Improving Silica Removal By EDI and GTM
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Electropure™ EDI Operating in 49 Countries
The Electropure™ EDI History

- **1977** Harry O’Hare EDI Prototype
- **1979** HOH Water Technology founded
- **1984** HOH EDI Patent Issued
- **1988** EPM series EDI
- **1996** HOH becomes Electropure
- **1999** Excellion™ IX Membrane Patents
- **1999** XL™ series EDI
- **2004** XL-HTS™ High Temperature Stable
- **2005** Electropure Management Buyout--SnowPure formed
- **2006** Electropure China Sales Office Opened
- **2007** XL-R™ series EDI improvements
- **2008** SnowPure International (Hong Kong) formed
- **2009** EXL™ series EDI introduced in China
- **2010** EXL™ series EDI introduced worldwide
- **2012** EXL-HTS high volume, high temperature for sanitization
- **2013** XL-DER EDI for Hemodialysis
Agenda

1. Importance of Silica for Power Plants
2. Old EDI Model: Working Bed - Polishing Bed
3. New EDI Model: Electropure Specific Ion Model
4. Discussion: Specific RO-EDI Cases
5. Rules to Optimize SiO$_2$ in EDI
Silica is Important in Power Plants and Electronics

Semiconductor Fabs
\[ \text{SiO}_2 < 0.1 \text{ ppb} \]

Combined Cycle High Pressure Boilers
\[ \text{SiO}_2 < 5 \text{ ppb} \]
Old EDI Model: Working Bed-Polishing Bed

Pure Water

Feed from RO

“WORKING BED”

“POLISHING BED”

10 μS

0.5 μS

18 MΩ
Electropure’s New Specific Ion Model

I: $H^+ \cdot OH^-$
II: $Na^+ \cdot Cl^- \cdot Ca^{+2} \cdot Mg^{+2} \cdot SO_4^{-2}$
III: $HCO_3^- \cdot CO_2(g)$
IV: $SiO_2 \cdot H_3BO_3$

Class 4 Transfer Region
Extensive Water Splitting
“Polishing”

Removal of $HCO_3^-$

All $CO_2$ to $HCO_3^-$
Bulk Conductivity Removed

pH to 7.0 in feed
$H^+$ and $OH^-$ in balance
Forces on Cations in EDI

- **Force 1:**
  - Electrical Attraction to resin
  - $K$, Selectivity Coefficient

- **Force 2:**
  - Electrical attraction to electrodes
  - $E$, Charge/Mass

- $K$, Selectivity Coefficient
  - $\text{Ca}^{+2} > \text{Mg}^{+2} > \text{K}^{+} > \text{Na}^{+} > \text{H}^{+}$
- $E$, Electrical Force/Mass
  - $\text{H}^{+} > \text{Mg}^{+2} > \text{Ca}^{+2} > \text{Na}^{+} > \text{K}^{+}$
Forces on Anions in EDI

- **Force 1:**
  - Electrical Attraction to resin
  - $K$, Selectivity Coefficient

- **Force 2:**
  - Electrical attraction to electrodes
  - $E$, Charge/Mass

$K$, Selectivity Coefficient:
- $SO_4^{2-} > Cl^- > OH^- > HCO_3^- > HSiO_3^-$

$E$, Electrical Force/Mass:
- $OH^- > Cl^- > SO_4^{2-} > HCO_3^- > HSiO_3^-$
Electropure’s 4 Classes of Ions

<table>
<thead>
<tr>
<th>Electropure™ Ion Class</th>
<th>Characteristics</th>
<th>Example Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class 1</td>
<td>Low Selectivity High Mobility</td>
<td>H⁺ OH⁻</td>
</tr>
<tr>
<td>Class 2 “Conductivity”</td>
<td>High Selectivity Medium Mobility</td>
<td>Ca⁺² Mg⁺² Na⁺ Cl⁻ SO₄²⁻</td>
</tr>
<tr>
<td>Class 3 “Bicarbonate”</td>
<td>Low Selectivity Low Mobility Moderate Charge, Polar at pH 7</td>
<td>HCO₃⁻ pK = 6.3</td>
</tr>
<tr>
<td>Class 4 “Weakly Ionized Ions”</td>
<td>Very Low Selectivity Very Low Mobility Low charge at pH 7</td>
<td>HSiO₃⁻ pK = 9.8 H₄BO₄⁻ pK = 9.3</td>
</tr>
</tbody>
</table>
Class 1: \( H^+ \) and \( OH^- \)

