INTRODUCTION

- Esa Vakkilainen: Leading Technology Specialist – Recovery
- Explanation of what recovery department of Bell Bay Pulp Mill does
- Recovery of Bell Bay pulp mill is accepted modern technology (AMT) and best available technology (BAT)
- All the pictures shown in the following presentation are indicative of the used technology, but details are specific to individual vendor design
Recovery systems are the core component of a kraft pulp mill. The three purposes of recovery systems are:

- Regeneration of chemicals used in cooking
- Destruction of waste streams generated elsewhere in the mill
- Production of steam for turbine and process

**RECOVERY CYCLE MISSION**

**RECOVERY CYCLE**

**RECOVERY CYCLE**
TERMINOLOGY

- “weak black liquor” is liquor from the brown stock washing, usually 14-20 % ds
- “strong black liquor” is high concentration liquor from the evaporation, usually >70 % ds
- “green liquor” is solution from the recovery boiler containing chemicals mixed with water
- “white liquor” is solution containing regenerated chemicals to be used in cooking
- “lime” is a solid stream containing mainly CaO
- “lime mud” is a solid stream containing mainly CaCO₃

BASIC CHEMICAL REACTIONS DURING COOKING

- To properly appreciate the purpose of the recovery system it is necessary to understand the basic chemical reactions that facilitate the generation of cooking chemicals used in the pulping process
- The proposed mill uses sodium compounds as the main cooking chemical
- The sodium compounds are first introduced (with chips and water and additional heat) in the digester where cooking occurs
- The active agents in the cooking process are sodium hydroxide (lye) and sodium sulfide
- During the cooking process, which causes the separation of fibres from the wood chips, these active chemicals became inactive sodium compounds such as sodium carbonate (washing soda), sodium sulfate (Glauber’s salt) and others

THE PURPOSE OF THE RECOVERY SYSTEM

- The purpose of the recovery system is to return the inactive sodium compounds at the end of the cooking process into active compounds that can be reused at the beginning of the cooking process
- The active sodium compounds take their present form in white liquor that comes from the causticizing plant
- The inactive sodium compounds are first introduced to the recovery system as part of the weak black liquor that is emitted from the cooking process
**Terminology**

The active sodium chemicals in the cooking process are referred to as alkali.

The total alkali represents all sodium compounds present in the liquor.

The active alkali represents those sodium compounds that are the main cooking agents.

The effective alkali is a term used to describe the relative strengths of sodium compounds as cooking agents – e.g., in the case of sodium sulfide it is only half the amount of the substance that is effective in the cooking process.

<table>
<thead>
<tr>
<th>Total alkali</th>
<th>NaOH+Na₂CO₃+Na₂S+Na₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>or all Na-compounds</td>
</tr>
<tr>
<td>Active alkali</td>
<td>NaOH + Na₂S</td>
</tr>
<tr>
<td>Effective alkali</td>
<td>NaOH + ½ Na₂S</td>
</tr>
</tbody>
</table>

**Cooking – Alkali and Woodchip Volumes**

- Leaving aside temperature and time of cooking, the successful cooking process is dependent upon achieving a correct balance between the volume of wood chips and the amount of effective alkali.

- Too little alkali will result in uncooked pulp or pulp that has a higher lignin residue which can only be removed through higher chemical loads in the bleaching phase.

- Too much alkali will result in overcooked pulp which damages the fibres.

**Black Liquor**

- Weak black liquor is produced in the cooking process and is separated from the fibres in the washing stage where it is pumped from washers at 14 – 16 % dry solids concentration

- Several small streams are added to or removed from the black liquor:
  - soap (softwood only) + residue from chemicals manufacture
  - NCG + biosludge + ash

- Concentrated to strong black liquor leaves the evaporation process at 80 % dry solids

- Black liquor contains:
  - Water
  - Organic residue from pulping (that part of wood that does not end up as pulp)
  - Inorganic cooking chemicals (mostly spent)
COMPOSITION OF BLACK LIQUOR

The chemical compounds that make up solids in black liquor are as follows:

<table>
<thead>
<tr>
<th>Organic</th>
<th>Weight % by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orgamics (including organic Na and S)</td>
<td>78</td>
</tr>
<tr>
<td>Degraded lignin</td>
<td>37.5</td>
</tr>
<tr>
<td>Isosaccharine acids</td>
<td>22.6</td>
</tr>
<tr>
<td>Aliphatic acids</td>
<td>14.4</td>
</tr>
<tr>
<td>Resin and fatty acids</td>
<td>0.5</td>
</tr>
<tr>
<td>Polysaccharides</td>
<td>3.0</td>
</tr>
<tr>
<td>Inorganics</td>
<td>22</td>
</tr>
<tr>
<td>NaOH</td>
<td>2.4</td>
</tr>
<tr>
<td>NaHS</td>
<td>3.6</td>
</tr>
<tr>
<td>Na2CO3 and K2CO3</td>
<td>9.6</td>
</tr>
<tr>
<td>Na2S2O3 and Na2SO3 and Na2Sx</td>
<td>5.2</td>
</tr>
<tr>
<td>Na2SO4 and K2SO4</td>
<td>0.5</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.5</td>
</tr>
<tr>
<td>Non process elements (Si, Al, Fe, Mn, Mg, etc.)</td>
<td>0.2</td>
</tr>
</tbody>
</table>

