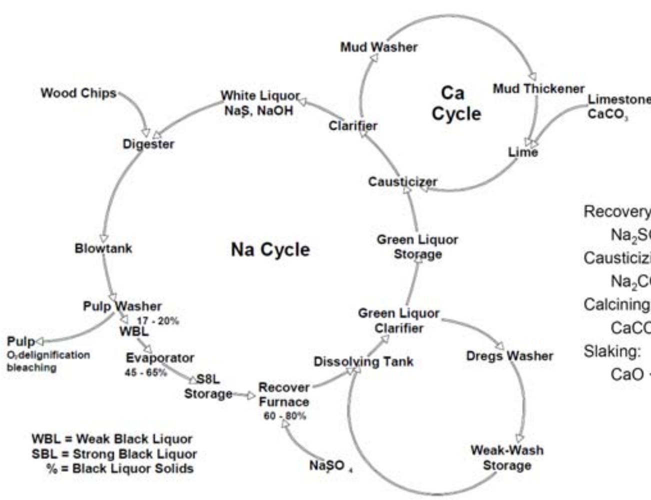
Kraft Pulping

Kraft Cycle



Recovery Furnace:

$Na_2SO_4 + 2C + heat \longrightarrow Na_2S$

Causticizing:

$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3$

Calcining:

$CaCO_3 + heat \longrightarrow CaO + CO_2$

Slaking:

$CaO + H_2O \longrightarrow Ca(OH)_2 + heat$

Standard terms

Total chemical:	All Na salts
Active alkali:	$NaOH + Na_2S$
Effective alkali:	$NaOH + 1/2\ Na_2S$
Sulphidity:	$Na_2S/(NaOH + Na_2S)$
Total alkali:	$NaOH + Na_2S + Na_2CO_3 + Na_2SO_4$
Total titratable alkali:	$NaOH + Na_2S + Na_2CO_3$

(Usually expressed in equivalents of Na_2O)
in North America as lb/ft^3 or g/L as Na_2O
International as g/L as Na_2O or NaOH

Chemical composition for bleachable pulp grades

	White Liquor (g/L as Na_2O)	Black Liquor (g/L as Na_2O)
NaOH	65 – 75	10 – 15
Na_2S	25 – 35	6 – 10
Na_2CO_3	10 – 15	
Na_2SO_4	<2	
Active Alkali	~100	13 – 20
Effective Alkali	~85	11 - 17

Kraft Chemical Charges

Pulp Grade	Active Alkali (% on od wood)	Sulfidity (%)	Liquor/Wood (vol/wt)
SW Bleachable	16 – 18	30	4:1
HW Bleachable	14 – 16	25	3:1
SW Liner	12 – 13	25	4:1

Hydrolysis of sodium sulfide

$$Na_2S + H_2O \rightleftharpoons NaOH + NaHS$$

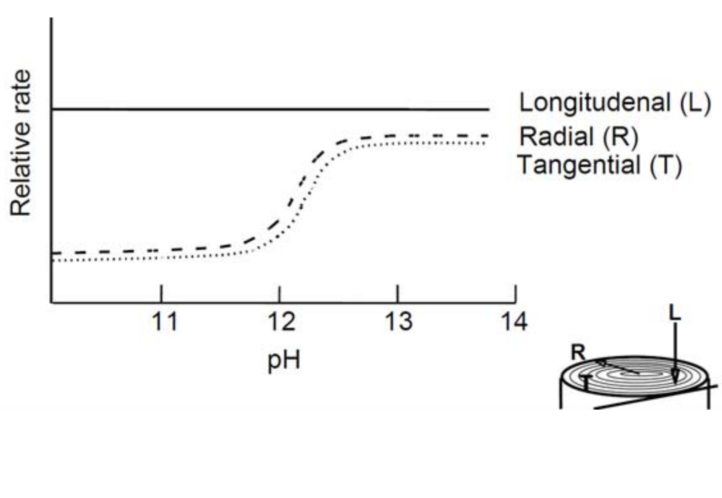
$$NaHS + H_2O \rightleftharpoons NaOH + H_2S$$

(The second reaction is not significant at the pH levels of kraft liquors)

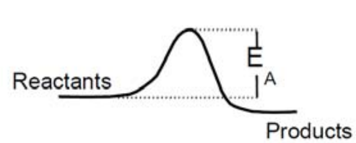
Sequence of Events in kraft pulping

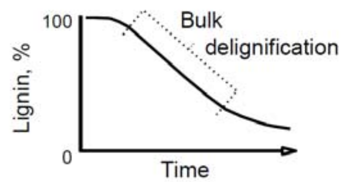
- Provide a pathway for liquor penetration into the wood matrix
- Diffusion of HS^- and OH^- ions throughout the fibre matrix
- Reactions with the wood components
- Diffusion of reaction products to the chip surface
- Dispersion of reaction products in the black liquor

Diffusion of white liquor ions into wood matrix



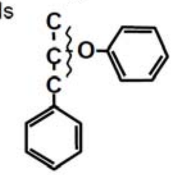
Major reactions in kraft puling



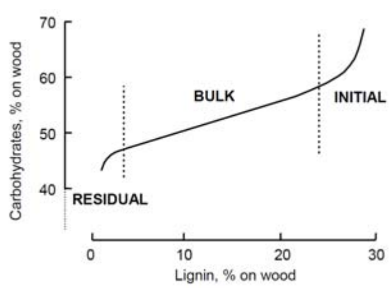


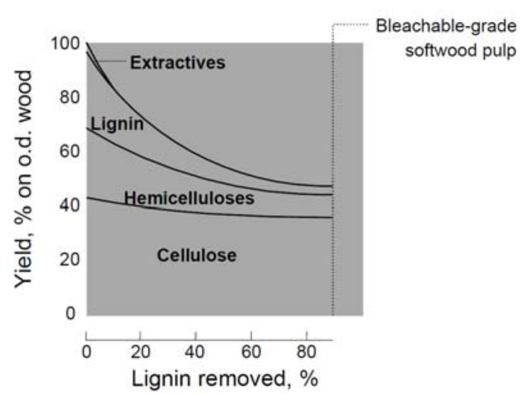
	E_A, kJ/mol
Kraft	~140
Kraft-AQ	~130
Sulfite	70-90

Principal reaction is breaking beta-aryl-ether bonds



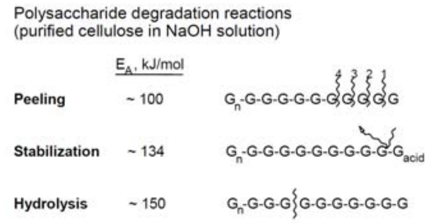
Delignification occurs in three phases





Carbohydrate reactions

- Alkaline swelling of the fibre wall
- Alkaline dissolution of carbohydrates
- Precipitation of dissolved carbohydrates onto fibres
- Alkaline hydrolysis of acetyl groups
- Alkaline "peeling" of cellulose
- Stopping reactions
- Alkaline hydrolysis of β-glycosidic bonds



Reaction Kinetics

$$-\frac{dL}{dt} = k[L]^a\,[OH^-]^b\,[HS^-]^c$$

L	= lignin content (% on o.d. wood)
a,b,c	= reaction order constants
t	= time (hours)
k	= reaction constant f (T, wood species, etc.)

