Brightening with Chlorine Dioxide: The D1 and D2 stages

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PAPTAC Bleaching Committee, Fall 2015 Meeting
Nanaimo, BC – September 21, 2015

ClO_2 Brightening Stages (D1 & D2)

- Purpose
  - To brighten pulp to desired target
  - To eliminate shives
  - To decolourize bleachable dirt
- Options
  - D_1 – single ClO_2 stage
  - $D_1E_2D_2$ or D_1EpD_2 – two ClO_2 stages with full alkaline extraction in-between (with or without peroxide reinforcement)
  - $(D_1E_2)D_2$ – two ClO_2 stages with simple neutralization in between, without washing (also known as "DnD")
  - D_1D_2 – two ClO_2 stages with only washing in between

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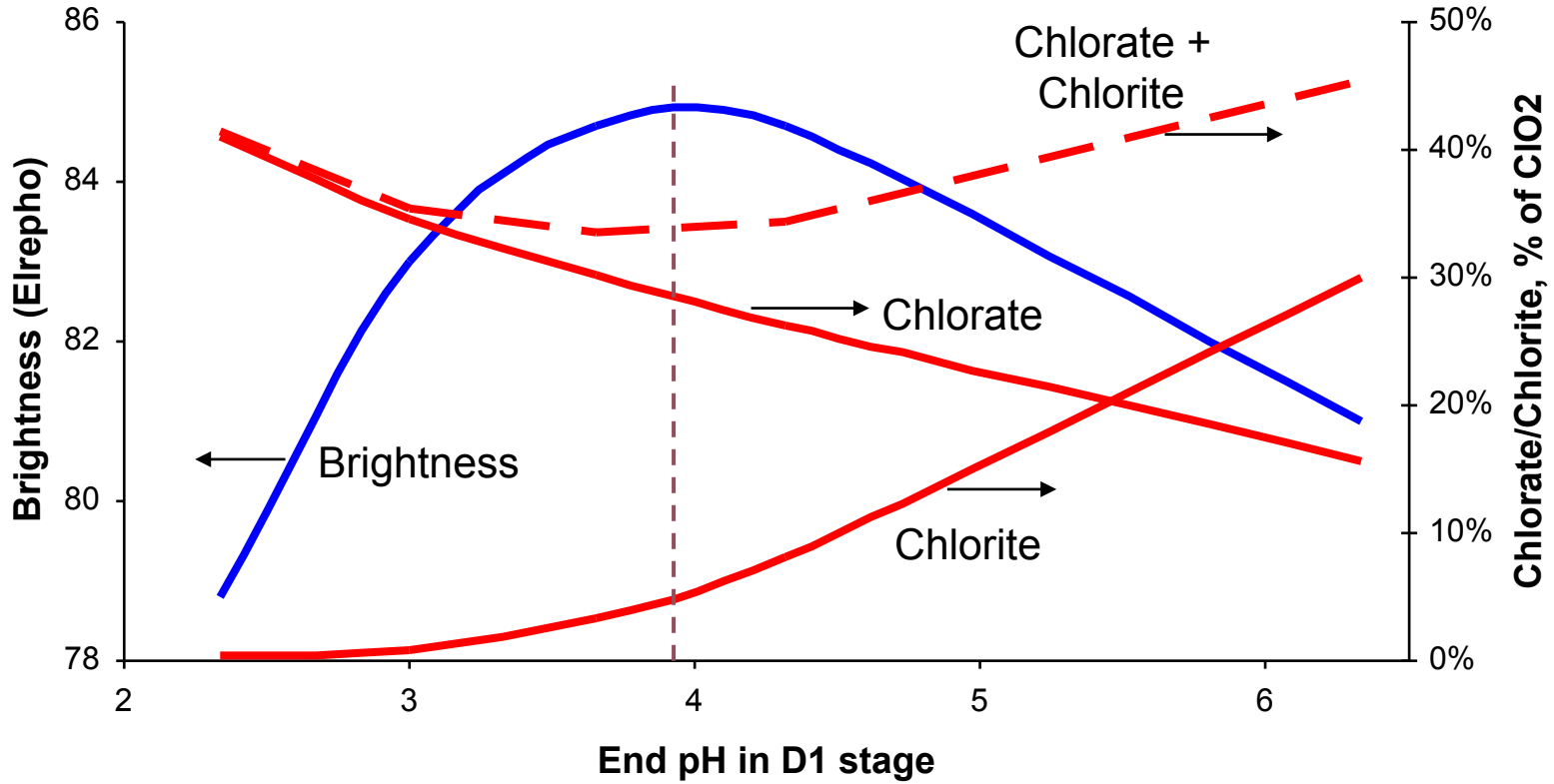
ClO_2 Brightening Stages (D1 & D2)

1) Impact of pH
2) Time & Temperature
3) Impact of Eop Washing
4) D1-stage Brightness Development
5) Brightness Reversion or Brightness Loss?

Effect of D1-stage pH on Brightness

Rapson's pH-Brightness curve; optimum end pH for brightening is 3.8-4.0.
Lab bleaching using 5-kappa SWD and 1% ClO_2 (10 kg/odmt)

