FIRST EXTRACTION STAGE
DEDED

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OUTLINE

- Extraction Stage Basics
- E Stage
- EO Stage
- EOP Stage

PURPOSE OF THE FIRST EXTRACTION STAGE

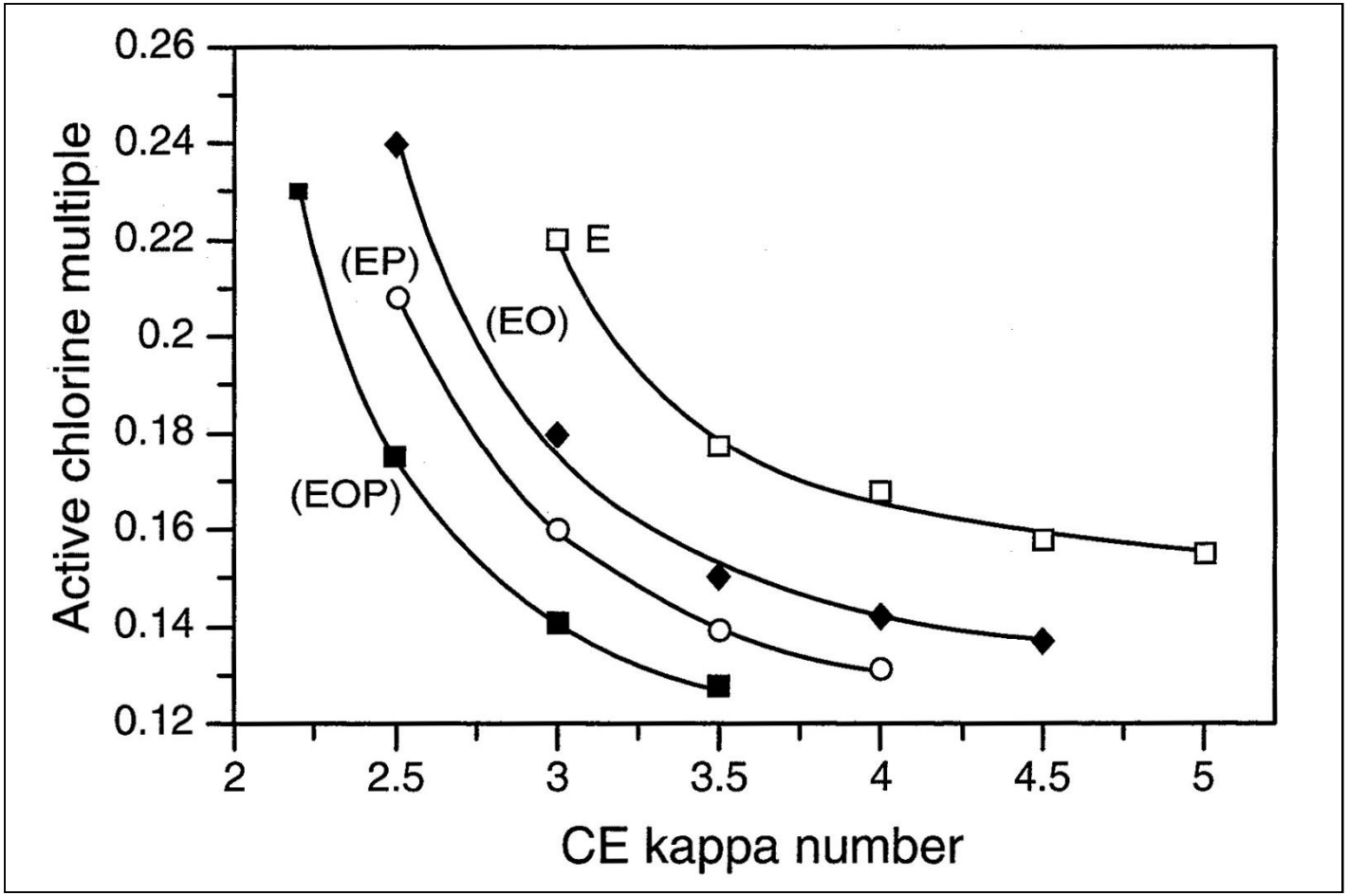
- Solubilize chlorinated and oxidized lignin and other colored components (and remove by washing)

- Additional delignification/brightening if reinforced with O_2 and/or H_2O_2

EVOLUTION OF THE EXTRACTION STAGE IN N. AMERICA

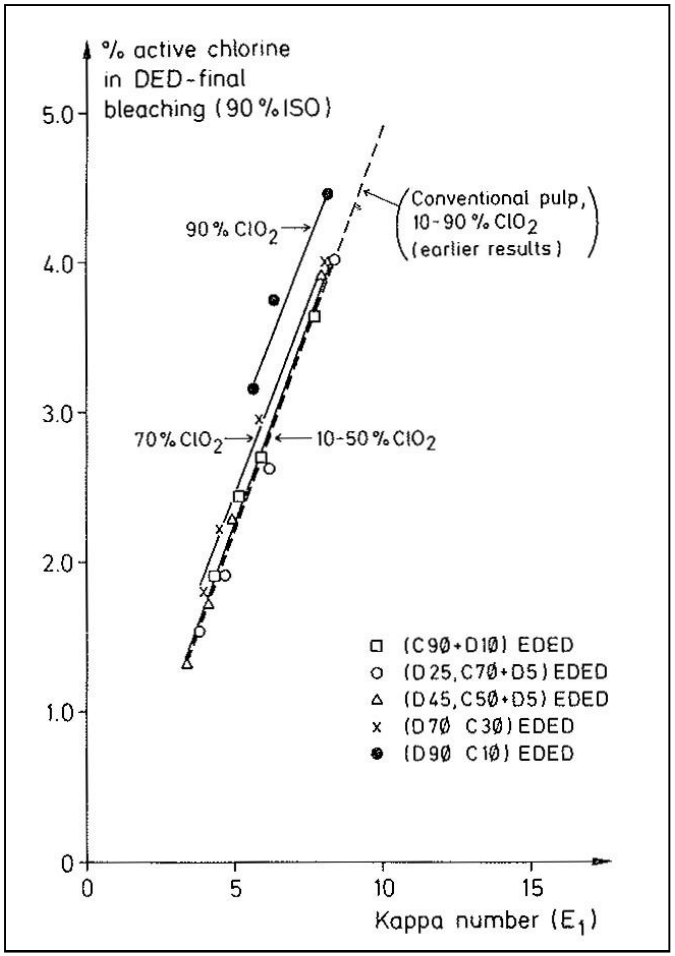
- E (1900's to current) → EO (1980's to current) → EOP (1990's to current)
- Newer options include pressurized stages:
  - (OO), (OP), (PO)
  - Few installations in N. America
- EOP is most common
  - But there are still E, EO, and EP stages in operation

HIERARCHY OF DELIGNIFICATION EFFICIENCY IN ALKALINE EXTRACTION

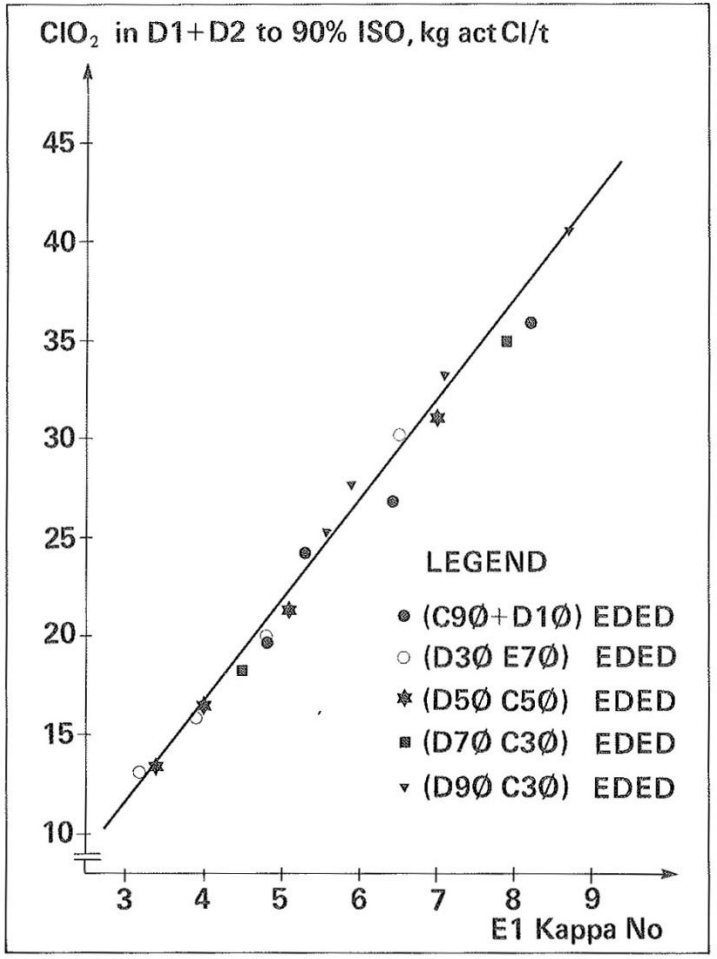


Reference: Pulp Bleaching – Principles & Practice, edited by Dence and Reeve
Original work by Carmichael *et al*, 1986 TAPPI Journal

