Application of I.E.R. for industry

- Water treatment for boiler
- Purification of medicine
- Purification of sugar
- Water treatment for power plants
- Ultra pure water for LSI
- Purification of amino acid

Ion exchange resins
Uses of I.E.R. in Japan

Share of DIAION 40%

- Water treatment: 37%
- Special uses: 4%
- Boiler: 5%
- Steam power plant: 3%
- Atomic power plant: 4%
- Ultra Pure water: 9%
- Catalyst: 7%
- Sugar: 8%
- Pharmacuticals: 5%
- Separation Process: 3%
- Amino acid & Nucleic acid: 3%
Manufacturing Process of I.E.R

Polymerization

\[ \text{Polymerization} \quad + \quad \text{DVB} \quad + \quad \text{porous agent} \]

\[ \text{cross-linked polystyrene} \]

gel  porous  High-porous

Amination

Anion exchange resin

Chelate resin

Sulfonation

Cation exchange resin

Synthetic Absorbent

Manufacturing Process of I.E.R
Physical Structure of I.E.R

- **Porous Type**
  - Macro pore: (10 - 10,000 Å)

- **Gel Type**
  - Micro pore: (0 - 300 Å)

- **High Porous Type (Macroreticular)**
  - Macro pore: (10 - 1,000 Å)

**Cross Linkage (DVB %)**
- Porous, Gel: 2 - 16%
- High por.: >15%

**Reaction Rate**
- Porous > Gel > High Porous
# Product List of DIAION® & its Applications

<table>
<thead>
<tr>
<th>Basic Structure</th>
<th>Gel</th>
<th>Porous</th>
<th>Highy Porus</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Types &amp; Classes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cation Exchange Resins</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strongly acidic cation e.r.</td>
<td>SK</td>
<td>PK</td>
<td>HPK</td>
<td>Water treatment&lt;br&gt;Refining sugar solutions&lt;br&gt;Separation of Fructose, Amino acid, Catalyst</td>
</tr>
<tr>
<td>R-SO3・Na</td>
<td>U</td>
<td>B K</td>
<td>R K P C</td>
<td></td>
</tr>
<tr>
<td>Weakly acidic cation e.r.</td>
<td></td>
<td></td>
<td>WK</td>
<td>Recovery of metals&lt;br&gt;Water treatment</td>
</tr>
<tr>
<td>R-COO・H , etc.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Anion Exchange Resins</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strongly basic anion e.r.</td>
<td>SA</td>
<td>PA</td>
<td>HPA</td>
<td>Water treatment&lt;br&gt;Refining sugar solutions&lt;br&gt;Purification of drugs&lt;br&gt;Separation of Amino acid,</td>
</tr>
<tr>
<td>R-N(CH3)3・Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-N(CH3)2(C2H4OH)・Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weakly basic anion e.r.</td>
<td></td>
<td></td>
<td>WA</td>
<td>Water treatment&lt;br&gt;Decolorization of sugar solution</td>
</tr>
<tr>
<td>R-N(CH3)2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Special Resins</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chelating resins</td>
<td></td>
<td></td>
<td>CR</td>
<td>Recovery of metals&lt;br&gt;Brine purification</td>
</tr>
<tr>
<td>ex. R-N-(CH2COOH)2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthetic absorbents</td>
<td></td>
<td></td>
<td>HP</td>
<td>Purification of drugs</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HPMG</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SP</td>
<td></td>
</tr>
<tr>
<td>Protein separating agents</td>
<td></td>
<td></td>
<td>FP</td>
<td>Protein separation</td>
</tr>
</tbody>
</table>

*other: resins for ultra pure water, mixed resins, powdered resins, etc.*
## DIAION® line up & Crosslinkage

<table>
<thead>
<tr>
<th>DVB (%)</th>
<th>S.A.Cation</th>
<th>S.Anion; Type I</th>
<th>S.Anion; Type II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gel</td>
<td>Gel</td>
<td>Gel</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>PA306</td>
</tr>
<tr>
<td>4</td>
<td>SK104</td>
<td>SA11A</td>
<td>SA21A</td>
</tr>
<tr>
<td>6</td>
<td>SK1B</td>
<td>SA12A SA10A</td>
<td>PA308 PA312</td>
</tr>
<tr>
<td>8</td>
<td>SK11B</td>
<td>PK216</td>
<td>PA308 SA20A</td>
</tr>
<tr>
<td>10</td>
<td>SK110</td>
<td>PA316</td>
<td>PA408</td>
</tr>
<tr>
<td>12</td>
<td>SK112</td>
<td></td>
<td>PA412</td>
</tr>
<tr>
<td>14</td>
<td>PK228</td>
<td></td>
<td>PA418</td>
</tr>
</tbody>
</table>
Influence with Crosslinkage (DVB%)

< Efficiency of IER is decided by Crosslinkage >

Capacity: high cross > low cross  
Reaction Rate: low cross > high cross
※8～12% is used for water treatment

DVB vs Moisture & Capacity (gel cation)  
Reaction Rate (Na adsorption of gel cation)
Strongly Acidic Cation E. R.

