# **Chemical Recovery Island**

# **Recovery Cycle Mission**

The three purposes of recovery systems are:

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

#### **Over all view of Pulp and Paper Industry**



## Kraft pulp mill: recovery cycle

The process steps included:

- Evaporation (from weak black liquor to strong black liquor)
- Recovery boiler (combustion of strong black liquor and reduction of sodium sulfate to sodium sulfide)
- Smelt dissolution (Green Liquor production)
- Re-causticization (Reaction of green liquor with calcium oxide to make white liquor and calcium carbonate)
- Lime cycle (burning lime from calcium carbonate to calcium oxide)

# To keep in memory

The 4 process steps 4 C's

Concentration – Evaporation

Combustion - Recovery boiler

Causticization – Re-causticization

Calcination - Lime cycle

#### What's Black Liquor?

- Complex mixture
- Spent pulping chemicals (Inorganic salts, caustic, etc.)
- Organic matter (Lignin) dissolved from the wood
- Non-Process-Elements (NPE) such as K, Cl, etc.
- Brought in with wood, water and fresh chemicals
- No purge points: Constantly recycled

#### **Black Liquor Properties**

- Chemical composition
- > Major role on the performance of the evaporators
- >  $Na_2SO_4$ ,  $Na_2CO_3$  co-precipitate at high solids
- Risk of scale formation
- Critical physical properties
- Boiling Point Rise (BPR)
- Viscosity which impacts heat transfer

#### **Black Liquor evaporation**

- Black liquor recovered from pulping contains 14-17% dissolved solids
- These solids are composed of about 1/3 inorganic chemicals that were in the white liquor added to the digester
- The remaining 2/3 consist of the organic chemicals extracted from the wood
- Black liquor must be concentrated to above 60% solids so that it will burn without supplemental fuel

Black liquor + Heat→Strong Black liquor + Water + SteamCondensate + Steam→Clean + Dirty condensate + NCGBlack liquor→Black liquor + Soap (only softwood)

#### **Evaporator Focus on**



#### **Evaporation capacity**

- Typically expressed as ton H<sub>2</sub>O/h or kg H<sub>2</sub>O/s
- Evaporation capacity is determined by the heating surface area(A), available temperature drop(T) and overall heat transfer coefficients
- Process governed by the heat transfer law



#### **Basics of evaporation**

Steam to next effect

Heat evaporates water (= steam) from black liquor

Drier black liquor is removed



Steam from previous effect

Steam condenses releasing heat

Condensates are removed

## **Basics of evaporation**

- Multi effect evaporation (MEE), 6-7 effects
  - 1 st effect uses primary LP & MP steam
  - 2-7 effects use secondary vapor
  - last effect vapor is condensed with cooling water in surface condenser
  - evaporation done mainly by secondary vapor



## **Basics of evaporation**

The more effects the better is the steam economy

• But the higher is the equipment cost



### Modern evaporator train



### Foul condensate formation

- Each time black liquor is evaporated it forms steam that may be used at another stage
- 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
  - in cooking

## Treatment of foul condensates

- 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
  - –located between effects 1 and 2



### Treatment of foul condensates

- The higher is the condensate quality demand
  - the more foul condensate is segregated
  - the more stripping vapor is used
  - the more stripper losses are generated
    - foul condensate heating
    - vapor losses to stripper of gas & trim condenser
    - stripped condensate taken out hot
- The more expensive equipment

## **Evaporator types**

- Thermal evaporation
  - rising film evaporator
  - falling film evaporator
  - film inside the heating surface
  - film outside the heating surface
- Forced circulation
- Direct contact evaporation
- Mechanical vapor recompression evaporation

#### **TYPES OF EVAPORATOR**





#### **Preference of application**

#### **Falling Film Evaporator**

- Film formed by mechanical means (Distribution plate)
- High turndown, can handle higher viscosity (Gravity helps)
- Primary technology worldwide for concentrations up to 50%TS
- Can operate at low  $\Delta T$
- Flexible (High turndown)
- Good resistance to scaling
- Moderate HP consumption
- Easily automated
- Foams easily at low %TS

#### **Rising Film Evaporator**

- Liquor film formed by generated vapors from boiling liquor at the bottom of the tubes
- Poor turndown, can't handle high viscosities, minimum  $\Delta T$  requirement
- Was the workhorse of the Industry, now found only in older mills
- Low operating cost.
- Low propensity for foaming.
- Low liquor viscosity and high flowrate are ideal conditions.
- Only used today in WBL preevaporation where foaming is an issue.

