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DIAION®

Ion Exchange and Water Treatment

Mitsubishi Chemical Corporation
Separation Material Department

2009/04

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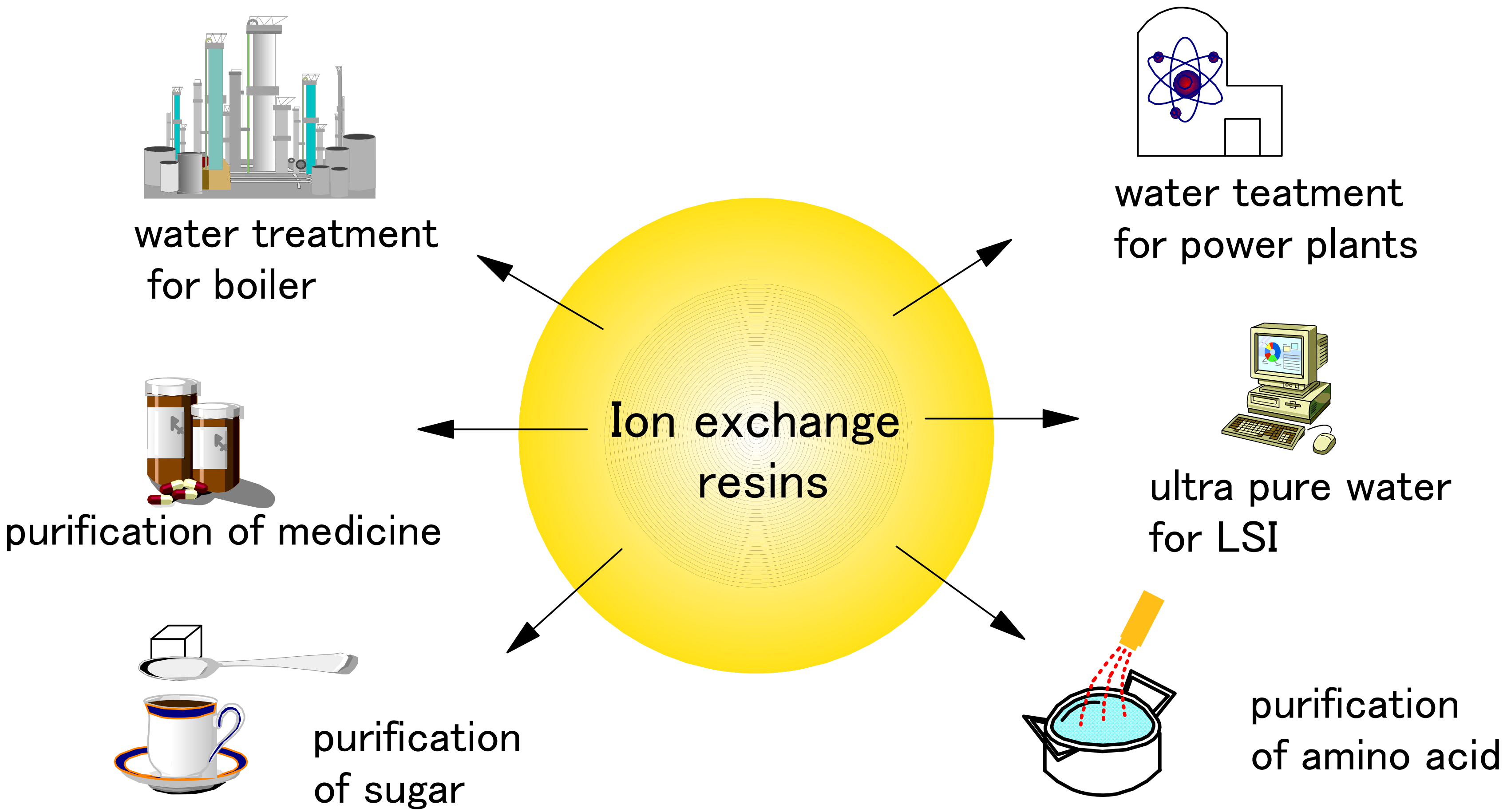
Application of I.E.R. for industry



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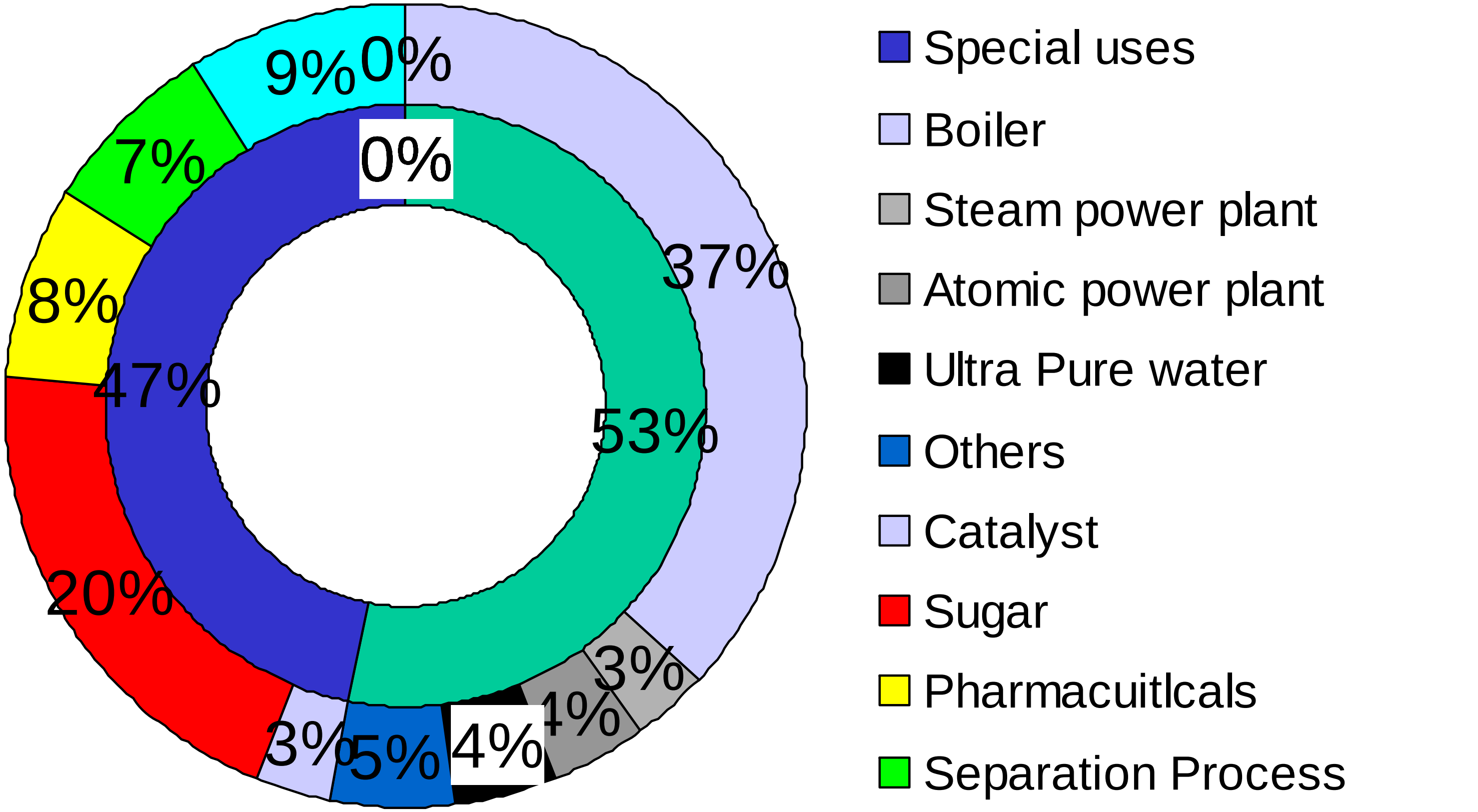
Uses of I.E.R. in Japan

