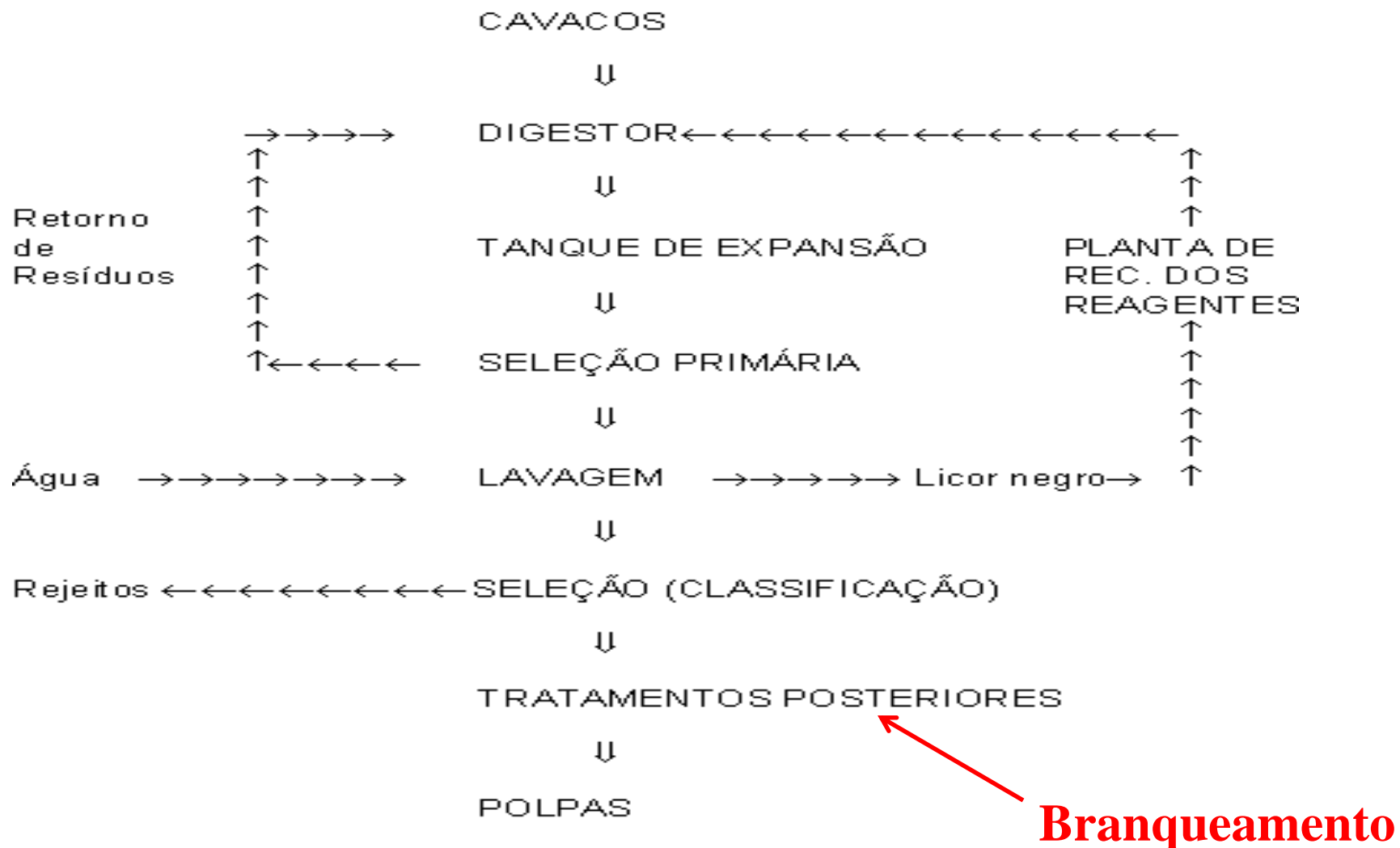


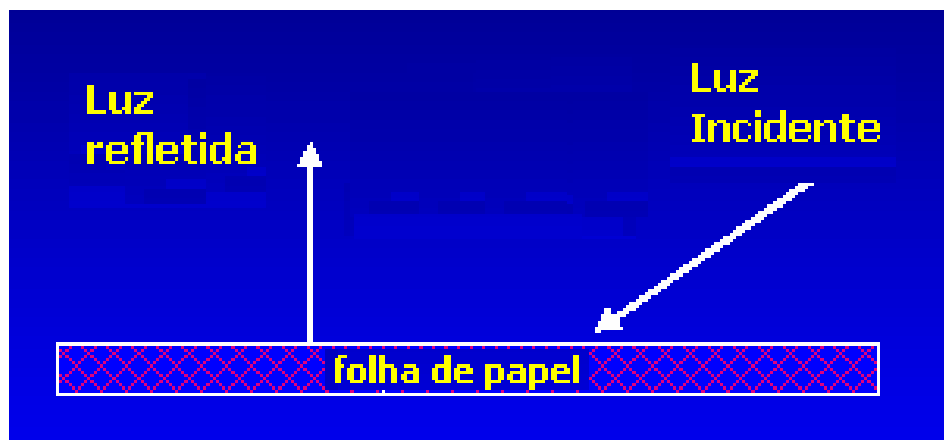
Diagrama simplificado do processo kraft



Branqueamento de polpas celulósicas

Dois tipos básicos:

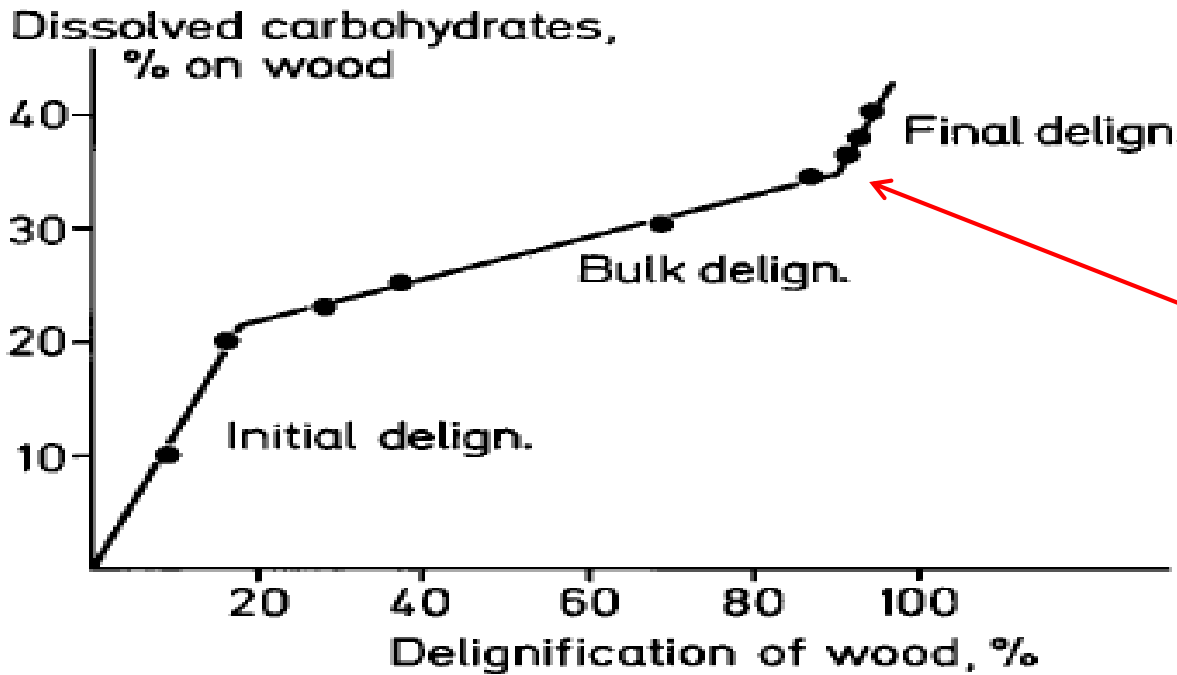
- a) eliminação de material responsável pela cor - usado em polpas químicas
- b) transformação do material responsável pela cor em substâncias mais claras - usado em polpas mecânicas



