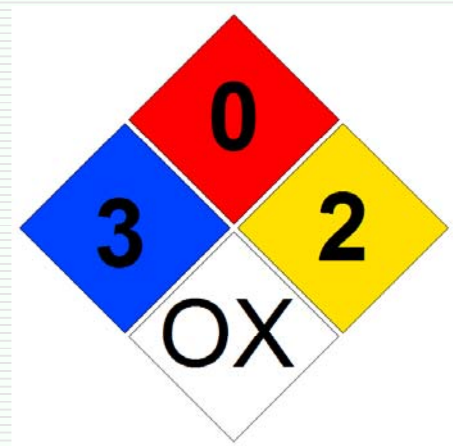
Hydrogen Peroxide Bleaching

Fundamental Overview

H_2O_2

- NAME: Hydrogen Peroxide; Hydrogen Dioxide; Albone; Inhibine; Perhydrol; Peroxan; Oxydol; Hydroperoxide; Hioxy; Dihydrogen Dioxide;
- CAS No.: 7722-84-1
- MOLAR MASS: 34.0147 g/mol
- APPLICATIONS: Pulp and paper, chemical synthesis, environmental uses, including water treatment, textiles, mining, electronics, food and cosmetic.

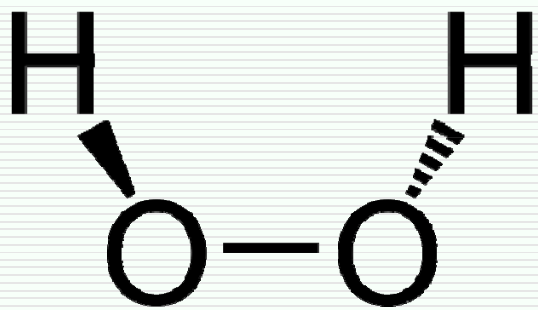


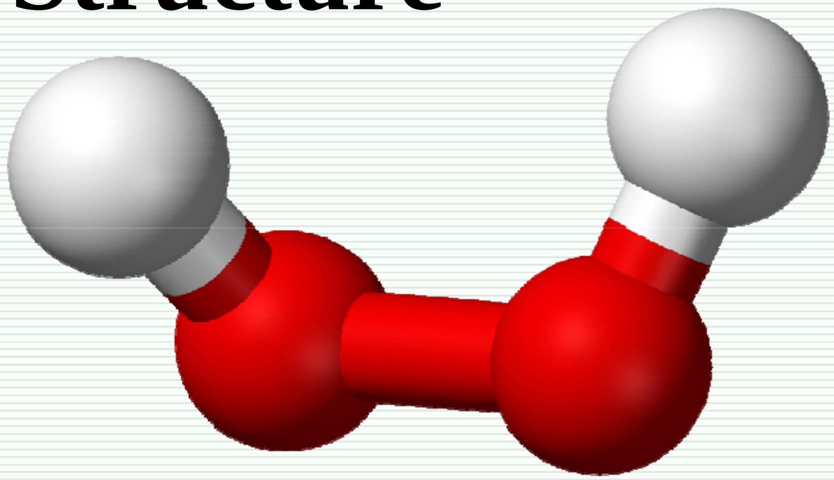
Note: Usage of hydrogen peroxide requires specialized training and equipment beyond the level of this overview

Hydrogen Peroxide

- H_2O_2 is a very pale blue liquid, slightly more viscous than water, that appears colorless in dilute solution.
- First isolated in 1818 by Louis Thénard.
- Naturally produced in organisms as a byproduct of oxygen metabolism. Nearly all living things possess enzymes known as peroxidases, which harmlessly and catalytically decompose low concentrations of hydrogen peroxide to water and oxygen.
- Commercially available as water solutions in the concentrations range of 3-90% w/w.
- World production in 2008 3 million metric tons with annual growth of 4%. In 2006 bulk 30% H_2O_2 sold for around \$0.54 per kg.

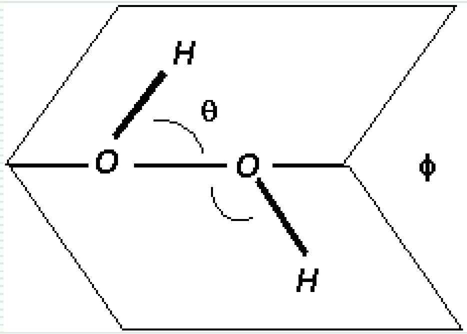
Hydrogen Peroxide Molecular Structure





Hydrogen peroxide adopts a **"skewed" shape**, due to repulsion between the lone pairs on the oxygen atoms. Despite the fact that the O-O bond is a single bond, the molecule has a remarkably high **barrier** to complete **rotation of 29.45 kJ/mol**; this is also caused by the lone pair repulsion.

Properties of H_2O_2 Molecule



Bond angles:	Θ (H-O-O angle): 95° ± 2° Φ (Dihedral angle): 120° ± 3° Ref: Gmelin "Handbuch der Anorganischen Chemie", *Suerstoff* – syst. 3, Lief. 7-8 Auflage – Weinheim – VERLAG Chemie, p.429 (1966)
Bond length:	O-H: 0.097 ± 0.001 nm - Ref: P.A. Giguere and O. Bain, *J.Phys.Chem*. 56:340-42 (1952) O-O: 0.149 ± 0.001 nm - Ref: S.C. Abrahams, et.al., *Acta Cryst*. 4:15-20 (1951)
Bond strength:	HO-OH: 51 ± 1 kcal/mole - Ref: J.A. Kerr, *Chem.Rev.* 66:465 (1966) H-OOH: 90 ± 2 kcal/mole - Ref: J.A. Kerr, *Chem.Rev.* 66:465 (1966)
Dipole moment:	μ = 2.26 D

Note: The H_2O_2 molecule has no center of symmetry

Select Molecular Structure Data

		Wave Number, cm^{-1}
Vibration	O-H stretching	3610
	Symmetric bending	1295
	O-O stretching	890
	Torsional oscillation	520
	O-H stretching	3610
	Unsymmetrical bending	1266
Moments of inertia ($g.cm^2$)		$I^A = 2.78 \times 10^{-40}$
		$I^B = 34.0 \times 10^{-40}$
		$I^C = 33.8 \times 10^{-40}$
		$I^{red} = I^A/4 = 0.696 \times 10^{-40}$
Barrier restricting internal rotation:		V^o = 3.5 kcal/mole
Absolute entropy:		S^o298.16 = 55.66 cal/mole °K

P.A. Giguere, I.D. Liu, J.S. Dugdale, J.A. Morrison. Can. J. Chem., 74:3715 (1952)

Notes: 1. In rotation as a whole, the molecule remains rigid.
2. Vibration may be considered to be harmonic oscillations.

Hydrogen Peroxide: physical properties

Aqueous solutions of H_2O_2

Concentration	35%	50%	70%
Appearance	Clear Colorless Odorless And Waterlike		
Active Oxygen	16.5% min	23.5% min	32.9% min
Specific gravity	1.133	1.196	1.288
Boiling point	108 °C	114 °C	126 °C
Viscosity	1.81	1.89	1.93
Freezing point	-33 °C	-52 °C	-40 °C
Apparent pH	2.5	1.8	0.5

H_2O_2:Related Electrochemical Values

H_2O_2 contains oxygen in a state of oxidation midway between molecular oxygen and water.

