INORGANIC DEPOSITS

- Scope of Problem
- Sources
- Problem Areas in Mill
- Analytical Methods
- Water Chemistry
- Scale Formation
- Treatment Options

OmniKlir, Inc.
SCOPE OF PROBLEM

Loss in Productivity
PRODUCTIVITY LOSSES

- Downtime
- Machine Breaks
- Reduced Machine Speed
- Formation Problems
- Reduced Efficiency

OmniKlir, Inc.
COST OF DOWNTIME

- Loss of Profits on tons not produced

Example:

$300/ton \times 20\ ton/hr = $6,000/hr

OmniKlir, Inc.
SECONDARY EFFECTS

- Decreased Equipment Life
- Corrosion
- Lower Quality Product
- Increased Cost
INORGANIC DEPOSITS

Sources of Components

OmniKlir, Inc.
SOURCES OF INORGANIC DEPOSITS

- Wood
- Water
- System Additives
- Secondary Fiber
- Byproducts of Pulping & Bleaching
WOOD COMPONENTS

- Calcium
- Magnesium
- Manganese
- Iron
- Barium
- Silica

OmniKlir, Inc.
VARIABILITY OF WOOD

- Bark
- Wood Species
- Lignin & Tannin
- Complexes with Fiber
- Location
- Sand & Dirt

- 10 x minerals in wood
- HW > SW
- Bleaching
- "Ion Exchange"
- Local Minerals
- Washing

OmniKlir, Inc.
WATER

- Calcium
- Magnesium
- Bicarbonate/Carbonate
- Iron
- Manganese
- Silicate
SYSTEM ADDITIVES

- Fillers
  - CaCO3
  - Kaolin
  - TiO2
  - Structured Pigments

OmniKlir, Inc.
SYSTEM ADDITIVES

- Aluminum compounds
  - Alum
  - Sodium Aluminate
  - Polyaluminum Chloride
SYSTEM ADDITIVES

- Calcium
- Deinking
- Make-up Lime
- White Liquor Carryover
- CaCO3 Filler
- Water

OmniKlir, Inc.
SYSTEM ADDITIVES

- Silicate, Silica
  - Bleaching
  - Defoamer
  - Dirt
  - Sand
  - Fillers

OmniKlir, Inc.
BYPRODUCTS OF PROCESS

- **Oxalate**
  - Breakdown of cellulose
  - Most likely in bleaching

- **Lignin Modifications**
  - Vary ability to bind metals
  - Oxidation releases metals
  - Soft scale
KRAFT PULP MILL PROBLEM AREAS

- Scale
  - Digesters
  - Evaporators
    * Hard Scale
    * Soft Scale
  - Liquor Lines
  - Washers (w or w/o pitch)
  - Sewer Lines
  - Pumps

OmniKlir, Inc.
KRAFT MILL DEPOSIT TYPES

- Calcium Carbonate
- Pitch/Calcium Carbonate
- Silica
- Silicates (calcium or magnesium)
- Calcium Sulfate
- Barium Sulfate

OmniKlir, Inc.
MECHANICAL PULPING PROBLEM AREAS

- Trouble Spots
  - Refiners
  - Grinders
  - Chests
  - Screens
  - Lines
  - Pumps
- Combined with Fiber or Pitch

OmniKlir, Inc.
MECHANICAL PULP MILL DEPOSITS TYPES

- Alumina
- Barium Sulfate
- Silicates
- Manganese Dioxide
- Calcium Oxalate
BLEACH PLANT PROBLEM AREAS

- Scale
  - Washers
  - Liquor Lines
- Tower
- Chests
- Pumps

OmniKlir, Inc.
BLEACH PLANT DEPOSIT TYPES

- Calcium Carbonate
- Calcium Oxalate
- Silicates
- Barium Sulfate
- Manganese Dioxide
- Iron Oxide
DEINK PLANT DEPOSITS

- Calcium Carbonate
- Calcium soaps
- Silicates
- Fillers

OmniKlir, Inc.
PAPER MILL PROBLEMS

- Scale
  - Chests
  - Lines
  - Cleaners
  - Headbox
  - Machine Frame
  - Pumps
PAPER MACHINE PROBLEMS