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 ² /g)	Índice de resistência ao rasgo (mN.m ² /g)
NSSC, branqueada	1.32	10.7
NSSC, não branqueada	0.96	8.7
Kraft, branqueada	0.96	9.2
Kraft, não branqueada	1.08	7.6
Soda, branqueada	0.60	6.1
Soda, não branqueada	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 ¹⁾	HexA ^{1, 2)}	Non-lignin ^{1, 3)}
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	Cl_2
Extração	E	NaOH
Hipocloração	H	NaClO
Dióxido de Cloro	D	ClO_2
Oxigênio	O	O_2 e NaOH
Peróxido de Hidrogênio	P	H_2O_2
Ozônio	Z	O_3

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

Chemical	kg active chlorine/kg
Chlorine (Cl_2)	1
Chlorine dioxide (ClO_2)	2.63
Sodium hypochlorite (NaClO)	0.95

Sequências típicas do branqueamento

Polpas Kraft

(CD)(EO)DED – comuns até 1995

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

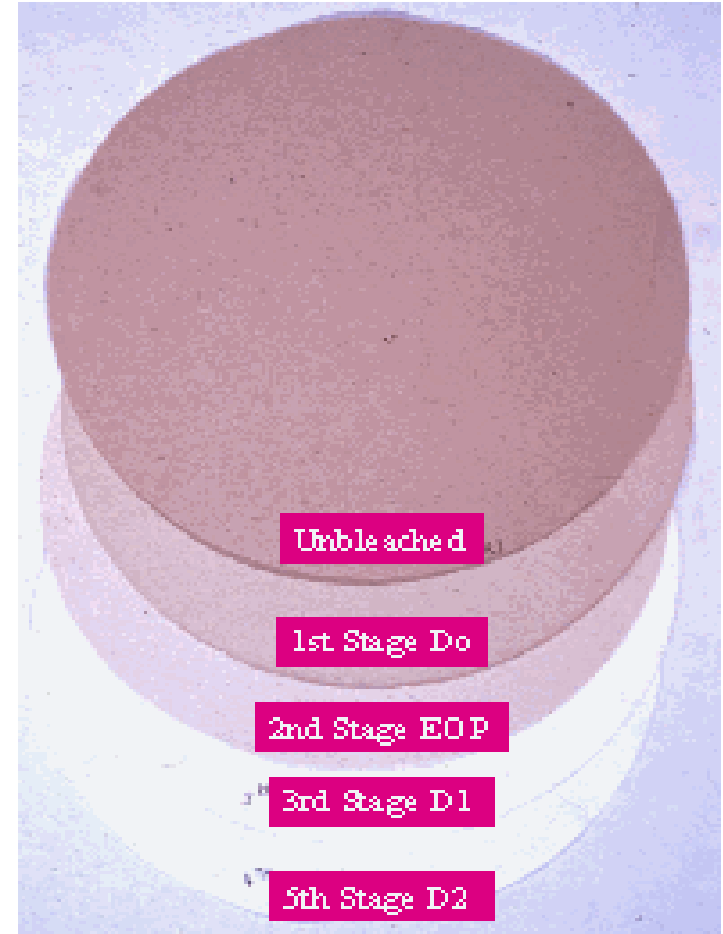


OD(EOP)D – requeridas por legislação e/ou mercado

Polpas mecânicas

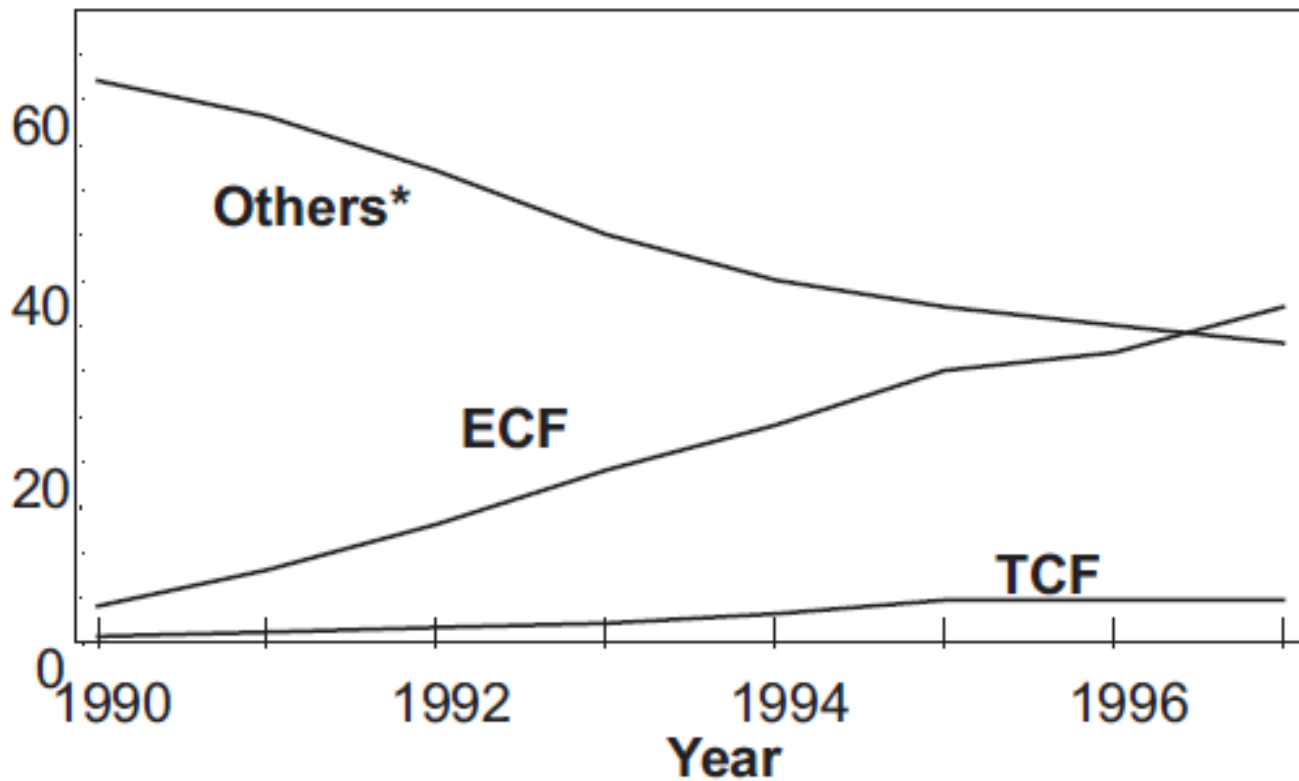
HP

P



World Production of Bleached Kraft Pulp

Mton/a



Source: AET

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

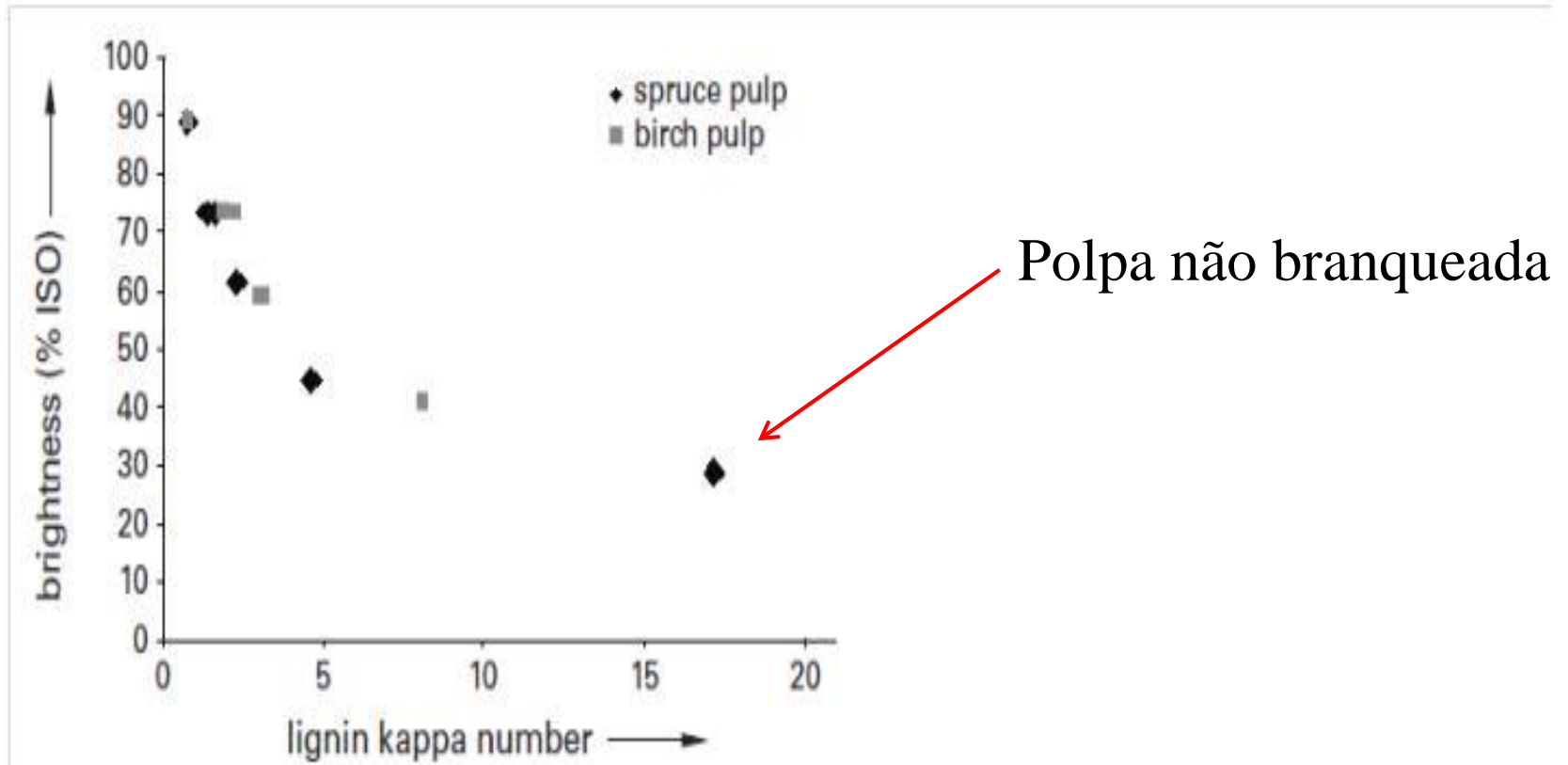
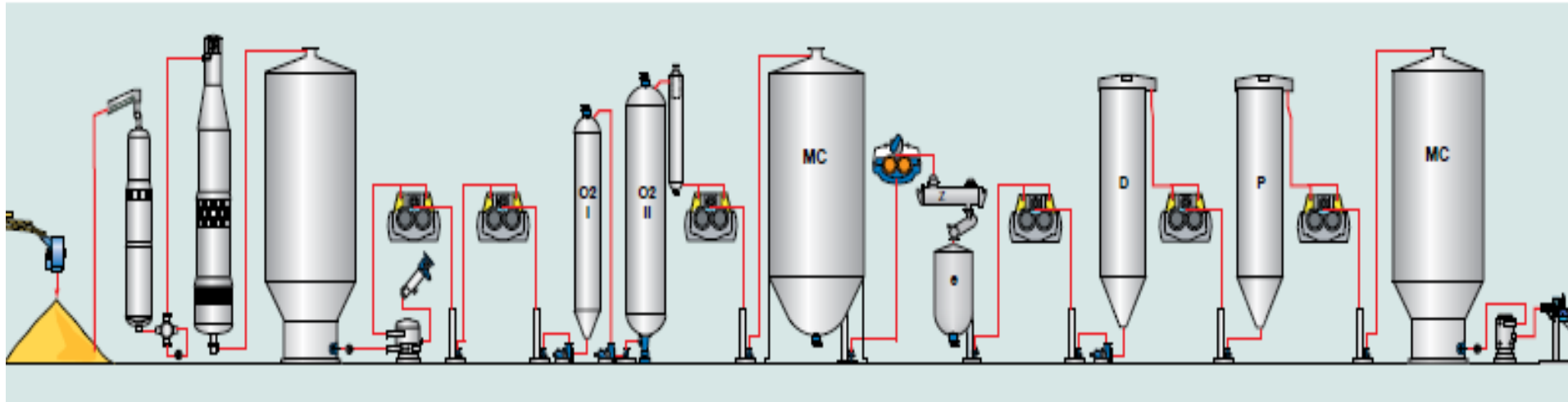


Figure 9.2. Brightness development for industrial kraft pulps as a function of the content of lignin, measured as lignin kappa number. Bleaching sequences: ODEQP (spruce) and OQ(OP)Q(PO) (birch).

↑
↑
Primeira etapa é com O₂

Sequências industriais de branqueamento



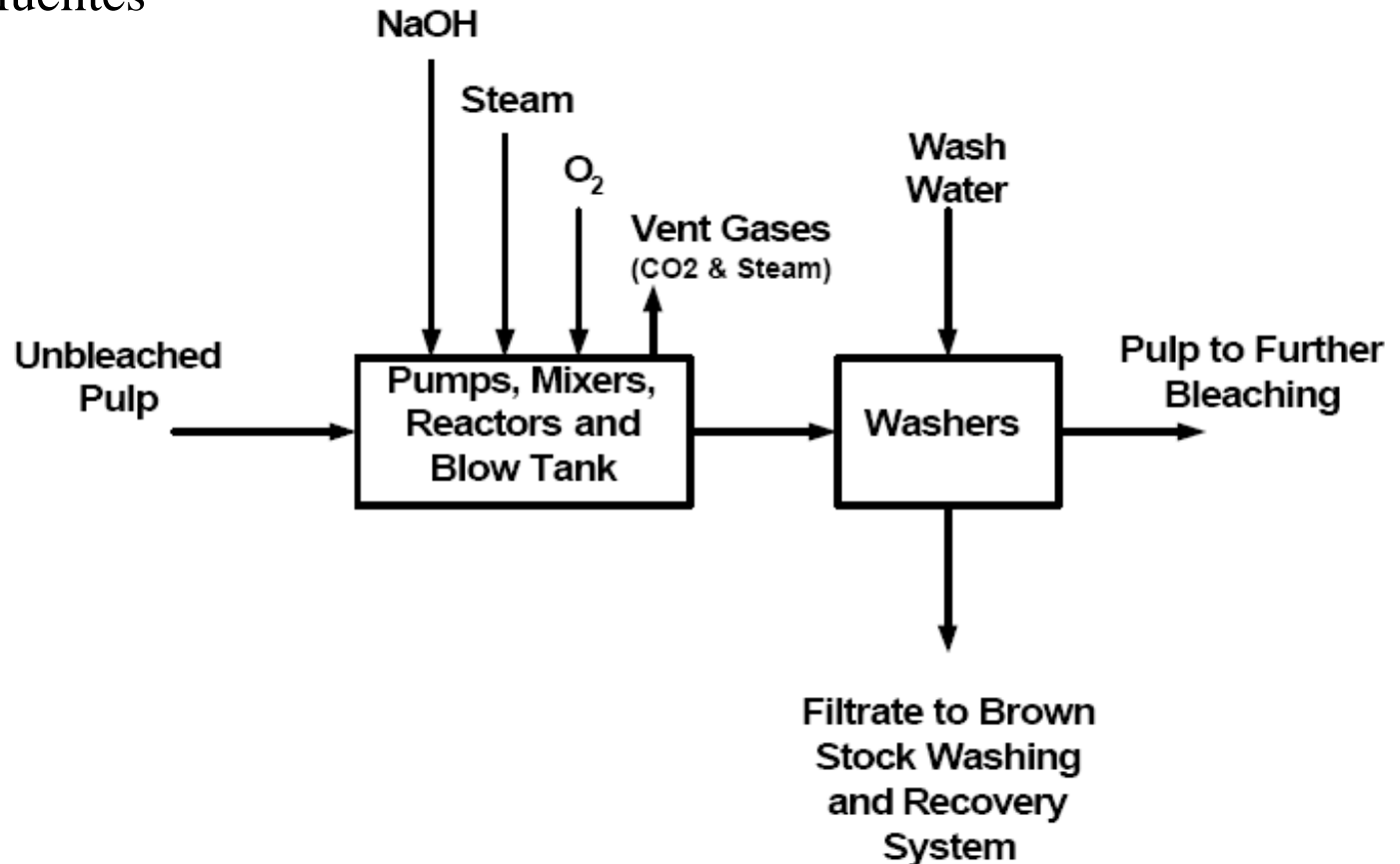
Aqui começa, efetivamente, o branqueamento

