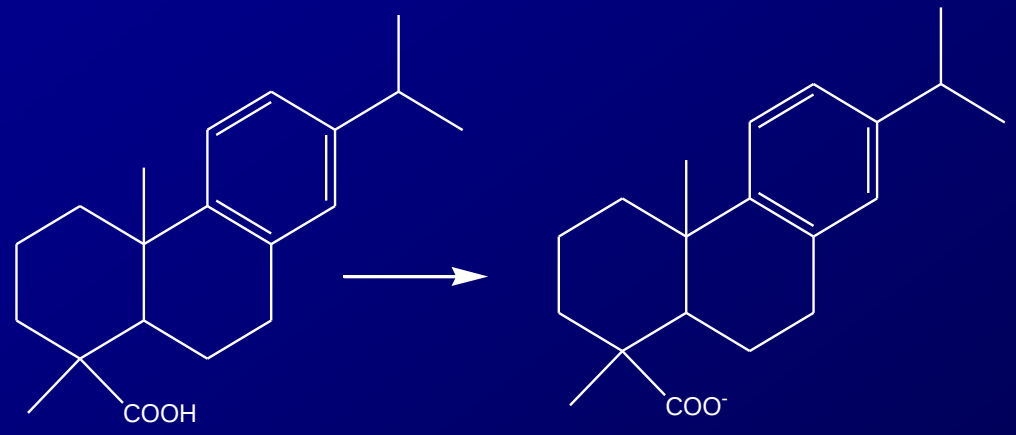
$pK_a = \sim 3.4$

Lignin Oxidation and Dissolution



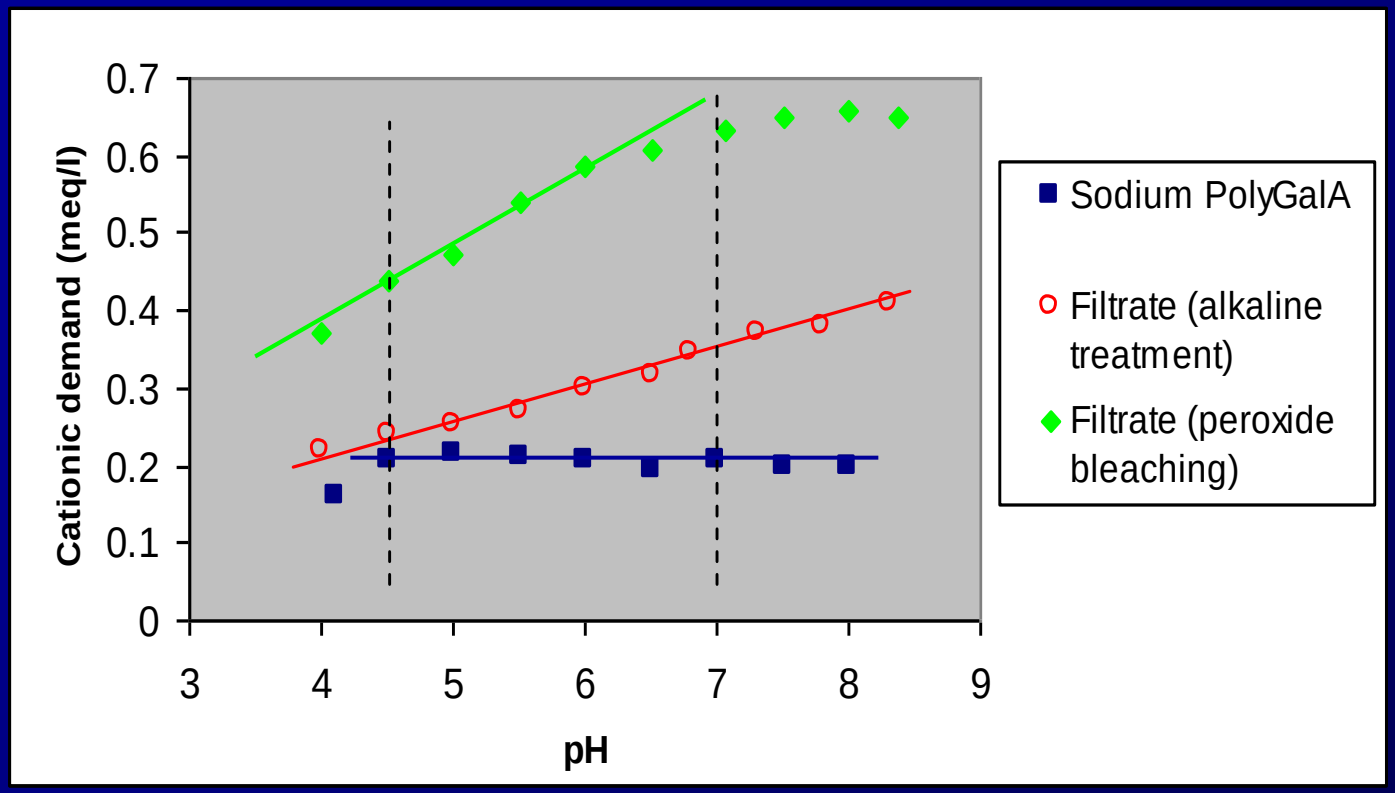
Extractives

- Dissolved and dispersed extractives
  - Example: resin acids, fatty acids



