Chapter 3

Cooking Chemistry with Additives

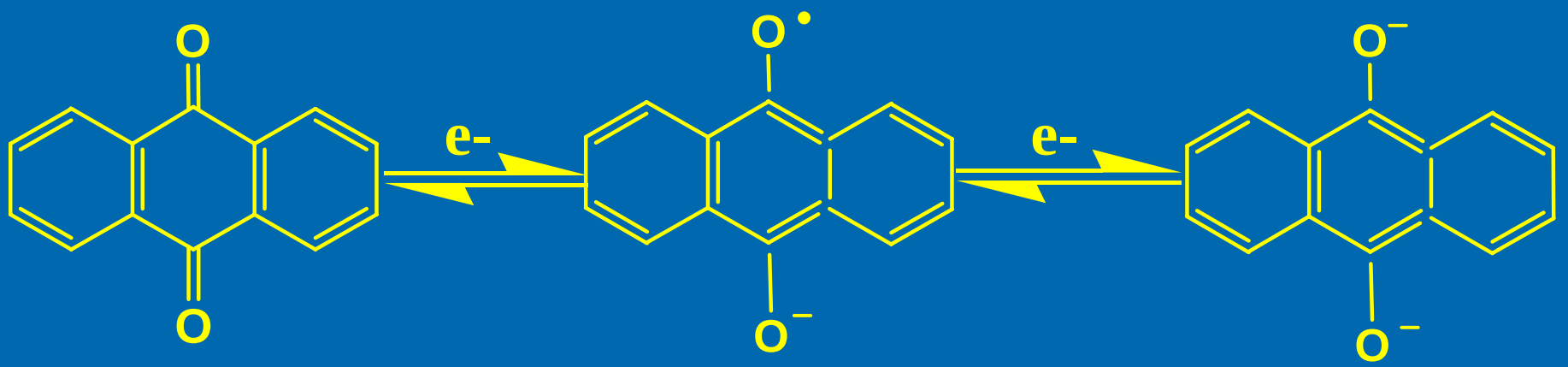
3.1 The Aims of Using Additives in Cooking

- accelerating the delignification rate
- increasing the delignification selectivity
- increasing pulp yield
- improving pulp properties
- eliminating or reducing air pollution

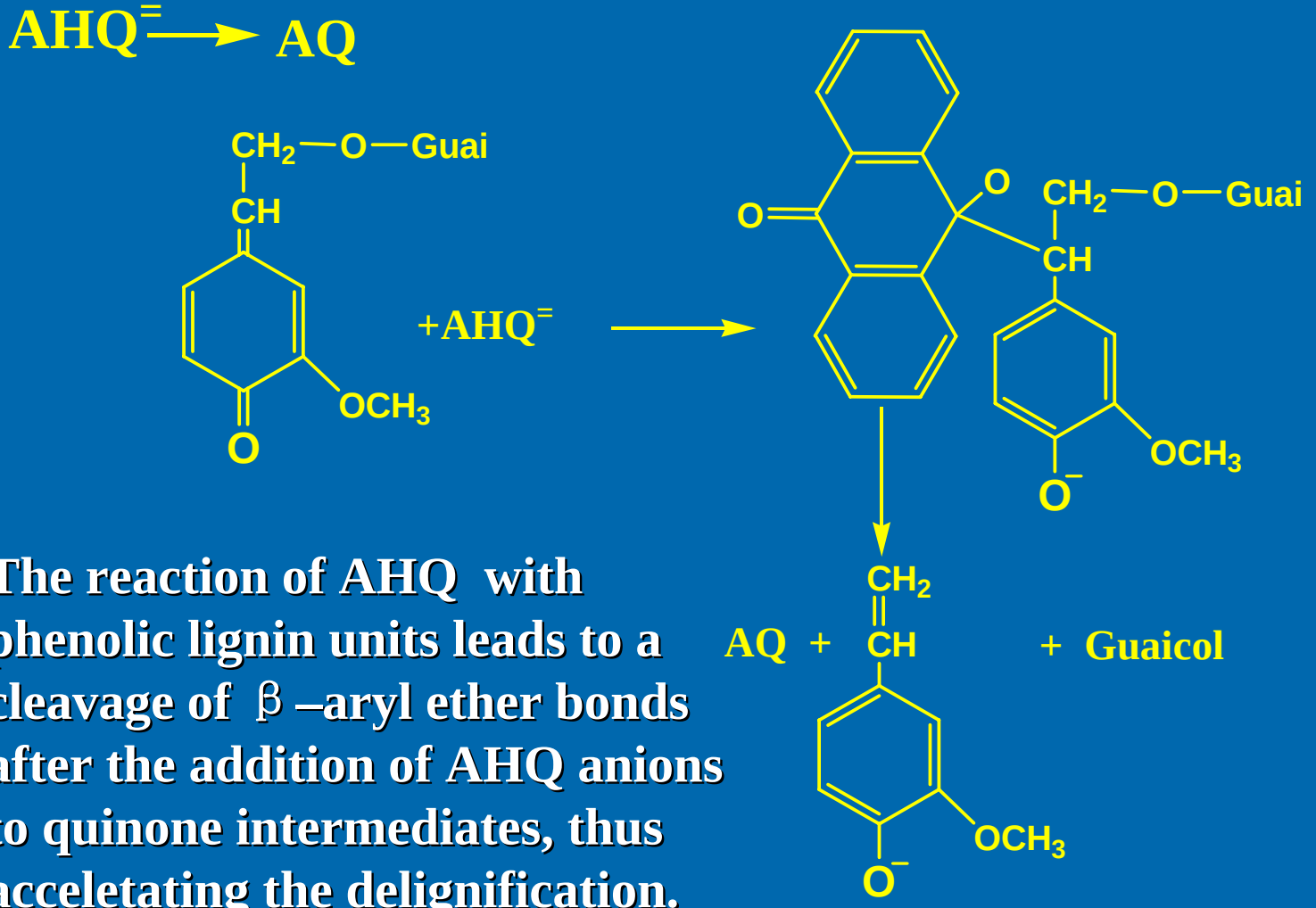
3.2 Adding anthraquinone (AQ) or its derivatives