- Fillers Deposits
  - Headbox
  - Machine Frame
  - Chests
  - Savealls

OmniKlir, Inc.
PAPER MILL DEPOSIT TYPES

- Fillers
- Alumina
- Iron Oxide
- Barium Sulfate
- Calcium Carbonate
- Calcium Oxalate
ANALYTICAL METHODS

- Atomic Absorption
- X-ray Fluorescence
- Microscopic Examination
- Wet Chemistry
- Speck & Spot Analyses
ATOMIC ABSORPTION

- Best Suited for Soluble Water Components
- Deposits must be Digested
- Extremely Accurate
- Laboratory Procedure Only
X-RAY FLUORESCENCE

- Sample must be Dried
- Small Sample Size
- Mapping Capabilities
- Laboratory Technique Only
MICROSCOPIC EXAMINATION

- Morphology of Particles
- Other Gross Contaminants
- Extent of Fiber & Fines
- Done at the Mill

OmniKlir, Inc.
WET CHEMISTRY

- Best Suited for Water Components
- Deposit Samples must be Digested
- Traditional
- High Accuracy
- Laboratory Method

OmniKlir, Inc.
SPECK & SPOT ANALYSIS

- Rapid Tests
- Semi-quantitative
- Identify Organic Components
- Mill Determination
- Good Problem Solving Tool

OmniKlir, Inc.
WATER CHEMISTRY IN PAPER MAKING

Solubility, Precipitation, and Scale Formation
# Solubility of Salts in Water

<table>
<thead>
<tr>
<th></th>
<th>Cl-</th>
<th>HCO3-</th>
<th>OH-</th>
<th>NO3-</th>
<th>CO3---</th>
<th>SO4--</th>
<th>PO4---</th>
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<tbody>
<tr>
<td>Na, K, NH4</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<tr>
<td>H+</td>
<td>S</td>
<td>CO2</td>
<td>H2O</td>
<td>S</td>
<td>CO2</td>
<td>S</td>
<td>S</td>
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<tr>
<td>Ca++</td>
<td>S</td>
<td>SS</td>
<td>VSS</td>
<td>S</td>
<td>I</td>
<td>VSS</td>
<td>I</td>
</tr>
<tr>
<td>Mg++</td>
<td>S</td>
<td>S</td>
<td>I</td>
<td>S</td>
<td>VSS</td>
<td>S</td>
<td>I</td>
</tr>
<tr>
<td>Ba++</td>
<td>S</td>
<td>VSS</td>
<td>S</td>
<td>S</td>
<td>VSS</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>Sr++</td>
<td>S</td>
<td>VSS</td>
<td>SS</td>
<td>S</td>
<td>I</td>
<td>VSS</td>
<td>I</td>
</tr>
<tr>
<td>Fe++</td>
<td>S</td>
<td>SS</td>
<td>VSS</td>
<td>S</td>
<td>VSS</td>
<td>S</td>
<td>I</td>
</tr>
<tr>
<td>Fe+++</td>
<td>S</td>
<td>I</td>
<td>I</td>
<td>S</td>
<td>I</td>
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<td>I</td>
</tr>
<tr>
<td>Al+++</td>
<td>S</td>
<td>NP</td>
<td>I</td>
<td>S</td>
<td>NP</td>
<td>S</td>
<td>I</td>
</tr>
<tr>
<td>Cu++</td>
<td>S</td>
<td>I</td>
<td>I</td>
<td>S</td>
<td>I</td>
<td>S</td>
<td>I</td>
</tr>
</tbody>
</table>

S: > 5000 ppm
S: 2000 - 5000 ppm
SS: 20 - 2000 ppm
<: < 20 ppm

OmniKlir, Inc.
SOLUBILITY PRODUCT CONSTANT

\[ \text{CA} \rightarrow \text{C}^+ + \text{A}^- \]

\[ K_{sp} = \frac{[\text{C}^+][\text{A}^-]}{[\text{CA}]} \] (Slightly Soluble)

\[ K_{sp} = [\text{C}^+][\text{A}^-] \] (Very Low Solubility)

