Basic Ion Exchange and Applications

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ResinTech, Inc.

- Bill Koebel
- Northeast Regional Sales Manager
- Ion Exchange Resins and Activated Carbon
- Experts in water and wastewater ion exchange applications
ResinTech History

- Founded in 1986
- Located in West Berlin, NJ
  - Processing plant
  - Laboratories
  - Sales & Marketing
  - Warehousing
- Other Warehouses
  - Florida
  - Texas
  - California
ResinTech Services

- Technical
  - Resin Rating Projections
  - Laboratory analysis
  - Resin selection
  - Troubleshooting
  - Comprehensive website

- People
  - All sales staff technical experts
  - Available by phone, fax, or email for immediate assistance
Applications

- Pharmaceutical
- Semiconductor
- Textile
- Automotive
- Electroplating
- Beverage
- Hemodialysis
- Pulp & Paper
- Nuclear Power
- Aquaculture
- Laboratory
- Portable exchange
- Residential
- EDM
- Remediation
- Municipal
Topics of Discussion

- History
- How resins are made
- Basic Terminology
- Ion Exchange Process
- Resin Types
- Basic Applications
- Q & A
Desalting of brackish waters mentioned in:
  - The Bible & Ancient Greeks
  - Sir Francis Bacon

1850 - Thompson & Way report to Royal Agriculture Society
  - Exchange of ions in soil
  - Attributed to aluminum silicates

1858 - Eichorn proves reaction is reversible
Synthetic Exchangers

- **1905** - Gans develops synthetic exchanger
  - Called Zeolites, from Greek words *Zein* and *Lithos*
- **1913** - First synthetic zeolites marketed in America
- **1944** - D’Alelio develops cation exchanger based on styrene/DVB copolymer
- **1948** - Anion exchanger developed
Ion Exchange Today

- Tiny plastic beads that have been chemically activated
- They are manufactured products that are made from petrochemical based monomers
Make the Beads

- Styrene
- DiVinyl Benzene (Crosslinkage)
- Suspension Polymerization
- No Water Content
- Neither Cation or Anion resin
- Beads are called co-polymer
- Functionalized to an Ion Exchange resin
Material Properties

- Size between 16 to 50 U.S. Mesh
- Resistance to fracture
- Insoluble
- Permanently attached sites
- High capacity for ions
- Temperature effects negligible
What is Ion Exchange?

- Exchange of undesirable ions for desirable ones
- Selectivity drives the reaction
- The process is reversible via regeneration
Definition of Ions

- Cations – Positively charged ions dissolved in solution
- Anions – Negatively charged ions dissolved in solution
- Law of Electroneutrality – In any solution the number of cations equals the number of anions
Basic Products

- Cation Resins
- Anion Resins
- Mixed Bed Resins
- Selective Resins & Zeolites
Cation Resins

- Used to remove cations from water
  - Hardness, Heavy Metals or all cations
- Strong Acid Cation
  - Typically use Na\(^+\) or H\(^+\) forms
- Weak Acid Cation
  - Typically use Na\(^+\) or H\(^+\) forms
## Common Cations

<table>
<thead>
<tr>
<th>Element</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Fe^{2+}</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca^{2+}</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg^{2+}</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na^{+}</td>
</tr>
<tr>
<td>Potassium</td>
<td>K^{+}</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H^{+}</td>
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</tbody>
</table>
Anion Resins

- Used to remove anions from water
  - Complexes, oxy anions (Cromate, Sulfate, etc.)
- Strong Base Anion
  - Typically use Cl\(^{-}\) or OH\(^{-}\) forms
- Weak Base Anion
  - Typically use Cl\(^{-}\) or free base forms
# Common Anions

<table>
<thead>
<tr>
<th>Anion</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphate</td>
<td>$\text{PO}_4^{\text{-3}}$</td>
</tr>
<tr>
<td>Sulfate</td>
<td>$\text{SO}_4^{\text{-2}}$</td>
</tr>
<tr>
<td>Nitrate</td>
<td>$\text{NO}_3^{-}$</td>
</tr>
<tr>
<td>Chloride</td>
<td>$\text{Cl}^{-}$</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>$\text{HCO}_3^{-}$</td>
</tr>
<tr>
<td>Hydroxide</td>
<td>$\text{OH}^{-}$</td>
</tr>
</tbody>
</table>
Selective Resins & Media

