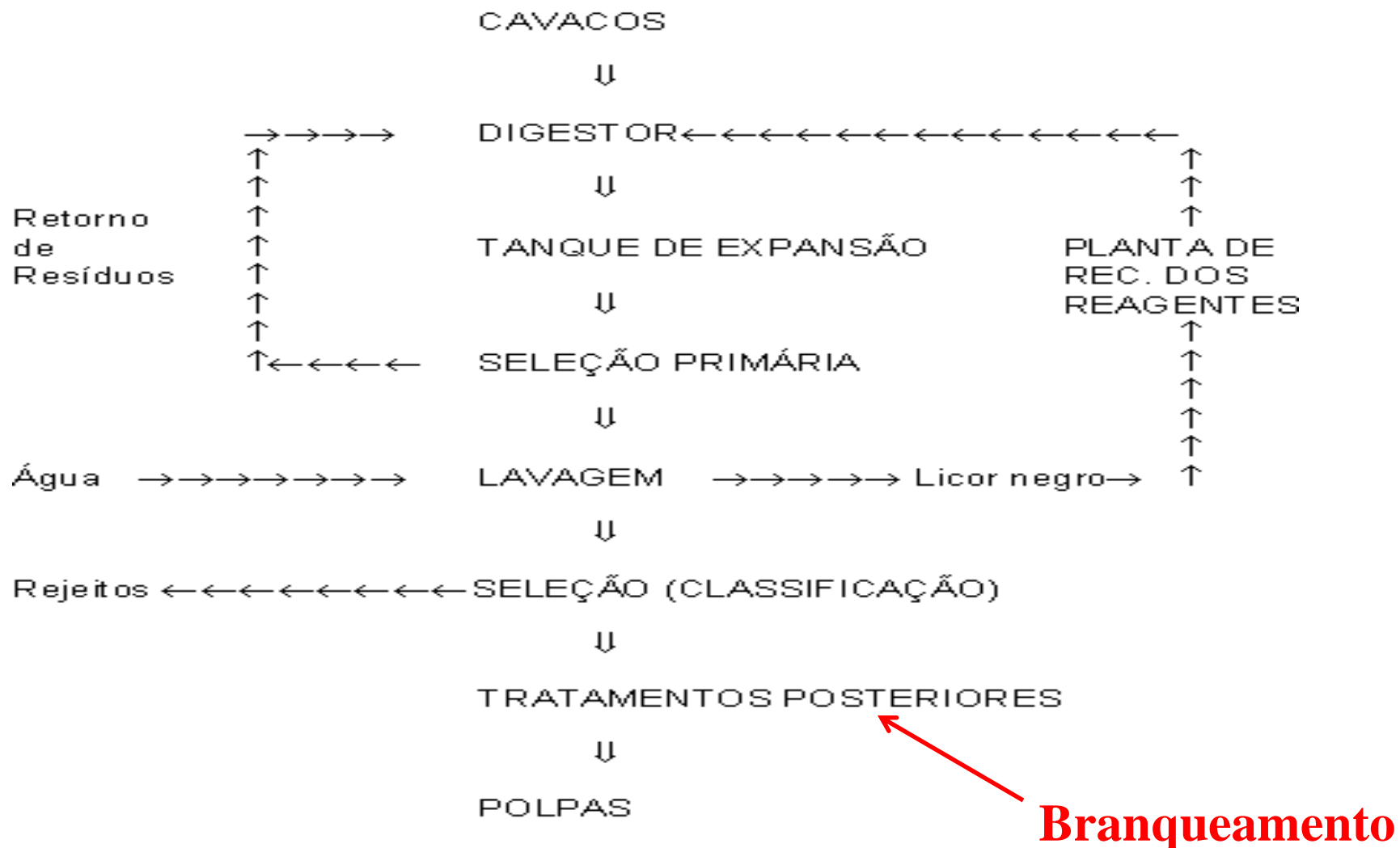


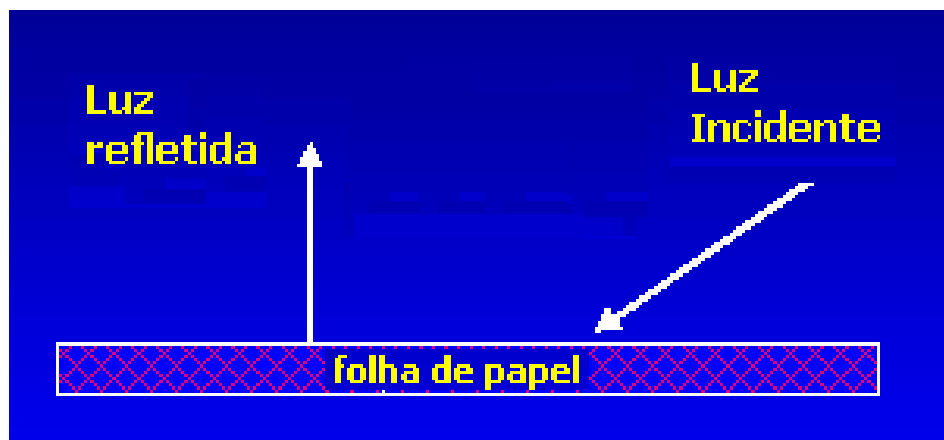
# Diagrama simplificado do processo kraft



# Branqueamento de polpas celulósicas

Dois tipos básicos:

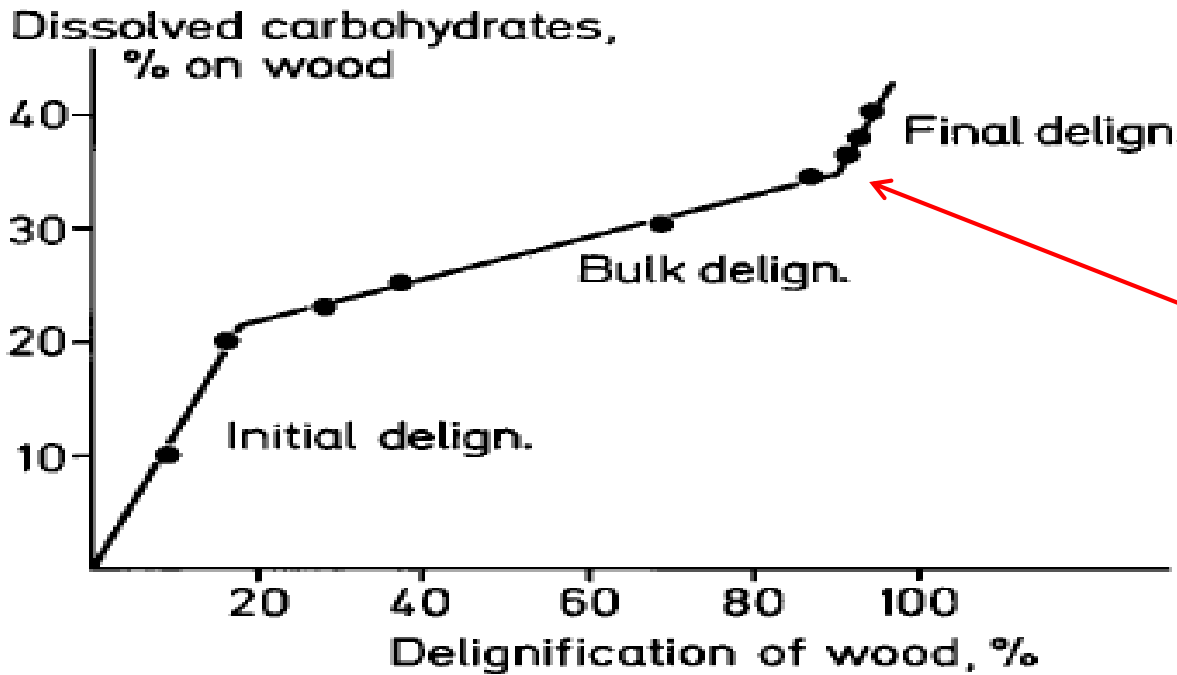
- a) eliminação de material responsável pela cor - usado em polpas químicas
- b) transformação do material responsável pela cor em substâncias mais claras - usado em polpas mecânicas



TIPO DE PAPEL	ALVURA %ISO
Impressão/cópia	80-90 ou maior que 90
Jornal	60-70
Embalagem (sacos)	25-30

**Pense:** Porque o branqueamento é necessário na polpação química???

Processo	Índice de resistência ao estouro (kPa.m <sup>2</sup> /g)	Índice de resistência ao rasgo (mN.m <sup>2</sup> /g)
NSSC, <b>branqueada</b>	1.32	10.7
NSSC, <b>não branqueada</b>	0.96	8.7
Kraft, <b>branqueada</b>	0.96	9.2
Kraft, <b>não branqueada</b>	1.08	7.6
Soda, <b>branqueada</b>	0.60	6.1
Soda, <b>não branqueada</b>	0.78	7.6



Remover lignina após este estágio no reator de polpação alcalina, representa perda expressiva de rendimento

**Pense:** O que será removido das polpas químicas com os agentes de branqueamento??

Table 9.1. Contributions to the kappa number from lignin, hexenuronic acid and "non-lignin" structures in various unbleached pulps (Li 1999).