• Insoluble in any solvents and strongly acidic like HCl or H₂SO₄

Ion Exchange Reaction

/<Neutralization>
\[ R\text{-SO}_3\text{H} + \text{NaOH} \rightarrow R\text{-SO}_3\text{Na} + \text{H}_2\text{O} \]

/<Salt Splitting>
\[ R\text{-SO}_3\text{H} + \text{NaCl} \rightarrow R\text{-SO}_3\text{Na} + \text{HCl} \]

/<Softening>
\[ 2R\text{-SO}_3\text{Na} + \text{CaCl}_2 \rightarrow (R\text{-SO}_3)\text{Ca}_2 + 2\text{NaCl} \]

Selectivity (in dilute solution)
\( (\text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}) > (\text{NH}_4^{+} > \text{K}^{+} > \text{Na}^{+} > \text{H}^{+}) \)

Regeneration
\[ (R\text{-SO}_3)\text{Ca}_2 + 2\text{HCl} \rightarrow 2R\text{-SO}_3\text{H} + \text{CaCl}_2 \]
More regenerates is required than the ex. Capacity.
Weakly Acidic Cation E.R.

- Insoluble in any solvents and show weakly acidic like carboxylic acids.
- Dissociation occurs in H₂O above pH 4.

**Ion Exchange Reaction**

WK react only with base, not with neutral salt.

\[
\begin{align*}
R-\text{COOH} + \text{NaOH} & \rightarrow R-\text{COONa} + \text{H}_2\text{O} \\
2R-\text{COOH} + \text{Ca(HCO}_3\text{)}_2 & \rightarrow (R-\text{COO})_2 \text{Ca} + 2\text{H}_2\text{CO}_3
\end{align*}
\]

**Selectivity**

\[H^+ > (\text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}) > > > \text{Na}^+\]

**Regeneration**

Salt form is easily regenerated with theoretical amount of regenerant.

**Hydrolysis**

\[
R-\text{COONa} + \text{H}_2\text{O} \rightarrow R-\text{COOH} + \text{NaOH}
\]
## Difference between Strongly and Weakly acidic Cation E.R.

<table>
<thead>
<tr>
<th></th>
<th>Strongly acidic C.E.R. (SK1B)</th>
<th>Weakly acidic C.E.R. (WK40)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Capacity</td>
<td>2 meq/mL-R</td>
<td>4.6 meq/mL-R</td>
</tr>
<tr>
<td>pH range</td>
<td>From 1 to 14</td>
<td>Above 4</td>
</tr>
<tr>
<td>Regeneration</td>
<td>Difficult</td>
<td>Easy</td>
</tr>
<tr>
<td>Volume change</td>
<td>Small</td>
<td>Big (e.g. Ca/H=1.1, Na/H=1.6)</td>
</tr>
<tr>
<td>Application</td>
<td>Widely used</td>
<td>Suitable for containing large amount of HCO$_3^-$, With hardness.</td>
</tr>
</tbody>
</table>
Strongly Basic Anion E. R

- Insoluble in any solvents and strongly basic like NaOH, KOH

**Ion Exchange Reaction**

*Neutralization*

\[
\text{R}_4\text{-NOH} + \text{HCl} \rightarrow \text{R}_4\text{-NCl} + \text{H}_2\text{O}
\]

*Salt Splitting*

\[
\text{R}_4\text{-NOH} + \text{NaCl} \rightarrow \text{R}_4\text{-NCl} + \text{NaOH}
\]

\[
\text{R}_4\text{-NOH} + \text{SiO}_2 \rightarrow \text{R}_4\text{-NHSiO}_3
\]

**Selectivity (in dilute solution)**

\[
\text{SO}_4^{2-} > \text{NO}_3^- > \text{HSO}_4^- > \text{Cl}^- > \text{HCO}_3^- > \text{SiO}_2 > \text{OH}^- 
\]

**Regeneration**

\[
\text{R}_4\text{-NCl} + \text{NaOH} \rightarrow \text{R}_4\text{-NOH} + \text{NaCl}
\]