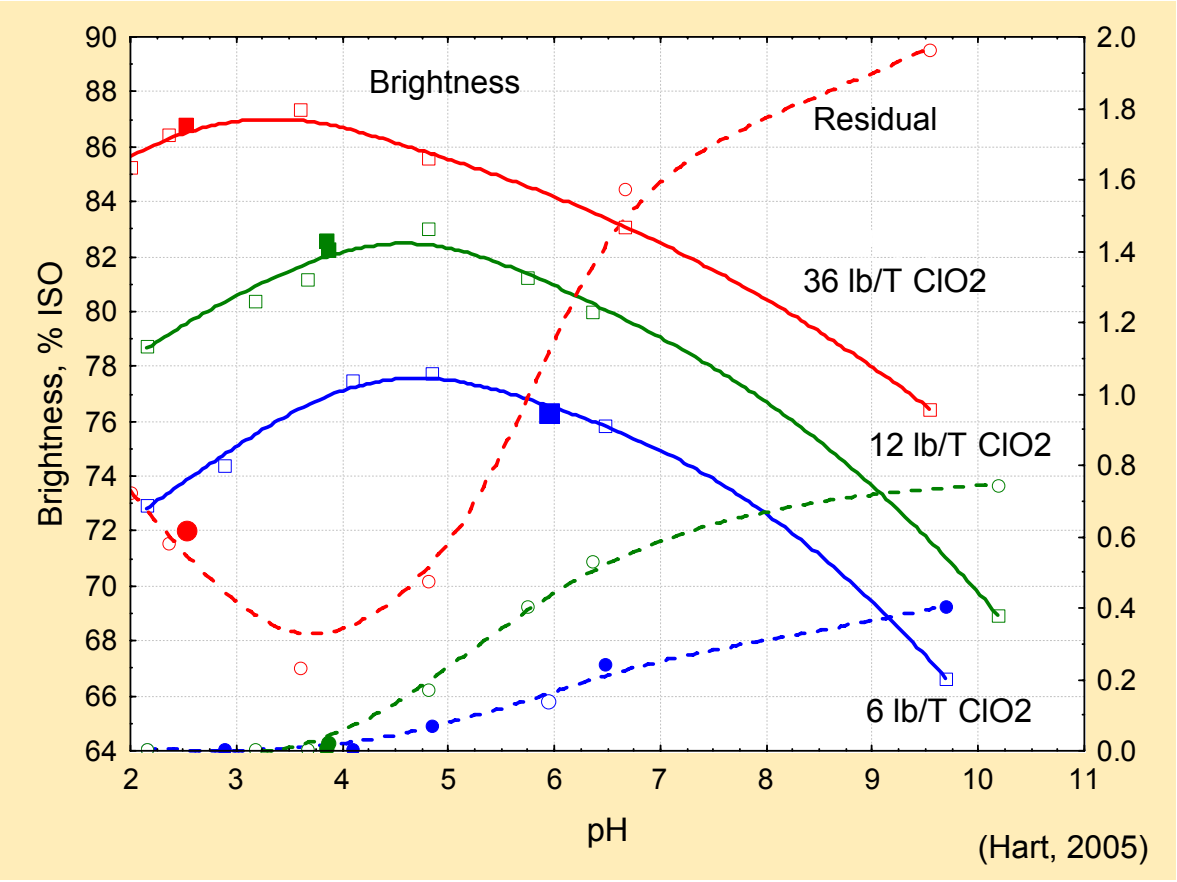


(Rapson, 1979)

Effect of pH on Brightness (SWD)

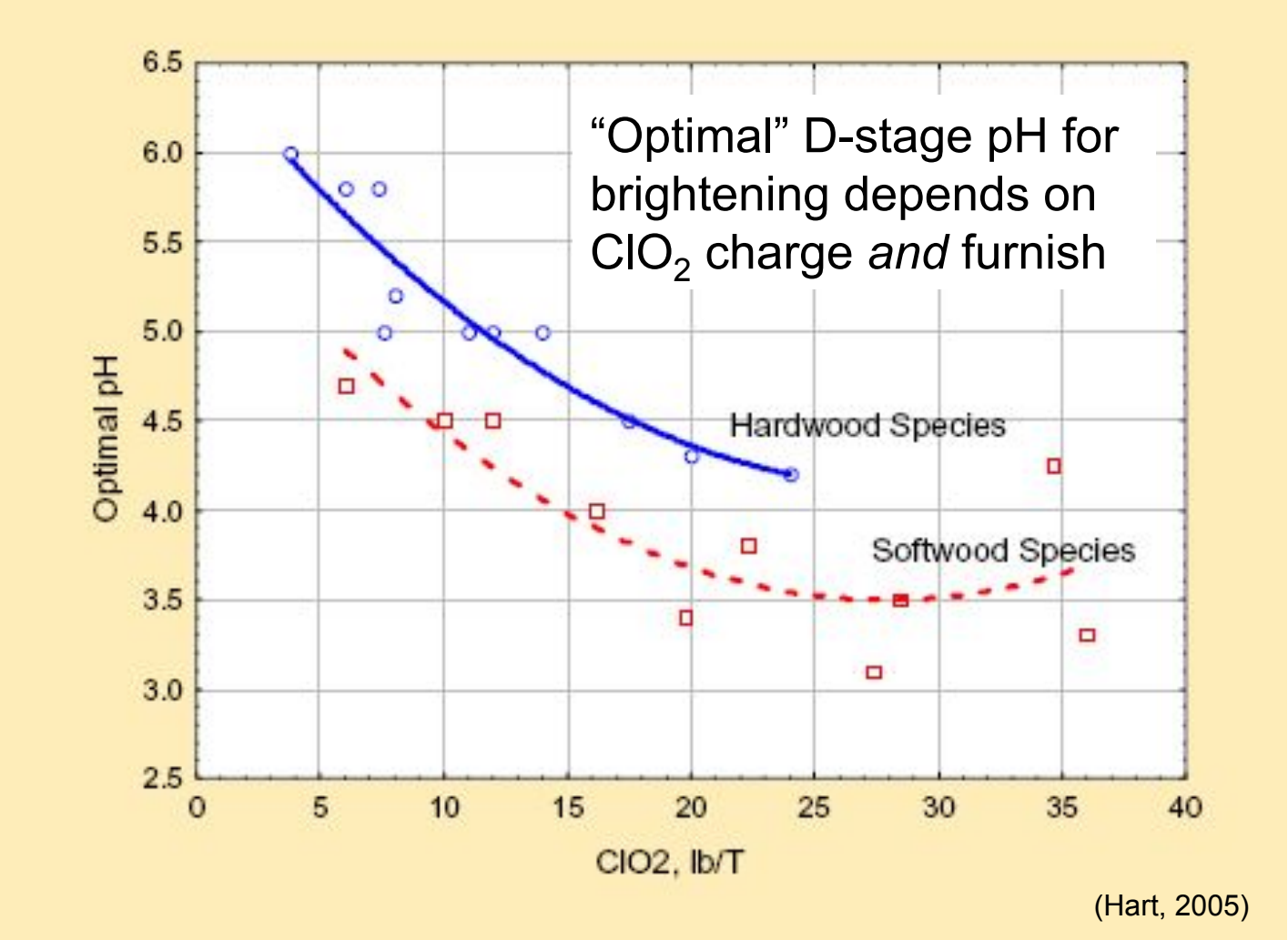
- New studies carried out to vary Rapson's conditions:
- For softwood pulp with high ClO_2 charges, the optimum D1-stage end pH was close to 3.8
- However at lower ClO_2 charges, the optimum end pH increased
- Results even more pronounced for HWD

