Delignification in the First Stage of the Bleach Plant

Principles and Practice

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The Bleach Plant

Outline

- Definitions and Fundamentals
- Delignification with Chlorine Dioxide ClO_2
  - Elemental Chlorine Free (ECF) Bleaching

First Stage of Bleaching

- Purpose
  - to remove residual lignin from unbleached pulp
  - to assist bleaching of shives
- How
  - through substitution and oxidation reactions with lignin
  - which in part allows the lignin to dissolve in water; and
  - makes the lignin soluble in the subsequent extraction stage

Definitions

- Elemental Chlorine Free "ECF" is the term used when chlorine dioxide (ClO_2) has fully replaced chlorine gas (Cl_2) in the first stage of bleaching
  - 1 kg of ClO_2 is equivalent to 2.63 kg of Cl_2 on an oxidizing equivalent basis
  - 1 kg of ClO_2 transfers the same amount of electrons as 2.63 kg of Cl_2
- In bleaching stage designations the following terms may be used for the first stage:
  - D, D_0, D_{100}

Definitions

- Kappa Factor is defined as:
  - Weight percent equivalent chlorine applied to the unbleached pulp divided by the unbleached pulp kappa number
  - i.e., 6 % equivalent chlorine applied to 30 kappa no. unbleached pulp

    Kappa Factor = 6/30 = **0.20**
- Kappa Factor is the same as:
  - Active chlorine multiple
  - Equivalent chlorine multiple

Chlorine Dioxide Delignification
(Elemental Chlorine-Free, ECF)

- Driving forces
- Chemistry
- Delignification
- Process conditions
  - pH
  - Consistency
  - Temperature
- Industry practice

Driving Forces for ECF

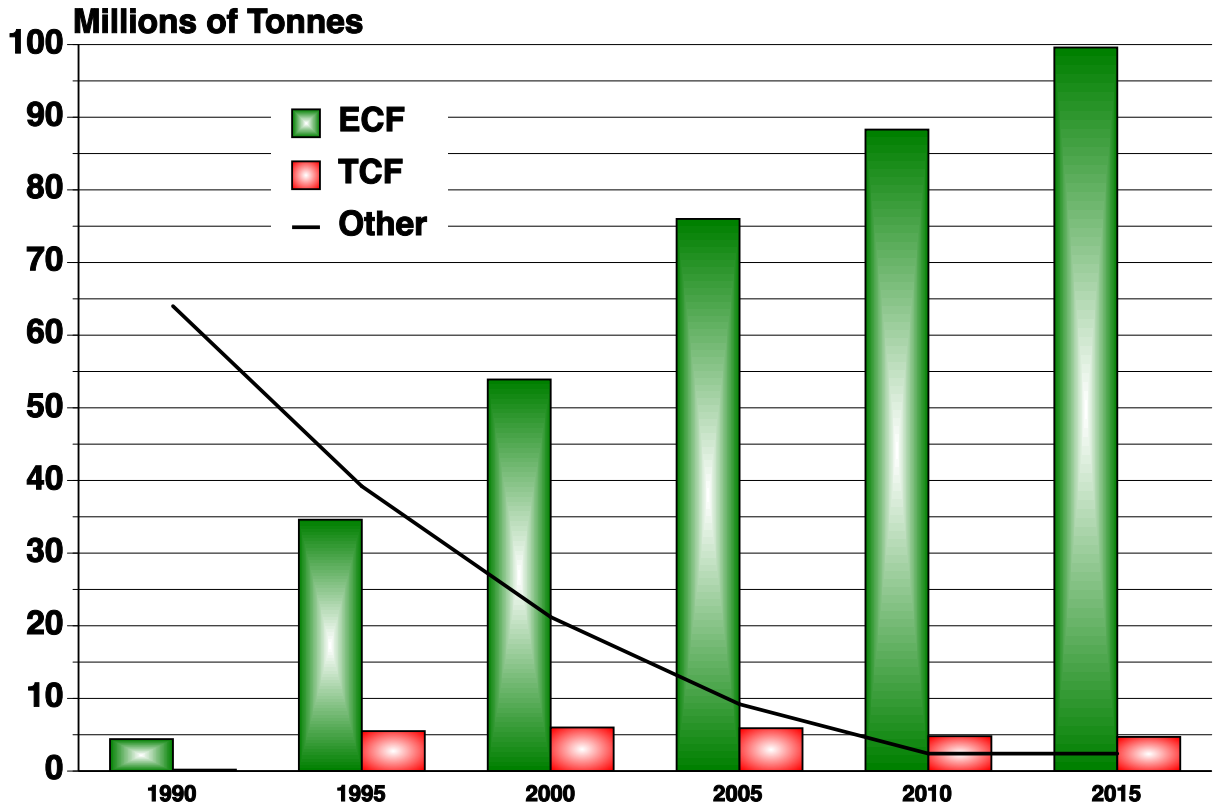
- Environmental
  - Elimination of dioxins, furans, polychlorinated phenols
  - Decrease chloroform, AOX and color discharges
- Market
  - Meet demand for Elemental Chlorine Free pulp
- Regulatory
  - Compliance with the Canadian Environmental Protection Act
  - Compliance with US EPA “Cluster Rules”

Impact of ECF on Bleaching Effluent

- Dioxins and furans non-detectable
- Tri-, tetra-, penta- chlorinated phenols non-detectable
- AOX decreased
- EOX decreased
- Chloroform decreased
- Color decreased
- Acidity decreased

Growth of ECF

- The production of bleached chemical pulp using Elemental Chlorine Free (ECF) technology based on ClO_2 has grown steadily
- In 2015 ECF represents ~ 95% of production
- TCF is declining and represents < 5% of production



Chemistry of ClO_2 Delignification

- ClO_2 + Lignin $\xrightarrow{\text{Acid}}$ oxidized lignin + Cl^-

- Lignin is
  - Fragmented
  - Oxidized
  - Ionized
  - Solubilized partially in the first stage and more so in the subsequent extraction stage

ClO_2 Reaction with Carbohydrates

- Aldehyde groups ⟶ Carboxyl groups
- No carbohydrate degradation
- Minimum viscosity loss
- High selectivity to lignin

ClO_2 Decomposition

- Decomposition in the gas phase:
  - $ClO_2 \longrightarrow 1/2\ Cl_2 + O_2$
- Decomposition in solution:
  - $ClO_2^- + HClO \longrightarrow ClO_3^- + Cl^- + H^+$

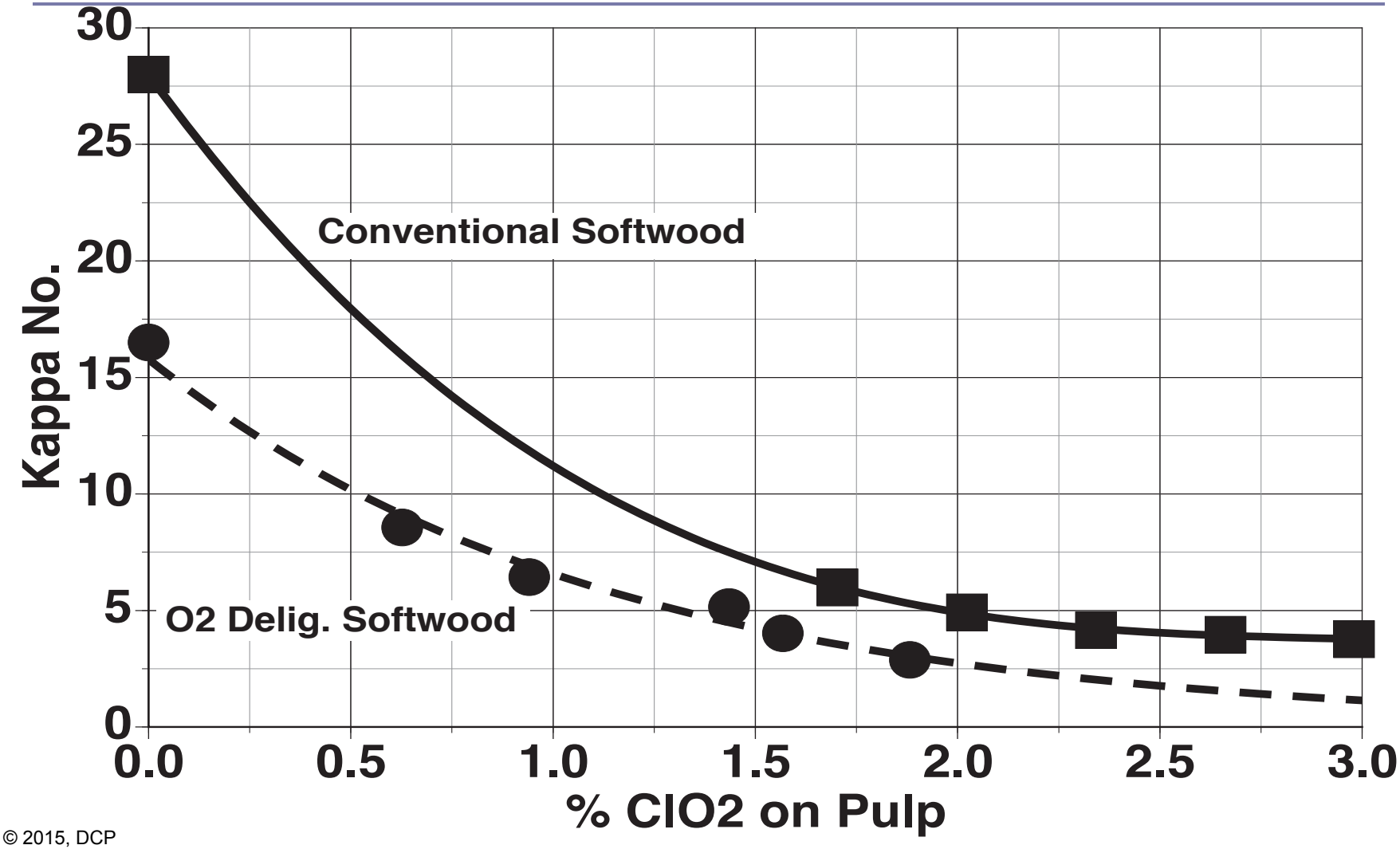
ClO_2 Reaction Products

- ClO_3^- chlorate ion — unreactive
- ClO_2^- chlorite ion — unreactive at pH > 5
- HClO, Cl_2 hypochlorous acid, chlorine — forms organochlorine
- Cl^- chloride ion — HCl formation