More regenerates is required than the ex. Capacity.
## Comparison of Type I and Type II resins

<table>
<thead>
<tr>
<th></th>
<th>Type I</th>
<th>Type II</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Exchange group</strong></td>
<td>Trimethylammonium R-N-CH₃ CH₃</td>
<td>Dimethyloethanolamine R-N-C₂H₄OH CH₃</td>
</tr>
<tr>
<td><strong>Diaion</strong></td>
<td>SA10A, SA12A, SA11A PA300 series HPA25</td>
<td>SA20A, SA21A PA400 series HPA75</td>
</tr>
<tr>
<td><strong>Basicity</strong></td>
<td>Strongly basic</td>
<td>Strongly basic, but slightly weaker than Type I</td>
</tr>
<tr>
<td><strong>Ease of regeneration</strong></td>
<td>Regeneration is difficult and a large quantity of regenerant is required.</td>
<td>Regeneration is facile and economical.</td>
</tr>
<tr>
<td><strong>Leakage in exchange of weak acids. (SiO2)</strong></td>
<td>Only slight (SiO2 spec. 0.1ppm at Co-CR)</td>
<td>Slightly weaker (SiO2 spec. 0.2ppm at CoCR )</td>
</tr>
<tr>
<td><strong>Chemical stability</strong></td>
<td>Cl form : up to 80 °C OH form : up to 60 °C</td>
<td>Cl form : up to 60 °C OH form : up to 40 °C</td>
</tr>
<tr>
<td><strong>Regeneration</strong></td>
<td>Counter current regen.</td>
<td>Co-current regen.</td>
</tr>
</tbody>
</table>
Difference between type I and type II SBAnion

Reg. Efficiency : Type II > Type I
SiO2 leakage : II > I
BTC : II > I
Degradation when using for water treatment (SB-Anion type I, II)

As for type 2,

- Degradation of SSC is big.
- Influence of oxygen is big.
Weakly Basic Anion E.R.

- Insoluble in any solvents and show weakly basic like NH₄OH.
- Dissociation occurs in H₂O under pH 9.

**Ion Exchange Reaction**

WA react only with strong acids or NH₄Cl, not with neutral salts or carboxylic acid

\[
R_3\text{-NOH} + \text{HCl} \rightarrow R_3\text{-NCl} + \text{H}_2\text{O}
\]

\[
R_3\text{-NOH} + \text{NH}_4\text{Cl} \rightarrow R_4\text{-NCl} + \text{NH}_4\text{OH}
\]

**Selectivity**

\[
\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-
\]

**Regeneration**

\[
R_3\text{-NCl} + \text{NaOH} \rightarrow R_4\text{-NOH} + \text{NaCl}
\]

Salt form is easily regenerated with theoretical amount of regenerant.
## Selectivity coefficients for SK

<table>
<thead>
<tr>
<th>Type of ion</th>
<th>D.V.B.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4%</td>
</tr>
<tr>
<td>Li⁺</td>
<td>1.00</td>
</tr>
<tr>
<td>H⁺⁺</td>
<td>1.32</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1.58</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>1.90</td>
</tr>
<tr>
<td>K⁺⁺</td>
<td>2.27</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>2.46</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>2.67</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>4.73</td>
</tr>
<tr>
<td>Te²⁺</td>
<td>6.71</td>
</tr>
<tr>
<td>UO₂²⁺</td>
<td>2.36</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>2.95</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>3.13</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type of ion</th>
<th>D.V.B.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4%</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>3.23</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>3.29</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>3.37</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>3.42</td>
</tr>
<tr>
<td>Be²⁺</td>
<td>3.43</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>3.45</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>4.15</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>4.70</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>6.56</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>7.47</td>
</tr>
<tr>
<td>Cr²⁺</td>
<td>6.6</td>
</tr>
<tr>
<td>Ce²⁺</td>
<td>7.5</td>
</tr>
<tr>
<td>La²⁺</td>
<td>7.6</td>
</tr>
</tbody>
</table>
Selectivity of ion

Selectivity: II valence > I valence
MW range > small

2R-Mg + Ca → 2R-Ca + Mg
2(R-Na) + Mg → 2R-Mg + 2Na
R-H + Na → R-Na + H

By Selectivity, ion is separated
Degradation of I.E.R(1)  
*S.A. Cation E.R*

**Phenomenon**
A. Increasing of moisture content and leakage  
B. Decreasing of I.E. capacity per volume

**Reason**
Irreversible swelling by oxidation

**Counter measure**
   (The degree of oxidation depends temperature, pH, Fe,Cu..)
2. To use high cross linkage resin.  
   (ex. to change from SK1B to SK110,SK112)
Decomposition of S.A.Cation

