ENVIRONMENTALLY FRIENDLY PROCESS IMPROVEMENTS USING CARBON DIOXIDE

Ann-Charlotte „Lotta“ Jansson, Linde AG, Linde Gas Division

Monica Ortiz-Cordova, Linde Canada Limited

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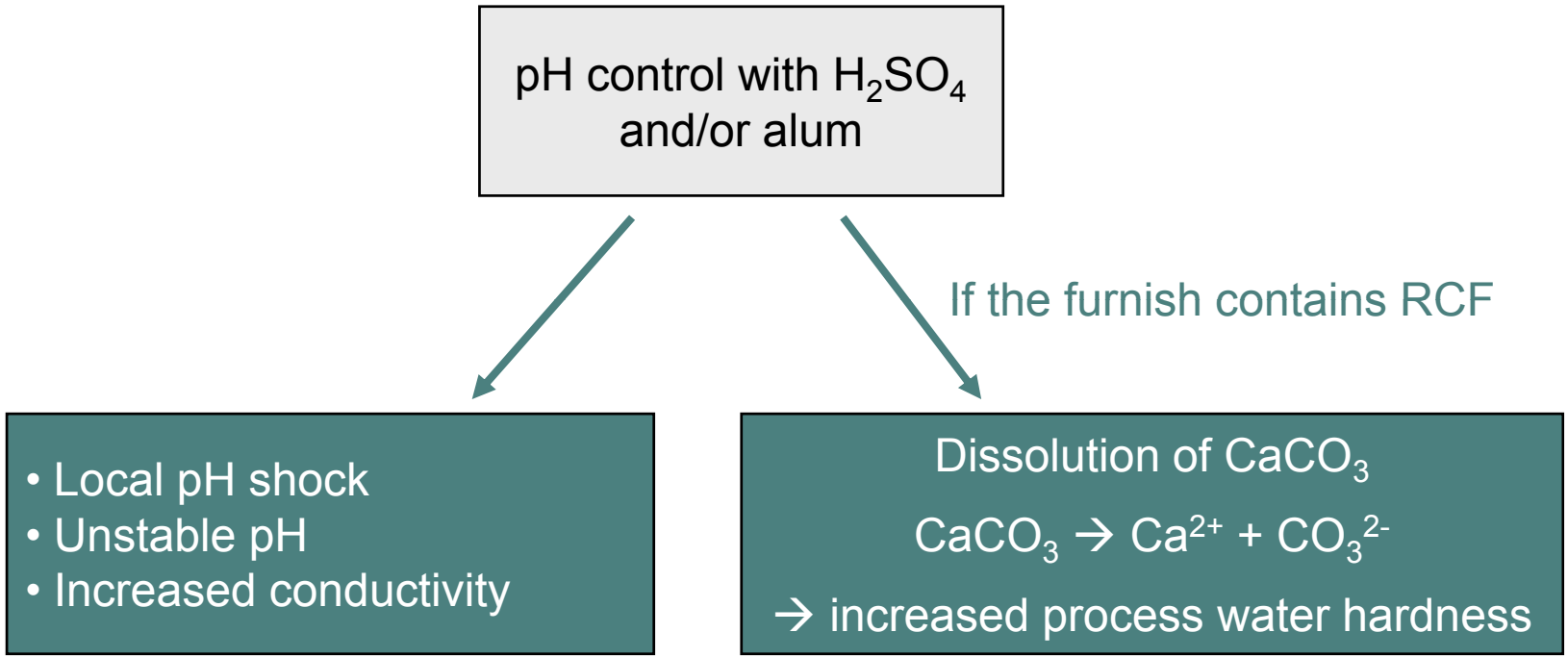
RETHINK PAPER:
Lean and Green