Softwood: D_1 stage: 4.1 kappa, 71°C for 180 min.



Note: (20 lb/T = 10 kg/mt = 1% on pulp)

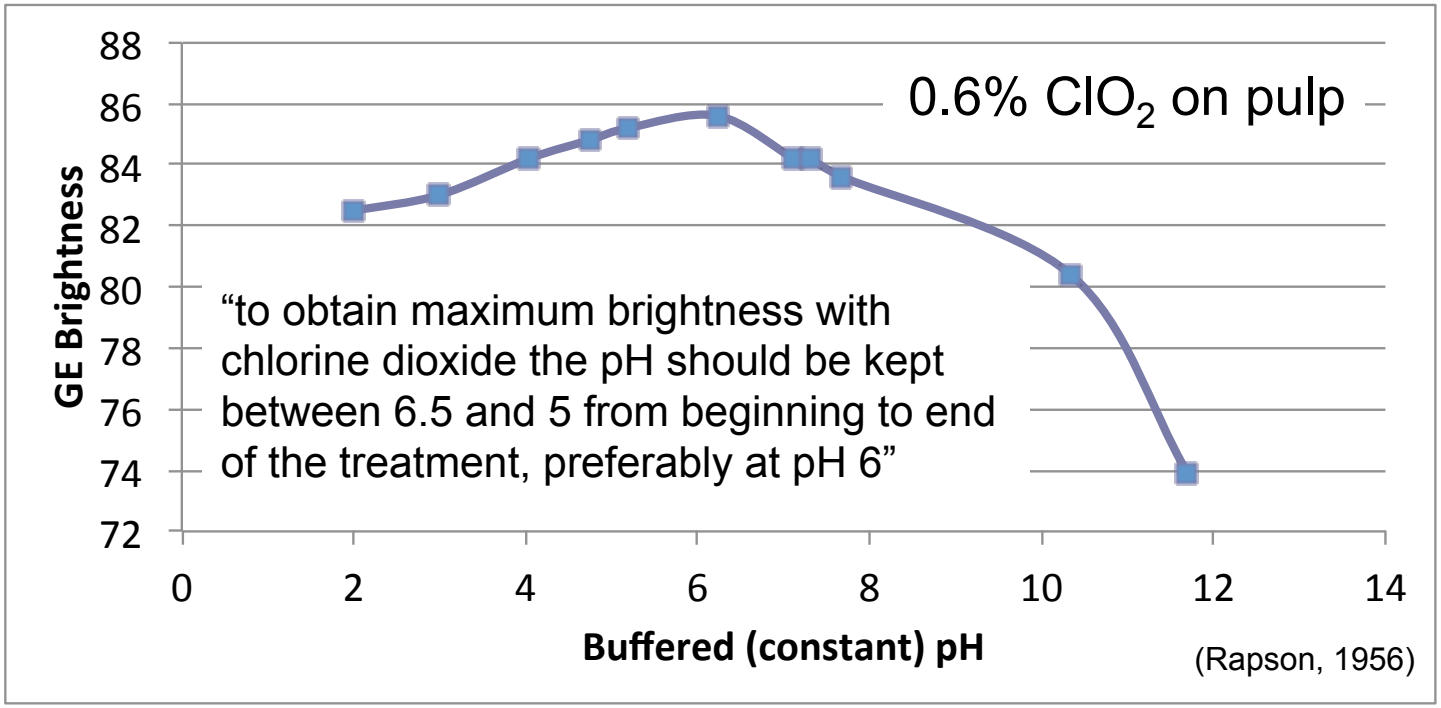
Impact of D1-stage pH (II)



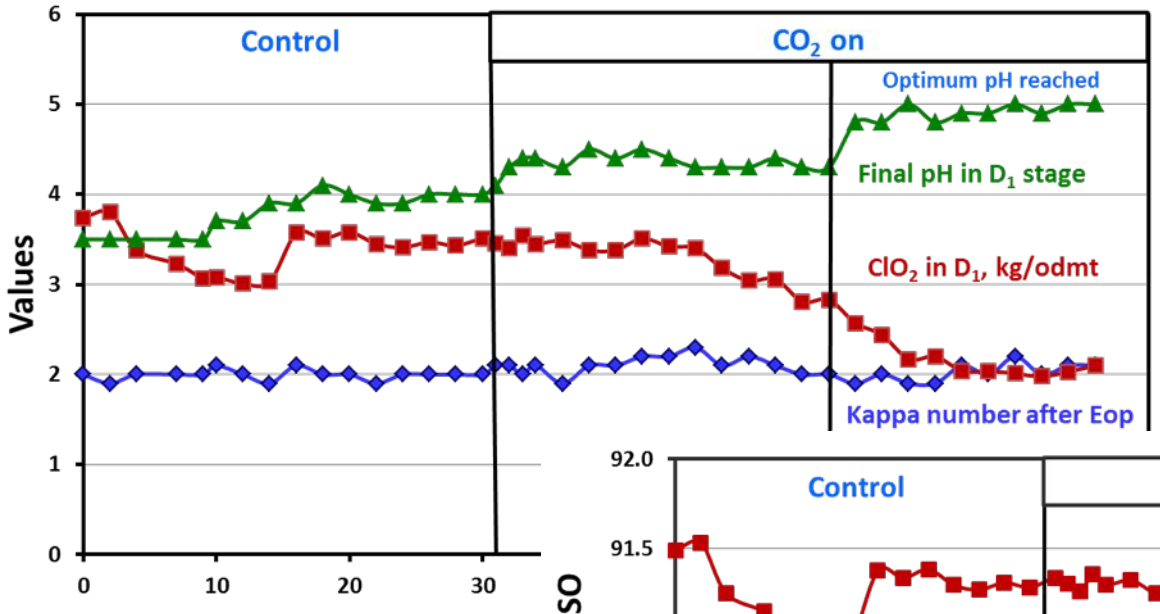
(Hart, 2005)