(1) Electrochemical reduction in anthraquinone pulping

AQ $\longrightarrow$ **AHQ** $^{=}$ **anthrahydroquinone anion , very soluble**

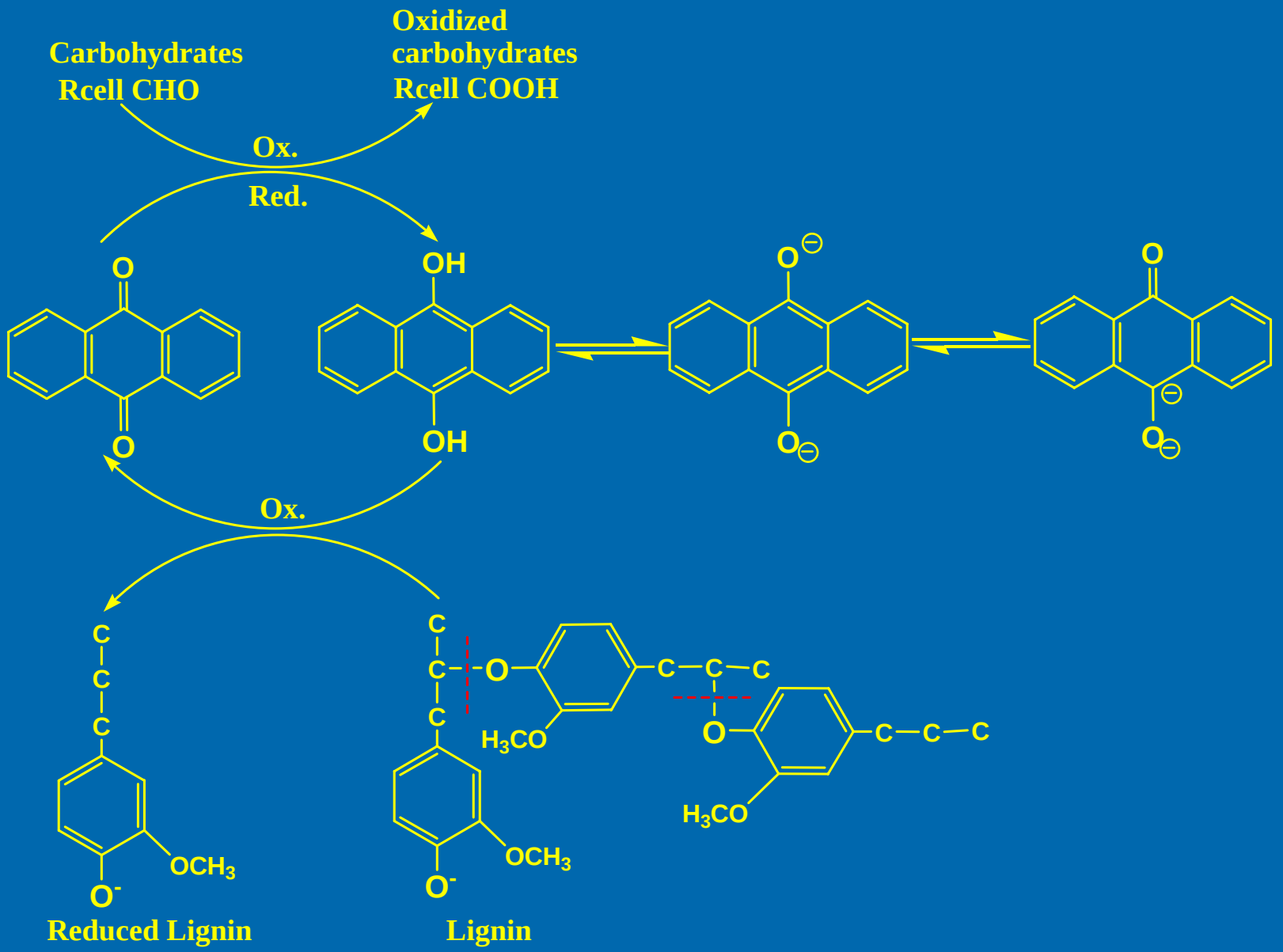


(2) Oxidation process in anthraquinone pulping



The reaction of AHQ with phenolic lignin units leads to a cleavage of β –aryl ether bonds after the addition of AHQ anions to quinone intermediates, thus acceletating the delignification.