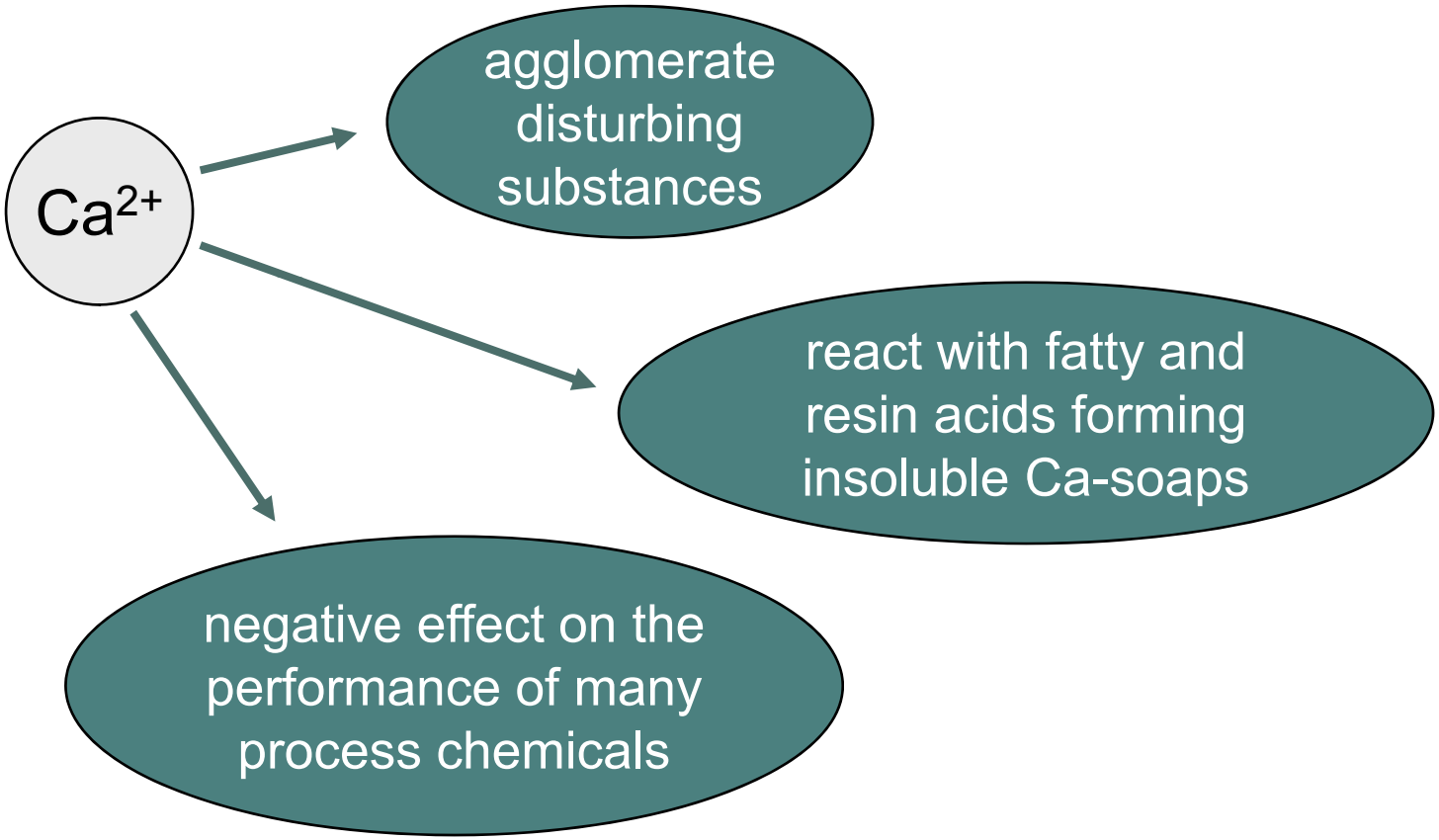
Introduction

- Carbon dioxide – environmentally friendly process chemical
- Process improvements
- Easier to reduce fresh water consumption