Relative rate of reaction

$$k = Ae^{-E_a / RT}$$

k = rate constant
A = pre exponential factor
E_a = activation energy
R = ideal gas constant
T = temperature (°K)

$$rel.\ rate = \frac{k_T}{k_{373}} = \exp\left(-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{373}\right)\right)$$

Pulping kinetics

- H-Factor

$$H = \int_0^t \frac{k_T}{k_{373}} dt$$

for E_a = 32 kcal/mole
R = 1.986 cal/(mole·K)

$$H = \int_0^t \left(e^{43.20 - \frac{16113}{T(t)}}\right) dt$$

- Delignification rate

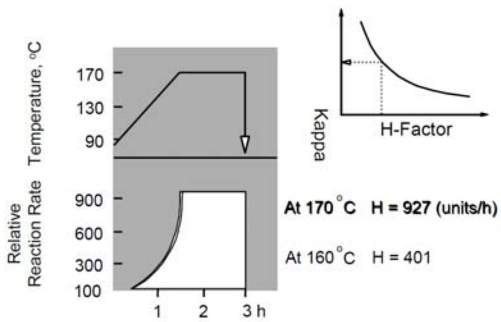
$$-\frac{dL}{dt} = k[L]^1[OH^-]^b[HS-]^c$$

for $[OH^-]$ and $[HS^-] \cong$ constant during bulk delignification

$$\ln\frac{L_o}{L} = k_{373}[OH^-]^b[HS^-]^c \int_0^t \frac{k(t)}{k_{373}} dt = K \cdot H$$

where $K \cong$ constant

H-Factor Calculation



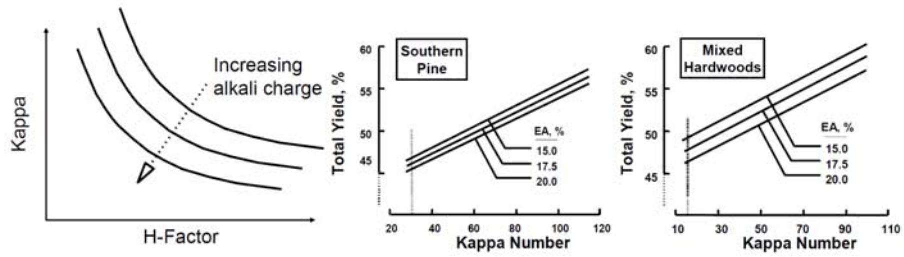
Time from start of Cook (h)	Temp (°C)	Relative Reaction Rate	Avg. Rate	Time Interval (h)	H
0.00	80	0	0	0.25	0
0.25	95	0	2	0.25	1
0.50	110	3	9	0.25	2
0.75	125	15	41	0.25	10
1.00	140	66	163	0.25	41
1.25	155	258	590	0.25	148
1.50	170	921		Total Rise	202
…..	…..	…..	921	1.50	1380
3.00	170	921		Whole Cycle	1582

$$H = \int_0^t \left(e^{43.20 - \frac{16113}{T(t)}} \right) dt$$

Variables in kraft pulping

Process Variables	Wood Variables
Alkali applied	Species
Cooking temperature	Tree component
Time-to-temperature	Quality
Time-at-temperature	Chip quality
Liquor-to-wood ratio	
Liquor sulfidity	

Effect of Alkali

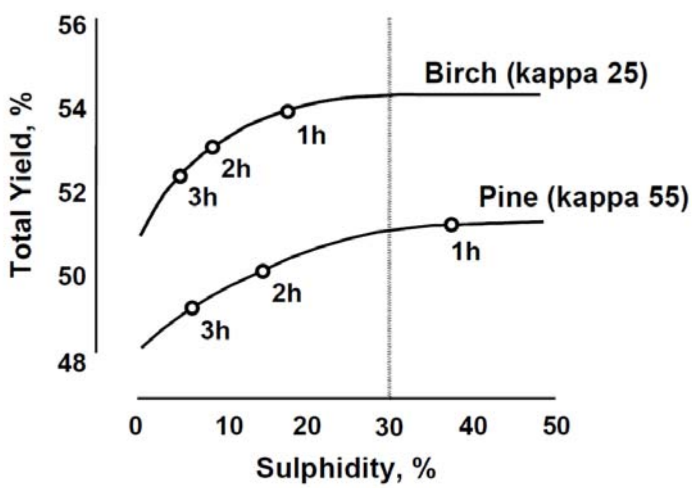


Pulp yield = A - B[($\log_{10}$ H)(EA)^n]
(n = 0.4 for softwoods)

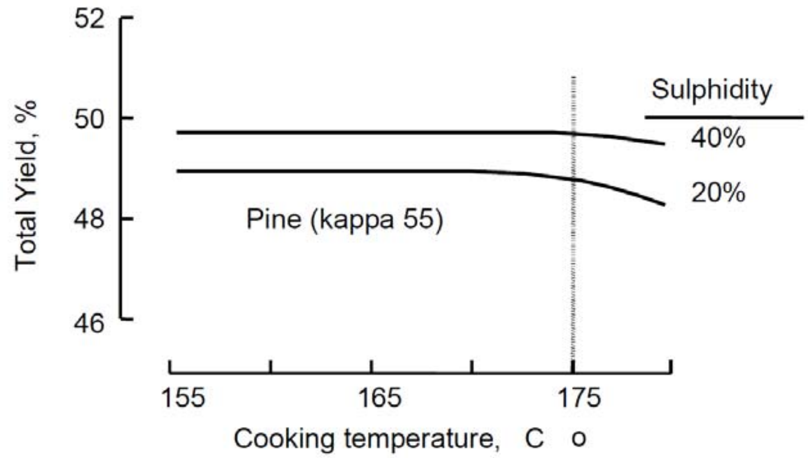
For six softwoods:
Range: 0.07 - 0.15%
Mean: 0.09%