(3) Redoxylic action of anthraquinone



AHQ acts the function as Na_2S

$AHQ^{=} \longrightarrow AQ \quad SH^{-} \longrightarrow S^{\circ}$

SAQ—Soluble anthraquinone

THAQ—Tetrahydroanthraquinone

DDA—Dihydrodihydroxylanthracene

DHAQ—Dihydro anthraquinone

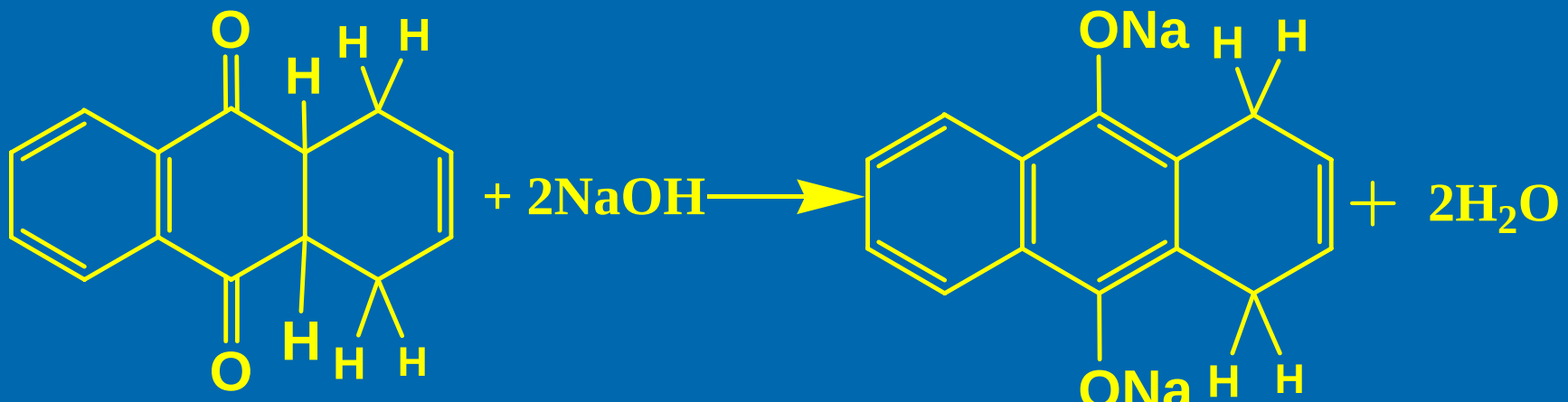
- **Improved selectivity of Pulp**
  - **Minimum cellulose loss**
  - **Maximum lignin removal**

Oxidative stabilization of reducing end-groups against the endwise peeling reaction

- **For lower kappa number**
  - **Same yield**
  - **Same black liquor solids/ton pulp**