Structure of SAC

Hydration:
- thermal decomposition (>120°C)
  \[ \text{R-SO}_3\text{H} + \text{H}_2\text{O} \rightarrow ① \text{R-OH} + \text{H}_2\text{SO}_3 \]
  \[ \rightarrow ② \text{R-H} + \text{H}_2\text{SO}_4 \]

Oxidation:
- decomposition of copolymer matrix
  ※Main decomposition in case of water treatment
  Oxidizing agents, Metals (Cu, Fe, Al etc)

Products:
① \( \text{H}_2\text{SO}_3 \)
② \( \text{H}_2\text{SO}_4 \)
③ Polystyrene Sulfonic Acid
Relation between Crosslinkage and Oxidative Degradation of SAC

Tolerance to Oxidation: 12 > 10 > 8 (DVB%)
Cause of Oxidation of IER

Oxidizing agents: O₂, Cl₂, H₂O₂, NaClO₃
Oxidation accelerates with Catalyst effect by metals (Cu, Fe, Al)

Cl₂ Tolerance of SK1B

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Maximum Cl₂ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5–10</td>
<td>0.6</td>
</tr>
<tr>
<td>10–15</td>
<td>0.4</td>
</tr>
<tr>
<td>15–20</td>
<td>0.2</td>
</tr>
<tr>
<td>20–25</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Degradation of I.E.R(2)
S.B. Anion E.R

Phenomenon
A. Decreasing of total capacity or salt splitting capacity.
B. Decreasing of moisture content.
C. Increasing of silica leakage.
D. Decreasing of reaction rate.

Reason
1. Thermal decomposition of resin.
2. Oxidative decomposition.
3. Organic contamination.

Counter measure
1. Refilling the resin.
2. Removal of oxidizing agents by pretreatment.
3-1. Removing of organic compound by pretreatment such as A.C.
3-2. To use porous resin. (e.g. PA312, PA418)
3-3. Treatment by HCl or NaOH + NaCl for recovery.
Decomposition of S.B. Anion (Type I)

Structure of SBA

Weak basicity

Detach

products

(CMethylamin=WBA-Resin)

(S)B Anion (Type I)

SBA are decomposed by heat and oxidation
Organic contamination and reaction rate

- Diffusion in solution
- Film diffusion
- Particle diffusion

Organic substance (Resin)
Comparison between Gel and Porous (Adsorption of organic substance)

Test condition
IER : R-Cl 15 mL
Organic sub. : Fast Green FCF 30 ppm
(dye MW=808)
Used Resin : after 80 cycle (water treatment)
Comparison between Gel and Porous (Efficiency of 2B3T-water treatment)

Comparison between PA418/SA20A
COD, CL reakage
Resin: after 80 cycle use in many COD areas (in Japan)
Selection of DIAION® for water treatment (1)

**CATION**

There are a larger amount of oxidizing agents in influent water.

The influent water contains a large quantity of HCO$_3^-$, and Ca$^{2+}$, Mg$^{2+}$ & total ions.

(Standard)  ↓  SK1B

- **yes**  →  SK110, SK112

- **yes**  →  WK40-SK1B  (4B5T)

- **yes**  →  WK40-SK112L  (D.L)
Selection of DIAION®
for water treatment (2)

ANION

You want to make much of regeneration cost or quality of effluent water. Co-current regen.

- yes → SA20A

There are a large amount of natural organic substance in influent water.

- yes → PA312, PA418

The influent water contains a large quantity of mineral acids.

- yes → WA30-SA12A (4B5T)
- yes → WA30-SA10DL (D.L)
System when there are many organic substance

4B5T

WK40 → SK1B → DG → WA30 → PA312

4B5T

SK1B → DG → PA418 → SK1B → PA312

2B3T

SK1B → DG → SA10DL → WA30

Dual layers Bed
This system suitable for treating water with a very large quantity of HCO3-, hardness and total ions.
Other Applications

- Effluent treatment & recovery of valuable materials.
- Foodstuffs and food additives.
  - Refining of sugar solution.
  - Separation of amino acids.
- Purification of chemicals.
  - Purification of brine
- Separation and purification of antibiotics
- Catalyst of chemical material manufacture

→ DIAION® manual (II)
Home Page of DIAION

http://www.diaion.com

● Introduction of product
  Specification and application

● Mail for question and data request

● There is English version