E1 KAPPA IS A GOOD INDICATOR OF ClO_2 DEMAND IN FOLLOWING STAGES



Reference: Germgård, "Optimized Prebleaching of Softwood Kraft Pulps of Low Kappa Numbers," Proceedings of 1984 TAPPI Pulping Conference

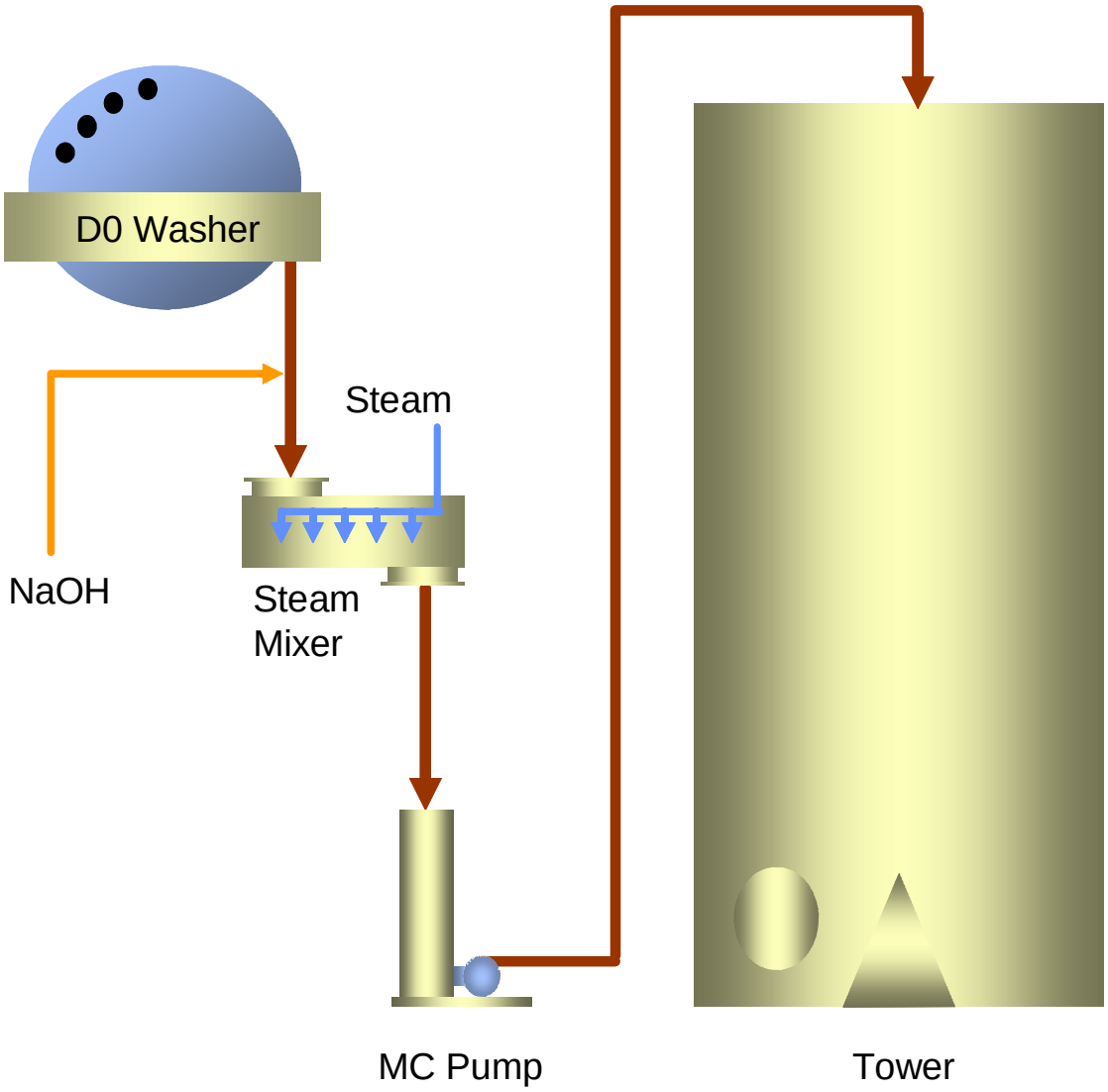


Reference: Axegard, "Effect of ClO2 Substitution on Bleaching Efficiency and Formation of Organically Bound Chlorine," Proceedings of 1984 TAPPI Pulping Conference

OUTLINE

- Extraction Stage Basics
- E Stage
- EO Stage
- EOP Stage

CHEMICAL ADDITION IN E CONFIGURATION



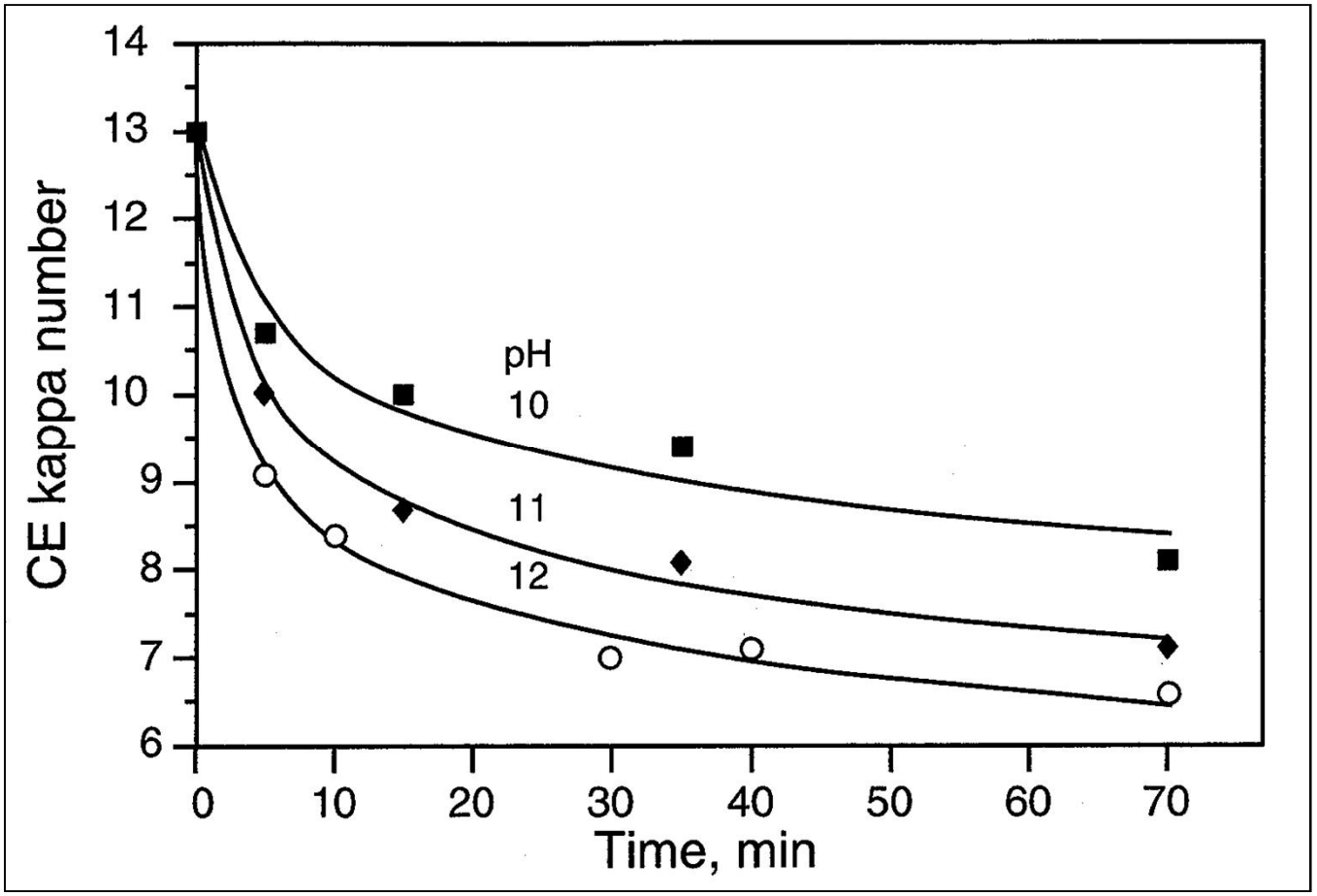
REACTIONS IN THE EXTRACTION STAGE

- Solubilization and removal of the major portion of chlorinated lignin through reaction with alkali
- Saponification of fatty acids and resin acids present in the pulp
- Removal of the hemicellulose from the fiber
- Degradation of the chain length of the polysaccharin content of the fiber