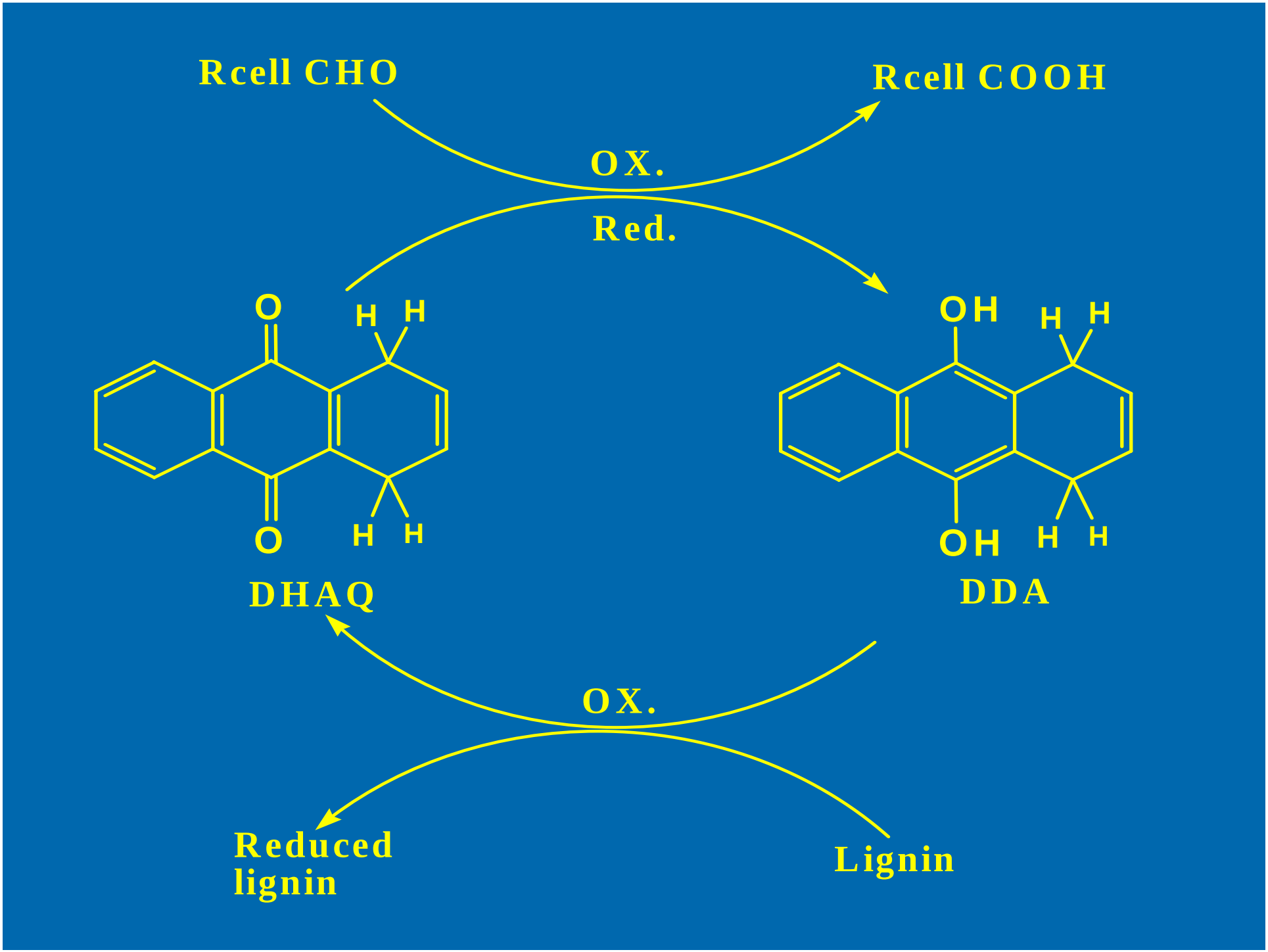
(4) Adding THAQ

THAQ can dissolved in alkaline solution which is favorable for even cooking



THAQ

Na_2DDA

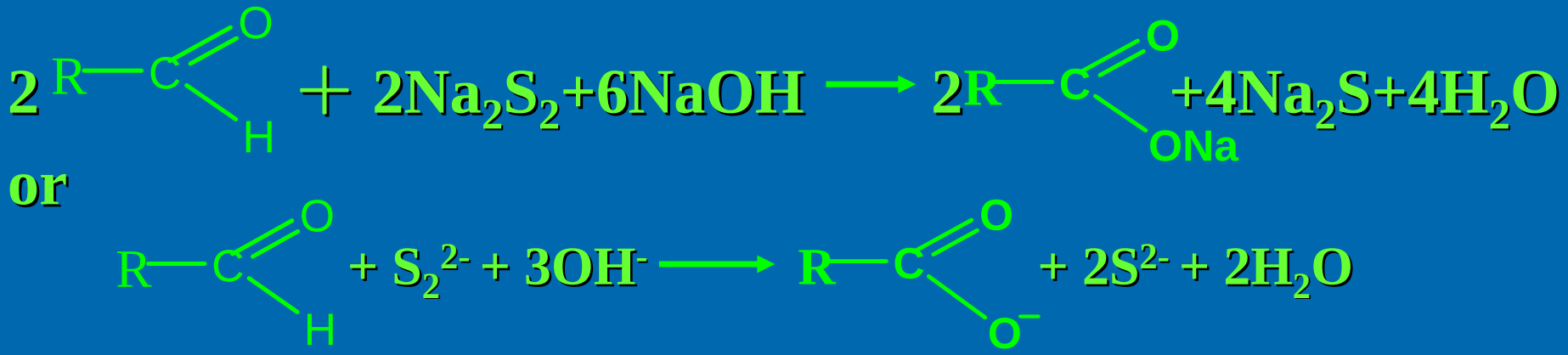

Rcell CHO
Rcell COOH
OX.
Red.
O
H H
O
H H
DHAQ
OH
H H
OH
H H
DDA
OX.
Reduced lignin
Lignin

3.3 Adding polysulfide

PS—inorganic oxidizing agent

1) PS Reactions in Pulping

- **Stabilization of carbohydrates—Prevents peeling reaction**



or

- **Thermal decomposition (>120~130℃)**

$$4Na_2S_2 + 6NaOH \longrightarrow 6Na_2S + Na_2S_2O_3 + 3H_2O$$

2) Production of PS Liquor

$$4Na_2S + O_2 + 2H_2O \longrightarrow 2Na_2S_2 + 4NaOH$$

Side Reaction

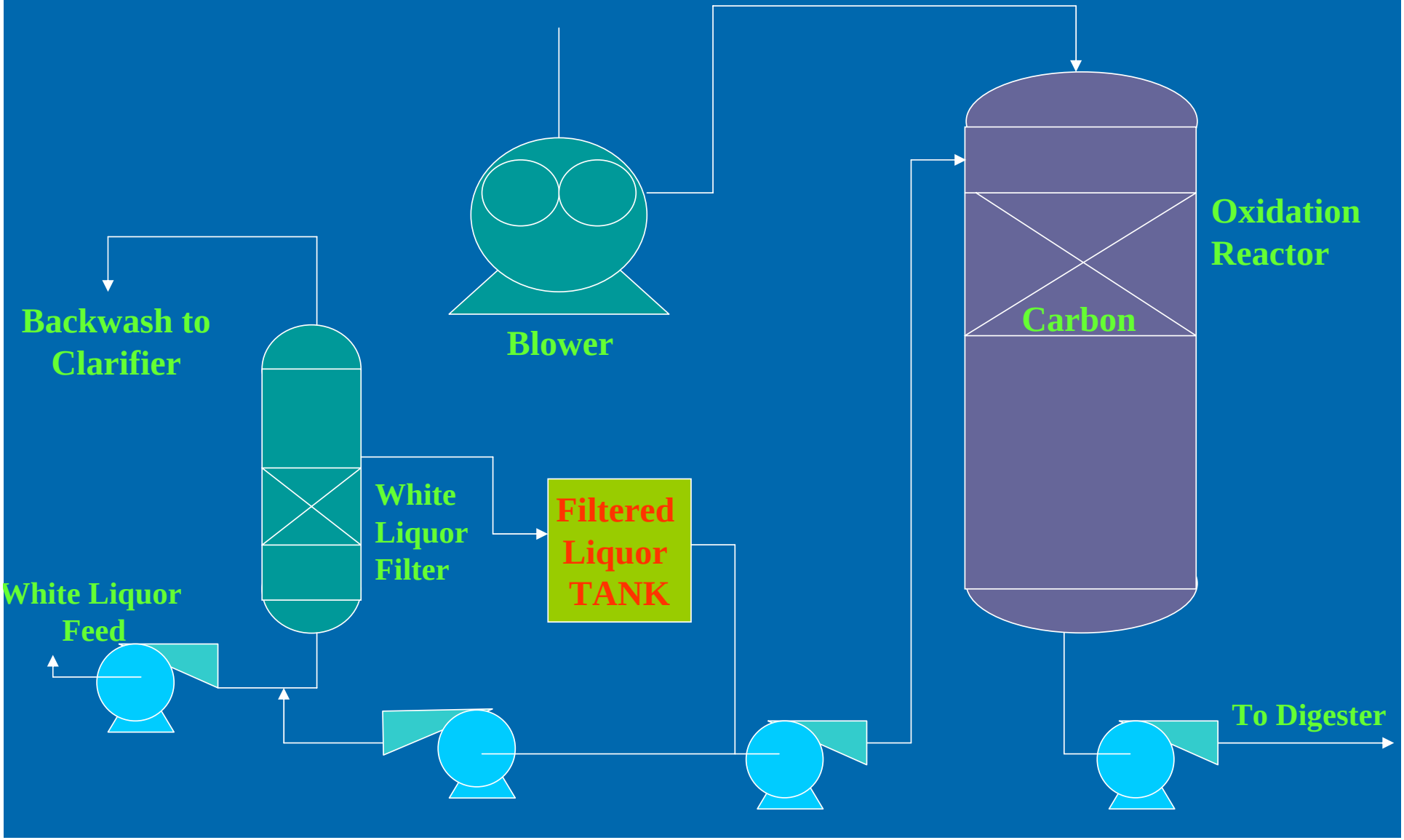
$$2Na_2S + 2O_2 + H_2O \longrightarrow Na_2S_2O_3 + 2NaOH$$