* Concentration Expressed in Moles/Liter

OmniKlir, Inc.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility Product Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaSO₄</td>
<td>1.1 x 10⁻¹⁰</td>
</tr>
<tr>
<td>BaCO₃</td>
<td>2.6 x 10⁻⁹</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>5.0 x 10⁻⁹</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>7.9 x 10⁻⁶</td>
</tr>
<tr>
<td>CaOxalate</td>
<td>2.0 x 10⁻⁸</td>
</tr>
<tr>
<td>Ca₃(PO₄)₂</td>
<td>2.0 x 10⁻³³</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>3.7 x 10⁻⁵</td>
</tr>
<tr>
<td>Fe(OH)₂</td>
<td>1 x 10⁻¹⁴</td>
</tr>
<tr>
<td>Fe(OH)₃</td>
<td>2 x 10⁻₃⁹</td>
</tr>
<tr>
<td>Al(OH)₃</td>
<td>1 x 10⁻⁹</td>
</tr>
<tr>
<td>Mg(OH)₂</td>
<td>5.7 x 10⁻¹²</td>
</tr>
</tbody>
</table>
CARBON DIOXIDE CHEMISTRY

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 + \text{NaOH} & \rightleftharpoons \text{NaHCO}_3 + \text{H}_2\text{O} \\
\text{NaHCO}_3 + \text{NaOH} & \rightleftharpoons \text{NaCO}_3 + \text{H}_2\text{O}
\end{align*}
\]
CaCO₃ + H₂CO₃ → Ca²⁺⁺ + 2HCO₃⁻⁻
Ca²⁺⁺ + CO₃⁻⁻ → CaCO₃
Ca²⁺⁺ + HCO₃⁻ + OH⁻ → CaCO₃↓ + H₂O
Ca²⁺ + 2HCO₃⁻ → Δ CaCO₃↓ + CO₂↑

OmniKlir, Inc.
CARBON DIOXIDE SPECIES vs. pH

Fraction of Total Carbon Dioxide

pH

CO3 or bound CO2
HCO3 of half bound CO2
H2CO3 or CO2 gas

OmniKlir, Inc.
CALCIUM CARBONATE SCALE

- Heating $2 \text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{CO}_2 \uparrow$
- $\text{OH}^- + \text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$
- $\text{CaCO}_3$ has Inverse Solubility with Temperature

OmniKlir, Inc.
ALKALINITY TITRATION

ppm H2SO4 added

pH Value

NaOH

Na₂CO₃

P Endpoint

M Endpoint

OmniKlir, Inc.
SCALE FORMATION

Precipitation of insoluble compounds from water, which adheres to a surface.

OmniKlir, Inc.
SCALE FORMATION PROCESS

Transportation ➔ Dissolution ➔ Deposition ➔ Problems

OmniKlir, Inc.
REQUIREMENTS FOR SCALE FORMATION

- Supersaturation
- Nucleation
- Contact Time

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NEGATIVE EFFECTS OF SCALE

- Heat Transfer Loss
- Flow Restriction
- Washing Problems
- Inaccurate Flow Measurements
- Formation Problems
- Stock Lumps
- Picking

OmniKlir, Inc.
MINERAL SCALE

% Reduction in Heat Transfer Coefficient

Scale Thickness (in.)

Al₂O₃
CaCO₃
CaSO₄
Clay
SiO₂

OmniKlir, Inc.
HANDLING DEPOSIT PROBLEMS

Treatment Options

OmniKlir, Inc.
TREATMENT OPTIONS

- Pretreatment to remove dissolved & suspended solids
  - Softening
  - Ion exchange
  - Filtration
  - Coagulation
  - Reverse osmosis

OmniKlir, Inc.
WATER PRETREATMENT

Raw Water

Screens

Sedimentation

Clarification

Lime Softening

Aeration

Chlorination

Filtration

Adsorption

Ultrafiltration

Reverse Osmosis

Ion Exchange

Electro-dialysis

Pure Water
TREATMENT OPTIONS

- Leave solids in and treat to prevent deposition
  - Scale Inhibitors
  - Antifoulants
  - Sludge conditioners
  - Flocculants
  - Coagulants
  - Dispersants