COMPOSITION OF EUCALYPTUS BLACK LIQUOR

Black liquor solids is comprised of the following elements:

<table>
<thead>
<tr>
<th>Element</th>
<th>Typical</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon, %</td>
<td>34.8</td>
<td>33 - 37</td>
</tr>
<tr>
<td>Hydrogen, %</td>
<td>3.3</td>
<td>2.7 - 3.9</td>
</tr>
<tr>
<td>Nitrogen, %</td>
<td>0.2</td>
<td>0.1 - 0.6</td>
</tr>
<tr>
<td>Oxygen, %</td>
<td>35.5</td>
<td>33 - 39</td>
</tr>
<tr>
<td>Sodium, %</td>
<td>19.1</td>
<td>16.2 - 22.2</td>
</tr>
<tr>
<td>Potassium, %</td>
<td>1.8</td>
<td>0.4 - 9.2</td>
</tr>
<tr>
<td>Sulfur, %</td>
<td>4.1</td>
<td>2.4 - 7.0</td>
</tr>
<tr>
<td>Chlorine, %</td>
<td>0.7</td>
<td>0.1 - 3.3</td>
</tr>
<tr>
<td>Inert, %</td>
<td>0.5</td>
<td>0.2 - 3.0</td>
</tr>
</tbody>
</table>

STRONG BLACK LIQUOR

Strong black liquor is comprised of the following elements:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>g/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>19</td>
</tr>
<tr>
<td>K</td>
<td>1.6</td>
</tr>
<tr>
<td>S2-</td>
<td>1.93</td>
</tr>
<tr>
<td>CO3-</td>
<td>6.2</td>
</tr>
<tr>
<td>SO3-</td>
<td>0.1</td>
</tr>
<tr>
<td>H</td>
<td>3.3</td>
</tr>
<tr>
<td>N</td>
<td>0.1</td>
</tr>
<tr>
<td>Heating value, HHV MJ/kgds</td>
<td>14.0</td>
</tr>
</tbody>
</table>

Figures are given to show indicative magnitude of the various chemical compounds.
FROM BLACK TO WHITE LIQUOR

- The strong black liquor that comes from the evaporator fuels the recovery boiler.
- The recovery boiler is also fuelled by a number of other sources (eg NCG, methanol, occasionally natural gas etc).
- Everything that is not destroyed in the recovery boiler becomes smelt, which takes the form of a hot molten ash flow.
- The smelt is mixed with weak white liquor from the causticizing plant to produce green liquor.
- The green liquor reacts with lime in the slaker to produce:
  - Lime mud; and
  - White liquor.
- The lime mud goes to the lime kiln where it is returned to lime.
- The white liquor goes to the digester at the beginning of the cooking process – completing the regeneration of the alkali compounds.

TERMINOLOGY

The efficiency of the process of regenerating black liquor (post cooking) to reusable white liquor (at the start of the cooking process) is measured by the ratio of active sodium cooking agents produced from the total amount of sodium compounds arriving into the recovery system.

This ratio can be monitored at various stages in the recovery process (some continuously and others by sample).

Causticizing efficiency  \[ \frac{\text{NaOH}}{\text{NaOH} + \text{Na}_2\text{CO}_3} \]

Reduction efficiency  \[ \frac{\text{Na}_2\text{S}}{\text{Total S}} \]

DEPARTMENTS AND STREAMS DISCUSSED

MAJOR DEPARTMENTS
- Evaporation
- Recovery boiler
- Lime kiln
- Causticizing
- Power boiler
- NCG collection

MINOR DEPARTMENTS
- Cl-K removal
- Condensate stripping
- Spill collection
- Methanol liquefaction
- Soap removal (with softwood only)

MAJOR STREAMS
- Weak black liquor
- Strong black liquor
- Smelt
- Green liquor
- White liquor
- Lime
- NCG
- CNCG
- Water
- Steam
Evaporation of weak black liquor to separate water and create a combustible product – strong black liquor.