Packaging Papers at Neutral/Pseudo-Neutral pH



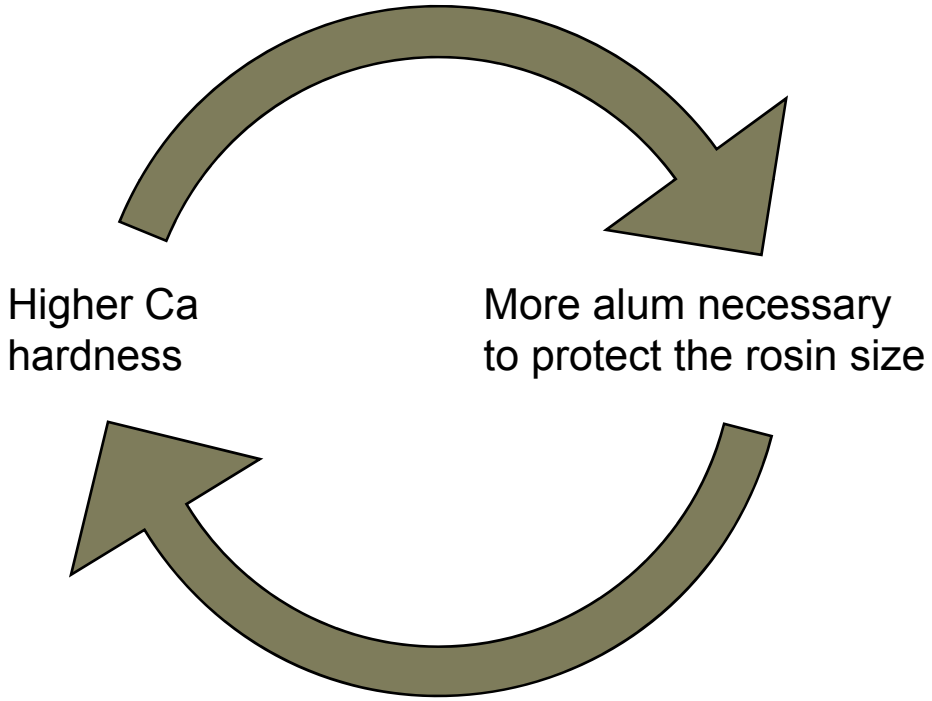
Negative Impact of Dissolved Calcium Ions on Papermaking



Effect of Calcium Ions on Rosin Sizing

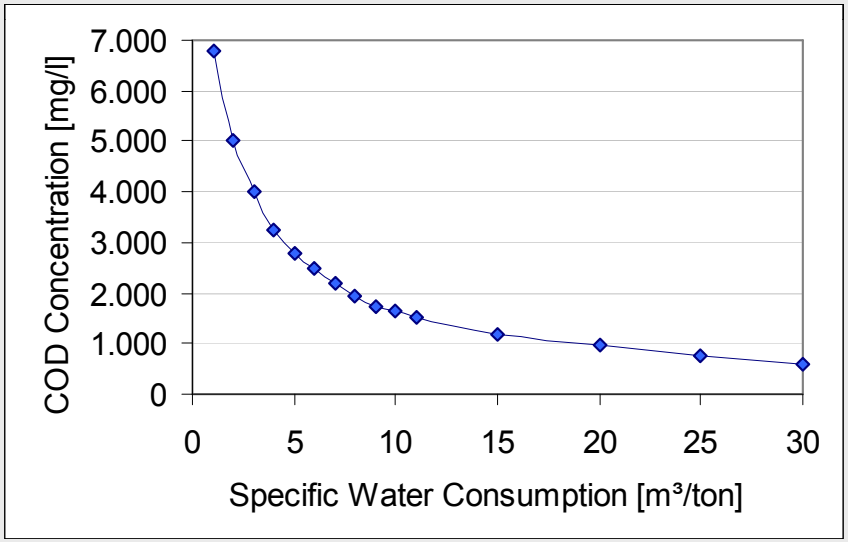
Low calcium hardness is better than total absence of calcium (Lab studies by Farley 1992)