## Falling film evaporator film inside tubes

- Gravity pulls liquor downwards (window during rain principle)
- Liquor inside the tubes
  Steam outside the tubes
- Fouls with high solids liquor
- Sold as 3 7 effect



## Falling film evaporator film outside tubes

 Gravity pulls liquor downwards (window during rain principle) Liquor outside the tubes Steam inside the tubes Used with high solids liquor Sold as 1 - 3 effect and as concentrator



### Forced circulation evaporator

- Pump forces liquor through
  - heat exchanger
- Liquor inside the tubes
- Steam outside the tubes
- Used with high solids liquor
- Sold as 1 3 effect and
  - as concentrator



#### Lamella type evaporator



## **Evaporator** scaling

- Soap and tall oil scaling
  - soap sticks to the surface
  - soap carries fibre and calcium
  - most of tall oil soap separates at 25-30%ds
- Lignin scaling
  - precipitation at pH < 11</p>

### **Evaporator** scaling

#### Falling film lamella

- Resistant to scaling
- "Self-cleaning"
- Tolerates even nonsoluble scaling





#### **Tube evaporator**

- Plugging under severe scaling conditions
- Non-soluble scaling requires mechanical or chemical cleaning

## Typical process challenges

PROBLEM	ROOT CAUSE	SOLUTION
HEAT TRANSFER SURFACE SCALING	<ul> <li>Low alkali (lignin precipitation)</li> <li>High soap &amp; fiber content</li> <li>High Ca, Si, Al concentrations</li> </ul>	<ul> <li>Ash mixing</li> <li>Wash sequences</li> <li>Soap skimming <ul> <li>Calcium deactivation reactor</li> <li>Liquor heat treatment (LHT)</li> </ul> </li> </ul>
FOAMING IN BACK END EFFECTS	• Low dry solids %	Sweetening of WBL to over 20 %
POOR CONDENSATE QUALITY	<ul> <li>Too much MeOH in WBL</li> <li>Colour in condensate, caused by too high evaporation rate &amp; carry over</li> <li>Smell &amp; high COD, improper segregation of VOC's</li> <li>Liquor or fibers in fiber line foul condensate</li> </ul>	<ul> <li>Low secondary vapor velocities in shell</li> <li>Droplet separators</li> <li>Proper segregation in lamellas</li> <li>Dedicated condensation packages</li> <li>Duct stripper</li> </ul>
HIGH DRY SOLIDS	<ul> <li>High viscosity</li> <li>Fouling</li> <li>Poor heat transfer</li> <li>Corrosion (high Effective Alkali)</li> </ul>	<ul> <li>High 1'st effect temp (MP-steam)</li> <li>High circulation rate in 1'st effect</li> <li>Liquor heat treatment (LHT)</li> <li>Ash mixing</li> <li>Wash sequences</li> <li>Duplex in HD-concentrator</li> </ul>

#### Principle of operation:

Recovery Boiler operation of firing Heavy Black Liquor (HBL) to produce steam for power generation and Green liquor



### Purpose of the recovery boiler

#### • Recovery of Chemicals = Chemical Reactor

 recovery of chemicals from the black liquor through combustion (reduction) to be used for cooking chemical preparation

#### • Recovery of Energy = Steam Boiler

 burn the organic materials in the black liquor and produce energy (steam, electricity)



## Modern recovery boiler

> 100 bar

- Steam pressure
- Steam temperature
- Capacity
- Dry solids content
- re > 500 °C > 5 000 tds/d t > 80 %
- Combustion air from several levels
  DNCG combustion (Diluted gases)
- Additional fuels
  - CNCG (strong gases)
  - methanol
  - turpentine
  - biosludge
  - soap



## Effects of dry solids

- + Steam generation increases (less water to the furnace)
- + Less flue gases
- + Lower SO<sub>2</sub> emissions
- Less desuper heating
- More heating surface
- Viscosity increases
- black liquor flashing, fouling