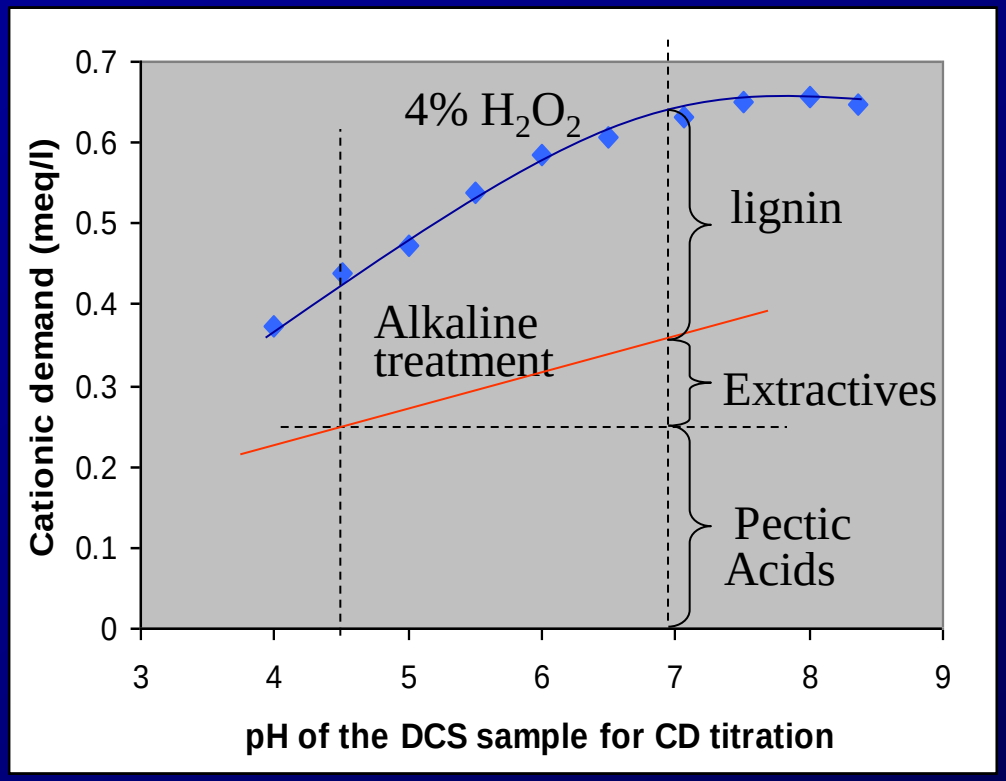
Resin acids
pKa= ~5.5-6.4

Anionic Trash Measured at Various pH



- The measured amount of anionic trash is pH-dependent.
- But the cationic demand of pectic acids is pH-independent from 4.5 to 7.