The three main processes that occur in the evaporator are:

- Black liquor + Heat ➔ Strong Black liquor + Water + Steam
- Condensate + Steam ➔ Clean + Dirty condensate + NCG
- Black liquor ➔ Black liquor + Soap (only soft wood)
HOW EVAPORATOR EFFECT WORKS

Steam to previous effect

Heat evaporates water (=steam) from black liquor

Drier black liquor is removed

Steam from previous effect

Steam condenses releasing heat

Condensates are removed

OPERATION OF AN EVAPORATOR EFFECT

Steam from previous effect

Condensate to either process or stripper

Steam to next effect

Black liquor from lower solids effect

Black liquor to higher solids effect

EVAPORATION
The Evaporation plant carries on a number of simultaneous processes which as well as producing strong black liquor for the recovery system, includes:
- Separation from the black liquor of:
  - Soap (only in softwood production)
  - Turpentine
  - Methanol
- Production of clean condensate for mill use e.g. washing of lime mud

These processes are undertaken in a way that maximizes the efficient use of energy e.g. as evaporation is done in stages which allows 1 kg of steam to evaporate more than 7 kg of water.

“condensates” are liquids produced from vapour when they are cooled by condensation. They comprise mainly of water.
- Clean condensates are formed when pure steam condenses.
- Foul condensates are formed when steam originating from black liquor is cooled.
FOUL CONDENSATE FORMATION

- Each time black liquor is evaporated it forms steam that may be used at another stage in the process.
- When that steam is cooled it condenses to form a liquid that contains mainly water with some other substances that condense at the same temperature as water.
- There are three main places in the pulp mill where foul condensates are formed:
  - Evaporation plant;
  - NCG handling; and
  - In cooking.
- In each of these three cases the condensate contains TRS and volatile carbohydrates (e.g. methanol) and as a result the condensate has a level of odour depending the composition.
- Cleaner condensate fractions are reused in parts of the mill processes that are not sensitive to slight contamination (e.g. pulp washing).
- All other foul condensate (smelly) streams are fed to the stripper where they are cleaned.

CONDENSATE HANDLING

TREATMENT OF FOUL CONDENSATES

- Foul condensates are produced at
  - digester
  - evaporation
  - condensing in NCG lines
- Foul condensates contain
  - methanol
  - malodorous sulfur compounds
  - turpentine
  - red oil (eucalyptus only)
  - water
- Steam is used in the stripper to remove contaminants
- Evaporator and stripper are integrated to get better heat economy.
SOFT WOOD PRODUCTION ONLY - SOAP SEPARATION

SPILL COLLECTION
- Mill is designed to collect all spills
- Each department has a spill recovery system, which will recover all contaminated spills, emptying equipment or tanks to a spill liquor sump
- Spills from sumps pumped to spill collection tank $4500 \text{ m}^3$
- Weak liquor tanks have typically spare capacity to store spills or liquors from departments under maintenance.

OBJECTIVES OF EVAPORATOR
- Use of AMT and BAT technology
- Final black liquor concentration high enough to minimize SO$_2$ and TRS emissions
- Capacity large enough to accommodate spills
- High number of effects for energy efficiency
BELL BAY EVAPORATOR

- Seven+ effects for good steam economy
- Weak BL dry solids design 13.4 % (low to give reserve)
- Strong BL dry solids 80 % (with ash)
- Integrated stripper
- Possibility to handle biosludge
- Possibility to separate soap during softwood operation
- 10 % additional capacity reserve to process spills
- Enclosed methanol treatment to minimize odour

RECOVERY BOILER

Refer to Volume 6: “3.8.5 Recovery Boiler” p. 75

Mission –
- Combustion of organics (lignin, hydrocarbons, organic acids etc) in black liquor
- Regeneration of chemicals
- Production of heat and power
ADDITIONAL TERMINOLOGY

• “air” is air drawn from the atmosphere by fans for combustion
• “firing liquor” is high concentration strong black liquor from evaporation, stored at 80 % dry solids
• “flue gases” are gaseous the products of combustion
• “smelt” is a molten chemical ash from recovery boiler
• “vent gases” comprise a mixture of water vapor and air from dissolving tank
• “ash” is a solid stream of mostly sodium salts

RECOVERY BOILER

The four main processes that occur in Recovery Boiler are:

\[
\begin{align*}
\text{C} + \text{O}_2 & \rightarrow \text{CO}_2 + \text{Heat} \\
\text{Na}_2\text{SO}_4 + 2\text{C} & \rightarrow \text{Na}_2\text{S} + 2\text{CO}_2 \\
\text{H}_2\text{S} + 1.5\text{SO}_2 & \rightarrow \text{SO}_3 + \text{H}_2\text{O} \\
2\text{NaOH} + \text{SO}_2 + 0.5\text{O}_2 & \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}
\end{align*}
\]