High calcium hardness has a negative effect



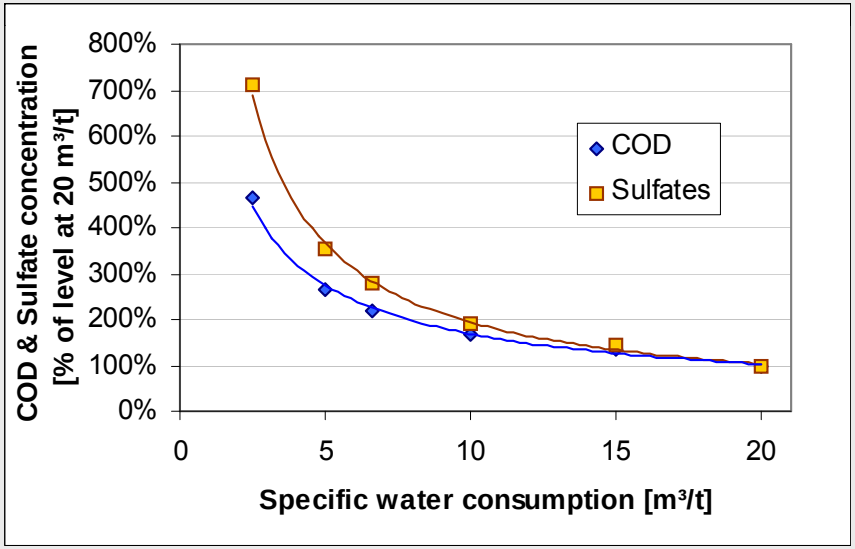
Change in COD and Sulfur Load when Reducing Specific Water Consumption

COD dependence on fresh water consumption for mechanical fiber containing printing grades



Source: Möbius (1993)

Inorganics have low affinity to fibers → accumulate faster than organic substances



Source: Data from Hermosilla et.al. (2010)

Improved Pulp Washing with Carbon Dioxide

- Patented method
- Reduces carry-over from the fiber line to the paper machine and/or
- Reduces the wash water usage
- Other possible benefits are
  - increased runnability and capacity
  - reduced effluent load
  - reduced maintenance cost
  - reduced defoamer consumption

Carbon Dioxide-Based Applications for Papermaking

- Patented methods
- Based on CO_2 only or on a combination of CO_2 and NaOH
- Dissolution of $CaCO_3$ can be significantly reduced or completely avoided
- Improved pH stability

Applications based on the use of carbon dioxide only, such as **CODIP™** and **GRAFICO™** will hereafter be referred to as the **"CO_2 method"**

Carbon Dioxide-based Applications Prevent Dissolution of Calcium Carbonate

- No pH shock at the addition point
- Increased concentration of carbonates
- pH stabilization

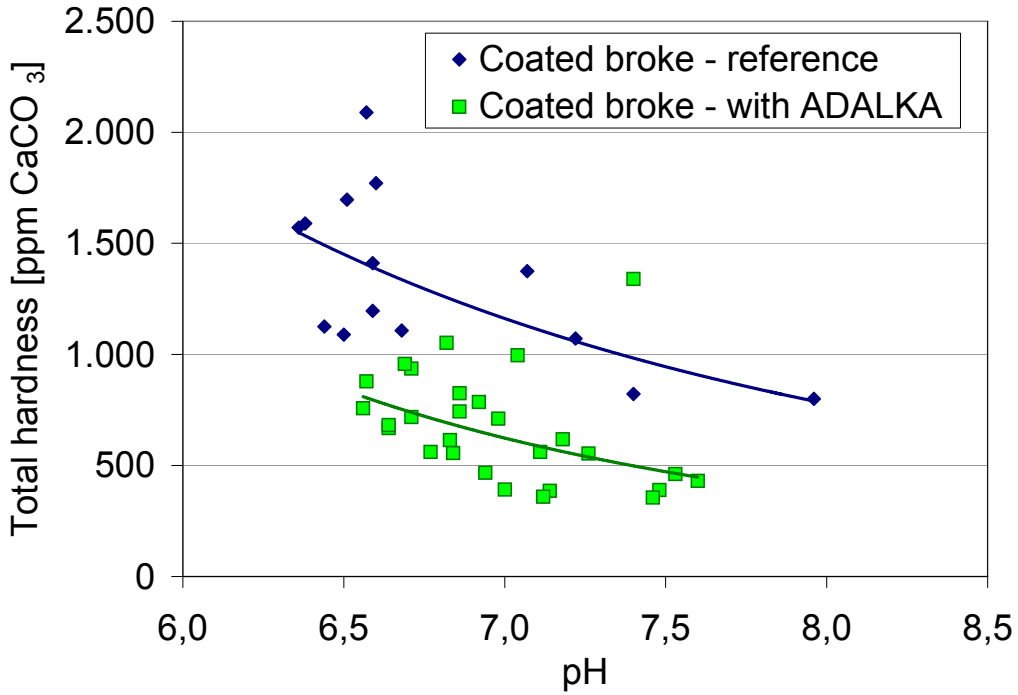
$CaCO_3$ (s) ↔ Ca^{2+} (aq) + CO_3^{2-} (aq)