### **Recovery boiler process**



#### **Recovery boiler main parts**

- **1.Superheaters (1B, 2, 3, 4, 1A)**
- 2.Bullnose/nose arch
- 3.Black liquor nozzle openings
- 4.Start-up burners



5.Steam drum 6.Boiler generating bank 7.Economizers 1 and 2 8.Rearwall screen 9. Furnace screen 10.Ash hoppers (3 pcs.) 11.Feedwater tank 12.Ash conveyors **13.Downcomers 14.NCG ducts 15.Tertiary air ducts 16.Secondary air ducts 17.Primary air ducts 18.Smelt spouts 19.Dissolving tank** 20.Mixing tank (\*) Electrostatic precipitator

#### Steam Drum

The chemical feed pipe is used to inject chemicals into the boiler to maintain the proper pH and phosphate balance in the boiler water.

- The vortex eliminators are used to reduce the swirling motion of the water as it enters the down comers.
- The cyclone steam separators remove moisture from the steam.
- The surface blow pipe is used to remove suspended solid matter that floats on top of the water and to lower the steam drum water level, when necessary. The surface blow pipe is also used to blow water out to lower the chemical level in the boiler when it becomes too high.



## Natural circulation Steam Drum Downcomer Furnace tubes Steam bubbles

 Driving force is static pressure difference between water in downcomers and water- steam mixture (emulsion) in furnace tubes

$$\Delta P_{\text{losses}} = (\rho_{\text{water}} - \rho_{\text{mixture}}) \times g \times h$$

Heat

- Pressure increase reduces driving force
- Heat to tubes by radiation and convection

## Natural circulation





- 1 Water flows downwards to furnace bottom and boiler bank
- 2 Water-steam mixture rises up in furnace wall tubes and in boiler bank panels
- 3 Water-steam mixture flows to the drum where water and steam are separated
## Furnace process

•Black liquor is injected into the recovery boiler from a height of 5...8 meters

•Combustion air is injected at three different zones in the boiler

•Burning black liquor forms the char bed at the bottom of the boiler, where complicated reactions occur

Smelt is drained from the boiler and is dissolved with weak white liquor to form green liquor, which contains the recovered cooking chemicals
High pressure steam is generated from feed water by heat releasing from combustion reactions



# **Chemical reactions in furnace**

- Drying
  - water is evaporated
- Devolatilization
  - droplet size increases
  - gases are released
- Char burning
  - carbon is burned off
  - inorganic salts melt, reactions
- Upper furnace reactions
  - volatiles combustion
  - formation of sodium sulphate and sodium carbonate



## **Objectives of Air System:**

- Supply Air for complete combustion.
- 3Ts (Time , Temperature and Turbulence)
  - Control the temperature and environment around char bed
- Minimize the carryover of black liquor spray.
- Minimize the Emission.
- Achieve uniform flow and temperature entering the super heater tube banks

## Role of Air system:

	Primary air	<ul> <li>Primary air controls the char bed of perimeter.</li> <li>Primary air keeps smelt hot and fluid.</li> <li>Hot air improves combustion stability.</li> </ul>	Air System Components (3-Levels)
/	Secondary air	<ul> <li>Control the char bed height</li> <li>Secondary air burns char and volatiles</li> </ul>	(J-Levels)
	Tertiary air	<ul> <li>Complete mixing and burning of Combustible Gases (CO ,H2S)</li> <li>It is essential for staged combustion</li> </ul>	



## Air flow Arrangement:

Primary Air Arrangement

Slide 11

- Many, small ports on all four walls feed air to perimeter of the char bed
- Isolation dampers control local burning rates
   and bed shape
- Hot air improves combustion stability







## Black liquor system:

- Black liquor system preparing liquor for firing.
- It contains Firing pump, AMT, Indirect heater ,Direct heater and Spray guns.
- HBL concentration 65% to 85% and liquor temperature is 125 to 130 deg Celsius.