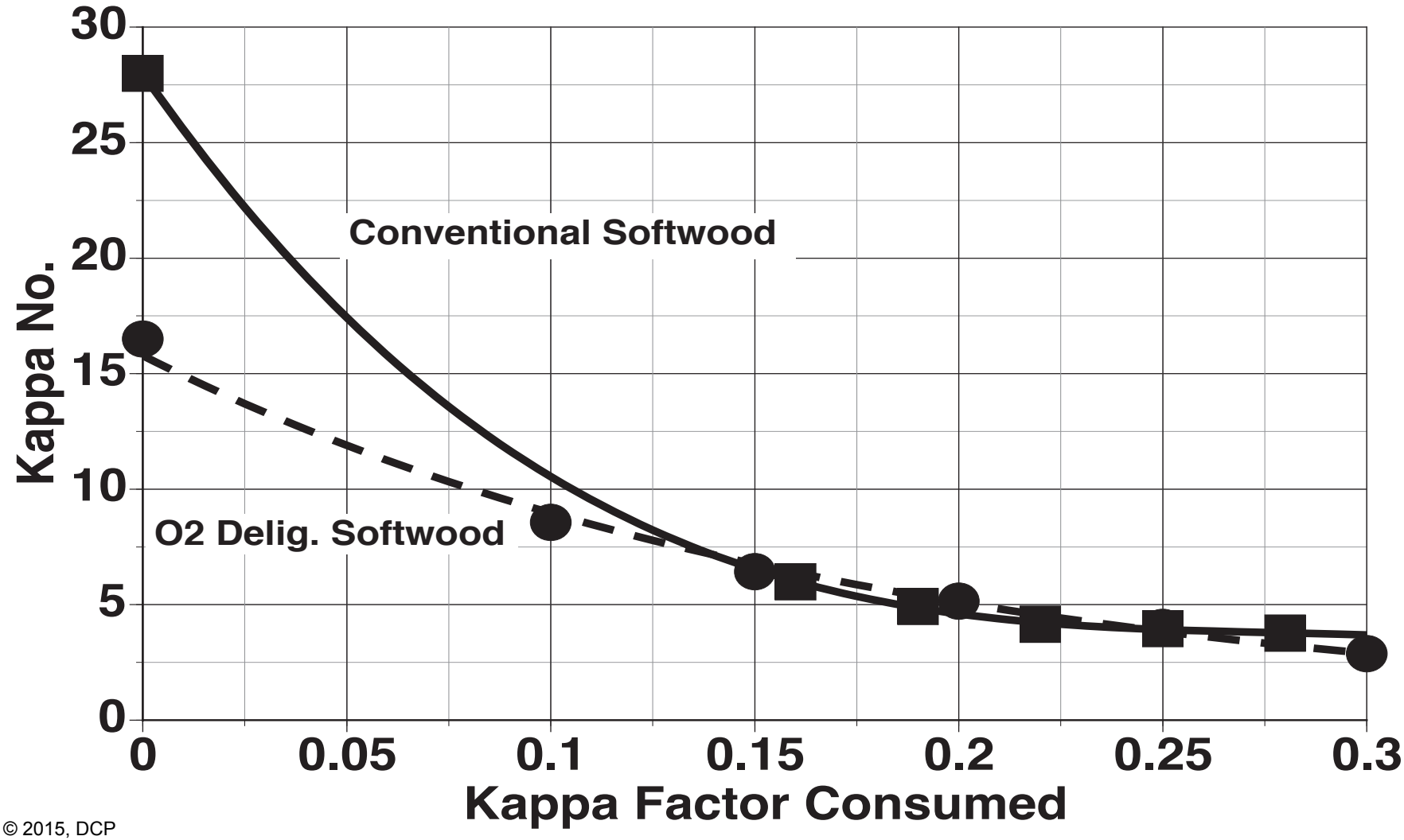
ClO_2 Delignification Variables

- Hardwood or Softwood
- Incoming Kappa Number
  - Conventionally Delignified
  - Oxygen Delignified
- ClO_2 Chemical Charge (Kappa Factor)
- Reaction Temperature & Time
- Reaction pH
- Consistency
- Carryover of Dissolved Organic Material