RECOVERY BOILER - STEAM

Steam generated by the recovery boiler is used in series:

- To power the turbo generator unit supplying electricity to the whole of the mill (with potential for some power to be sold on the grid); and
- As the source of clean steam servicing a variety of other mill processes across the whole of the mill.
RECOVERY BOILER IN SWEDEN

FIRING LIQUOR TO FURNACE

COMBUSTION AIR AND FLUE GAS
BLACK LIQUOR AND ASH

• Bell Bay Recovery 43
• Electrostatic precipitator 1
• Electrostatic precipitator 2
• TIC
• LIC
• Firing liquor storage
• Furnace
• Mix tank
• Boiler bank
• Economiser
• Dump tank
• Spill liquor
• Strong liquor from evaporation plant
• Intermediate liquor from/to concentrator
• Electrostatic precipitator 3
• Vent to DNCG Scrubber
• Vent to DNCG Scrubber
• Steam

BLACK LIQUOR SYSTEM

• Black liquor concentrated to 80 % dry solids
• Pressurized liquor tank used to store as fired liquor
• Separate liquor loop to collect ESP and BB ash and mix it in the evaporator with evaporated liquor
• Strong black liquor fired to the boiler through liquor guns

OPTIMUM FIRING REQUIREMENTS

• Selection of suitable air pattern
• Selection of suitable liquor gun operating parameters; type, pressure, temperature
• Adjusting for changes in liquor properties
ELECTROSTATIC PRECIPITATORS

MIXING TANK
- Black liquor sprayed to the top
- BB, ECO and ESP salt ash dropped from the top
- Rotating rotor with blades mixes ash with black liquor

FURNACE FLOOR
- Smelt out Frozen smelt layer
DISSOLVING TANK

- Molten smelt drops to the dissolving tank
- Smelt is dissolved in water
- Dissolving is a violent action with noise, heat and vibration
- Weak white liquor is introduced to the tank to replace lost liquid
- The combination is green liquor which then goes to the causticizing plant

**Green liq.**

Smelt

Weak WL

Vent gases

DISSOLVING TANK

**Smelt**

Smelt is comprised of the following elements and chemical compounds:

- Na, g/kgds: 416.5
- K, g/kgds: 72.1
- Cl, g/kgds: 118.1
- C, g/kgds: 8.78
- N, g/kgds: 74.1
- O, g/kgds: 245.2
- Na₂S, g/kgds*: 3.12
- Na₂CO₃, g/kgds*: 592.9
- Na₂S₂O₃, g/kgds*: 692.9
- Na₂SO₄, g/kgds*: 23.7

*both sodium and potassium salts, presented as sodium salts

Figures are given to show indicative magnitude of the various chemical compounds.
OBJECTIVES OF RECOVERY BOILER

- Use of AMT and BAT technology
- Final black liquor concentration high enough to minimize SO2 and TRS emissions
- Possibility of handling biosludge and soap
- Possibility of firing 100 % CNCG
- Possibility of firing 100 % DNCG
- After consultation and review the further objective of minimizing dust emissions below AMT was emphasized

TYPICAL RECOVERY BOILER

- pressure 85 bar
- steam temp 480 °C
- capacity 2400 tds/d
- improved air system
- stationary firing
- single drum construction

BELL BAY RECOVERY BOILER

- pressure 104 bar
- steam temp 505 °C
- capacity 4100 tds/d
- multi level air
- firing of CNCG
- firing of DNCG
- firing of DTVG
- firing of biosludge
- very high dry solids 80 %
- target dust 30 mg/m³
- target TRS <1 ppm
RECAUSTICIZING

Refer to Volume 6: "3.8.6 Recausticizing" p. 78

Mission –
Production of white liquor for cooking by converting sodium carbonate to hydroxide with lime and removal of non process elements

This image is indicative only and does not purport to show all features of AMT technology.
**ADDITIONAL TERMINOLOGY**

- “green liquor dregs” are solids separated from green liquor by filtration
- “slaker grits” are solids separated during lime addition
- “burnt lime” is a solid stream from lime kiln containing mainly CaO
- “makeup lime” is an incoming solid stream containing mainly CaO
- “secondary condensates” are condensates from the evaporator plant containing mainly water

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**RECAUSTICIZING**

The three main processes that occur in Recausticizing are:

\[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \]

\[ \text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow 2\text{NaOH} + \text{CaCO}_3 \]

- solids in liquor → solids + liquor

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**RECAUSTICIZING**

There are three processes undertaken in the recausticizing stage:

- Cooking liquor is produced from green liquor by adding slaked lime which produces white liquor and lime mud (calcium carbonate)
- Lime mud (calcium carbonate) is fed into lime kiln to produce lime
- Process residue is purged as dregs and grits
RECAUSTICIZING UNIT OPERATIONS