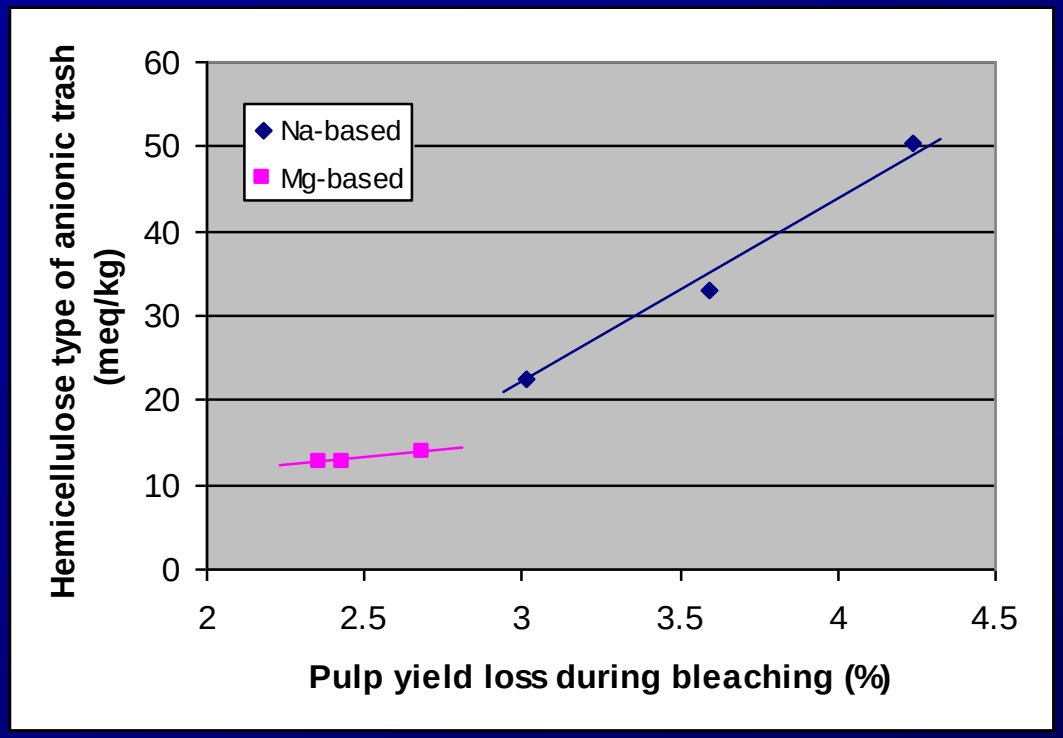
Estimation of the Contribution of Pectic Acids, Lignin and Extractives to the Total Anionic Trash



The increase of cationic demand with pH is due to:

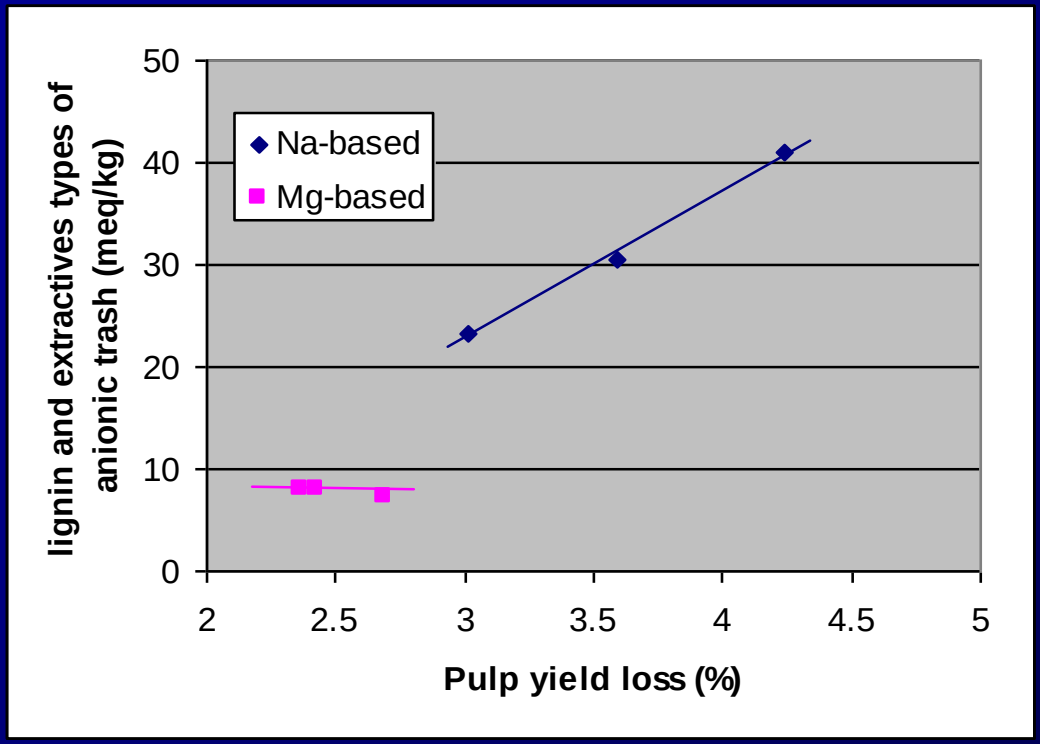
- Extractives
- Oxidized lignin

Hemicellulose Type of Anionic Trash in Peroxide Bleaching of the Eucalyptus CTMP



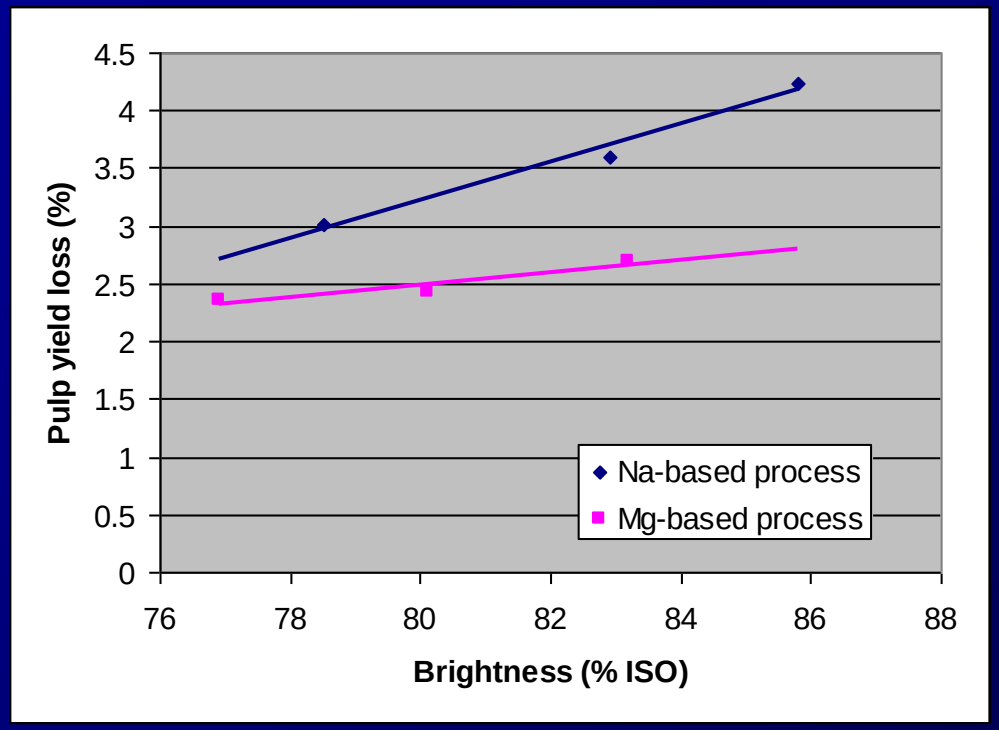
Measured as the cationic demand of filtrate measured at pH 4.5

Lignin and Extractives Types of Anionic Trash in Peroxide Bleaching of the Eucalyptus CTMP



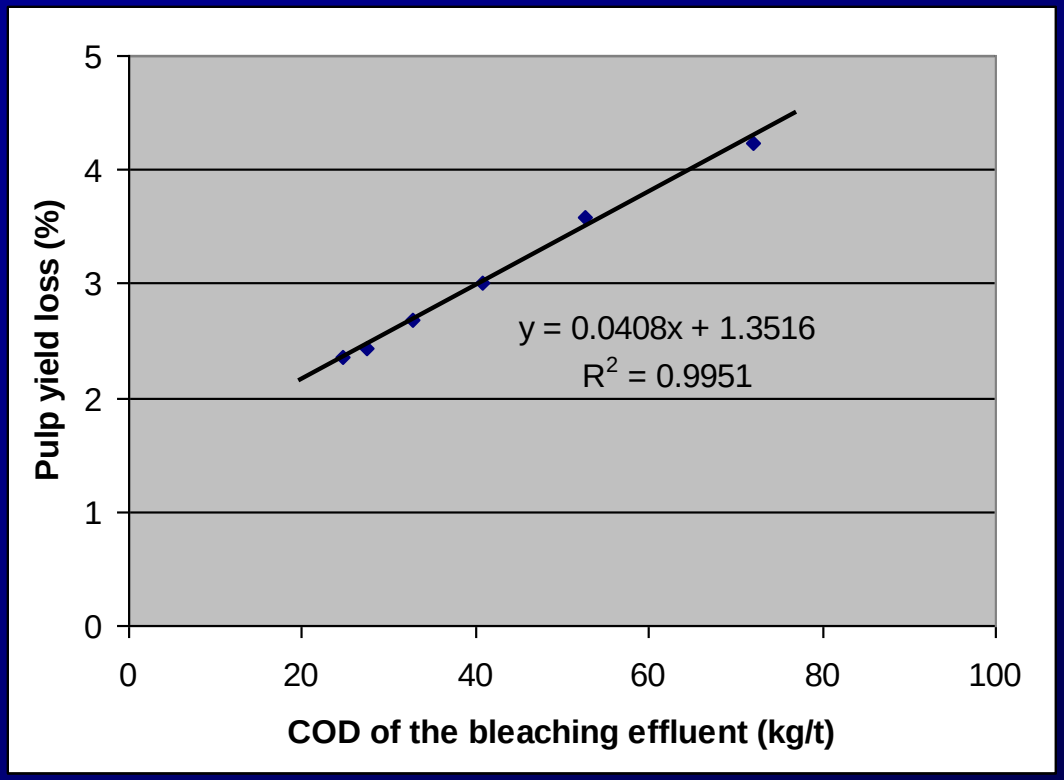
Difference of filtrate cationic demand measured between pH 7.0 and 4.5

Comparison of Pulp Yield Loss at Various Brightness Levels



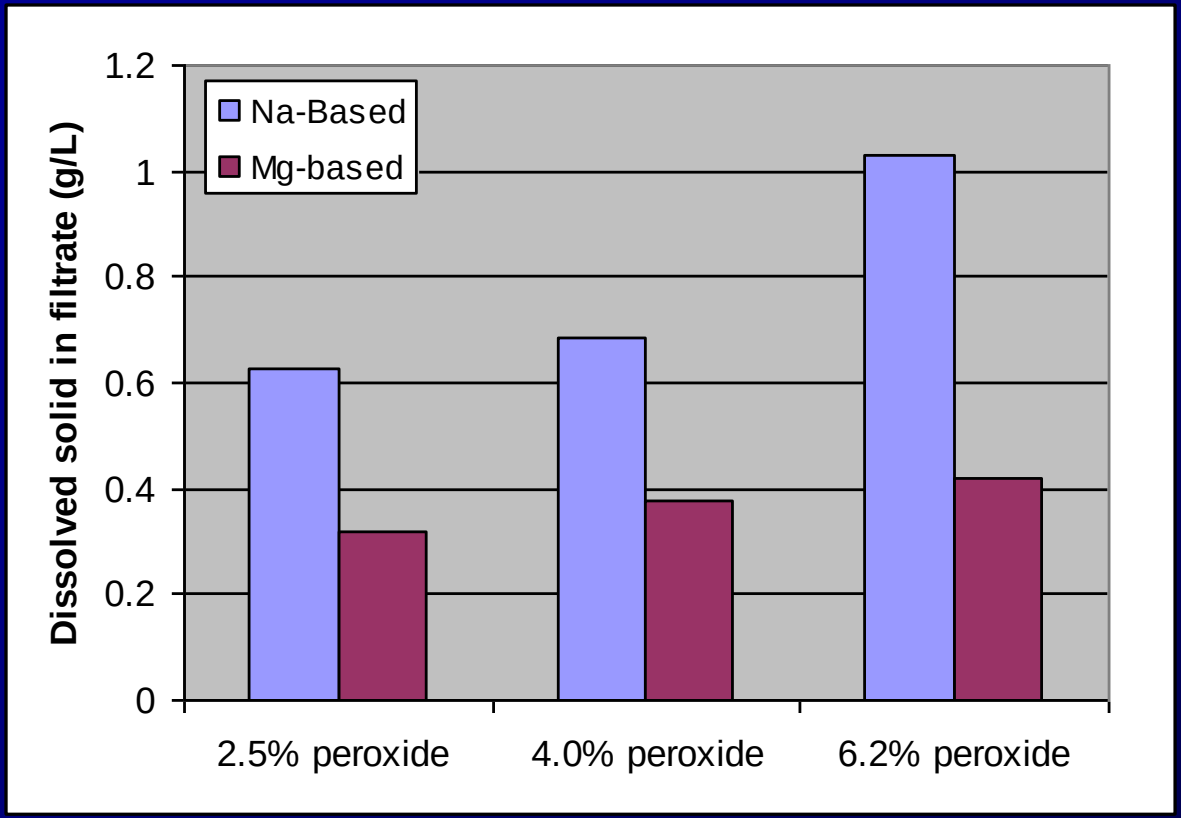
- Lower yield loss for the Mg- based process.

Correlation of Pulp Yield Loss and COD

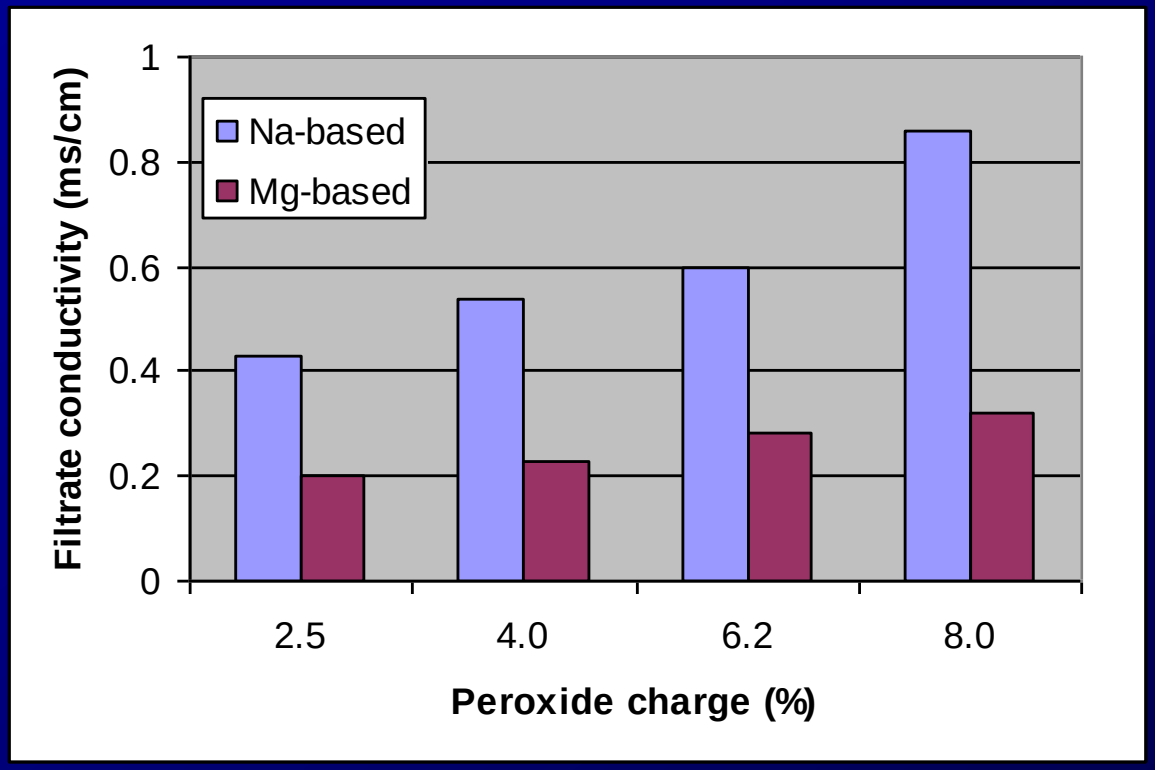


- The same correlation for both the NaOH-based and $Mg(OH)_2$-based processes

Dissolved Solid (HC system)



Filtrate Conductivity (HC System)



Summary

- Under the optimized conditions, the Mg process in the HC system gives 1-2 units lower brightness than the Na process at the same peroxide dosages.
- The Mg process requires higher temperature and longer retention time to reach the brightness targets.
- At a similar brightness, the Mg process has
  - 50-80% less anionic trash
  - 40-50% less COD,
  - 20-30% less loss of pulp yield
  - 50-60% less dissolved solid
  - 50-60% less conductivity

Conclusions

- The $Mg(OH)_2$-based process has been successfully implemented in a number of mills in N.A.
- In comparison with the NaOH-based process, the $Mg(OH)_2$-based process offers:
  - Lower bleaching cost
  - Similar or slightly lower brightness
  - Higher light scattering coefficient
  - Higher pulp yield
  - Lower COD
  - Less anionic trash

Acknowledgements

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