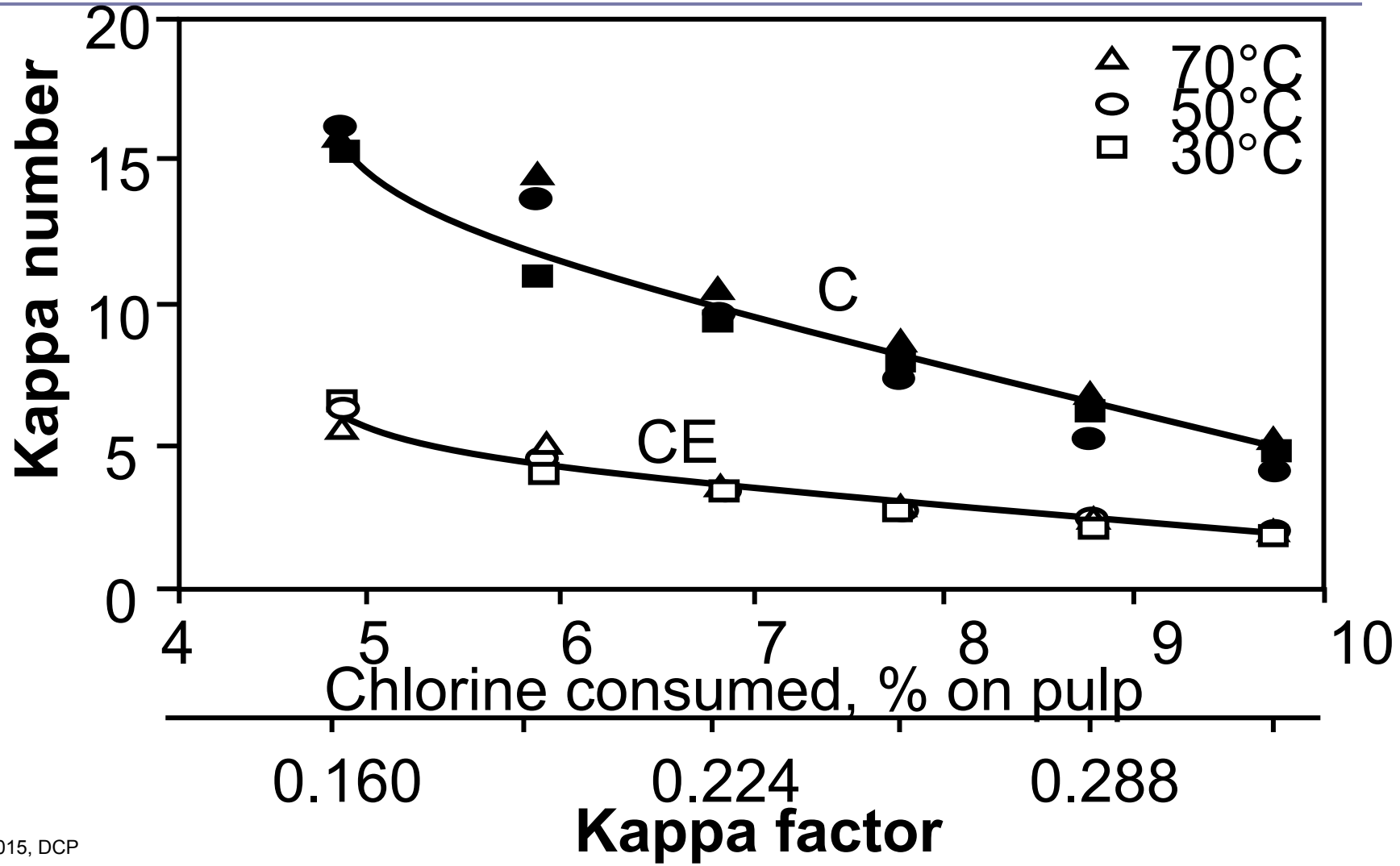
Delignification with ClO_2



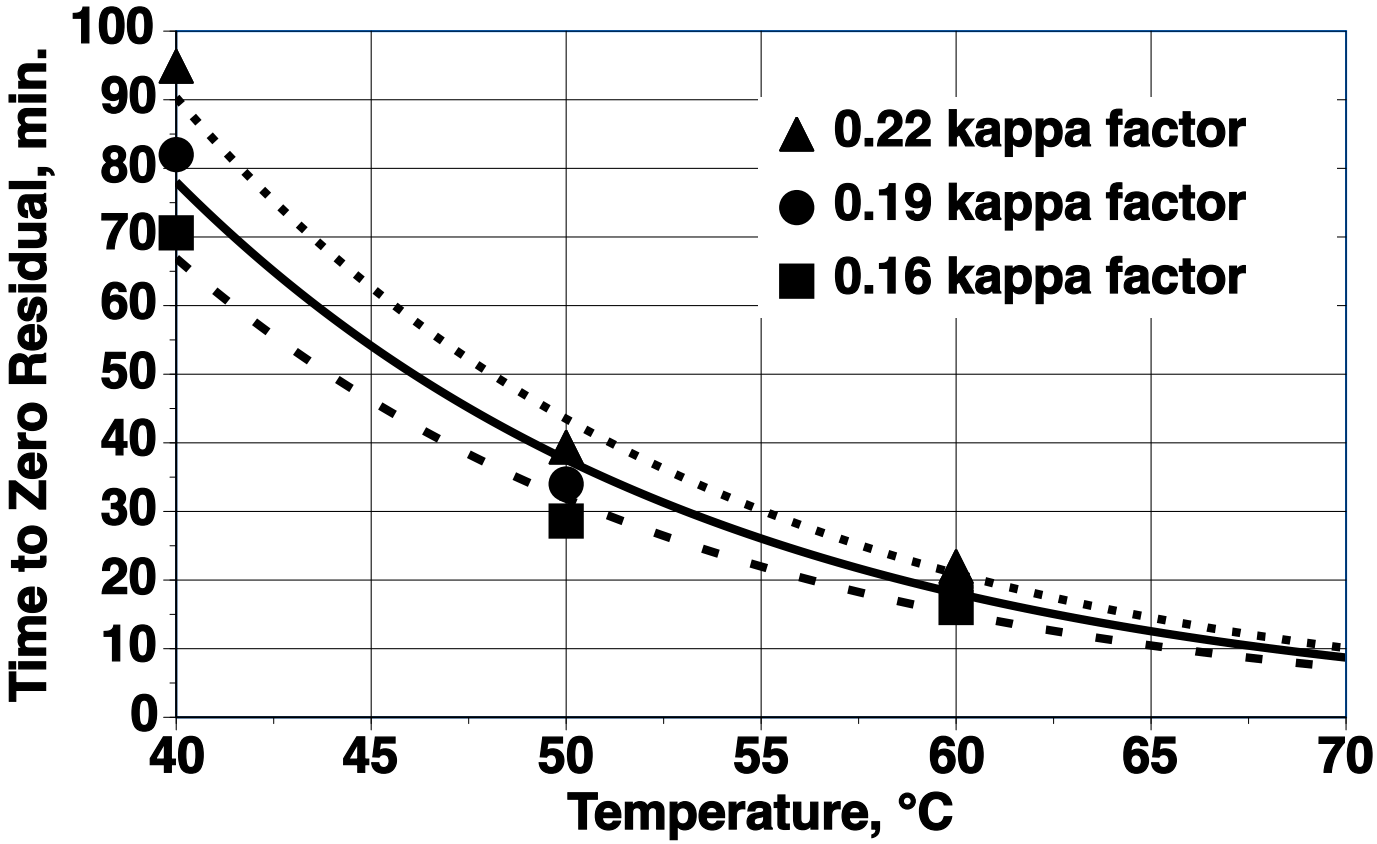
Delignification with ClO_2



Delignification with Cl_2: Effect of Temperature

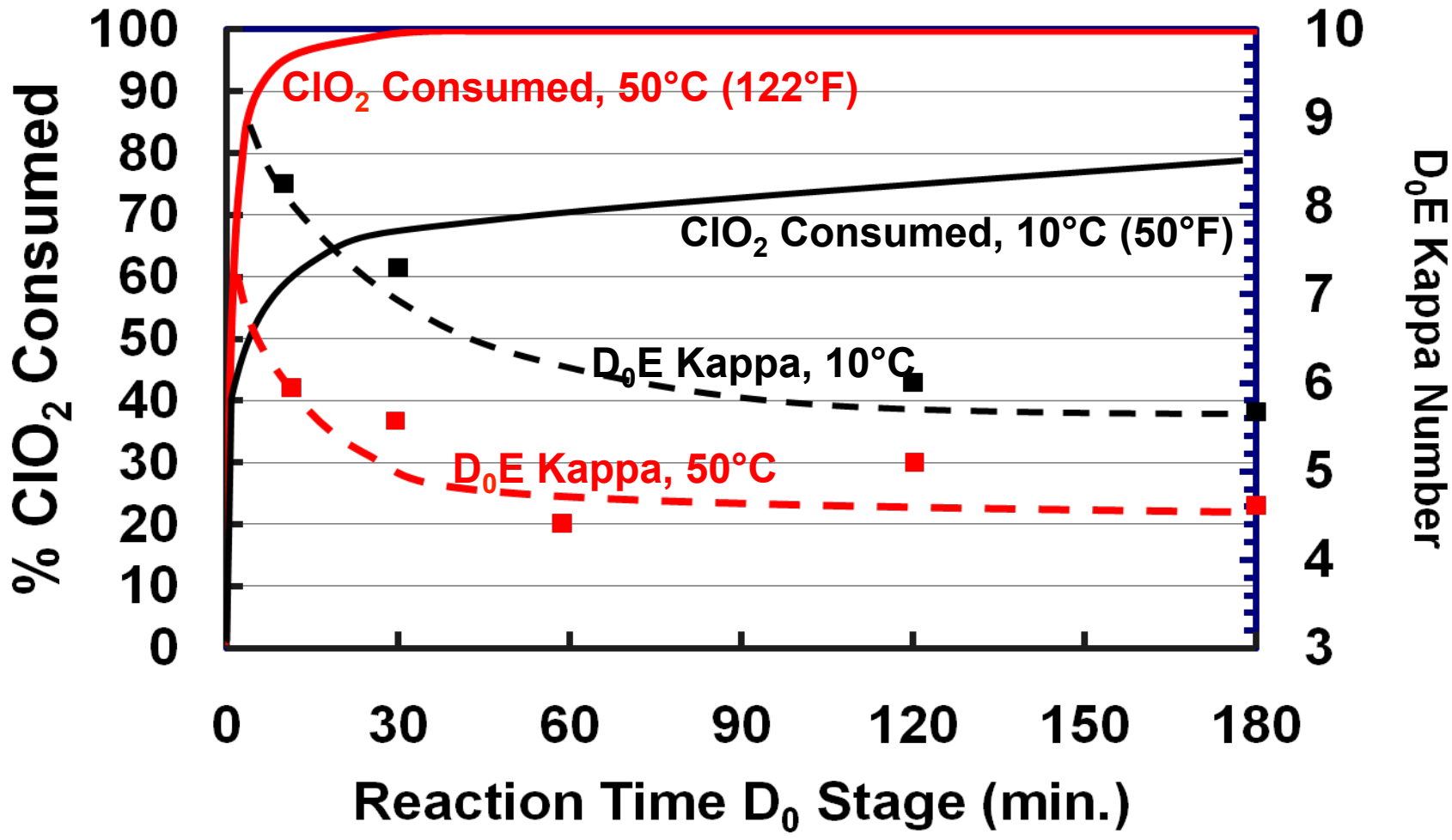


Delignification and Temperature



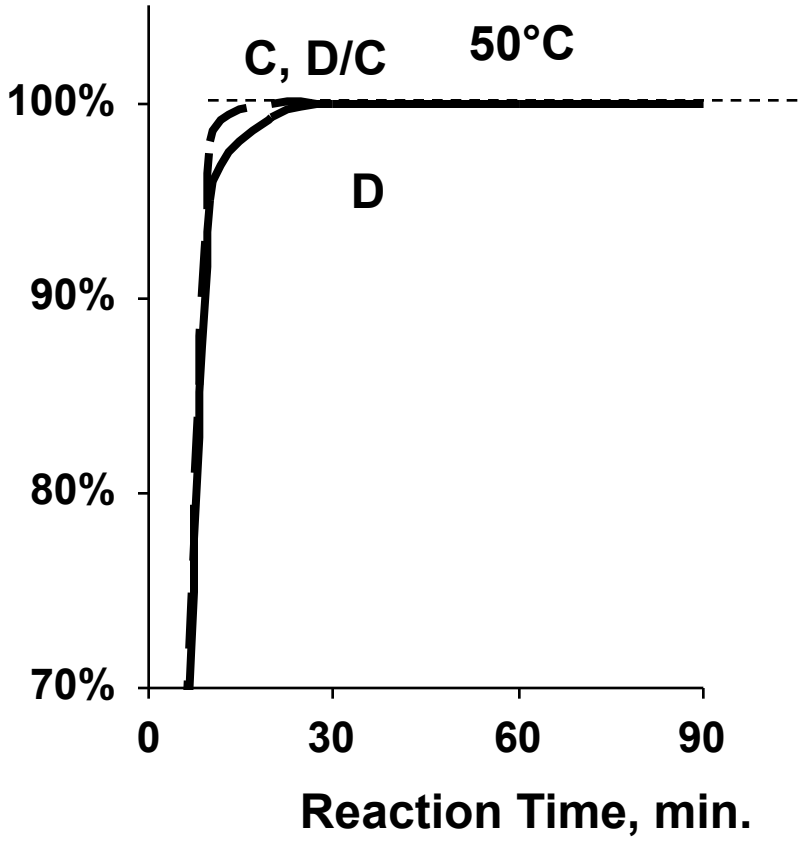
Delignification and Temperature

30 Kappa No. Softwood Kraft: 0.18 Kappa Factor



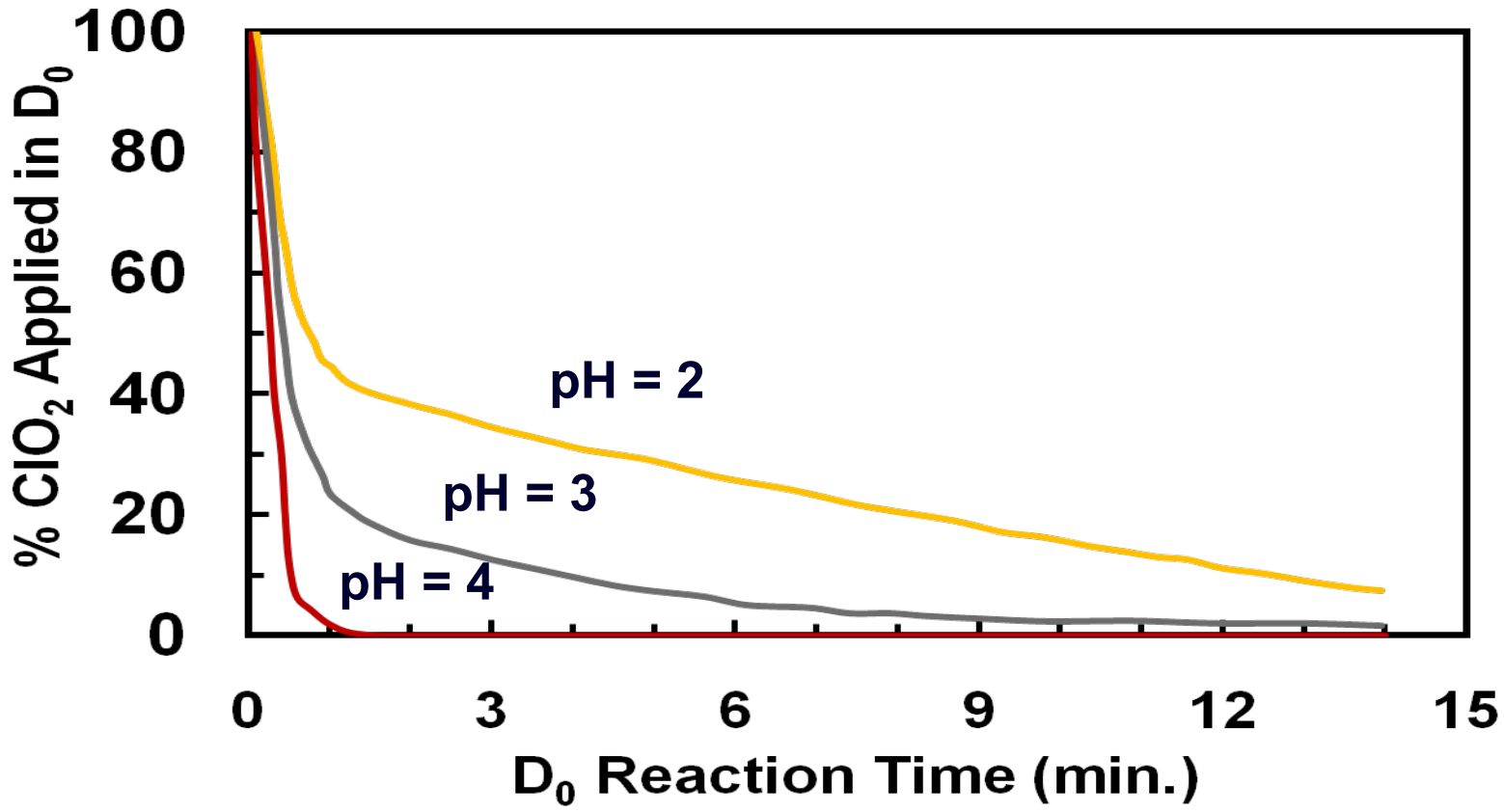
Reaction Rate

- At 50°C (122°F) the rates of chlorine dioxide consumption and delignification are indistinguishable from those of chlorine
- Two-thirds of the lignin in a kraft pulp can be solubilized in 4 seconds and 85% in 30 seconds.
  - *Ref. Pulp Bleaching: Principles and Practice. Pages 247, 264*