Share of DIAION
40 %



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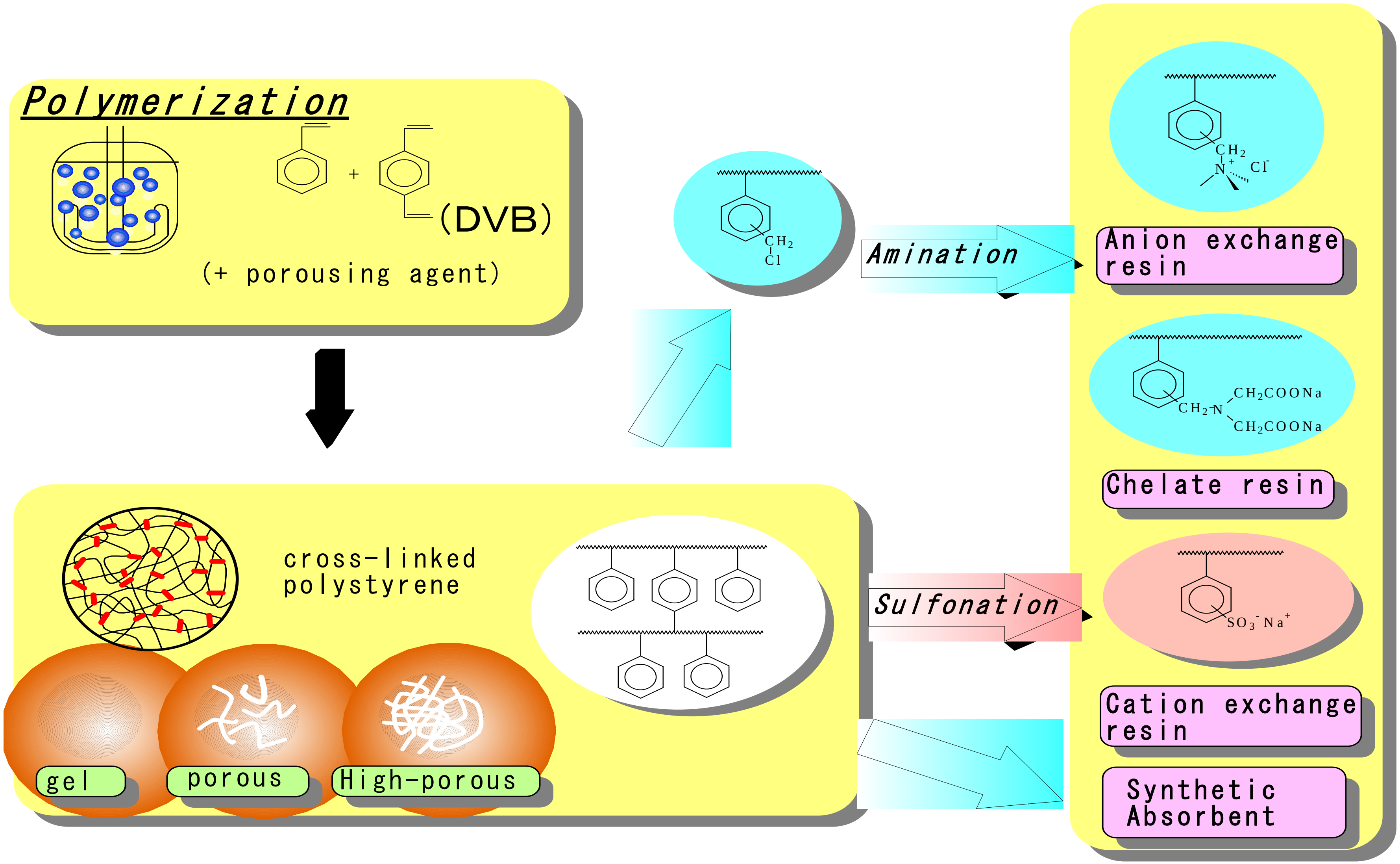
Manufacturing Process of I.E.R



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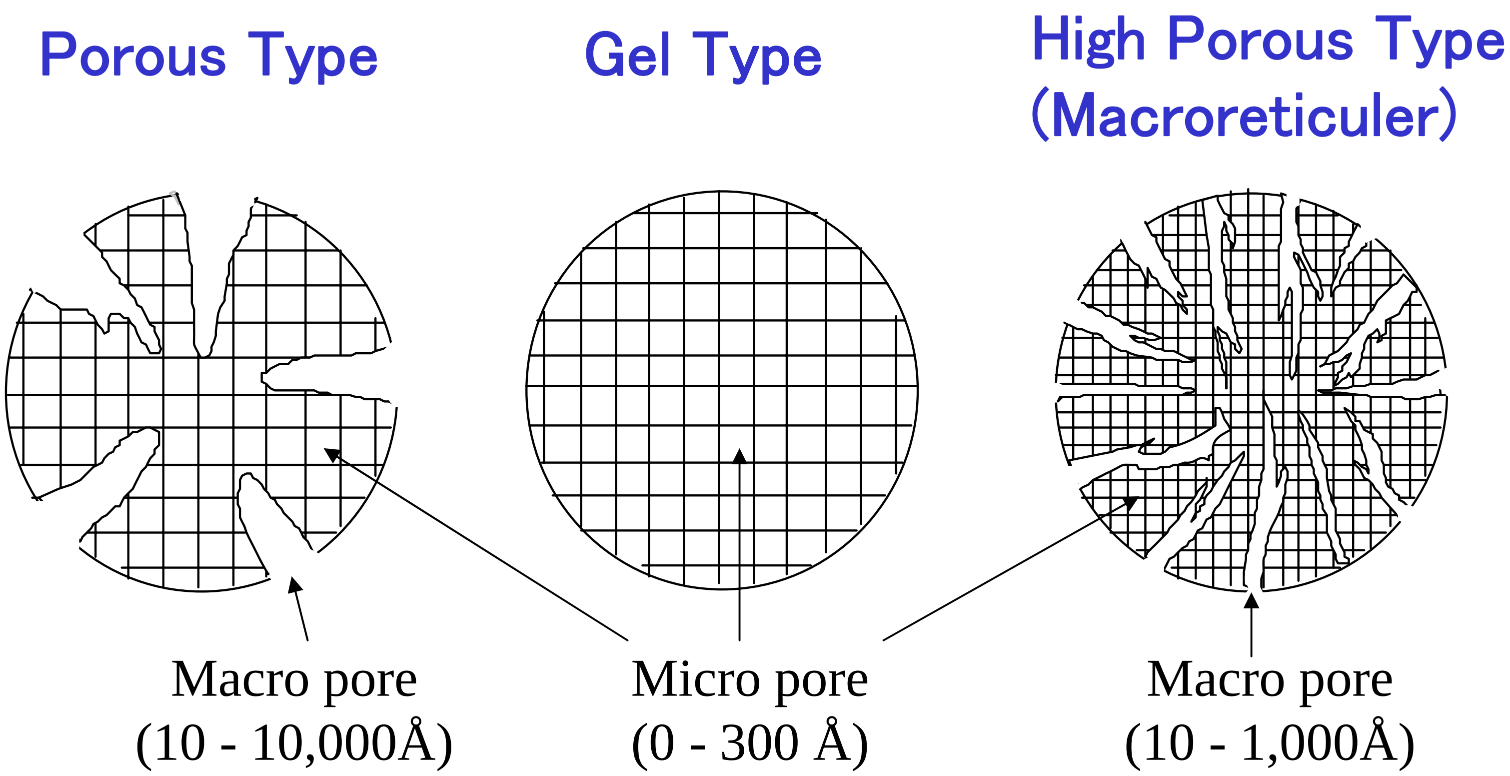
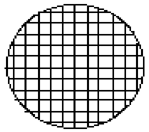
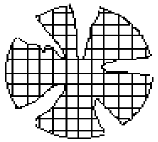
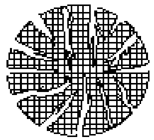
Physical Structure of I.E.R



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

Product List of **DIAION®** & its Applications

Basic Structure / Types & Classes	Gel	Porous	Highy Porus	Applications
				
Cation Exchange Resins				
Strongly acidic cation e.r. R-SO3·Na	SK UBK	PK	HPK RCP	Water treatment Refining sugar solutions Separation of Fluctose, Amino acid, Catalyst
Weakly acidic cation e.r. R-COO·H , etc.			WK	Recovery of metals Water treatment
Anion Exchange Resins				
Strongly basic anion e.r. R-N(CH3)3·Cl R-N(CH3)2(C2H4OH)·Cl	SA	PA	HPA	Water treatment Refining sugar solutions Purification of drugs Separation of Amino acid,
Weakly basic anion e.r. R-N(CH3)2			WA	Water treatment Decolorization of sugar solution
Special Resins				
Chelating resins ex. R-N-(CH2COOH)2			CR	Recovery of metals Brine purification
Synthetic absorbents			HP HPMG SP	Purificasion of drugs
Protein separating agents			FP	Protein separation

other;resins for ultra pure water, mixed resins, powdered resins, etc..