• Used to remove various ions from water
  – Heavy metals most common

• Chelating Resins
  – Typically use Na\(^+\) or H\(^+\) forms
  – Many types
Ion Exchange Processes

- Softening
- Dealkalization
- Deionization
- Nitrate removal
- Condensate polishing
- Pollution control
Selectivity

- The attraction, of one ion over another, to an ion exchange resin
- Function of ion charge, size and concentration
- For SACs and SBAs:
  - Bigger the ion, higher the charge, the more selective the ion becomes
  - I.e. -3>-2>-1 and +3>+2>+1
Inside the Resin Bead

**PS-DVB Resin bead**

**Polymer chains (polystyrene- PS)**

**Crosslinks between polymer chains (DVB)**
Inside the Resin Bead

Functional sites on polymer
Inside the Resin Bead

Functional sites shown occupied by regenerant ions (i.e. H+)
The Resin Bead in Action

Water contacts resin beads. Beads are ~50% water.
Water containing unwanted ions, in contact with water inside beads, allows ions to diffuse in/out of beads.
The Resin Bead in Action

**Calcium** ions enter

**Hydrogen** ions are exchanged and exit producing improved water
Ion Exchange - High Purity Water

C: Carbon

A: Resin

- $H^+$
- $Na^+$
- $SO_4^{2-}$
- $Mg^{2+}$
- $HCO_3^-$
- $Ca^{2+}$
- $Cl^-$
- $OH^-$

Exchange process:

C (Carbon) absorbs $H^+$ and releases $OH^-$

A (Resin) absorbs $OH^-$ and releases $H^+$
Ion Exchange - High Purity Water
Ion Exchange - High Purity Water

- H^+ 
- HCO_3^- 
- SO_4^{2-} 
- Cl^- 
- OH^- 
- Na^+ 
- Mg^{2+} 
- Ca^{2+} 

(+), (-)
<table>
<thead>
<tr>
<th><strong>Definition Chelating Resin</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chela:</strong> Gr. The pincer like claw(s) of a crab, lobster, or scorpion.</td>
</tr>
<tr>
<td><strong>Ligand:</strong> The chemical term for an electron pair donor (Lewis base) when it forms a bond with a metal cation.</td>
</tr>
<tr>
<td><strong>Chelating Resin:</strong> Ion exchange resins that have ligands that can bond with metal cations. The ligands may be in addition to or in place of conventional ion exchange sites.</td>
</tr>
<tr>
<td><strong>Selectivity:</strong> The preference of an ion exchange material for a particular ion. Selectivity is always relative to a particular operating condition.</td>
</tr>
</tbody>
</table>
Chelating Lobster

Lobster

Fish

Chela
Chelating & Selective Resins

- True Chelating Resins
  - Iminodiacetate (SIR-300)
  - Aminophosphonic (SIR-500)
  - Picolyamine (SIR-1000)

- Selective Resins
  - Thiol (SIR-200)
  - Thiouronium (SIR-400)
  - Exhausted Weak Base (WBMP & SIR-700)
  - Natural Zeolites (SIR-600, greensand, & others)
  - Weak Acid Cation Resins (WACG & WACMP)
  - Nitrate & Perchlorate Selective (SIR-100 & SIR-110)
What Makes a Chelating Resin Selective?

- **Ionic Charge (Valence)**
  - Most chelating resins prefer di-valent ions to mono-valent or tri-valent ions, because the chelant group has two “Chela” (claws).

- **Hydrated Ionic Radius**
  - When the size of the hydrated radius of the ion closely fits the space between the “Chela” the resin is very selective for that particular ion.

- **Ligand Bonding**
  - Nitrogen (and oxygen) can possess an exposed electron pair, making them Lewis bases (electron pair donors). Metals that are Lewis acids form ligands with Lewis bases.
Iminodiacetate Chelant
“SIR-300”

Sodium Form (unstable charge balance)

Copper Form (very stable charge balance)

Ligand bonding
Iminodiacetate Chelant (SIR-300) Operating Limits

- **Dissolved Solids**
  - Unaffected by Sodium and other Group 1A metals (except hydrogen)
  - Practically unaffected by Calcium and other Group 2A metals
  - Selectivity is affected by other complexing agents
    - EDTA blocks exchange entirely for many metals
    - Ammonia affects exchange significantly
    - Chloride has a minor effect on selectivity