Basic process elements

Filter—— for preparation of clean white liquor

Reactor—— for oxidation of sulfide to polysulfide

Process for Generation of Polysulfide Liquor (Orange Liquor)



Liquor Quality		White Liquor Feed	Orange Liquor Product
NaOH	g/L	72	89
Na_2S	g/L	34	13
AA	g/L	106	103
EA	g/L	89	96
Sulfidity	%	32	12
Polysulfide	S g/L	0	7.5

3）Polysulfide Corrosion

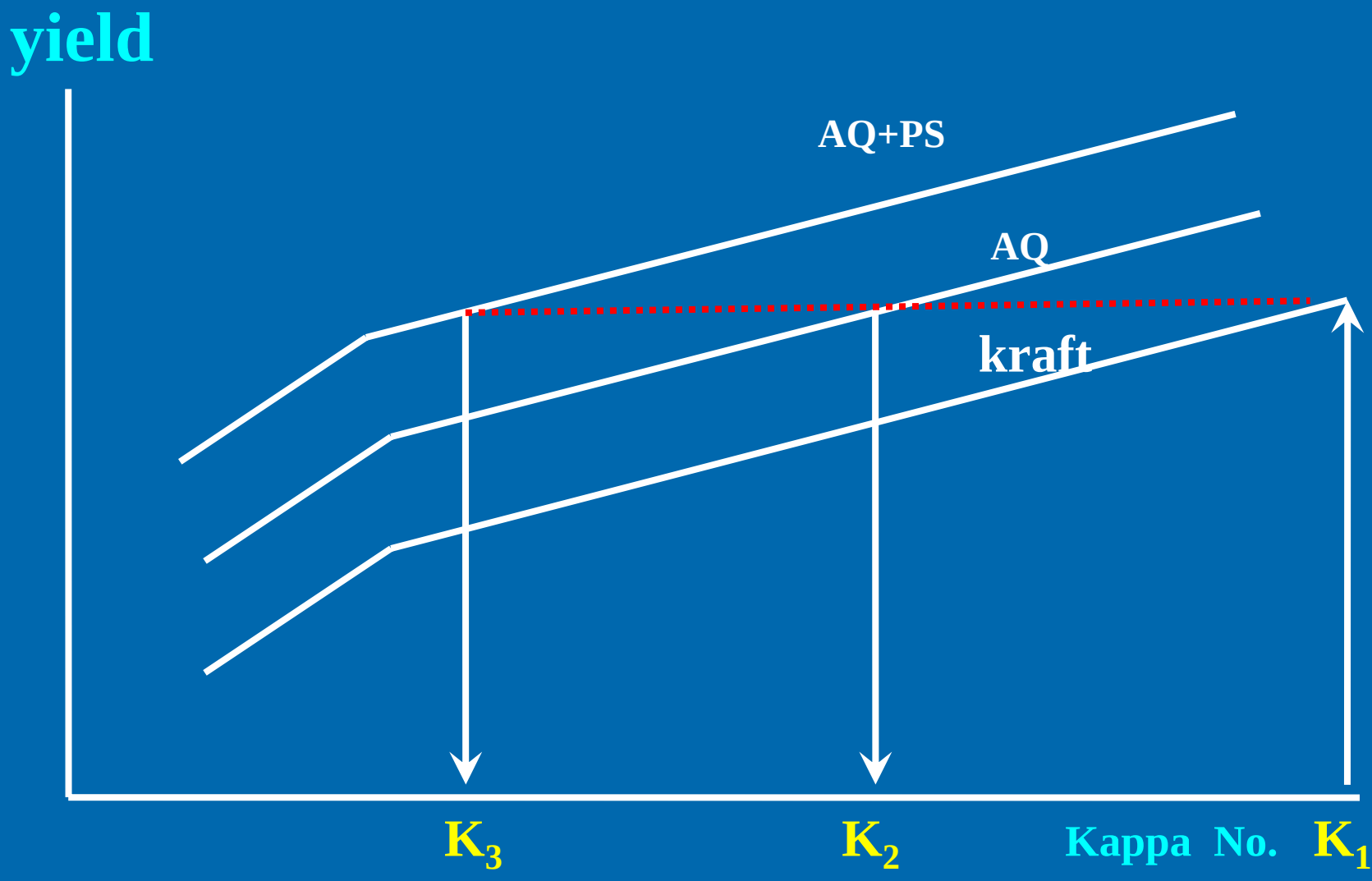
- PS has sharp corrosion peak @1g/L
- PS pulping liquor @5～8 g/L－Highly passivating
- Operating mills report no corrosion problems
- No PS downstream of digester