PROCESS VARIABLES AFFECTING EXTRACTION STAGE PERFORMANCE

- Caustic application (pH)
- Temperature
- Time
- Consistency

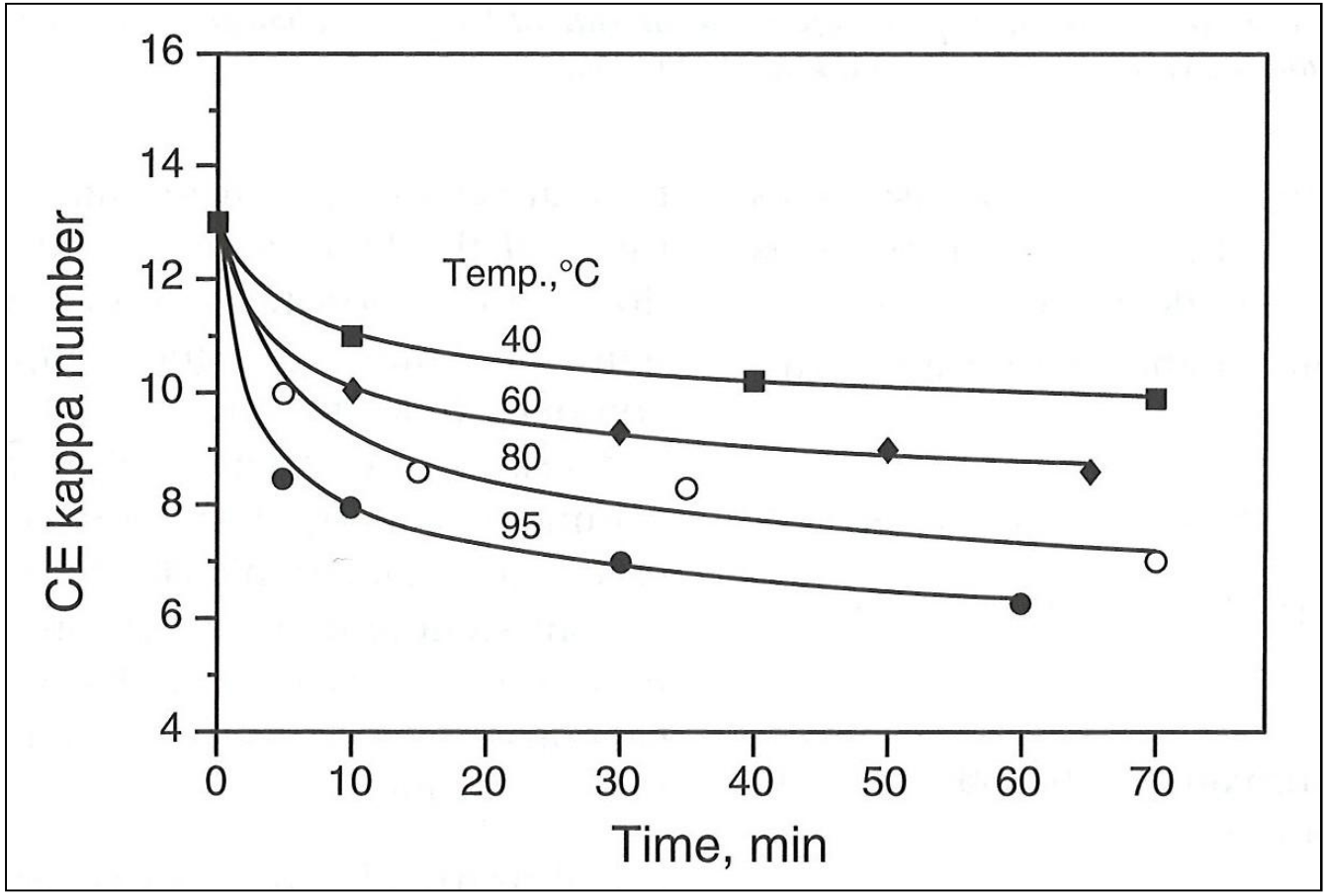
EFFECT OF pH ON ALKALINE EXTRACTION



Chlorinated Softwood Kraft Pulp
Reference: *Pulp Bleaching - Principles and Practices*, Dence & Reeve
Original Work by Axegård, 1979 Svensk Papperstidn

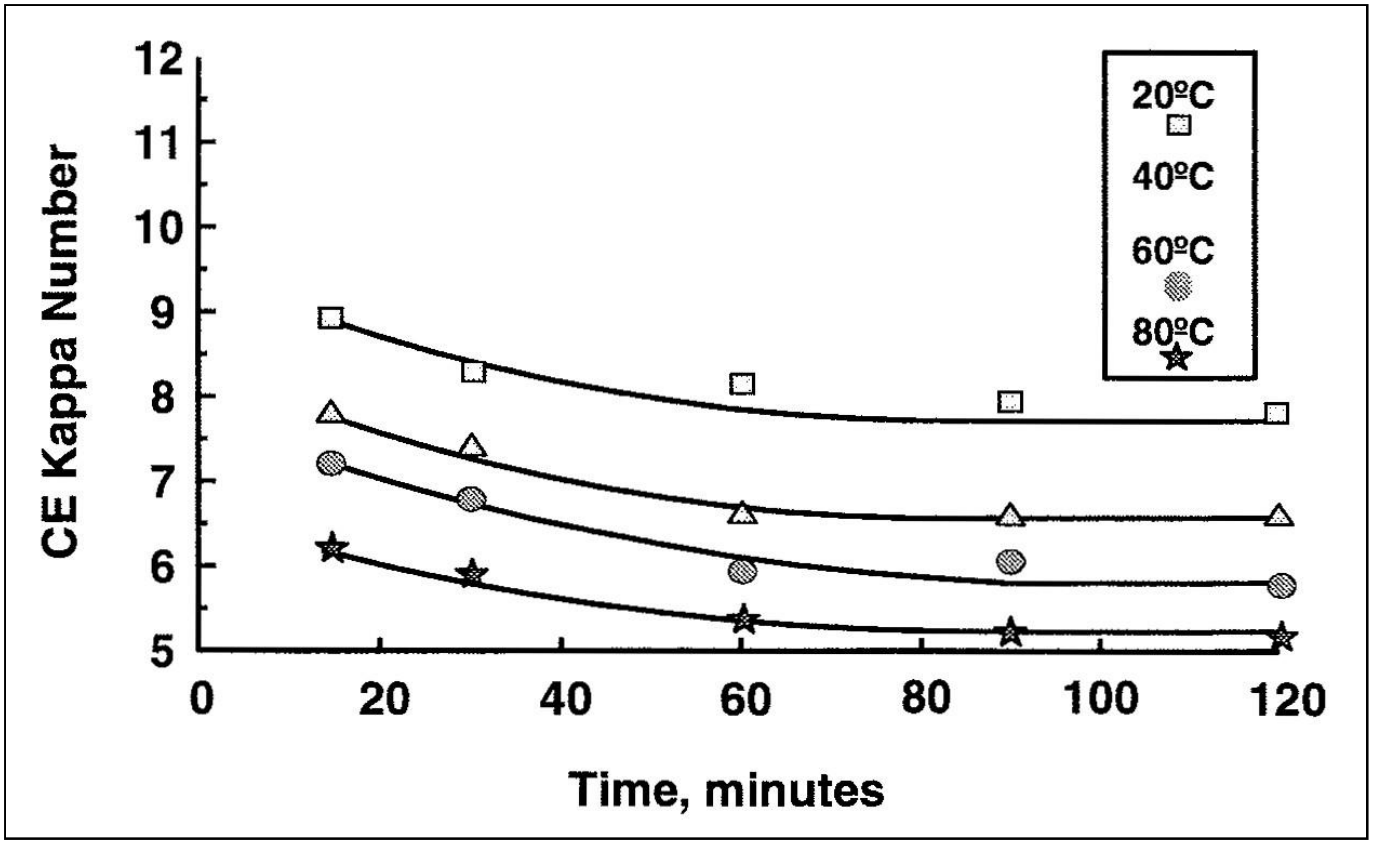
Note: All pH values are measured on a cooled sample at 25 C