For five hardwoods:
Range: 0.25 - 0.60%
Mean: 0.41%

Effect of sulfidity



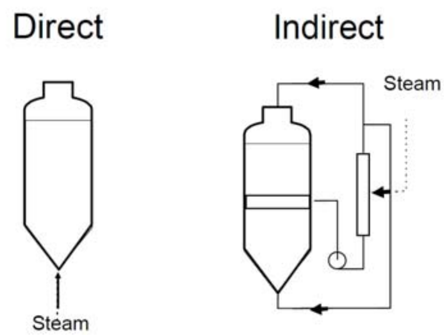
Effect of temperature



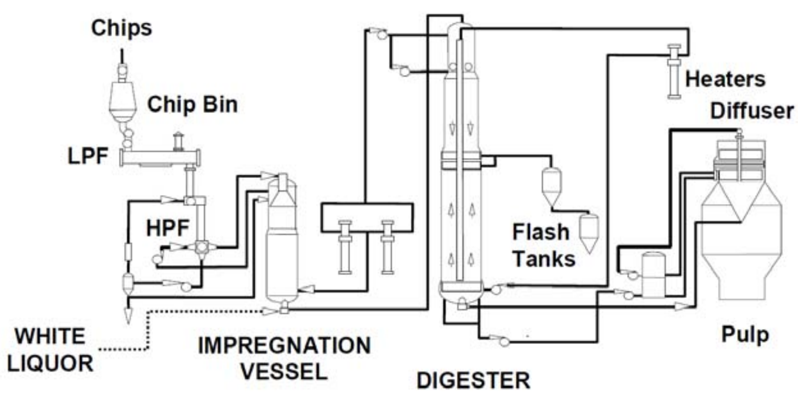
Effect of species on yield

	CHEMICAL COMPOSITION, %			PULP YIELD, %	
	Cellulose	Hemicellulose	Lignin		
White Spruce	44	29	27	48	Kappa 30
Jack Pine	41	30	29	46	
Balsam Fir	44	27	29	45	
White Birch	41	40	19	51	Kappa 15
Maple	41	35	24	49	
Aspen	53	31	16	56	

Batch Pulping

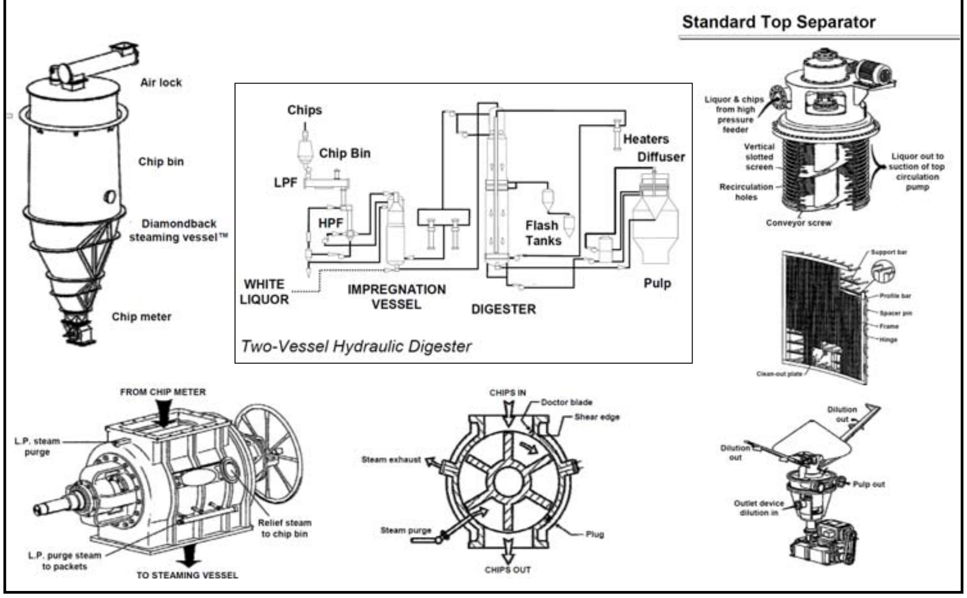


Continuous kraft pulping

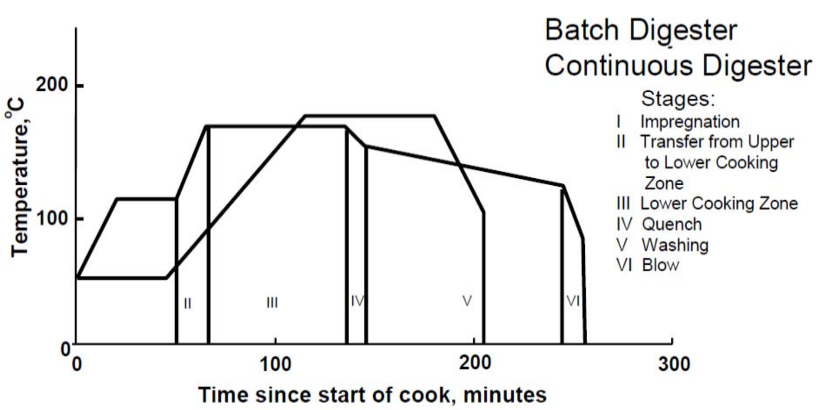


Two-Vessel Hydraulic Digester

Continuous kraft pulping equipment

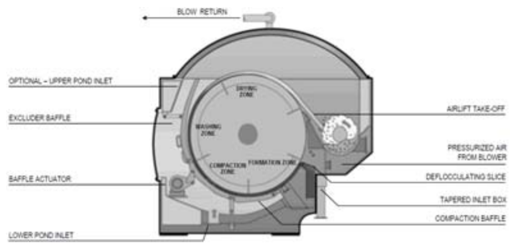


Temperature profile through continuous pulping process



Pulp Washing

- Washing removes ‘black liquor’ from pulp
- Black liquor goes to recovery
- Pulp goes to screening and bleaching

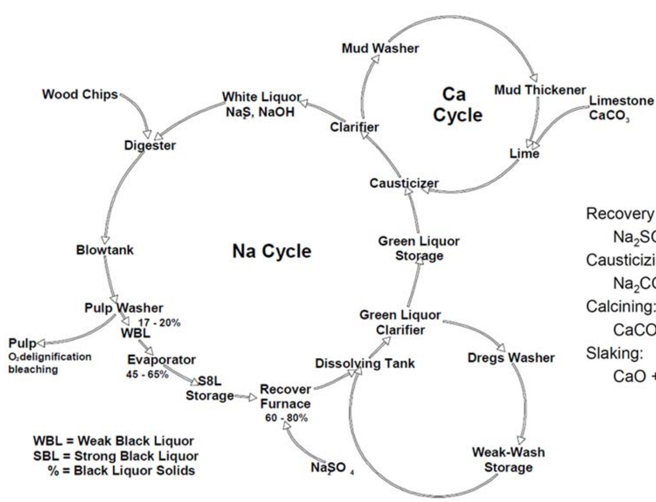


Recovery

Purposes of Chemical Recovery

- Regeneration of alkali: it regenerates the sodium hydroxide consumed in the cook
- Chemical conversion: it converts all sulphur compounds in black liquor into Na_2S
- Elimination of pollution: destruction of organic matter dissolved in liquor during pulping stage
- Heat generation: nearly all the heat requirements for the pulping operation are produced