1: \( H^+ \) \( OH^- \)
2: \( Na^+ \) \( Cl^- \) \( Ca^{+2} \) \( Mg^{+2} \) \( SO_4^{-2} \)
3: \( HCO_3^- \) \( CO_2(g) \)
4: \( SiO_2 \) \( H_3BO_3 \)

Zone 1 pH adjustment
Class 2: Easy Ions

1: H⁺ OH⁻
2: Na⁺ Cl⁻ Ca⁺² Mg⁺² SO₄⁻²
3: HCO₃⁻ CO₂(g)
4: SiO₂ H₃BO₃

Zone 1 pH adjustment

Zone 2: Conductivity Removal
CO₂ → HCO₃⁻
Class 3: Bicarbonate Ion $\text{HCO}_3^-$

1: $\text{H}^+$ $\text{OH}^-$
2: $\text{Na}^+$ $\text{Cl}^-$ $\text{Ca}^{+2}$ $\text{Mg}^{+2}$ $\text{SO}_4^{-2}$
3: $\text{HCO}_3^-$ $\text{CO}_2(\text{g})$
4: $\text{SiO}_2$ $\text{H}_3\text{BO}_3$

Zone 1: pH adjustment

Zone 2: Conductivity Removal $\text{CO}_2 \rightarrow \text{HCO}_3^-$

Zone 3: $\text{CO}_2$ Removal
Class 4: Difficult Ions 
(SiO$_2$)

1: H$^+$ OH$^-$
2: Na$^+$ Cl$^-$ Ca$^{+2}$ Mg$^{+2}$ SO$_4^{-2}$
3: HCO$_3^-$ CO$_2$(g)
4: SiO$_2$ H$_3$BO$_3$

Zone 1 pH adjustment

Zone 2: Conductivity Removal
CO$_2$ $\rightarrow$ HCO$_3^-$

Zone 3: CO$_2$ Removal

Zone 4: SiO$_2$ Removal
Water Splitting H$_2$O $\rightarrow$ H$^+$ OH$^-$

Slide 15
Case of high or low pH in EDI feed

1: H⁺ OH⁻
2: Na⁺ Cl⁻ Ca⁺² Mg⁺² SO₄⁻²
3: HCO₃⁻ CO₂(g)
4: SiO₂ H₃BO₃

Weakly Ionized
Bicarbonate HCO₃⁻
Conductivity
pH high or low
Case: High conductivity in EDI feed

1: H⁺ OH⁻
2: Na⁺ Cl⁻ Ca²⁺ Mg²⁺ SO₄²⁻
3: HCO₃⁻ CO₂(g)
4: SiO₂ H₃BO₃

Bicarbonate HCO₃⁻

High Conductivity
RO is bad

pH near 7.0
Case: High CO$_2$ + HCO$_3^-$ in EDI feed

1: H$^+$ OH$^-$
2: Na$^+$ Cl$^-$ Ca$^{+2}$ Mg$^{+2}$ SO$_4^{2-}$
3: HCO$_3^-$ CO$_2$(g)
4: SiO$_2$ H$_3$BO$_3$

High CO$_2$ + HCO$_3^-$

Good RO (1-pass or 2-pass)
Low Conductivity

pH near 7.0
EDI Optimized for Removal of Silica

1. pH in Control (6.5 to 7.5)
2. High Rejection RO
3. CO₂ Removal System (GTM)
4. Voltage Is Not Too Low

Tall Bed for Polishing
Lots of Water Splitting
High residence time

– SiO₂ & HSiO₃⁻
  – H₃BO₃ & H₄BO₄⁻
– HCO₃⁻
– Na⁺ Cl⁻ Ca²⁺
  – Mg²⁺ SO₄⁻²
– H⁺ OH⁻

Low CO₂ + HCO₃⁻
Low Conductivity
pH near 7.0
EDI “How Does It Work” Summary

- Silica < 5 ppb
- Working Bed-Polishing Bed EDI Model
- Electropure Specific Ion EDI Model
- Electropure's 4 Classes of ions
- Optimization Rules for SiO$_2$
  - pH of Feed (RO permeate) near 7
  - High rejection RO System
  - Removal of CO$_2$
  - Voltage is High-Good Water Splitting
How does EDI remove CO$_2$ and SiO$_2$?