Accelerated Lab Corrosion Rates

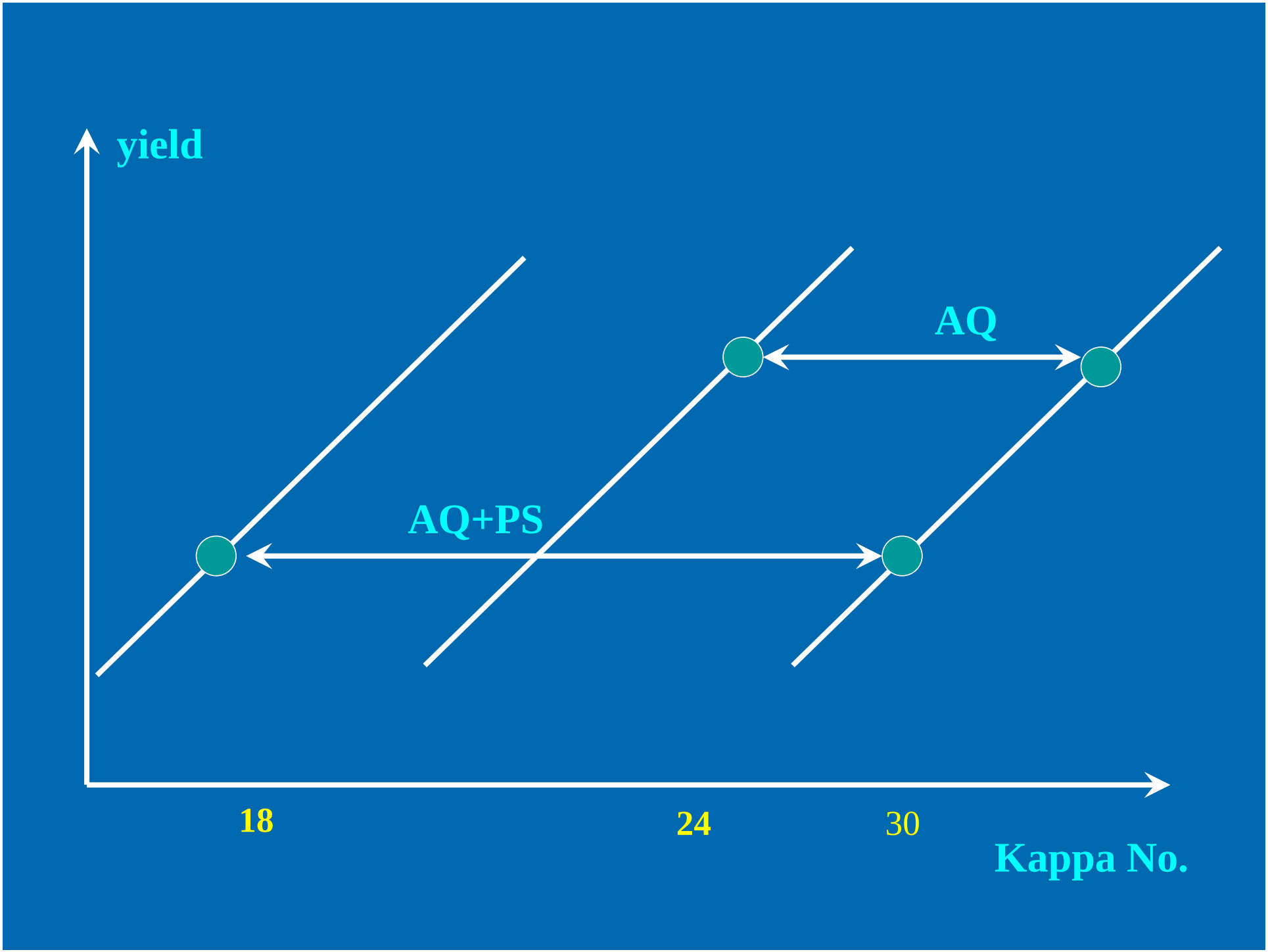
Liquor	Corrosion rate（in/yr）
White Liquor	2。60（6.6mm/y）
	2。11（5.4mm/y）
PS Liquor	003（0.076mm/y）
	005（0.13mm/y）