- Smelt dissolving tank (in recovery boiler area)
  Molten smelt from recovery boiler and weak white liquor are mixed to produce green liquor
- Raw green liquor stabilization tank
  Variations in green liquor composition are reduced by sufficient retention time
- Green liquor filtration
  Particles in green liquor are removed by filtration
- Slaker
  Lime and green liquor are mixed to produce white liquor
- Causticizers
  Three or more agitated tanks in series are used to ensure as complete a reaction as possible
- White liquor filtration
  Lime mud is separated from white liquor by filtration

GREEN LIQUOR HANDLING
GREEN LIQUOR, CLARIFIED GREEN LIQUOR, DREGS

Green liquor is comprised of the following elements and chemical compounds:

- Na, g/kgds: 90.8
- K, g/kgds: 14.5
- SNa, g/kgds: 24.1
- ClNa, g/kgds: 1.9
- S-, g/kgds: 19.1
- NaOH, g/kgds: 18.8
- Na₂S, g/kgds: 42.7
- Na₂CO₃, g/kgds: 134.9
- Na₂SO₃, g/kgds: 1.41
- Na₂SO₄, g/kgds: 7.08
- Na₂S₂O₃, g/kgds: 8.7
- Total alkali, g NaOH/l: 165.2
- Active alkali, g NaOH/l: 62.7
- Effective alkali, g NaOH/l: 40.7

Figures are given to show indicative magnitude of the various chemical compounds.

DISTRIBUTION OF ELEMENTS IN GREEN LIQUOR

<table>
<thead>
<tr>
<th>Element</th>
<th>% dissolved</th>
<th>% in dregs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>&gt;97</td>
<td>&lt;3</td>
</tr>
<tr>
<td>K</td>
<td>&gt;97</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Cl</td>
<td>&lt;100</td>
<td>&lt;0</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;3</td>
<td>&gt;97</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;6</td>
<td>&gt;94</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;11</td>
<td>&gt;89</td>
</tr>
<tr>
<td>Al</td>
<td>92</td>
<td>8</td>
</tr>
<tr>
<td>Si</td>
<td>99.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Analysis is given to show indicative magnitude of various chemical compounds.
REMOVAL OF ELEMENTS FROM GREEN LIQUOR

<table>
<thead>
<tr>
<th></th>
<th>Raw green liquor</th>
<th>Filtered liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium (Ca) mg/l</td>
<td>53</td>
<td>1.3</td>
</tr>
<tr>
<td>Magnesium (Mg) mg/l</td>
<td>90</td>
<td>17</td>
</tr>
<tr>
<td>Iron (Fe) mg/l</td>
<td>17</td>
<td>66</td>
</tr>
<tr>
<td>Manganese (Mn) mg/l</td>
<td>18</td>
<td>23</td>
</tr>
<tr>
<td>Copper (Cu) mg/l</td>
<td>1.3</td>
<td>0.88</td>
</tr>
<tr>
<td>Phosphate (P) mg/l</td>
<td>43.5</td>
<td>41.2</td>
</tr>
</tbody>
</table>

Ref: Chemical pulping, Gullischen and Fogelholm

GREEN LIQUOR FILTRATION

- Green liquor contains usually 800-1200 ppm of impurities called dregs
- Impurities originate from raw material sources, primarily wood chips
- Dregs contain almost all the minerals in the wood
- Dregs only place where these minerals are removed
- Often separate stabilization tank to minimize variations in:
  - density
  - temperature
  - flow
- Storage after filtration
PRINCIPLE OF CROSS FILTRATION

- Liquid flows downward on the surface of the filter element.
- Pressure difference is maintained across filter element such as $P_1 > P_2$
- Liquid is forced through filter element by pressure difference
- Particles in the liquid stream experience two forces
  - Downward force $F_f$
  - Sideways force $F_p$
- If particle cross section $A_f$ is larger than filter element cross section $A_p$ then particle is trapped on the surface of the filter element

NPE'S IN RECOVERY CYCLE

Analysis is given to show indicative magnitude of various chemical compounds.
PROCESS STEPS

- Once green liquor is produced to a stabilized concentration it is mixed with lime and the slaking process commences.
- The lime reacts with the water in the green liquor producing slaked lime.
- Slaking occurs in a short time
- Slaked lime then begins to react with sodium carbonate in the green liquor which produced lime mud and sodium hydroxide (white liquor).
- This second reaction is called causticizing and occurs in the causticizing tanks, long residence time needed to complete reactions.
- The lime mud goes to the lime kiln to produce lime.
- The white liquor is then used in the digester.