Kraft cycle



Recovery Furnace:

$$Na_2SO_4 + 2C + heat \longrightarrow Na_2S$$

Causticizing:

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3$$

Calcining:

$$CaCO_3 + heat \longrightarrow CaO + CO_2$$

Slaking:

$$CaO + H_2O \longrightarrow Ca(OH)_2 + heat$$

Main Chemical Reactions in Recovery Process

1. Reduction in recovery furnace

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2\, CO_2$$

2. Causticizing

$$Na_2CO_3 + CaO + H_2O \rightarrow 2NaOH + CaCO_3$$

3. Calcining

$$CaCO_3 \rightarrow CaO + CO_2$$

Black Liquor Properties Which Have Strong Effects on Recovery

1. Concentration of black liquor
2. Liquor viscosity $\rightarrow$ sprayability, evaporation capacity
3. Organic-inorganic ratio of black liquor solids
4. Heating value of liquor $\rightarrow$ composition of organics, O/I ratio, liquor oxidation, dead load of inorganics, soap content

Heat Transfer in Evaporators

Evaporators are heat transfer devices with a heat supply and heat sink

- Heat supply: latent heat of steam and condensate flash
- Heat usage: sensible heat (to bring liquor to boiling) & latent heat (to evaporate water)

Steam economy ~ evaporation efficiency = kg of water evaporated per kg of steam used (4.5 - 6.0 kg/kg in the multiple effect evaporators)

Several different types of evaporator technologies can / have been used.

Multiple Effect Evaporators

- Steam is fed to only one evaporator body
- The steam condensate, and vapour from liquor evaporation in that body, are "flashed" to a second evaporator operating at lower pressure
- Water evaporated in effect n is used for heating effect n+1
- Liquor and steam flow are counter-current
- The multiple effect principle results in very high steam economy and low evaporation costs

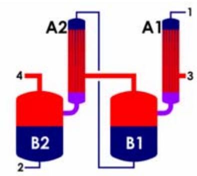


diagram of a double-effect falling film evaporator. Condensing vapors from flash tank B1 heat evaporator A2. 1=feed, 2=product, 3=steam, 4=vapors

http://en.wikipedia.org/wiki/Multiple-effect_evaporator

Disadvantages

- Heat transferred in each effect is roughly equal. If U in effect # 1 drops by 50 % (due to scaling), the evaporation capacity of a six effect system is reduced by 17 %
- Foaming and liquor entrainment in the vapour stream lead to steam side fouling and corrosion
- Stripping of sulphur gases from the liquor can result in non-condensable gas blanketing, which effectively reduces the area available for heat transfer

Black Liquor Oxidation

- Essential for odor reduction prior to recovery furnace
- Two types of systems:
  - Weak black liquor (15-20% solids)
  - Strong black liquor (40-50 solids)
- Foam from the soaps/fats from the tree is a major problem .. Need de-foaming systems
- Purpose to oxidize residual Na2S to Sodium Thiosulfate
- First stage can be on WBL or SBL. Second stage should be before direct contact evaporators.

Black Liquor Oxidation

$$2Na_2S + 2O_2 + H_2O \rightarrow Na_2S_2O_3 + 2NaOH$$

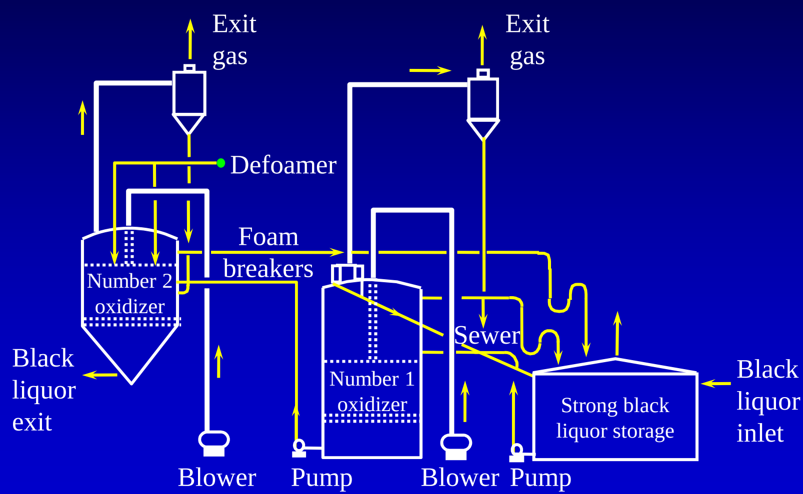
sodium thiosulphate

$$4CH_3SH + O_2 \rightarrow 2(CH_3)_2S_2 + 2H_2O$$

methyl mercaptan → dimethyl disulphide

Both Na2S and CH3SH are the largest contributors to TRS (Total Reduced Sulphur) emission non-compliance