OmniKlir, Inc.
TREATMENT OPTIONS

- Leave solids in and allow deposits to form - then remove periodically
  - Chemical removal - boilouts
  - Mechanical removal - hydroblasting
  - Combination programs
DEPOSIT CONTROL
ALTERNATIVES

Inorganic Materials
CALCIUM CARBONATE

- PULP MILL
  - Liquor Clarification
  - pH Control
  - Condensate for Pulp Washing
  - Higher Flow Rates
  - Acid cleaning
  - Water Softening
  - "Dispersants"

OmniKlir, Inc.
CALCIUM CARBONATE

- PAPER MILL
  - pH Control
  - Water Softening
  - Improve Retention
  - Dispersants
  - Boilouts
BARIUM SULFATE

- PULP MILL
  - Reduce H2SO4
  - Reduce Alum
  - Reduce soda loss
  - Boilouts
  - Dispersants

- PAPER MACHINE
  - Reduce Alum
  - Reduce soda loss
  - Dispersants
  - Boilouts

OmniKlir, Inc.
MANGANESE DIOXIDE

- Water Softening
- Chlorination of Mill Water
- Chelating Agents
- boilouts

OmniKlir, Inc.
IRON OXIDES

- Water Softening
- Chlorination of Mill Water
- Corrosion Inhibitors in Mill Water
- Low Iron Alum
- Chelating Agents
- Boilouts
SILICA & SILICATES

- Silicate Reduction (Bleaching)
- Water Softening
- Improved Chip Washing
- Switch Defoamers
- Improved Retention
FILLER DEPOSITS

- Wet End Chemistry
  - Improve Retention
  - Aluminum Chemistry
  - pH Control
- Dispersants
- Boilouts

OmniKlir, Inc.
WET END CHEMISTRY

- Fiber source & properties
- Machine design
- Fillers
- pH
- Water chemistry
- Coagulants
- Flocculants
- System charge

OmniKlir, Inc.
ALUMINUM SPECIES vs. pH

Fraction of Aluminum

pH

0 0.2 0.4 0.6 0.8 1

3 4 4.25 4.5 4.75 5 5.25 5.5 5.75 6 7 8 9 10 11

Al+3

Al+2

Al8(OH)20+4

Al(OH)3

Al(OH)4−
ALUMINA DEPOSITS

- Avoid pH shock
- Check for overuse
- Clarified White Water vs. Fresh Water
- Change feed points
SCALE INHIBITION

Mechanisms for Control

OmniKlir, Inc.
HISTORICAL PERSPECTIVE

- Potato starch reported effective for boiler scale - 1821
- First scale control patent - 1869
LANGUAGE OF SCALE CONTROL

- Chelation
- Sequestration
- Complexation
- Antiprecipitation
- Threshold treatment
- Dispersant
- Deflocculant
- Antinucleation agent
- Modification
- Surface Modification
- Crystal modification
- Peptization

OmniKlir, Inc.
CHELATION

- Co-ordinate bonds with cations
- Interfere with the thermodynamics of crystal formation
CHELANTS & SEQUESTERANTS

- EDTA
- DTPA
- NTA
- Citrate
- Gluconate
- Tartrate
- Hexametaphosphate
- Polyphosphate
- Phosphonates
- Phosphate esters
- Lignosulfonate
- Tannin
CRYSTAL MODIFIERS

- Adsorb at surface of crystals
- Distort scale crystals as they grow
- Interfere with kinetics of crystal formation

OmniKlir, Inc.
THRESHOLD INHIBITORS

- Hexametaphosphate
- Polyphosphate
- Phosphonates
- Phosphate esters
- Lignosulfonate
- Tannin

- Polyacrylates
- Polymethacrylates
- Polymaleates
- Polyphosphonate
- CMC
- Alginates

OmniKlir, Inc.
DISPERSANTS

- Anionic Charge (increase repulsion)
  - Lignosulfonate
  - Tannin
  - Polyphosphates
  - Acrylic polymers
  - Sulfonate polymers
  - Copolymers & terpolymers

OmniKlir, Inc.
INORGANIC DEPOSITS CONTROL

- Know the entire process
- Understand your options
- Evaluate the economics of treatment
- ACTION Plan
INORGANIC DEPOSIT CONTROL

The key to improved runnability.