### Spout system:

- Molten smelt is produced within the recovery boiler is removed from the furnace through the smelt spouts into a dissolving tank, where its is dissolved to form green liquor.
  - Smelt shattering jets are used to break up the smelt stream as it out the furnace to prevent the accumulation of the molten smelt within the dissolving tank





## Spout system:

Spouts are covered with water cooled jackets. Spout cooling water systems are designed to minimize the pressure inside the spout while providing an adequate flow of cooling water



# Smelt-water explosion

- Even a small amount of water mixed with molten smelt at high temperature can cause it
  - purely physical phenomenon
- Water turns into steam in few ms
  - sudden evaporation causes increase of
     volume and a pressure wave of
     10 100 000 Pa
  - sufficient to cause furnace walls to bend
- Furnace equipped with a weak corner to control the direction of explosion



#### Soot blower:

- A soot blower is a device for removing the soot that is deposited on the furnace tubes of a boiler during combustion.
- Wall Blowers also known as IRs (Insertable Rotating)
- Long Retractable Soot Blower (LRSB)
- Air Heater Blower.
- Steam blowing medium (steam)

# Deposit Removal with Sootblowers



Electrostatic precipitator :

An electrostatic precipitator (ESP) is an device that removes dust particles from a flowing gas (such as air) using the force of an induced electrostatic attraction





#### Deaerator:

- A deaerator is a device that removes oxygen and other dissolved gases from water, such as feed water for steam-generating boilers.
- Dissolved oxygen in feedwater will cause serious corrosion damage in a boiler by attaching to the walls of metal piping and other equipment and forming oxides (rust).
- Dissolved carbon dioxide combines with water to form carbonic acid that causes further corrosion



#### Deaerator:

- Oxygen scavenging chemicals are very often added to the de aerated boiler feed water to remove any last traces of oxygen that were not removed by the de aerator.
  - $\succ$  sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>),
    - hydrazine (N<sub>2</sub>H<sub>4</sub>), Ethylenediaminetetraaceticacid (EDTA),
  - Diethyl hydroxylamine(DEHA),
  - Nitrilotriacetic acid (NTA)



## Indirect heat exchanger:

• A heat exchanger is a device used to transfer heat between two or more fluids.

•Types of flow are Counter Flow ,Co current Flow and Cross flow



shell side out

## **Boiler accessories:**

#### Air pre heater:

The function of air pre-heater is to increase the temperature of air before enters the furnace.

#### **Economizer:**

- waste heat of the flue gases is utilised for heating the feed water.
- To recover some of the heat being carried over by exhaust gases.
- heat is used to raise the temperature of feed water supplied to the boiler.
- Evaporative capacity of the boiler is increased.
- Overall efficiency of the plant is increased.

## **Boiler** accessories:

#### **Super heaters:**

- super heater is to increase the temperature of the steam above its saturation point.
- Super heaters are heat exchangers in which heat is transferred to the saturated steam to increase its temperature.

#### Feed water pump:

Feed pump is a pump which is used to deliver feed water to the boiler.

## **Boiler Mountings:**

## Water level indicator:

- fitted in front of the boiler and generally present two in number.
- It is used to indicate the water level inside the boiler. It shows the instantaneous level of water that is present inside the steam boiler

#### Pressure gauge:

- measure the pressure of the steam inside the boiler.
- The pressure gauges generally used are of Bourden type
  Feed check valve:
- Regulates the supply of water which is pumped into the boiler by feed pump.
- Non-return valve and fitted to a screwed spindle to regulate the lift.

## **Boiler Mountings:**

**Safety valves:** 

- It prevent explosion due to excessive internal pressure.
- When the internal pressure inside the boiler exceeds its working pressures than the safety valves blow off the steam and maintains the internal pressure.

## **Steam stop valve:**

- Control the flow of steam from the boiler to the main steam pipe.
- To completely shut off the steam supply when required.

## **Boiler Mountings:**

#### **Blow off cock:**

To discharge the scale, mud and sediments which gets collected at the bottom of the boiler.

#### **Fusible plug:**

- It is fitted to the crown plate of the furnace or firebox.
- Its function is to extinguish fire in the furnace when the water level in the boiler falls to an unsafe limit.
- This avoids the explosion that may takes place because of the overheating of the furnace plate.

