Bleaching of Pulp And Its Chemistry, A Brief Introduction

ARVIND KUMAR SHARMA
SCIENTIST-B

Crash Course on paper making for non paper, June 03, 2025
Hotel Vivanta, New Delhi Dwarka,

INDEX

Objective of Bleaching of Pulp

- **High brightness of pulps.**
- **Brightness stability by removing chromophoric structures.**
- **High pulp cleanliness by removing extractive and other contaminants.**
- **High cellulose content.**

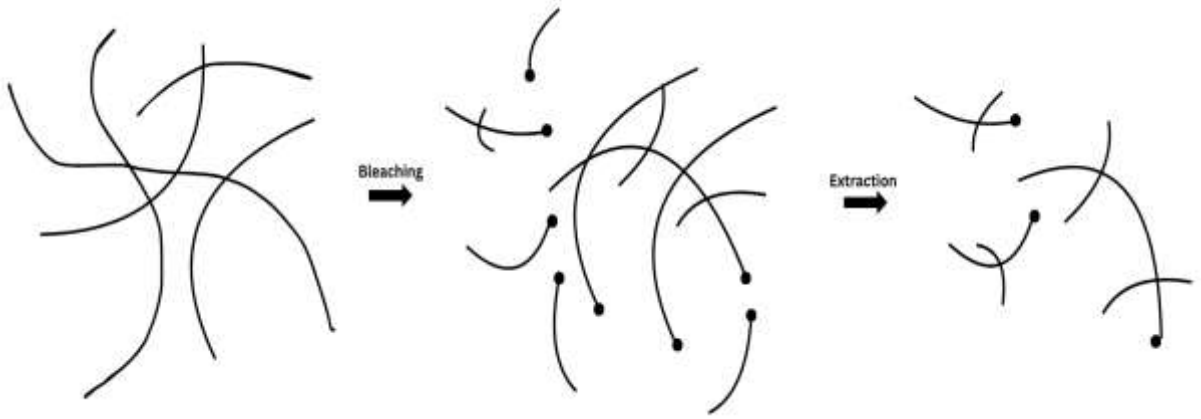
These objective must be achieved without compromising the strength of the final product.

Bleaching

Two principally different methods

➢Lignin removing bleaching

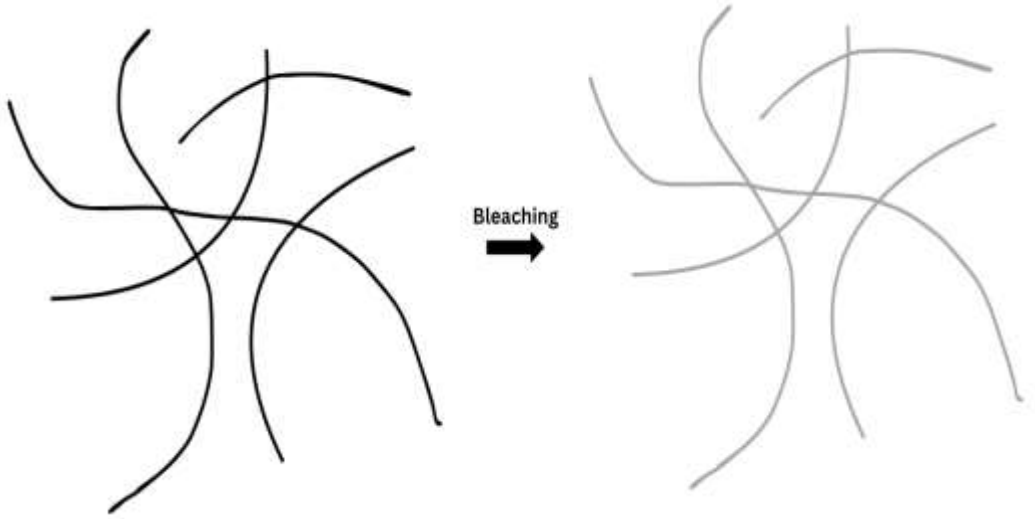
- No lignin – no color
- Break up lignin molecules into smaller fragments.
- Make the fragments water soluble by introducing hydrophilic groups
- Suitable for chemical fiber



➢Lignin preserving bleaching/brightening

The lignin is not removed from the fiber, but color is removed

- High yield pulps (mechanical, Chemimechanical-----)
- Make the lignin brighter



Chemicals Used For Bleaching

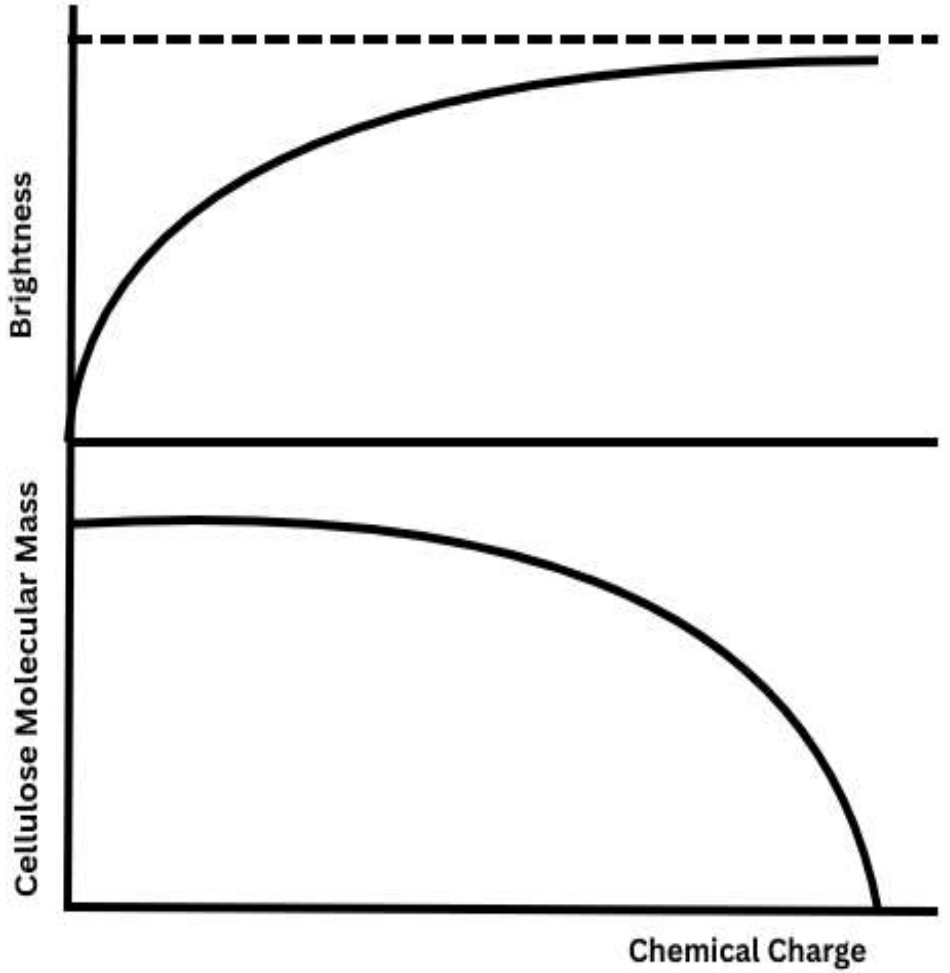
- Chlorine (Cl_2) – C
- Hypochlorite (ClO^-) – H
- Chlorine dioxide (ClO_2) – D
- Alkali (NaOH) – E
- Ozone (O_3) – Z
- Peroxide (H_2O_2) – P
- Complexing agent – Q
- Peracids – Pa, Ca
- Bisulfite
- Dithionite (hydrosulfite) – Y
- Formamidinic sulfonic acid – FAS
- Enzyme (xylanase) – X
- Enzyme (laccase) – L

