Raffinate regeneration of ion-exchange softeners in the Beet Sugar Industry

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WHAT IS RAFFINATE?

- CSB: Concentrated Separator By-product
- HSC: Holly Sugar Concentrate
- SMS: Soluble Molasses Solids
- Rest Fraction
- Non Sugar Fraction from Molasses desugarization
Thin Juice
(Ca, Mg, Na, K,..)

**PROCESS PRINCIPLE**

Exchange of divalent ions which form scaling in the evaporators for monovalent species with gel or macroreticular cationic resins.

**Production:**

\[
2 \text{R-Na} + \text{Ca}^{++} \rightarrow \text{R}_2\text{Ca} + 2 \text{Na}^+ \\
2 \text{R-K} + \text{Ca}^{++} \rightarrow \text{R}_2\text{Ca} + 2 \text{K}^+
\]

**Regeneration:**

\[
\text{R}_2\text{Ca} + 2 \text{Na}^+ \rightarrow 2 \text{R-Na} + \text{Ca}^{++} \\
\text{R}_2\text{Ca} + 2 \text{K}^+ \rightarrow 2 \text{R-K} + \text{Ca}^{++}
\]

**Equilibrium law:**

\[
\frac{[\text{Ca}]}{[\text{K}^+]^{2}} = K \left( \frac{C_R}{C_F} \right) \left[ \frac{\text{Ca}}{K^2} \right]
\]
APPLEXION IX THIN JUICE SOFTENING

PROCESS ECONOMICS

- TRUE Ca REMOVAL FROM THIN JUICE
- IMPROVED SUGAR QUALITY (LOW TURBIDITY)
- ENERGY SAVINGS (HIGHER HEAT TRANSFER COEFFICIENT)
- LESS EVAPORATORS SCALING, LESS EVAPORATORS CLEANING
- BETTER FILTRABILITY OF THICK JUICE
- MOLASSES SUITABLE FOR ION EXCLUSION
- LOWER MAINTENANCE COST
- BETTER PROTECTION OF HIGH PERFORMANCE EVAPORATORS (PLATES/TUBULAR)
- EXTENDED SHELF LIFE OF SOFT THICK JUICE
IX THIN JUICE SOFTENING

AVAILABLE REGENERANT FOR INDUSTRIAL APPLICATIONS

- SODIUM CHLORIDE
  - Dilution of treated juice
  - Hot water consumption
  - NaCl consumption and waste waters
  - Sugar losses in molasses
- SULFURIC ACID on Weak Acid Cation
  - High Capacity
  - Risk of invert production
- DECALCIFIED JUICE & NaOH (NRS)
  - Simple, effluent free
  - Operation at < 50°C
- THICK JUICE
- GREEN II SYRUP (GRYLLUS)
  - Dilution of Green II
- MOLASSES
- CHROMATOGRAPHY RAFFINATE FRACTION
IX Raffinate regeneration

Typical clear thin juice solution
- 16 Brix, Total Cation ~ 50 meq/l
- Na + K ~ 43 meq/l of juice
- Ca ~ 7 meq/l

Available Raffinate solution
All Non Sugar ends up in the raffinate which contains ALL the original monovalents
IX Raffinate regeneration

Typical NaCl regeneration

2BV of a 10% NaCl solution or 1.83 eq/l or 3.4 eq/l.

Operating capacity ~0.75 eq/l.

The raffinate shall be preconcentrated up to 25 Brix to be effective.
IX Raffinate regeneration

Industrial Trials results

**OBJECTIVE:**

ACHIEVE >90% DIVALENT REMOVAL WITH A REGENERATION WITH RAFFINATE

**TEST CONDITIONS**

<table>
<thead>
<tr>
<th>Regeneration rate</th>
<th>Regenerant excess</th>
<th>Regenerant as 25 Bx</th>
<th>% Ca removal</th>
<th>Capacity Leakage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,5 eq/lr</td>
<td>218 %</td>
<td>1 BV</td>
<td>92 %</td>
<td>0,67 eq/l</td>
</tr>
<tr>
<td>2,3 eq/lr</td>
<td>322 %</td>
<td>1,5 BV</td>
<td>96 %</td>
<td>0,70 eq/l</td>
</tr>
<tr>
<td>3,0 eq/lr</td>
<td>423 %</td>
<td>2 BV</td>
<td>97 %</td>
<td>0,71 eq/l</td>
</tr>
</tbody>
</table>