LIME FEEDER

LIME SLAKER
SLAKING CHEMISTRY

A. Slaking in water
B. Slaking in green liquor

CAUSTICIZING CHEMISTRY

- Slaking  \[ \text{CaO} (s) + \text{H}_2\text{O} (aq) \leftrightarrow \text{Ca(OH)}_2 (s) \]
  \[ +1130 \text{ kJ/kg CaO} \]

- Causticizing  \[ \text{Ca(OH)}_2 (s) + \text{Na}_2\text{CO}_3 (aq) \leftrightarrow 2\text{NaOH} (aq) + \text{CaCO}_3 (s) \]
  \[ -560 \text{ kJ/kg CaO} \]

CAUSTICIZERS
DREGS FILTER

DREGS WASHING
- 3-8 % of suspended solids in green liquor
- Sodium recovery
- Drum filter with precoat
  - Coating with lime mud of 50-10 mm thick
  - dry solids 40 – 50 %

DREGS FILTER, FINLAND
WHITE LIQUOR

- Final product from causticizing system
- Cooking chemical to the digester
- Active ingredients NaOH and Na₂S

WHITE LIQUOR TYPICAL ANALYSIS

White liquor is comprised of the following elements and chemical compounds:

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (g/kgds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>78.0</td>
</tr>
<tr>
<td>K</td>
<td>14.1</td>
</tr>
<tr>
<td>S₄O₆²⁻</td>
<td>22.4</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>1.7</td>
</tr>
<tr>
<td>S²⁻</td>
<td>18.0</td>
</tr>
<tr>
<td>NaOH</td>
<td>88.2</td>
</tr>
<tr>
<td>Na₂S</td>
<td>41.8</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>40.3</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.1</td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>0.99</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>8.99</td>
</tr>
<tr>
<td>Total alkali, g NaOH/l</td>
<td>161.6</td>
</tr>
<tr>
<td>Active alkali, g NaOH/l</td>
<td>131.2</td>
</tr>
<tr>
<td>Effective alkali, g NaOH/l</td>
<td>109.8</td>
</tr>
</tbody>
</table>

Analysis is given to show indicative magnitude of various chemical compounds.
OBJECTIVES OF CAUSTICIZING

- Use of AMT and BAT technology
- High active alkali concentration
- High causticity
- High reduction
- Clean white liquor to minimize chemical consumption
- Efficient lime mud washing

CAUSTICIZING IN BELL BAY

- White liquor active alkali (NaOH) g/l 136
- White liquor sulfidity % 32
- Causticity % 82
- Reduction efficiency % 95
- Green liquor filtration
- White liquor filtration
- Capacity m³WL/d 10 000

LIME KILN

Refer to Volume 6: "3.8.7 Lime Kiln" p. 79
The two main processes that occur in Lime Kiln are:

- Lime mud + Heat → \( \text{CaCO}_3 \) + vapour
- \( \text{CaCO}_3 \) + Heat → \( \text{CaO} \) + \( \text{CO}_2 \)
LIME PRODUCT QUALITY

- Ideal reburnt lime forms soft pebbles of approx. 2 cm in diameter pebbles
- Reburnt lime quality is judged in terms of:
  - availability - refers to the fraction of lime (as CaO) in the reburnt lime product
  - residual calcium carbonate
  - reactivity
  - particle size

<table>
<thead>
<tr>
<th></th>
<th>Fresh lime</th>
<th>Reburnt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, kg/l</td>
<td>1.6</td>
<td>&gt;2.2</td>
</tr>
<tr>
<td>Porosity, %</td>
<td>50</td>
<td>&lt;34</td>
</tr>
<tr>
<td>Surface area, m²/g</td>
<td>&gt;1.0</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Reactivity, °C/min</td>
<td>&gt;10</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>

From, Adams, 1997

LIME KILN FUELS

- natural gas
- fuel oil (not burned due to environmental reasons)
- hydrogen
- odorous gases (option)
- methanol (option, methanol burning decreases CO₂ from mill)
PHOSPHOROUS

- Phosphorous
  - is one of the elements that is present in the woodchip at the start of the process.
  - does not react at any stage in the recovery process – in other words it survives the evaporation and boiler.
  - forms calcium phosphate by reacting with lime during the causticizing stage.
- Over time the build up of calcium phosphate affects the efficiency of the lime production and must be removed.
- This calcium phosphate can be commercially disposed of along with lime kiln ESP dust as fertiliser, however in the Bell Bay case it has been counted as a solid waste to the landfill.