D1 Bleaching at *Constant* pH

Earlier studies by Rapson used laboratory buffer solutions (phosphates) to maintain a *constant* pH.

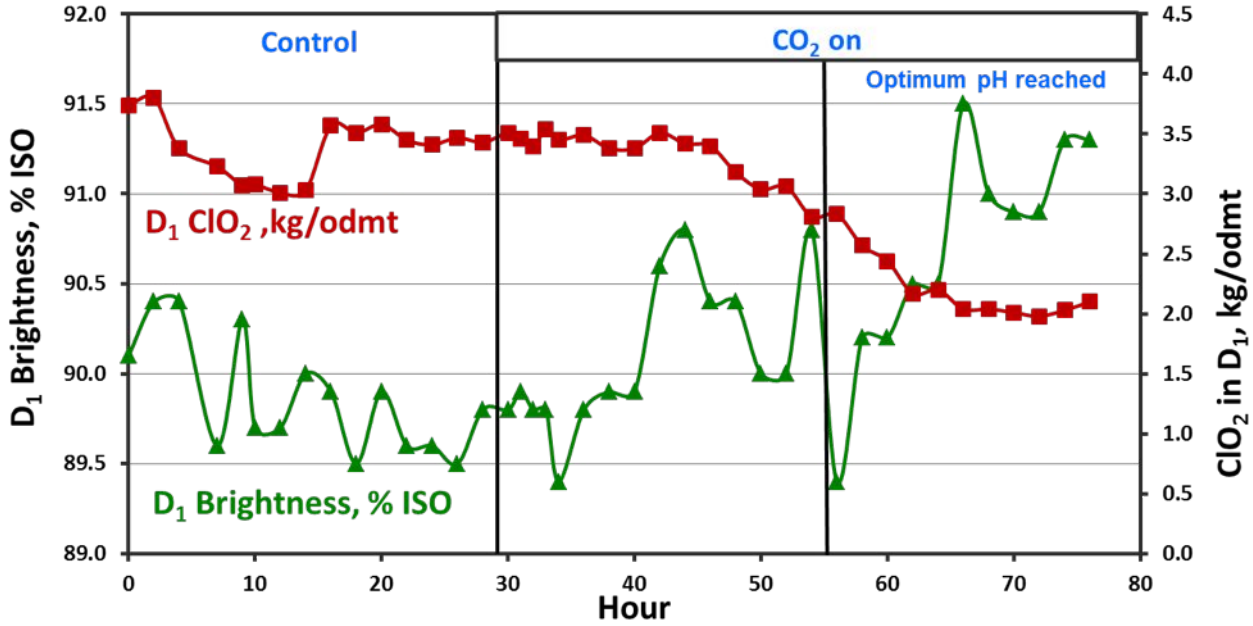


"Near Neutral" Brightening



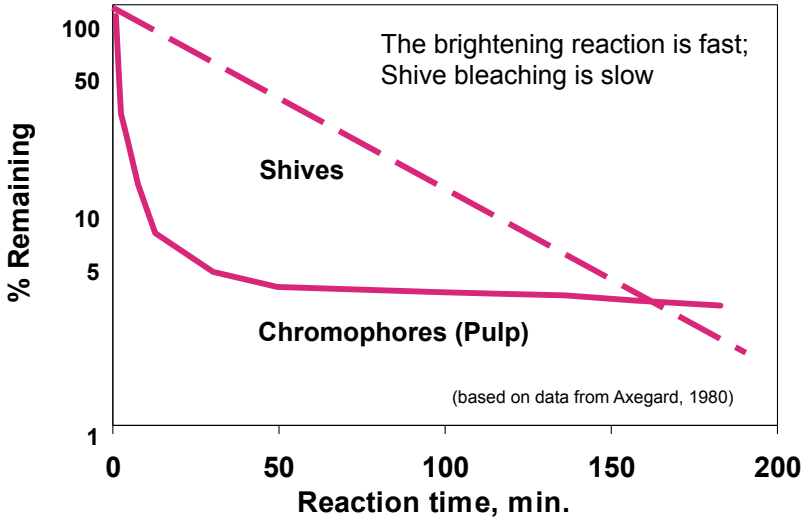
Buffering the final D stage with $NaHCO_3$ allows for higher pH and more efficient use of ClO_2

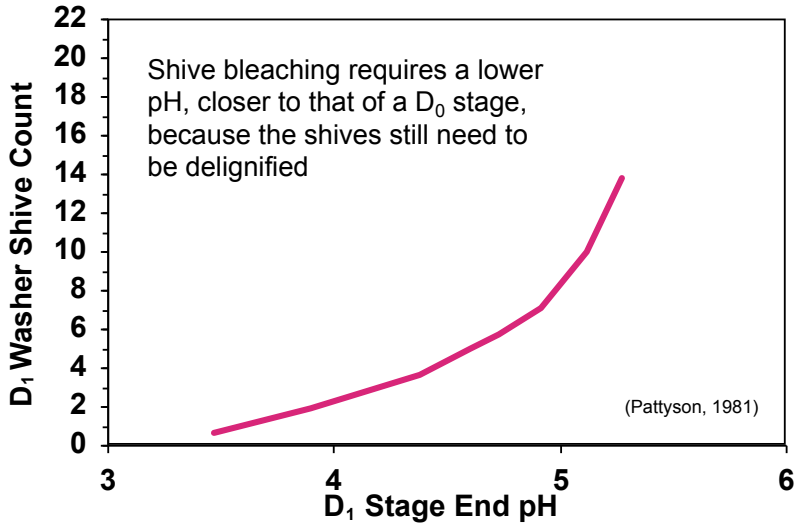
(Audet, 2014)