	Reduction →
Oxygen Moiety	$O_2 \leftrightarrow H_2O_2 \leftrightarrow H_2O$
Oxygen Valence	0 -1 -2
	← Oxidation

$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ $E^o = -0.682$ V

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $E^o = 1.776$ V

For perhydroxyl ion (HO_2^-):

$OH^- + HO_2^- \rightarrow O_2 + H_2O + 2e^-$ $E_B^o = 0.084$ V

$3OH^- \rightarrow HO_2^- + H_2O + 2e^-$ $E_B^o = -0.87$ V

H_2O_2:Related Electrochemical Values

Reaction	Potential, Volts
$HO_2 + H^+ + e^- \leftrightarrow H_2O_2$	1.5
$O_2 + H_2O + 2e^- \leftrightarrow HO_2^- + OH^-$	-0.076
$O_2 + 2H_2O + 2e^- \leftrightarrow H_2O_2 + 2OH^-$	-0.146
$HO_2^- + H_2O + 2e^- \leftrightarrow 3OH^-$	0.87

Heat for formation (ΔH_f^o) for:

$HO^\bullet$	9.2 ± 1 kcal/mole
HO_2^-	5.3 ± 2 kcal/mole

Ref: J.A. Kerr, Chem.Rev. 66:465 (1966)

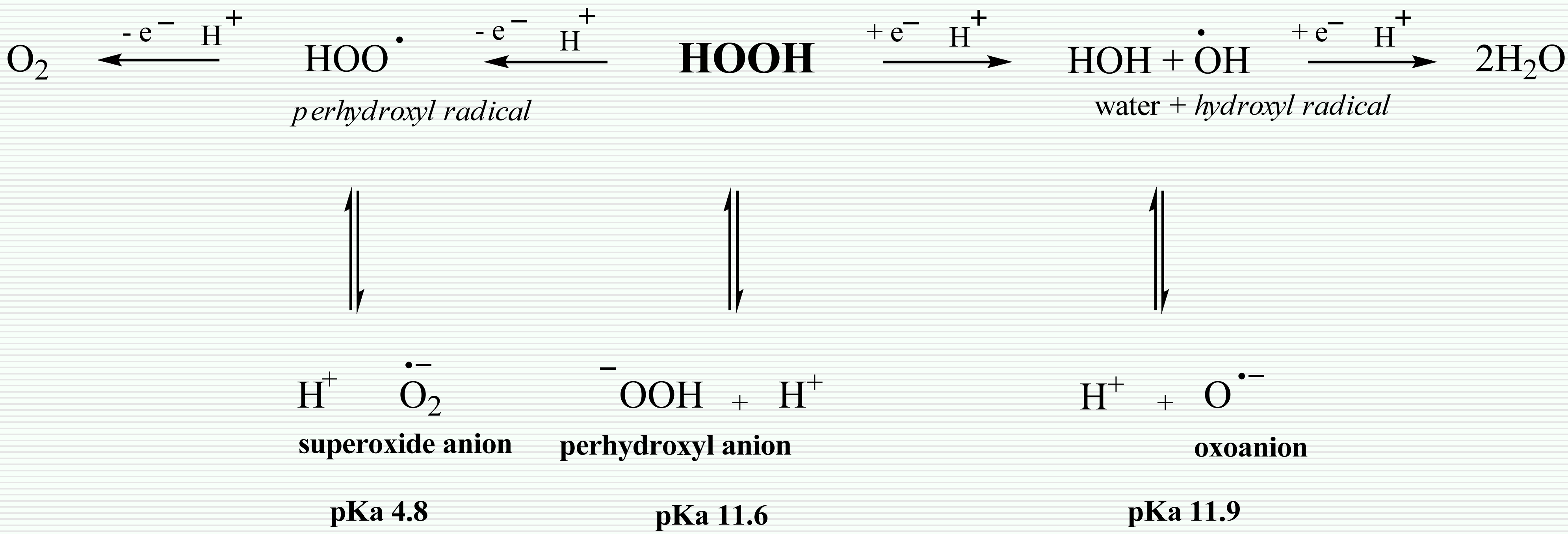
Chemistry of Hydrogen Peroxide. Decomposition

- Thermodynamically, hydrogen peroxide is unstable as is shown by the following equation:

  $$½H_2O_2\ (l) \rightarrow ½H_2O\ (l) + O_2\ (g) \quad \Delta G° = –119.2\ kJ/mol$$

- The reaction from left to right is a spontaneous process and is accompanied by a decrease of free energy. However, the decomposition of H_2O_2 at 25°C in the absence of catalysts is slow. Platinum, silver, copper, cobalt, manganese dioxide, iron, etc. are catalysts, which accelerate its decomposition. There are also a few stabilizers such as, acids, acetanilide, stannates and pyrophosphates.
- Commercial grades of hydrogen peroxide are often quite stable, typically losing less than 1% relative strength per year.

Possible Redox reactions of H_2O_2



Chemistry of Hydrogen Peroxide Redox reactions

- H_2O_2 is a powerful oxidizer

Oxidant	Oxidation potential, V
Fluorine	3.0
Hydroxyl radical	2.8
Ozone	2.1
Hydrogen peroxide	1.8
Potassium permanganate	1.7
Chlorine dioxide	1.5
Chlorine	1.4

Redox chemistry of H_2O_2

Perhydroxyl anion

$$HOOH \rightleftharpoons {}^{-}OOH + H_2O$$

pK_a 11.62

The principal reactive species in peroxide bleaching systems is the perhydroxyl ion

Reactions of H_2O_2 in presence of transition metal (M)

$$H_2O_2 + M \rightarrow HO\cdot + HO^- + M^+$$
$$H_2O_2 + HO^- \rightarrow HO_2^- + H_2O$$
$$HO_2^- + M^+ \rightarrow HO_2\cdot + M$$
$$HO_2\cdot + HO^- \rightarrow O_2^{\cdot -} + H_2O$$

$$O_2^{\cdot -} + M+ \rightarrow O_2 + M$$
$$O_2^{\cdot -} + HO\cdot \rightarrow O_2 + HO^-$$
$$2O_2^{\cdot -} + H_2O \rightarrow O_2 + HO_2^- + HO^-$$

The essential element of any proposed peroxide decomposition sequence is a transition metal catalysis step