$Ks.p(CaCO_3) = [Ca^{2+}][CO_3^{2-}]$

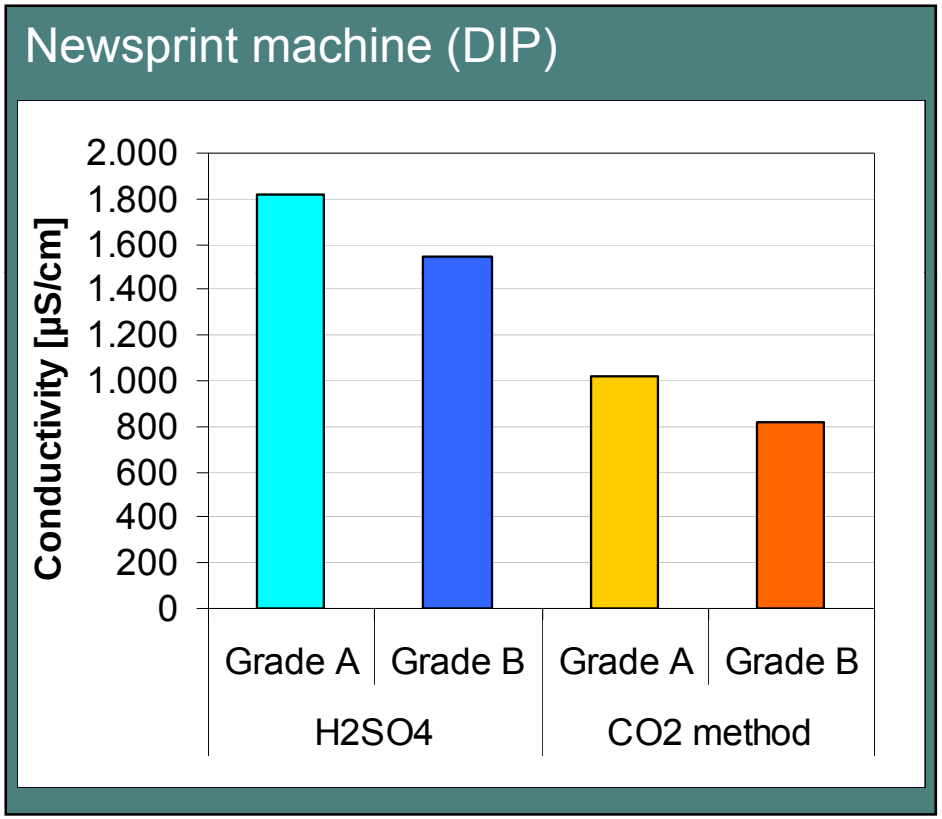
$Ks.p(CaCO_3) = [Ca^{2+}][CO_3^{2-} + \mathbf{CO_3^{2-}\ (added)}]$