## Customer outputs:

	Source of input	input	process	output	Customer outputs
	Evaporator	ESP ash mixed with HBL	•Heating of Heavy Black liquor	HP steam	Boiler house
	Deilerhouse	steam steam •Heating of Furnace oil •Heating of Primary and	Condensate	Boiler house	
/	boller nouse	Furnace oil	<ul> <li>Secondary air</li> <li>Collection of Condensate</li> <li>Handling of ESP Ash</li> <li>Production of HP steam (64</li> </ul>	Flue gas	
	Recausticizer	Weak white Liquor	<ul><li>ksc) and supplied to 16 MW</li><li>Turbo generator for power</li><li>generation</li><li>Production of green liquor and</li></ul>	Green liquor	Recausticizer
	Atmosphere	Air	supplied to Recausticizing plant	ESP Ash	Bagged and sent to authorised vendors

## Boiler tube failure:

Creep:

Creep is a time-dependent deformation that takes place at elevated temperature under mechanical stresses, such failure results in overheating or overstressing the tube material.

Fatigue:

Fatigue is a phenomenon of damage accumulation caused by cyclic or fluctuating stresses, which are caused by mechanical loads, flow induced vibration.

Dissimilar Metal Weld (DMW) Failure: Material fails at the ferritic side of the weld, along the weld fusion line. A failure tends to be catastrophic in that the entire tube will fail across the circumference of the tube section.

## Boiler tube failure:

Erosion :

Erosion is metal removal caused by particles striking the metal's surface.

Corrosion:

Deterioration and loss of material due to chemical attack.

#### Internal corrosion:

hydrogen damage, acid phosphate corrosion, caustic gouging, and pitting

### External corrosion:

water wall fireside corrosion, super heater (SH)/re heater (RH) fireside corrosion, and ash dew point corrosion



## **Useful numbers**

<ul> <li>ADt (bleached)</li> </ul>	1.3 - 2.0	tds
• Dry solids (virgin)	65 - 83	%
<ul> <li>Density</li> </ul>	1.35 - 1.43	kg/l
• HHV	13.0 - 15.0	MJ/kgds
<ul> <li>Furnace bottom loading</li> </ul>	18 - 25	tds/d/m <sup>2</sup>
	3.0 - 4.0	MW/m <sup>2</sup>
<ul> <li>Steam production</li> </ul>	3.0 - 4.5	kg/kgds

# Liquor spraying

- Target
  - spray the liquor evenly on the charbed
  - optimize the droplet size
- Liquor gun openings on all walls
- Locations adjusted to the air system between secondary and tertiary air ports









# **Smelt and green liquor**

 Smelt is molten inorganic chemicals produced in the reducing zone of furnace

<ul> <li>Sodium carbonate</li> </ul>	Na <sub>2</sub> CO <sub>3</sub>	(65 75 %)
<ul> <li>Sodium sulfide</li> </ul>	Na <sub>2</sub> S	(20 25 %)
<ul> <li>Sodium sulfate</li> </ul>	$Na_2SO_4$	(2 3 %)

- Green liquor is a mixture of smelt from RB and Weak White Liquor from Causticizing Plant
  - temperature at dissolving tank outlet
     95 ... 98 °C
  - dregs content (unburned carbon)
     500 ... 1000 mg/l
  - reduction efficiency (in smelt):
    93 ... 97
    - $Na_2S/(Na_2S + Na_2SO_4)$
    - increasing reduction efficiency decreases steam production

%

# Modern white liquor plant





## Basic flow chart:



# Re causticizing Plant

## Mission:

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



# 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
- Make-up lime is an incoming solid stream containing mainly CaO

# Recausticizing

The three main processes that occur in recausticizing are:





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 RB 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 removed by filtration