Black Liquor Oxidation Process



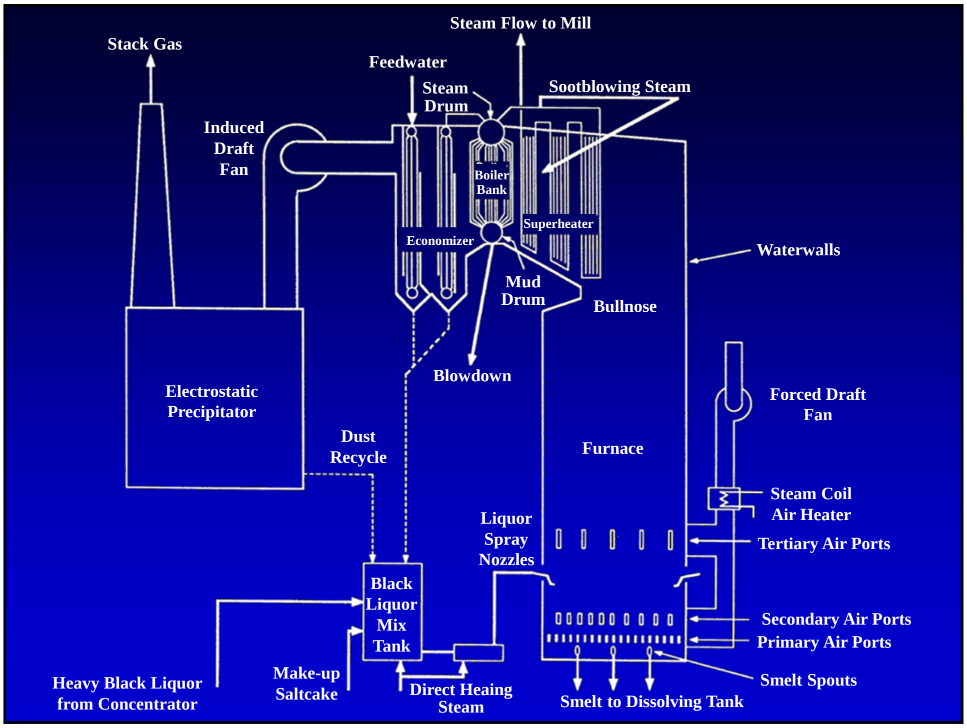
Recovery Boiler

- The recovery boiler process has several unit processes:
  - Combustion of organic material in black liquor to generate steam
    - Send to turbine for energy production
  - Reduction of inorganic sulfur compounds to sodium sulfide, which exits at the bottom as smelt
  - Production of molten inorganic flow of mainly sodium carbonate and sodium sulfide, which is later recycled to the digester after being re-dissolved
  - Recovery of inorganic dust from flue gas to save chemicals (sulphor and sodium)
  - Production of sodium fume to capture combustion residue of released sulfur compounds

CMPC Celulosa Santa Fe Recovery boiler is one of the newest boilers in South America

Howe Sound Pulp and Paper Recovery boiler

http://en.wikipedia.org/wiki/Recovery_boiler



Corrosion in Recovery Furnace

- Floor tube cracking and hydroxide attack around air ports are problems in boilers with composite tubes
- Reactions between H_2S and CH_3SH and iron in carbon steel can cause rapid corrosion of water wall tubes
- Corrosion close to the surface of the mud drum is problematic in boilers with two drums
- Acidic corrosion, below the dew point of gases, can reduce the electrostatic precipitator efficiency and lifetime

Objectives of Recausticizing

- Regenerate NaOH
- Produce enough white liquor for cooking (and other needs)
- Produce a high quality liquor at minimal cost

Definitions

$$\text{Causticity} = \frac{NaOH}{NaOH + Na_2CO_3} \times 100$$

$$\text{Causticizing efficiency} = \frac{NaOH_{wl} - NaOH_{gl}}{(NaOH_{wl} - NaOH_{gl}) + Na_2CO_3} \times 100$$

$$\text{Total titratable alkali} = TTA = NaOH + Na_2S + Na_2CO_3$$

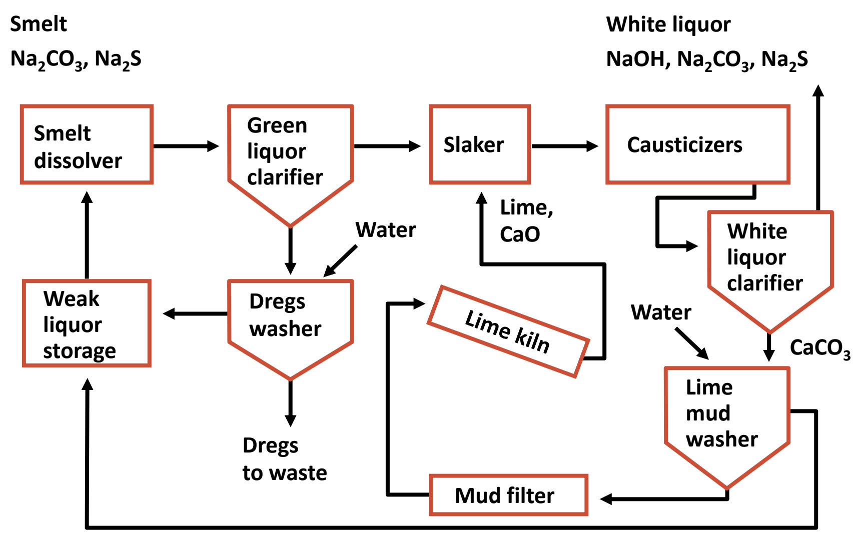
Recausticization Reactions

$$CaCO_3 \xrightarrow{heat} CaO + CO_2$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

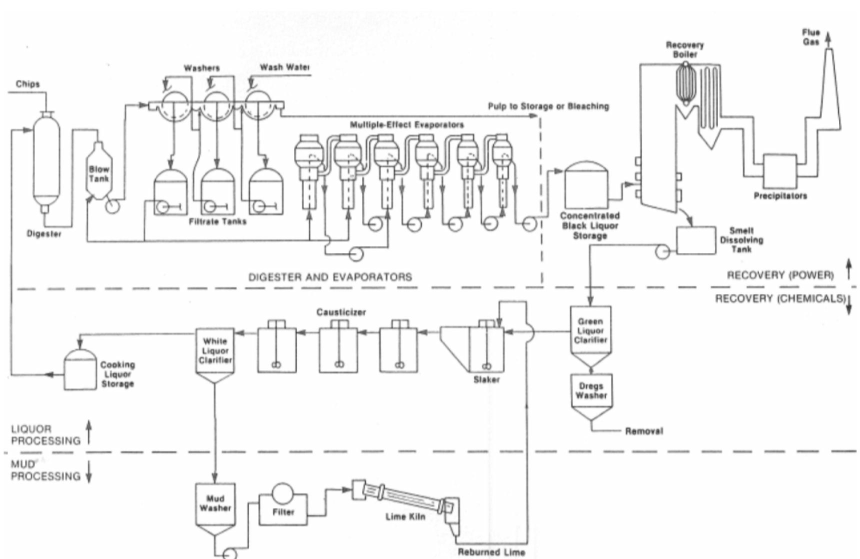
$$Ca(OH)_2 + Na_2CO_3 \longrightarrow 2NaOH + CaCO_3$$

Recausticizing



Lime Kiln

Overview of Kraft liquor cycle



Smook 1992

Chemical Pulp Bleaching I
Overview

- Objectives and goals
- Bleaching chemistries used
  - Reactions with lignin and cellulose
  - Typical bleaching conditions
  - Bleaching kinetics
- The bleaching stage
- Delignification partial sequences
- Brightening partial sequences

Why Pulps can be Bleached

- Cellulose is almost colourless
- Lignin - can be removed or modified to absorb less light

Objectives of Pulp Bleaching

"To produce a strong, bright and clean pulp in an environmentally friendly manner at minimum cost."