Reactions of radicals in subsequent stage

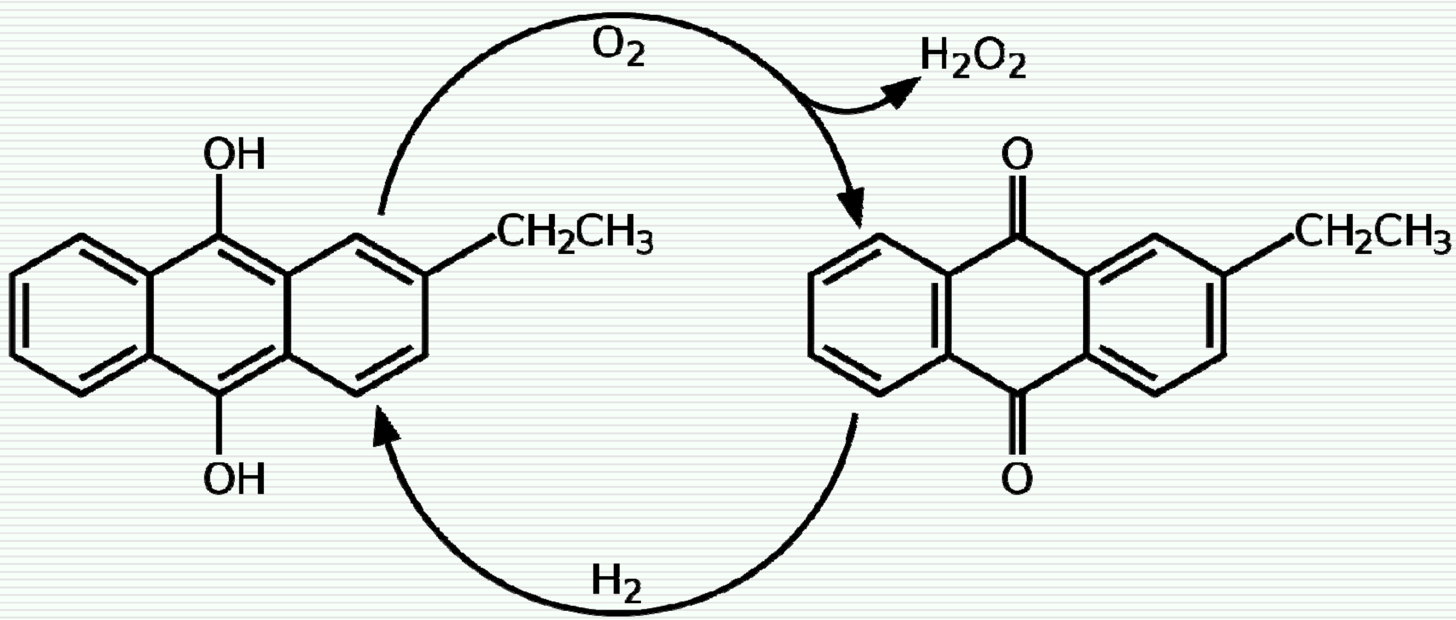
$HO\cdot + HO_2^- \rightarrow H_2O + O_2^{\cdot -}$

$HO\cdot + M \rightarrow HO^- + M^+$

$HO\cdot + HO\cdot \rightarrow H_2O_2$

Chemical Process Employed In The Industry For Generation of H_2O_2

Today, hydrogen peroxide is manufactured almost exclusively by the autoxidation of a 2-alkyl anthrahydroquinone (or 2-alkyl-9,10-dihydroxyanthracene) to the corresponding 2-alkyl anthraquinone. Major producers commonly use either the 2-ethyl or the 2-amyl derivative.



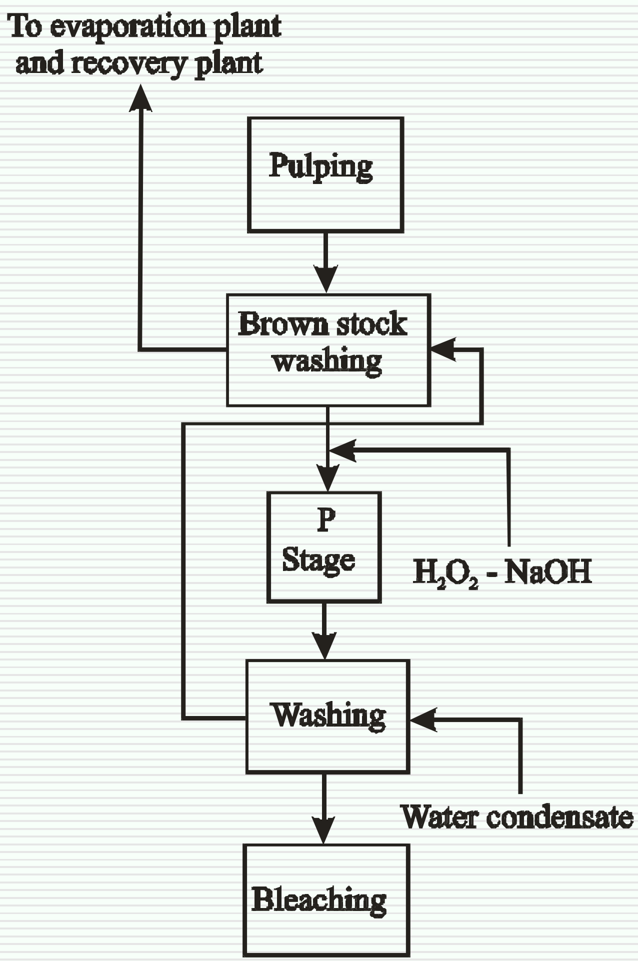
Typical stages of ECF Bleaching Sequences

Abbreviation	Name
O	oxygen delignification
P	hydrogen peroxide
D	chlorine dioxide
E	alkaline extraction
H	hypochlorite
Pac	peroxy acid (peracid)
Z	ozone

Bleaching Sequences Comprised Of A Hydrogen Peroxide Delignification Stage

Sequence	Pulp type
OPDED	Softwood kraft
PPDED	Softwood kraft
OPOPP	Softwood and hardwood kraft
OPD	Hardwood kraft
PDP,PDPD	Softwood sulfite
PHDH	Softwood sulfite
(PO) (PO)	Softwood kraft
(EOP) P	Softwood and hardwood sulfite
PPacP	Softwood sulfite
OPZ	Hardwood kraft
OPZP	Softwood kraft
(EOP) Z P	Hardwood and softwood sulfite

MINOX Process



- H_2O_2 directly applied to the unbleached pulp

<u>P reaction conditions</u>

Time 30-60 min

Temp 60-105

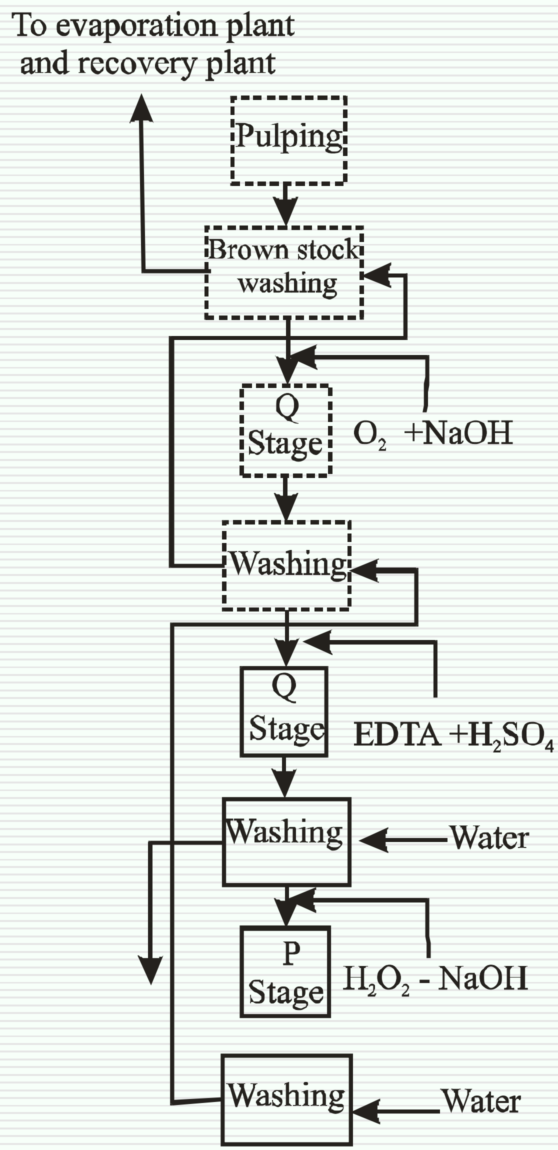
Charge: both H_2O_2 and NaOH 0.5% on pulp