O₂ é considerado etapa de deslignificação ou pré-branqueamento

Deslignificação com O₂

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



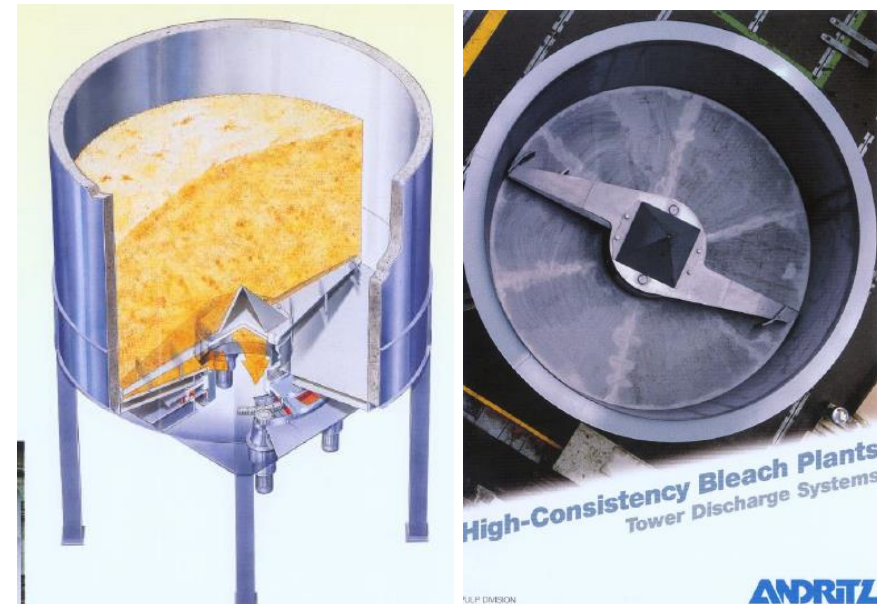
Sistemas industriais para a etapa de deslignificação com O₂

Oxygen delignification Metso



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

	1 st stage	2 nd 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



O₂ 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.

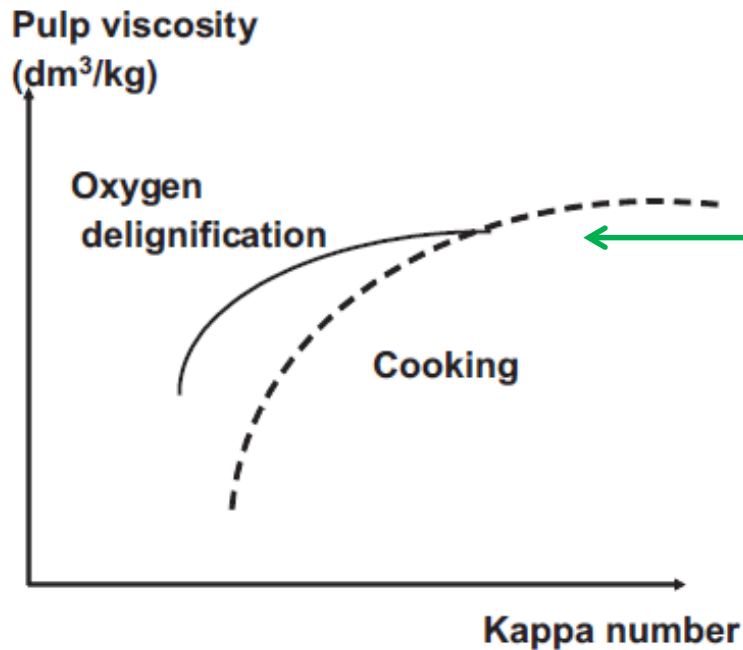
Pulp	Kappa No	Lignin ¹⁾	HexA ^{1,2)}	Non-lignin ^{1, 3)}
Spruce, unbleached	22.5	17.2	1.3	4.0
Spruce, after O-stage	10.7	4.6	1.2	4.9
Birch, unbleached	13.8	8.1	4.7	1.0
Birch, after O-stage	9.6	3.2	4.3	2.1

¹⁾ calculated in Kappa number units

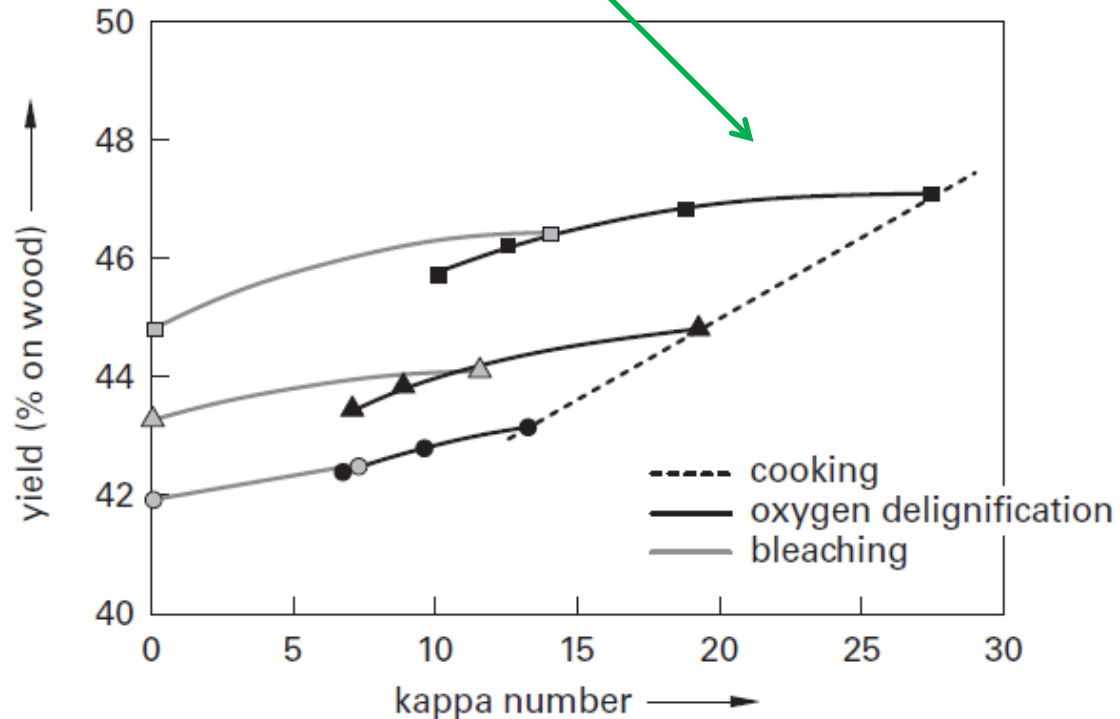
²⁾ HexA = hexenuronic acid

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

Sequências industriais que incluem a etapa de pré-deslignificação com O₂ em meio alcalino