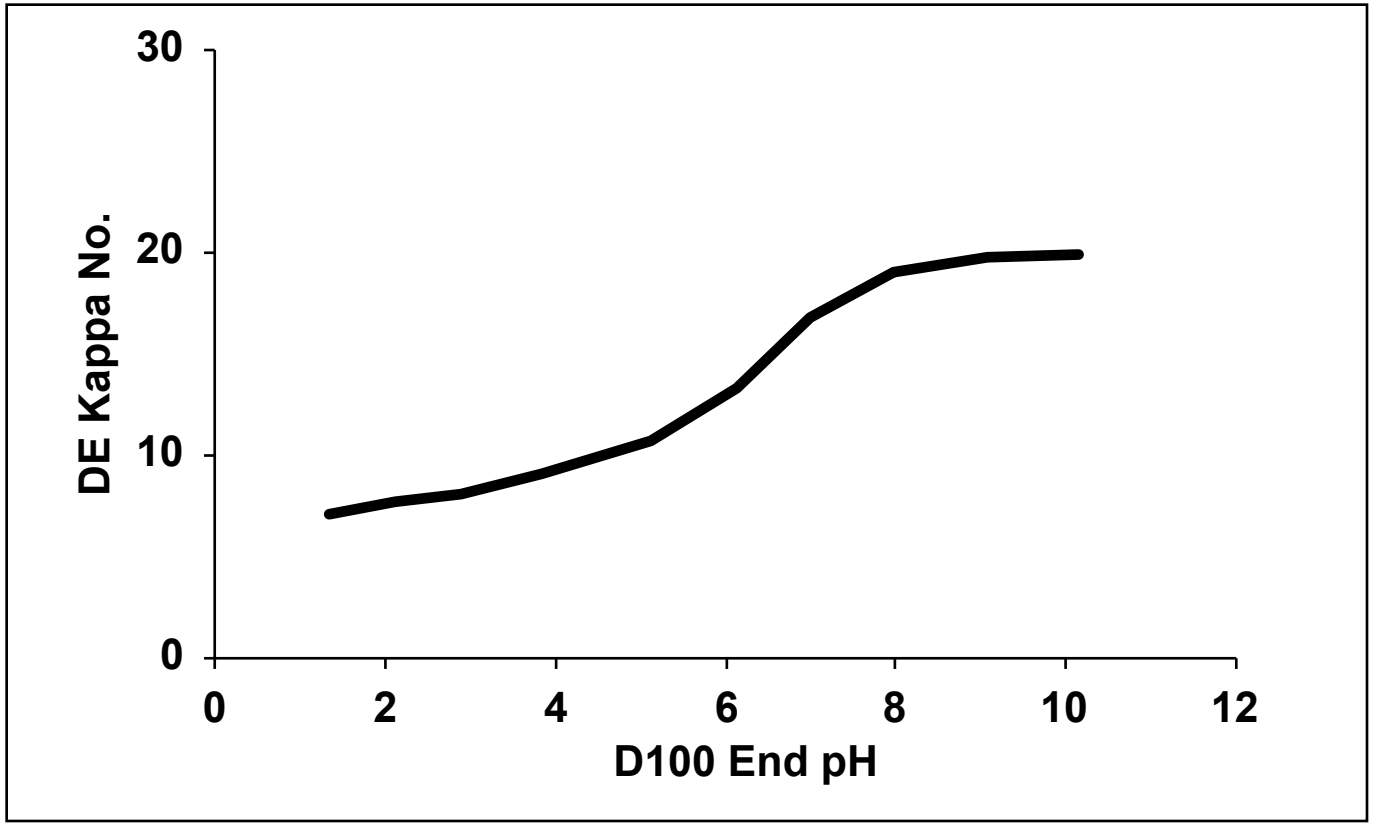


Impact of pH on Reaction Rate

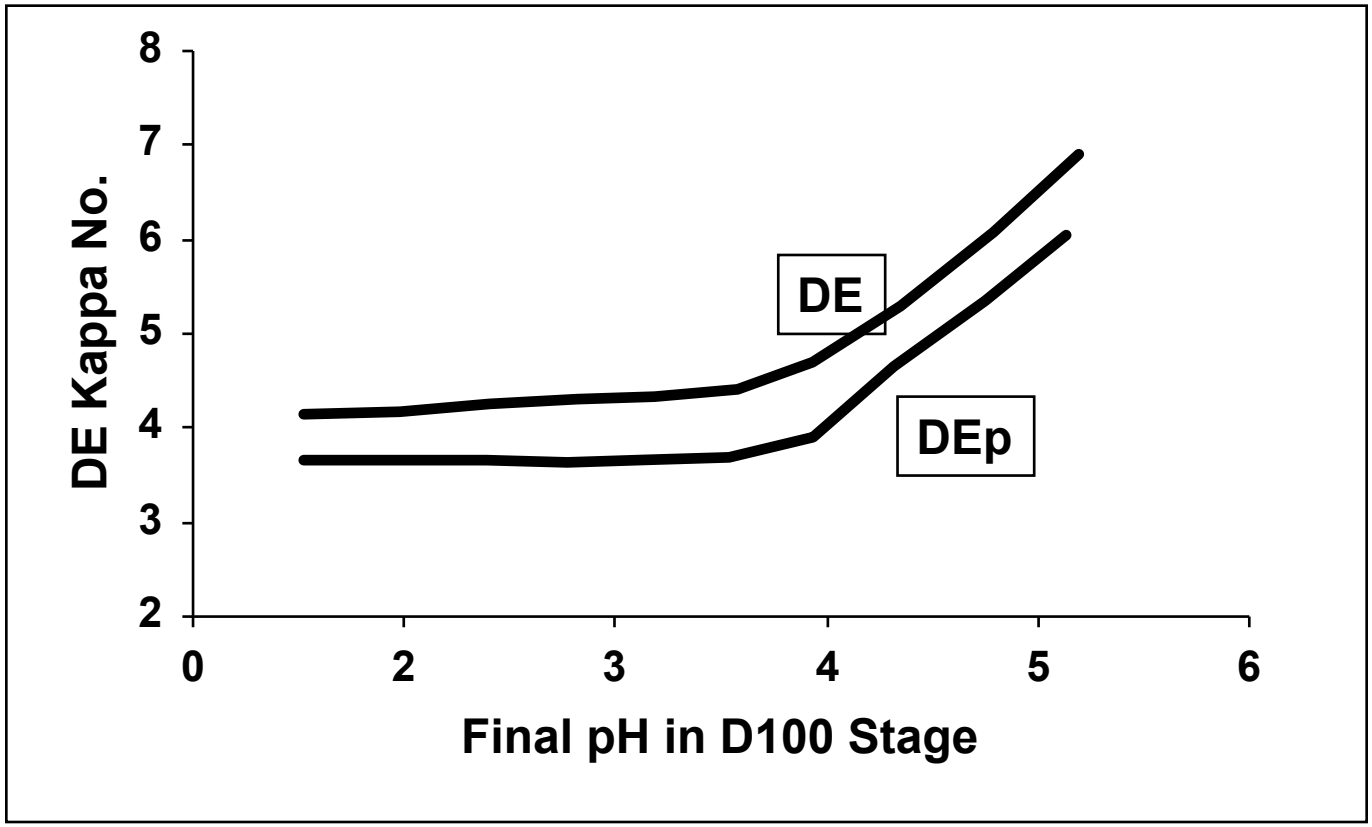
15 Kappa No. Softwood Kraft, 45°C D_0 Stage



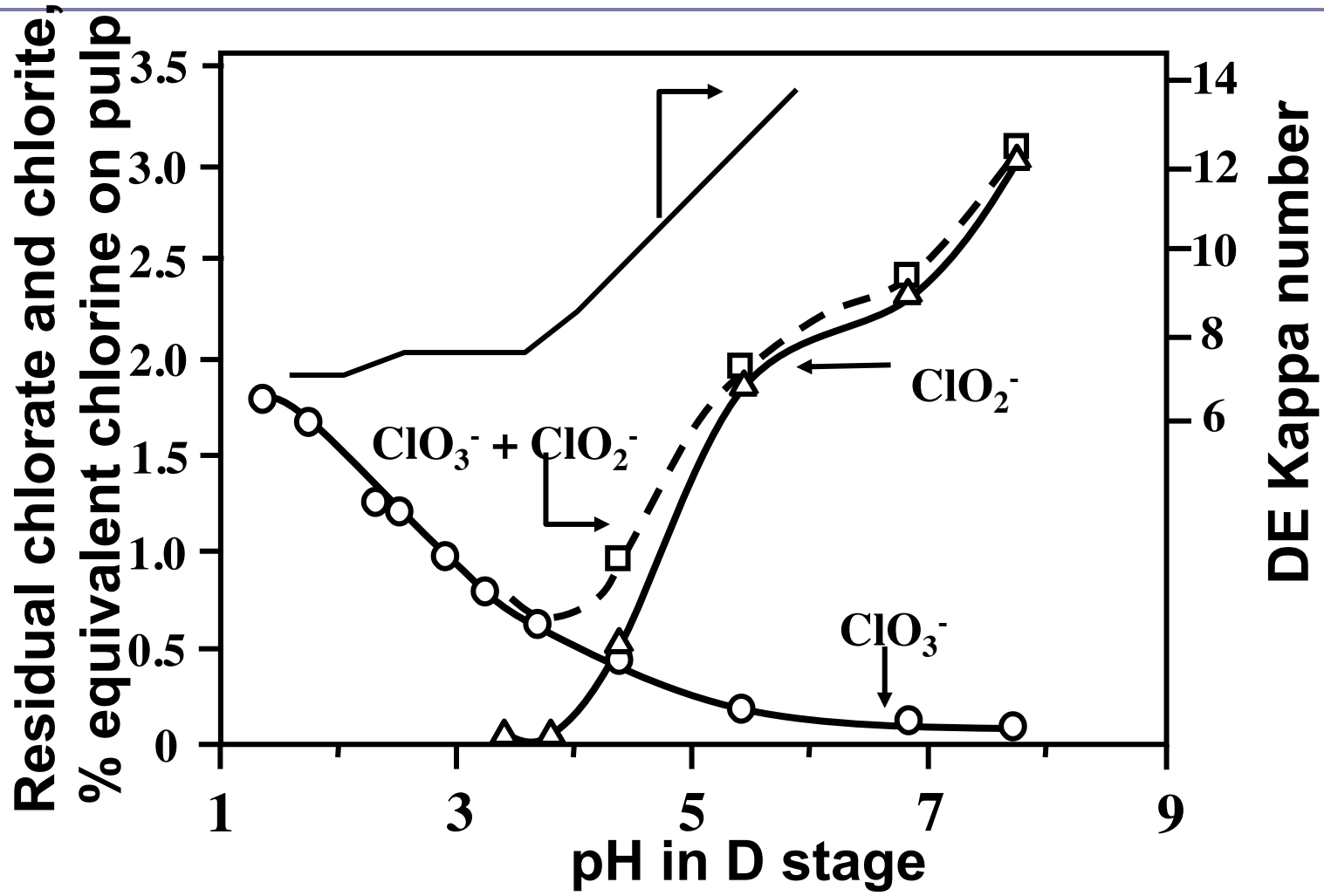
Impact of pH on Softwood Delignification



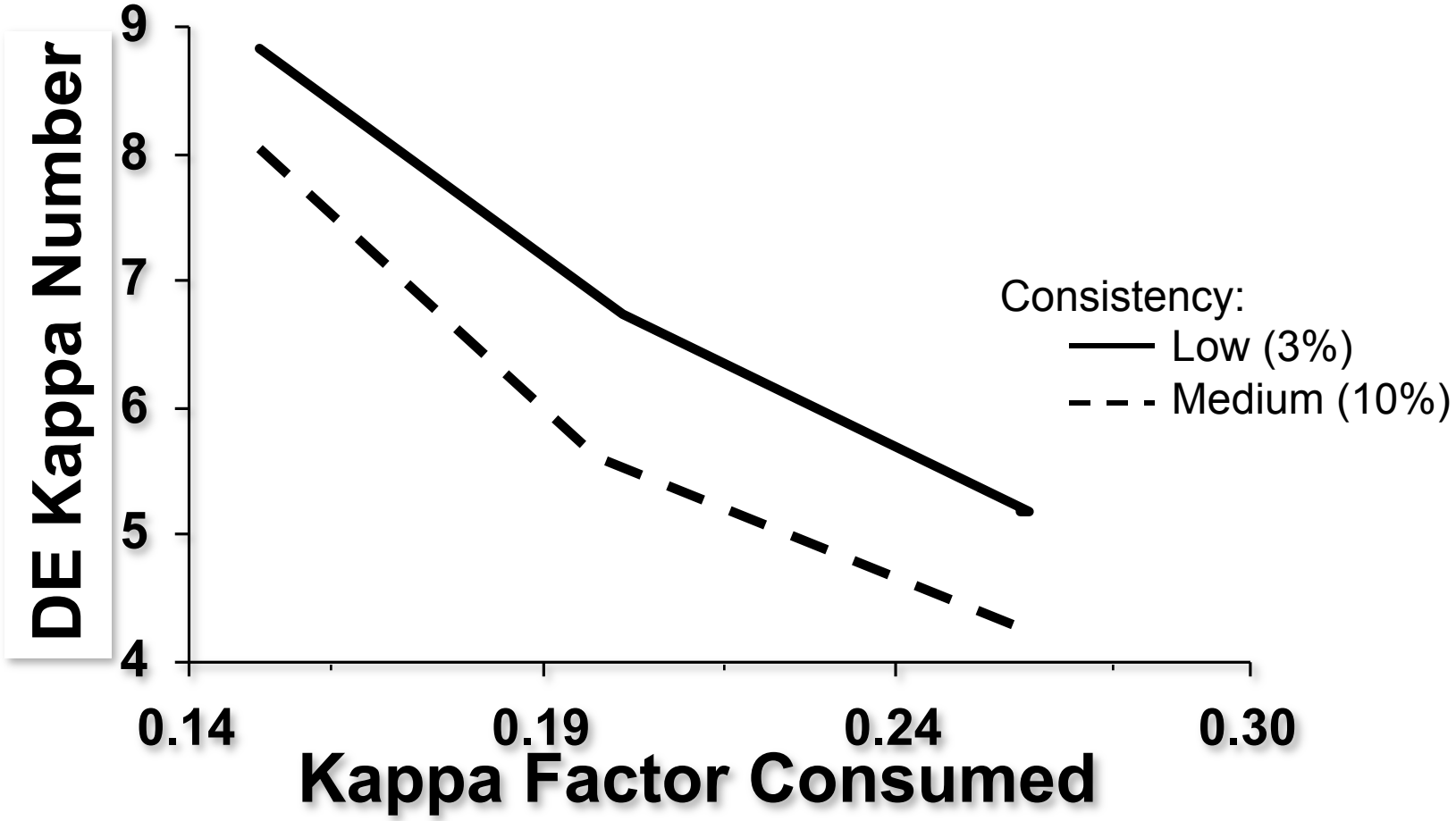
Effect of pH on ECF Hardwood Delignification