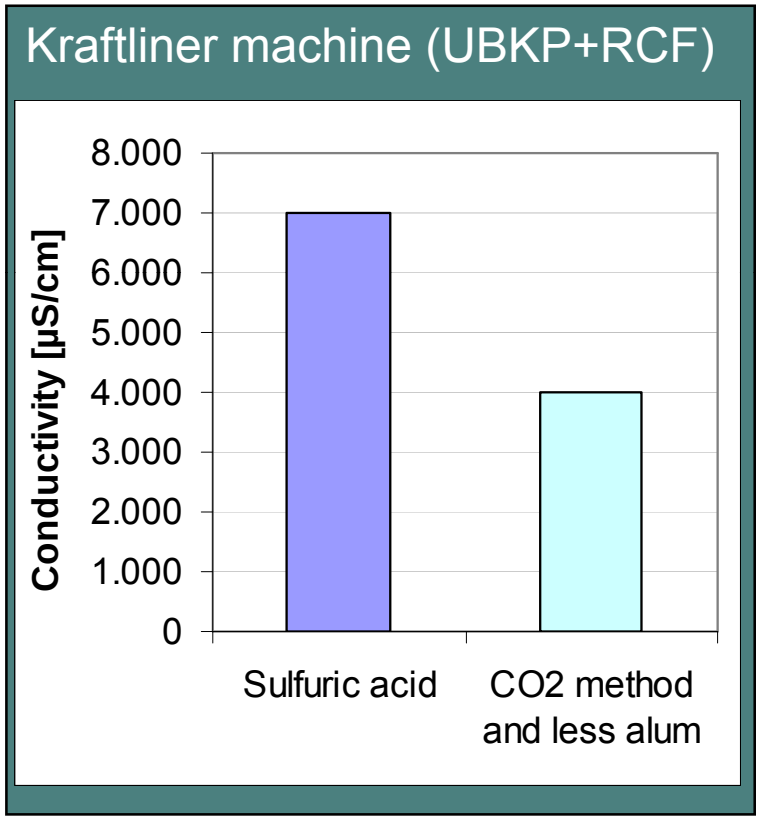
Acid neutralization:
$HCO_3^- + H^+ \leftrightarrow H_2CO_3$

Base neutralization:
$HCO_3^- + OH^- \leftrightarrow H_2O + CO_3^{2-}$



Lower Conductivity When Using the CO_2 Method





Less Pitch Deposits When Using the CO_2 Method

pH shocks and high concentrations of dissolved calcium can trigger deposition of pitch

Process

Unbleached Kraft, RCF, Rosin sizing

Problem

Ca-resinate deposits

Carbon dioxide based solution

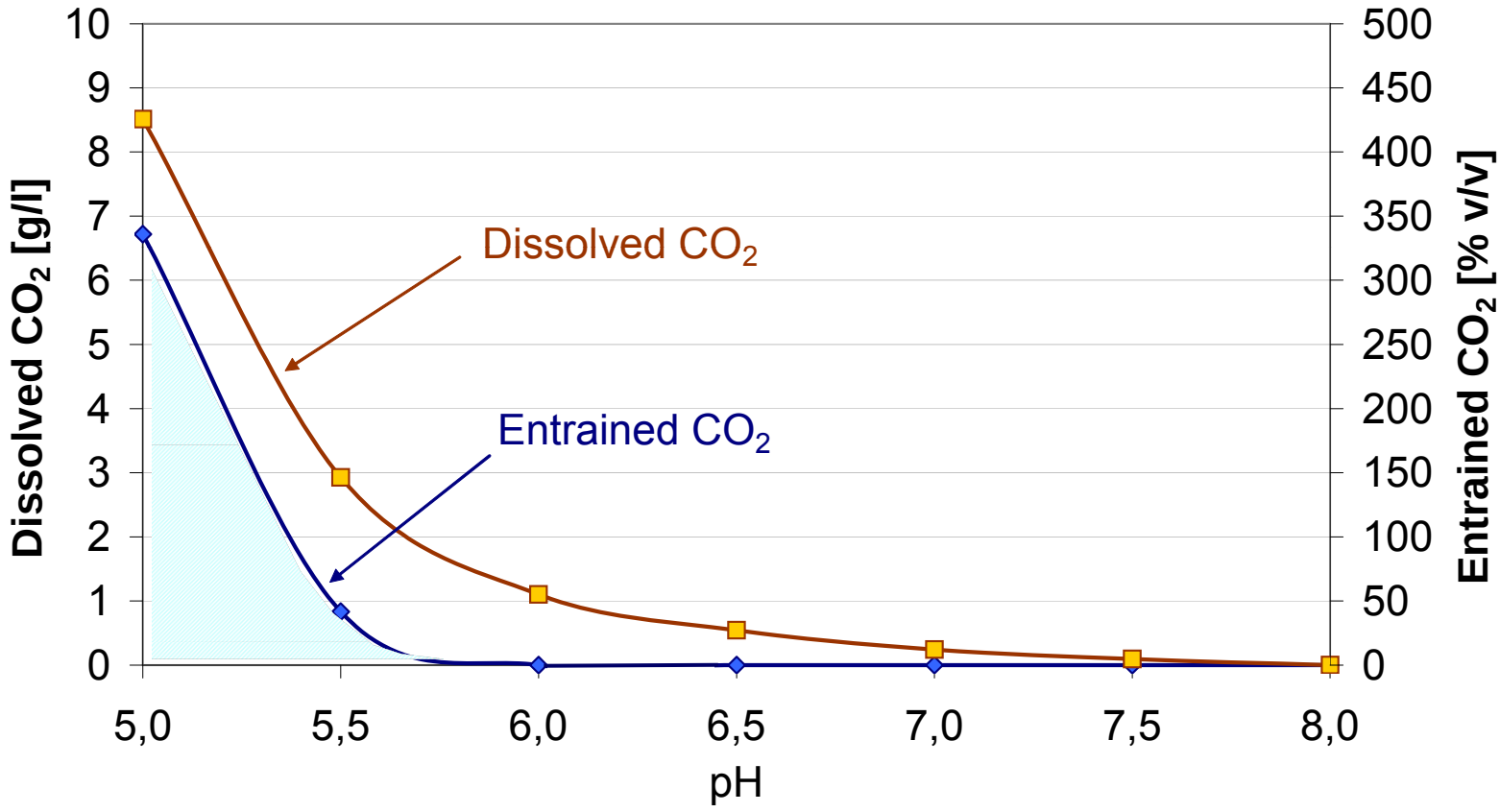
Change from using H_2SO_4 and alum to using the CO2 method and less