pH 10.2 on average

Consistency 10-12%

Delignification limited to about 20%

LIGNOX Process



<u>P reaction conditions</u>

Time 40-90 min

Temperature 60-85 °C

Charge 0.2-0.5 % H_2O_2

pH 9.5-11.0

Consistensy 10-12%

Delignification up to 50%

<u>Q reaction conditions</u>

Time 40-90 min

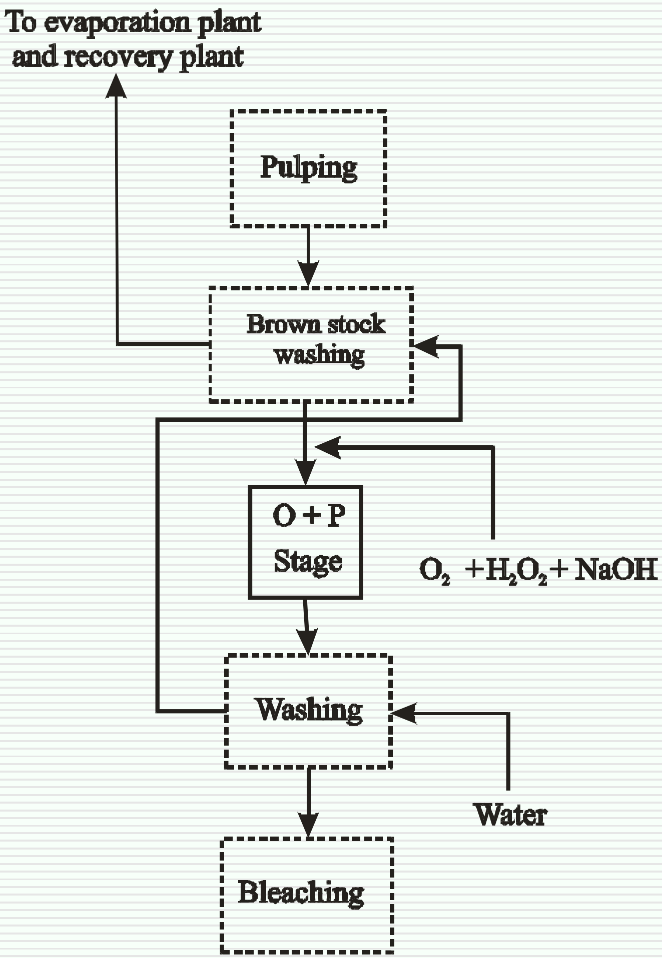
Temp.: 60-85 °C

Charge 0.2-0.5% EDTA

pH 6.5-6.9

Consistensy 4-5%

Combined Oxygen-H_2O_2 Process



<u>P reaction conditions</u>

Time 50-120min

Temp 50-70 °C

Charge up to 0.5% H_2O_2

pH 5-7

Consistency 12%

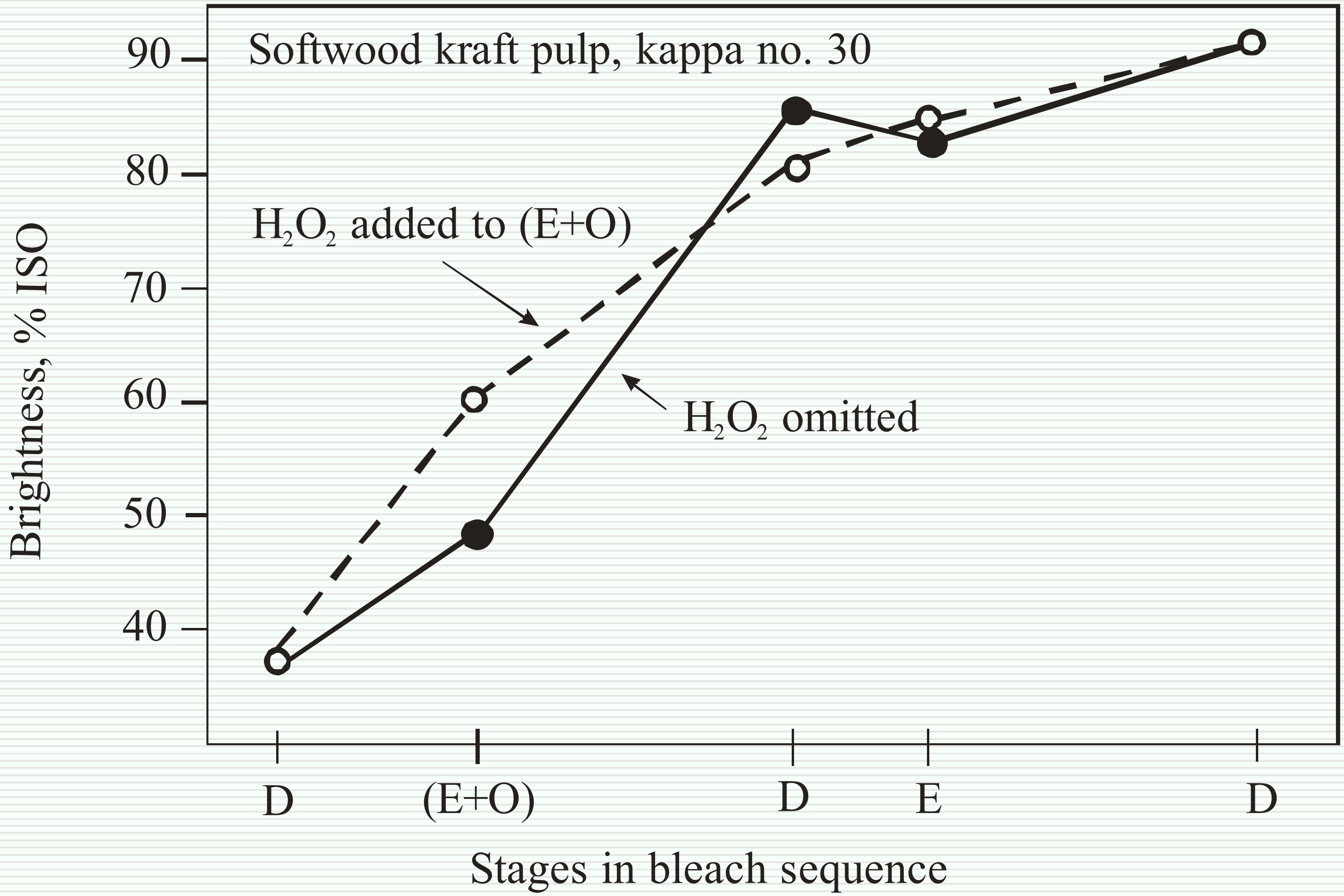
60% kappa number reduction

Select Process Parameters Employed With H_2O_2

Eop - also written as (E+O+P)

- Peroxide 0.1 - 0.6%
- Temp.: 55 – 85 ^oC (typically 70 °C)
- $pH_{initial}$ 10.5 pH_{final} 9.0-9.5
- amount of NaOH less than 0.5% on pulp
- Time: 50 – 140 min
- O_2: 0.5 - 0.7% $_{consumed}$
- Pulp consistency desired 10%
- Brightness 45-58% ISO
- first extraction stage

Select Process Parameters Employed With H_2O_2



Effect of peroxide addition in an (E+O) stage on brightness at the end of each stage in a D(E+O)DED sequence.