Impact of pH on Delignification



Impact of Consistency



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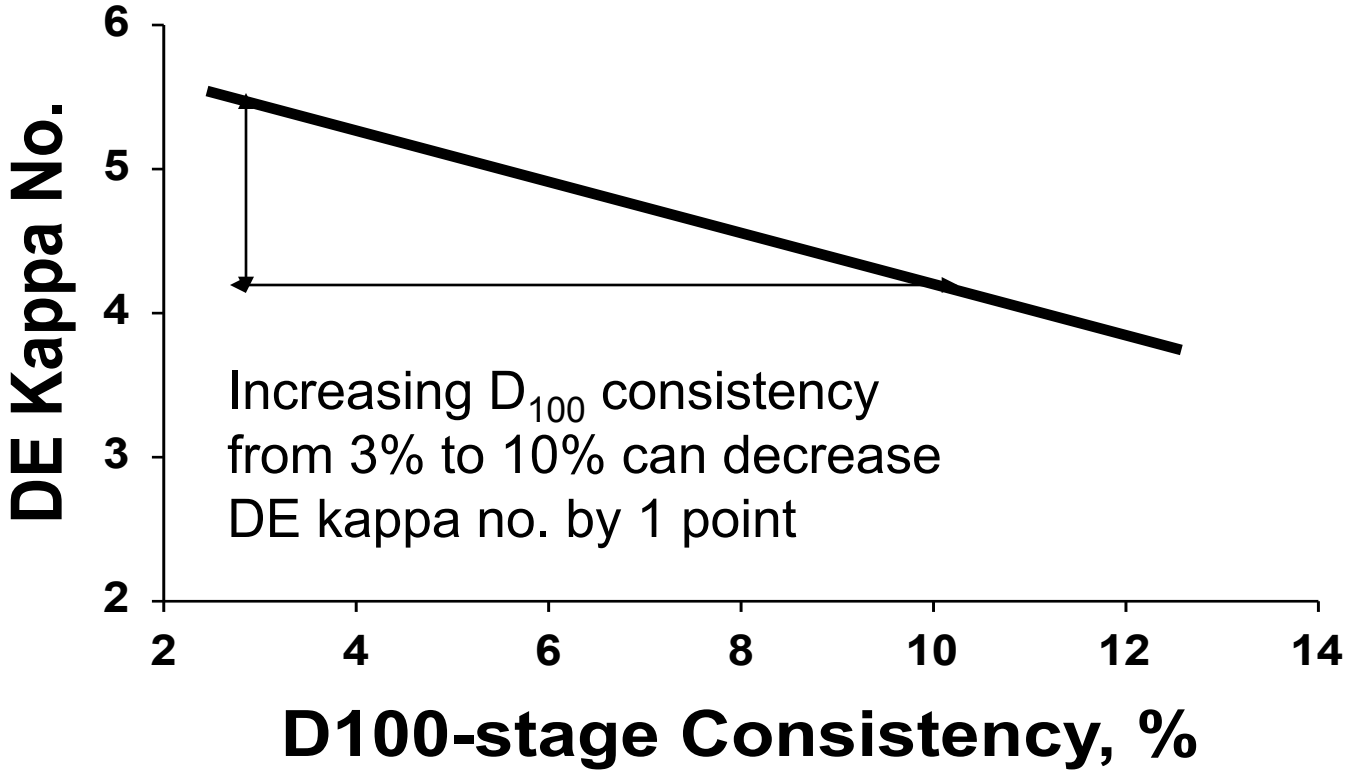
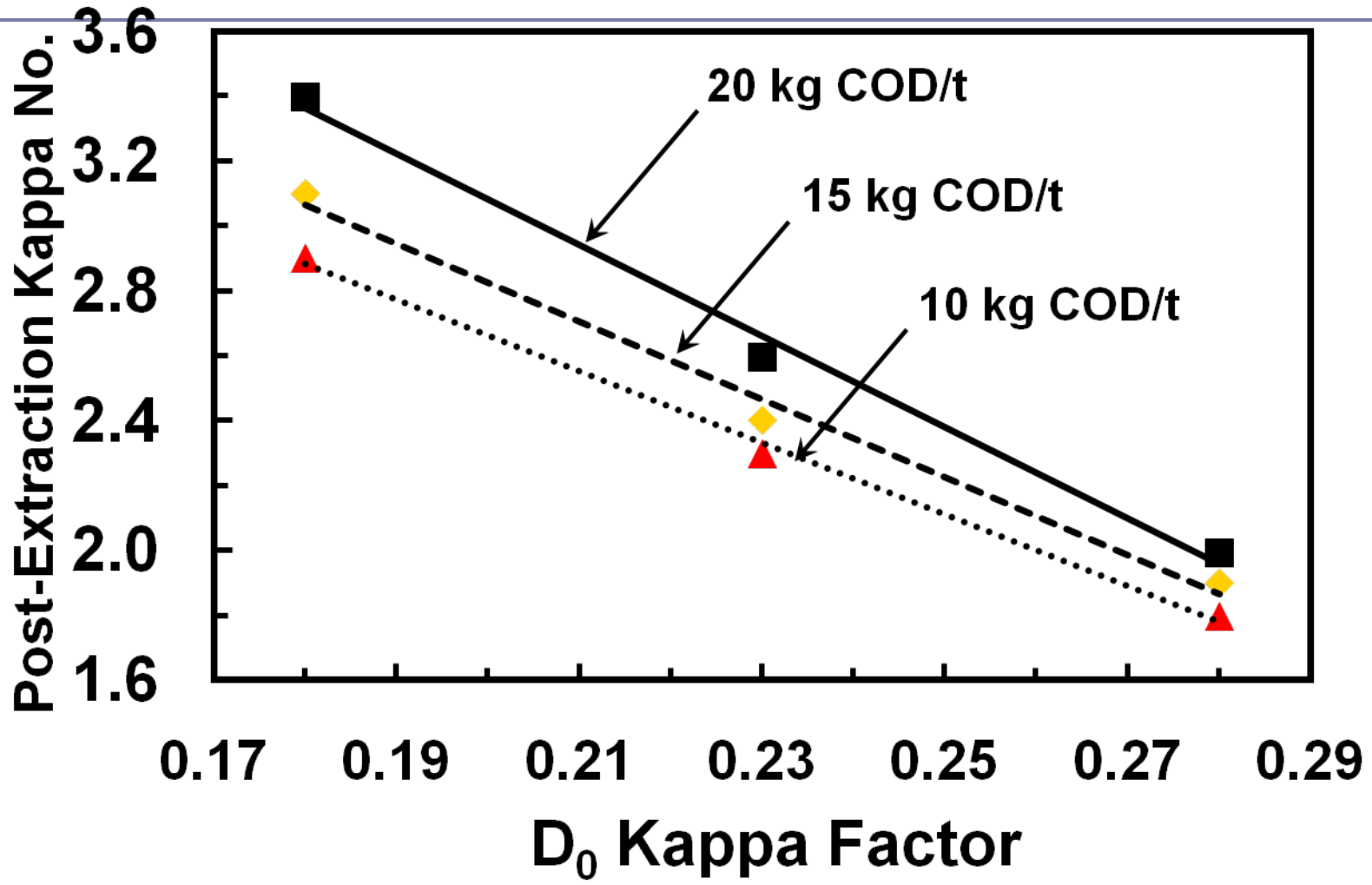
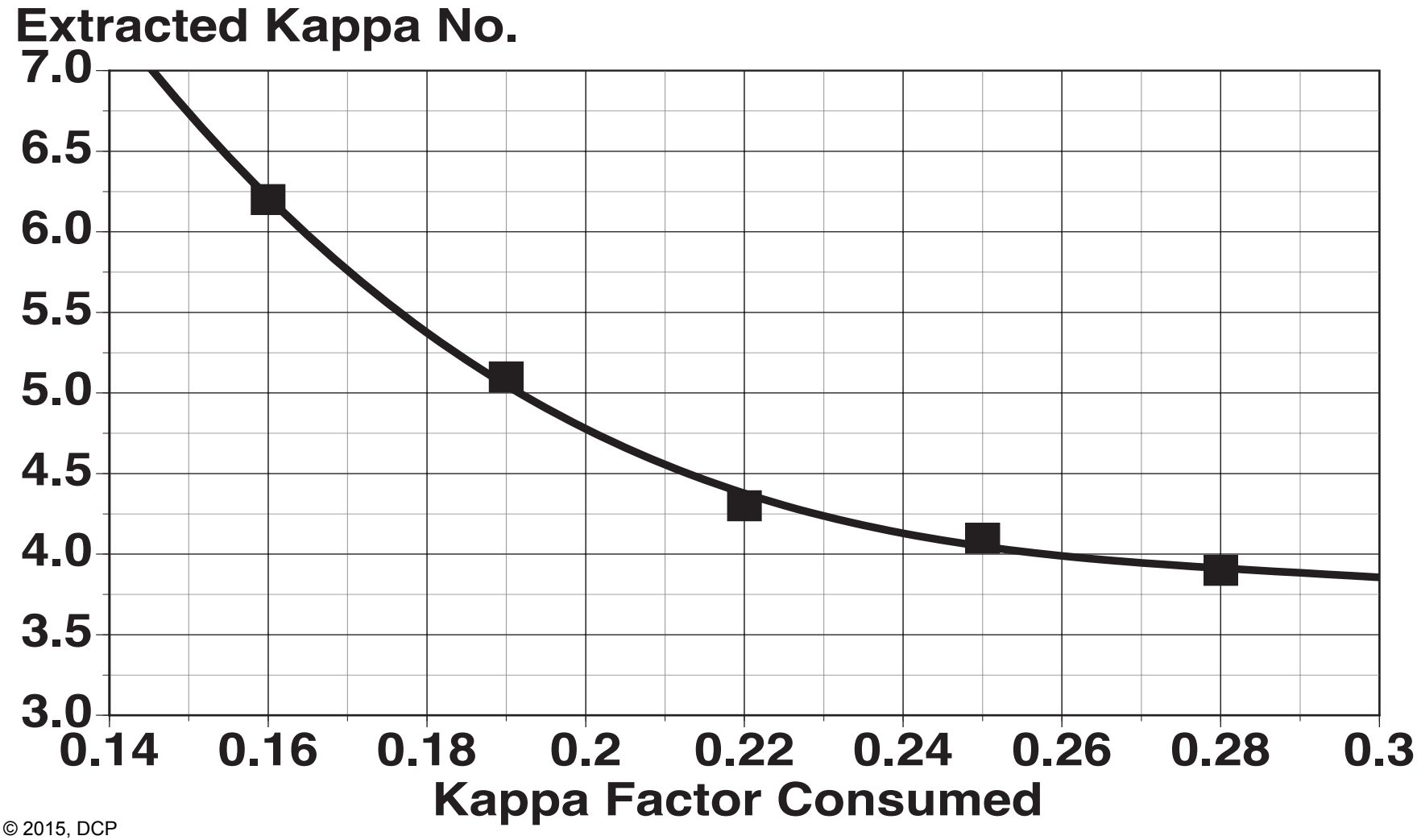