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DIAION® line up & Crosslinkage

<table>
<tr><th rowspan="2">DVB (%)</th><th colspan="2">S.A.Cation</th><th colspan="2">S.Anion; Type I</th><th colspan="2">S.Anion; Type II</th></tr>
<tr><th>Gel</th><th>Porous</th><th>Gel</th><th>Porous</th><th>Gel</th><th>Porous</th></tr>
<tr><td>3</td><td></td><td></td><td rowspan="4">SA11A
SA12A
SA10A</td><td>PA306</td><td rowspan="4">SA21A
SA20A</td><td></td></tr>
<tr><td>4</td><td>SK104</td><td>PK208</td><td>PA308</td><td>PA408</td></tr>
<tr><td>6</td><td></td><td></td><td>PA312</td><td>PA412</td></tr>
<tr><td>8</td><td>SK1B</td><td>PK216</td><td>PA316</td><td rowspan="2">PA418</td></tr>
<tr><td>10</td><td>SK110</td><td>PK220</td><td></td><td></td><td></td></tr>
<tr><td>12</td><td>SK112</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>14</td><td></td><td>PK228</td><td></td><td></td><td></td><td></td></tr>
</table>

Influence with Crosslinkage (DVB%)

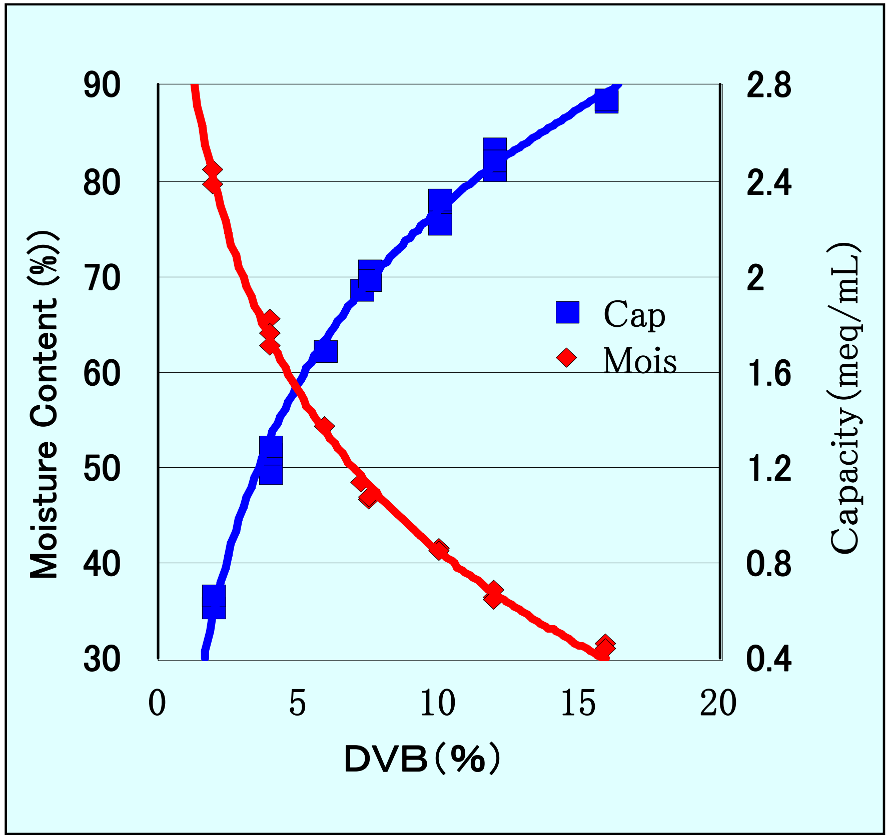
＜ Efficiency of IER is decided by Crosslinkage ＞

Capacity : high cross > low cross

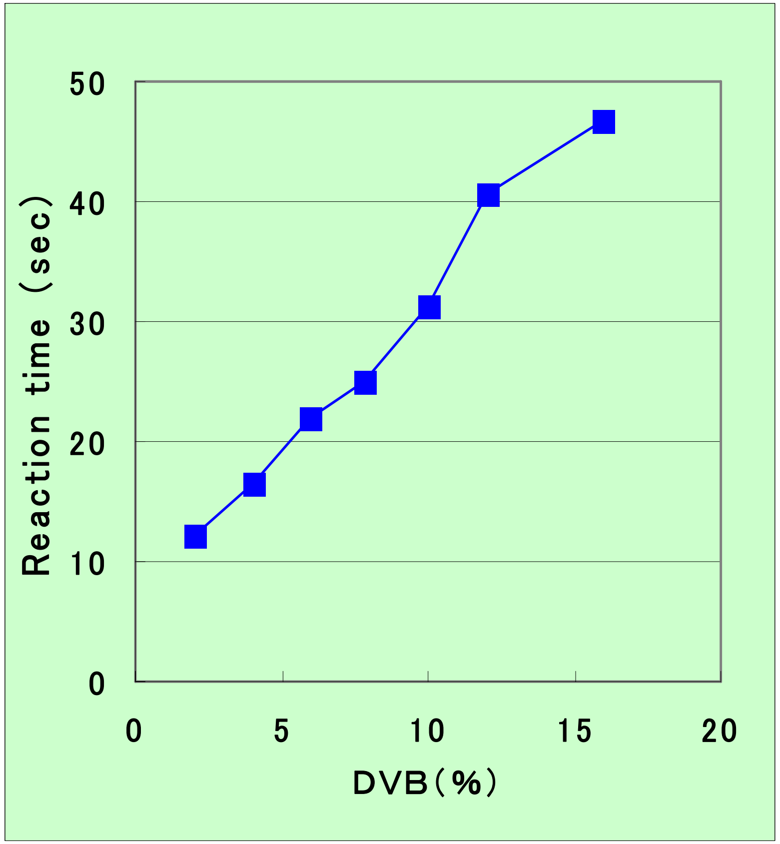
Reaction Rate : low cross > high cross

※8～12% is used for water treatment

DVB vs Moisture & Capacity (gel cation)



Reaction Rate (Na adsorption of gel cation)



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Strongly Acidic Cation E. R.

- Insoluble in any solvents and strongly acidic like HCl or H_2SO_4

Ion Exchange Reaction

<Neutralization>

$$R\text{-}SO_3H + NaOH \longrightarrow R\text{-}SO_3Na + H_2O$$

<Salt Splitting>

$$R\text{-}SO_3H + NaCl \longrightarrow R\text{-}SO_3Na + HCl$$

<Softening>

$$2R\text{-}SO_3Na + CaCl_2 \rightarrow (R\text{-}SO_3)_2Ca + 2NaCl$$

Selectivity (in dilute solution)

$$(Ba^{2+} > Ca^{2+} > Mg^{2+}) > (NH_4^+ > K^+ > Na^+ > H^+)$$

Regeneration

$$(R\text{-}SO_3)_2Ca + 2HCl \longrightarrow 2R\text{-}SO_3H + CaCl_2$$

More regenerates is required than the ex. Capacity.

Weakly Acidic Cation E.R.

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- Insoluble in any solvents and show weakly acidic like carboxylic acids.
- Dissociation occurs in H_2O above pH 4.

Ion Exchange Reaction

WK react only with base, not with neutral salt.

$$R\text{-}COOH + NaOH \longrightarrow R\text{-}COONa + H_2O$$

$$2R\text{-}COOH + Ca(HCO_3)_2 \rightarrow (R\text{-}COO)_2\ Ca + 2H_2CO_3$$

Selectivity

$$H^+ > (\ Ba^{2+} > Ca^{2+} > Mg^{2+}) >>> Na^+$$

Regeneration

Salt form is easily regenerated with theoretical amount of regenerant.

Hydrolysis

$$R\text{-}COONa + H_2O \longrightarrow R\text{-}COOH + NaOH$$

Difference between Strongly and Weakly acidic Cation E.R.

	Strongly acidic C.E.R. (SK1B)	Weakly acidic C.E.R. (WK40)
Total Capacity	2 meq/mL-R	4.6 meq/mL-R
pH range	From 1 to 14	Above 4
Regeneration	Difficult	Easy
Volume change	Small	Big (e.g. Ca/H=1.1 Na/H=1.6)
Application	Widely used	Suitable for containing large amount of HCO_3^- , With hardness.

Strongly Basic Anion E. R

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

Ion Exchange Reaction

<Neutralization>

$R_4\text{-NOH} + HCl \longrightarrow R_4\text{-NCl} + H_2O$

<Salt Splitting>

$R_4\text{-NOH} + NaCl \longrightarrow R_4\text{-NCl} + NaOH$

$R_4\text{-NOH} + SiO_2 \longrightarrow R_4\text{-NHSiO}_3$

Selectivity (in dilute solution)