Select Process Parameters Employed With H_2O_2

Ep

- Peroxide: 0.2 - 0.6%
- Temp. 65-85^{o}C
- $pH_{initial}$ 10.5 pH_{final} 9.0-9.5
- NaOH up to 0.5% on pulp
- Time: 45 - 120 min.
- second extraction stage

P

Peroxide: 2.5-3.0%

Temp. 65- 85^{o}C

pH 10.5-11.8

NaOH 0.2-0.5%

Kappa no. 4-10

Time: 45 - 120 min.

Select Process Parameters Employed With H_2O_2

PO

- Requires pre Q-stage
- Peroxide: 0.5 - 3.0%
- Temp: 100 - 110^oC
- Time: 60 - 120 min
- O_2: 75 - 120 psi
- Stabilizer EDTA or DTPA up to 0.2%
- NaOH 0.5% on pulp

- Brightening and delignifying

Typically
19-27 % delignification for SW
22-33 % delignification for HW

Select Process Parameters Employed With H_2O_2

P_{HT}

- Pre Q stage preferred
- Peroxide 0.5 - 3.0%
- Temp.105 - 110°C for 5-15 min
  90 - 98°C for 180 - 240 min
- O_2: 70 - 120 psi
- Stabilizer EDTA up to 2 kg per ton of pulp (0.2%)
- Consistency 10-20%
- pH 9.5-11.8
- NaOH 0.5%

- Brightening 8-10 points ISO
- Delignifying

Typically
21-28 % delignification for SW
25-34 % delignification for HW

Select Process Parameters Employed With H_2O_2

Typical bleaching sequences used in North America

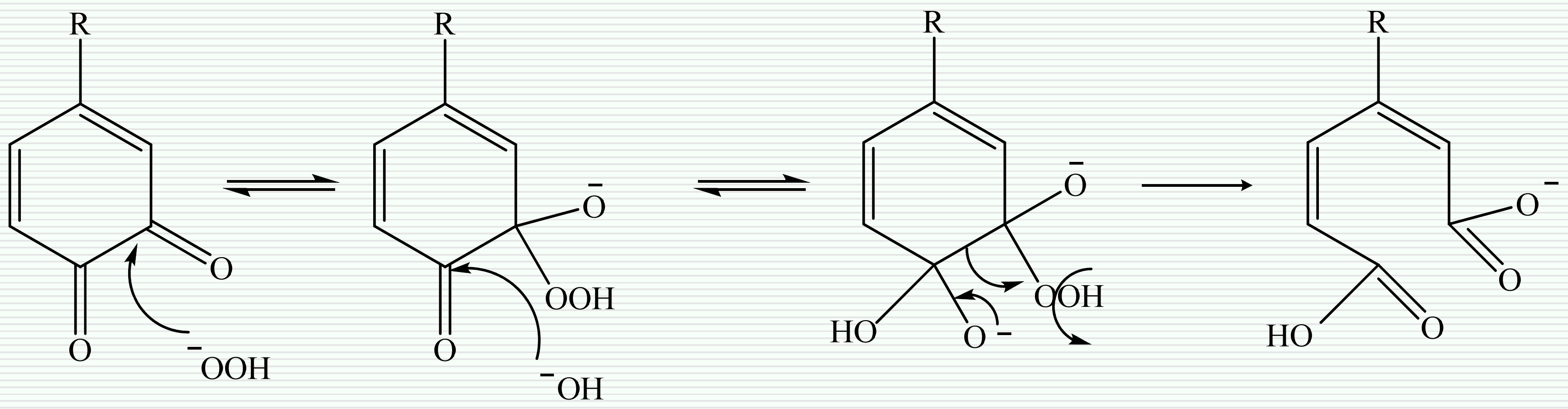
Primarily ECF

- D(Eop)DED
- D(Eop)DEpD,
- OD(Eop)D or OD(Eop)DEpD
- D(Ep)DED

HD (High Density) storage (0.1 - 0.2% P, pH approx. 9)

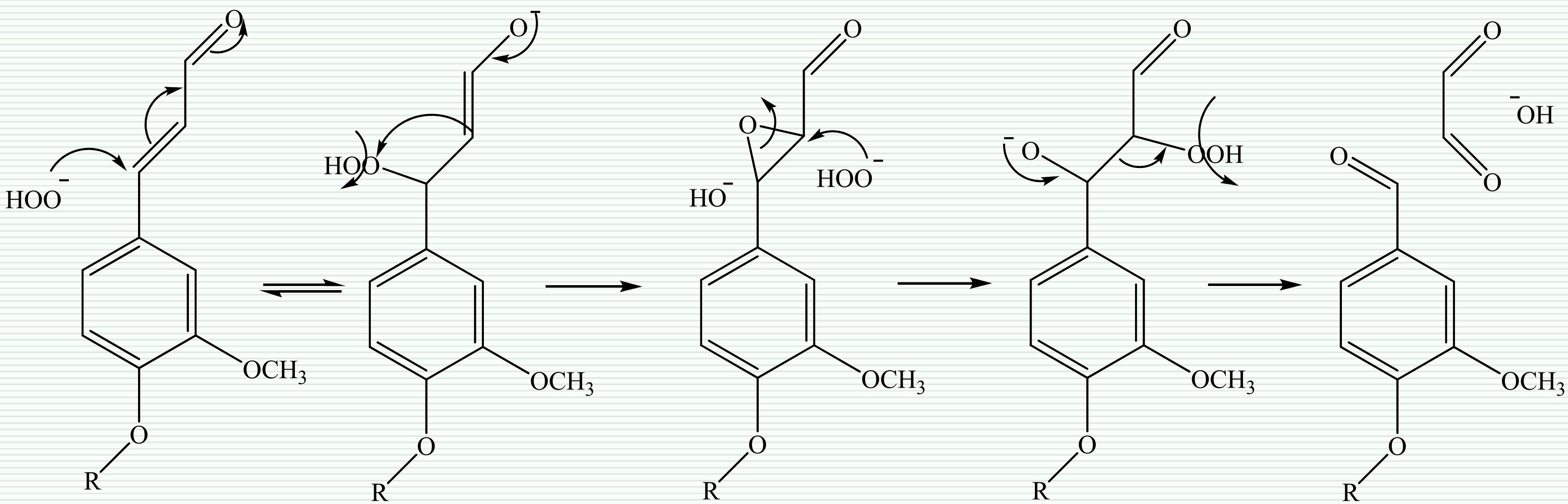
H_2O_2 Bleaching Chemistry

- Addition to quinones:



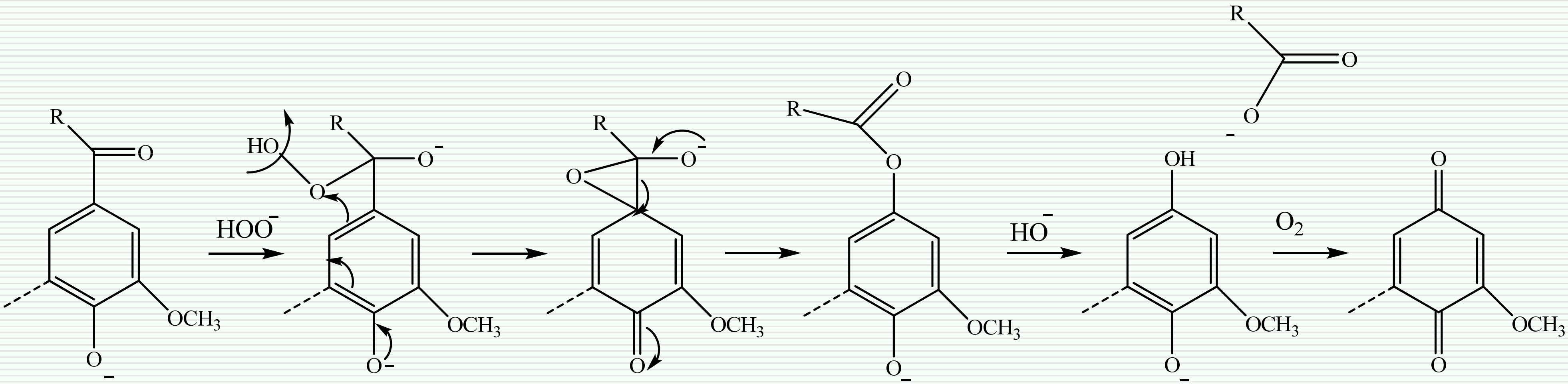
H_2O_2 Bleaching Chemistry

- Michael addition to conjugated carbonyl structures



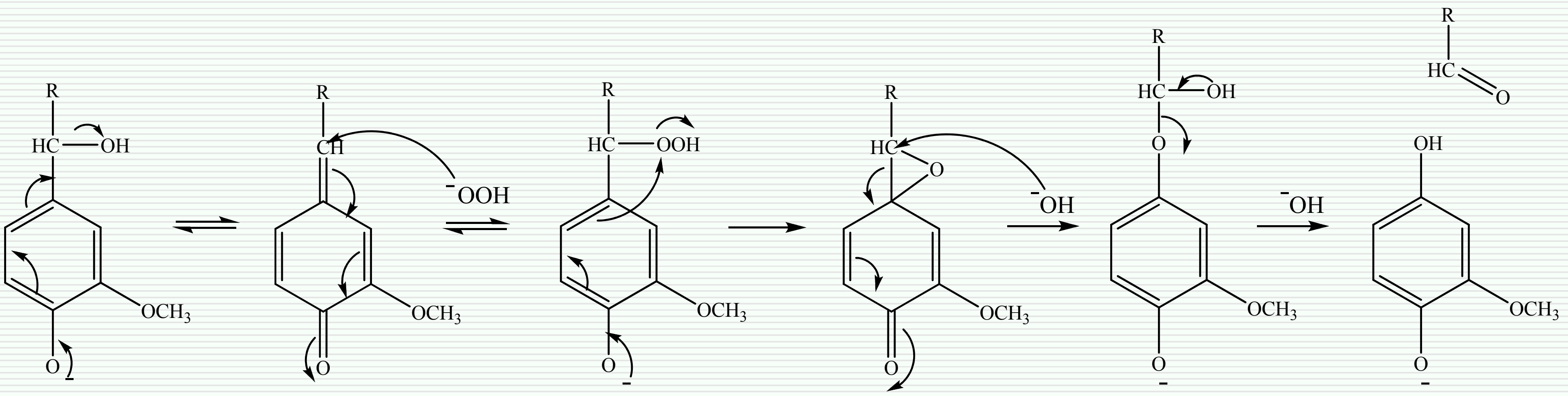
H_2O_2 Bleaching Chemistry

- Dakin reaction



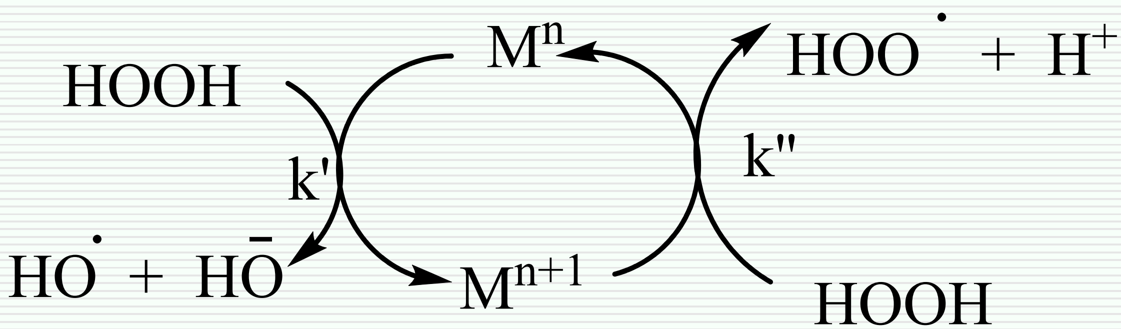
H_2O_2 Bleaching Chemistry

- 'Dakin-like' reaction



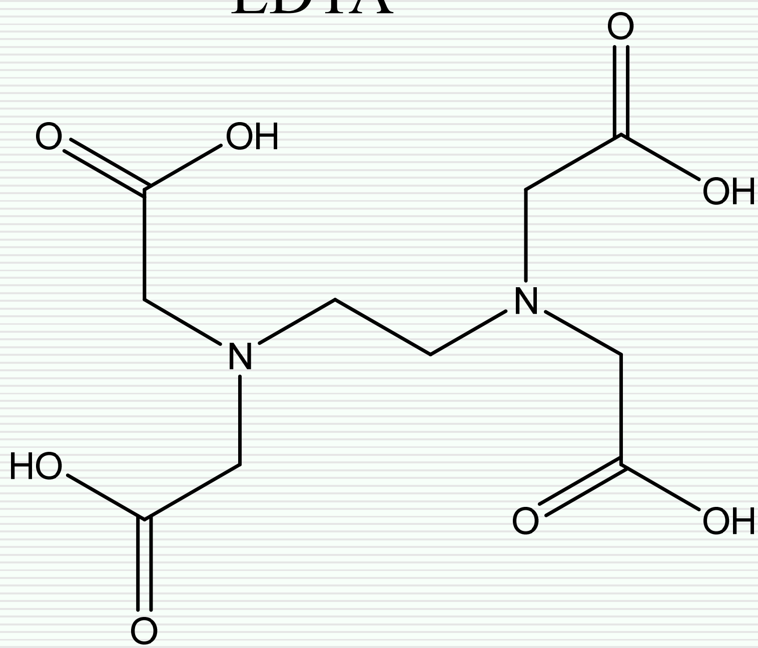
H_2O_2 Bleaching ChemIstry: Effect Of Metal Ions On Reaction

- Hydrogen peroxide is also very sensitive to traces of transition metal ions, particularly iron, copper and manganese, which catalyze its decomposition (Brown and Abbot 1995).