Bleaching Shives

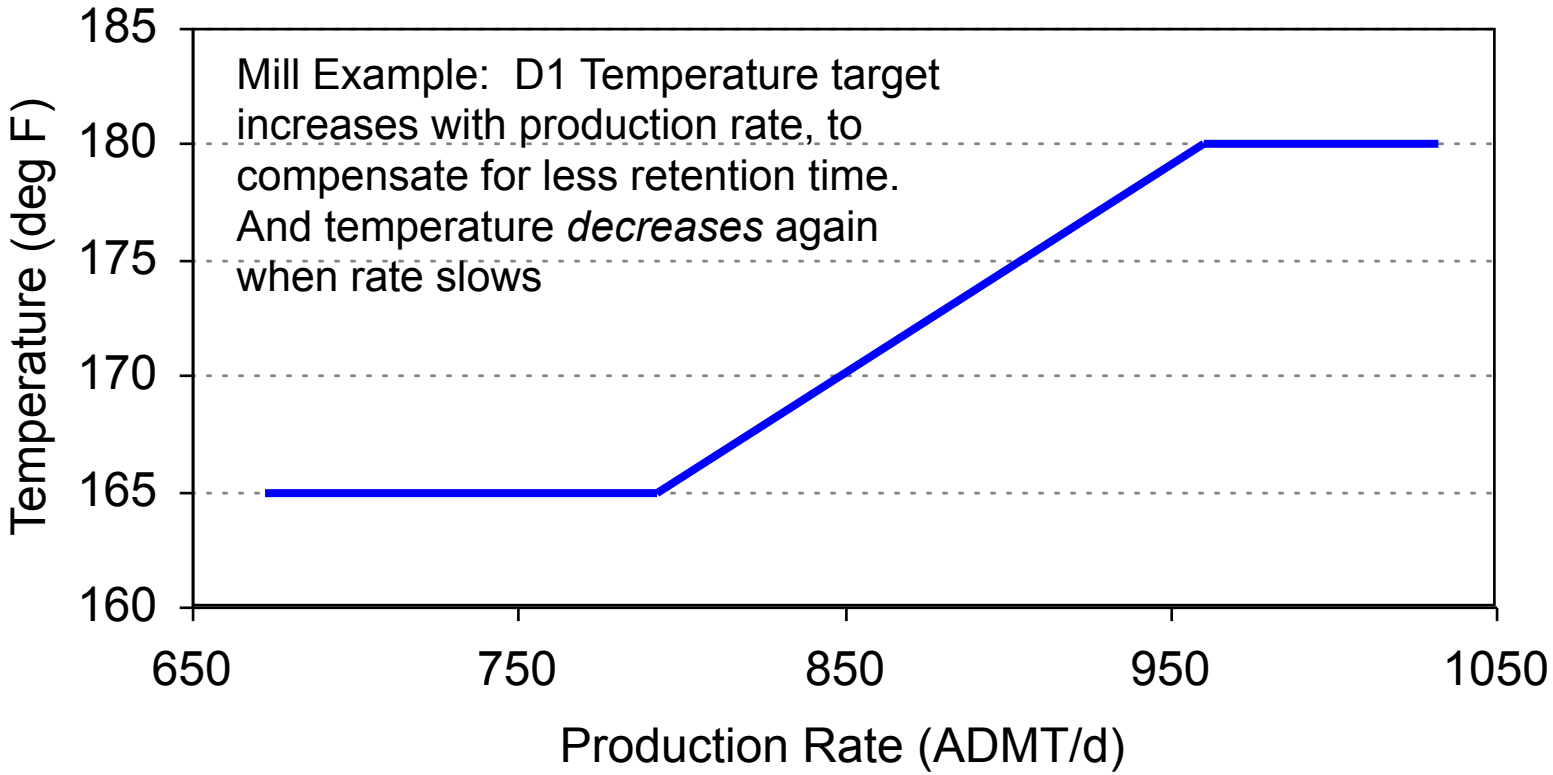
- Shive bleaching is favoured by:
  - Long reaction time (time needed for penetration)
  - Lower temperature (shives bleach slower than fibres)
  - Lower pH (delignification vs. brightening)
- Because of long retention time, D1 stage is the preferred bleaching stage to remove shives
- Lower pH in D1 means a trade-off between brightness development and shive removal
  - Must keep end pH <3.5