- EDI removes charged ions
- CO$_2$ and SiO$_2$ are not charged
- How to optimize EDI Systems to remove CO$_2$ and SiO$_2$
CO₂ Chemistry

\[
\text{CO}_2 \text{ (gas) } + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \text{ (carbonic acid)}
\]

\[
\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \text{ (bicarbonate)}
\]

\[
\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \text{ (carbonate)}
\]
CO$_2$ Chemistry and pH

CO$_2$ + H$_2$O $\Leftrightarrow$ H$_2$CO$_3$

H$_2$CO$_3$ $\Leftrightarrow$ H$^+$ + HCO$_3^-$  \hspace{1cm} pH = 6.4

HCO$_3^-$ $\Leftrightarrow$ H$^+$ + CO$_3^{2-}$ \hspace{1cm} pH = 10.3
CO$_2$ Chemistry and pH
CO$_2$ Chemistry and pH
CO₂ in RO-EDI Systems

Normal 1-pass RO:
\[ \text{pH} = 5.8-6.4 \]

CO₂

EDI: \[ \text{pH} = 7.0 \]
CO₂ + HCO₃⁻
SiO$_2$ Chemistry and pH

\[ \text{SiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4 \]
\[ \text{H}_4\text{SiO}_4 \rightleftharpoons \text{H}^+ + \text{H}_3\text{SiO}_4^- \]

\[ \text{pH} = 9.8 \]

Silica is charged only above pH 9.8
CO₂ and SiO₂ Conclusions

- RO: at pH < 6.4 CO₂ is difficult to reject
- RO: at pH < 9.8 SiO₂ is difficult to reject
- EDI: at pH = 7.0 HCO₃⁻ is weak
- EDI: at pH = 7.0 H₄SiO₄ is weak
- GTM: at pH < 6.0 GTM is very good for CO₂
RO and CO$_2$

1. Use Corosex to remove CO$_2$ before the RO
2. pH in 1-pass RO above 6.8
3. Raise pH in 2-pass RO to above 8.3
RO Option #1 (Corosex™)

- pH 5.5
  - CO₂ high
- pH 7.0
  - HCO₃⁻ low
- pH 7.0
  - HCO₃⁻ low
- pH 6.7
  - HCO₃⁻ very low

Corosex™ (MgO) + Calcite (CaCO₃) ~ 10:90
Softener
- Ca²⁺
RO
pH 7.3
HCO₃⁻ to drain
RO Option #2 (pH >6.8)

- pH 5.5
- CO$_2$ high
- Add NaOH
- pH 7.0
- HCO$_3^-$ high
- RO
- pH 6.7
- HCO$_3^-$ low
- pH 7.3
- HCO$_3^-$ to drain
RO Option #3 (2-pass RO high pH)

pH 6.3
CO₂ high

RO #1
pH 6.5

Add NaOH
pH ~ 8.3

RO #2
pH 8.5
HCO₃⁻ to drain

pH 7.0
HCO₃⁻ very low

pH 6.5
GTM (Gas Transfer Membrane) and CO₂

- Use GTM (Liqui-Cel™) to remove CO₂ after the RO
- pH must be right for GTM
  - GTM removes CO₂ (gas) not HCO₃⁻
  - pH should be < 6.0
RO-GTM Option

- Add Acid
- pH 6.0-6.3
- CO₂ high

- pH < 6.0
- CO₂ high

Vacuum
- CO₂ to drain

Liqui-Cel™

- CO₂ + HCO₃⁻ < 1-2 ppm
EDI Pretreatment Options

• Corosex™ removal of CO₂
• RO removal of CO₂ pH > 6.6
• 2-pass RO pH > 8.3
• RO-GTM pH < 6.0
EDI Pretreatment Options

- pH 7.0
- pH 8.3
- Corosex™ +Calcite
- Liqui-Cel™
Conclusion for CO₂

- pH is important
  - pH < 6.4 (for GTM)
  - pH > 6.4 (for RO)
- Remove CO₂ before EDI
- Remove CO₂ in EDI (pH = 7.0)
Conclusion for SiO$_2$

- pH is important
  - $H_3SiO_4^-$ above pH = 9.8
- SiO$_2$ competes with HCO$_3^-$ and Cl$^-$
  - $SiO_2$ HCO$_3^-$ Cl$^-$
  - HCO$_3^-$ and Cl$^-$ are stronger
- Use EDI pretreatment
  - CO$_2$ and conductivity removal
- EDI will remove up to 99% of SiO$_2$
  - 0.200 ppm $\to$ 2 ppb SiO$_2$