- Regeneration with raffinate is achieving the expected goals
- It must be preconcentrated up to 25 Brix to be effective
- The process is **effluent free** since the hard raffinate can be further concentrated to be sold as animal feed.
- Using this technology the regenerant is **free of charge**
IX Raffinate regeneration

Challenging issues for Beet Sugar Factories using raffinate as a regenerant:

- Corrosive solution (high salinity, high temperature)
- Very high color (up to 100,000 Icumsa)
- Very low sugar purity (15-20% sucrose purity)

The industrial implementation must be optimized in order to minimize any back-mixing:

- Colorants transfer from raffinate to thin juice
  (Production of white sugar from standard liquor A)
- Sucrose transfer from thin juice to raffinate
  (Sugar loss to hard raffinate)
IX Raffinate regeneration

Process solutions developed by Applexion:

- Columns and piping in stainless or lined steel
- Co-current regeneration with controlled water flush between thin juice softening and raffinate regeneration
- Typical process sequence:
  - Thin juice 15 Bx 120 Bed Volumes
  - Water flush 0.5 Bed Volume
  - Soft raffinate 25 Bx 1.5 Bed Volume
  - Water flush 1 Bed Volume
IX Raffinate regeneration

Limitation of back-mixing and dilutions:

- Sugar transfer from thin juice to raffinate: not more than 0.1 increase in the raffinate purity
- Color transfer from raffinate to thin juice: not more than 3% increase in the color of soft thin juice (2,000 to 2,050 Icumsa)
- Evaporation of the water flush:
  - in thin juice evaporator: 0.5% increased capacity
  - in hard raffinate evaporator: 2% increased capacity
IX Raffinate regeneration

Main information for a typical US Beet Sugar factory:

- Slicing capacity: 8,000 tons beet/day
- Operating days: 250 days/year
- Thin juice hardness: 90 mg CaO%Bx

NRS regeneration

- NaOH expense @$400/ton: $440,000/year

Raffinate regeneration

- Molasses to IEP: 600 tons molasses/day
- Raffinate used for regeneration: 20% of all raffinate
- Sugar loss to raffinate @$400/ton: $20,000/year
- Additional thin juice evaporation: $23,000/year (5 effects, $12/ton of steam)
- Additional raffinate evaporation: $60,000/year (4 effects, $12/ton of steam)
Raffinate regeneration is a very cost effective and environmental friendly new technology available to the Beet Sugar Industry, for which APPLEXION has now developed the implementation expertise.
Abstract

During the last decade or so, a significant part of the US Beet Sugar Industry has introduced thin juice softening by ion-exchange in their operations. In addition to the many benefits associated with ion-exchange softening (true removal of Ca from juice and molasses, less evaporators scaling/cleaning, increased heat transfer coefficients, reduced sugar turbidity), thin juice softeners allow for the production of soft molasses for chromatographic separation. One-third of the US beet sugar factories include an Ion-Exclusion Process in their operations for the recovery of sugar, and sometimes betain, from molasses. About half of the US beet sugar factories already soften their thin juice by ion-exchange: 25% use a weak cation resin and regeneration with dilute sulfuric acid; 25% use a strong cation resin and NRS regeneration with soft thin juice and caustic soda. Eighty percent of the US factories working on beet molasses separation also use ion-exchange softening of thin juice. For those factories, Applexion/ASI have developed an efficient and cheap regeneration process, using raffinate. Raffinate is the by-product from molasses chromatographic separation; it contains 90% of the non-sugars and 10% of the sugar from the molasses. Its concentration in monovalent cations (K, Na) has been enriched during the multiple-stage crystallization, and during the chromatographic separation. One liter of raffinate 25 Brix has the same regeneration power as one liter of a 10% NaCl solution. Unlike other regenerants, it is available for free from the molasses separation plant. This new softening process is available for the Cane and the Beet Sugar Industries. When used in the Beet Sugar Industry, one must take great care to avoid backmixing of sugar and colorants between thin juice and raffinate. Therefore, counter-current regeneration and small intermediate water flush have been introduced in the process available to the Beet Sugar Industry for the production of white sugar. Raffinate regeneration of thin juice softeners can be done very efficiently, using an inexpensive strong cation resin, for only a fraction of the operating cost of the existing weak cation and NRS juice softeners.