D_1-stage Temperature & Time

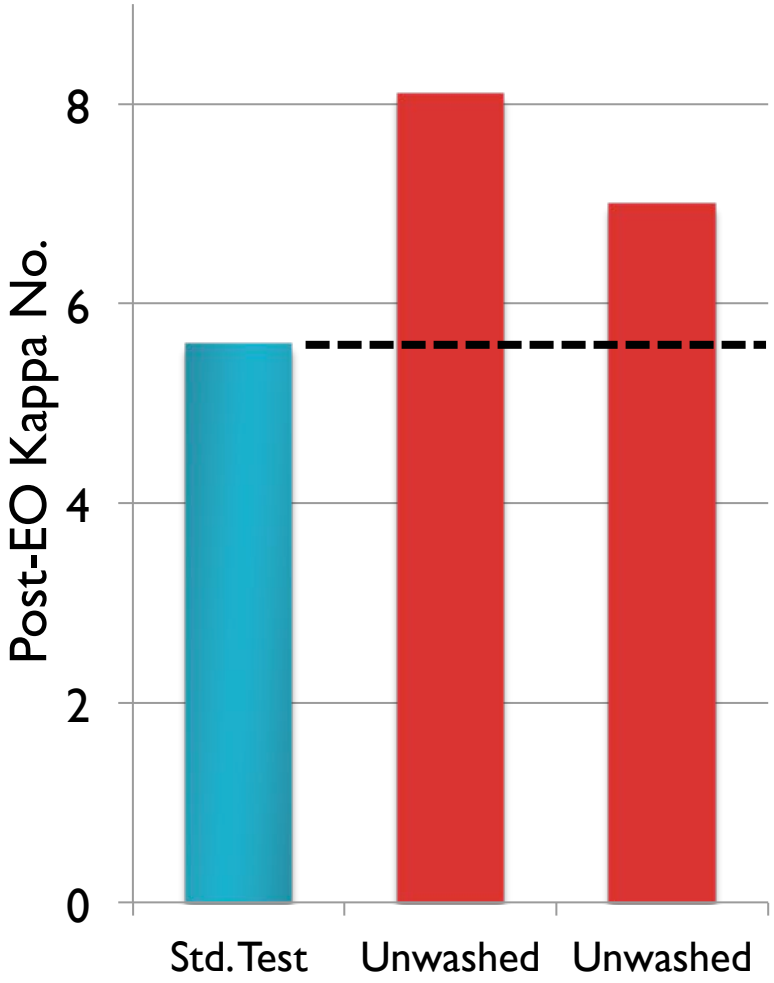
Higher temperatures make ClO_2 react ***faster***, not better.
Rule-of-thumb: an increase of 10°C (18°F) doubles the rate of reaction



Eop Washer Carryover

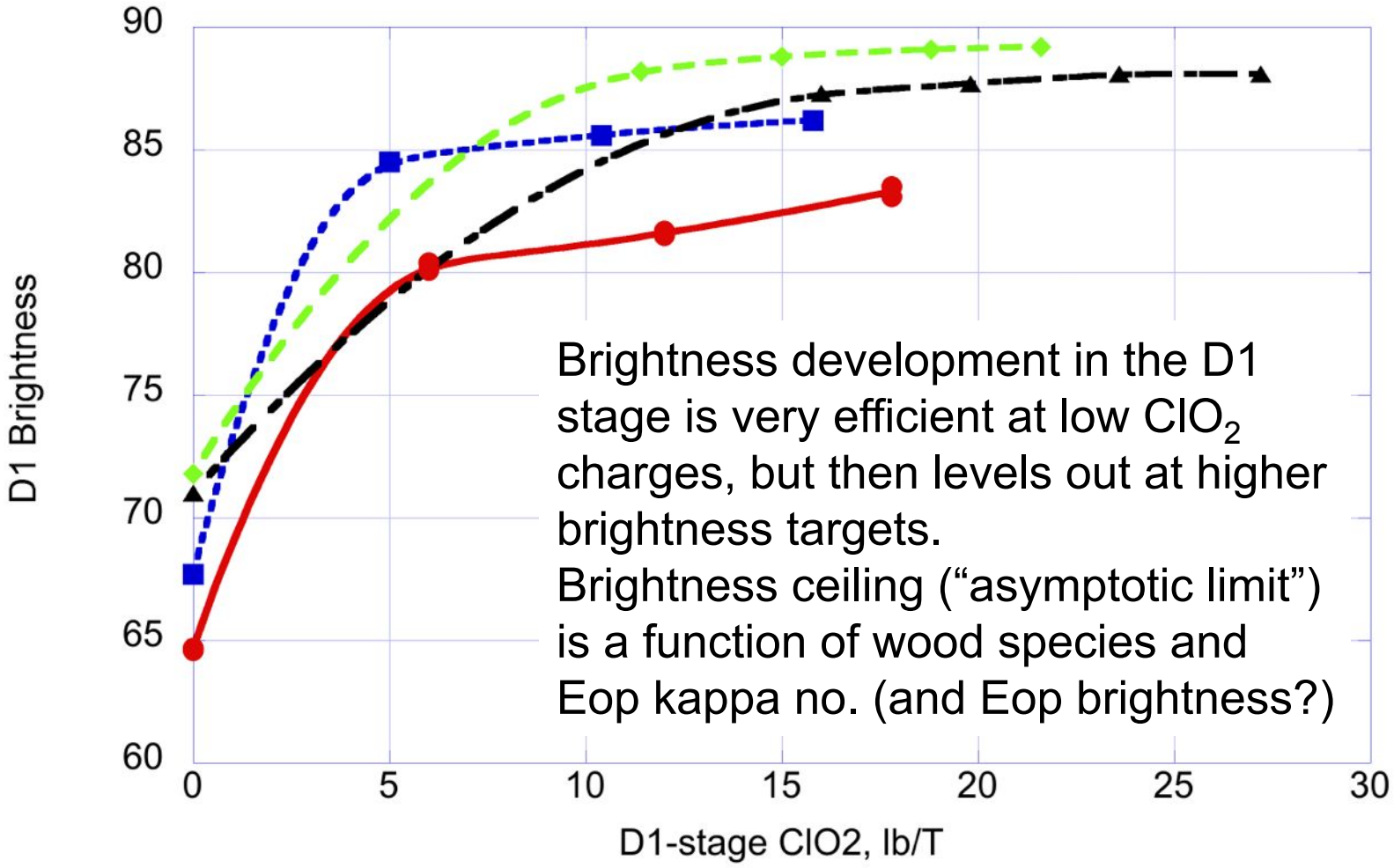
Eop washer carryover consumes ClO_2 in the D1 stage