EFFECT OF TEMPERATURE ON REACTION RATE DURING ALKALINE EXTRACTION



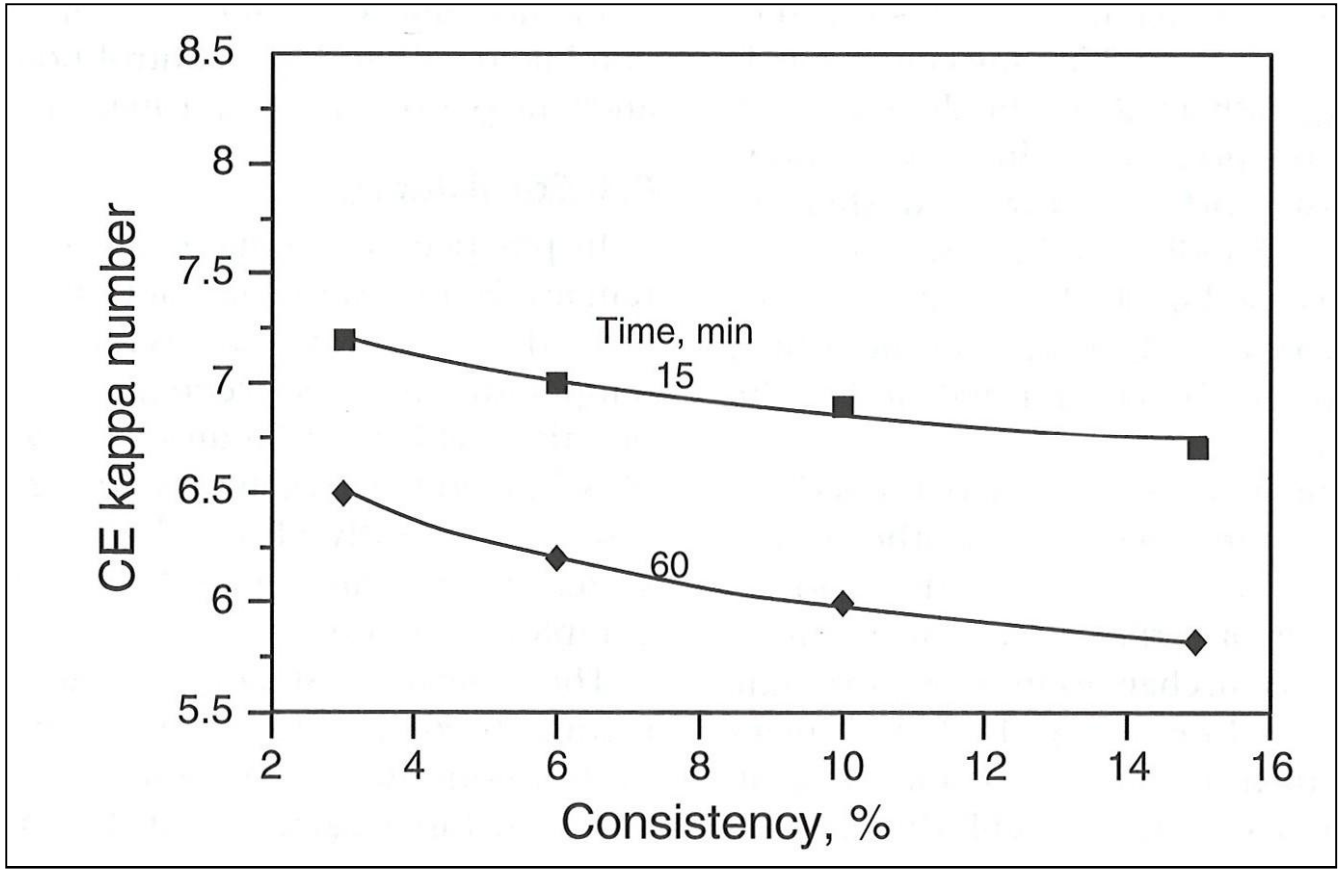
Chlorinated Softwood Kraft Pulp
Reference: *Pulp Bleaching - Principles and Practices*, Dence & Reeve
Original Work by Axegård, 1979 Svensk Papperstidn

EFFECT OF TIME AND TEMPERATURE ON ALKALINE EXTRACTION



Reference: Berry, “Extraction and Peroxide,” 2001 TAPPI Pulp Bleaching Course Notes

EFFECT OF CONSISTENCY AND TIME ON ALKALINE EXTRACTION



Softwood Kraft Pulp
Reference: *Pulp Bleaching - Principles and Practices*, Dence & Reeve
Original Work by van Lierop *et al*, 1986 Pulp and Paper Canada

CONDITIONS FOR ALKALINE EXTRACTION

- Typical time = 60 – 90 minutes
- Typical temperature = 75 - 85° C
- Typical pH = 10 – 10.5 (@25° C)
- Typical consistency = 10 – 12% AD

OUTLINE

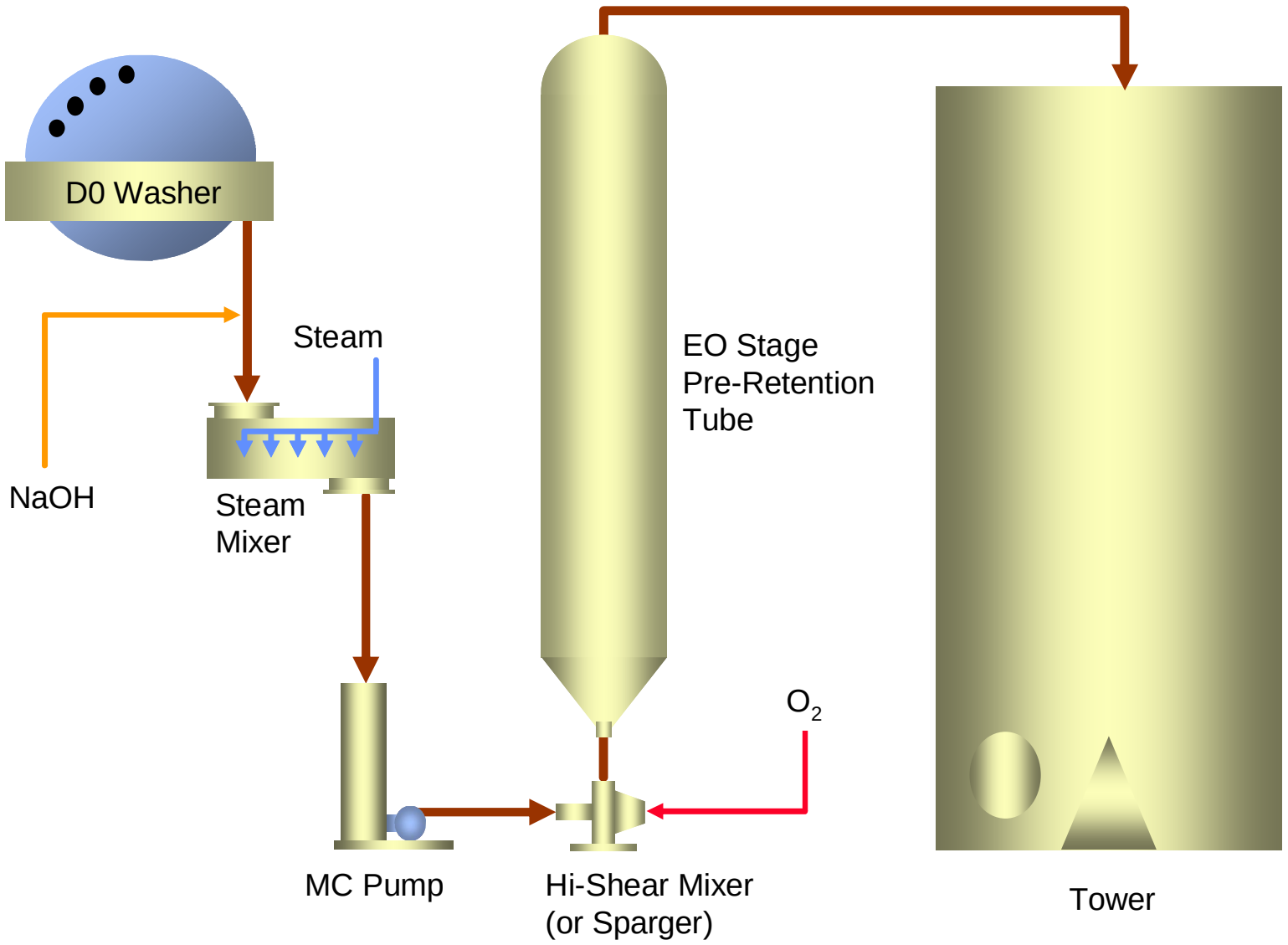
- Extraction Stage Basics
- E Stage
- EO Stage
- EOP Stage