Interrupção prematura do cozimento é vantajoso



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

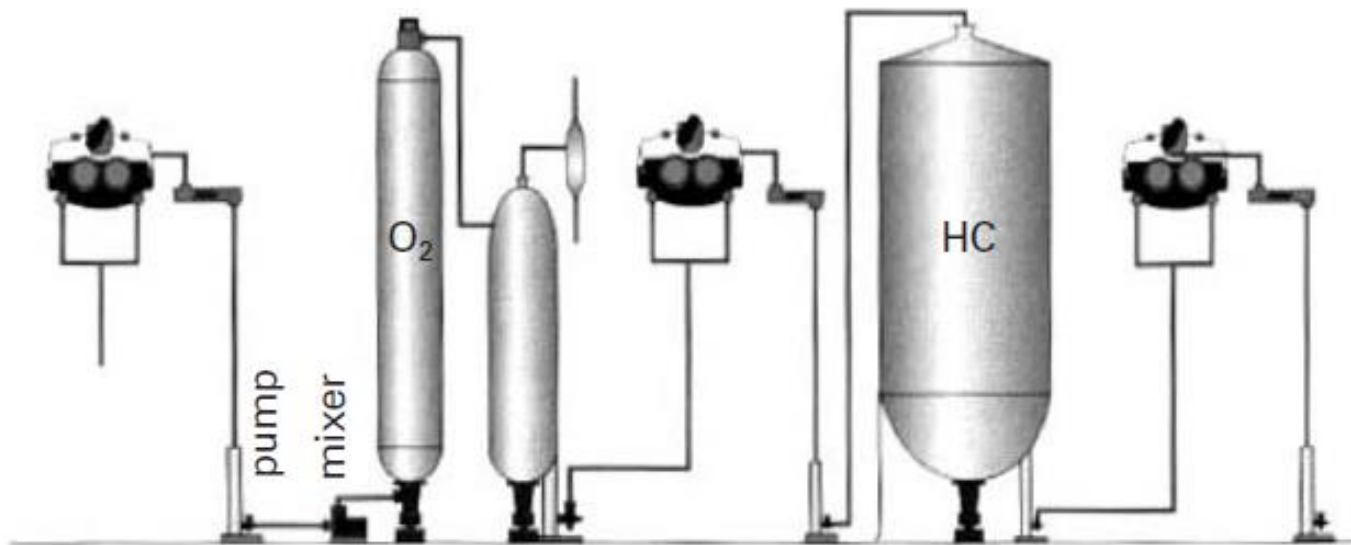


Figure 10.10. A medium consistency oxygen delignification stage consisting of a wash press, a transportation screw, a stand-pipe with a pump, a mixer and a reactor with a following blow tank, a wash press, a HC tower (buffer tank) and a final wash press. (Metso Paper).

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

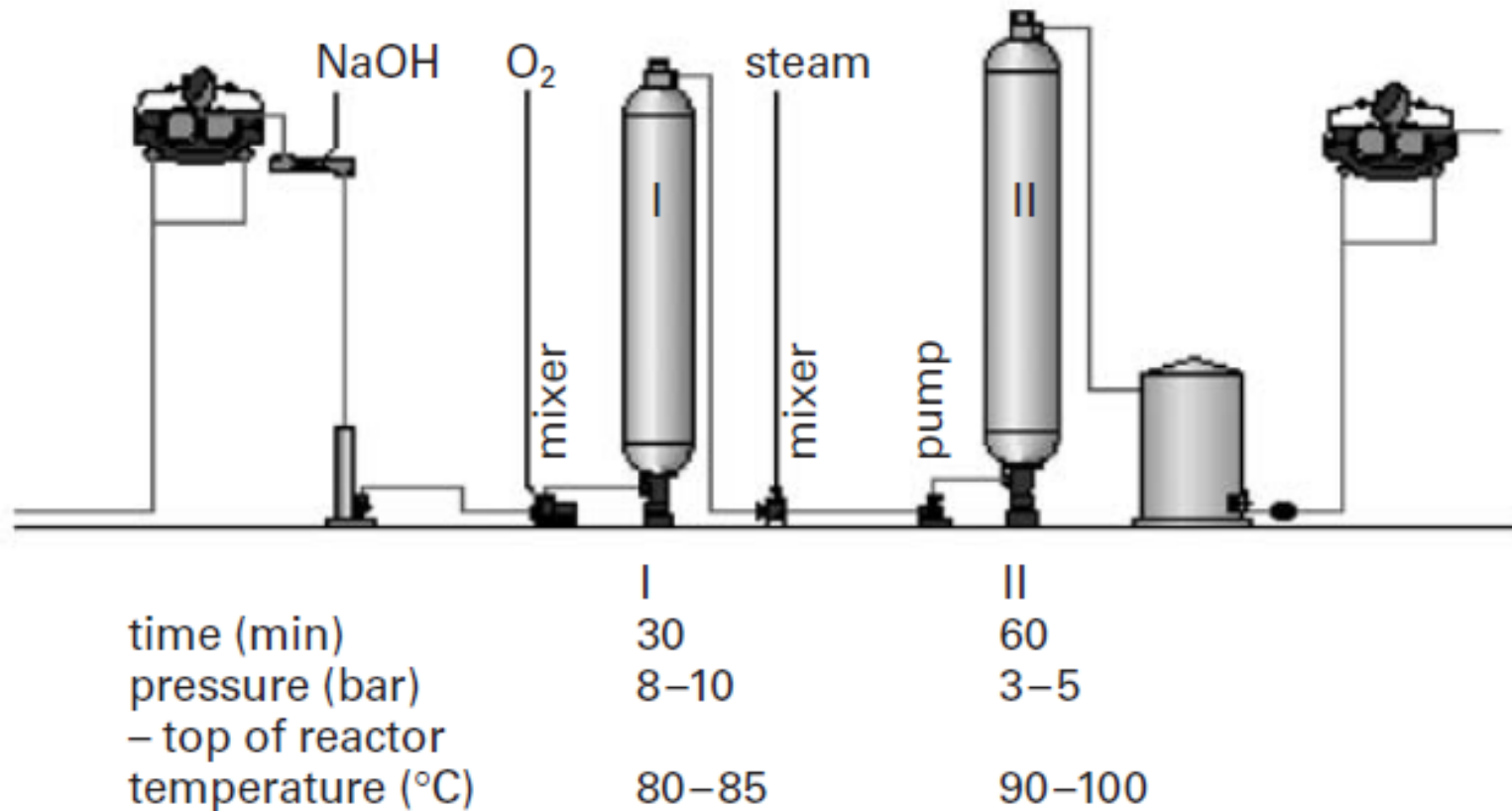


Figure 10.11. A medium consistency oxygen delignification stage with two reactors, 10.10. (Metso Paper).

Dois estágios O_2

Reações de O₂ e espécies reativas de oxigênio (ROS)

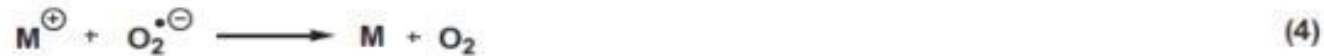
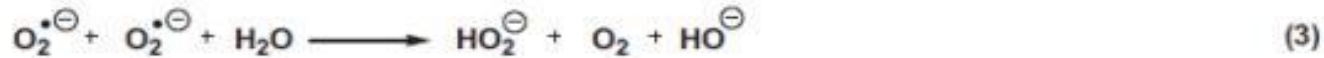
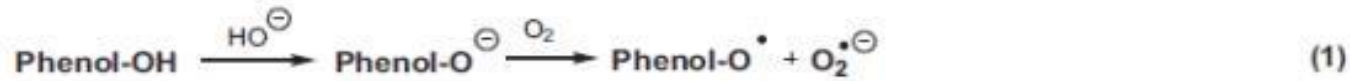
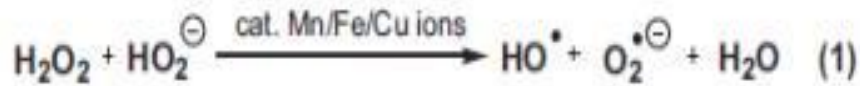


Figure 9.7. Initial reactions in the alkaline oxygen oxidation of lignin and polysaccharides (reaction 1 and 2) together with major decay reactions of the superoxide radical (reaction 3 and 4).

A reação com a lignina leva à redução do O₂ a radical superóxi ânion que pode desproporcionar em O₂ e H-O-OH





Formação indesejável de OH radical

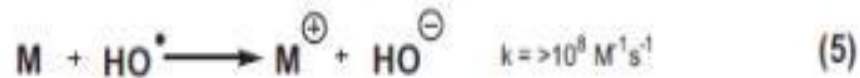
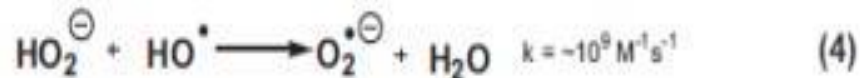
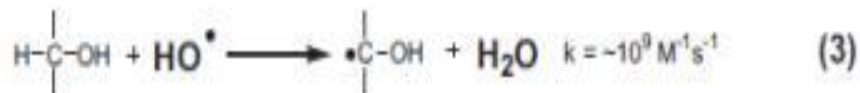
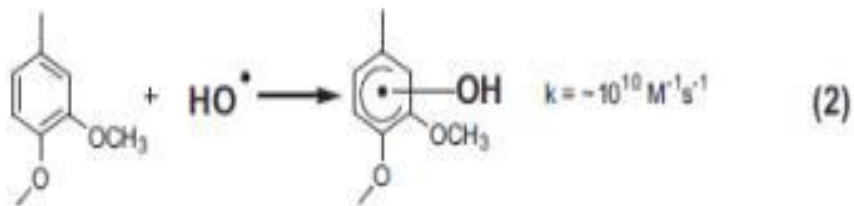


Figure 9.8. Formation of hydroxyl radicals by decomposition of hydrogen peroxide and various decay reactions of hydroxyl radicals (with approximate reaction rates).