# **Recausticizing unit operations**

- •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

## Equipment loading rates

Equipment	English Units		Metric units	
Raw Green Liquor Stabilization	hrs	2 - 4	hrs	2 - 4
Green Liquor Clarifier	ft/hr	1.3-1.8	m/hr	0.4-0.55
Dregs washer (sedimentation)	ft²/Ton/d	100	m²/tonne/d	10.3
Dregs filter (precoat)	lb/hr/ft <sup>2</sup>	2.5-3.5	kg/hr/m <sup>2</sup>	12-17
Slaker (clarifiers)	min.	10-15	min.	10-15
Slaker (pressure filters)	min.	15-25	min.	15-25
Causticizers (clarifiers)	min.	90	min.	90
Causticizers (pressure filters)	min.	150-180	min.	150-180
White Liquor (WL) Clarifier				
Unit type	ft²/Ton/d	9 - 10	m <sup>2</sup> /tonne/d	0.92-1.0
Tray type	ft²/Ton/d	14 - 16	m²/tonne/d	1.43-1.64
WL Pressure filter (tube type)	usgpm/ft <sup>2</sup>	0.6	$L/min/m^2$	25
WL Pressure disc filter	usgpm/ft <sup>2</sup>	1.0	$L/min/m^2$	40
Lime Mud Washer				
Unit type	ft²/Ton/d	7 - 8	m²/tonne/d	0.72-0.82
Tray type	ft²/Ton/d	12 - 14	m <sup>2</sup> /tonne/d	1.23-1.43
LMW Pressure filter (tube type)	usgpm/ft <sup>2</sup>	0.73	$L/min/m^2$	30
LM Filter	Ton/d/ft <sup>2</sup>	0.6 - 0.75	tonne/d/m <sup>2</sup>	5.9-7.3

Note: Above loading rates should be used in conjunction with an analysis of the existing or proposed system making allowance for future changes in the plant capacity.

The above loading rates are only a guide. Please check with your equipment supplier for the recommended loading rates.

# **Recausticizing Process**


#### WHITE LIQUOR PRESSURE DISC FILTER



#### Green liquor

Na	g/kgds	90.8
K	g/kgds	14.5
S <sub>tot</sub>	g/kgds	24.1
Cl <sub>tot</sub>	g/kgds	1.9
S <sup>2-</sup>	g/kgds	19.1
NaOH	g/kgds	18.8
Na <sub>2</sub> S	g/kgds	42.7
Na <sub>2</sub> CO <sub>3</sub>	g/kgds	134.9
$Na_2SO_3$	g/kgds	1.41
$Na_2S_2O_3$	g/kgds	7.08
$Na_2SO_4$	g/kgds	8.7
Total alkali	g NaOH/I	165.2
Active alkali	g NaOH/I	62.7
Effective alkali	g NaOH/I	40.7

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

# White liquor definitions and reactions

White Liquor (WL)	Definitions	Reactions
<ul> <li>Containing small amount Suspended Solids (SS) &lt; 20 mg/l</li> <li>Concentration is given g as Na<sub>2</sub>O/liter or g as NaOH/liter</li> <li>Main compounds as NaOH are: <ul> <li>NaOH are:</li> <li>Na<sub>2</sub>S</li> <li>40 g/l</li> <li>Na<sub>2</sub>CO<sub>3</sub></li> <li>20 g/l</li> <li>NaOH</li> <li>100 g/l</li> <li>Na<sub>2</sub>SO<sub>4</sub></li> <li>10 g/l</li> <li>Suspended Solids &lt; 20 mg/l</li> </ul> </li> </ul>	<ul> <li>Active Alkali (AA) – NaOH + Na<sub>2</sub>S</li> <li>WSA (Water Soluble Alkali) – Soluble Na as Na<sub>2</sub>O</li> <li>Causticizing Degree (CE) – NaOH/(NaOH + Na<sub>2</sub>CO<sup>3</sup>)</li> <li>Suspended Solids (SS) – Compound insoluble in WL</li> <li>Typically measured after White Liquor filter</li> <li>Concentration &lt; 20 mg/l, mainly CaCO<sub>3</sub></li> <li>Lime • Lime Kiln product or make-up lime • Mainly CaO &gt; 90%</li> <li>Lime Milk • GL + Lime</li> </ul>	<ul> <li>Lime slaking CaO + H<sub>2</sub>O -&gt; Ca(OH)<sub>2</sub> + 1130 kJ/kg</li> <li>Causticizing reaction Ca(OH)<sub>2</sub> + Na<sub>2</sub>CO<sub>3</sub> &lt;-&gt; 2 NaOH + CaCO<sub>3</sub></li> </ul>

# Green liquor filtration

- Green liquor contains 800-1 200 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

#### 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 reacts with sodium carbonate in the green liquor to 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