REASONS FOR OXYGEN REINFORCEMENT

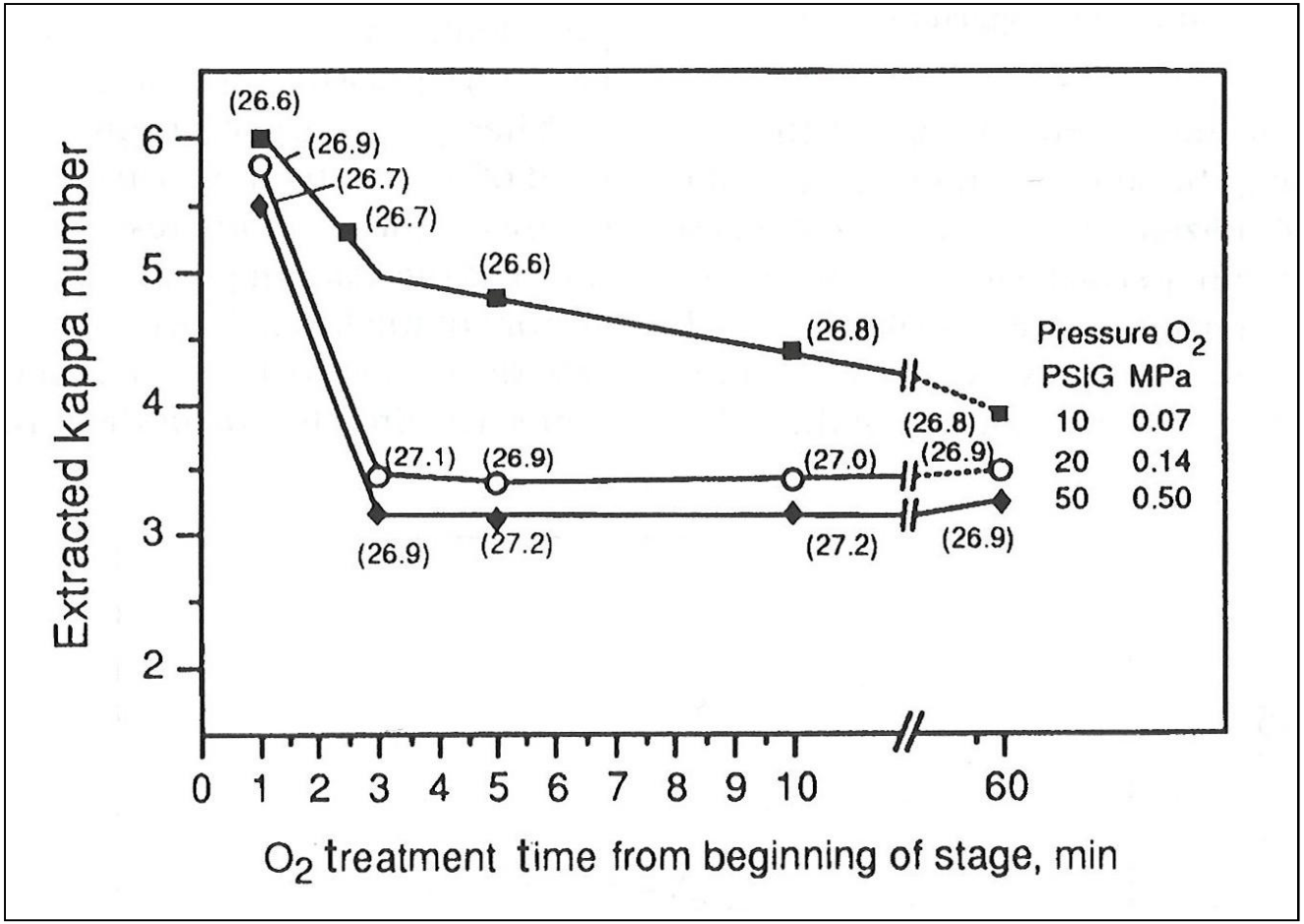
- Oxygen is inexpensive compared to other bleaching chemicals ⇨ Cost savings
  - Secondary reasons:
    - Environmental
    - Compensate for limited ClO_2 capacity
- Fairly easy and low capital upgrade
- Rule of thumb: 5 kg O_2 in Eo saves ~ 3 kg ClO_2 in D1*
  - BUT: Highly oxidized pulps are less responsive to O_2
  - “Leave something for the oxygen to work on”
- Most mills use oxygen reinforcement (with peroxide)

* Reference: *Pulp and Paper Manufacture, Volume 5 – Alkaline Pulping,* edited by Grace and Malcolm

CHEMICAL ADDITION IN EO CONFIGURATION



EFFECT OF PRESSURE AND TIME ON THE EO STAGE



Softwood Kraft Pulp
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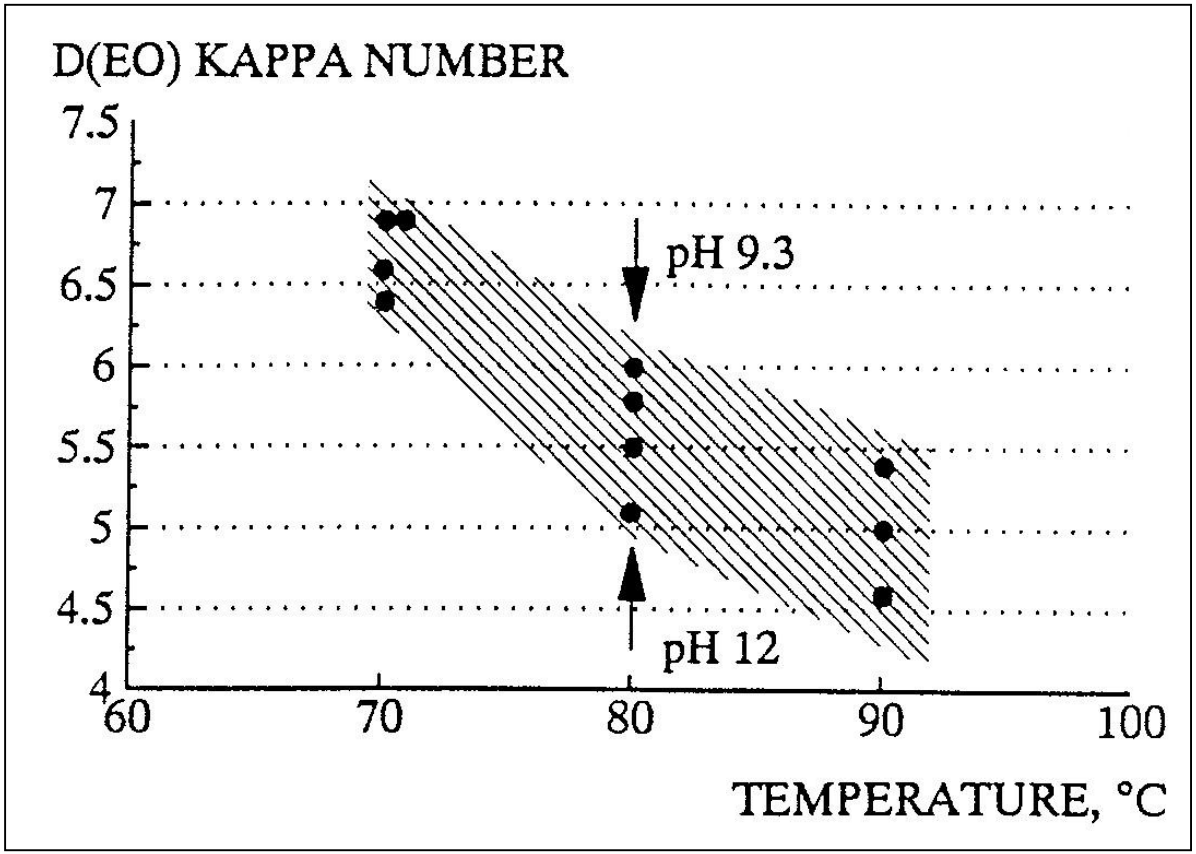
Original Work by van Lierop et al, Journal of Pulp & Paper Science, May 1986