Oxidation Equivalents

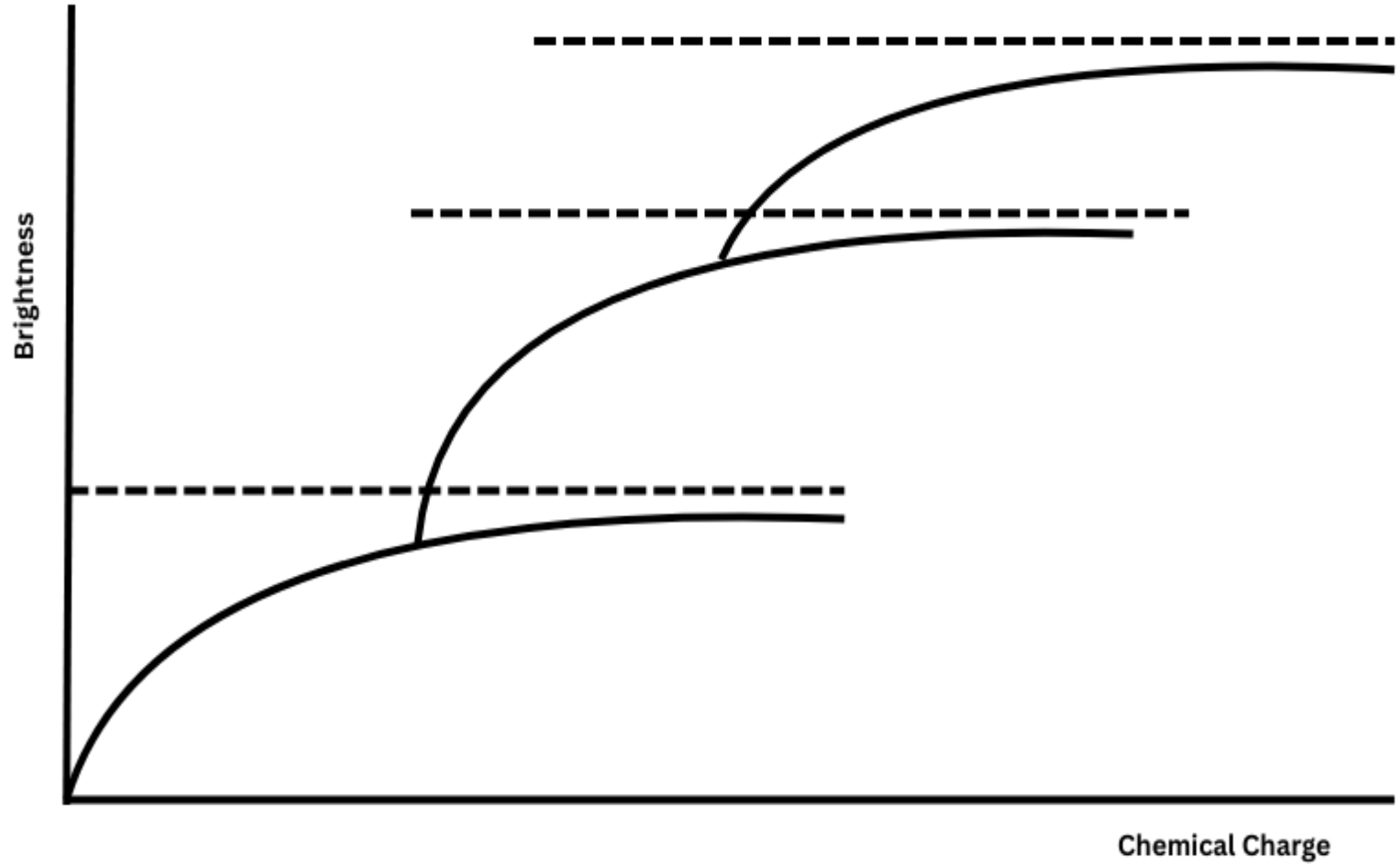
Bleach Chemical		Molecular Mass (g/mol)	Mole e^- /mole chemical	g/ mole e^-	OXE/kg
Cl_2	C	71	2	35.5	28.2
NaoCl	H	74.5	2	37.2	26.8
Clo_2	D	67.5	5	13.5	74.1
O_2	O	32	4	8	125
H_2O_2	P	34	2	17	58.8
O_3	Z	48	6	8	125

Effects of bleaching agents on brightness and cellulose molecular mass

- **Bleaching response decreases with increasing chemical charge**
- **Cellulose degradation increases with increasing chemical charge**
- **A bright fiber is usually no problem. The problem is how to obtain a sufficiently bright fiber with sufficient strength for a low cost**



Solution: Multistage Bleaching



Chemical and Mechanical pulp bleaching sequences

Chemical pulp bleaching sequence			Mechanical pulp bleaching sequence
Conventional	ECF	TCF	
CEpH	DEpD	OZP	QPP
CEpHH	ODEOpD	OZEpP	QPYP
CEopHD	OD/CEopD	OAZEp(PO)	QYP
OCEopHD	ODEopDP	OZ(EOP)P	PP
OD/CEpD	$OD_{ht}ZEpD$	OAZP	

Bleaching conditions for different bleaching sequences

Parameters	Conventional bleaching sequence					ECF bleaching sequence			
	O stage	C stage	Eop stage	H Stage	D stage	O stage	D_0 stage	Eop stage	D_1 stage
Consistency, %	10	8	10	10	10	10	8	10	5
Reaction time, min	90	30	90	120	180	90	60	90	60
Reaction temp, ^{0}C	90	Amb	70	40-45	80	90	75-80	70	80
pH	10.5-11.5	<2	11-12	9.5-10.5	3-4	11-12	2.5-3.0	11-12	3-4

Parameters	TCF bleaching sequence				QPP bleaching sequence		
	O stage	Z stage	Eop stage	P stage	Q stage	P stage	P stage
Consistency, %	10	25-30	10	10	10	10	10
Reaction time, min	90	5.0	90	120	60	120	120
Reaction temp, ^{0}C	90	30-40	70	70	60-65	70	70
pH	10.5-11.5	2-3	11-12	9-10	5-6	2.5-3.0	9-10