Results

Significantly reduced process water hardness

Equipment remains clean

Dissolved and Entrained Carbon Dioxide Generated from Dissolution of $CaCO_3$



Source: Redrawn from Grist & Canty (2006)

Big Bubbles are Difficult to Dissolve

The mass transfer equation:

$$N = k_1 \bullet a \bullet (C^* - C)$$

where

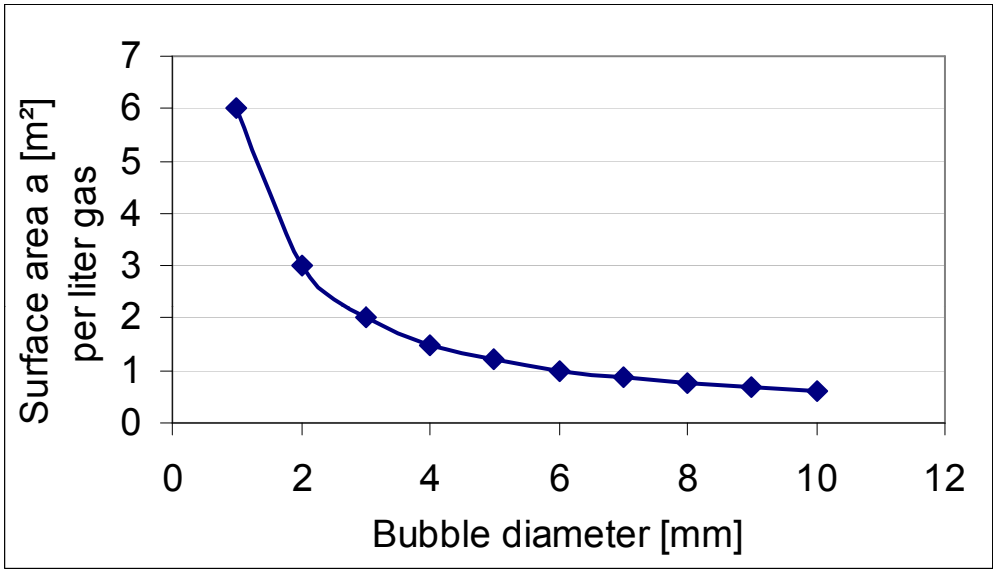
N = absorbed gas per unit time

k_1 = mass transfer coefficient

a = gas / liquid interfacial area per unit volume

C* = saturation concentration of the gas in the liquid phase

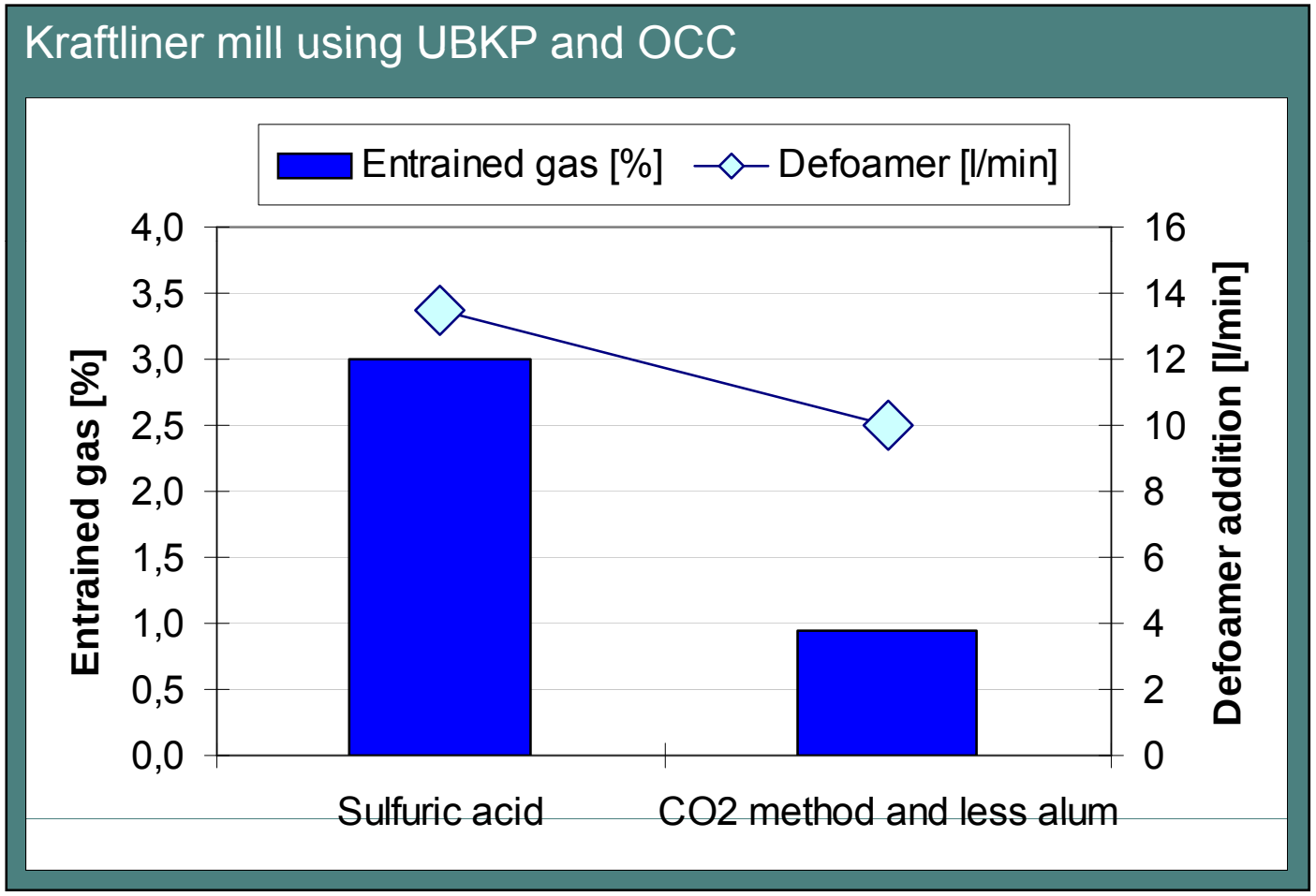
C = gas concentration in the liquid phase



For bubbles a = 6/d

The mass transfer rate is slower for larger bubbles

Reduced Amount of Entrained Gas When Using the CO_2 Method on a Kraftliner Machine



Environmental Benefits of Using the CO_2 Method

- Reduced conductivity
- Lower process water hardness
- Stable pH
  - Improved efficiency of process chemicals
  - Easier to further close the water circuit
  - Possibility of running the process at higher pH without generating calcium-resinate deposits
  - Improved efficiency of rosin sizing
- Easier to control the Na/S balance in closed Kraft mills

Thank You for Your Attention

References

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