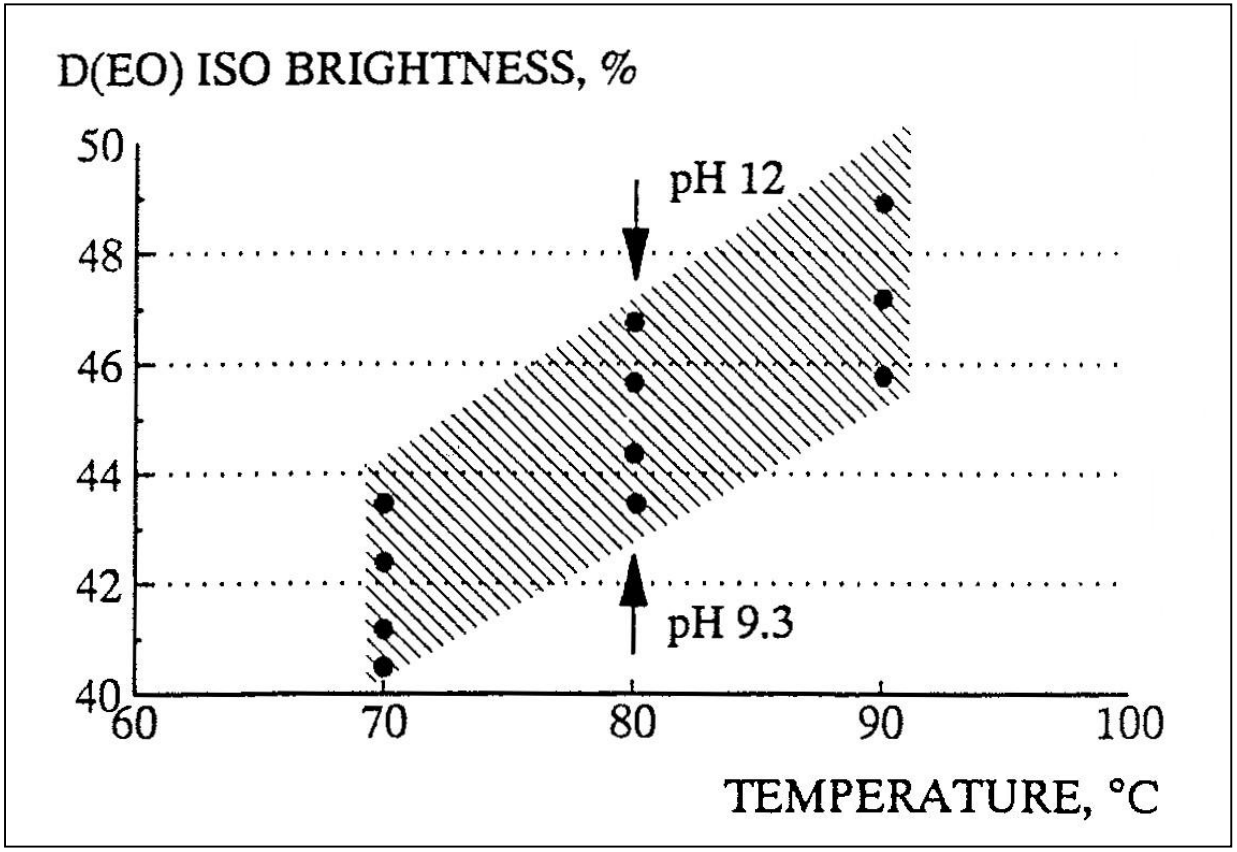
EFFECT OF pH AND TEMPERATURE IN EO STAGE



Note: All pH values are measured on a cooled sample at 25 C

ECF Southern Pine Kraft, Kappa # 24
Reference: Basta, *et al.*, "New and Improved Possibilities in D100 Bleaching," Proceedings of 1992 TAPPI Pulping Conference

EFFECT OF pH AND TEMPERATURE IN EO STAGE



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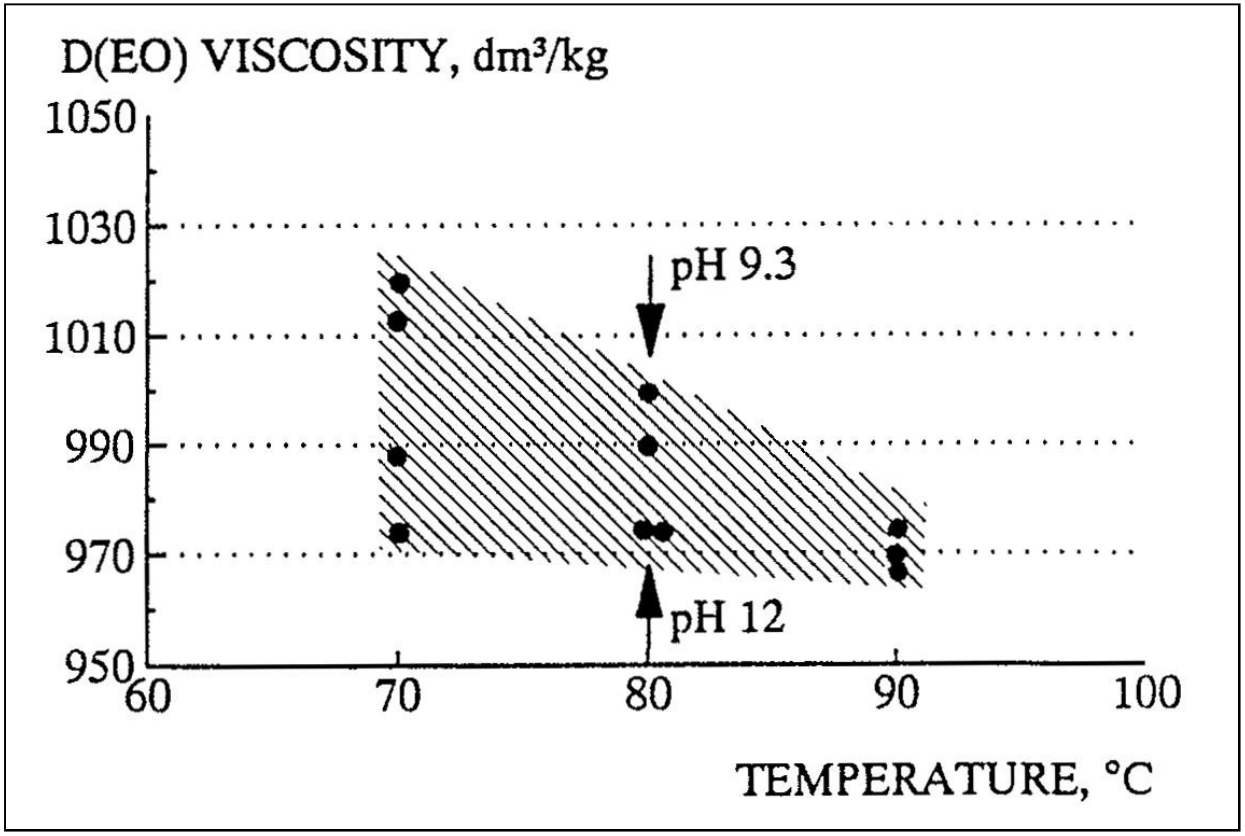
EFFECT OF pH AND TEMPERATURE IN EO STAGE



ECF Southern Pine Kraft, Kappa # 24
Reference: Basta, *et al.*, "New and Improved Possibilities in D100 Bleaching," Proceedings of 1992 TAPPI Pulping Conference

Note: All pH values are measured on a cooled sample at 25 C

CONDITIONS FOR OXYGEN REINFORCEMENT

- Typical O_2 charge = 5 kg/ADMT
- Minimum pressure of 140 kPa (20 psig) for 3 minutes
  - Upflow pre-retention tube (hydrostatic pressure only) is adequate
  - Pressurized tube can give better results (but must have proper safeguards – it's now a pressure vessel!)
- Hi-shear mixer
- Similar time, temperature, and consistency as for E stage