$SO_4^{2-} > NO_3^- > HSO_4^- > Cl^- > HCO_3^- > SiO2 > OH^-$

Regeneration

$R_4\text{-NCl} + NaOH \longrightarrow R_4\text{-NOH} + NaCl$

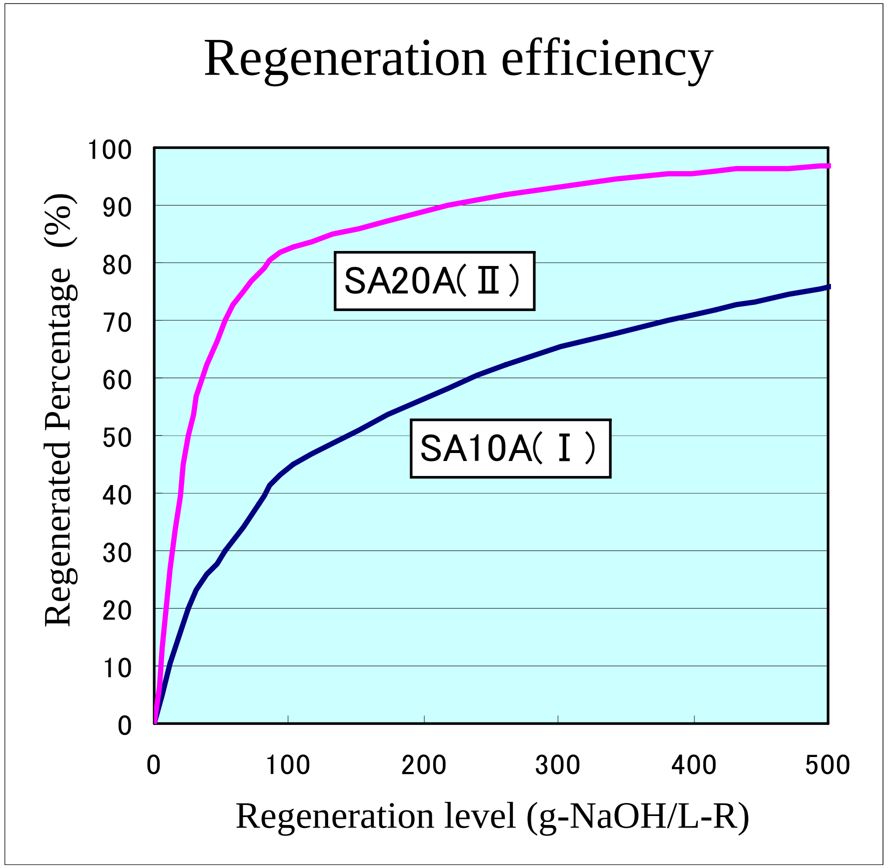
More regenerates is required than the ex. Capacity.

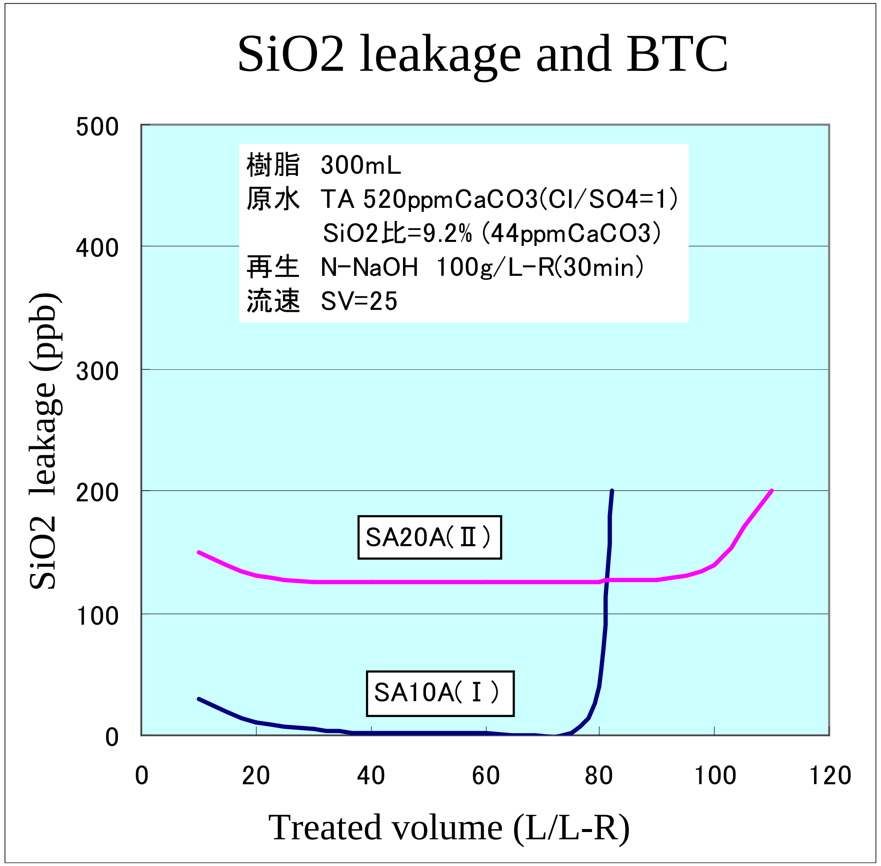
Comparison of Type I and Type II resins

	Type I	**Type II**
Exchange group	Trimethylammonium CH_3 $R\text{-}N\text{-}CH_3$ CH_3	Dimethlyethanolamine CH_3 $R\text{-}N\text{-}C_2H_4OH$ CH_3
Diaion	SA10A,SA12A,SA11A PA300 series HPA25	SA20A,SA21A PA400 series HPA75
Basicity	Strongly basic	Strongly basic, but slightly weaker than Type I
Ease of regeneration	Regeneration is difficult and a large quantity of regenerant is required.	Regeneration is facile and economical.
Leakage in exchange of weak acids. (SiO2)	Only slight (SiO2 spec. 0.1ppm at Co-CR)	Slightly weaker (SiO2 spec. 0.2ppm at CoCR)
Chemical stability	Cl form : up to 80 ^oC OH form : up to 60 ^oC	Cl form : up to 60 ^oC OH form : up to 40 ^oC
Regeneration	Counter current regen.	Co-current regen.

Difference between type Ⅰ and type Ⅱ SBAnion

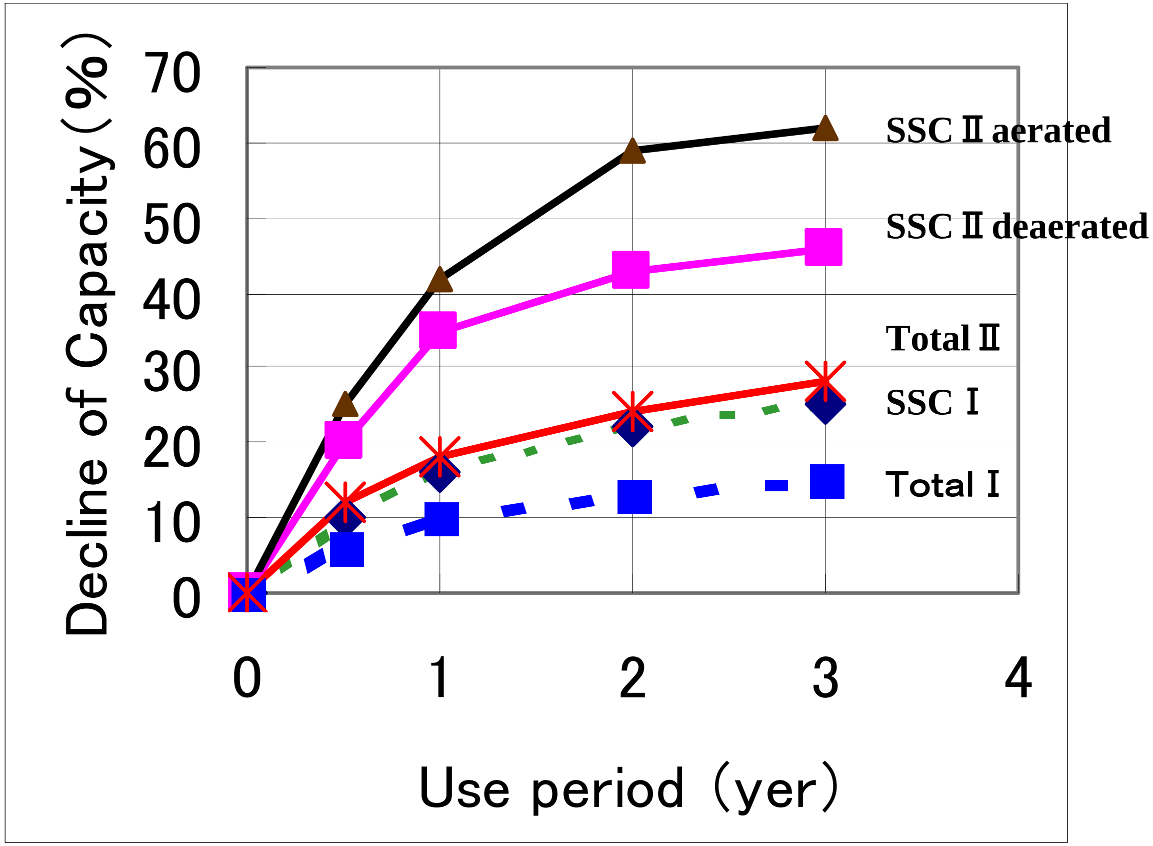
Reg. Efficiency : Type Ⅱ > Type Ⅰ
SiO2 leakage : Ⅱ > Ⅰ
BTC : Ⅱ > Ⅰ





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.

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- Insoluble in any solvents and show weakly basic like NH_4OH.
- Dissociation occurs in H_2O under pH 9.

Ion Exchange Reaction

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

$$R_3\text{-NOH} + HCl \longrightarrow R_3\text{-NCl} + H_2O$$

$$R_3\text{-NOH} + NH_4Cl \longrightarrow R_4\text{-NCl} + NH_4OH$$

Selectivity

$SO_4^{2-} > NO_3^- > Cl^-$

Regeneration

$$R_3\text{-NCl} + NaOH \longrightarrow R_4\text{-NOH} + NaCl$$

Salt form is easily regenerated with theoretical amount of regenerant.