Objectives of Pulp Bleaching

- Removal of the majority of lignin in the delignification stages: attain target kappa number
- Obtain target brightness levels in the brightening stages
- Preserve carbohydrates to maintain pulp yield and strength
- Treat the pulp uniformly
- Minimize all costs

What Happens During Bleaching?

- Pulp is made whiter and brighter
- Lignin, resins, metal ions, etc. are removed
- Pulp and fibre properties are altered (*e.g.* viscosity)
- Pulp is made suitable for its end use

Factors Affecting the Choice of the Bleaching Process Used

- Pulping process (kraft, soda or sulfite)
- Wood species
- End use of pulp
- Minimum colour reversion
- Environmental constraints
- Cost

Delignification and Brightening

- Pulp bleaching is accomplished in two stages: delignification and brightening
- Delignification removes the residual lignin (3 - 7%) that remains after cooking.
- Brightening is accomplished in a series of oxidation stages (one to four)
- Brightness ceiling typically 90%+ ISO

Control Targets in Bleaching

Lignin Content

Kappa Number
% lignin = 0.15 × kappa

Brightness

ISO Brightness
457nm light reflected from sheet under controlled conditions

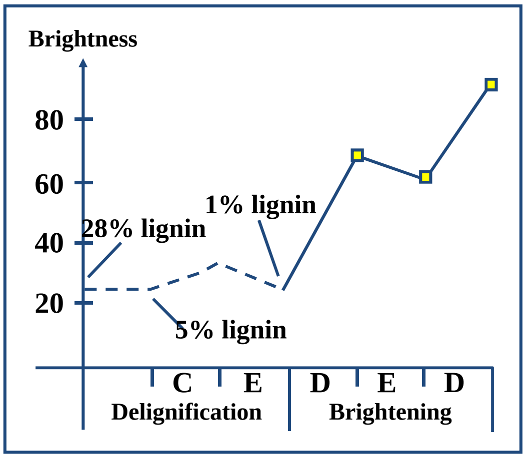
Bleaching Chemicals

Stage	Chemical Name	Symbol
C	Chlorine	Cl_2
D	Chlorine Dioxide	ClO_2
E	Sodium Hydroxide	NaOH
H	Sodium Hypochlorite	NaOCl
P	Hydrogen Peroxide	H_2O_2
O	Oxygen	O_2
Z	Ozone	O_3

Bleaching Variables

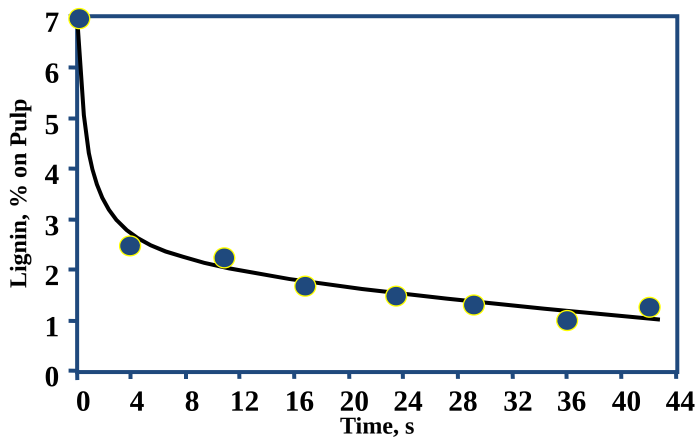
Variable	Expressed as:	Effect
Chemical		• chemical reactions
Pulp consistency	$C_m = \frac{mass\ of\ fibre}{total\ suspension\ mass}$	• chemical concentration • reaction rate • suspension rheology
Charge	wt/wt, %	• treatment • extent of reaction
Temperature	^{o}C	• reaction rate
Time	s/min/hr	• duration of reaction
pH	pH	• chemistry • reaction rate

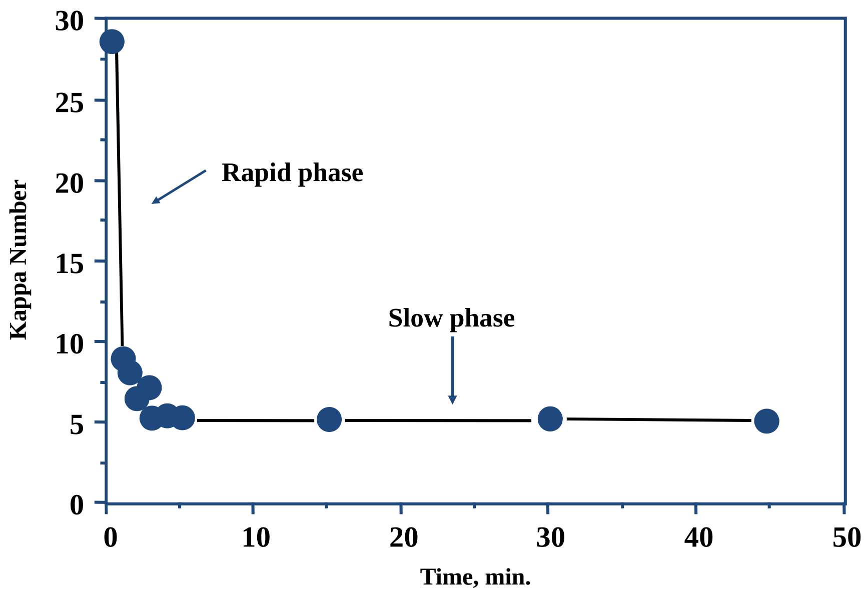
Brightness Development Across the Bleach Plant



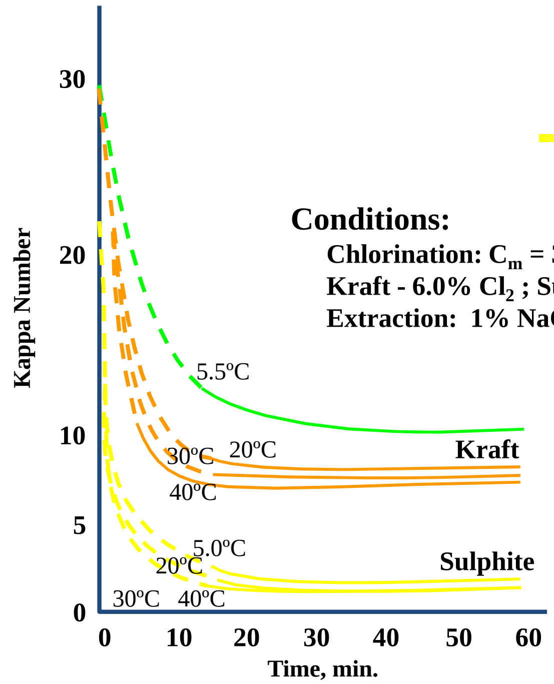
Delignification and brightness development