Chlorine free bleaching

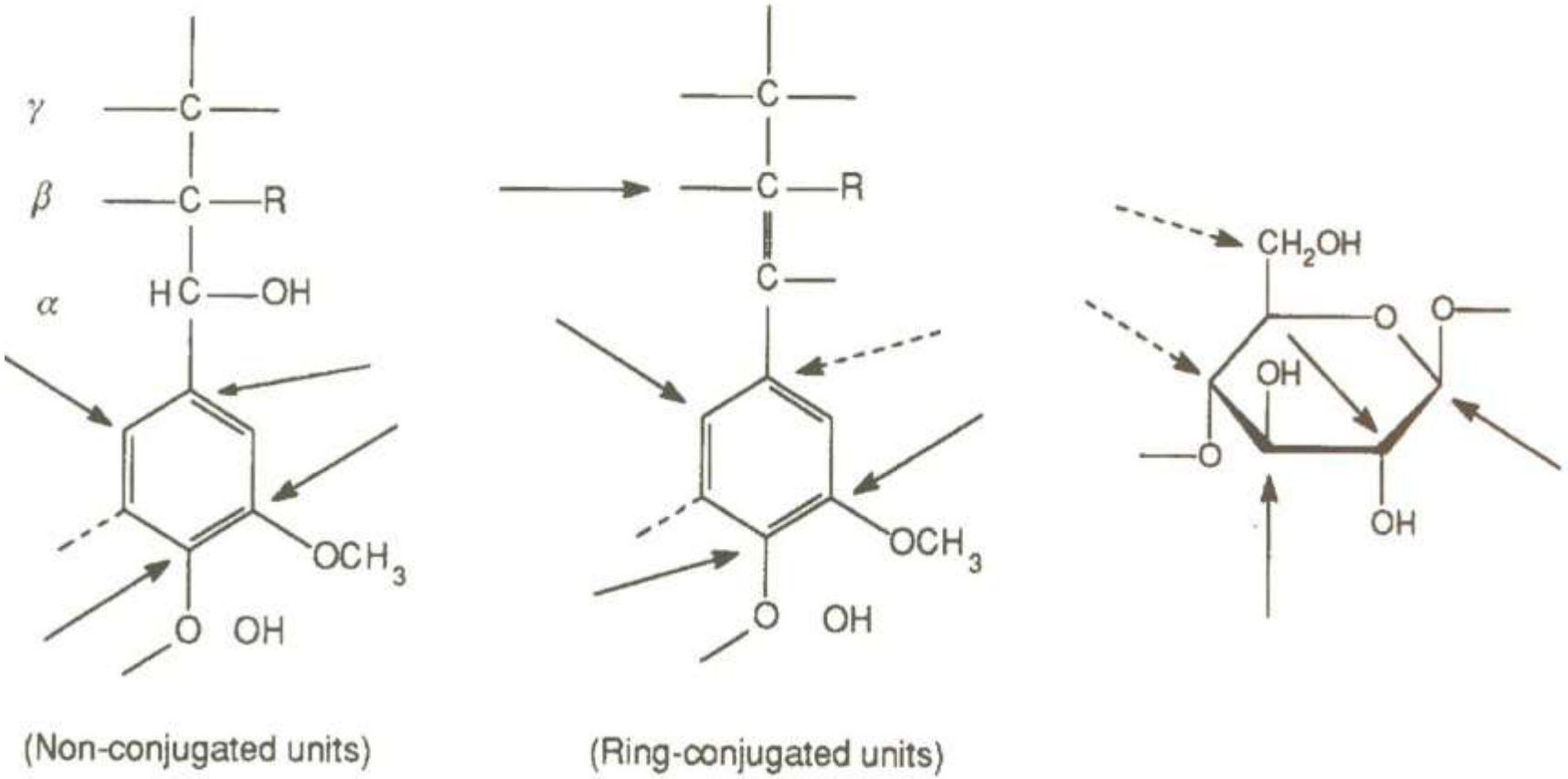
- Bleaching sequences of chemical fibres
- Elemental Chlorine Free (ECF):
  - Chlorine (Cl_2) is not allowed, other chlorine containing chemicals (ClO_2) are allowed Example: OD(EOP)D
- "ECF-light"
  - ECF sequences where the ClO_2 charge has been reduced by substituting chlorine free chemicals for ClO_2 in one or more stages: Example: OZ(EOP)DEP
- Total chlorine Free (TCF)

  -Neither chlorine(Cl_2) nor other chlorine- containing chemicals are allowed : Example: OZ(EOP)PP

Bleaching Reaction Mechanisms

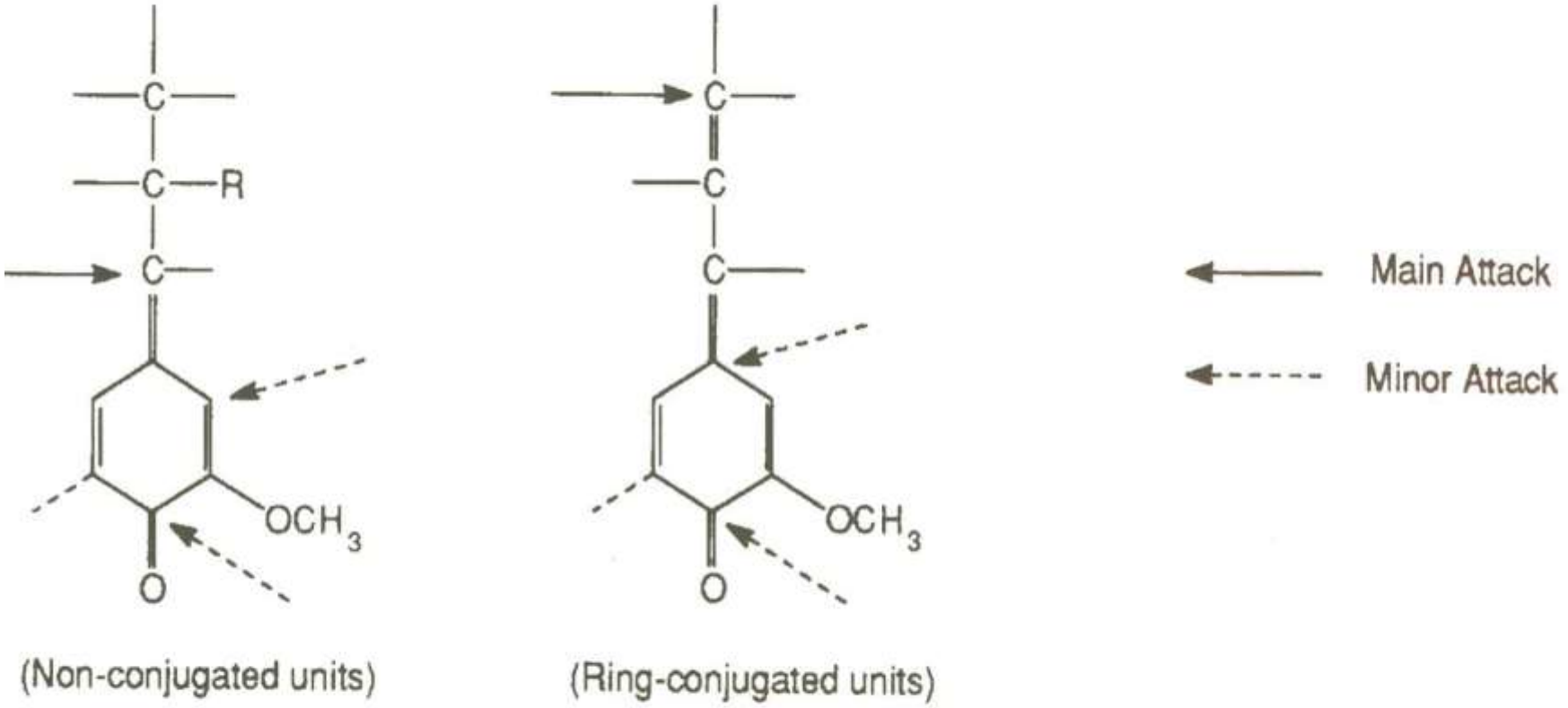
Reaction Mechanism	Bleaching chemicals	Target	Effect
Electrophilic reaction mechanism	Chlorine, Hypochlorous acid, Ozone, Chlorine dioxide and Paa	Unsaturated structures (-C=C-) [lignin, HexA, extractives]	Chlorination of lignin and Oxidation of lignin
Nucleophilic reaction mechanism	Sodium hydroxide, Hydrogen peroxide, Hypochlorous acid and Paa	Electrophilic carbon atoms, such as carbonyl structures (C=O) [lignin, extractives]	Brightening effect, oxidation of lignin
Radicals reaction mechanism	Chlorine dioxide, Ozone and Oxygen	Phenolic and non phenolic structures with ClO2, O3 and Phenolic structure with O2	Brightening effect, oxidation and chlorination of lignin

Electrophiles attack on lignin



Sites of Attack by Electrophiles

Nucleophiles Attack on Lignin



Sites of Attack by Nucleophiles

Bleaching Vs. Pulping

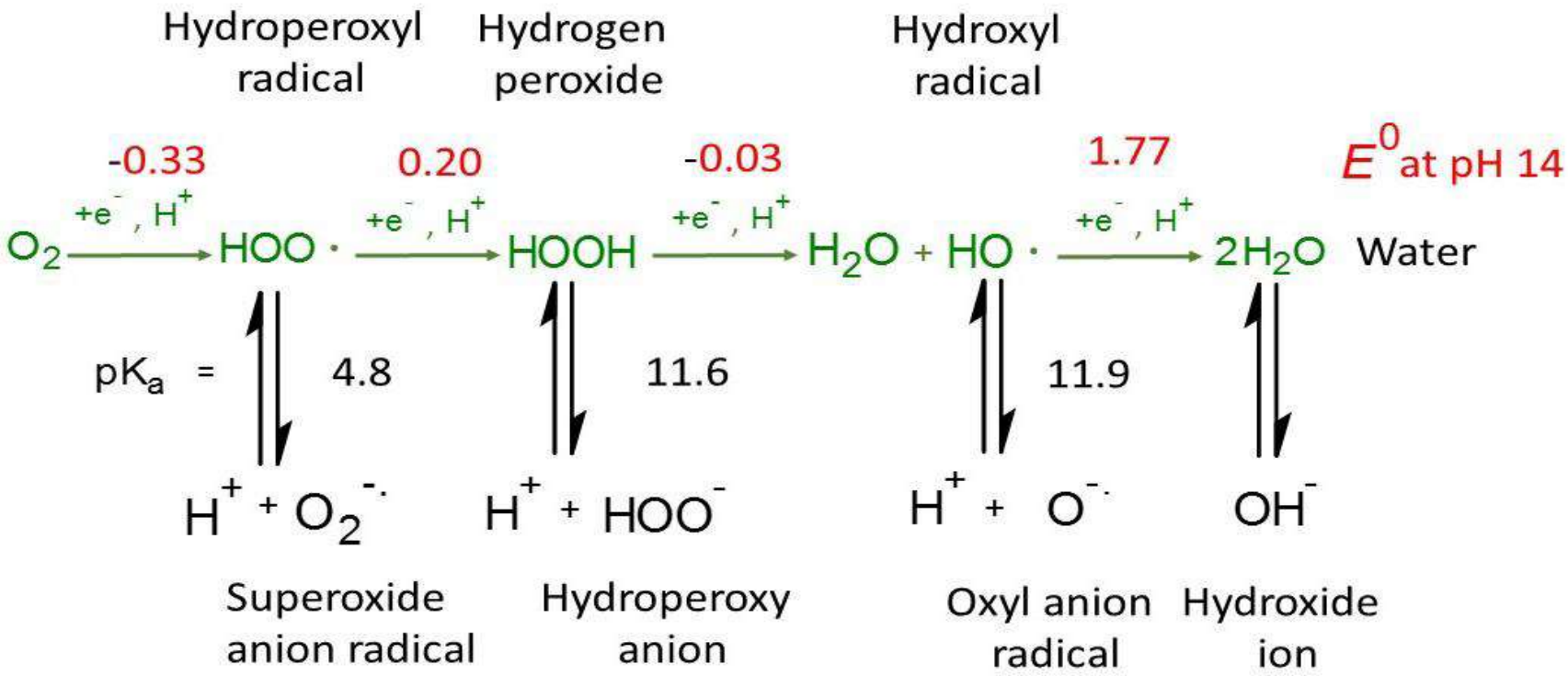
Compared to pulping, bleaching is

- is a delignification process
- Is more selective in terms yields and D.P
- Is more expensive per unit of lignin remove
- Removes less lignin
- Produce problematic effluent

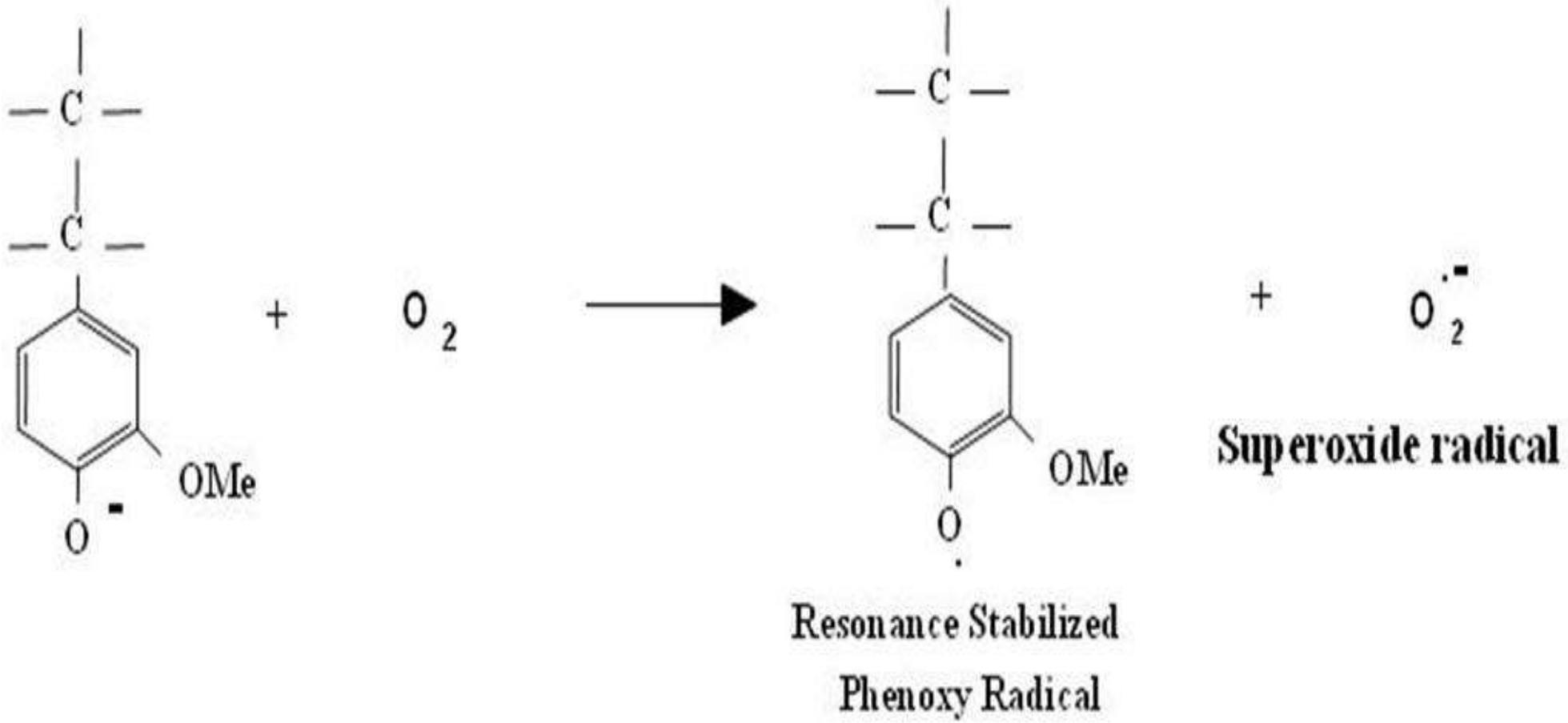
Oxygen Delignification - Purpose

- Extended lignin removal to minimize the volume of more expensive bleaching chemicals
- Minimize pulp degradation (cellulose loss)
- Reduce the amount of lignin to the bleach plant
- Minimize environmental load
- Reduce bleaching chemical demand

Stepwise Reduction of Oxygen To Water

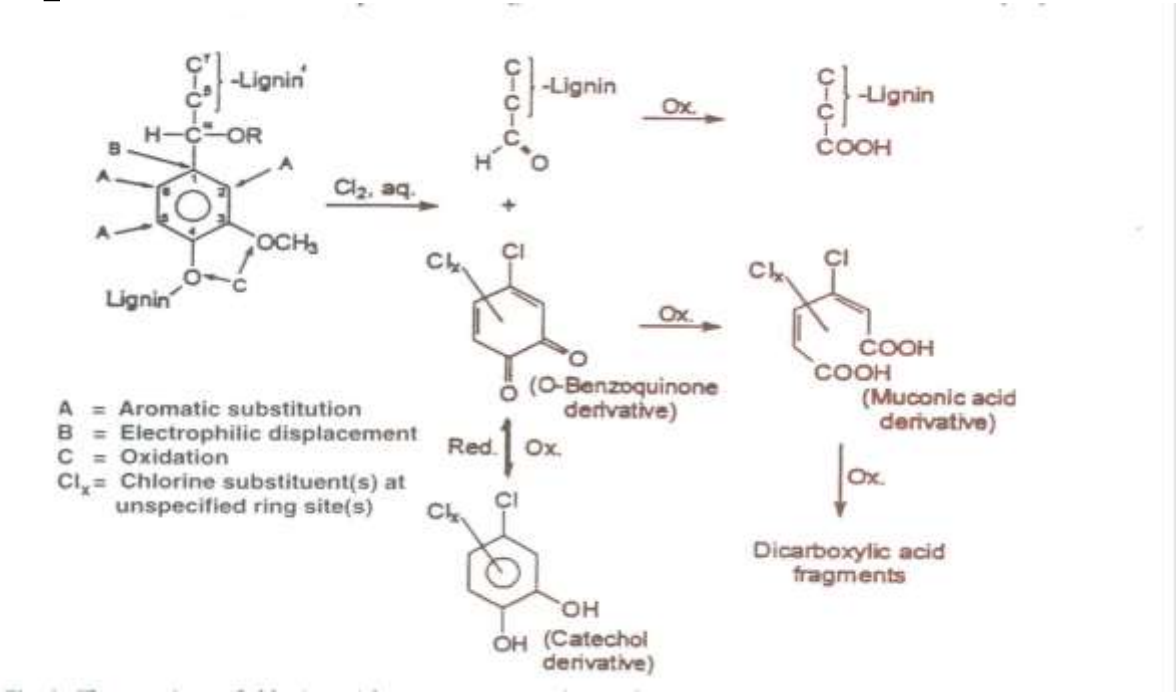


Oxygen and the lignin

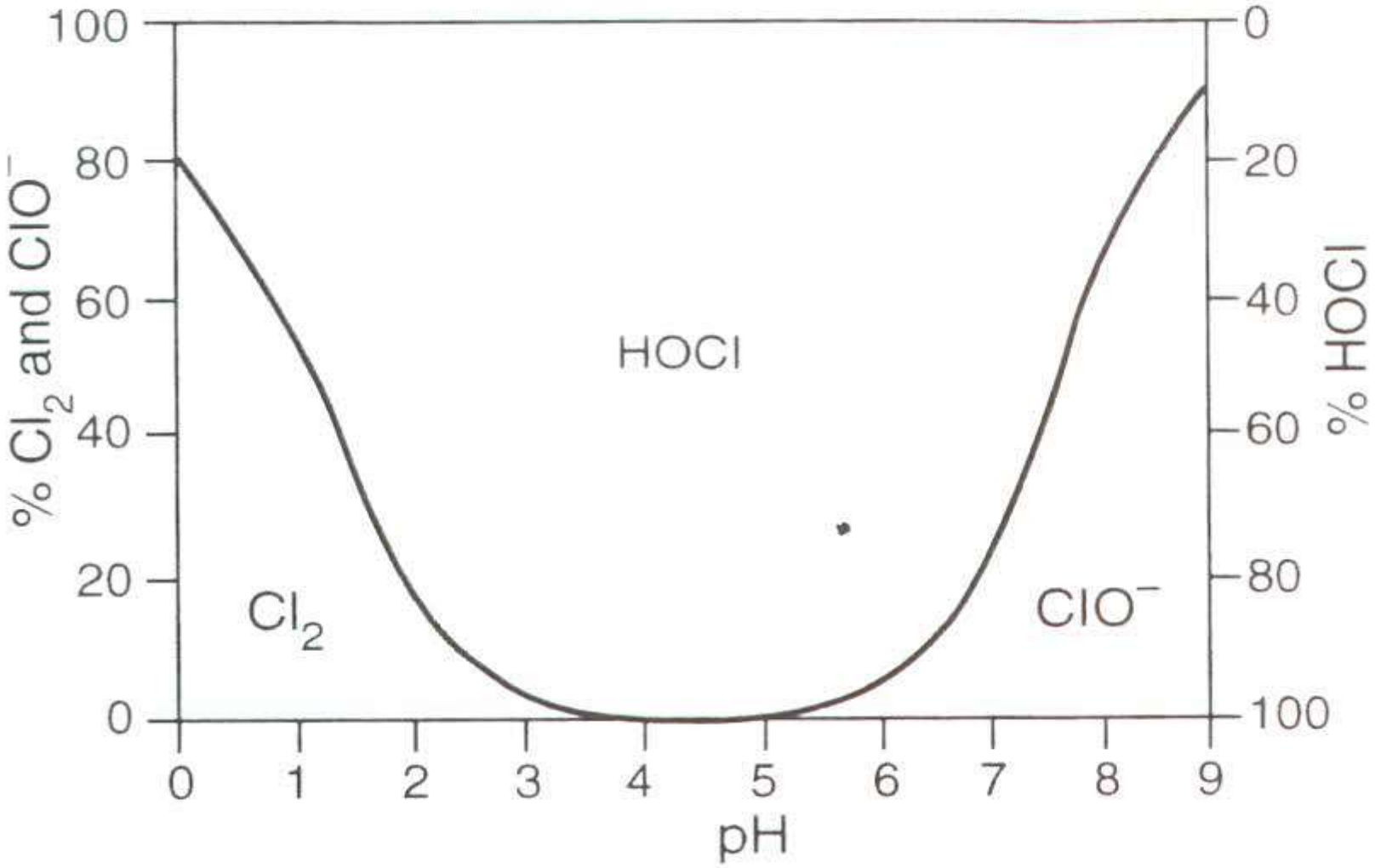


Chlorination stage- C stage

- Bleaching of chemical fibres
- Very effective bleaching agent for lignin degradation
- Pulp viscosity drop upto 15%
- Ability to remove dirt particles from pulp
- Reaction with lignin
  - Substitution reaction and electrophilic displacement reaction
  - Oxidation reaction
  - Catalytic hydrolysis reaction
  - Electrophilic addition reaction to carbon–carbon double bond



Effect of pH During Chlorination Stage



Extraction Stage – E stage

Objective:

- To remove chlorinated and oxidized lignin formed in the chlorination stage
- Dissolves 80 % residual lignin removed in early stages.
- To remove the physical barrier
  - Allow the exposure of unreacted lignin to further oxidation
- To generate new active groups on the remaining lignin structures
  - Allow reaction with the oxidizing agent used in the next stage
- To remove resins and fatty acids.
- Today, an oxidizing bleaching chemical (O_2 and H_2O_2) is often added as reinforcement.

O and/or P reinforced extraction

- Denoted (EO), (EP), (EOP)
- Increased delignification during extraction
- Increased brightness during extraction
- Reduced chemical consumption in later bleaching stage
- Less color in filtrate
- 5kg/ton O_2 or 1.5 kg/ton peroxide in E = 3kg/ton lower ClO_2 charge in D_1 for similar brightness

Hypochlorite – H stage

- The first pulp bleaching chemical (chemical fibers)
- Produced by alkalization of chlorine water

$$Cl_2 + 2\ NaOH \longrightarrow 2Na^+ + OCl^- + H_2O$$

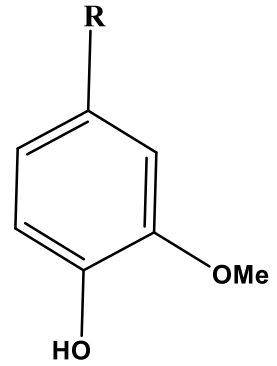
- Brightening bleaching chemicals
  - Decolourize some chromophoric structures by oxidation
- Maximum carbohydrate degradation at low and high pH

Chlorine dioxide -D stage

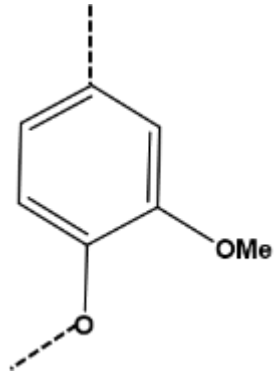
- **Chlorine dioxide is an efficient delignification agent for chemical fibre .**
- **Generated on site.**
- **High selectivity towards lignin**
- **Attack on aliphatic bonds of lignin and there by reduce color.**
- **Works as a radical scavenger there by protected cellulose against depolymerisation.**
- **Used for initial delignification and final bleaching.**
- **Compliance with strict environmental regulations**

Reactions of Chlorine Dioxide and lignin

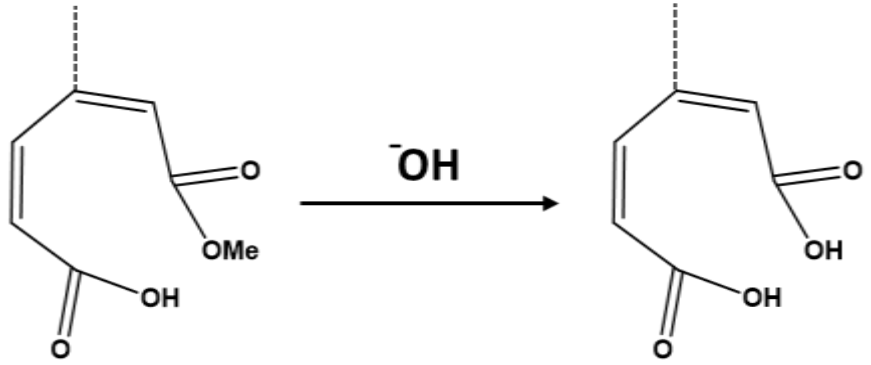
- Reacts fastest (i.e. preferably) with phenolic lignin structures



- Reacts slowly with non- phenolic lignin structures



- Degrades lignin forms muconic acid type structures



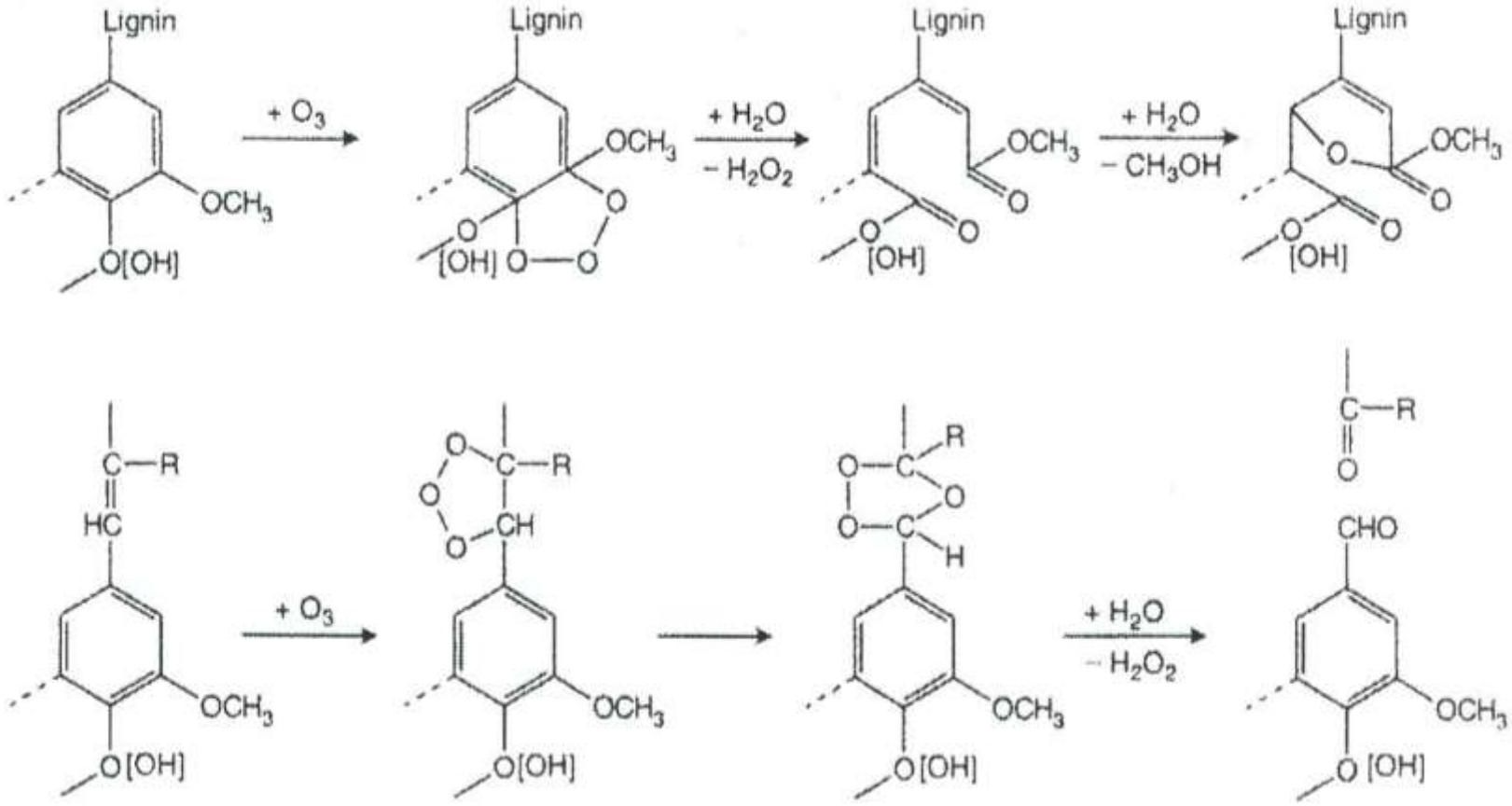
Advantages of Chlorine Dioxide With Pulp

- **High brightness of pulp**
- **Excellent for shive and dirt removal**
- **Substitute to Harmful Chlorine/Hypochlorite**
- **High strength pulp**
- **Brightness stability**
- **Reduce environmental problem**

Ozone (O_3) – Z stage

- **For chemical fibers**
- **Chlorine free bleaching chemical**
- **Produced on site from oxygen up to 12%(w/w)**
- **Strong oxidizing agent, fast reaction**
  - **Somewhat poorer selectivity than chlorine dioxide**
- **Normally early in the bleach sequence**
  - **Can be used in combination with chlorine dioxide – (DZ)stage**
- **Ozone is an oxidizing electrophilic reagent, which can oxidize**
  - **Free phenolic hydroxyl lignin structures**
  - **Non- phenolic hydroxyl lignin structures**
  - **Conjugated double bondlignin structures**

Reactions of Ozone With Pulp



Benefit of Ozone Bleaching

- Ozone is 10^6 times more reactive towards lignin than towards carbohydrates.
- Removal of hexeneuronic acid present in pulps
- Extractive content significant reduced
- Brightness stability
- Unfortunately, radicals formation i.e. superoxide, hydroxyl are very reactive towards carbohydrates.
- Addition to additives to retard carbohydrate decompositions of pulps.
- Compliance with strict environmental regulations

Hydrogen Peroxide (H_2O_2) -P

- For chemical or Mechanical fibers
- Some what different process condition
- Chlorine free bleaching chemical
- Wide spread use in TCF sequences for chemical pulps
- Less effective for delignification compared to ClO_2
- Very effective in final bleaching
- Works under alkaline condition: The reactive species is the prehydroxyl anion HOO-

Bleaching Chemical Characteristics, L=Low, M=Medium H=High

Bleaching chemicals	Eq.wt	Eq.Cl_2	Efficiency	Reactivity	Selectivity	Dirt Removal	Environmental implication
Cl_2	35.5	1.00	H	H	H	H	H
Clo_2	13.5	2.63	H	M	H	H	M
O_2	8	4.44	L	L	M	M	L
H_2O_2	17	2.09	L	L	M	L	L
O_3	8	4.44	H	H	M	L	L
NaoCl	37.2	0.93	M	M	M	H	H

Auxiliary Chemicals And Their Functions In Bleaching

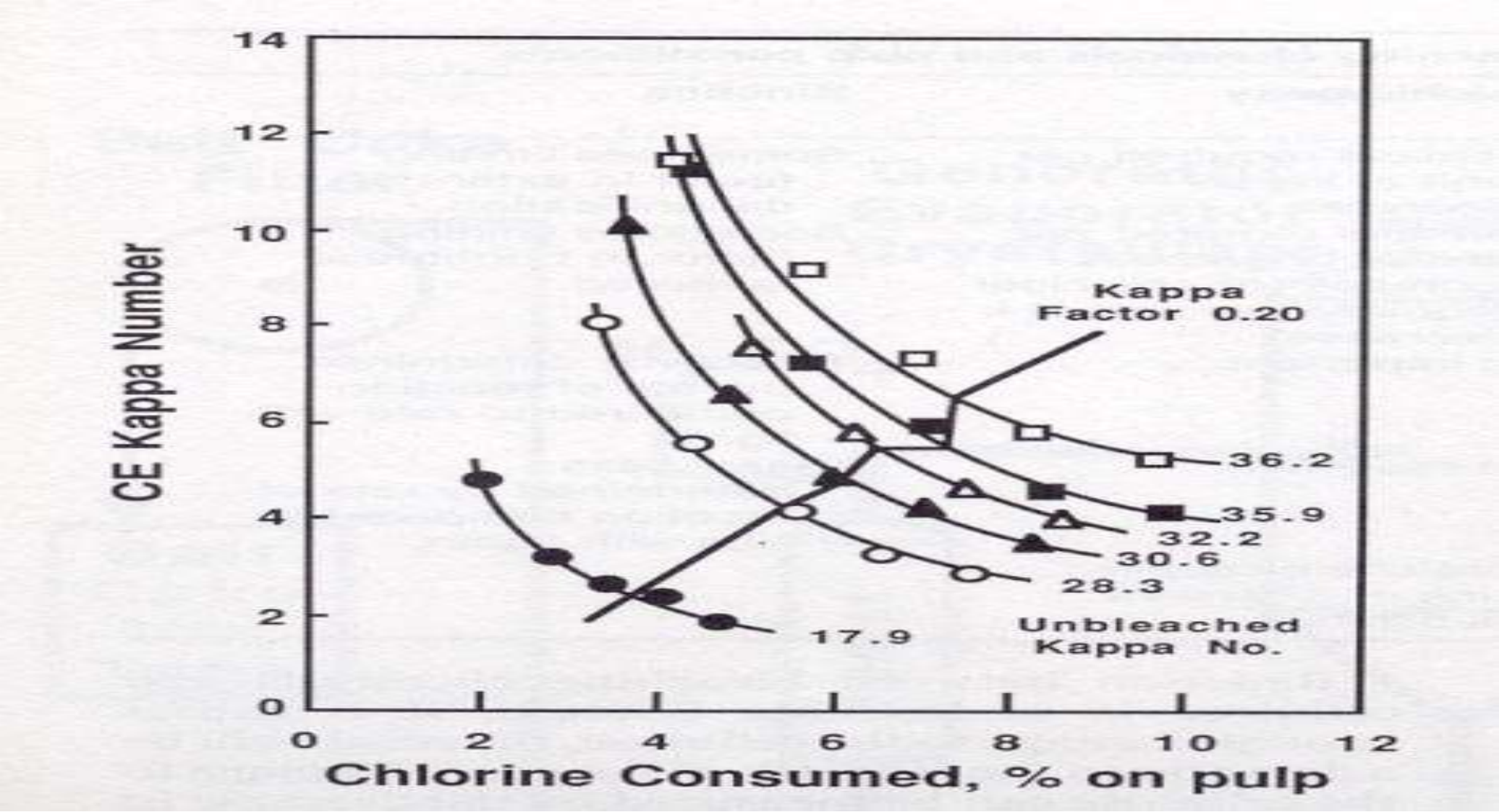
Bleaching chemicals	Function
Acid (A)	Removal of hexenueonic acid groups by acid hydrolysis
Alkali (E)	Dissolution of oxidized lignin residue after the First bleaching stage
Chelant (Q)	Removal of transition metals (Cu, Fe, Mn) which consume peroxide bleaching agent
Xylanase (X)	Degradation of surface lignin carbohydrate complexes

Conclusion

- **For chemical bleaching of pulps the main reaction mechanism is oxidation.**
- **For Mechanical bleaching of pulp describes the decolorization of chromophoric group of lignin.**
- **It is important to remember that depending on bleaching conditions different intermediate products are formed.**
- **Reactions of bleaching chemicals are often very complex due the formation of intermediate products.**

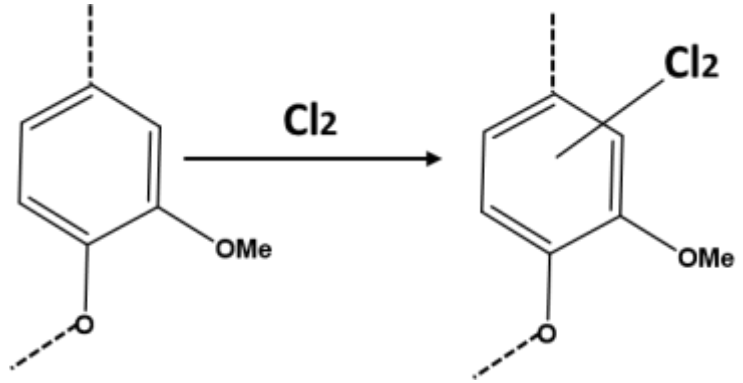
Thank you

Effect of % addition of chlorine (doze optimization)

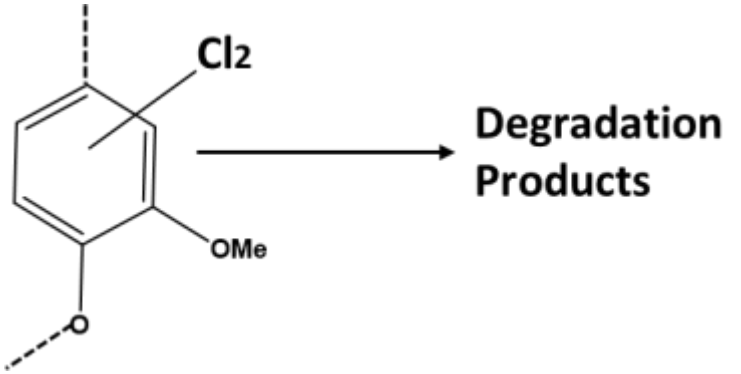


Reactions of Chlorine and lignin

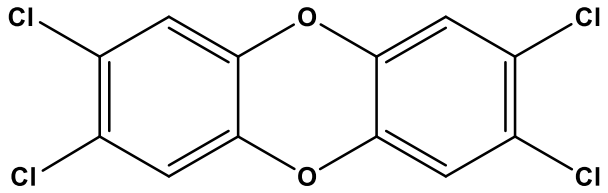
- Fast chlorination of the aromatic ring, at multiple site



- Slow fragmentation



- Cl_2 bound to the aromatic ring, yields polychlorinated (aromatic) compounds in filtrate- E.g. dioxins



Bleaching Chemical Characteristics

- **Equivalent weight**
- **Efficiency**
- **Reactivity**
- **Selectivity**
- **Particles bleaching ability**
- **Environmental Implication**

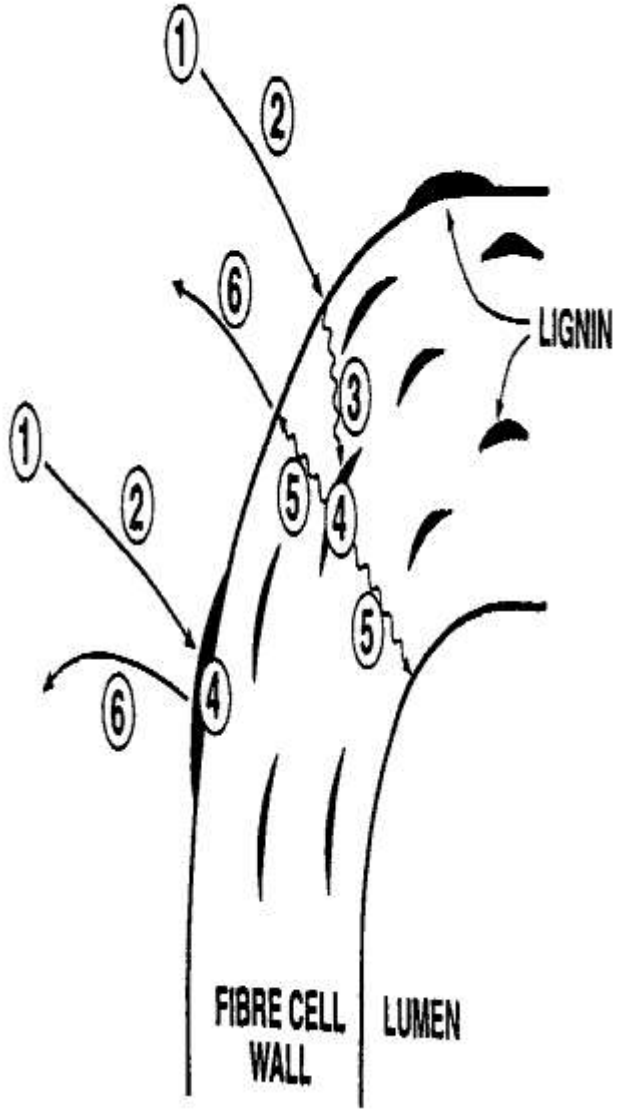
Reactivity and Selectivity

- **Reactivity may be defined in terms of the fraction of the residual lignin that the bleaching agent is practically capable of removing.**

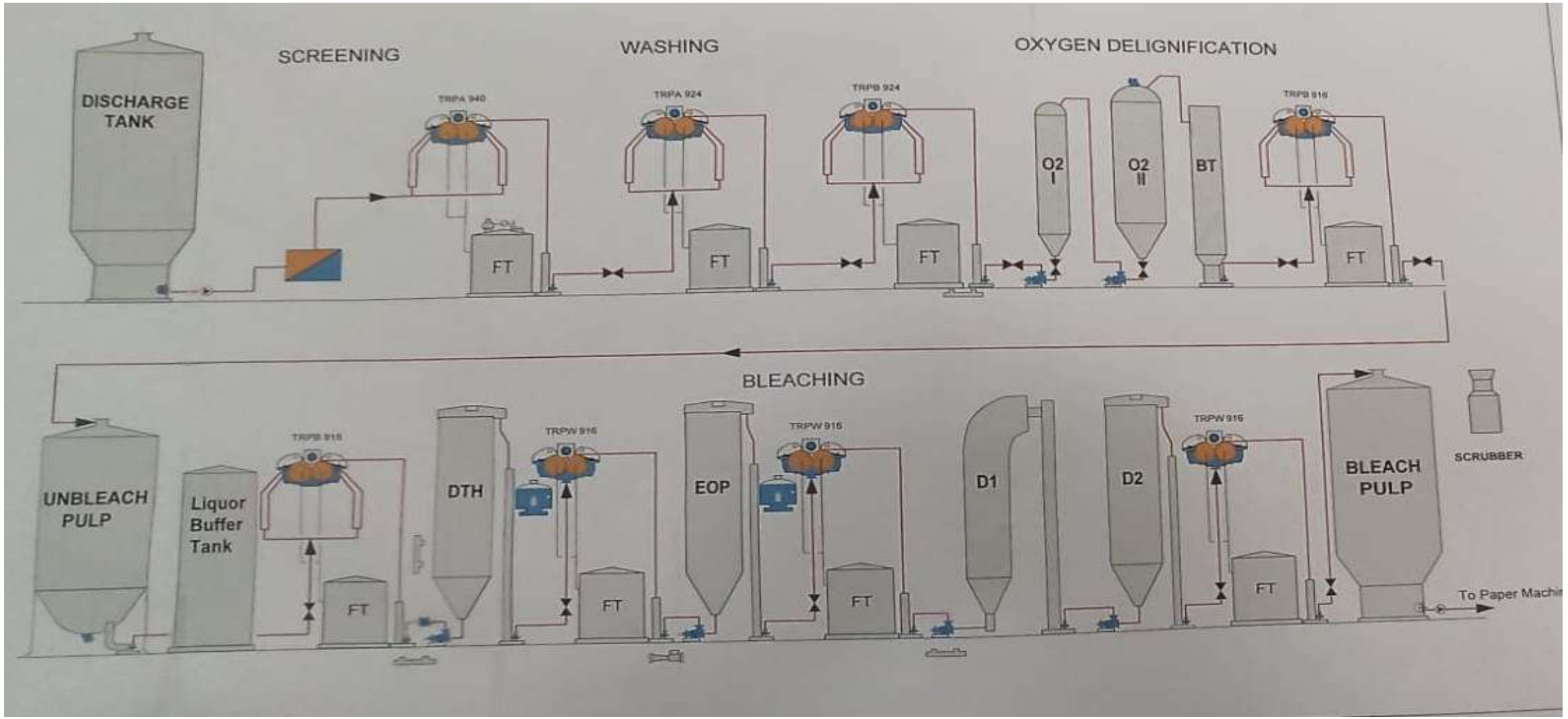
- **Selectivity is the degree of the residual lignin that the bleaching agent can remove lignin without dissolving or damaging the other components of the fiber, cellulose and hemicellulose.**

Mass Transfer in Pulp Bleaching

Step-1	▪Dissolution of a gaseous bleaching agents in to bleaching phase ▪The solubility of gas governs the rate of reaction.
Step-2	▪The transport of bleaching chemicals from the bulk phase onto the fiber surface ▪This rate is only dependent on mixing
Step-3	Diffusion of bleaching chemicals into the fiber cell wall where it is able to react with lignin or other cell wall components.
Step-4	Bleaching chemicals reaction itself
Step-5	Transport of the reaction products out of the cell wall
Step-6	Transport of the reaction products out into the bulk phase



ECF Bleaching Fibre Line



Technology Upgradation