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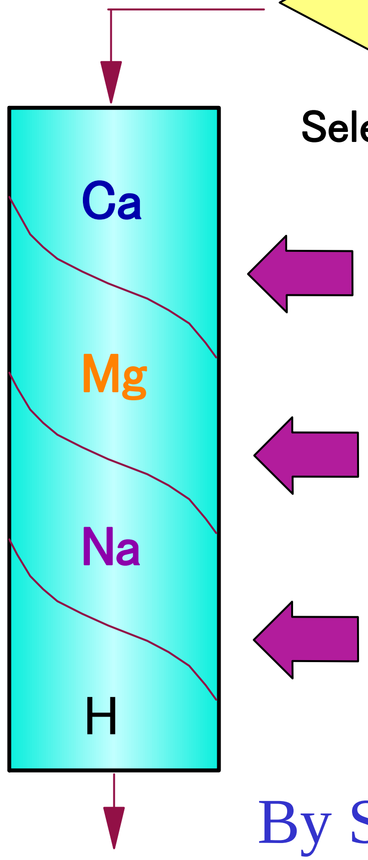
Selectivity coefficients for SK

Type of ion	**D.V.B.%**		
	4%	**8%**	**16%**
Li^{+}	1.00	1.00	1.00
H^{+}+	1.32	1.27	1.47
Na^{+}	1.58	1.98	2.37
NH_4^{+}	1.90	2.55	3.34
K^{+}+	2.27	2.90	4.50
Rb^{+}	2.46	3.16	4.62
Cs^{+}	2.67	3.25	4.66
Ag^{+}	4.73	8.51	22.9
Te^{2+}	6.71	12.4	28.5
UO_2^{2+}	2.36	2.45	3.34
Mg^{2+}	2.95	3.29	3.51
Zn^{2+}	3.13	3.47	3.78

Type of ion	**D.V.B.%**		
	4%	**8%**	**16%**
Co^{2+}	3.23	3.74	3.81
Cu^{2+}	3.29	3.85	4.46
Cd^{2+}	3.37	3.88	4.95
Mn^{2+}	3.42	4.09	4.91
Be^{2+}	3.43	3.99	6.23
Ni^{2+}	3.45	3.93	4.06
Ca^{2+}	4.15	5.16	7.27
Sr^{2+}	4.70	6.51	10.1
Pb^{2+}	6.56	9.91	18.0
Ba^{2+}	7.47	11.5	20.8
Cr^{2+}	6.6	7.6	10.5
Ce^{2+}	7.5	10.6	17.0
La^{2+}	7.6	10.7	17.0

Selectivity of ion

Ca++ , Mg++ , Na+



Selectyvity : Ⅱ valence ＞ Ⅰ valence
MW rage ＞ 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

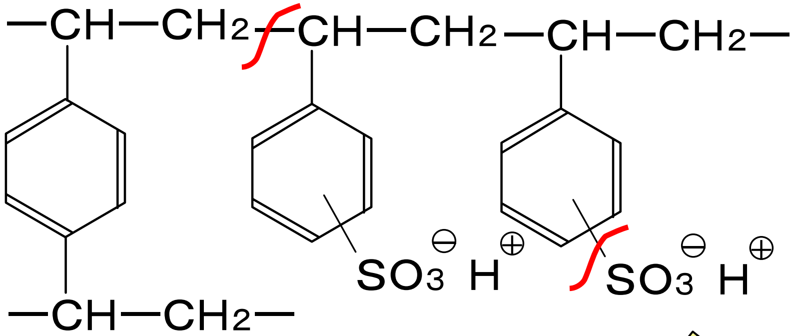
Irreversible swelling by oxidation

Counter measure

1. Removal of oxidizing agents by pretreatment (ex. Na_2SO_3, AC).
   (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

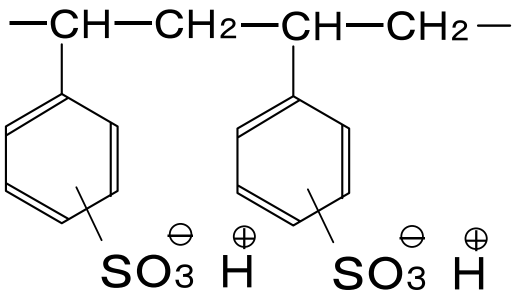
products

① H_2SO_3

② H_2SO_4

Oxidation

③ Polystyrene Sulfonic Acid



Hydration: thermal decomposition (>120℃)

R-SO3 H + H2O → ① R-OH + H2SO3

→ ② R-H + H2SO4

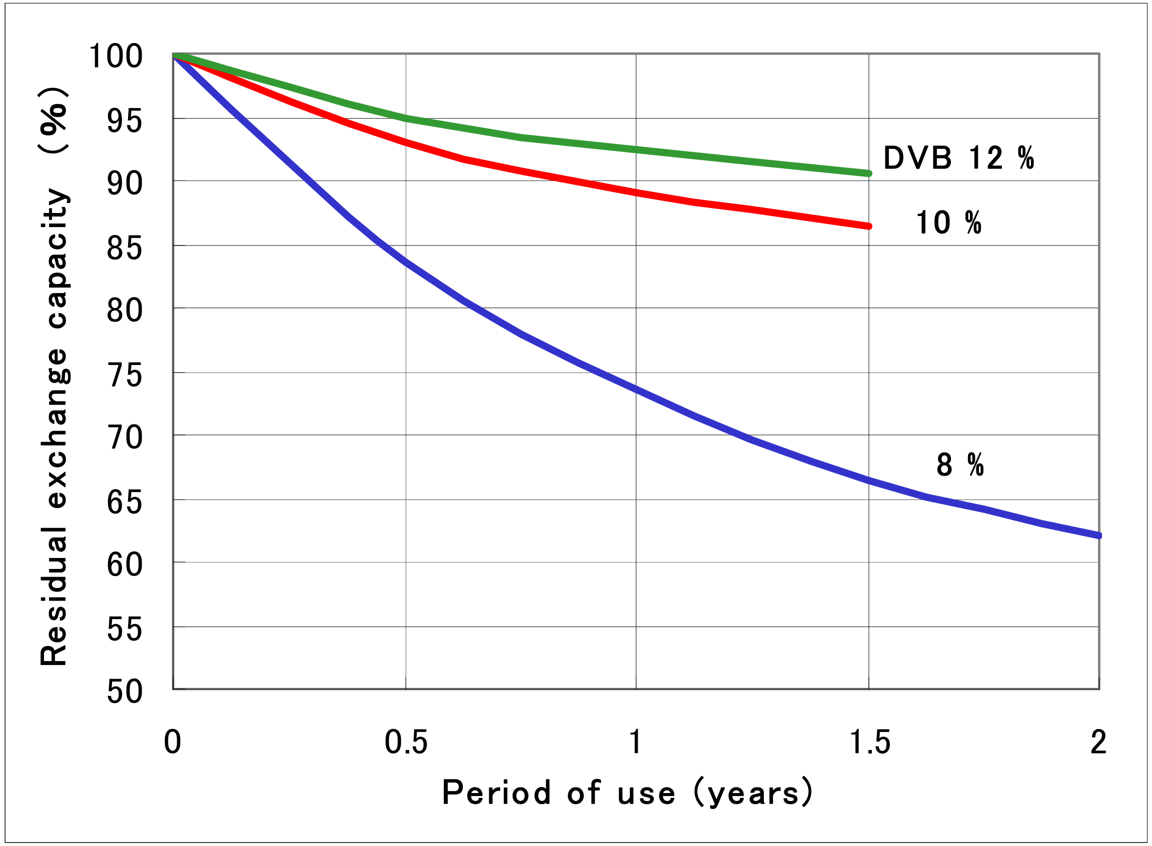
Oxidation: decomposition of copolymer matrix

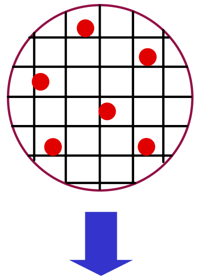
※Main decomposition in case of water treatment

Oxidizing agents, Metals (Cu,Fe,Al etc)

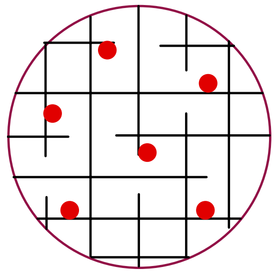
<u>Relation between Crosslinnkage and Oxidative Degradation of SAC</u>