Reações com lignina e polissacarídeos

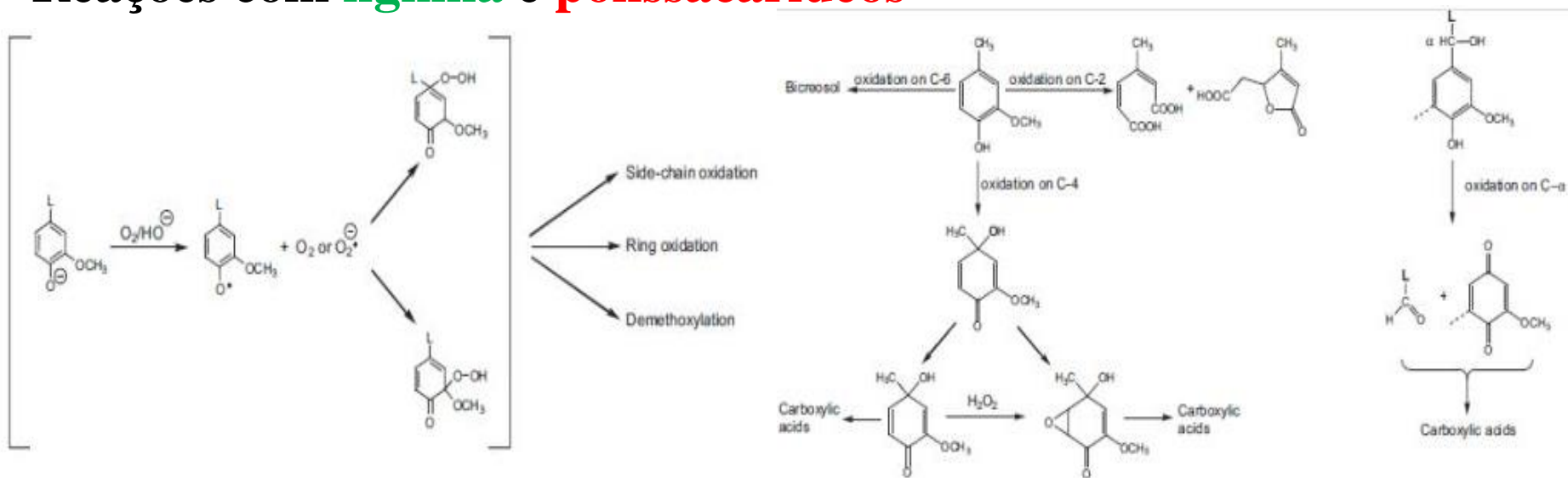


Figure 9.9. The initial reaction step in the oxidation of a phenol with oxygen in alkaline media.

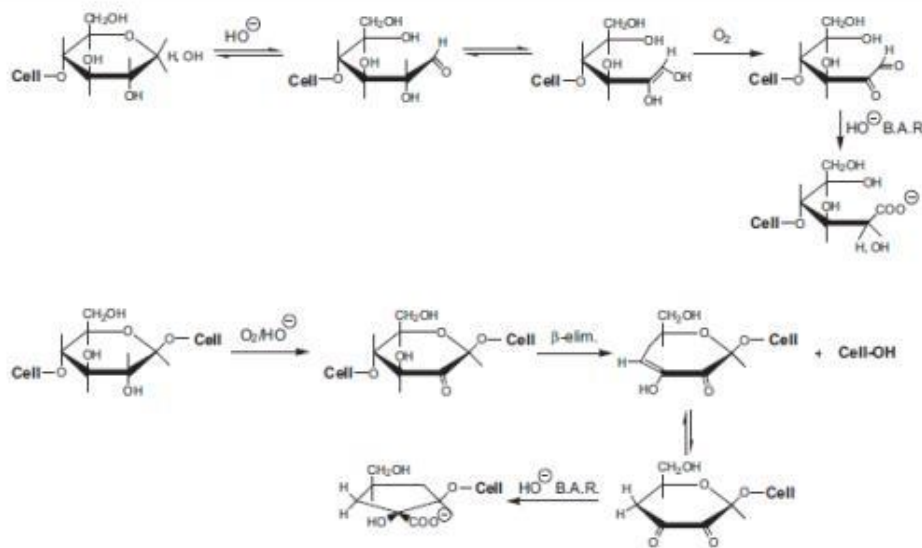


Figure 9.14. Major carbohydrate reactions in the O-stage. Oxidative stabilization of a reducing end group (upper reaction), oxidative cleavage of a polysaccharide chain (lower reaction). B.A.R. = benzilic acid rearrangement.

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 O₂ 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 _w lignin products	3.7
Polysaccharides ¹⁾	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

¹⁾ 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.

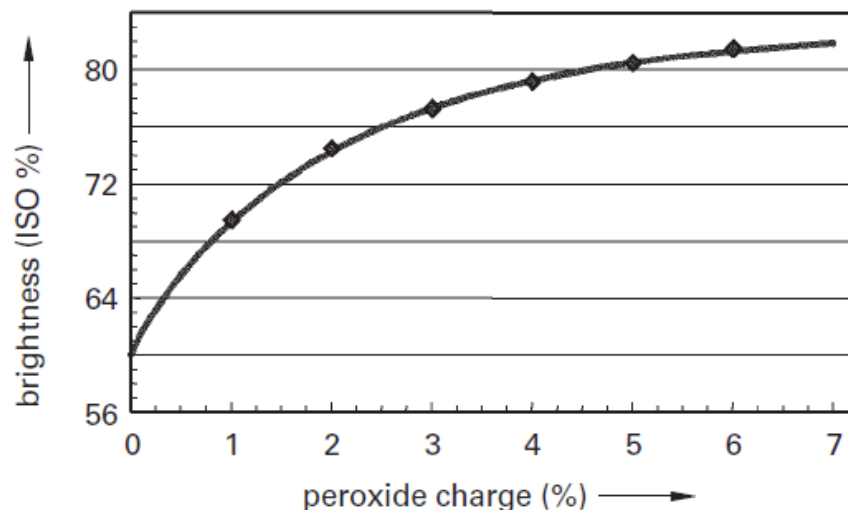
Pulp sample	Brightness, % ISO	Viscosity, dm ³ /kg	Kappa Number	Lignin ¹⁾	HexA ^{1, 2)}	Non-lignin ^{1, 3)}
after O-stage	59.1	920	9.6	3.2	4.3	2.1
after OQ(OP)	73.3	850	7.3	2.2	3.7	1.4
after OQ(OP)Q(PO)	89.0	710	4.6	0.8	3.0	0.8

¹⁾ calculated in Kappa number units

²⁾ HexA = hexenuronic acid

³⁾ 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)