ClO_2 Delignification – COD Carryover

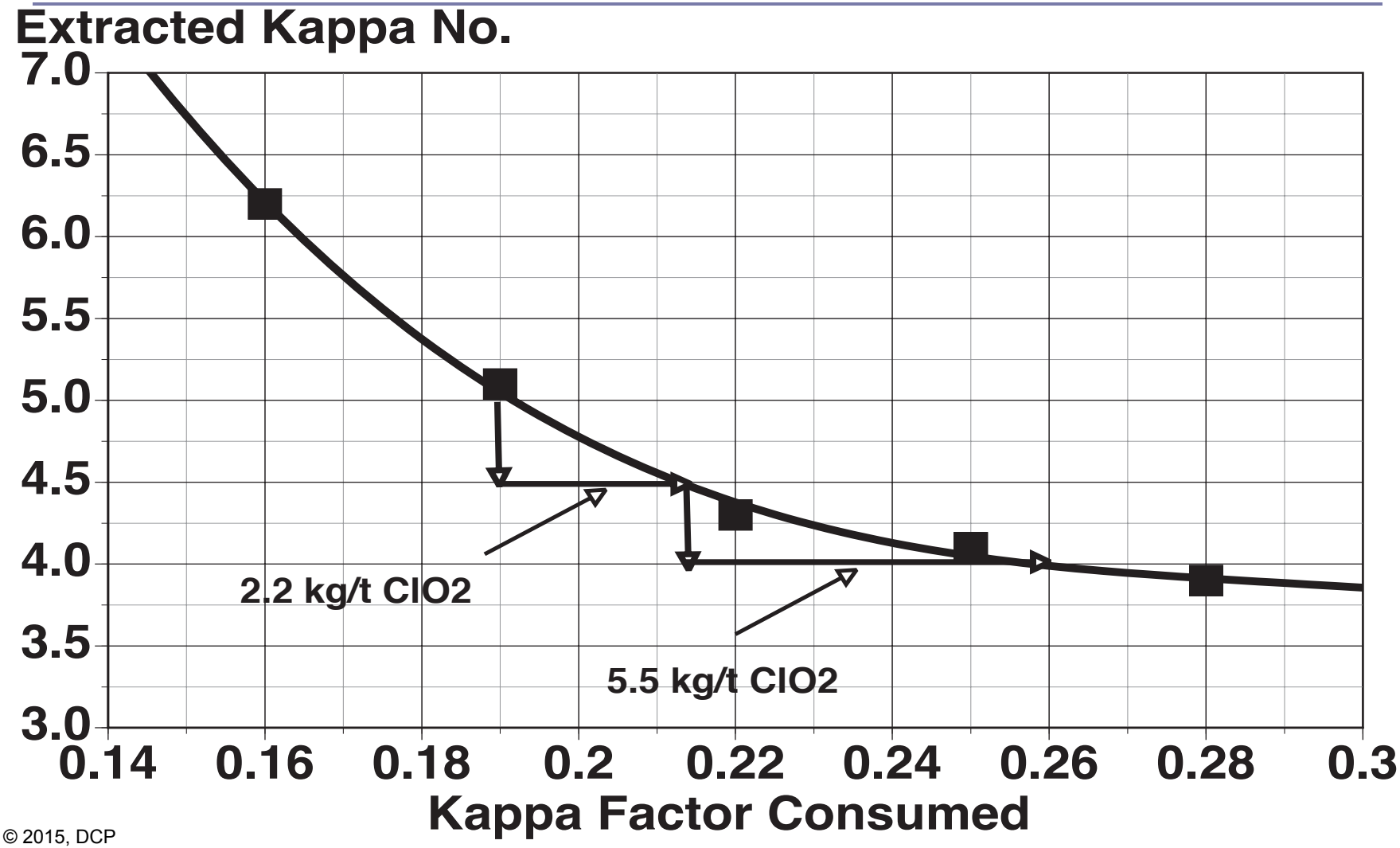
O_2 Delignified Softwood Kraft Pulp



Softwood Delignification



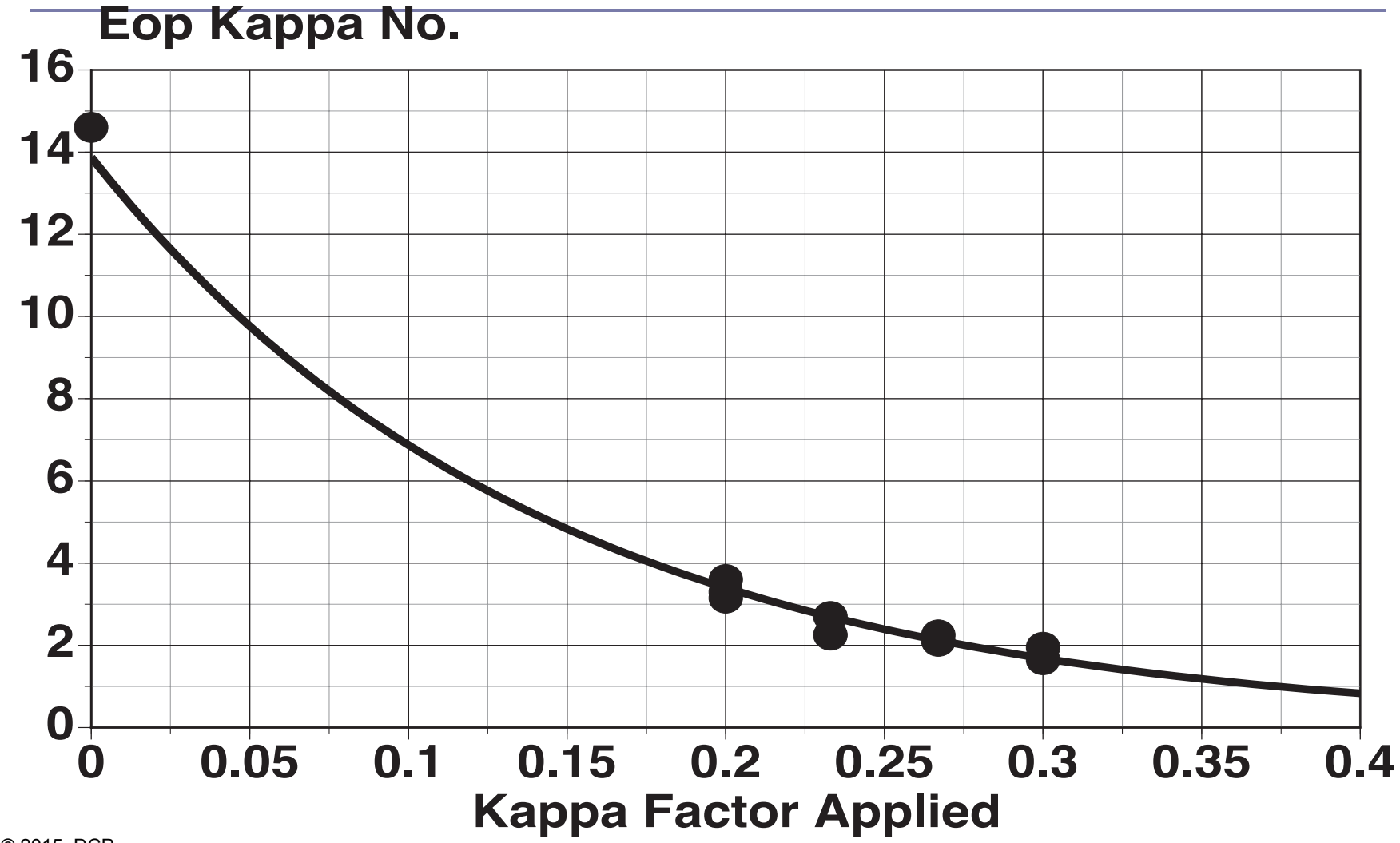
Softwood Delignification with ClO_2
29 kappa no.



Delignification with ClO_2

Oxygen Delignified Softwood

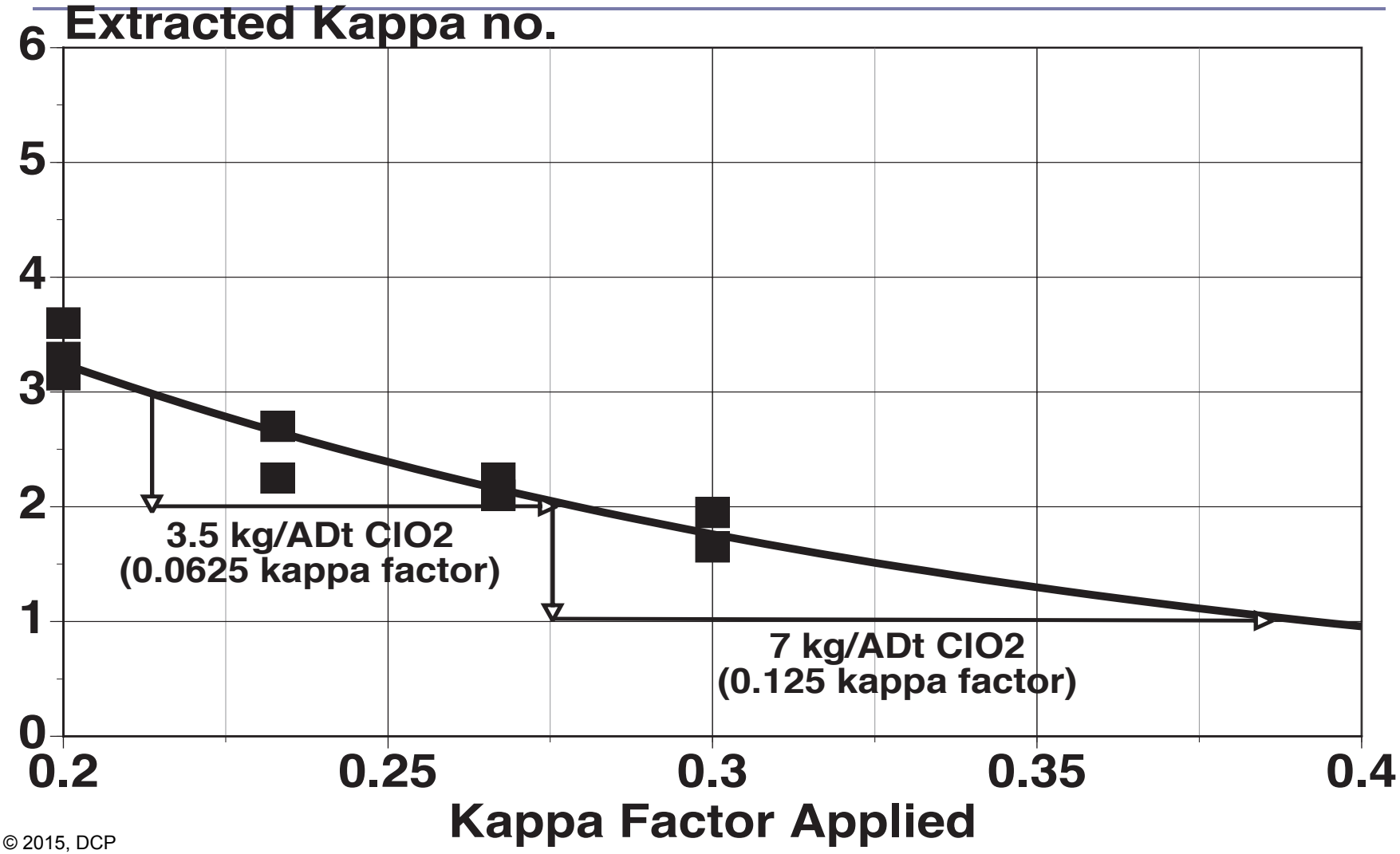
14.5 Kappa No.