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





Irreversible swelling
by oxidation



Decline of Cap.(meq/mL)
meq/g doesn’t change

Cause of Oxidation of IER

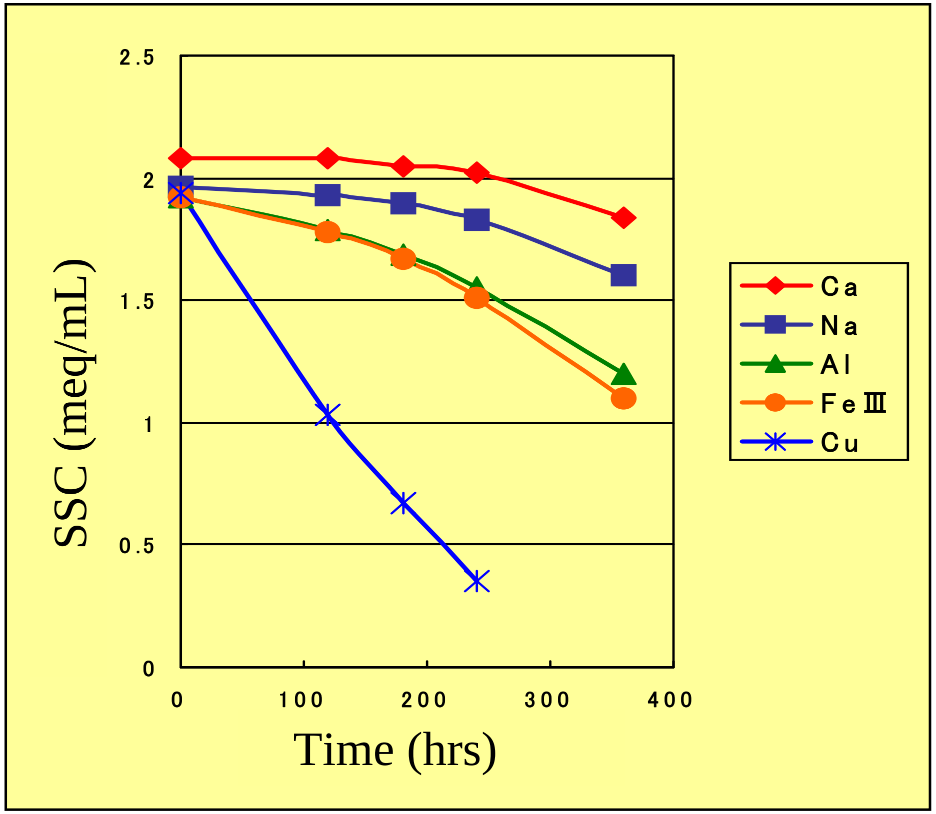
Oxidizing agents : O_2, Cl_2, H_2O_2, $NaClO_3$
Oxidation accelerates with Catalyst effect by
metals (Cu, Fe, Al)

Influence of metals

金属形SK1B 5 mL
10%H2O2 -100mL

Cl_2 Tolerance of SK1B

Temperature (℃)	Maximum Cl2 (ppm)
5–10	0.6
10–15	0.4
15–20	0.2
20–25	0.1



Degradation of I.E.R(2)

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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

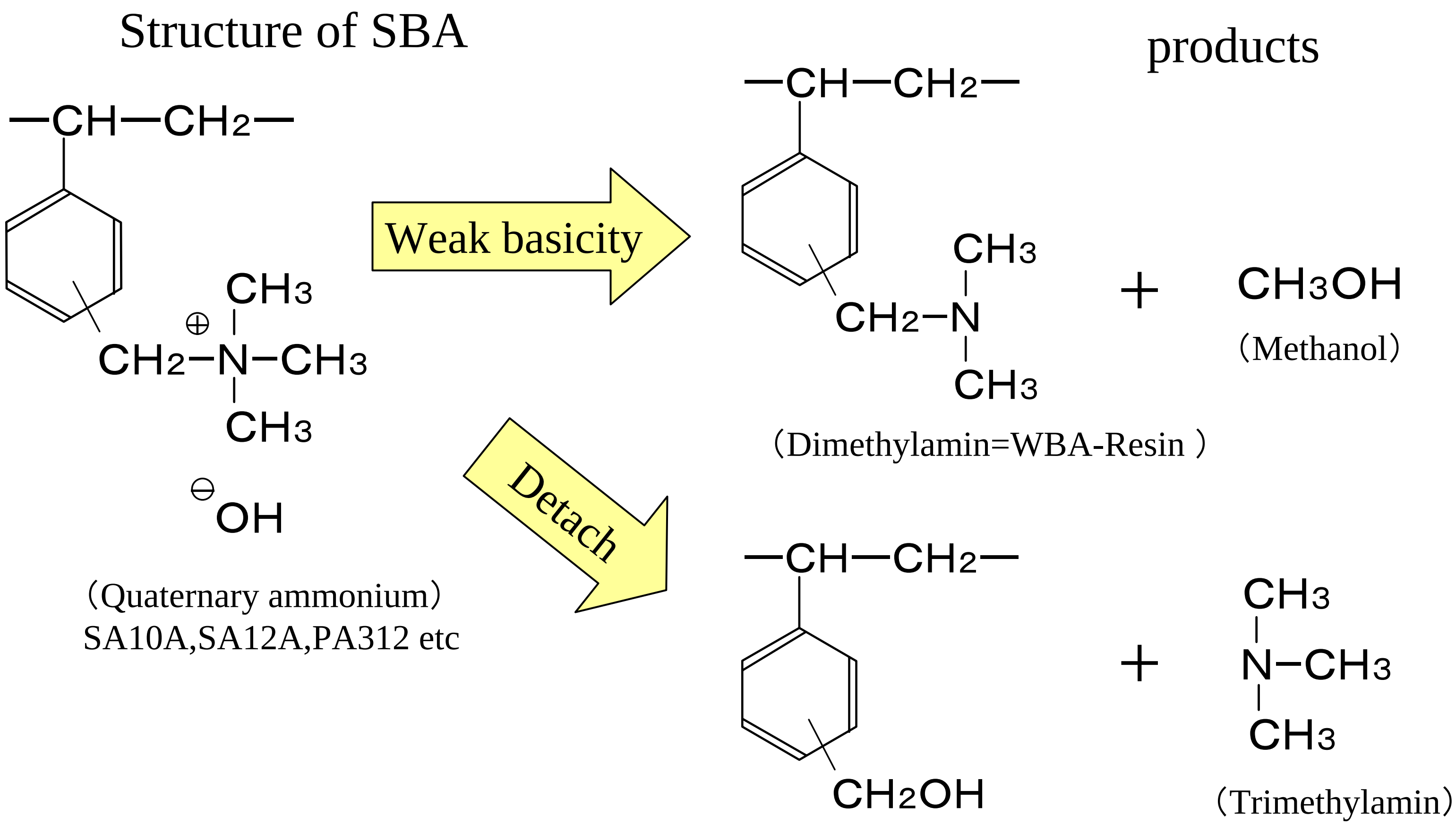
1. Refilling the resin.
2. Removal of oxidizing agents by pretreatment.

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)