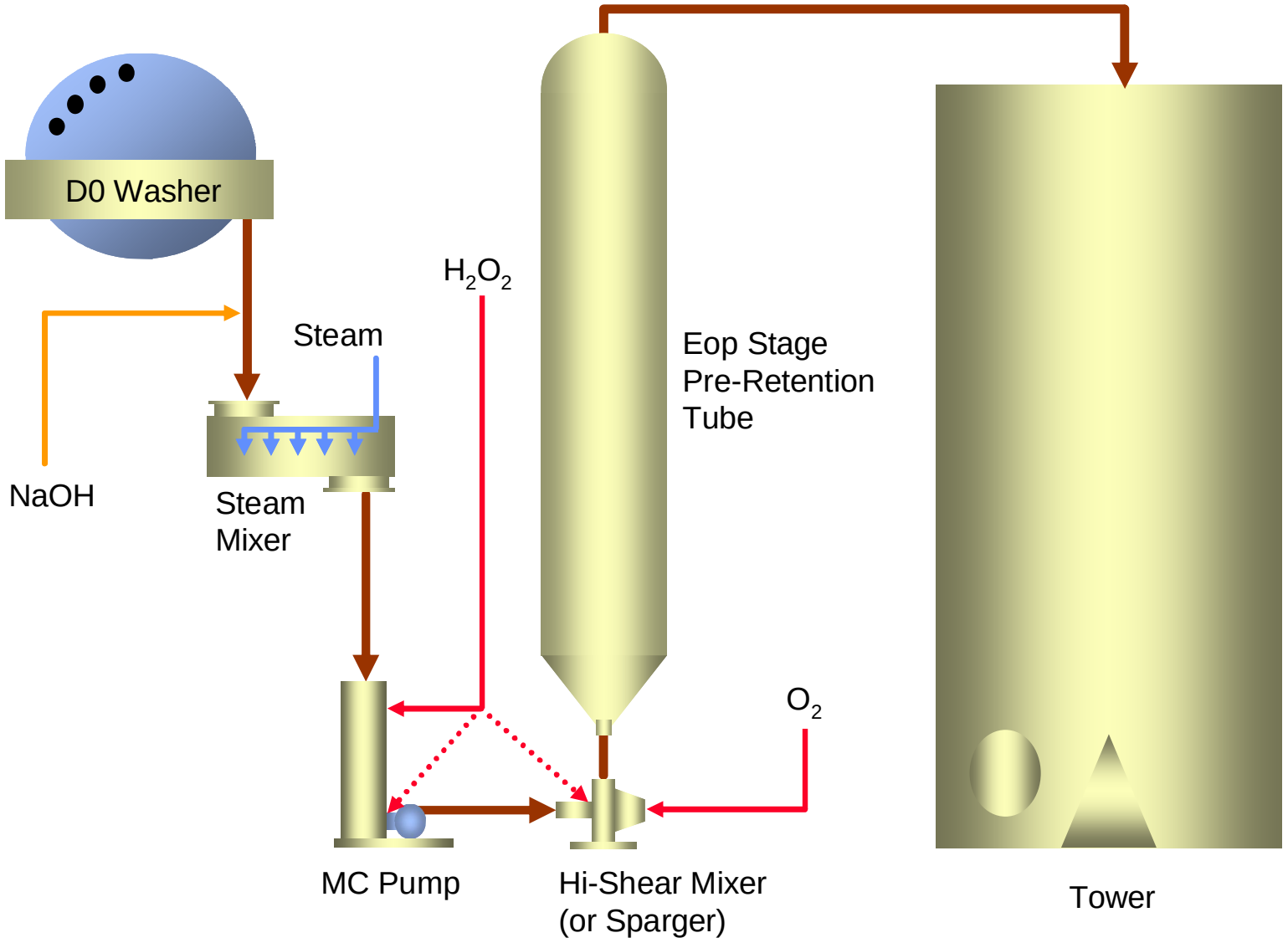
OUTLINE

- Extraction Stage Basics
- E Stage
- EO Stage
- EOP Stage

REASONS FOR PEROXIDE REINFORCEMENT

- Fairly easy and low capital upgrade
  - Cost savings
  - Environmental (AOX, effluent color, OX in pulp)
  - Compensate for limited ClO_2 capacity
- Rule of thumb: 1 kg H_2O_2 in Eop saves 1 – 1.5 kg ClO_2
  - Better results with SW compared to HW
  - BUT: diminishing returns with higher charges
  - BUT: Highly oxidized pulps are less responsive to H_2O_2
  - “Leave something for the peroxide to work on”
- Delignifies and brightens
- Most mills use peroxide reinforcement (with oxygen)

CHEMICAL ADDITION IN EOP CONFIGURATION



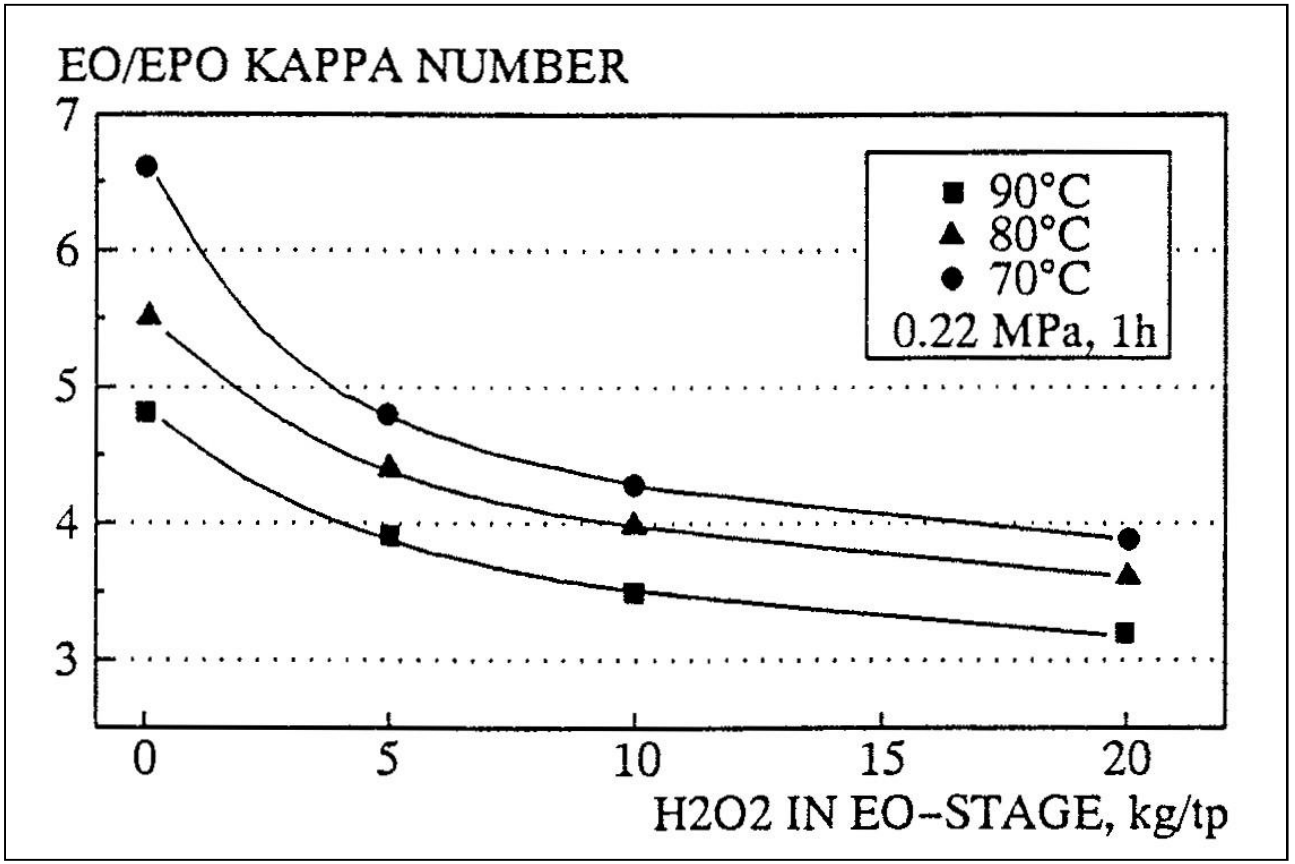
CHEMISTRY OF H_2O_2 BLEACHING

- H_2O_2 generally forms three intermediate reacting species:
  - Hydroxonium ion (HO+) under acidic conditions
  - Perhydroxl anion (HO_2-) under alkaline conditions
  - Hydroxyl radical (HO•) in presence of transition metals

EOP STAGE
IMPORTANT PARAMETERS

- H_2O_2 charge
- Terminal pH
- Residence time
- Temperature
- Pulp consistency
- Chemical mixing efficiency
- Pulp metal profile
- COD carryover from previous stage

EFFECT OF TEMPERATURE AND H_2O_2 CHARGE ON EOP STAGE



ECF Southern Pine Kraft Pulp, Kappa # 24, KF = 0.17
Reference: Basta, *et al.*, "New and Improved Possibilities in D100 Bleaching," Proceedings of 1992 TAPPI Pulping Conference

EOP STAGE OPERATING CONDITIONS
pH

- Optimum terminal pH generally 10.5 – 11.0 in EOP
- Positive effect in range of pH 10-12 on most pulp properties
- pH 12-14 results in H_2O_2 decomposition and negative effect on pulp properties