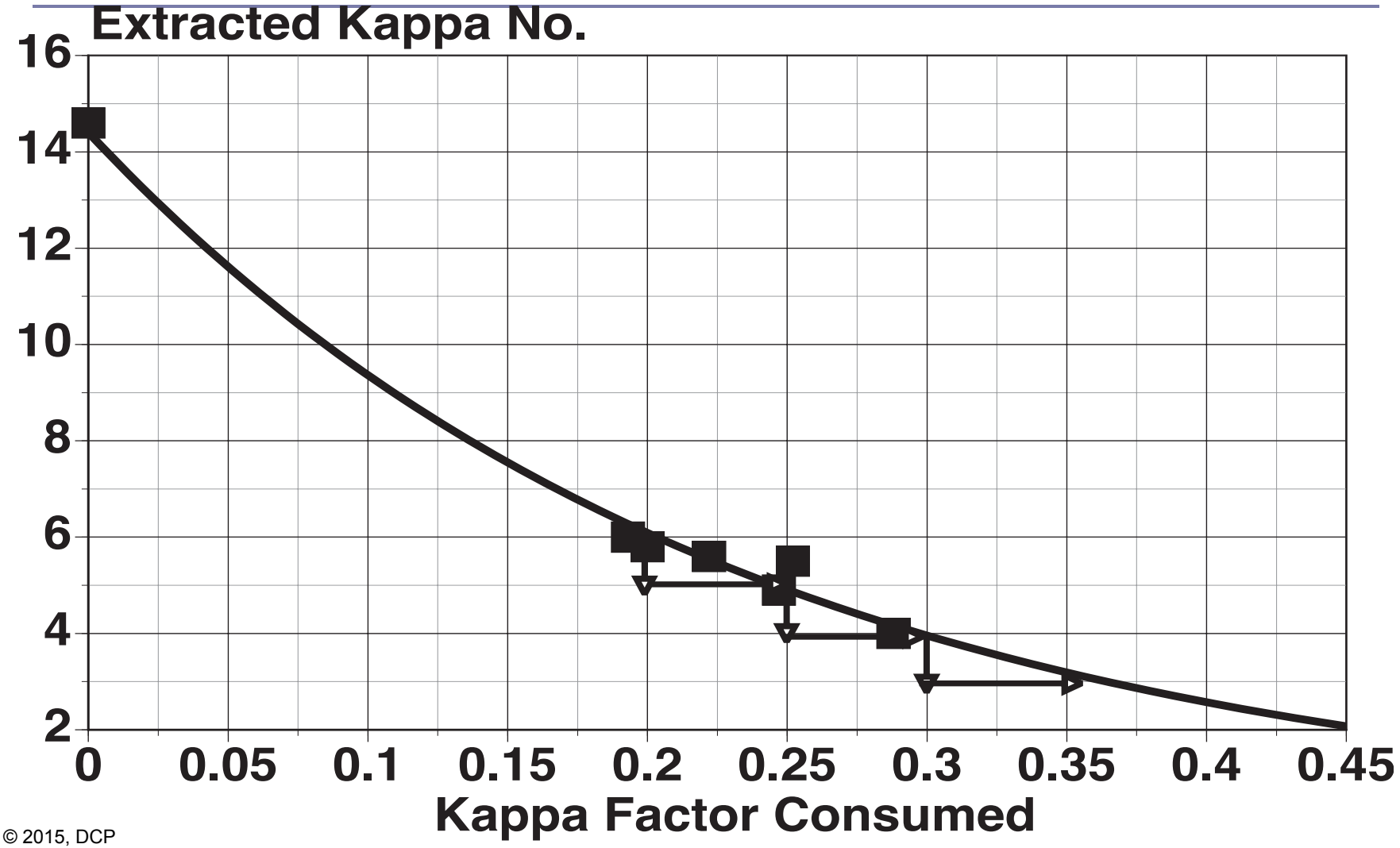
Delignification with ClO_2

Oxygen Delignified Softwood

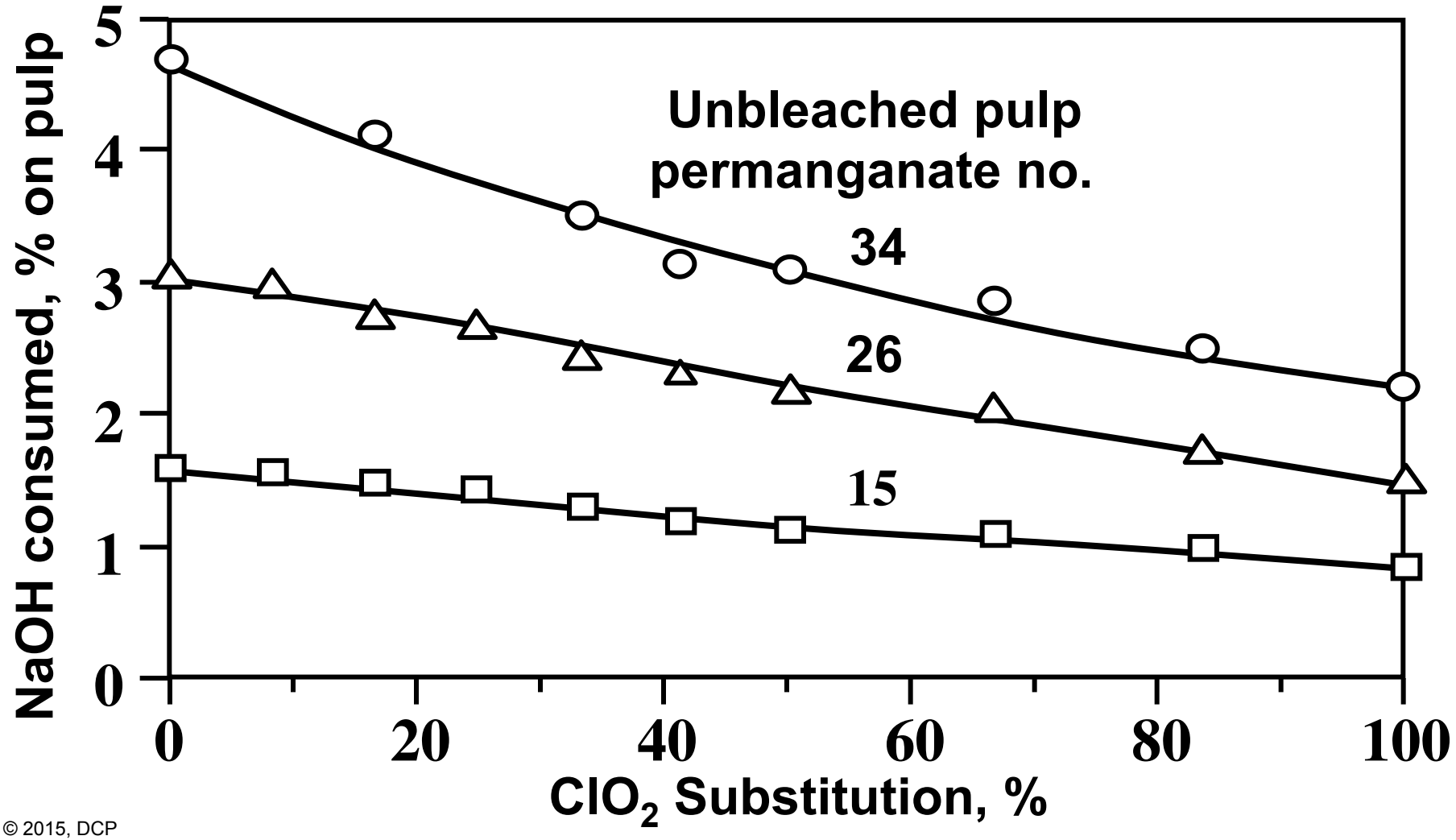
14.5 Kappa No.



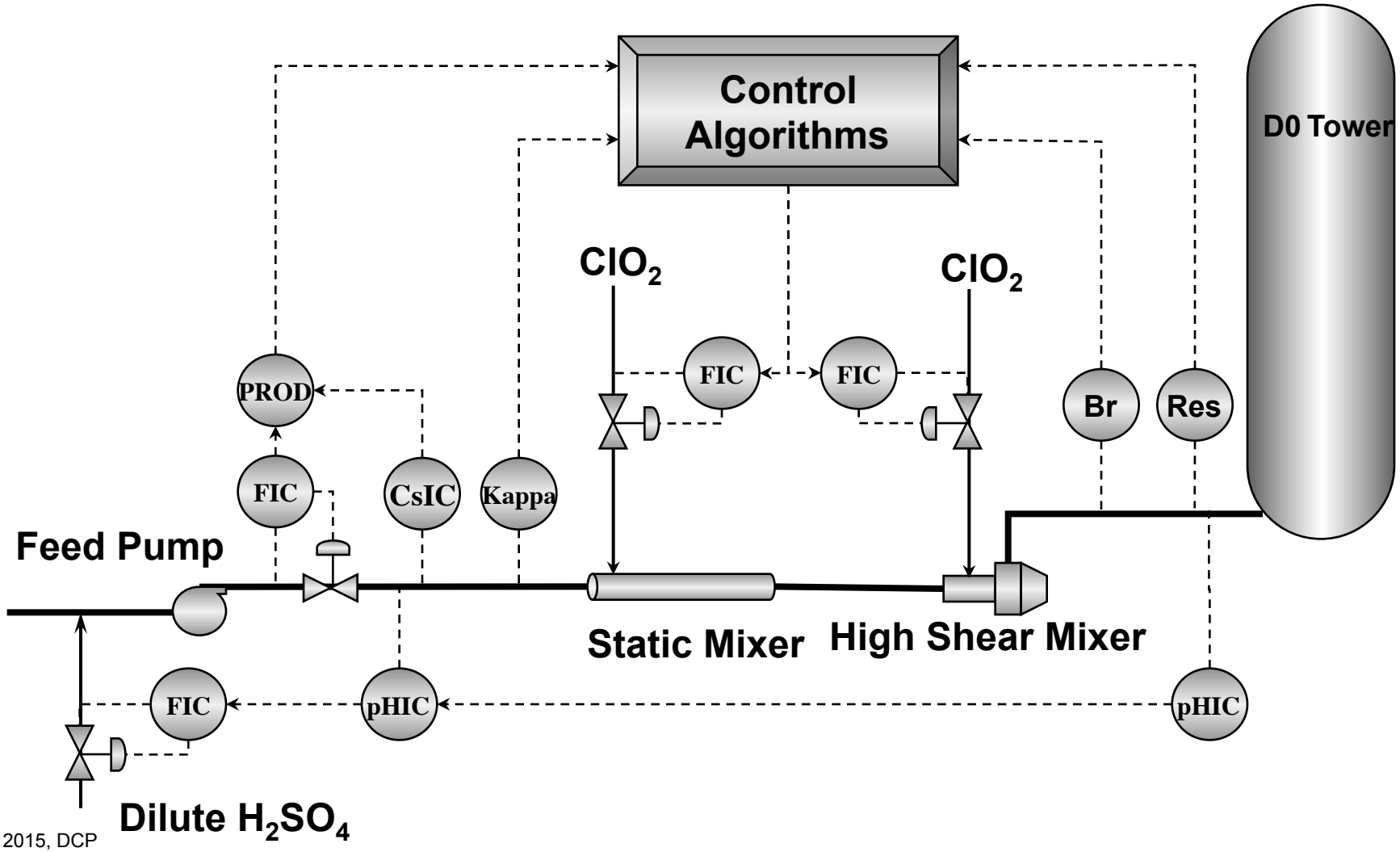
Hardwood Delignification with ClO_2
14.5 Kappa No.



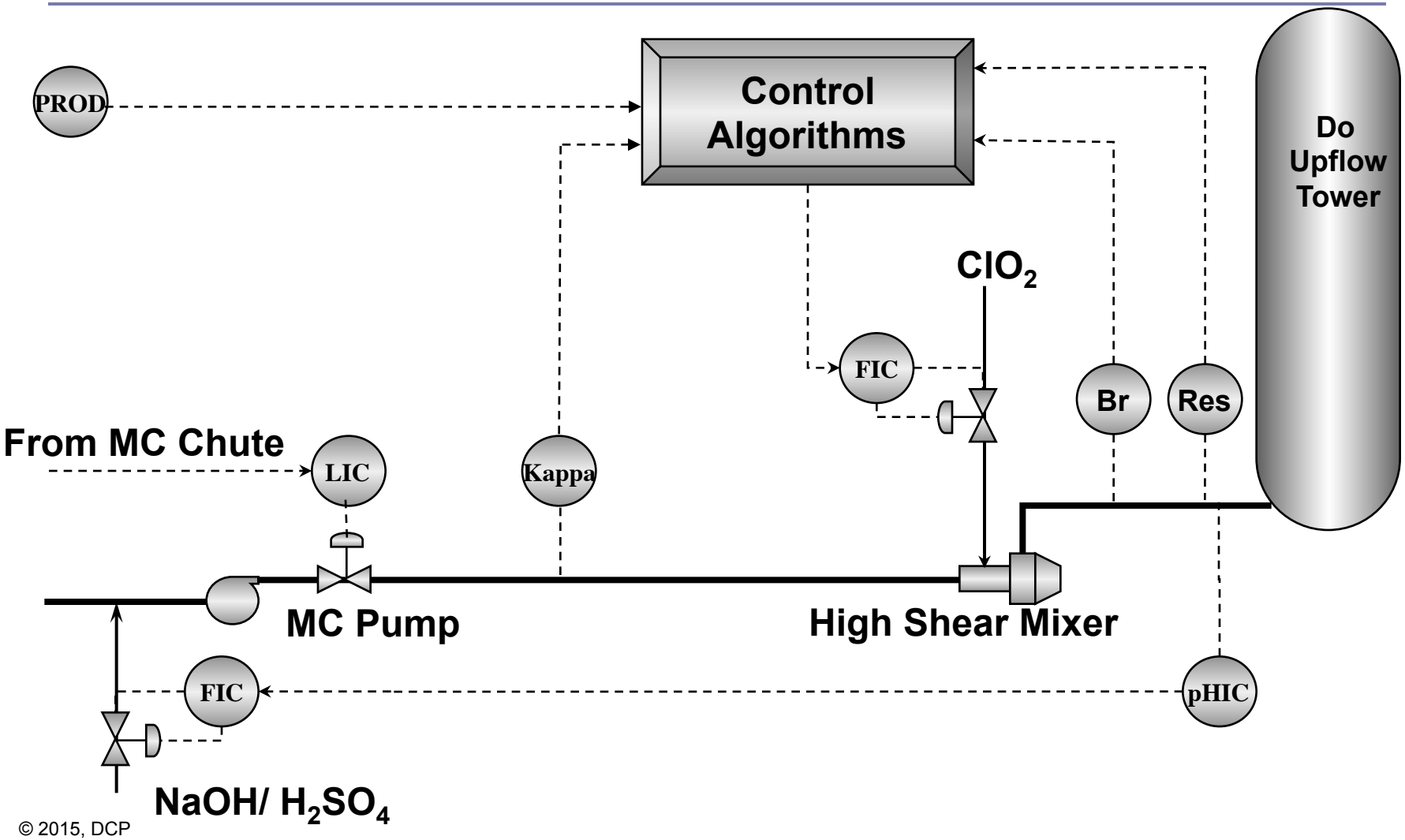
NaOH Consumption



Low Consistency ECF



Medium Consistency ECF



ECF Bleaching Practice

- Based on 2012/13 Pulp and Paper Technical Association of Canada (Paptac) Bleaching Committee Survey
- Responses from 23 mills with 37 ECF bleach lines or grades

