Composition, Removal and Prevention of Scales in Evaporators of Cane Sugar Factories

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Introduction – Why talking about Scales in Sugar Factories?

Dependence of Heat Transfer Coefficient on Scale Thickness
Materials and Methods

Scale composition

Scale analyses with a combination of specific modified methods including
- ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry),
- Ion Chromatography and
- Titration methods.

Trends in scale composition

Based on the results of about 10 000 analyses of scale samples from about 1000 factories from about 60 countries all over the world during the last 40 years.
Materials and Methods

Removal recommendations based on some thousand solving test with original scales.

Chemical cleanings have been done in hundreds of sugar factories all over the world during several decades.

Chemicals for cleaning

Alkaline step:

- **Caustic Soda** (NaOH)
- **Soda Ash** (Na₂CO₃)

and different **Dispersant** and **Wetting agents**

(own development).

Acid step:

- **Formic**, **Sulfamic**- or **Hydrochloric acid** with **Corrosion inhibitors**

(own development).
Scale prevention is based on experiences in hundreds of beet and cane sugar factories.

Chemicals for scale prevention: Polyacrylate based antiscalant (own development).
Scale forming compounds found in sugar industry

No „typical“ scale composition for beet or cane sugar industry

**Main scale compounds** or compounds that are essential for formation and/or removal of the scale:

**Ca-Salts**
- Oxalate
- Carbonate
- Sulfate / Sulfite
- Phosphate
- Aconitante
- Other Ca-containing Scales

**Silicates**

**Sugar Coal** and Caramelized Sugar

**Other inorganic or organic** scale compounds are rare but sometimes found.

Difficult to remove: scale formed from layers
## Scale Components found in Sugar Industry

**Different scale composition from effect to effect** in a factory.

<table>
<thead>
<tr>
<th>Scale Components</th>
<th>Cane sugar factory (Thailand)</th>
<th>Beet sugar factory (Russia)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>Evaporator</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO₃</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Ca₃(PO₄)₂</td>
<td>%</td>
<td>72,8</td>
</tr>
<tr>
<td>Ca-Oxalate</td>
<td>%</td>
<td>0,8</td>
</tr>
<tr>
<td>Organics and water</td>
<td>%</td>
<td>20,4</td>
</tr>
<tr>
<td>SiO₂</td>
<td>%</td>
<td>2,0</td>
</tr>
</tbody>
</table>
Calcium Oxalate

Occurrence: Found in beet and cane sugar factories.  
Source: From beet or cane.

Tendencies:  
Still the most important scale component in sugar industry  
Limiting compound for operation time of later effects if the juice is not treated.

Removal:  
Not soluble in alkaline or acid cleaning solutions, therefore a two step cleaning is necessary:  
1. Conversion of Oxalate to Carbonate with Na$_2$CO$_3$, NaOH, Dispersant and wetting agent.  
2. Acidic cleaning with inhibited acid.

Prevention:  
• Softening of thin juice (beet sugar).  
• Application of Polyacrylate based antiscalant.
Calcium Phosphate

**Occurrence:** Cane sugar factories.
**Source:** From cane.

**Tendencies:** Most important scale compound in first effects of cane sugar factories, limiting compound for operation time of early effects.

**Removal:**
Acidic cleaning with inhibited formic or hydrochloric acid.

**Prevention:**
- Optimization of juice purification process, especially at the sedimentation and filtration steps, because most Calcium Phosphate enter as particle into the evaporators.
- Application of Polyacrylate based antiscalant.
Calcium Phosphate

Prevention:
Influence of mixing the flocculant solution (conc.: 0.1 - 0.05 %) with the limed juice.

unstirred, unmixed
slow stirred, incomplete mixing
fast stirred, good mixing
**Calcium Sulfate** and **Calcium Sulfite**

**Occurrence:** Sugar factories with sulfitation, mainly in later effects or cane sugar factories in some areas

**Source:** Addition of SO$_2$ or (Bi-)Sulfite (sulfitation) or use of ammonia sulfate as fertilizer.

**Tendencies:** Increasing in cane sugar industry because of trend to low colour sugar.
In European beet sugar industry unimportant, even after the reintroduction of sulfitation, because of well controlled and low dosage of Bisulfites instead of gaseous SO$_2$.

**Removal:** Two step cleaning.
1. Conversion of Sulfate/Sulfite to Carbonate with Na$_2$CO$_3$, NaOH, dispersant and wetting agent.
   Conversion is recommended because Sulfite will form gaseous SO$_2$ if treated with acid directly.
2. Acidic cleaning with inhibited acid.

**Prevention:**
- Improved control of SO$_2$ dosage.
- Use of Bisulfite instead of gaseous SO$_2$.
- Application of Polyacrylate based antiscalant.
Calcium Aconitate

**Occurrence:** Cane sugar factories in South America.
**Source:** From cane.

**Tendencies:** Important scale component in South America, especially Brazil and Uruguay. In these countries limiting component for operation time of later effects if the juice is not treated.

**Removal:**
Acidic cleaning with inhibited formic acid.

**Prevention:**
Application of Polyacrylate based antiscalant.
Calcium Carbonate

Occurrence:
• In sugar factories with carbonatation in heat exchangers for limed/carbonated juice and sometimes first effects of evaporator stations.
  Source: Addition of milk of lime or Saccharate and CO₂ (carbonatation).

• In scale samples taken after alkaline treatment of Calcium Oxalate scales before acidic cleaning step (samples taken to check if conversion of Oxalate is complete).
  Source: Na₂CO₃ in the alkaline cleaning solution.

Tendencies:
Decreasing importance through reduced lime application and further optimization of carbonatation process.