Batch Digester Corrosion Rates（softwood，hardwood）

AQ－kraft	0.13 in/yr（0.33mm/y）
AQ/PS－kraft	0.006 in/yr（0.15mm/y）

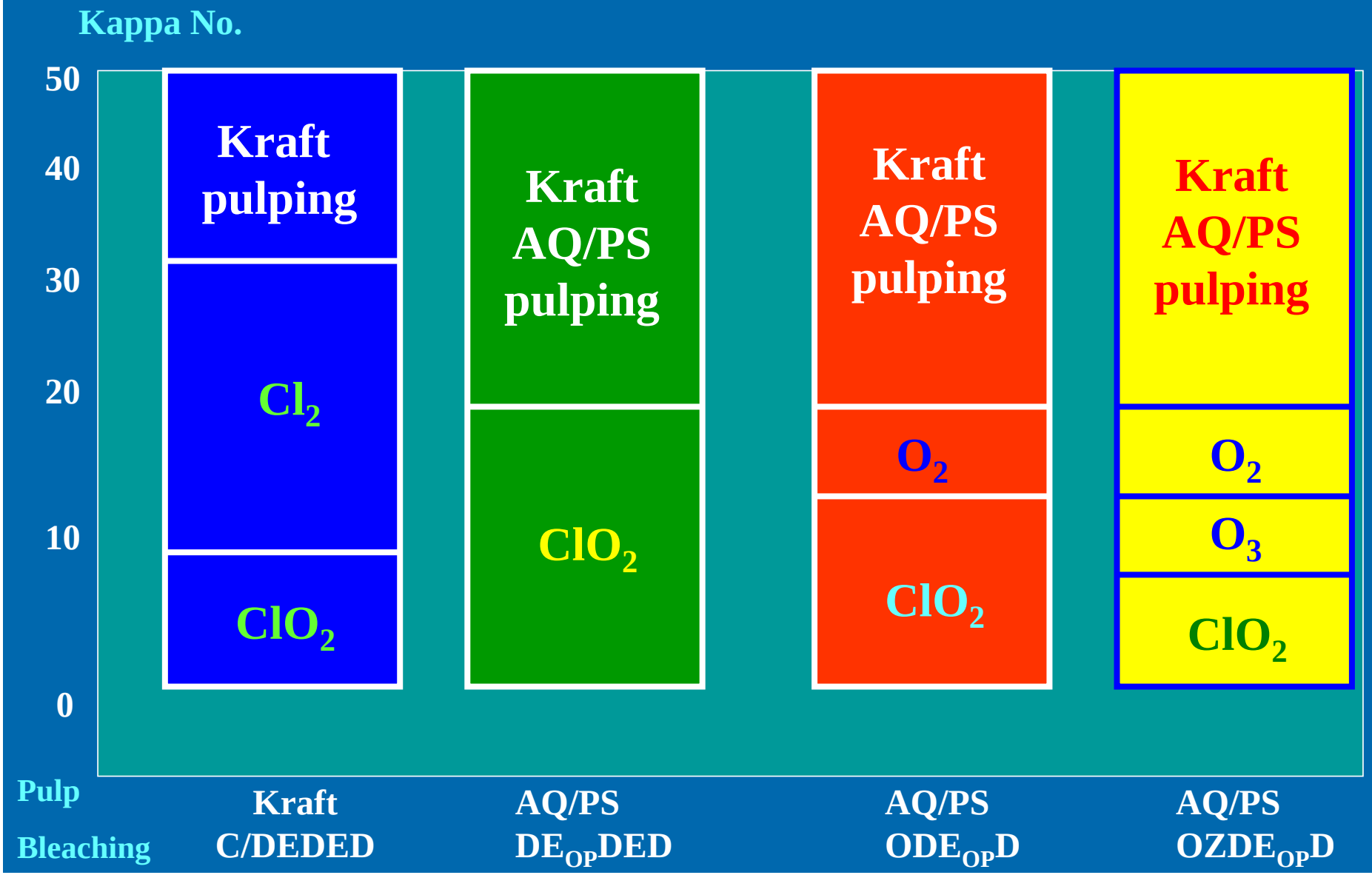


Softwood Extended Delignification (Recovery limited mill)

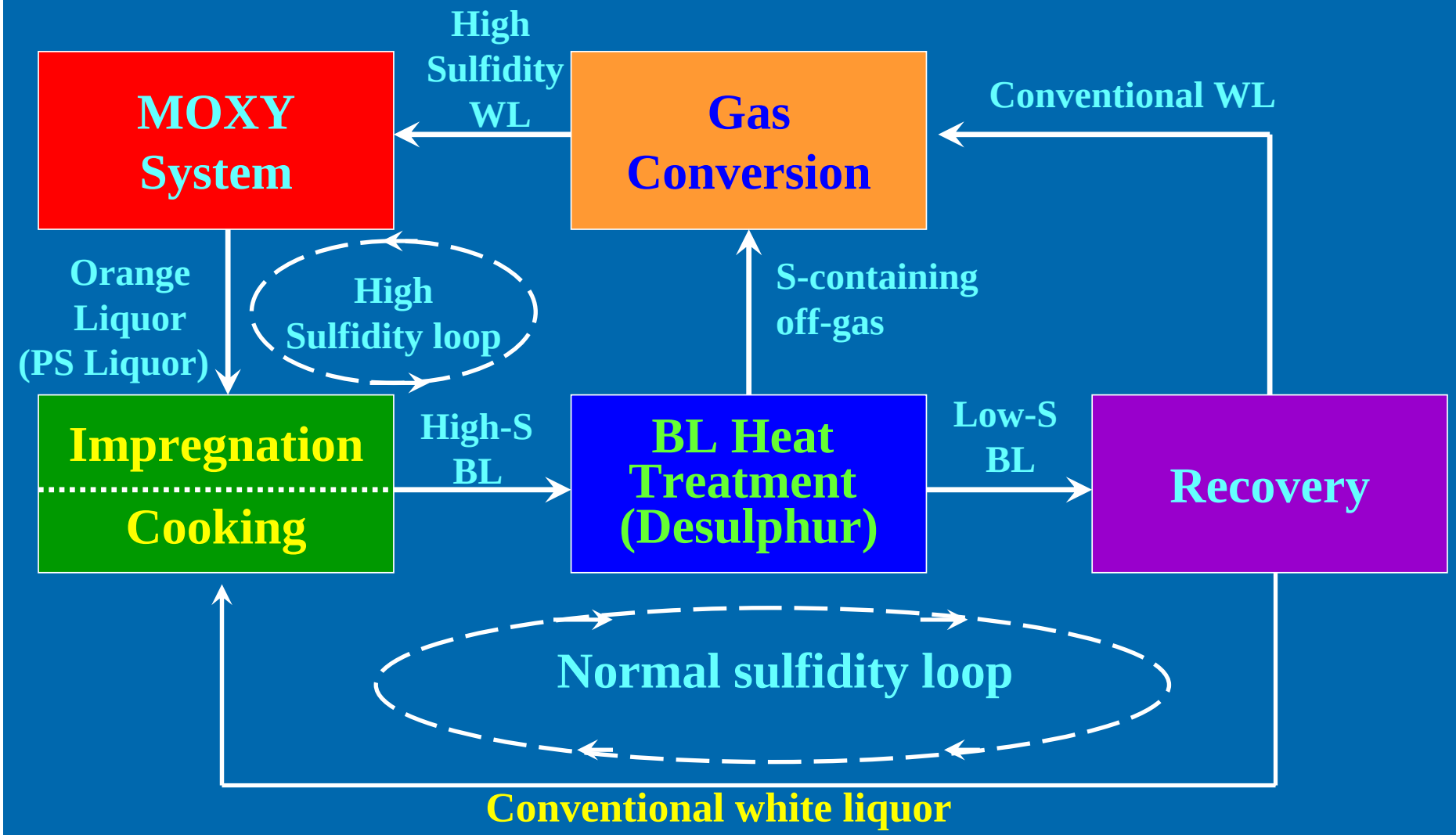

yield
AQ
AQ+PS
18
24
30
Kappa No.