Note: All pH values are measured on a cooled sample at 25 C

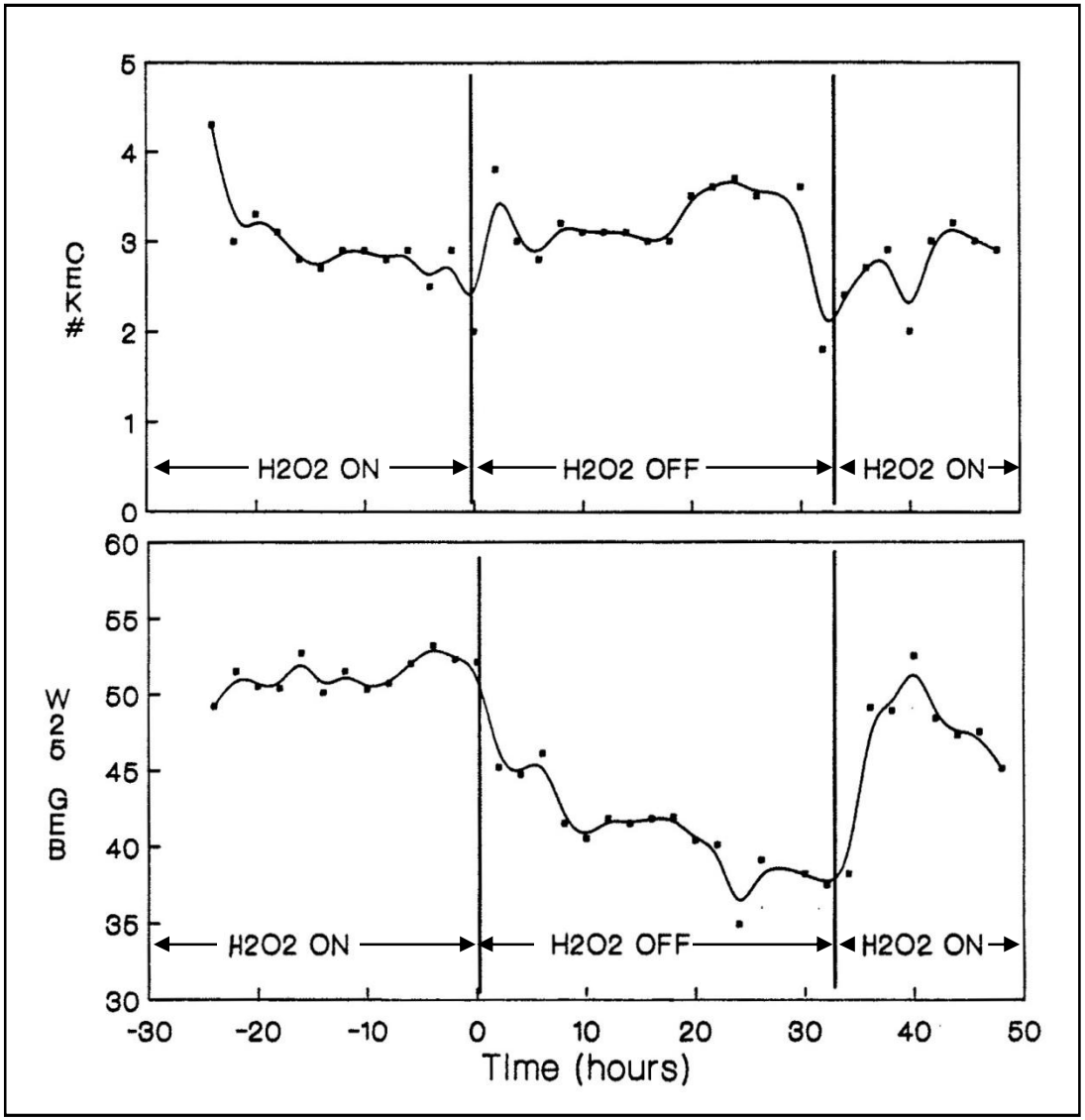
EOP STAGE OPERATING CONDITIONS
TIME

- Most EOP stages are approximately 60-90 minutes
- 90% H_2O_2 consumed within 10 minutes under mild conditions (60^o C, 0.2% H_2O_2)
- Usually no residual at end of EOP stage

METAL MANAGEMENT

- High content of alkaline metals (Mg, Ca) low concentration of transition metals (Mn, Fe, Cu) is desirable
- Low pH in the D0 stage will partially remove metals
- Chelants can be added to improve metal profile
- Normally in kraft process metal management is not a concern

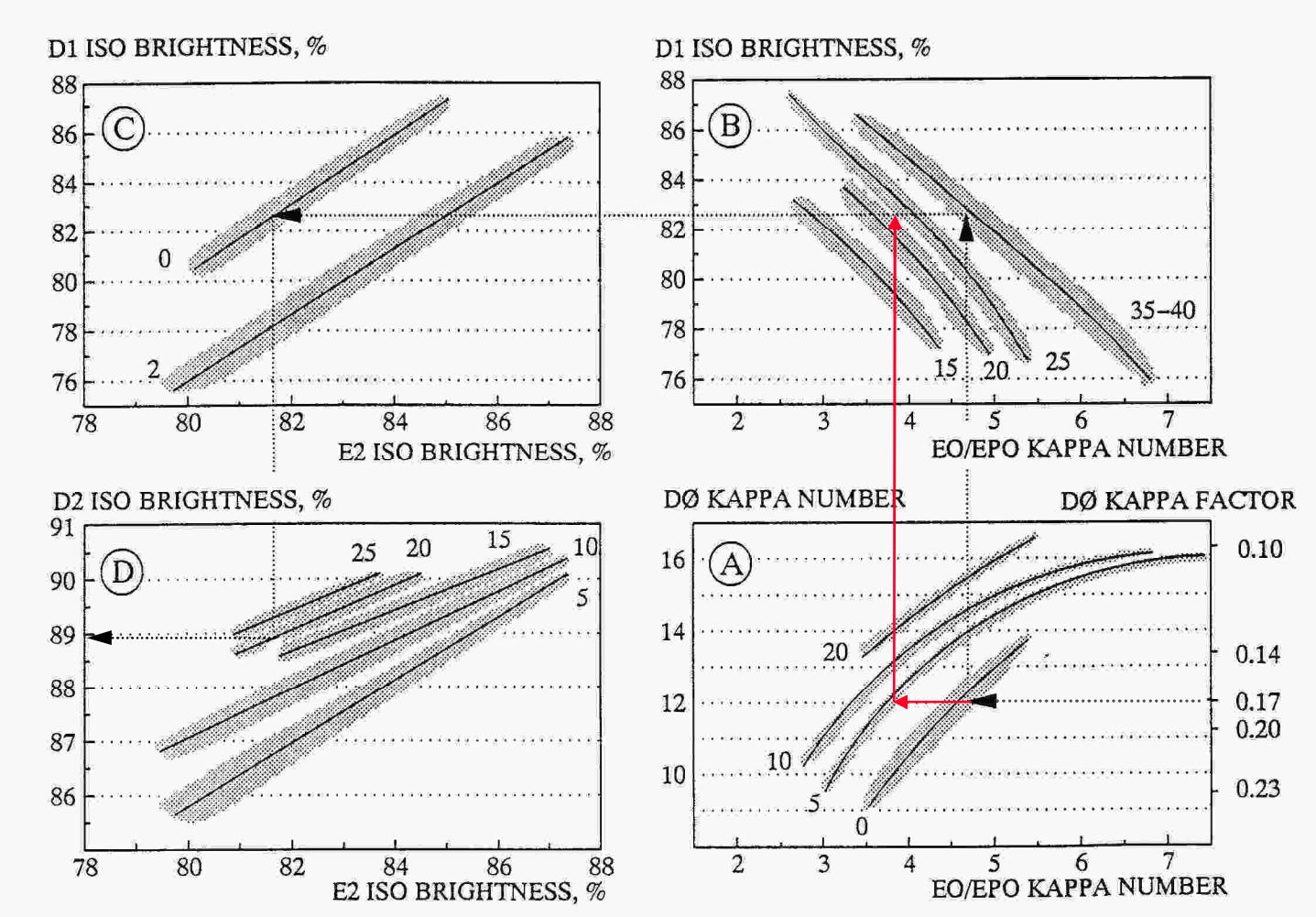
HOW TO MONITOR EOP PERFORMANCE?



- Kappa or K# is probably the best <u>absolute</u> measure of Eop performance, especially if an accurate Kappa analyzer is available
- For <u>routine</u> monitoring (not optimization or trials) using hand tests, brightness may be a more sensitive indicator at some mills

Mill data, Softwood Kraft pulp - K# and GE Brightness measured after Eop
Reference: Reid, “Peroxide Bleaching – Mill Experience,” 1991 CPPA Kraft Pulp Bleaching Course Notes

SUBSTITUTION OF PEROXIDE IN A FIVE-STAGE ECF SEQUENCE



Chemical charge in kg/tp (ClO_2 as aCl), ECF Southern Pine Kraft, Kappa number 24
Reference: Basta, *et al.*, "New and Improved Possibilities in D100 Bleaching,"
Proceedings of 1992 TAPPI Pulping Conference

EOP STAGE OPERATING CONDITIONS SUMMARY

- Typical H_2O_2 charge = 3 - 7 kg/t
- Replacement ratio 1.0 - 1.5 kg ClO_2 per kg H_2O_2
- Typical pH = 10.5 - 11.0
- Typical temperature range = 75 - 90^o C
  - Hotter is generally better
- Typical O_2 charge = 5 - 7 kg/t
- Separate NaOH and H_2O_2 and ensure thorough mixing
  - 5 - 10 wt % H_2O_2 can give better mixing
- Establish and monitor E-stage kappa or brightness target

Note: All pH values are measured on a cooled sample at 25 C

Questions ??