Removal: Cleaning with inhibited acid.

Prevention:
• During carbonatation process: unwanted.
• In first evaporator effects: optimization of carbonatation and filtration process, e.g. improved reaction times.
• Application of Polyacrylate based antiscalant.
Silicates

**Occurrence:** In beet and cane sugar factories. No simple monomer silicate, complex polymeric structures, in beet sugar factories often as Aluminium-, Magnesium- and/or Calcium-Silicates.

**Source:** From cane or from limestone.

<table>
<thead>
<tr>
<th></th>
<th>%</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>5,3</td>
<td>5,0</td>
<td></td>
</tr>
<tr>
<td>CaC₂O₄ • H₂O</td>
<td>&lt; 0,1</td>
<td>0,2</td>
<td></td>
</tr>
<tr>
<td>Org. Substances and Hydration Water</td>
<td>18,8</td>
<td>25,2</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>44,9</td>
<td>40,7</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20,3</td>
<td>18,9</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0,2</td>
<td>0,1</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>9,8</td>
<td>8,7</td>
<td></td>
</tr>
</tbody>
</table>

**Tendencies:**
Limiting compound for operation time of later effects if the juice is treated for Calcium scale prevention.
Increasing importance for European beet sugar industry because of longer campaigns
Removal:
1. Acidic cleaning with inhibited sulfamic acid or inhibited hydrochloric acid
2. Alkaline cleaning with NaOH and wetting agent.

Prevention:
In beet sugar factories:
Choose of limestone with low silicate content.
In beet sugar factories and refineries:
Silicate content increase with decrease of pH at application point,
therefore: No fresh milk of lime to second carbonatation.

Silicate in Carbonated Juice in Relation to pH of 1. Carbonatation

<table>
<thead>
<tr>
<th>pH</th>
<th>Silicon in mg / kg Drysubstance</th>
</tr>
</thead>
<tbody>
<tr>
<td>10,75</td>
<td>69,6</td>
</tr>
<tr>
<td>10,85</td>
<td>58,8</td>
</tr>
<tr>
<td>10,90</td>
<td>56,6</td>
</tr>
<tr>
<td>11,00</td>
<td>50,8</td>
</tr>
<tr>
<td>11,05</td>
<td>50,1</td>
</tr>
<tr>
<td>11,18</td>
<td>40,2</td>
</tr>
<tr>
<td>11,275</td>
<td>32,2</td>
</tr>
<tr>
<td>11,35</td>
<td>26,8</td>
</tr>
</tbody>
</table>

Data from: Devillieurs, Detavernier et Groult: "L'entartrage des évaporateurs au cours de la campagne 1975 - 1976" Sucrerie Française, 1976, p. 245 - 249
Prevention for cane sugar factories:
Application of Polyacrylate based antiscalant (reduction, but not 100% prevention).

<table>
<thead>
<tr>
<th>Effect</th>
<th>Without antiscalant</th>
<th>With antiscalant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>CaCO₃ %</td>
<td>3,8</td>
<td>16,8</td>
</tr>
<tr>
<td>CaHPO₄ %</td>
<td>&lt; 0,1</td>
<td>&lt; 0,1</td>
</tr>
<tr>
<td>Ca₃(PO₄)₂ %</td>
<td>8,1</td>
<td>5,4</td>
</tr>
<tr>
<td>CaSO₄ %</td>
<td>0,3</td>
<td>2,8</td>
</tr>
<tr>
<td>CaSO₃ %</td>
<td>&lt; 0,1</td>
<td>&lt; 0,1</td>
</tr>
<tr>
<td>CaC₂O₄ • H₂O %</td>
<td>2,5</td>
<td>6,5</td>
</tr>
<tr>
<td>Ca₃(C₆H₅O₇)₂ %</td>
<td>&lt; 0,1</td>
<td>&lt; 0,1</td>
</tr>
<tr>
<td>Ca₃(C₆H₃O₆)₂ • 3 H₂O %</td>
<td>&lt; 0,1</td>
<td>&lt; 0,1</td>
</tr>
<tr>
<td>Organic and water %</td>
<td>24,1</td>
<td>19,5</td>
</tr>
<tr>
<td>SiO₂ %</td>
<td>30,9</td>
<td>30,2</td>
</tr>
<tr>
<td>Al₂O₃ %</td>
<td>0,9</td>
<td>0,5</td>
</tr>
<tr>
<td>MgO %</td>
<td>0,4</td>
<td>0,3</td>
</tr>
<tr>
<td>Na₂O %</td>
<td>0,2</td>
<td>0,5</td>
</tr>
<tr>
<td>K₂O %</td>
<td>0,1</td>
<td>0,1</td>
</tr>
<tr>
<td>ZnO %</td>
<td>&lt; 0,1</td>
<td>&lt; 0,1</td>
</tr>
<tr>
<td>CuO %</td>
<td>&lt; 0,1</td>
<td>&lt; 0,1</td>
</tr>
<tr>
<td>Fe₂O₃ + FeO %</td>
<td>28,6</td>
<td>17,3</td>
</tr>
</tbody>
</table>
Sugar coal and caramelized sugar

Occurrence: By accidents, whenever sugar gets burned on hot surfaces.
Source: From sugar juice.

Tendencies:
Increasing importance with the success of falling film and plate evaporators in sugar industry because these evaporator types are more sensitive to sugar coal formation in case of break downs.

Removal:
Alkaline solution with suspension- and wetting agent.
Often removed but not 100% solved.

Prevention:
In some cases: optimization of juice distribution system.
Emergency system for water supply to evaporator in case of break down.