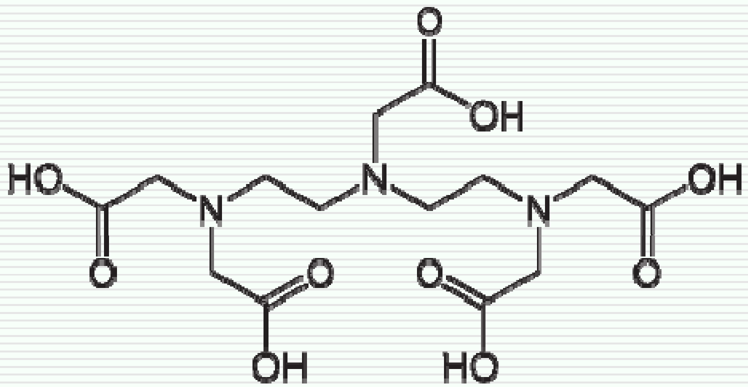
Chelating Agents

EDTA



ethylene-diamine-tetraacetic acid

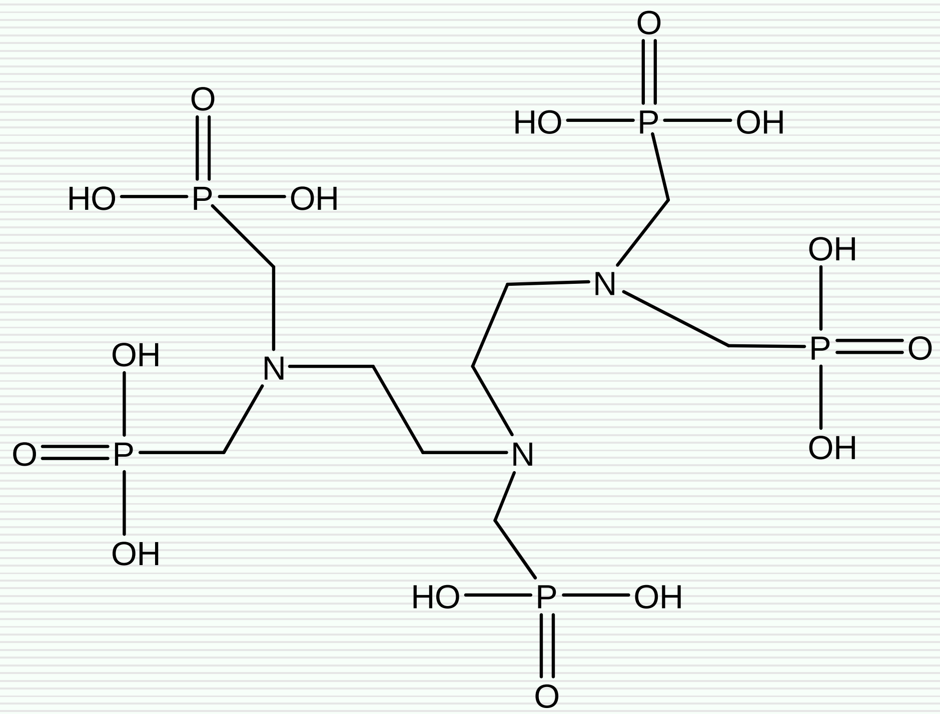
DTPA



diethylene-triamine-pentaacetic acid

H_2O_2 Bleaching Chemistry: Effect Of Metal Ions On Reaction. Chelating Agents

DMTPA



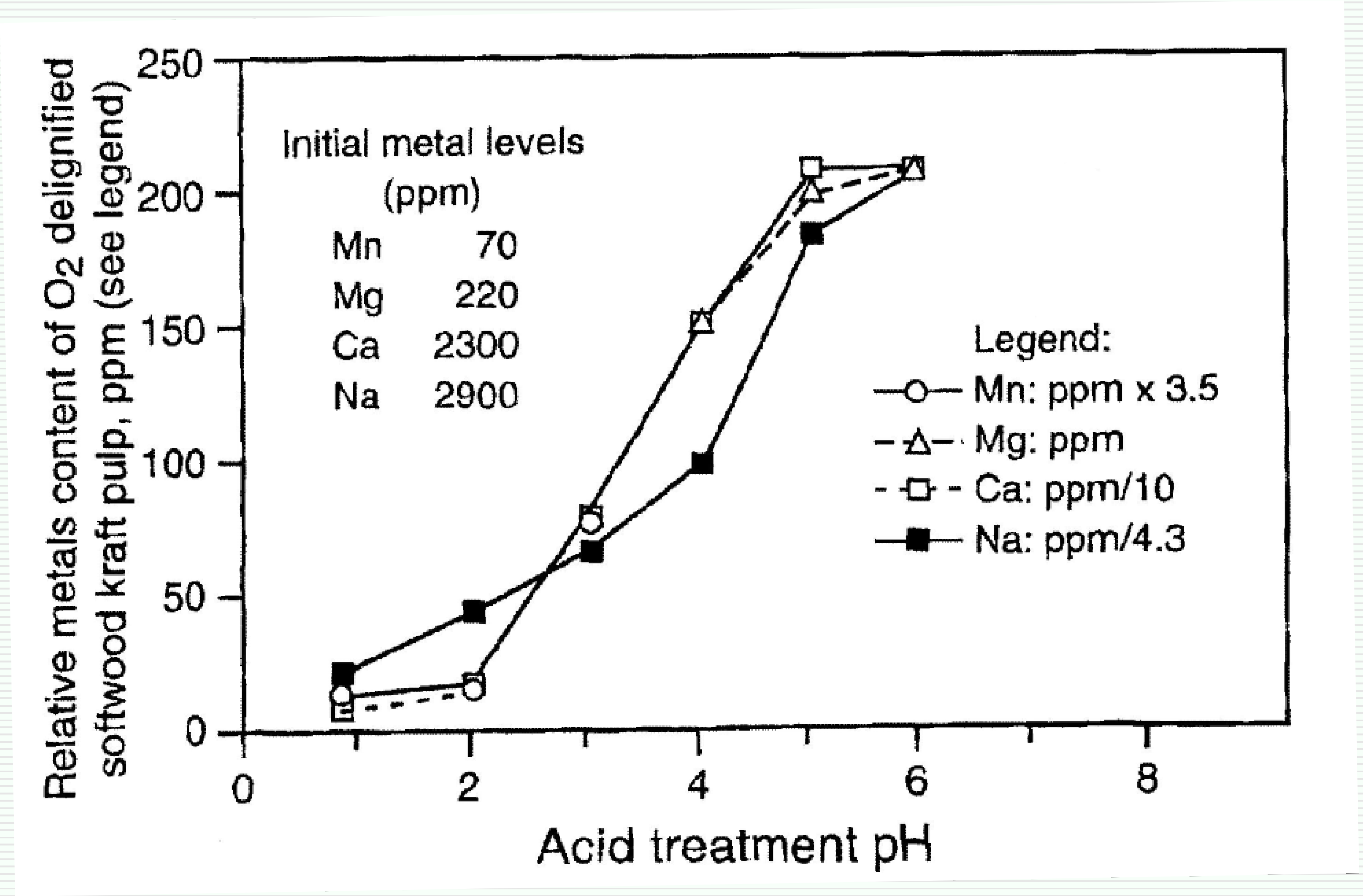
diethylene-triamine-methylene-phosphonic acid

Effect of chelation (Q stage) on metal content of softwood kraft pulps.