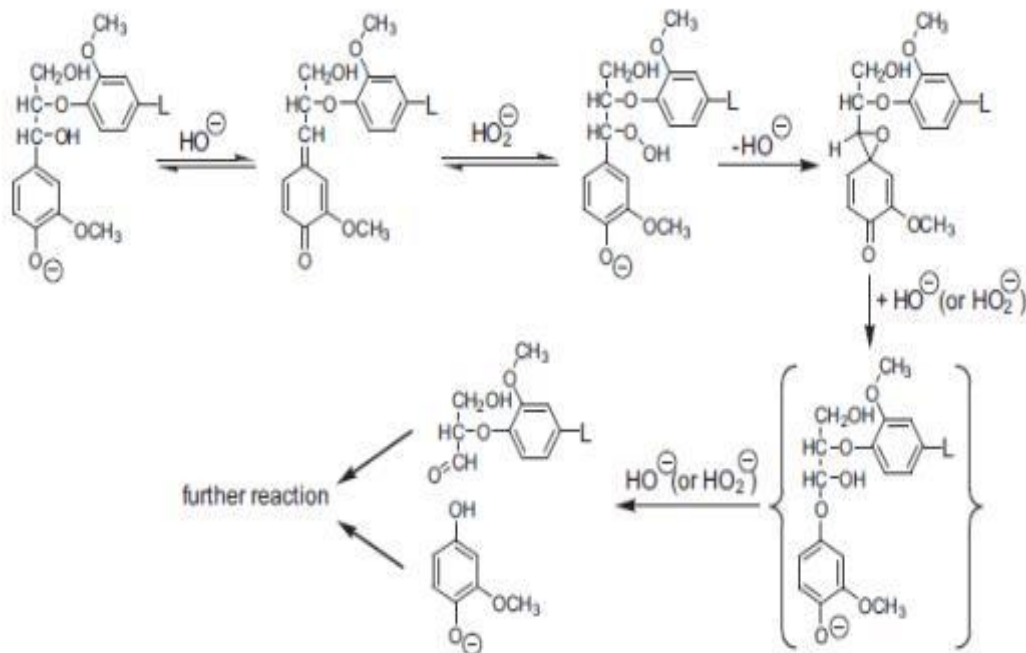


Figure 9.20. Side chain cleavage of a phenolic β -O-4 structure in lignin on oxidation with alkaline hydrogen peroxide. Reaction conditions for L (lignin)=H: 90 °C, 180 min (Heuts 1998).

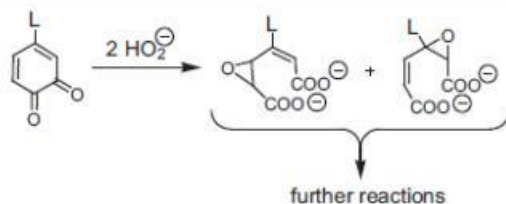


Figure 9.22. Oxidation of a quinone structure by alkaline hydrogen peroxide.

Branqueamento com dióxido de cloro

Chlorine dioxide bleaching



O 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 ClO_2 é dissolvido em água acidificada e usado como agente de branqueamento

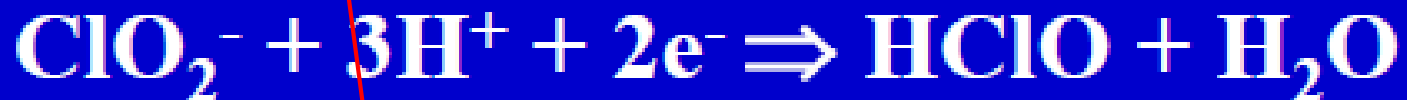
Conditions used in an industrial D0-stage

	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

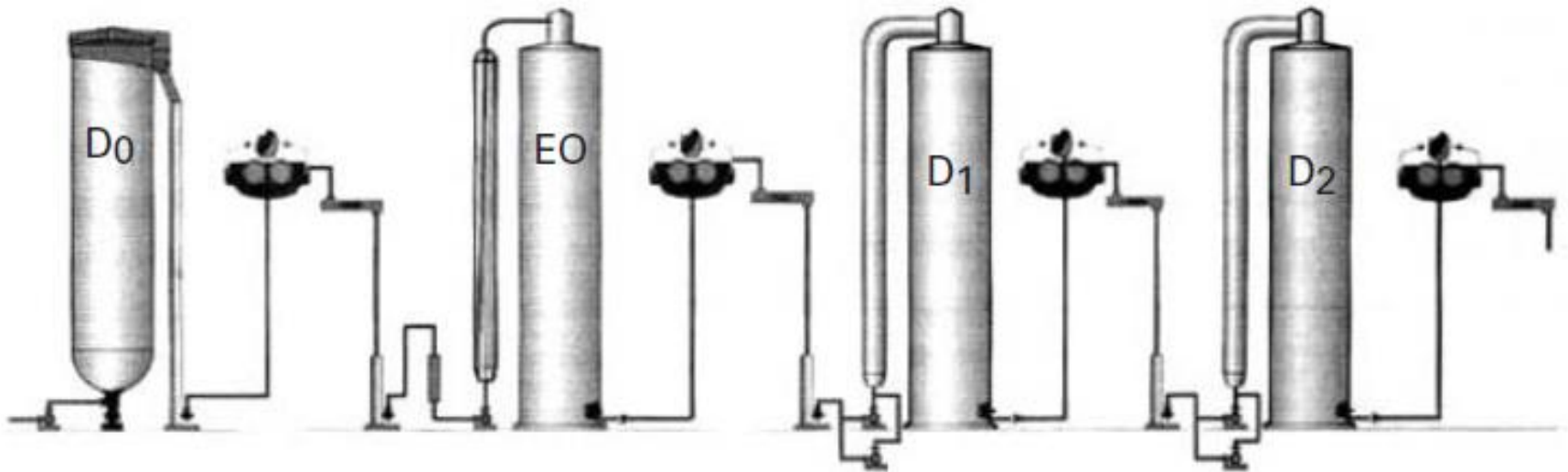


Figure 10.6. A bleaching sequence with four stages according to $D_0(EO)D_1D_2$. (Metso Paper).

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 ³ /kg	Kappa Number	Lignin ¹⁾	HexA ^{1, 2)}	Non-lignin ^{1, 3)}
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

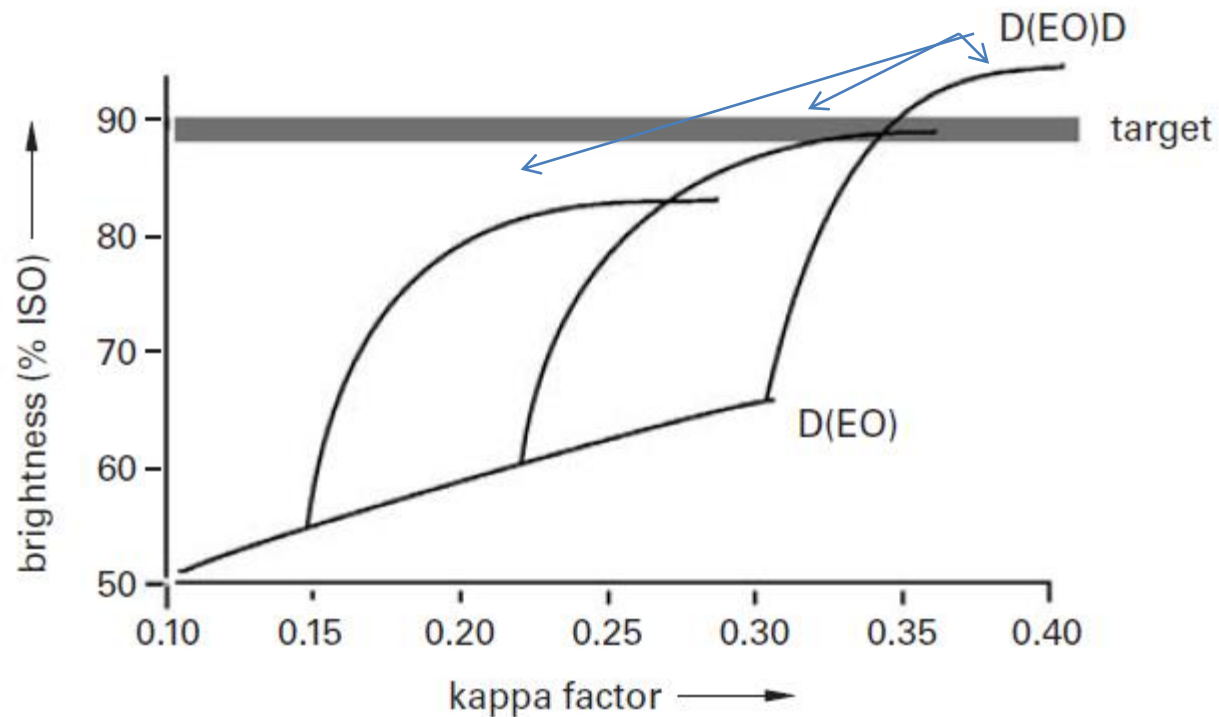
¹⁾ calculated in Kappa number units

²⁾ HexA = hexenuronic acid

³⁾ Non-lignin = unspecified but oxidizable structures

Adição do agente oxidante x eficiência

No caso da branqueamento com ClO_2 , é usual que 2 etapas proporcionem melhor efeito do que uma única carga