Pulp type, Kappa number	Lignin <sup>1)</sup>	HexA <sup>1, 2)</sup>	Non-lignin <sup>1, 3)</sup>
Pine kraft, 18.6	14.3	1.9	2.4
Pine soda/AQ, 18.9	16.8	0.3	1.8
Birch kraft, 13.6	6.5	4.5	2.6
Eucalyptus kraft, 17.2	9.0	7.4	0.8

1) calculated in Kappa number units

2) HexA = Hexenuronic acid

3) Non-lignin = non-specified but oxidizable structures

## Principais reagentes usados no branqueamento

Cloração	C	$\text{Cl}_2$
Extração	E	$\text{NaOH}$
Hipocloração	H	$\text{NaClO}$
Dióxido de Cloro	D	$\text{ClO}_2$
Oxigênio	O	$\text{O}_2$ e $\text{NaOH}$
Peróxido de Hidrogênio	P	$\text{H}_2\text{O}_2$
Ozônio	Z	$\text{O}_3$

**Table 10.2.** Active chlorine content in chlorine containing bleaching chemicals.

Chemical	kg active chlorine/kg
Chlorine ( $\text{Cl}_2$ )	1
Chlorine dioxide ( $\text{ClO}_2$ )	2.63
Sodium hypochlorite ( $\text{NaClO}$ )	0.95

## Sequências típicas do branqueamento

### Polpas Kraft

(CD)(EO)DED – comuns até 1995

D(EOP)DED – requeridas por legislação e/ou mercado

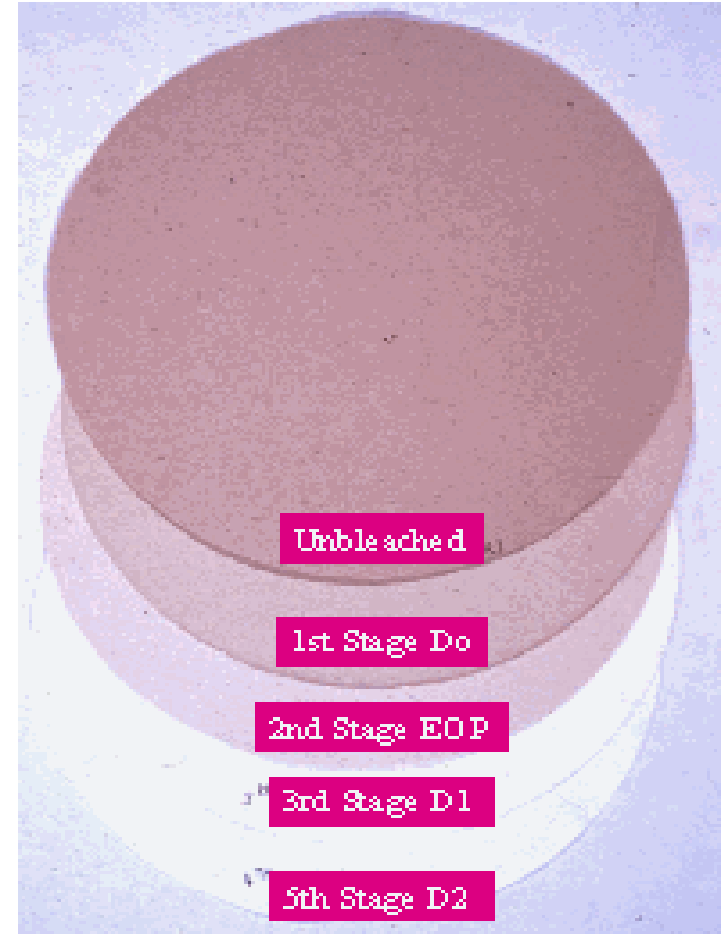


OD(EOP)D – requeridas por legislação e/ou mercado

### Polpas mecânicas

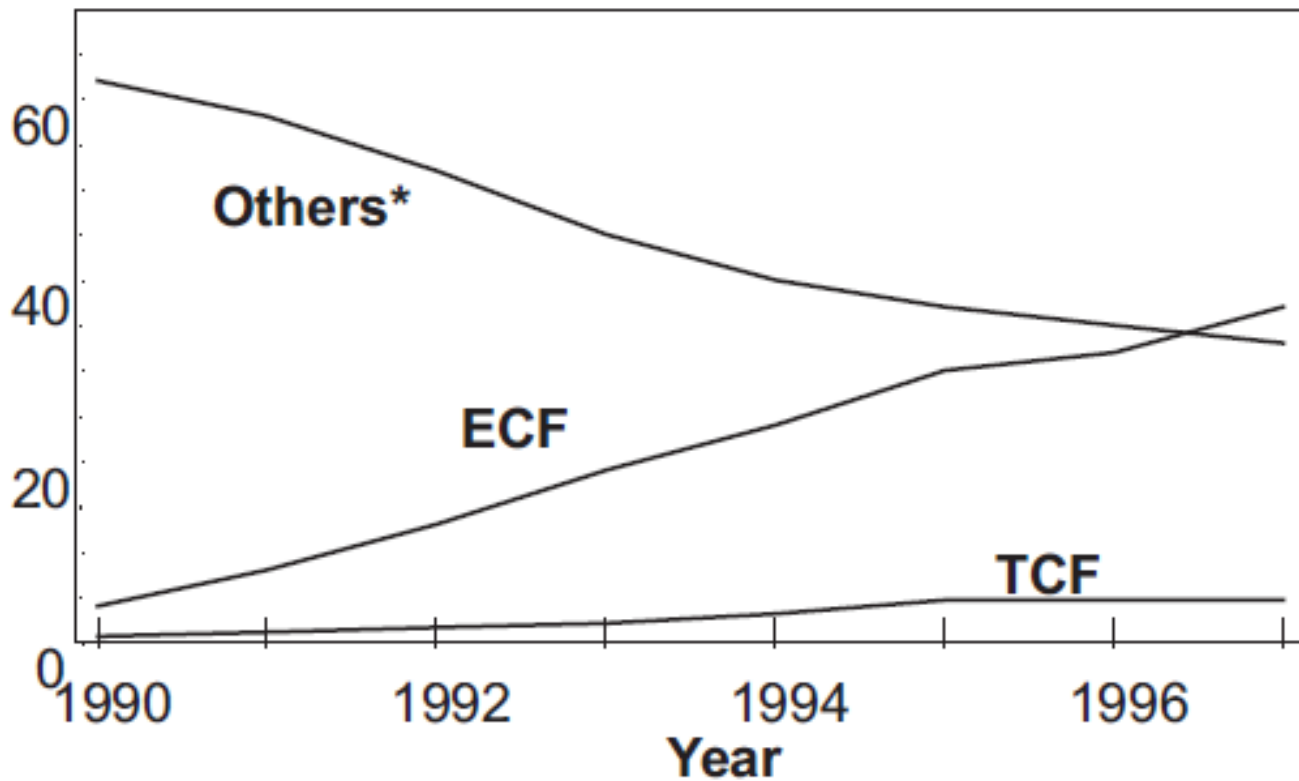
HP

P



# World Production of Bleached Kraft Pulp

Mton/a



Source: AET

# Alvura versus número Kappa durante o branqueamento de polpas Kraft em seqüências típicas de branqueamento

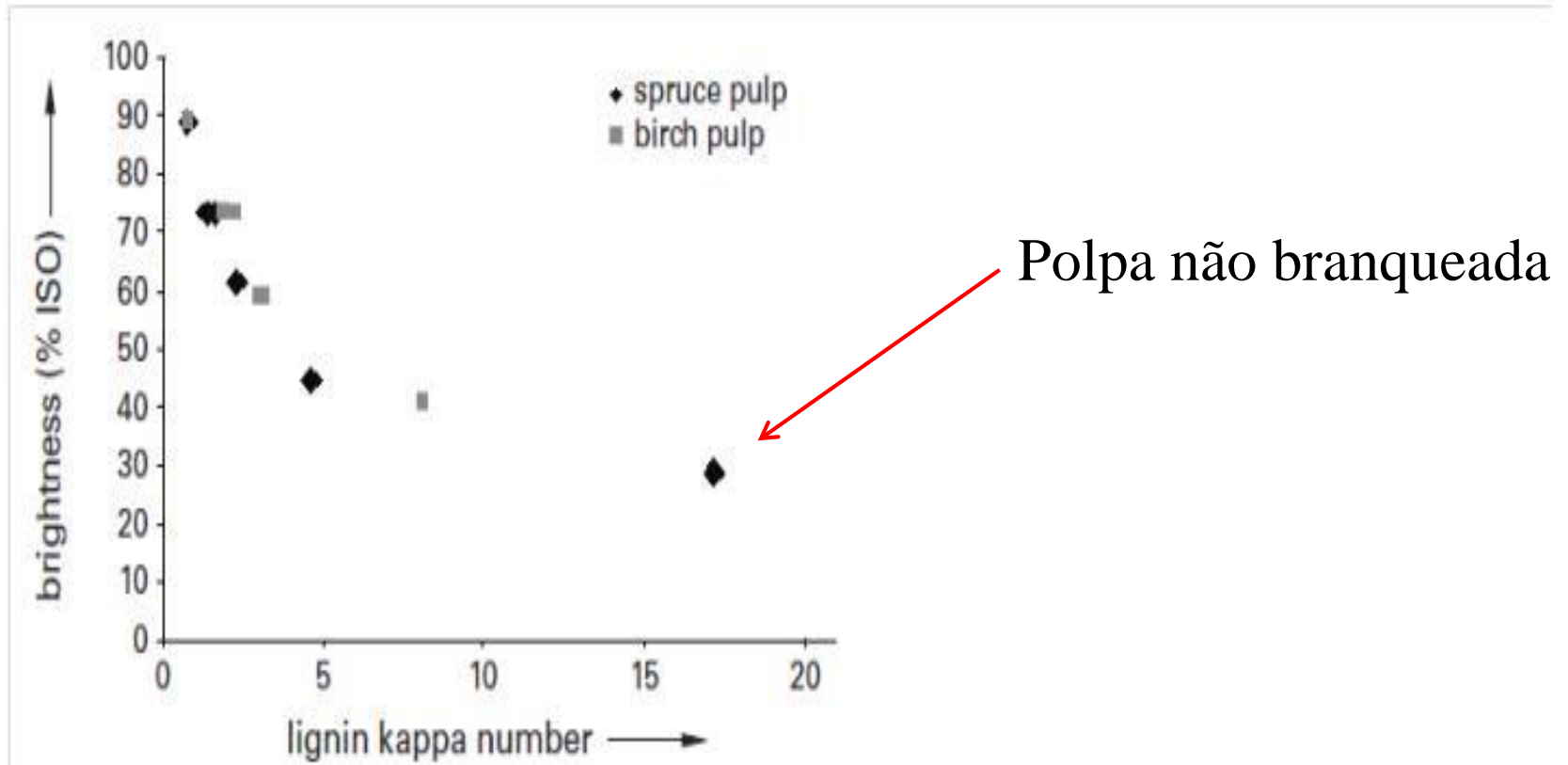
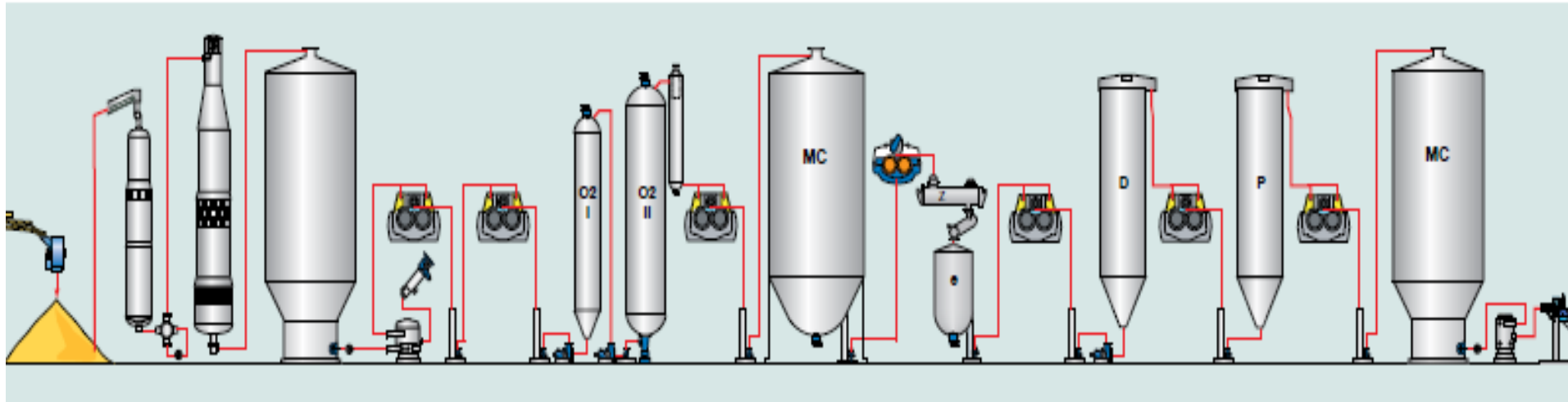


Figure 9.2. Brightness development for industrial kraft pulps as a function of the content of lignin, measured as lignin kappa number. Bleaching sequences: ODEQP (spruce) and OQ(OP)Q(PO) (birch).

↑  
↑  
**Primeira etapa é com O<sub>2</sub>**



# Sequências industriais de branqueamento



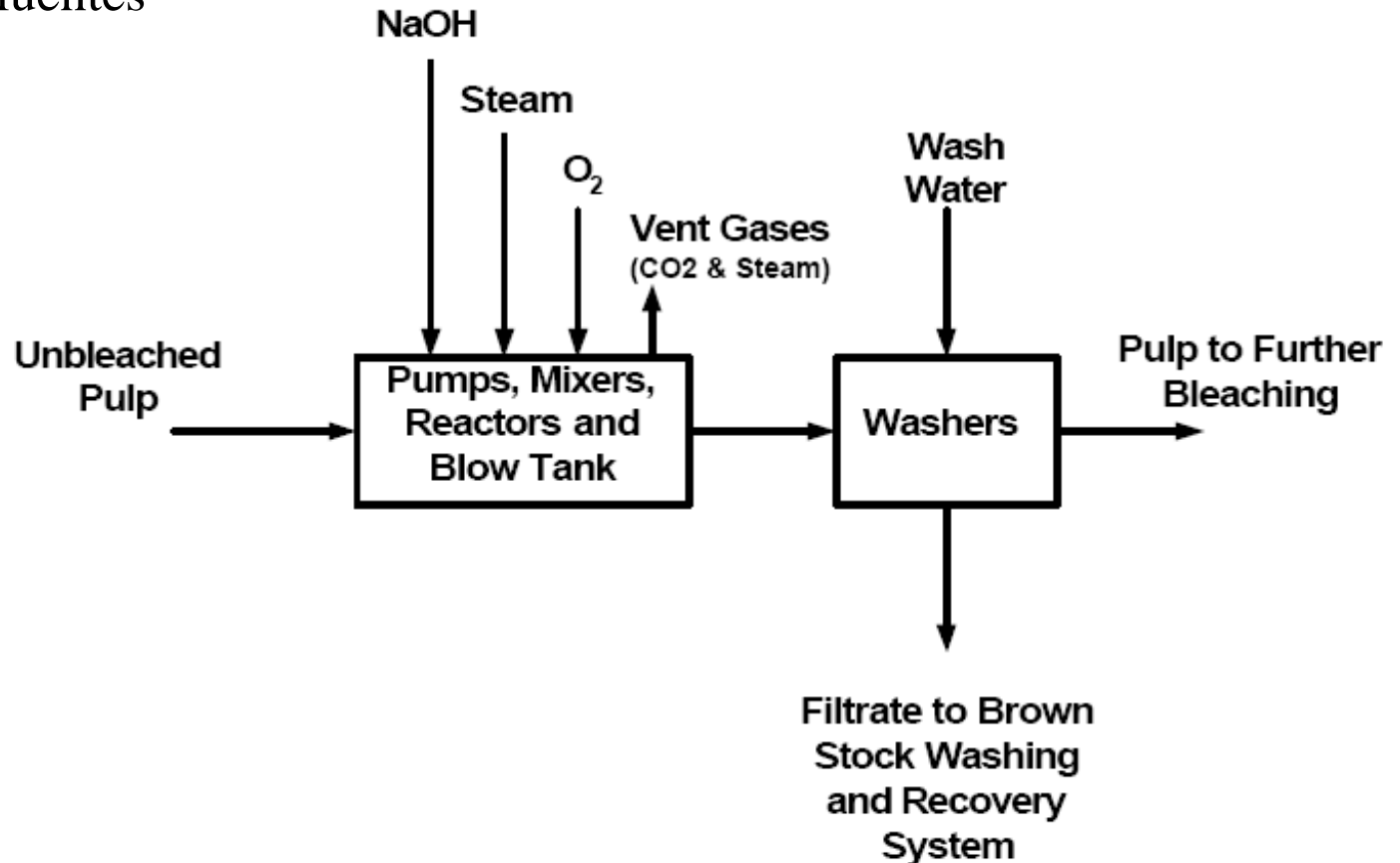
**Aqui começa, efetivamente, o branqueamento**

**O<sub>2</sub> é considerado etapa de deslignificação ou pré-branqueamento**

## Deslignificação com O<sub>2</sub>

Muitas vezes considerada como uma etapa de deslignificação adicional ao cozimento e não como etapa de branqueamento.

Efluente (água de lavagem gerado no processo) volta para o sistema de concentração e queima de licores de polpação e não se dirige ao sistema de tratamento de efluentes



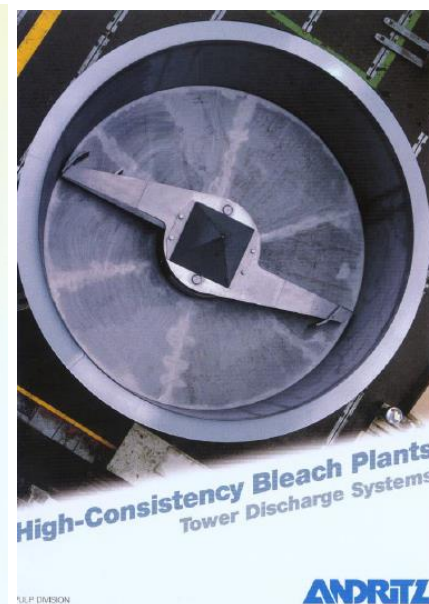
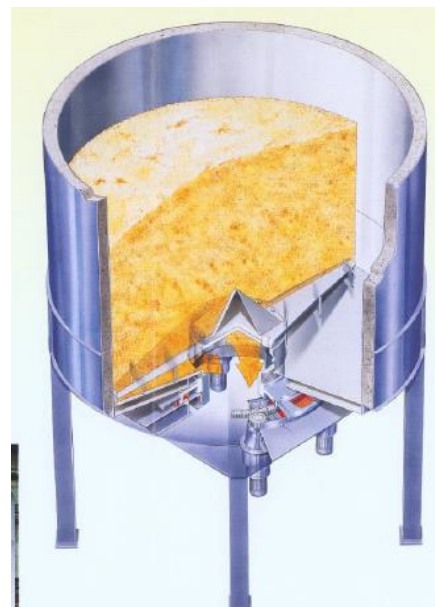
# Sistemas industriais para a etapa de deslignificação com O<sub>2</sub>

## Oxygen delignification Metso



Typical process conditions in the OxyTrac™ system for softwood pulp.

	1 <sup>st</sup> stage	2 <sup>nd</sup> stage
Residence time	30 min	60 min
Temperature	80-85 °C	90-105 °C
Consistency	≥ 11%	≥ 11%
Pressure (top)	8-10 bar	3-5 bar
Final pH value		10.5-11



## O<sub>2</sub> diminui número Kappa por remoção de lignina residual (não é útil para remoção de ácidos hexenurônicos)

Table 9.3. Changes in the contribution to kappa number from lignin, HexA and other oxidizable structures after an industrial O-stage of spruce and birch kraft pulps respectively.

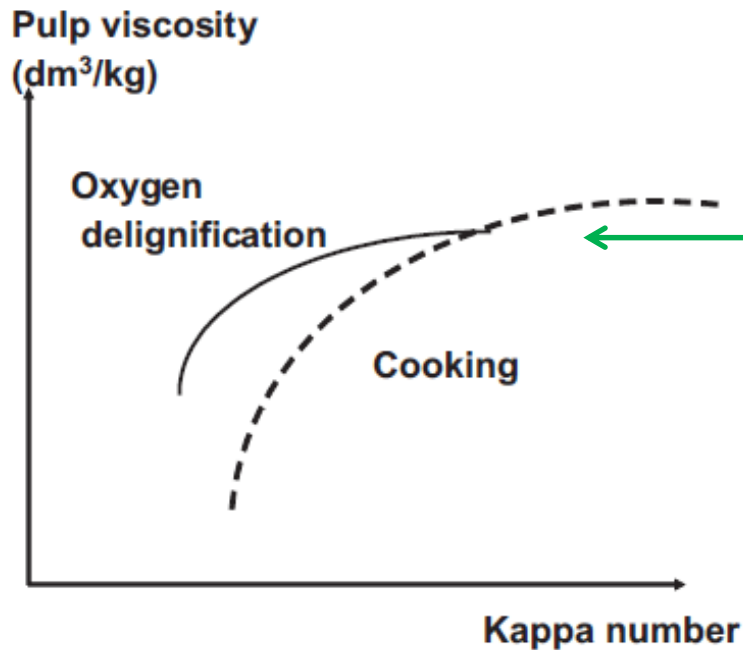
Pulp	Kappa No	Lignin <sup>1)</sup>	HexA <sup>1,2)</sup>	Non-lignin <sup>1, 3)</sup>
Spruce, unbleached	22.5	17.2	1.3	4.0
Spruce, after O-stage	10.7	4.6	1.2	4.9
Birch, unbleached	13.8	8.1	4.7	1.0
Birch, after O-stage	9.6	3.2	4.3	2.1

<sup>1)</sup> calculated in Kappa number units

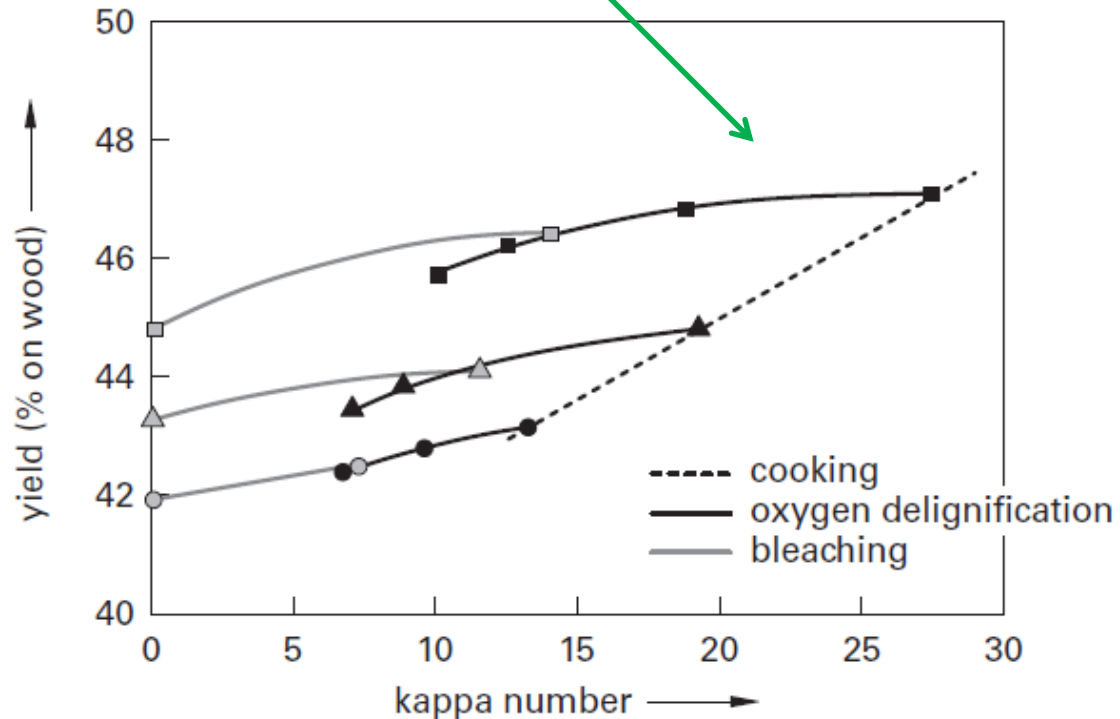
<sup>2)</sup> HexA = hexenuronic acid

<sup>3)</sup> Non-lignin = non-specified but oxidizable structures

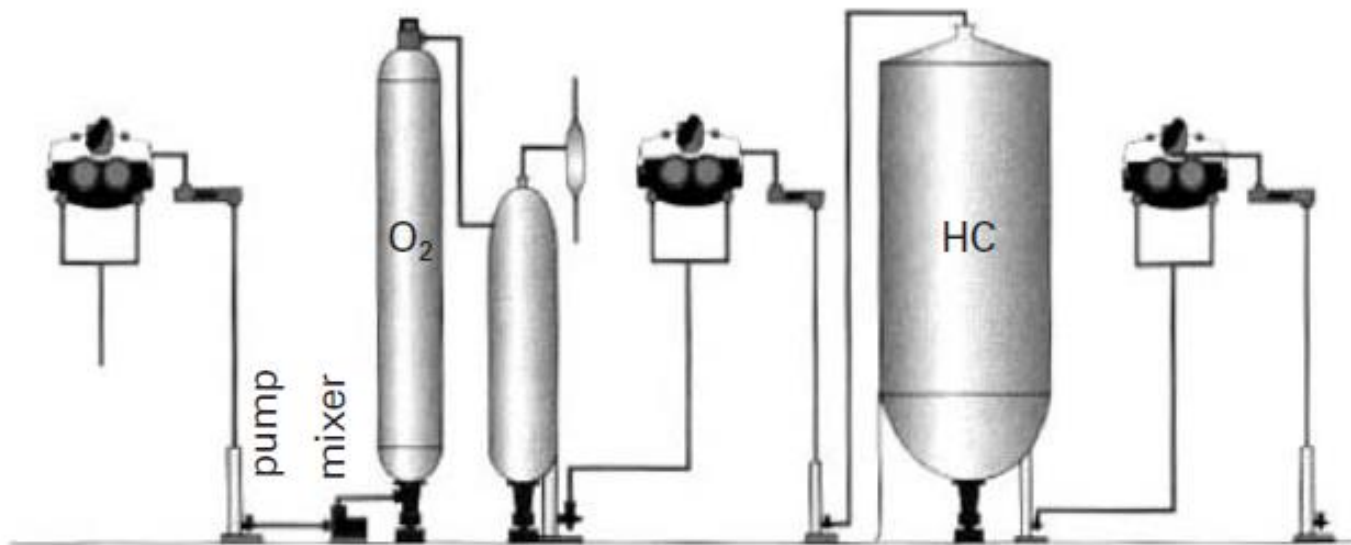
# Sequências industriais que incluem a etapa de pré-deslignificação com O<sub>2</sub> em meio alcalino



Interrupção prematura do cozimento é vantajoso

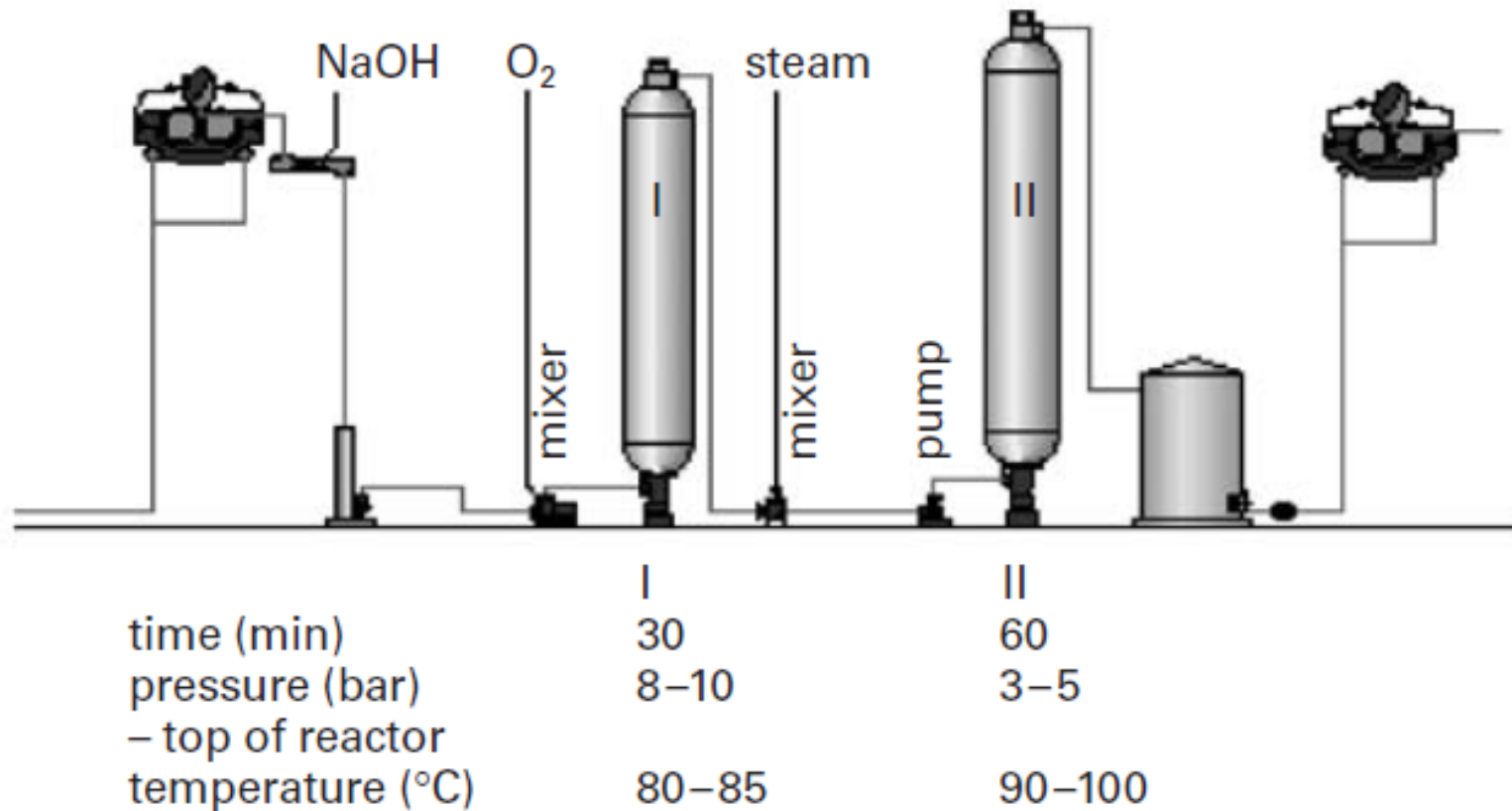


## Sequências industriais que incluem a etapa de pré-deslignificação com $O_2$ em meio alcalino



**Figure 10.10.** A medium consistency oxygen delignification stage consisting of a wash press, a transportation screw, a stand-pipe with a pump, a mixer and a reactor with a following blow tank, a wash press, a HC tower (buffer tank) and a final wash press. (Metso Paper).

## Sequências industriais que incluem a etapa de pré-deslignificação com O<sub>2</sub> em meio alcalino



**Figure 10.11.** A medium consistency oxygen delignification stage with two reactors, 10.10. (Metso Paper).

Dois estágios O<sub>2</sub>

## Reações de O<sub>2</sub> e espécies reativas de oxigênio (ROS)

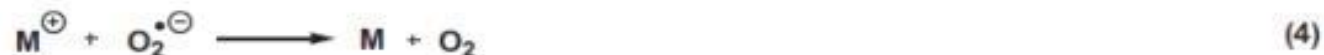
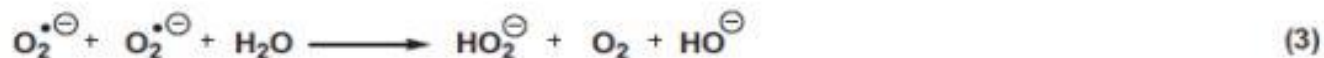
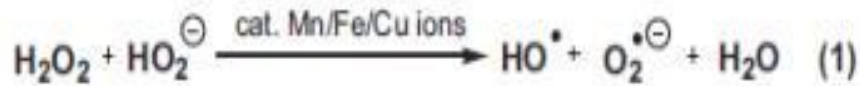


Figure 9.7. Initial reactions in the alkaline oxygen oxidation of lignin and polysaccharides (reaction 1 and 2) together with major decay reactions of the superoxide radical (reaction 3 and 4).

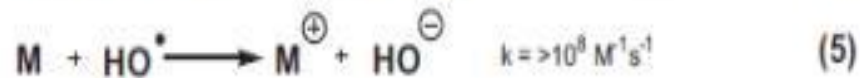
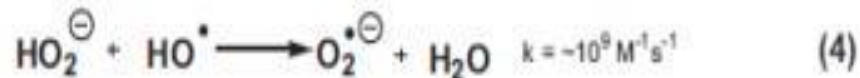
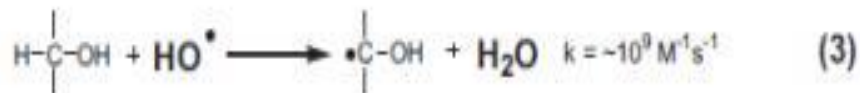
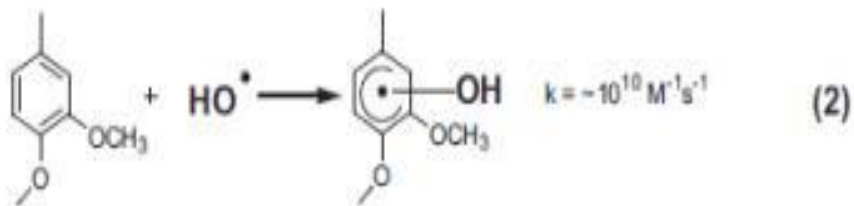
A reação com a lignina leva à redução do O<sub>2</sub> a radical superóxi ânion que pode desproporcionar em O<sub>2</sub> e H-O-OH







**Formação indesejável de OH radical**



**Figure 9.8.** Formation of hydroxyl radicals by decomposition of hydrogen peroxide and various decay reactions of hydroxyl radicals (with approximate reaction rates).

# Reações com lignina e polissacarídeos

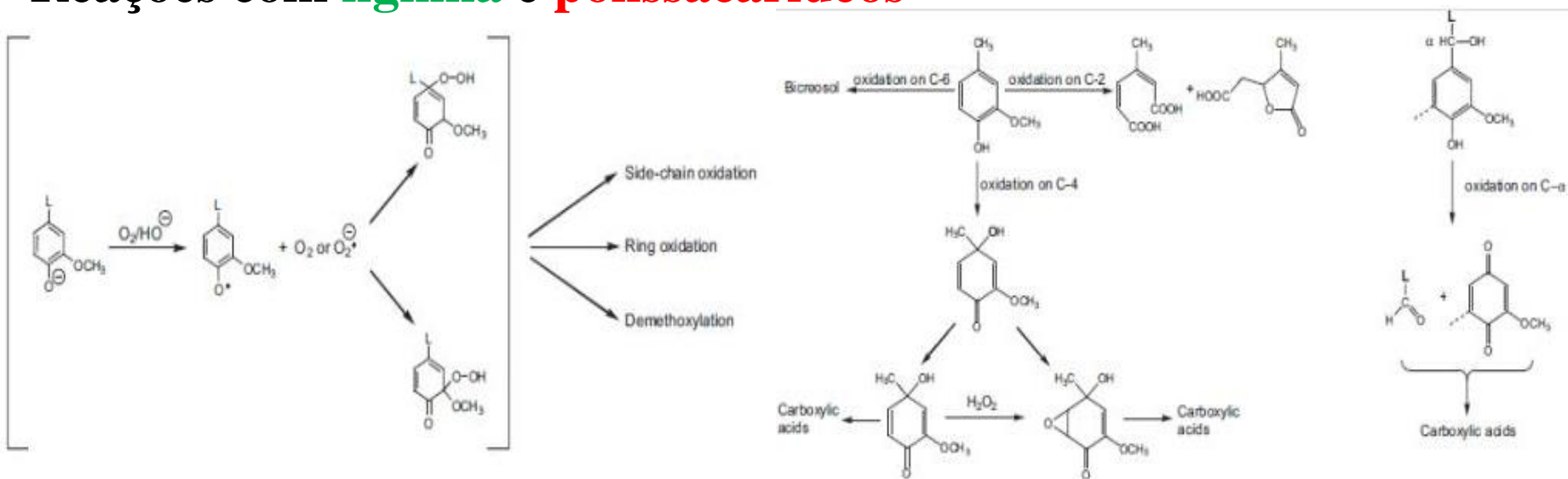


Figure 9.9. The initial reaction step in the oxidation of a phenol with oxygen in alkaline media.

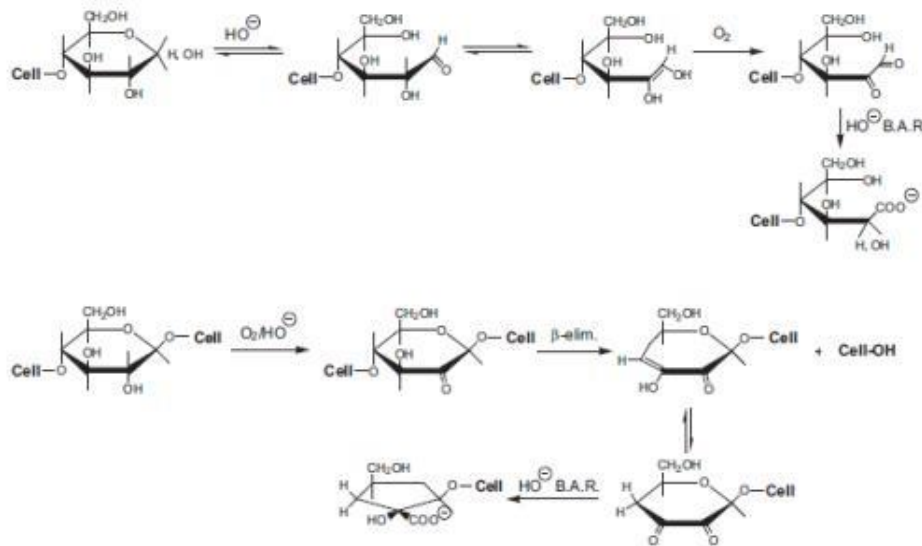


Figure 9.14. Major carbohydrate reactions in the O-stage. Oxidative stabilization of a reducing end group (upper reaction), oxidative cleavage of a polysaccharide chain (lower reaction). B.A.R. = benzilic acid rearrangement.

Reação com **lignina residual predomina**

Reação com **polissacarídeos pode ser evitada**

Composição química dos produtos detectados nos licores de reação de branqueamento de polpas com O<sub>2</sub> em meio alcalino

Table 9.2. Composition of the bleaching effluent obtained after oxygen delignification of a pine kraft pulp (Pfister and Sjöström 1979).

Compound	Amount, kg/tonne of pulp
Lignin	29
Low M <sub>w</sub> lignin products	3.7
Polysaccharides <sup>1)</sup>	4.5
Methanol	1.5
Carbon dioxide	7.5
Formic acid	3.0
Oxalic acid	1.1
Acetic acid	1.0
Glycolic acid	1.0
3,4-Dihydroxybutanoic acid	0.9
Minor acids, total	2.5

<sup>1)</sup> xylose as predominant sugar moiety

# Branqueamento com **peróxido de hidrogênio** (aplicável em polpas químicas e também em polpas mecânicas)

Peroxide bleaching Metso



Typical process conditions in a (PO)- and P-stage

	(PO)	P
Final pH value	9.5-11	9.5-10.5
Temperature	80-100 °C	80-85 °C
Pulp consistency	≥ 11%	≥ 11%
Time	60-120 min	60-180 min
Pressure (top)	3-5 bar	atmospheric



**Table 9.5.** Changes in brightness, viscosity and kappa number for an industrial birch kraft pulp after an O-stage and subsequent bleaching in a peroxide-based sequence. Contributions to the kappa number from lignin, hexenuronic acid and other oxidizable structures are also shown.

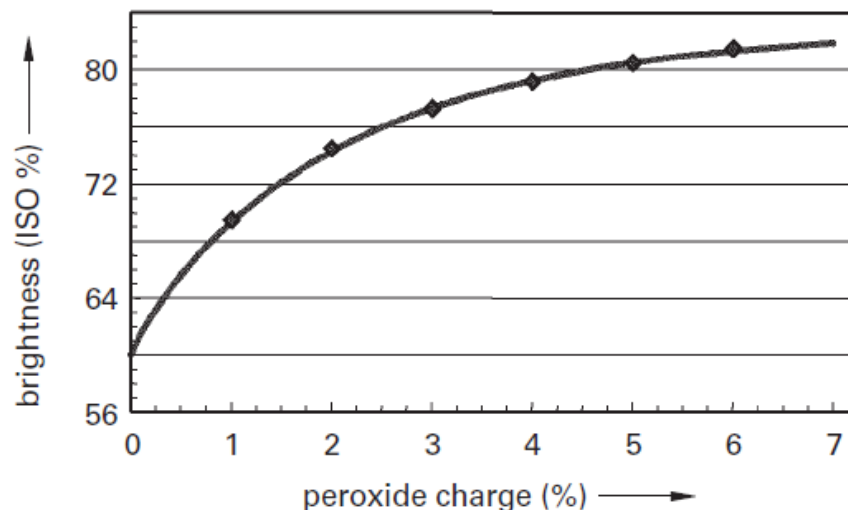
Pulp sample	Brightness, % ISO	Viscosity, dm <sup>3</sup> /kg	Kappa Number	Lignin <sup>1)</sup>	HexA <sup>1, 2)</sup>	Non-lignin <sup>1, 3)</sup>
after O-stage	59.1	920	9.6	3.2	4.3	2.1
after OQ(OP)	73.3	850	7.3	2.2	3.7	1.4
after OQ(OP)Q(PO)	89.0	710	4.6	0.8	3.0	0.8

<sup>1)</sup> calculated in Kappa number units

<sup>2)</sup> HexA = hexenuronic acid

<sup>3)</sup> Non-lignin = unspecified but oxidizable structures

**Peróxido de hidrogênio sobre polpas químicas**



**Peróxido de hidrogênio sobre polpas mecânicas**

**Figure 10.32.** The brightness of a TMP pulp versus the peroxide charge. Bleaching conditions used: 3 hours, 70 °C, 3 % silicate, 25% consistency, Spruce TMP, 60% ISO (Metso Paper).

# Reações da lignina com **peróxido de hidrogênio** (aplicável em polpas químicas e também em polpas mecânicas)

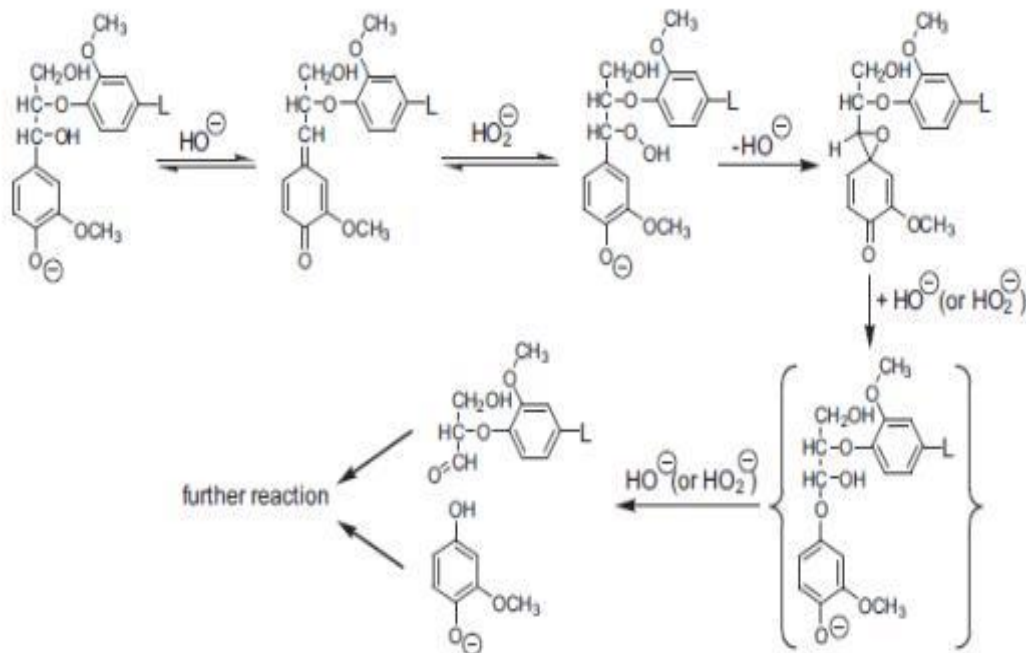


Figure 9.20. Side chain cleavage of a phenolic  $\beta$ -O-4 structure in lignin on oxidation with alkaline hydrogen peroxide. Reaction conditions for L (lignin)=H: 90 °C, 180 min (Heuts 1998).

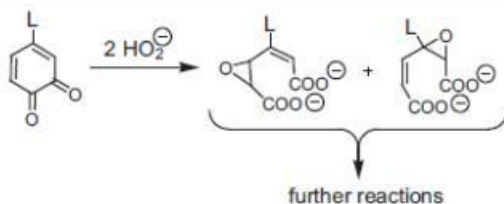


Figure 9.22. Oxidation of a quinone structure by alkaline hydrogen peroxide.

# Branqueamento com dióxido de cloro

## Chlorine dioxide bleaching



O  $\text{ClO}_2$  é um gás produzido in situ devido a sua grande instabilidade.

Oxidação de clorato de sódio em meio ácido pela redução de metanol.

O gás  $\text{ClO}_2$  é dissolvido em água acidificada e usado como agente de branqueamento

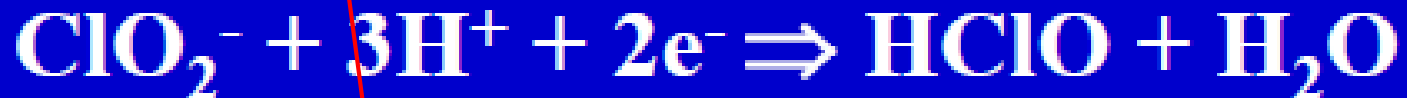
### Conditions used in an industrial D0-stage

	D0	Dht
Final pH value	2-3	2.5-3.5
Pressure	atmospheric	atmospheric
Pulp consistency	$\geq 11\%$	$\geq 11\%$
Temperature	45-85 °C	85-95 °C
Time	45-60 min	90-180 min

### Conditions in D1-stage and D2-stage:

	D1-stage	D2-stage
Final pH value	3.5-4.2	3.5-4.5
Temperature	65-75 °C	65-80 °C
Pulp consistency	$\geq 11\%$	$\geq 11\%$
Time	60-180 min	120-180 min
Pressure	atmospheric	atmospheric

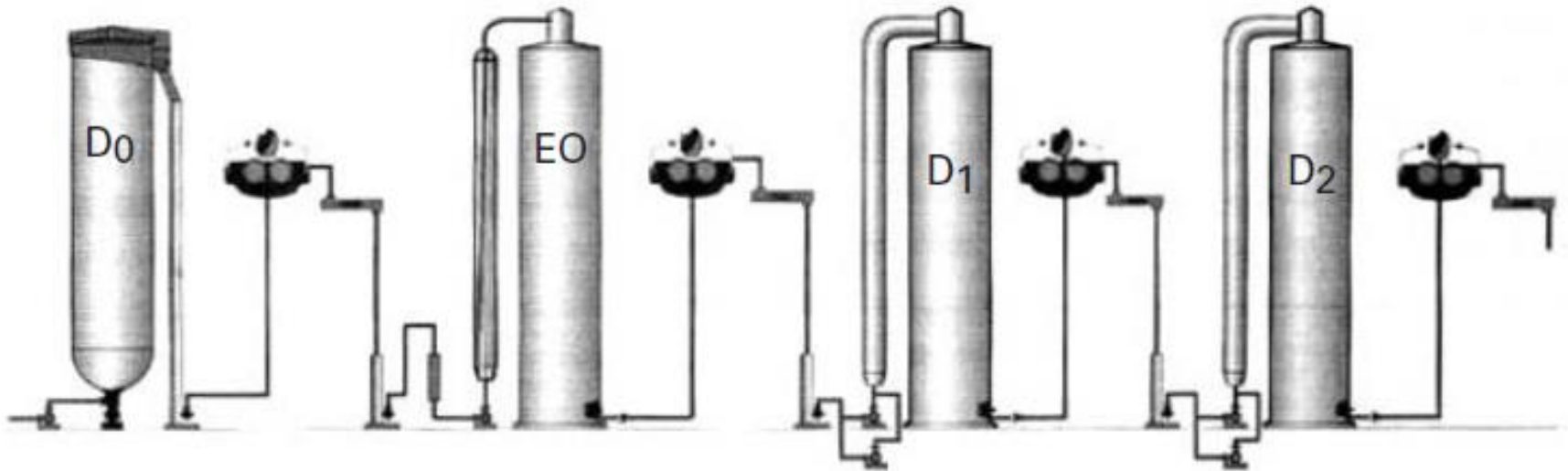
# Chemistry



Componentes passíveis de oxidação na polpa é que doam o elétron



# Sequências típicas do branqueamento



**Figure 10.6.** A bleaching sequence with four stages according to  $D_0(EO)D_1D_2$ . (Metso Paper).

## Dióxido de cloro sobre polpas químicas

**Table 9.6.** Changes in brightness, viscosity and kappa number for an industrial softwood kraft pulp after an O-stage and subsequent ECF-bleaching. Contributions to the kappa number from lignin, hexenuronic acid and other oxidizable structures are also shown.

Pulp sample	Brightness, % ISO	Viscosity, dm <sup>3</sup> /kg	Kappa Number	Lignin <sup>1)</sup>	HexA <sup>1, 2)</sup>	Non-lignin <sup>1, 3)</sup>
after O-stage	44.7	910	10.7	4.6	1.2	4.9
after ODE	73.3	850	3.3	1.6	0.8	0.9
after ODEQP	88.8	800	1.6	0.8	0.7	0.1

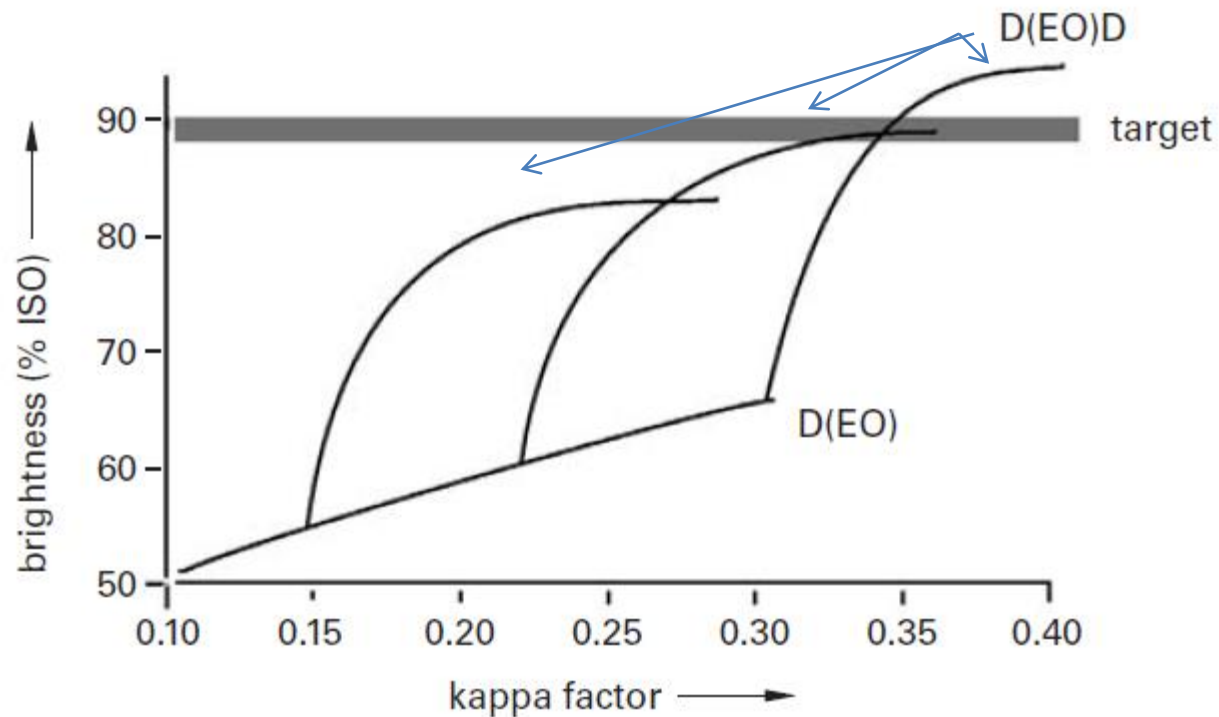
<sup>1)</sup> calculated in Kappa number units

<sup>2)</sup> HexA = hexenuronic acid

<sup>3)</sup> Non-lignin = unspecified but oxidizable structures

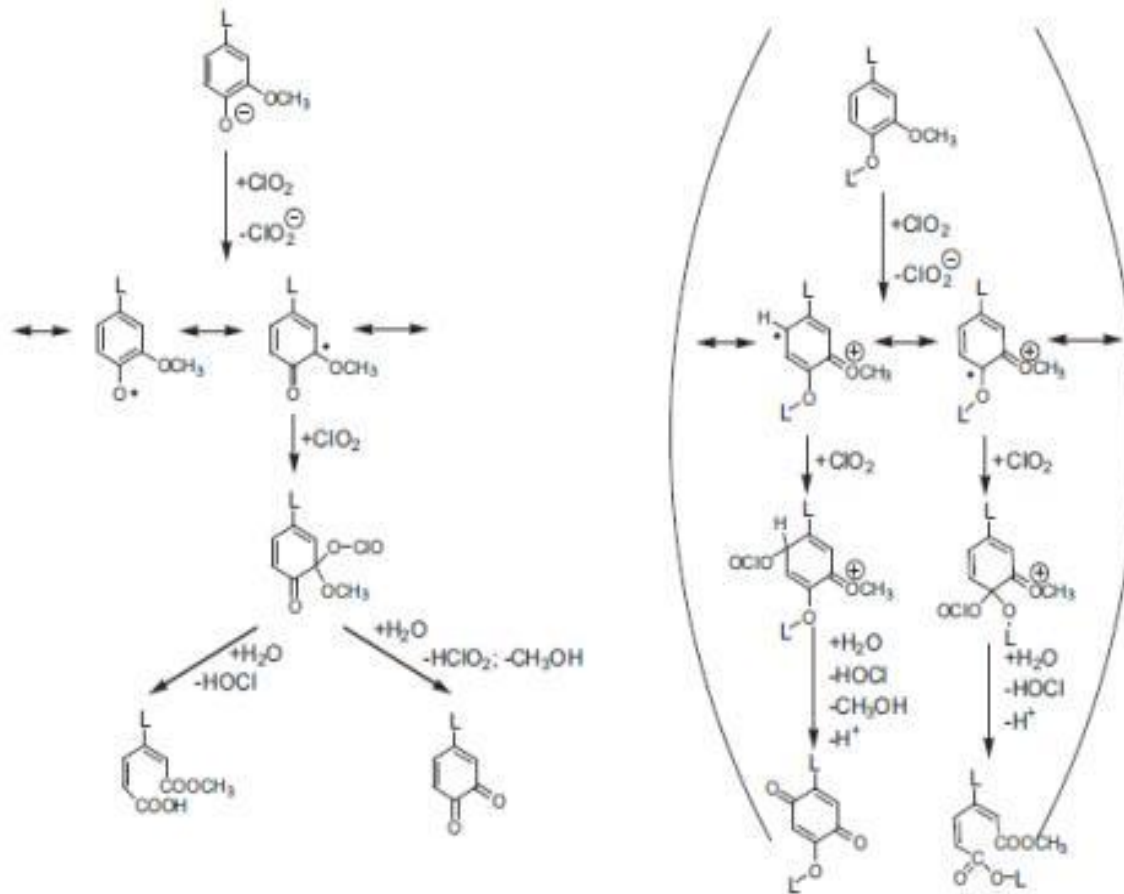
# Adição do agente oxidante x eficiência

No caso da branqueamento com  $\text{ClO}_2$ , é usual que 2 etapas proporcionem melhor efeito do que uma única carga



Proporcional a carga de  $\text{ClO}_2$

# Reações do dióxido de cloro com lignina



**Figure 9.25.** Reactions between a phenolic (left) and a non-phenolic (right) lignin structure respectively with chlorine dioxide under acidic conditions (Eriksson 1993). In benzylalcohol structures, a similar reaction will result in an oxidative elimination of the side chain. The reaction of non-phenolic lignin structures is less likely under technical pre-bleaching conditions.

# Resumo com cargas e condições usuais em cada etapa de branqueamento

## Conditions in the $D_0$ -stage

- pH 2–3
- 40–70 °C
- 3–4 % or 9–13 % pulp consistency
- 0.5–1.0 hours
- atmospheric pressure
- 1.0–2.0 x kappa number (aCl/t)

## Conditions in the $D_{1,2}$ -stages

- pH 3.0–4.0 in  $D_1$  and pH 3.5–4.5 in  $D_2$
- 55–75 °C in  $D_1$  and 60–85 °C in  $D_2$
- 9–13% pulp consistency
- 1–3 h
- atmospheric pressure
- $\Sigma$  4–6 x kappa number ( $E_1$ ) (a.Cl/t)
- $D_1/D_2$ -charge ratio usually 2/1–3/1

## Conditions in the Q-stage

– metal ion remover prior to P-bleaching

- pH 4–7 (9–10 in alkaline Q)
- pH 5–7
- 50–80 °C
- 9–13%
- 5 min–2h
- atmospheric pressure
- 2–4 kg EDTA or DTPA/t

## Conditions in the (PO)-stage

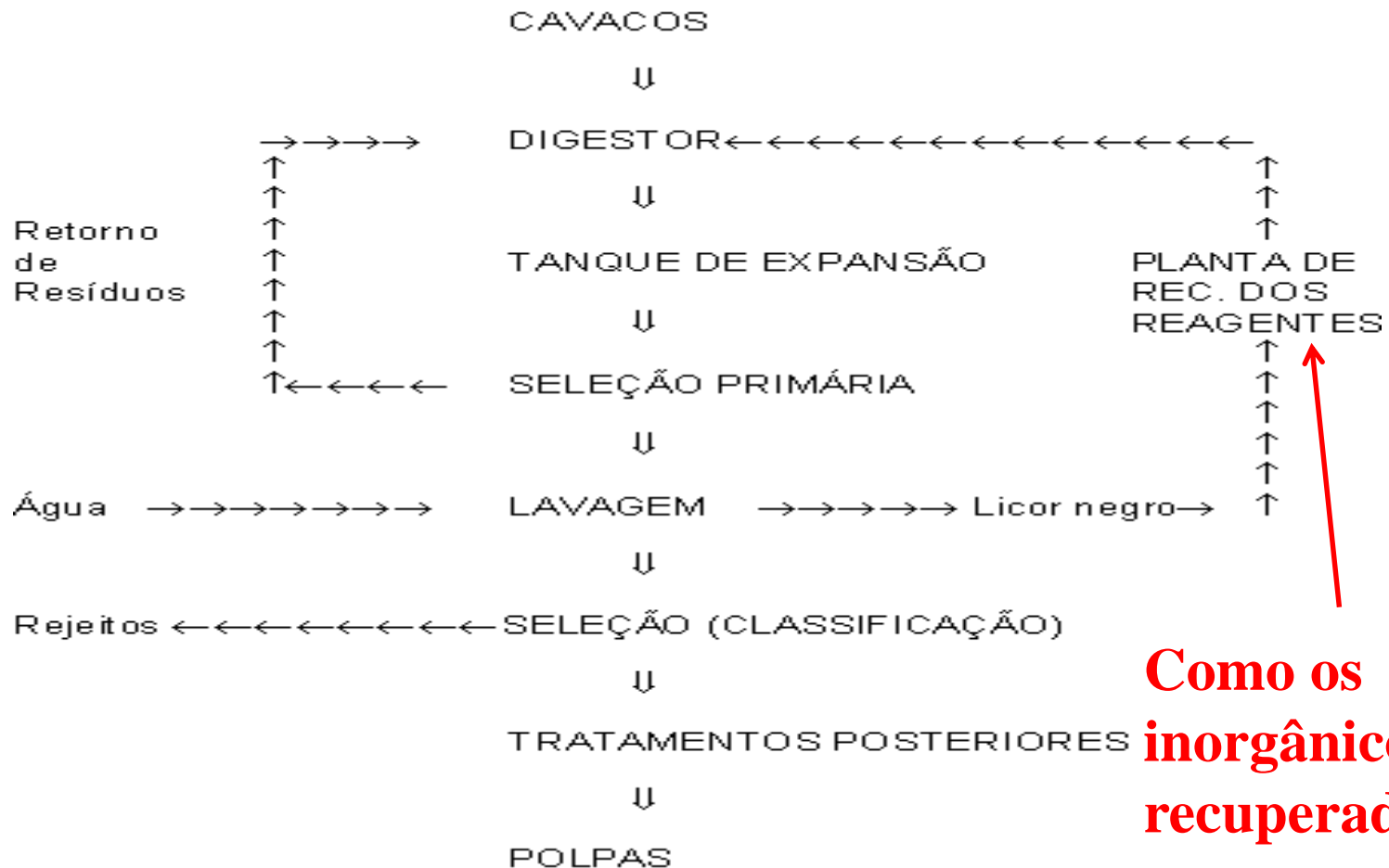
- pH 10.5–11.0
- 80–110 °C
- 9–13% pulp consistency
- 1–3 hours
- 3–8 bar
- 5–10 kg  $O_2$ /t and 5–40 kg  $H_2O_2$ /t

# Regeneração no processo kraft

*próxima aula*

## - recuperação de inorgânicos e produção de energia

Ref. básica para estudo: **Capítulos 12 e 13: Ek M, Gellerstedt G, Henriksson G. *Pulping Chemistry and Technology* (Volume 2). Berlin, Walter de Gruyter, 2009**



**Como os inorgânicos são recuperados?**