Rate of Lignin Removal in the Initial Stages of Kraft Pulp Chlorination





Pulp Chlorination



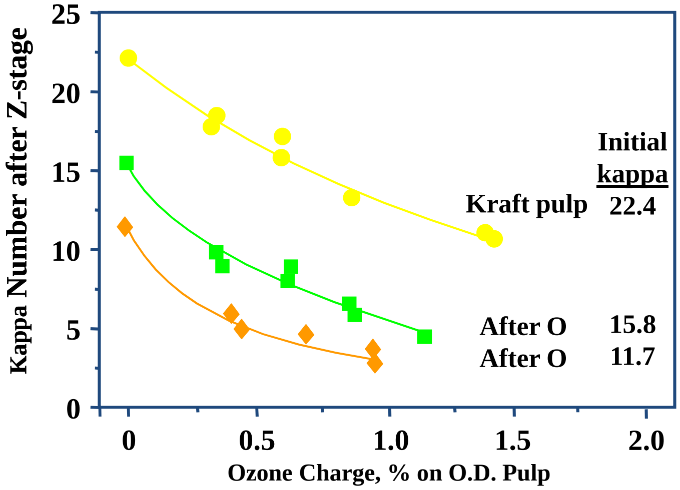
Conditions:

Chlorination: C_m = 3.0%
Kraft - 6.0% Cl_2 ; Sulphite - 5.0% Cl_2
Extraction: 1% NaOH, C_m = 5%, 50°C, 2 hr.

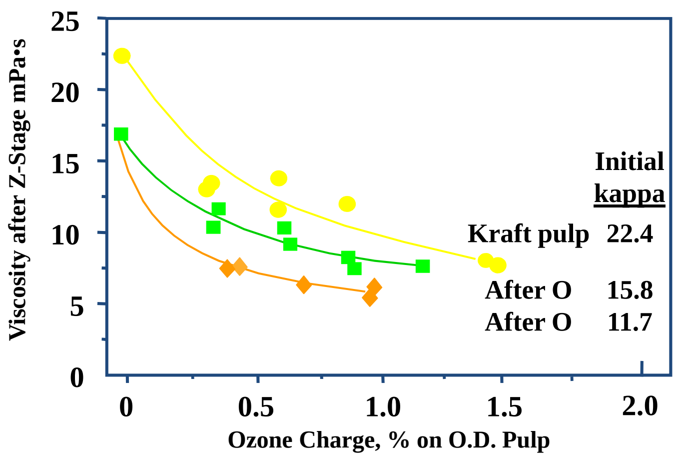
Ozone Delignification

- Ozone is a powerful oxidizing agent which reacts readily with most organic materials
- First patent describing the use of ozone in bleaching of fibres for papermaking issued in 1889
- Commercial implementation delayed due to technical issues (mixing, ozone generation), higher pulp production costs, and poorer pulp quality (lower strength, lower brightness)
- 13 installations by 1995
- Future D/Z?

Ozone Delignification



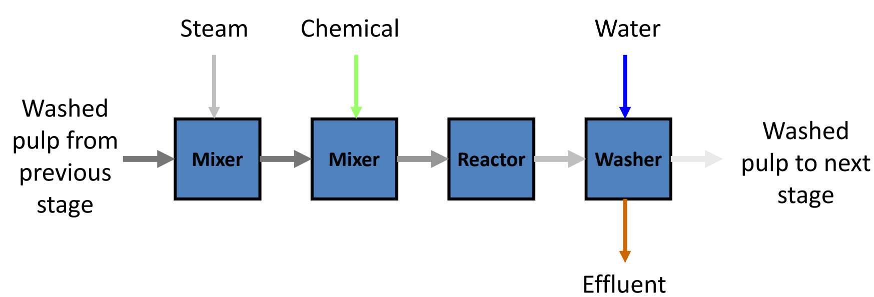
Ozone Delignification



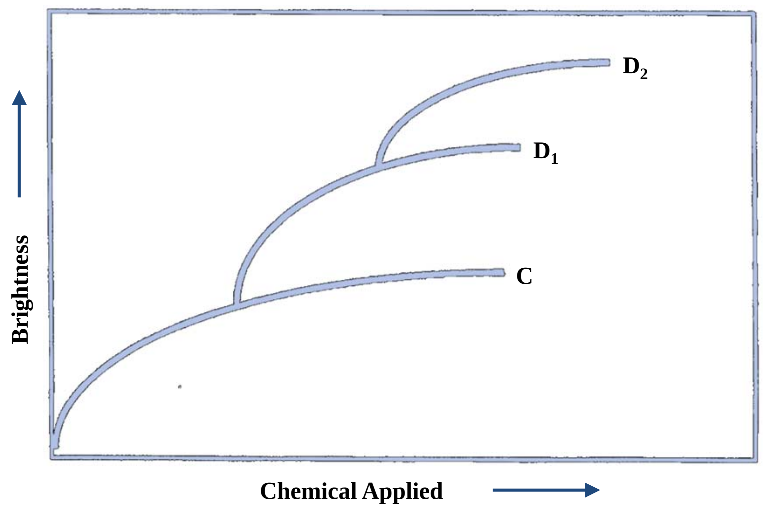
Chemical Pulp Bleaching II Overview

- Bleaching sequences
- D(EOP)D(EP)D sequence
- Bleaching equipment
  - washers
  - mixers
  - residence towers
- Challenges met in the 90's
- Challenges for the future - 2000 and beyond

The Bleaching Stage



Asymptotic Bleaching Levels



Bleaching Sequences

- Delignification Partial Sequences

  CE
  C_DE
  (DC)E
  C(EO)
  O(CE)
  ODE
  OD(EO)