## Slaking chemistry





# Causticizing chemistry

Slaking +1130 kJ/kg CaO

**CaO** (s) +  $H_2O$  (aq)  $\leftrightarrow$  **Ca(OH)**<sub>2</sub> (s)

Causticizing -560 kJ/kg CaO

 $Ca(OH)_2(s) + Na_2CO_3(aq) \leftrightarrow 2NaOH(aq) + CaCO_3(s)$ 

# **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
  - <u>- dry solids 40 50 %</u>

# White liquor

- Final product from causticizing system
- Cooking chemical to the digester
- Active ingredients NaOH and Na<sub>2</sub>S

# White liquor analysis

Na	g/kgds	78.0
K	g/kgds	14.1
S <sub>tot</sub>	g/kgds	22.4
Cl <sub>tot</sub>	g/kgds	1.7
S <sup>2-</sup>	g/kgds	18.0
NaOH	g/kgds	88.2
Na <sub>2</sub> S	g/kgds	41.8
Na <sub>2</sub> CO <sub>3</sub>	g/kgds	40.3
$Na_2SO_3$	g/kgds	0.1
$Na_2S_2O_3$	g/kgds	8.99
$Na_2SO_4$	g/kgds	0.5
Total alkali	gNaOH/I	161.6
Active alkali	gNaOH/I	131.2
Effective alkali	gNaOH/I	109.8

Analysis is given to show indicative magnitude of various chemical compounds

# **Objective** of causticizing

- High active alkali concentration
  - high causticity
  - high reduction
- Clean white liquor to minimize chemical consumption
- Efficient lime mud washing

# Causticizing in modern mill

<ul> <li>White liquor active alkali (NaOH)</li> </ul>	g/l	136
<ul> <li>White liquor sulfidity</li> </ul>	%	32
Causticity	%	82
<ul> <li>Reduction efficiency</li> </ul>	%	95
<ul> <li>Green liquor filtration</li> </ul>		
<ul> <li>White liquor filtration</li> </ul>		

• Capacity m<sup>3</sup>WL/d >10 000





Mission – Converting used lime mud into lime

### Lime kiln

• The main processes that occur in lime kiln are:



Lime mud + Heat	$\rightarrow$	CaCO <sub>3</sub>	+ vapor
CaCO <sub>3</sub> + Heat	$\rightarrow$	CaO	+ CO <sub>2</sub>

# 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

## Lime product quality

	Fres	sh lime	Reburnt
	Soft	Hard	
Density, kg/l	1.6	>2,2	1,7-2.1
Porosity, %	50	<34	44-67
Surface area, m <sup>2</sup> /g	>1.0	<0,3	0,21-0,43
Reactivity, °C/min	>10	<2	low
		From	Adams, 1997

# Lime kiln fuels

- Natural gas
- Fuel oil
- NCG's
- Methanol
- Gasification gas
- Saw dust
- Pet coke

#### Lime kiln

Lime mud + heat → burned lime + carbon dioxide
Adiabatic flame temperature 1750 °C



# Energy balance

	MJ/t CaO
Water heating & evaporation	2 0 9 0
Energy in kiln product and dust	140
Enthalpy of calcination	2 890
Enthalpy in CO <sub>2</sub> from calcination	90
Enthalpy of combustion products	410
Radiation loss	820
Total input	6 4 4 0

#### **OPERATIONS IN LIME KILN**

- Receiving of lime mud from recausticizing plant
- Filtering of Lime mud using LMCD filter and feed to lime kiln through conveyor
- Handling of Weak white liquor
- Handling of Limestone and Furnace oil as inventory
- Conversion of Lime mud into Burnt lime through calcination process
- Handling and supply of Burnt lime to recausticizing

#### **OPERATION:**

- The feed is given through the ribbon screw conveyor and it is fed inside the kiln
- The length of the kiln is +70 m long. (wet kilns)
- As the kiln rotates the feed gets rotates and the calcination reaction takes place which is the conversion of calcium carbonate to calcium oxide
- The furnace oil is heated up using heat exchangers and using suction and delivery strainers it is pumped to kiln where light up is done
- The product as it reaches the burner side it gradually enters the satellite coolers which brings down the temperature of lime using secondary fan
- The primary air is given for combustion using a fan in radial and axial direction
- The flue gas generated is sucked through the ID fan and the ash generated is collected in the ESP and sent inside to kiln again







#### Chain section



# **Baffles:**



#### Refractory inside kiln:







