The 9th International Colloquium on Eucalyptus Pulp, will be run together with the ABTCP 2020.
ECOBRIGHT - A BLEACHING TECHNOLOGY
IMPROVING COSTS, QUALITY AND ENVIRONMENT

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Why do we bleach our pulp?

Objectives of pulp bleaching are to

- increase **brightness** to meet product specifications (market demand!)
- stay within specified **colour** shade
- remove residual **lignin** from cooking process (kappa specifications)
- avoid **yellowing** (brightness reversion) during storage

and at the same time one should

- avoid to create too much **effluents** (COD)
- limit the **depolymerisation** of cellulose by alkali and oxidative bleaching agents
- minimize the use of **dangerous chemicals**
- reduce **yield losses** as far as possible
- limit energy consumption and **carbon footprint**
Main Pulp bleaching technologies

Different bleaching stages

- C...elementary chlorine widely substituted
- D...chlorine dioxide for delignification and bleaching
- O...oxygen mainly for delignification (ODL)
- Z...ozone for bleaching
- P...hydrogen peroxide (OP, PO, EOP, EP,...)

EcoBright shows improvement on
- yield
- effluents
- brightness
- depolymerisation
- chemical consumption
Mg(OH)₂ delivers exactly what is needed

Wanted
- Mg²⁺ to protect the fibres
- OH⁻ to control the pH value

Industry Practice
- Mg²⁺ SO₄²⁻ to protect the fibres
- Na⁺ OH⁻ to control the pH value

Mg(OH)₂ - delivers exactly what is needed
- Mg²⁺ to protect the fibres
- OH⁻ to control the pH value

Using 1 t Mg(OH)₂ substitutes
→ 2,0 t MgSO₄ plus
→ 1,4 t NaOH

<table>
<thead>
<tr>
<th></th>
<th>mol. weight</th>
<th>% Mg²⁺</th>
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<tbody>
<tr>
<td>MgSO₄ .7H₂O</td>
<td>246,5</td>
<td>10%</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>120</td>
<td>20%</td>
</tr>
<tr>
<td>Mg(OH)₂</td>
<td>58,3</td>
<td>42%</td>
</tr>
</tbody>
</table>

EcoBright contains more Mg²⁺ than MgSO₄

<table>
<thead>
<tr>
<th></th>
<th>mol. weight</th>
<th>% OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>40</td>
<td>43%</td>
</tr>
<tr>
<td>Mg(OH)₂</td>
<td>58,3</td>
<td>58%</td>
</tr>
</tbody>
</table>

EcoBright contains more OH⁻ than NaOH
In the ODL stage, Mg(OH)$_2$ limits the depolymerisation of cellulose still achieving the same kappa reduction.

- **viscosity values** comparable with magnesium sulfate
- Compared to no magnesium sulfate, EcoBright will increase the viscosity value after ODL stage
- Same achieved **kappa value** demonstrates a good selectivity
- A special **activated EcoBright A50** grade with more soluble magnesium ions was used in these trials
In a mill trial EcoBright has demonstrated the ability to reduce viscosity loss in the oxygen delignification stage.

- A trial was run in a hard wood production line where no magnesium was used in ODL stage.

- Compared to no magnesium addition, Mg(OH)$_2$ increased the viscosity after ODL stage by 84 ml/g in average.

- This mill has now been using Mg(OH)$_2$ for several years.
Optimal pH for peroxide stability

Optimised bleaching requires the peroxide to dissociate into its perhydroxyl anion whilst minimising the rate of auto-decomposition to unreactive oxygen.

- The **highest speed of auto-decomposition** is around pH=11.8 where 50% of H$_2$O$_2$ is in form of the perhydroxyl anion and 50% still exist as hydrogen peroxide.

- To avoid unwanted auto-decomposition the pH should stay away from this area.

- Mg(OH)$_2$ is **buffering the pH** to a lower value compared to caustic soda and helps to avoid too high pH-levels. In addition the magnesium ion has the ability to stabilise peroxide.
- Mg(OH)$_2$ used in a final P-stage with hardwood pulp shows increased brightness and strongly reduced COD values.

- The slightly higher final brightness with Mg(OH)$_2$ is due to an improved pH-curve in the P-stage causing better peroxide use.

- The most interesting effect here is the 35% reduction of the COD value in the wash water after the P-stage.
Results with Mg(OH)$_2$ and short fibres

- Mg(OH)$_2$ used in a final P-stage with hardwood pulp shows also increased viscosity and kappa value.
  
  ○ The introduced magnesium ions showed a positive effect on the fibre protection consequently the **viscosity increased** by 56 ml/g with the use of EcoBright instead of caustic soda.

  ○ The **kappa value** did slightly increase (0.4 units) which was appreciated by the mill.

  ○ Both viscosity increase and kappa increase have a **positive effect on the total yield**.

\[ \text{NaOH substituted by Mg(OH)2 in a hardwood line} \]
There is a clear correlation between the yield and the measured Chemical Oxygen Demand (COD) in the water

- When COD is measured in the water this is a clear indication that solid substances were made soluble in the process. Whatever is made soluble will finally disappear with the effluents and lower the yield of the process.

- For cellulose one can calculate that around 10-11 kg created O₂-demand are representing 10 kg of dissolved cellulose type material. This is well documented in literature. This means that each 11 kg created COD reflect a 1% yield loss or the other way round, 11 kg/t less COD in the water will increase the yield by 1%!
There is also a correlation between the yield and the measured intrinsic viscosity shown in several publications:

- The intrinsic viscosity indirectly measures the chain length of the cellulose molecule. The longer it is, the higher is the viscosity and the better are its strength properties.

- Chemical attack will partly reduce the chain length and shorter parts of the molecule get soluble and are lost in the water.

- One can estimate how much yield loss is linked to a certain loss of viscosity. In a thesis from the Univ. of Maine you find that a viscosity increase of 75 ml/g would correspond to around 1% yield increase which on an annual production can sum up to an impressive number of tonnes!
The D-stage is sensitive on pH: at pH=2-4 lignin removal is dominant while pH=4-6 better supports bleaching.

- The pH curve during the chlorine dioxide bleaching process is favouring either lignin removal (pH<~4) or brightness development at pH>~4.
- In this graph you can see that pH regulation with NaOH has a quite short optimal pH window for bleaching.
- Using Mg(OH)$_2$ opens a much longer optimal pH-window for brightness development.
- The consequence is a better brightness development or as a direct consequence a possible reduction of ClO$_2$. 

![Graph showing pH regulation and brightness development](image)
Another positive impact of magnesium hydroxide is the **lower frequency of hard deposits**.

The presence of magnesium ions has a very positive effect on the reduction of oxalate deposits so that the **use of Magnesium ions for deposit reduction even was patented in 1996!**

In a thesis it was demonstrated that 18% or less of the oxalate was in the precipitated form when Magnesium ions were present, while around 58% of the oxalate were precipitated as calcium oxalates in the absence of magnesium.

The much higher solubility of magnesium oxalate in combination with a higher affinity to oxalate than calcium explains why **the presence of magnesium in the bleaching process can significantly reduce harmful calcium oxalate deposits** in pulp mills by forming more soluble magnesium salts.
Mg(OH)$_2$ supports environmental targets

The United Nations Department of Economic and Social Affairs have defined a number of goals for a sustainable development. The use of Mg(OH)$_2$ in the bleaching process fits well to several of these targets:

**Mg(OH)$_2$ reduces organic substances in effluents** measured as COD. This keeps our rivers, lakes and oceans cleaner which is supporting the UN goals n° 6 “reducing pollution and minimizing release of hazardous chemicals” and n° 14 “reduce marine pollution of all kinds, in particular from land-based activities”

**Mg(OH)$_2$ helps to reduce the use of hazardous chemicals** which is well in line with some objectives as they are defined in the UN goal n° 12 “environmentally sound management of chemicals”

**Mg(OH)$_2$ increases the pulp yield** per ton of wood used. This is linked to a reduced COD creation and a better fibre protection that keeps the viscosity high. This better yield leads directly a lower demand of wood and is well in line with targets of the UN goal n° 15 “sustainable management of all types of forests”
Commercial drivers to use Mg(OH)$_2$

- Magnesium hydroxide can reduce chemical costs depending on local situation
  - As 1.0 kg Mg(OH)$_2$ can substitute 2.0 kg MgSO$_4$ plus 1.4 kg NaOH in most cases this is enough to save costs in such recipe.
  - In addition the better bleaching efficiency quite often leads to additional savings on hydrogen peroxide and chlorine dioxide, both costly bleaching chemicals

- As magnesium hydroxide causes a higher yield it consequently lowers wood consumption
  - the lower wood consumption not only saves money on the wood supply itself but also in the cooking process and following bleaching steps that work more efficient. Even only 1% higher yield has a huge impact considering annual productions of 1 million tons or more per mill!

- Lower fees for water emissions are a consequence of reduced COD with magnesium hydroxide
  - In some countries (e.g. Germany) mills have to pay fees depending on their COD emissions. A 25% to 40% reduction of COD creation has a potential for significant savings here.

- The reduction of oxalate deposits is another benefit where magnesium hydroxide can save costs for a mill due to lower cleaning costs and less down time caused by deposits in production equipment
Summary and Conclusions

- Magnesium hydroxide has shown numerous benefits in chemical pulp bleaching
  - It leads to a lower chemical consumption in several bleaching stages
  - It helps to increase the brightness achieved over the full process
  - It participates in the reduction of deposits especially calcium oxalate
  - It causes a higher yield by reducing the solubilisation of cellulose
  - It reduces the COD load in mill effluents
  - It helps to gain a higher viscosity hence better strength properties of the final pulp

Some or all of above benefits were always the drivers for the pulp mills in Europe and South America that started to implement magnesium hydroxide use in their bleaching process in the last few years.
Thank You very much

for your attention!