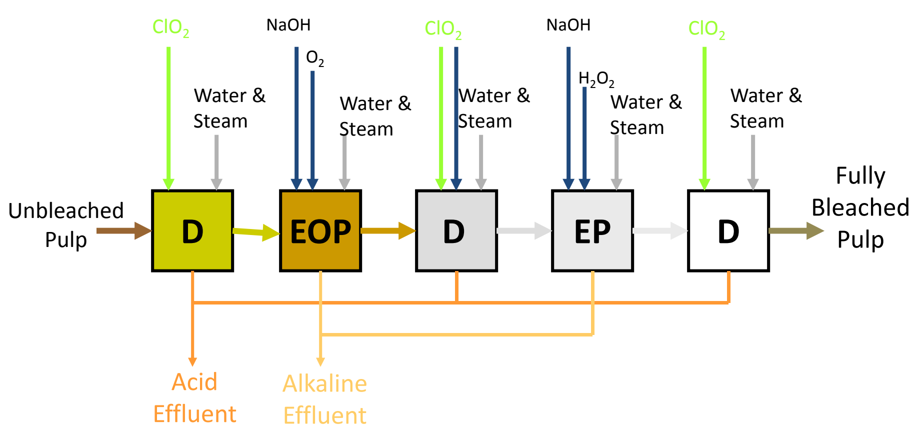
- Brightening Partial Sequences

  H
  D
  HD
  HDED
  DED
  D(EP)D

Bleaching Sequences

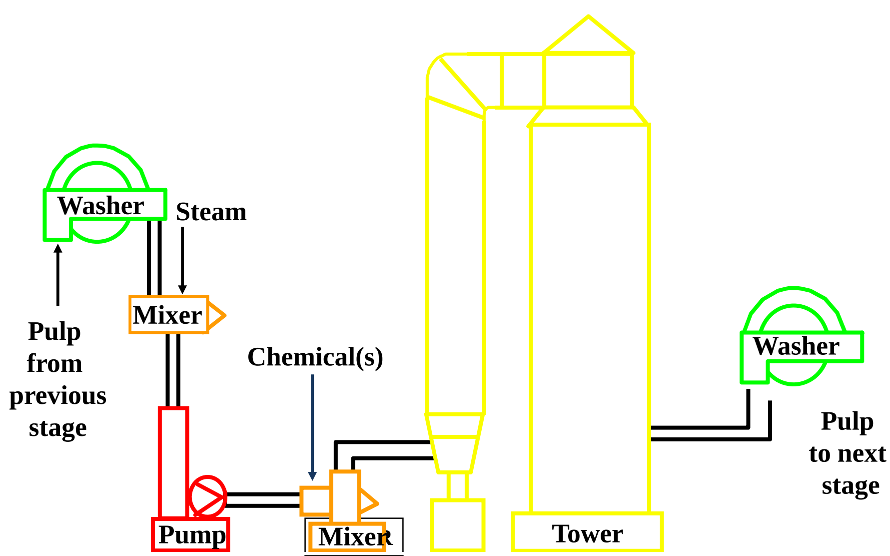
1970's	CEH
	CEHH
	CEDED
	C_DEDED (5-10% D)
	$(C_{30}D_{70})(E+O)DED$
	$O(D_{70},C_{25}D_5)(E+O)D$
1990's	OD(EOP)D(EP)D
	OZEP
Future	?

The D(EOP)D(EP)D Sequence



Typical Bleaching Conditions OD(EOP)D(EP)D

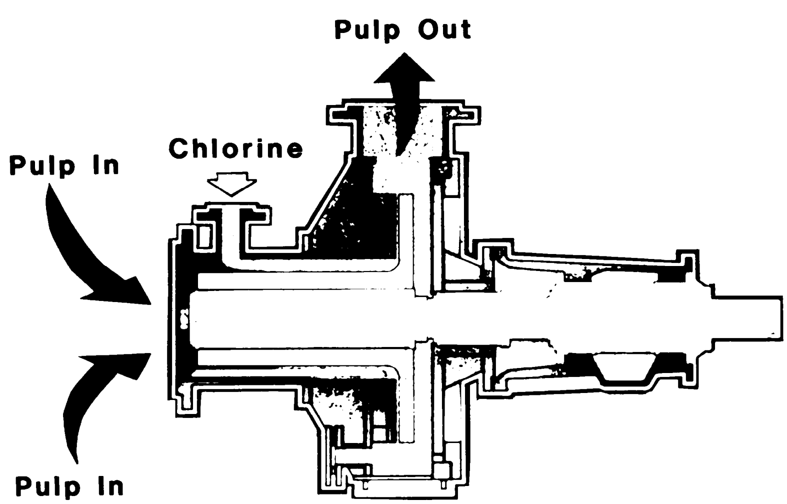
	O	D	EOP	D	EP	D
Chemical Applied, kg/t						
O_2	25	-	5	-	-	-
ClO_2	-	20	-	8	-	5
NaOH	25	-	25	5	5	-
H_2O_2	-	-	3	-	~3	-
Temperature, ^{o}C	95	50	70	70	70	70
Residence time, min	60	30	60	180	60	180
Residual Oxidant	yes	nil	-	tr	-	nil
Consistency, %	12	3	12	12	12	12
End pH	11+	2.5	10.5	3.5	10.5	4
kappa target	15	-	~3	-	-	-
Brightness target (ISO)	-	-	-	83	-	90



Bleaching Equipment

- Pumps
- Mixers
- Reactors (Residence Towers)
- Washers
- Sensors

Medium-Consistency Pulp Mixer



MC Mixer installation

Bleach Towers

Typical Tower Design

Stage	Consistency (%)	Residence Time (h)	Tower Configuration	Tower Aspect Ratio (H/D)
O	10 - 12 28 - 32	0.75 - 1.0 0.5	UF DF	7 - 10 3 - 4
C, (CD), D_{100}	3 - 4 10 - 12	0.5 - 1.0 0.5	UF UF	4 - 7 4 - 7
Z	10 - 12	0.05 - 0.08	UF	10 - 12
E_o, E_{op} (tube) E E_{op}	10 - 12	0.05 - 0.5 1.0 - 2.0 ~2.0	UF+ DF UF	9.5 4 - 5 4 - 5
H	10 - 12	0.5 - 3.5	DF	4 - 5
D	10 - 12	0.5 2.5 - 4.5 3.0 - 5.0	UF+ DF UF	9 5 5

Tower Design - In General

- Tower Configuration
- Low and Medium Consistency (3 - 12%)
  - Liquid chemicals: upflow or downflow
  - Liquid chemicals with high vapor pressure: upflow (tower or tube)
  - Gaseous chemicals: upflow (tower or tube)
- High Consistency (20% - 40%)
  - Downflow
- Aspect Ratio
- Low consistency: 4 - 7
- Medium consistency: no gas 4 - 7
  gas > 8

Future Trends in Bleaching

- Greater use of oxygen compounds
- Progressive system closure
- More efficient chemical use
  - carefully chosen kappa targets
  - improved chemical contacting/mixing
  - hexenuronic acid removal
  - new chemical additives