- White liquor TSS（Total suspended solids）－low uniform level
  - － Minimize Filter washing
  - － Maximize Catalyst Life
  - － Low operating cost for PS system
- White liquor sulfidity
  - － Uniformly high level to maximize PS
- Maximize ％ PS on wood
  - － To maximize yield potential at given kappa No.
- Uniform chip thickness
  - － To maximize penetration of AQ and PS
- Penetration of AQ/PS liquor at<130℃
  - － To maximize carbohydrate stabilization before reaching cooking temperature

4）Effect of pulping process options on bleaching chemical requirements for low AOX



Polysulfide Pulping System with Desulphur™
AHLSTROM KAMYR



3.4 Adding sodium borohydride

$NaBH_4$ — inorganic reducing agent

$$4RCHO + NaBH_4 + NaOH + H_2O \rightarrow 4RCH_2OH + NaBO3$$

borate

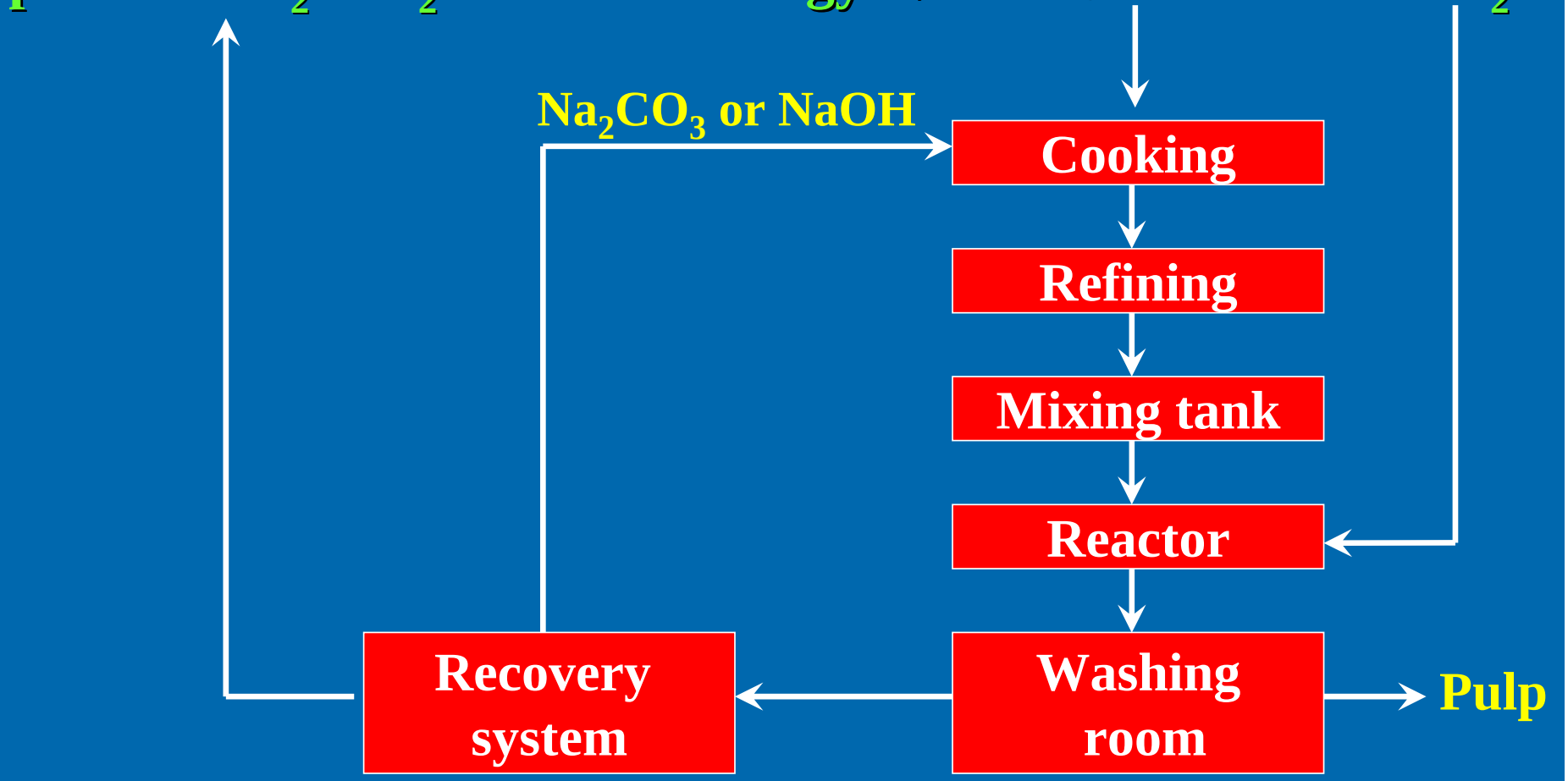
increasing pulp yield up to 6%

In hot （135℃） alkaline liquor

$$NaBH_4 + 2NaOH + H_2O \rightarrow 4H_2 + NaBO_3$$

3.5 Soda－Oxygen pulping

plant + CO_2 + H_2O + Solar energy →Fibrous materials + O_2



Advantages

a）Sulfur－free， no sulfur pollution

b）Meeting the regularity of ecologic circulation

c）Higher yield （compared with soda process）

Main problem

Low solubility of oxygen in alkaline liquor