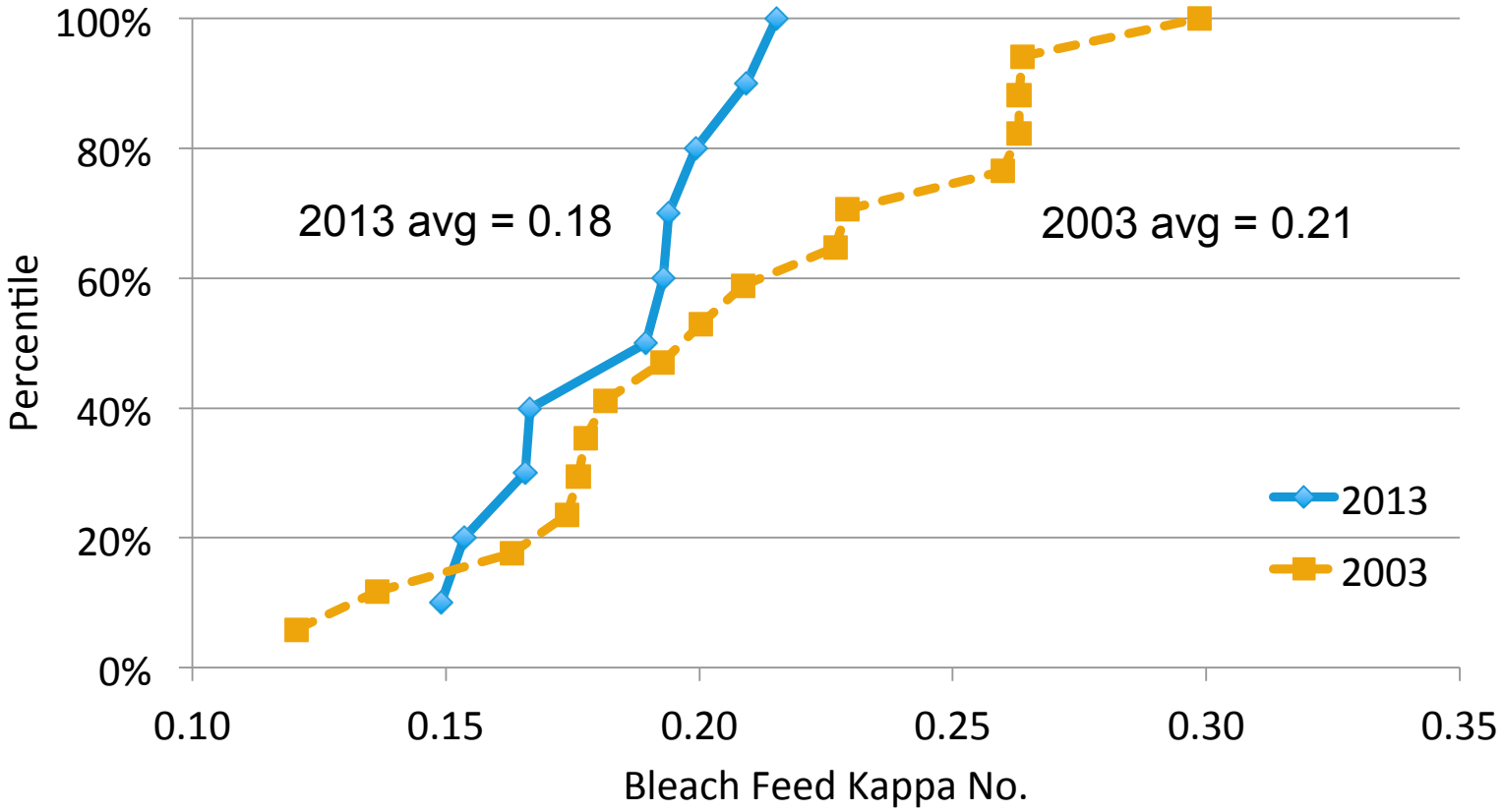
Do Stage

- Operating Conditions
  - 65% low cons. (LC) 35% medium cons. (MC)
  - 33 minutes retention time (25 to 75 min. range)
  - 50°C to 60°C
  - Operate to “zero” residual
  - End pH 1.5 – 3.0
  - Kappa Factor
    - Conventional Softwood 0.18 (0.15 – 0.22)
    - O_2-Softwood 0.27 (0.17 – 0.43)

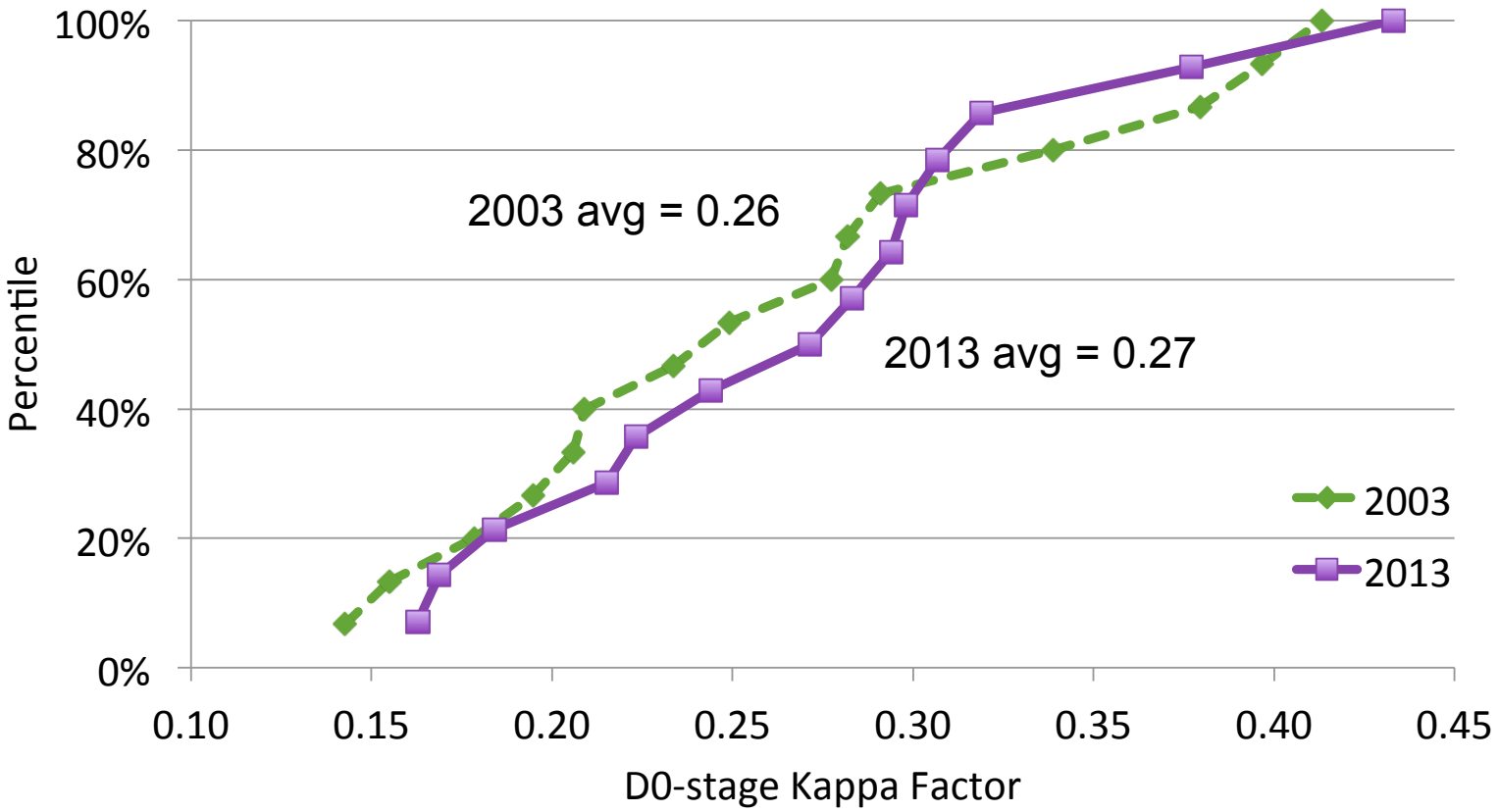
Do Stage Control

- All bleach plants have installed on-line Kappa Analyzers
- Most bleach plants use some form of Kappa Factor and compensated Kappa Factor control in D_0
- The majority of mills use the E_1-stage kappa no. for D_0/Eop control
- Few use post Eop brightness

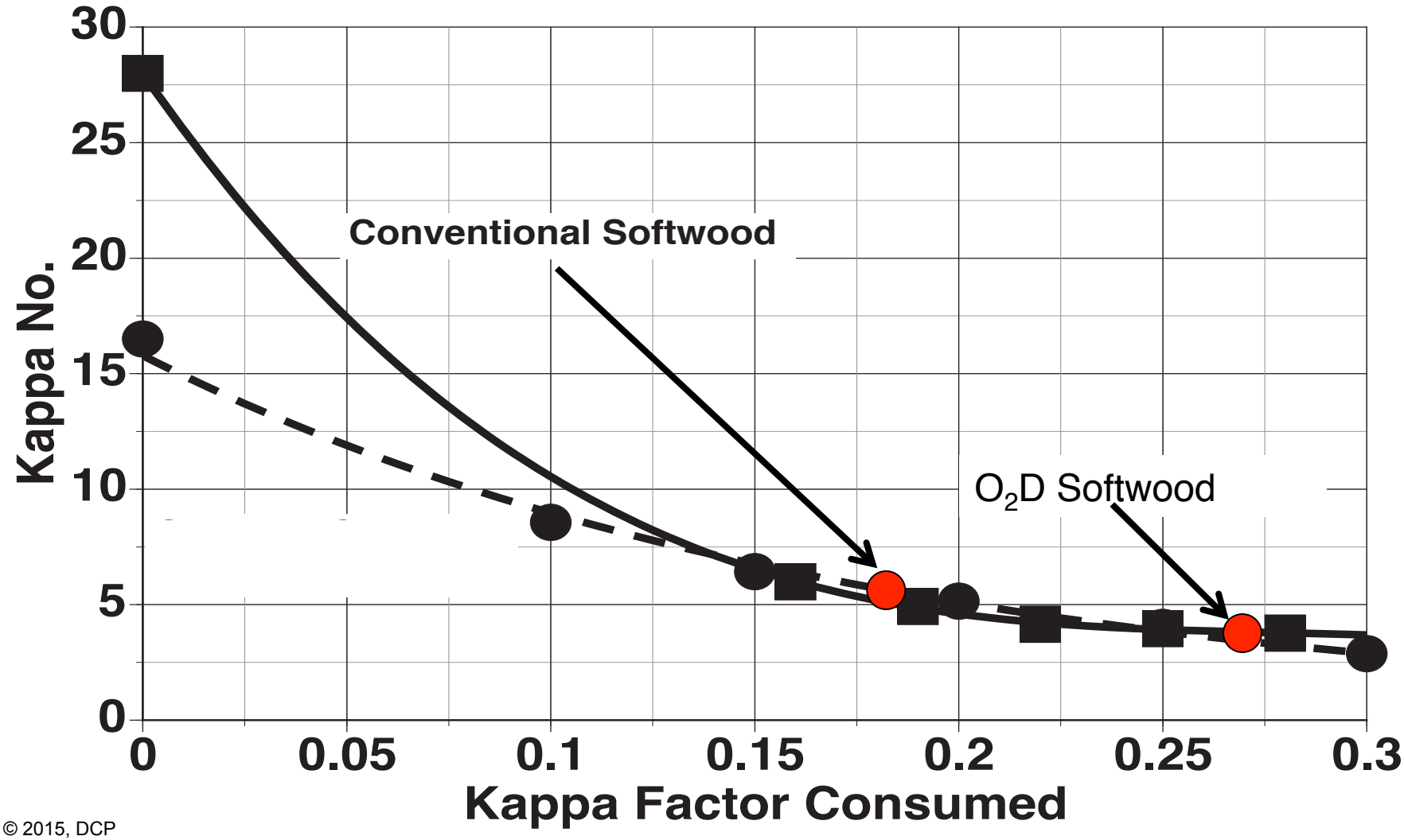
Conventional Softwood Do Kappa Factor



Oxygen Delignified Softwood Do Kappa Factor



Delignification with ClO_2



Thanks!