- **pH**
  - Optimum pH is usually slightly acidic
  - Selectivity is lower at high pH
  - Loses selectivity below pH of approx. 2.0
Iminodiacetate Chelant (SIR-300) Criteria for Selection

- Removal of divalent Group IV (transition) metals
- High TDS background (greater than 1000 ppm)
- Significant calcium concentration present (equal to or greater than the metal concentration)
- pH is slightly acidic (optimum pH is approx. 4)
Capacity of SIR-300 Various Metals (at saturation)

- Copper
- Nickel
- Iron
TDS Limits of various Resins Used for Metals Removal

- Strong Cation Resin (Hydrogen form) 500 ppm
- Strong Cation Resin (Sodium form) 1,000 ppm
- Weak Cation Resin (Sodium form) 10,000 ppm
- Chelating Cation Resin (Sodium form) no limit
- Mixed Bed Resin 500 ppm
What do we need to Know?

- Viability of ion exchange
  - TDS (or conductivity) with min and max if variable
  - pH and Temperature with min and max if variable
  - basic inorganic analysis of ions (Ca, Mg, Na, Cl, SO4)
  - presence or absence of oxidants
  - presence or absence of complexing agents
  - level and type of organic molecules
  - level of suspended solids
Definitions

- PPM (mg/l) – Parts per Million (milligrams per liter) a measure of the concentration of ions as defined by their weight
- “as CaCO₃” – A measure of the concentrations of ions based on the number of ionic charges.
- Grains – a very small unit of weight, originally equal to a grain of wheat.
Conversion Factors

- 7000 grains = 1 pound
- 17.1 PPM (as CaCO3) = 1 grain per gallon
- 7.48 gallons = 1 cubic foot
- 40% = resin void volume
Resin Selection

- Feedwater analysis
- Desired effluent quality
- Operating conditions
- Economics
- Type of equipment
- Regeneration chemicals available
Typical Resin Life

- Operating Life
  - Cation – 8 to 10 years
  - Anion – 4 to 6 years

- Factors
  - Oxidants
  - Temperature
  - Regeneration frequency
Factors Affecting Resin Performance

- Oxidation
  - Chlorine
  - Temperature
- Loss of capacity
- Fouling
  - Organic
  - Oil
- Loss of resin
  - Backwash loss
Equipment Troubleshooting

- Equipment Failure
- Distribution Problems
- Control malfunctions
- Operator error
- Changing Water analysis
Types of Waste Treated

- **Rinse Waters**
  - Acid and neutral Rinses
  - Alkaline cyanide Rinses
  - EDM Machines
  - PCB washers

- **Plating Baths**
  - Tri chrome

- **Wastewater**
  - End of pipe polishing
Typical Plating Rinse Tank Set-up

- Plating Bath
- Dead Rinse
- First Rinse
- Second Rinse
- Final Rinse

- Pre-filter
- IX Columns
- Sump
Misc Ion Exchange Possibilities

- Silver (and other precious metals)
- Lead (and other heavy metals)
- pH control (by ion exchange buffering)
- Fluoborate (and other exotic ions)
- Carbonate Removal (from cyanide baths)
Bulk Regeneration for base transition metals

- pH Adjustment
- Carbamate precipitation
- Filter Press
- Final Filtration
- Ion Exchange Polishing
Regeneration Sequence

- Backwash
- Chemical Injection
- Displacement / Slow rinse
- Fast Rinse
Backwash

- A flow of water is passed upward through the resin bed
- The resin bed expands and fluidizes
- Suspended solids are removed
- The resin bed is classified, increasing the void space
- Mixed bed backwash also serves to separate the cation and anion beads
Chemical Injection

- A dilute solution of acid or caustic flows through the bed
- The relatively high concentration of hydrogen or hydroxide ions causes a reverse exchange
- The resin is restored to the hydrogen or hydroxide form
Displacement Rinse

- Increases contact time between regenerant and the bottom of the bed
- Helps push remaining regenerant through the bed without significant mixing
- Begins the rinse process
Fast Rinse

- Removes the last traces of regenerant chemical from the resin
- Prepares the resin for the next service cycle
Effluent Water Quality

- Selectivity and Leakage – least strongly held ion first to come off
- Regeneration Dose – the higher the dose, the lower the leakage
Questions & Answer

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