SBA are decomposed by heat and oxidation

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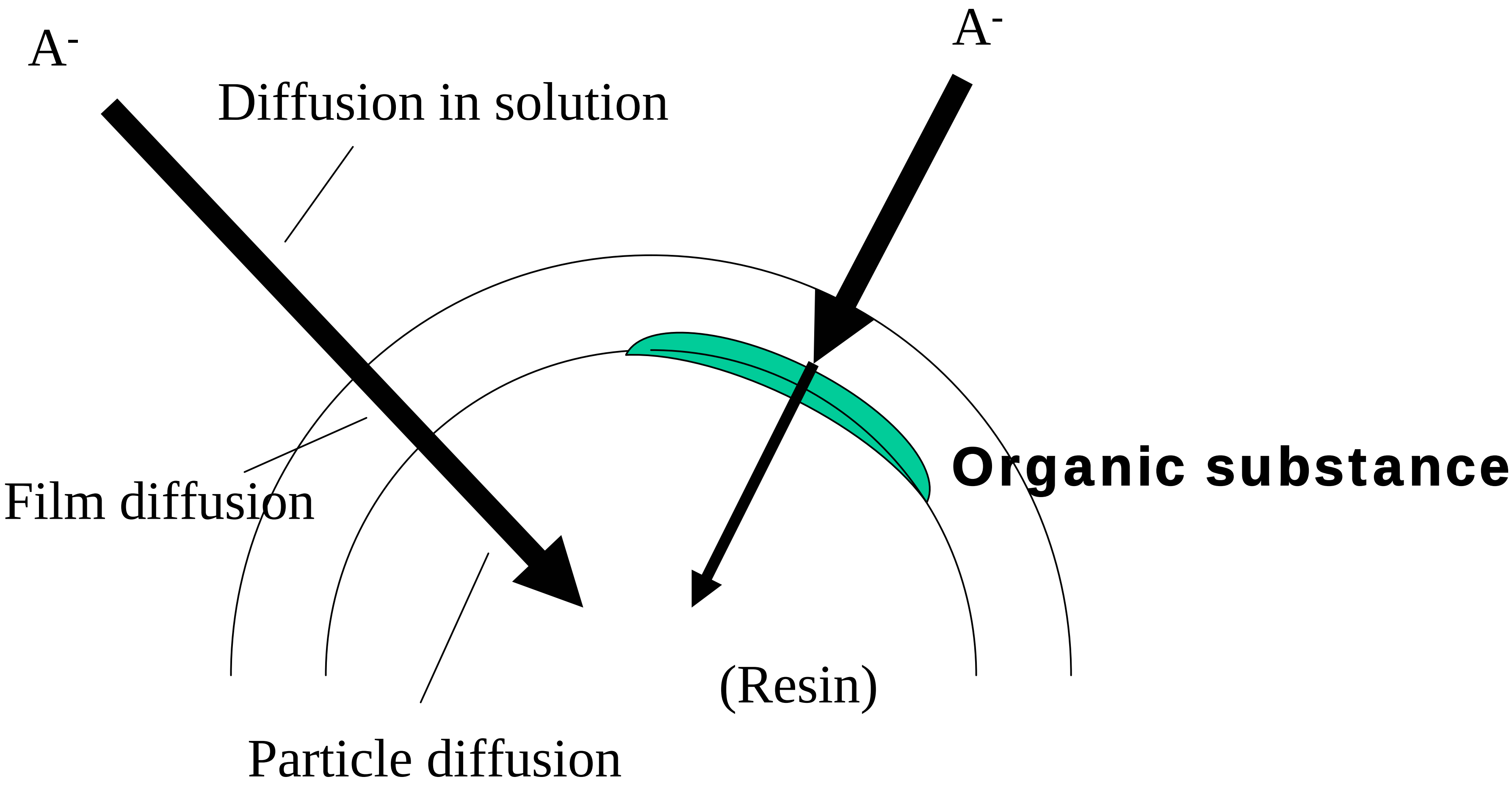
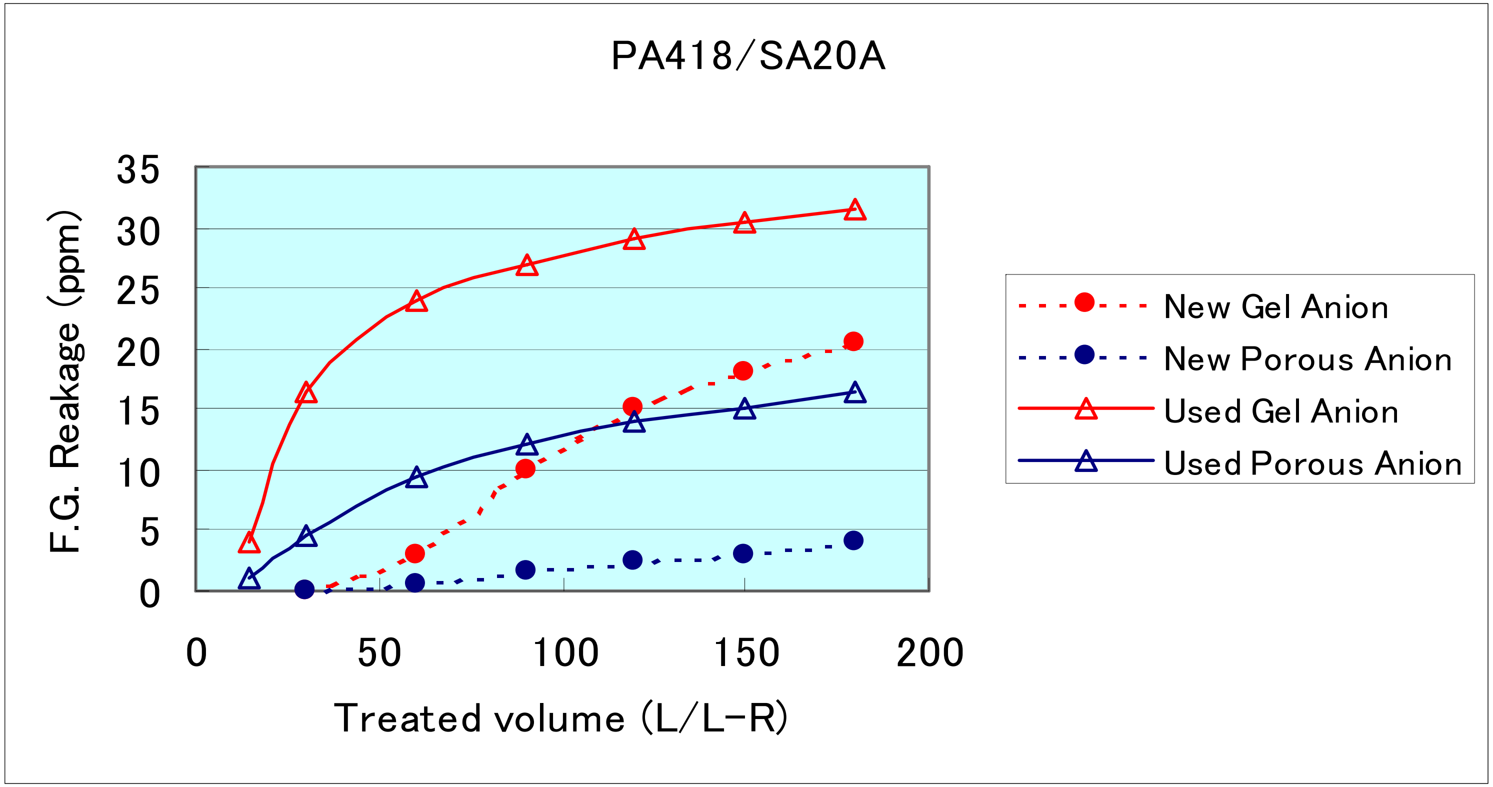
Organic contamination and reaction rate

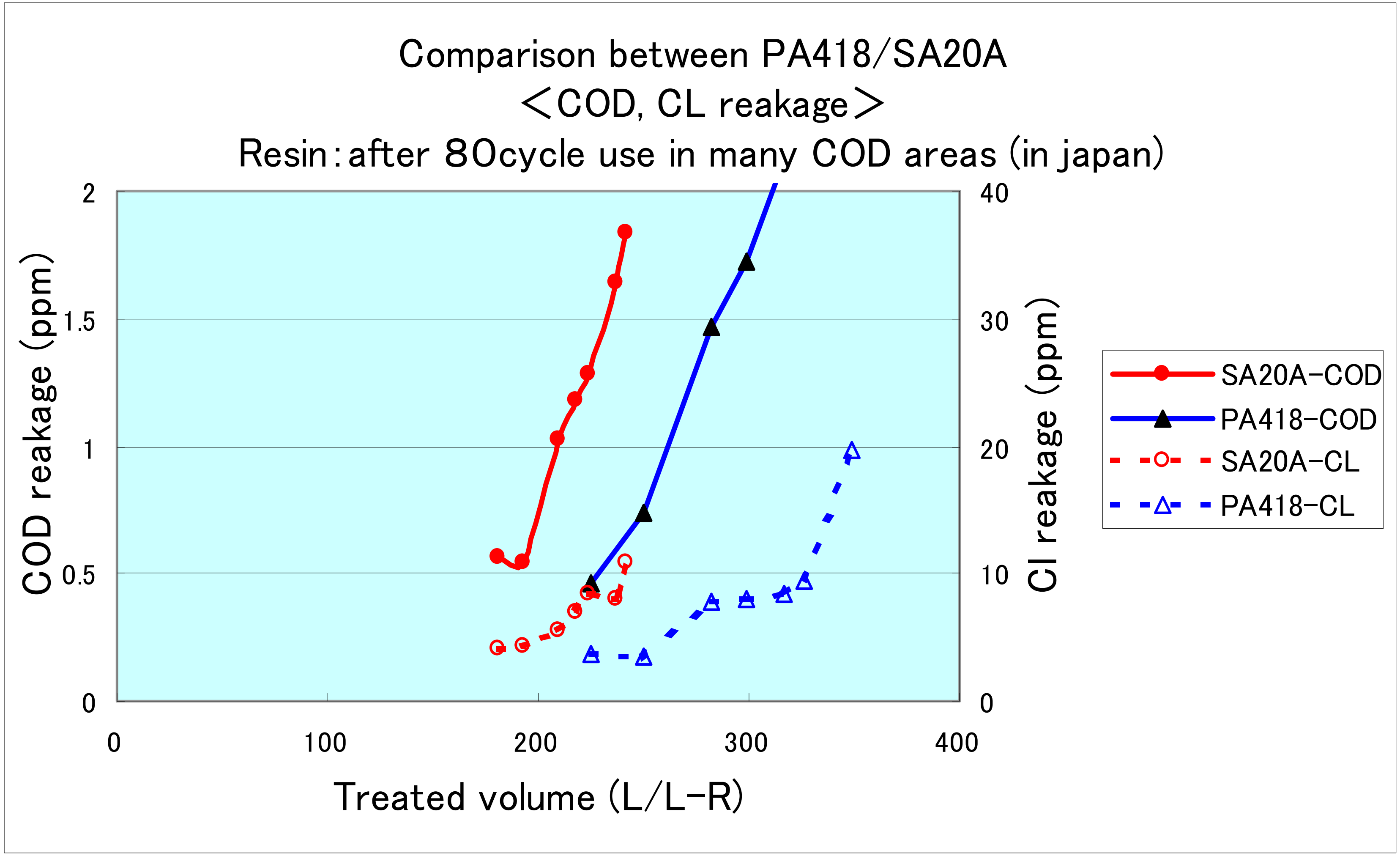


Comparison between Gel and Porous
(Adsorption of organic substance)