PHOSPHOROUS IN LIME CYCLE

DUST REMOVAL
LIME MUD DRYER

Fitting several burners to lime kiln

POWER BOILER

Refer to Volume 6: "3.8.9 Power Boiler" p. 81
The two main processes that occur in Power Boiler are:

- Biofuel + Air → Steam + Flue gas
- Waste stream + Air → Flue gas

POWER BOILER - STEAM

- Steam generated by the power boiler is used in series:
  - To power the turbo generator unit supplying electricity to the whole of the mill (with potential for some power to be sold on the grid); and
  - As the source of clean steam servicing a variety of other mill processes across the whole of the mill.
- Power boiler produces about 20% of the mill’s steam production.
**TERMINOLOGY**

- "HP steam" refers to high pressure steam from power boiler
- "Feedwater" refers to demineralized water
- "Biofuel" refers to sawdust, forest residue and fines
- "Air" refers to air drawn in by fans and used for combustion
- "Flue gases" refers to gaseous product of combustion of biofuel and air
- "Ash" refers to solid residue from combustion

**COMBUSTION IN BFB**

![Diagram of combustion in BFB]

**HYDROBEAM GRATE**
OBJECTIVES OF POWER BOILER

- Use of AMT and BAT technology
- Possibility to burn various fuels
  - fines from screening
  - Sawdust
  - forest residues
  - dewatered primary effluent sludge
- Big enough to start the mill
- After consultation and review the objective to minimize dust emissions below AMT was emphasized

BELL BAY POWER BOILER

- Bubbling fluidized boiler (BFB) with
  - Good turn down capability
  - Possibility to burn efficiently variety of fuels
- Main steam pressure 104 bar
- Main steam temperature 505 °C
- Steam generation capacity 55 kg/s
- Target dust 30 mg/m³
TURBOGENERATOR

Refer to Volume 6: "3.8.8 Turbogenerator" p. 80

TURBO GENERATOR

• The main source of electricity within the mill is derived from the
turbogenerator that is powered by steam created at the:
  - Recovery Boiler (80%); and
  - Power Boiler (20%).

• The turbogenerator is capable of producing more electricity than is
required to power the mill. The surplus is capable of being sold onto
the national grid.

TERMINOLOGY

• "HP steam" is high pressure steam from recovery boiler and
  power boiler
• "MP steam" comprises a number of medium pressure steam flows
  used in e.g. Sootblowing, cooking and air preheating
• "LP" is low pressure steam used all over the mill and especially in
  evaporating and pulp drying
• "Condensate" is here referring to clean condensate from fully
  expanded steam
The turbogenerator is a Back-pressure turbine which has a condensing tail and includes the following key features:

- Medium pressure extractions for various small steam users
- Low pressure extraction for main steam users
- Condensing tail for extracting electricity from extra steam (not used in the process)
- Expanding steam rotates generator which produces electricity
**TURBOGENERATOR IN BELL BAY**

- Inlet steam pressure: bar (a) 100
- MP3 bleed pressure: bar (a) 30
- MP2 bleed pressure: bar (a) 22
- MP1 extraction pressure: bar (a) 10
- Lower extraction pressure: bar (a) 4.5
- Condensing pressure: bar (a) 0.06
- Net output: MW 190

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**MALODOROUS GAS HANDLING (DNCG, CNCG)**

Refer to Volume 1: 6-329

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**BELL BAY NCG GAS DESTRUCTION OBJECTIVES**

- Collection of all DNCG from every department
- Collection of all CNCG from every department
- Three possible places to burn CNCG
- Three possible places to burn DNCG
- Use of AMT and BAT technology
- After consultation and review, the objective to minimize smell occurrences to fewer than AMT was emphasized
**TERMINOLOGY**

- "DNCG" refers to dilute non-condensable gases
  - DNCG is almost pure air with some smelly components
  - DNCG transported by fans
  - DNCG creates hazard if contaminants are enriched
- "CNCG" refers to concentrated non-condensable gases
  - CNCG has high heating value
  - CNCG transported by steam ejectors
  - CNCG creates hazard if diluted with air
- "condensates" refers streams of mainly water some of which contain impurities

**CNCG COLLECTION**

- Sources of CNCG are:
  - Evaporation plant surface condenser
  - Cooking plant
  - Stripping column
  - Foul condensate tank
  - Firing liquor tank
  - Concentrator (option)

- The path of CNCG from the source to the burners passes through water seal to prevent back flow;
- CNCGs are transported by steam ejector to avoid the risk of exposure to sparks;
- Stripper gases are transported separately because they contain flammable turpentine; and
- Pipelines and equipment are safeguarded with necessary vacuum / pressure relief devices.
BELL BAY CNCG DESTRUCTION

- Two units continuously in line
- Mainly burned in recovery boiler
- Some CNCG burned in NCG boiler to keep it warm and to make NaHSO₃
- Malfunction in RB -> CNCG turned to dedicated NCG boiler
- Malfunction in dedicated NCG boiler -> all CNCG burned in recovery boiler
- Third tier -> CNCG burned in spare NCG boiler