"Wet" Kappa No. Testing

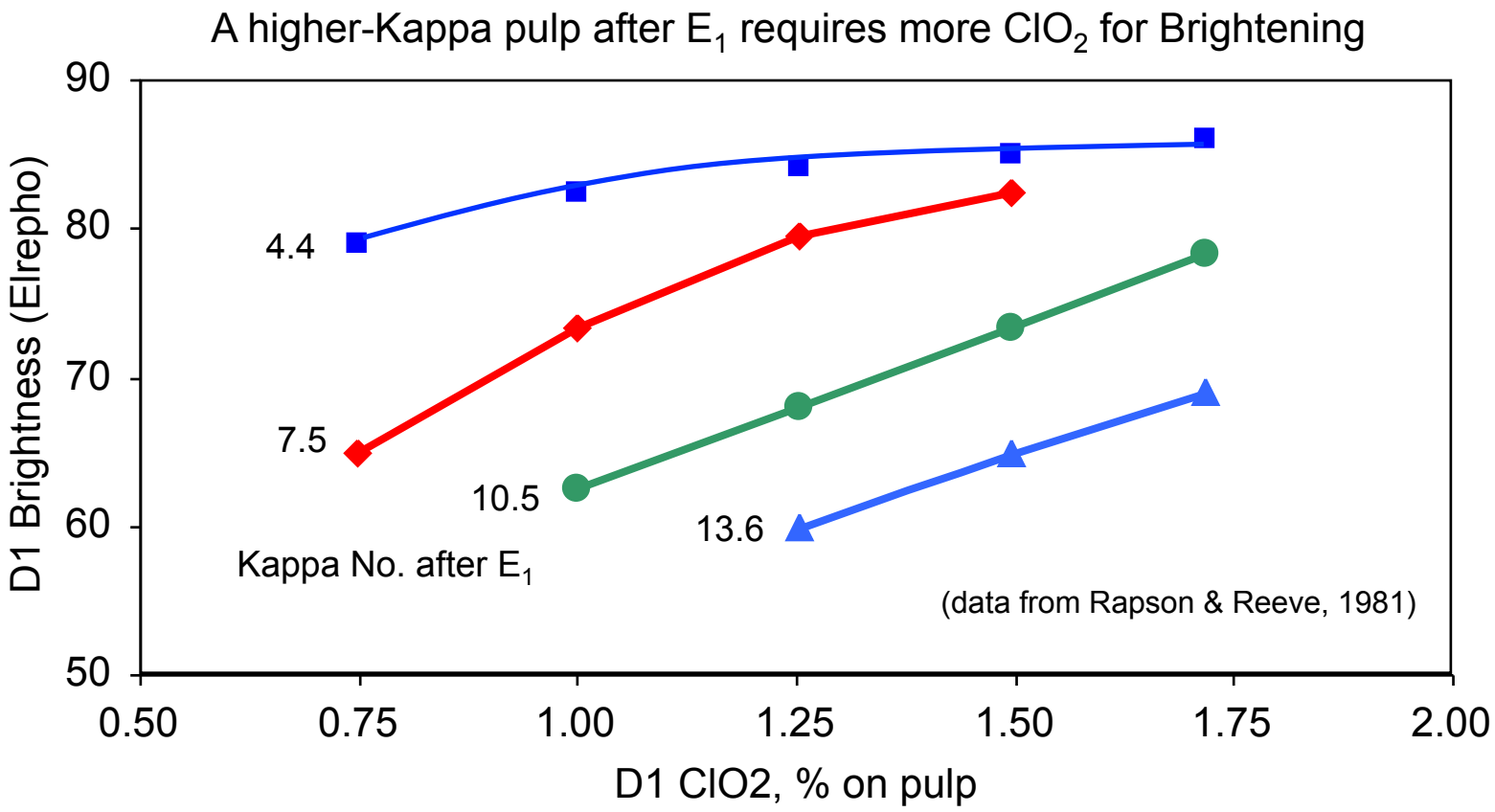


- "Wet" or "unwashed" kappa no. test includes the filtrate surrounding the pulp sample
  - Measures contribution of carryover
- Example on left indicates that on average, 25% of the ClO_2 added to the D1 stage is being consumed by EO carryover