Proporcional a carga de ClO_2

Reações do dióxido de cloro com lignina

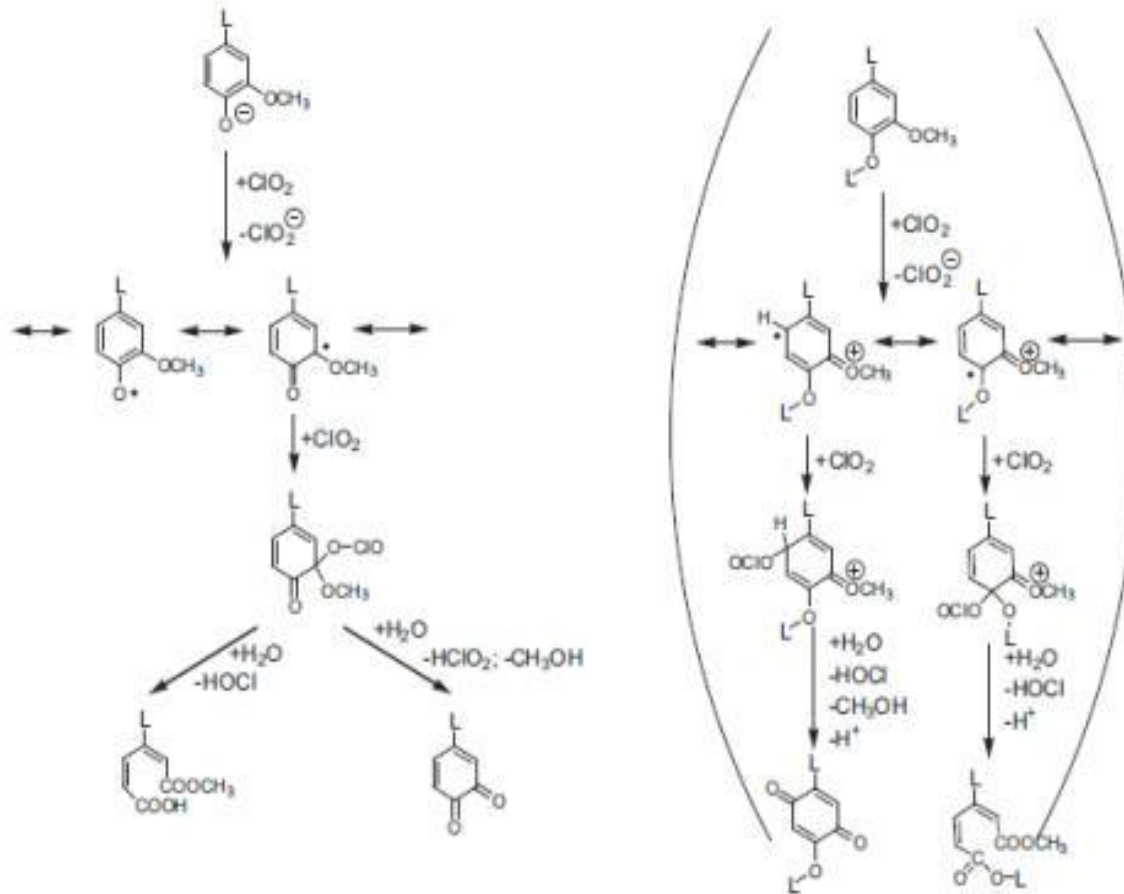


Figure 9.25. Reactions between a phenolic (left) and a non-phenolic (right) lignin structure respectively with chlorine dioxide under acidic conditions (Eriksson 1993). In benzylalcohol structures, a similar reaction will result in an oxidative elimination of the side chain. The reaction of non-phenolic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

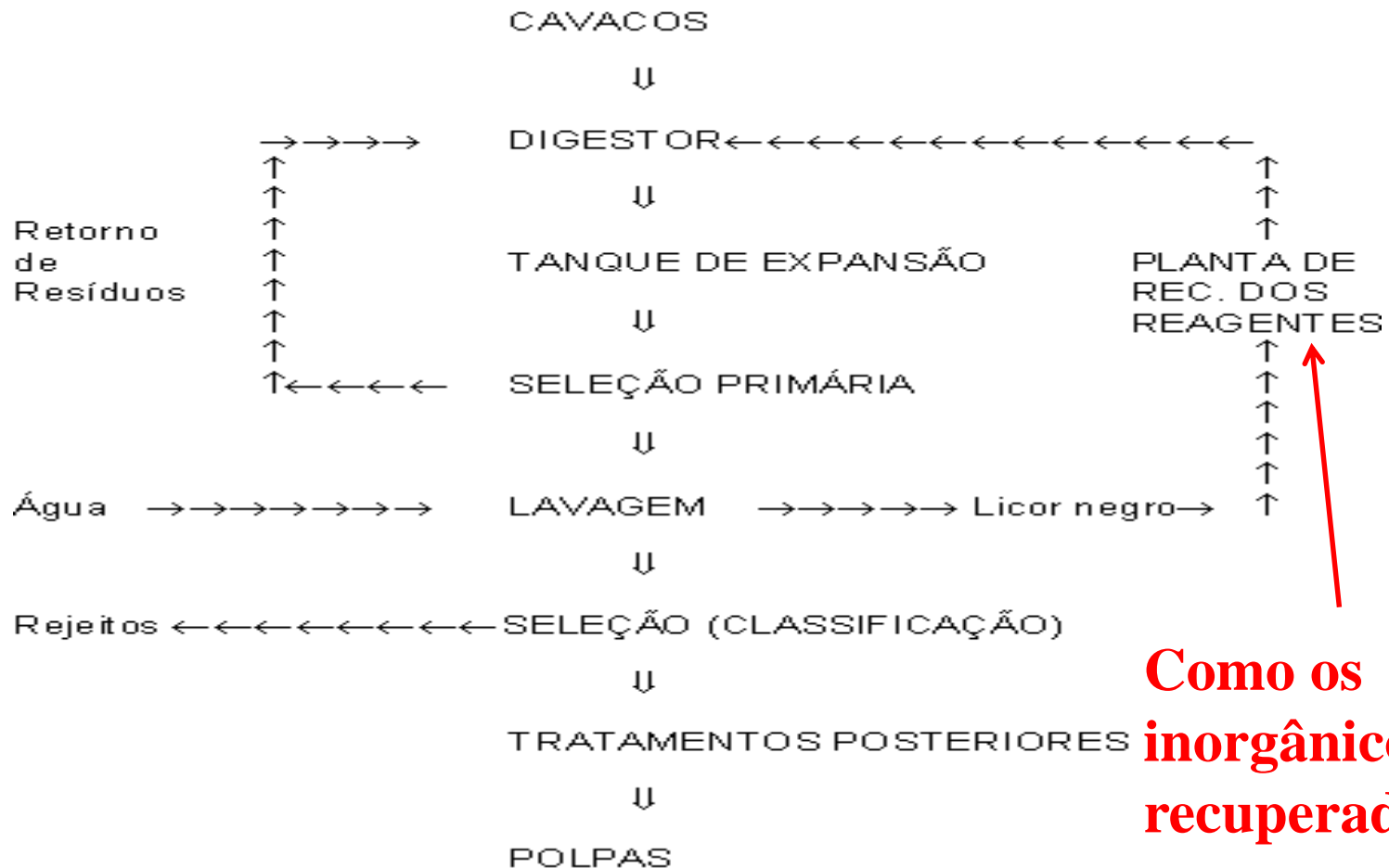
- pH 10.5–11.0
- 80–110 °C
- 9–13% pulp consistency
- 1–3 hours
- 3–8 bar
- 5–10 kg O_2 /t and 5–40 kg H_2O_2 /t

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?