BELL BAY NCG DESTRUCTION UNITS

- Recovery boiler
  - CNCG (main capacity 100%)
  - DNCG (main capacity 100%)
  - Methanol (small capacity 100%)
- NCG boiler
  - CNCG (some, spare capacity 100%)
  - DNCG (during shutdown, spare capacity 50%)
  - Methanol (main capacity 100%)
- Spare NCG boiler
  - CNCG (spare capacity 100%)
  - DNCG (spare capacity 50%)
- Lime kiln
  - DNCG (option, some)
  - Methanol (option)
- Power boiler
  - DNCG (spare capacity 100%)
- Stack
  - Separate inner stacks for DNCG and CNCG
BURNING OF CNCG - FLAME TUBE BOILER

- Independent of pulp production operations
- Sulfur may be removed from the pulp process
- Medium pressure steam production is possible
- Design pressure is 20 bar to avoid acid dew point
- Saturated steam produced
- Burner is a multi-fuel burner, which is suitable for burning support fuel together with strong gases

CNCG IN RECOVERY BOILER

- Dedicated nozzles to NCG, methanol and turpentine
- Placed in front wall
- In lower furnace
- Easy access

BURNING OF CNCG - FLUE GAS CLEANING

- Effective sulfur dioxide and dust removal from the gas
- Generation of sodium bisulfite for bleach plant pH-control
COLLECTION OF DNCG

- Collection points
  - All sulfur containing vents

- Handling
  - Gases are cooled and the moisture is removed before taking them to the incineration
  - The pipelines and equipment are safeguarded with necessary vacuum/pressure relief devices

DNCG TREATMENT SYSTEM

- Boiler building
- Chip bin
- Causticizing Tank farm
- Fiber line
- Condensing scrubber
- Collection fan
- Booster fan
- Supplement air heater
- Liquor clarifiers
- Evaporator plant
- Stack
- NCG boilers
- Power boiler
- Recausticizing

DNCG SCRUBBING

- Fibers are removed
- Gases are cooled
- Moisture removed
- Three main impurities
  - water soluble solid particles, e.g. from evaporation tank area
  - insoluble solid particles, e.g. from recausticizing
  - fibers from the fiber line sources
DILUTED NCG SAFETY FEATURES

The DNCG destruction system contains the following safety features:
- Dedicated nozzles for injection of DNCG into the furnace;
- Separation valves allowing rodding to facilitate removal of ash; and
- Condensate removal from lines

VENT GAS FROM DISSOLVING TANK Special Case

- This gas is formed when smelt falls into the dissolving tank at the base of the recovery boiler. This gas does not smell but it does contain some TRS and for this reason it has to be dealt with in the following way:
  - Fan draws vent gas from dissolving tank
  - Condenser used to reduce moisture
  - Scrubber used to reduce particulate content
  - Combined with hot air
  - Fan blows air/gas mixture to furnace and is burnt with other DNCGs
Apart from its role in the recovery system, the recovery boiler also forms part of another critical system in the mill – the destruction of waste streams generated by different processes across the whole of the mill.

In normal operating conditions there are two places for the destruction of NCGs:
- Recovery boiler; and
- NCG incinerator.

The are two categories of NCG:
- Diluted NCGs (DNCGs); and
- Concentrated NCGs (CNCGs)

CNCGs can be burnt at any time in both the recovery boiler and the NCG incinerator.
DNCGs are burnt only in the recovery boiler.

In the event of failure of the recovery boiler:
- DNCGs are redirected to the power boiler for incineration. There is also the capacity for destruction of DNCGs in the lime kiln if they are produced in close proximity to the kiln;
- CNCGs continue to be burnt in the main NCG incinerator but in addition a second incinerator is activated so that the capacity for destruction of CNCGs is not reduced.

In the event of a failure of the main NCG incinerator, the second incinerator will work in tandem with the recovery boiler;

In the event that both the recovery boiler and the main NCG incinerator have failed:
- DNCGs will be burnt in the power boiler; and
- CNCGs will be burnt in the second NCG incinerator.

Both the recovery boiler and both NCG incinerators have built in over design capacity.
HIGH AVAILABILITY

- Compared to other mills, the Bell Bay mill has high availability.
  - Each CNCG system will be statistically available for approximately 99% of the time.
  - Each DCNG system will be statistically available for approximately 96% of the time.

- In the typical AMT CNCG system (2-tier) the statistical unavailability amounts to about 2-3 failures of 15 minutes per year.
  - The introduction of a third tier reduces this period to about 30 seconds per year.

- In the typical AMT DNCG system (1-tier) the statistical unavailability amounts to about unavailability of one day per month.
  - The introduction of a third tier reduces this period to about 30 minutes per year.