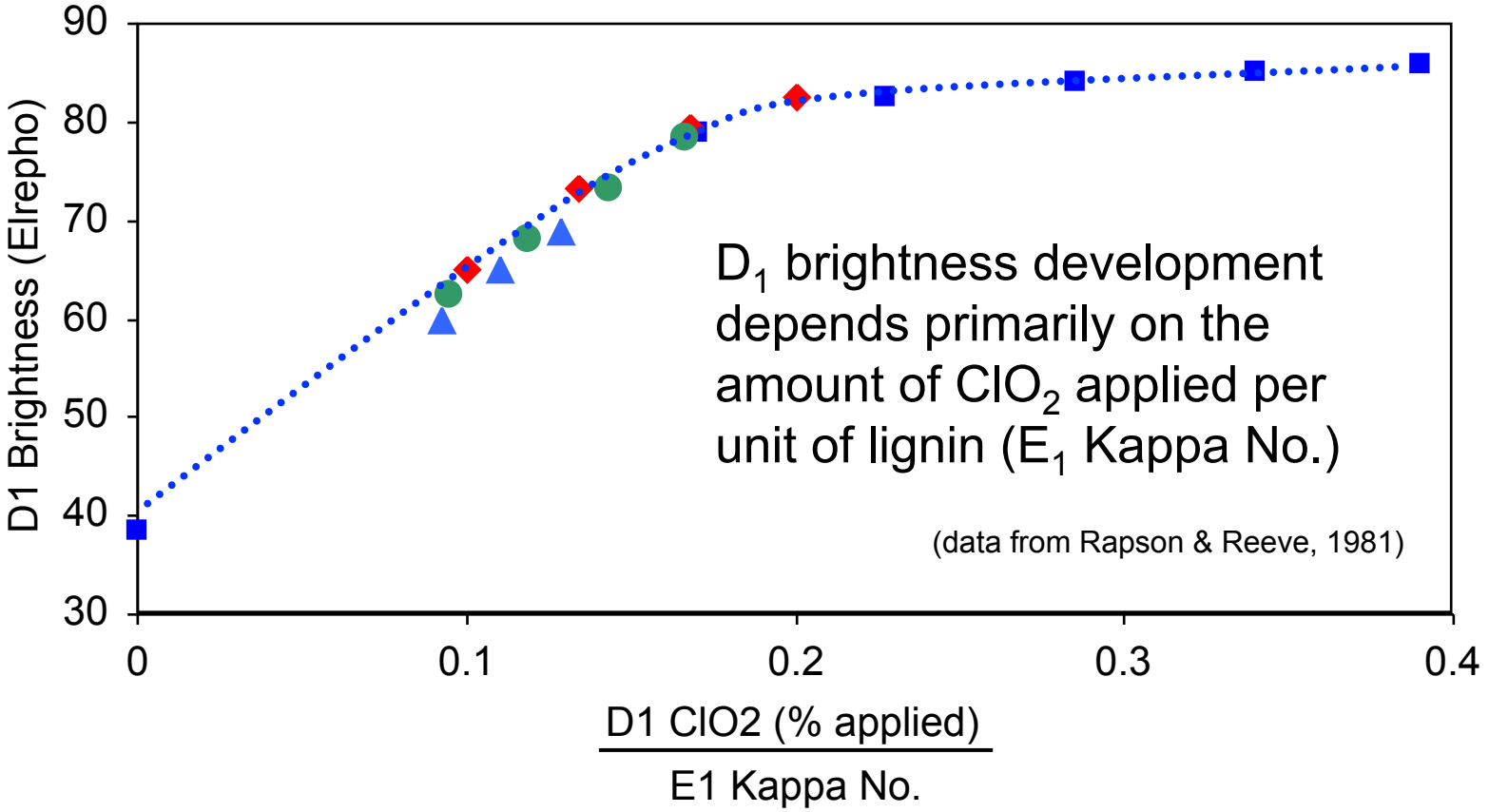
D1 Brightening - Hardwood



D_1-stage Brightening

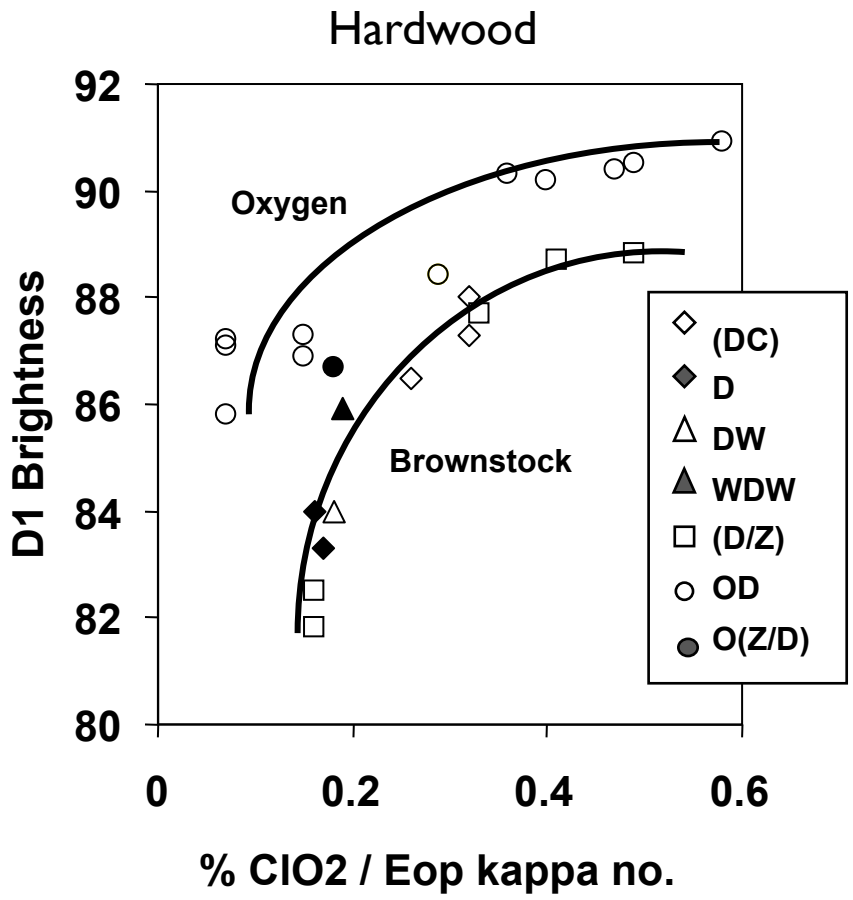


D_1-stage Brightness Development



Chlorine Dioxide Brightening

- D_1-stage brightening efficiency depends on the ClO_2 charge and the Eop Kappa No.
- For HWD, D_1-stage brightening efficiency decreases when ClO_2 use exceeds ~0.25% ClO_2 per Eop kappa no. (~2.5 kg/mt or ~5 lb/T per kappa)



(McDonough, 1999)

Brightness Reversion

- Light, heat, certain chemicals, and aging can all form (or re-form) chromophores in the pulp
  - Fibres will absorb more light and brightness is decreased
  - “yellowing”
- Possible causes:
  - Zero residual & high temperature in tower, before dilution/neutralization and washing
  - Residual lignin
    - Poor Eop extraction stage
  - Oxidized cellulose
    - Hypochlorite, Ozone, even ClO_2 under wrong conditions
  - Drying or baling at high temperature
- Reversion cannot be reversed without adding more bleaching chemicals

Brightness Loss

- A decrease in brightness that takes place when light-absorbing chemicals are deposited onto the fibres
- Possible causes:
  - Caustic
  - Dyes
  - Poor-quality white water
  - Metal ions
    - esp. Manganese (forms MnO_2)
- Brightness loss can be reversed if the material can be washed out of the pulp

Reversion or Loss?

- Check brightness measurement
  - Different brightness meters in different departments?
  - Different procedures for testing or handsheet-making?
- Check effects of wash water & white water; compare handsheets made with:
  - Deionized water
  - Acidified DI water (loss)
  - White water (loss)
  - Filtered white water (loss)

ClO_2 Brightening Stages: D1 & D2

- Thank you
- Questions?