Test condition
IER : R-Cl 15 mL
Organic sub. : Fast Green FCF 30ppm
(dye MW=808)
Used Resin : after 80cycle (water treatment)



Comparison between Gel and Porous
(Efficiency of 2B3T-water treatment)



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Selection of DIAION® for water treatment (1)

CATION

↓

There are a larger amount of oxidizing agents in influent water. — yes → **SK110,SK112**

↓

The influent water contains a large quantity of HCO_3^-, and Ca_2^+, Mg_2^+ & total ions. — yes → **WK40-SK1B** (4B5T) / **WK40-SK112L** (D.L)

↓ (Standard)

SK1B

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Selection of DIAION® for water treatment (2)

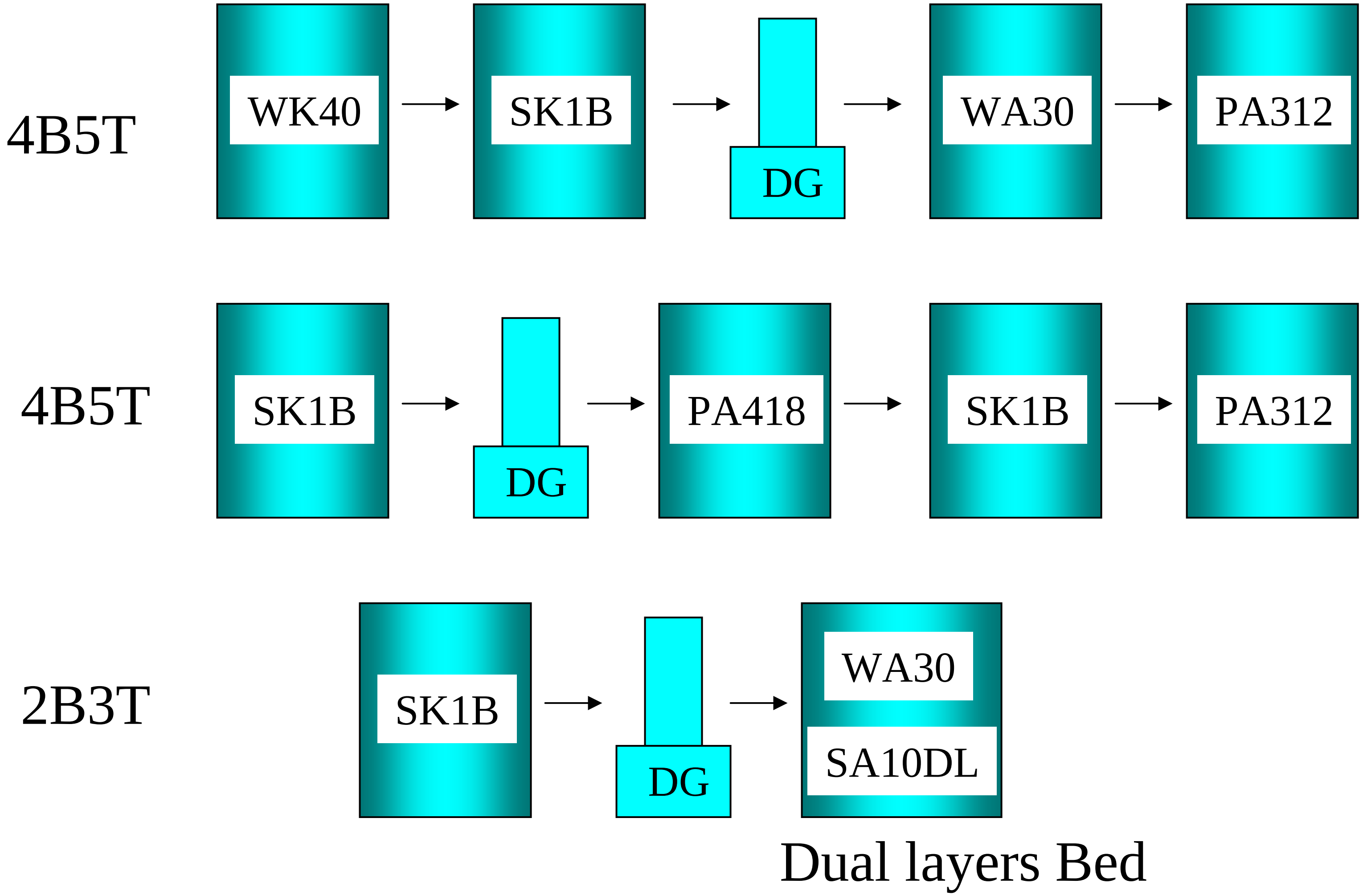
ANION

- 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) / **WA30-SA10DL** (D.L)

↓

SA12A

System when there are many organic substance



4B5T system

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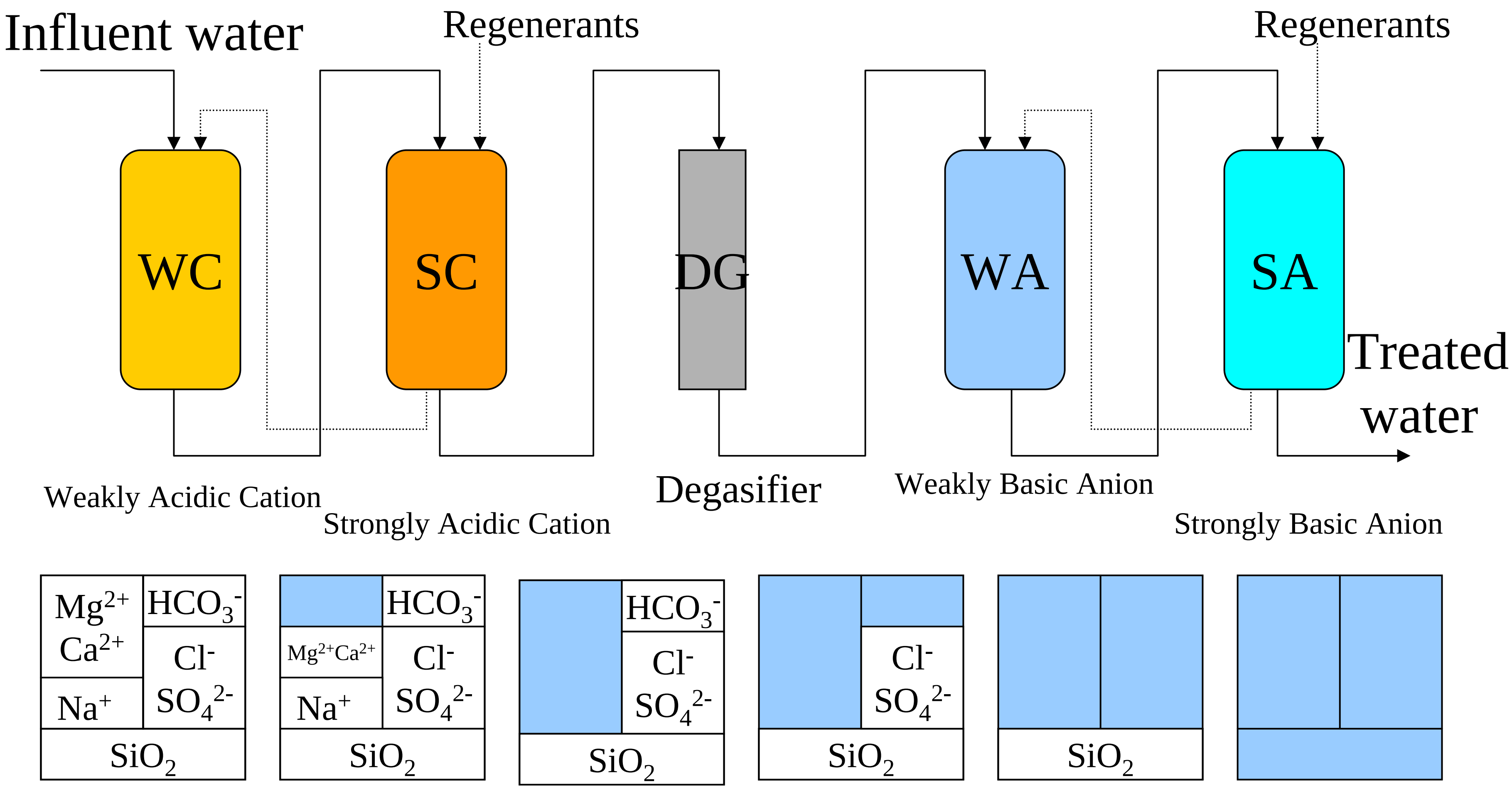

This system suitable for treating water with a very large quantity of HCO3-, hardness and total ions.

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**