Metal content, ppm

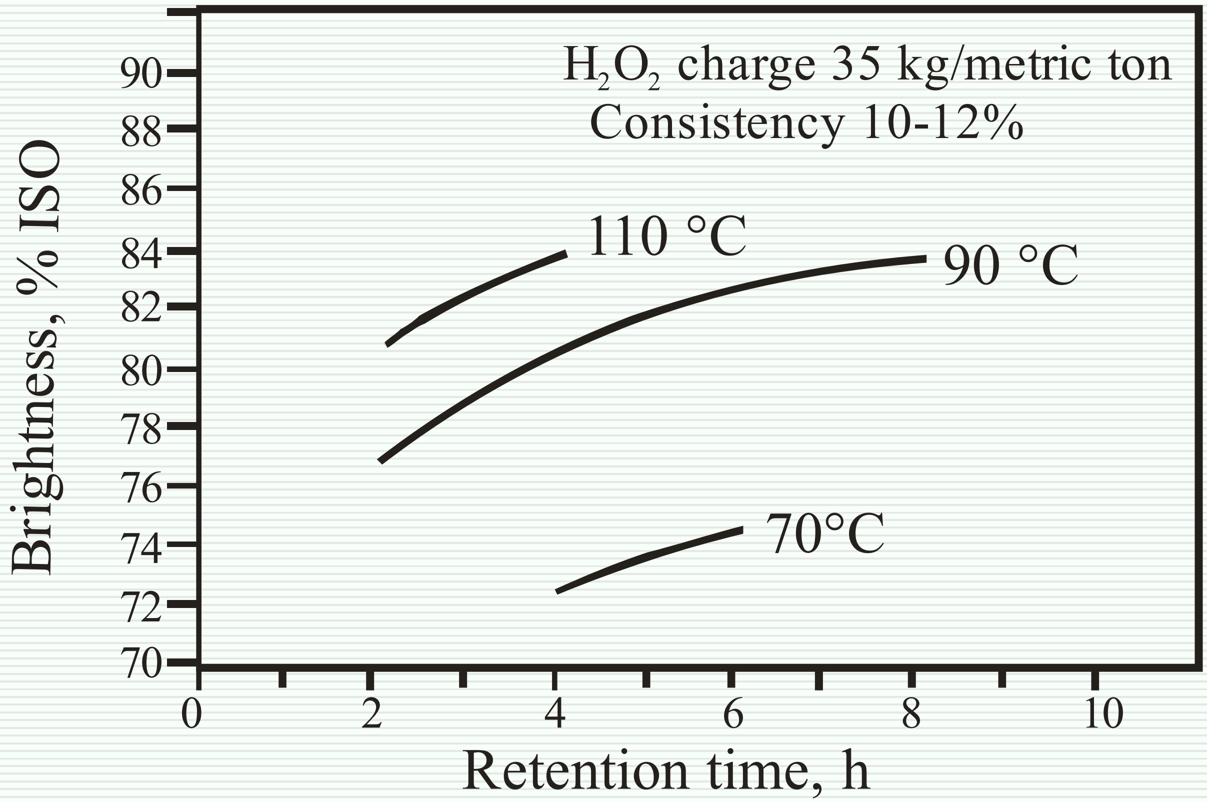
	Ca	**Mg**	**Fe**	**Mn**	**Cu**
Before chelation	1400	300	11	47	0.6
After chelation	500-1000	120-280	6-8	<5	0.1-0.2
Q-stage conditions: 0.2% EDTA on oven-dry pulp, 90°C, 1 h, pH 5-7					

H_2SO_4 wash out metals



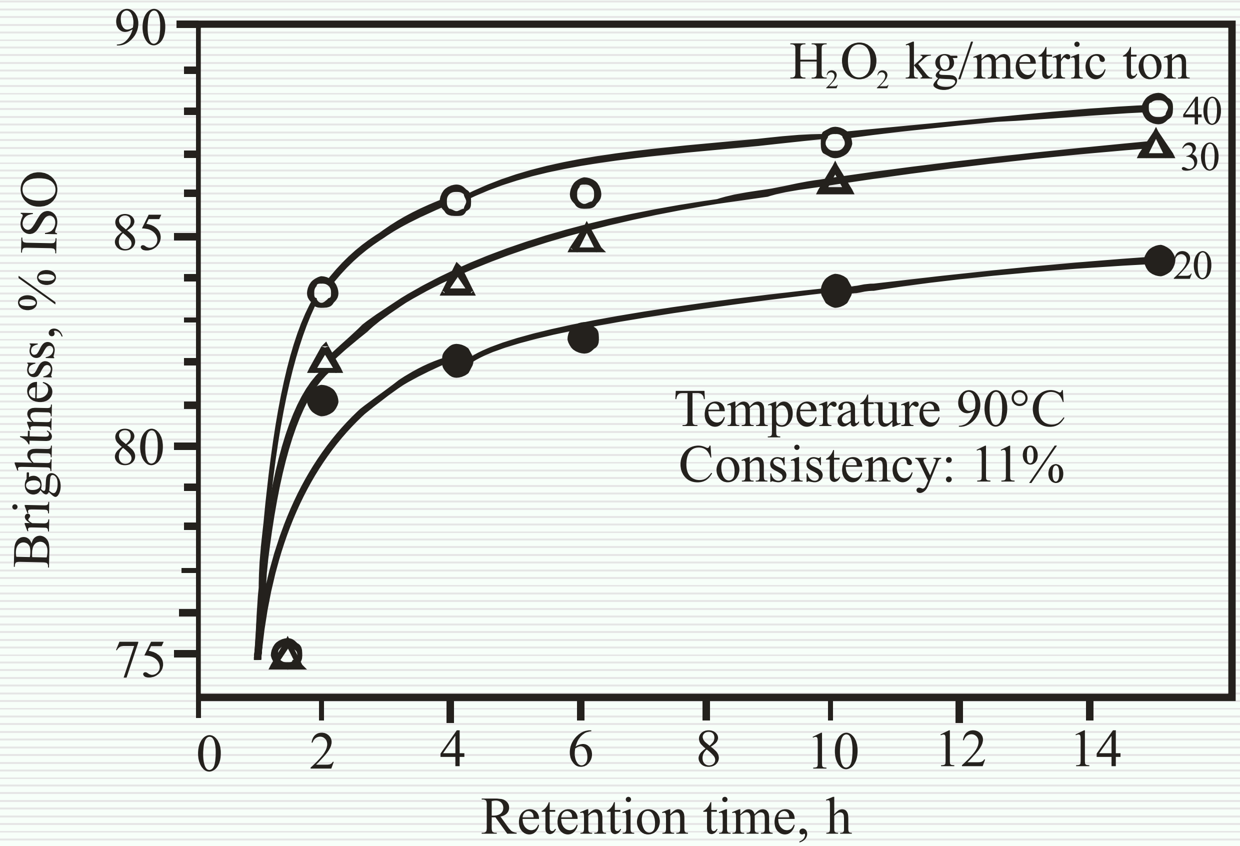
Effect of acid-pretreatment pH on the removal of metals from an oxygen-delignified softwood kraft pulp

H_2O_2 Bleaching Chemistry: Effect of Temperature



Effect of temperature on the rate of bleaching of an oxygen delignified softwood kraft pulp (kappa No. 6) bleached with hydrogen peroxide.

H_2O_2 Bleaching Chemistry: Effect Of Peroxide Charge On Brightness



Effect of peroxide charge on the rate of bleaching of an oxygen-delignified hardwood kraft pulp (kappa No. 11) bleached with hydrogen peroxide.