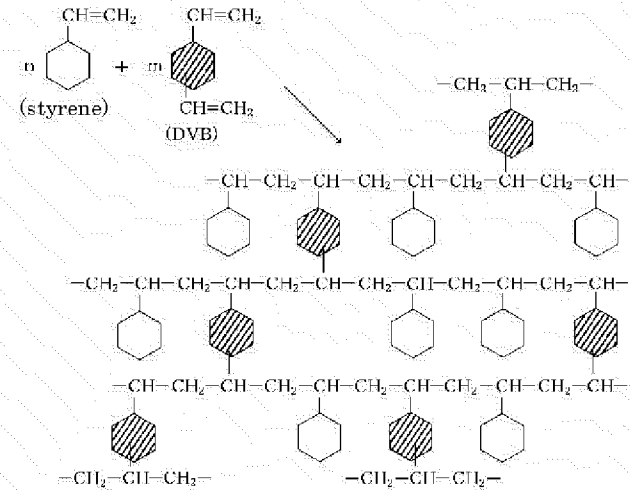


Chapter I Properties of Ion Exchange Resins

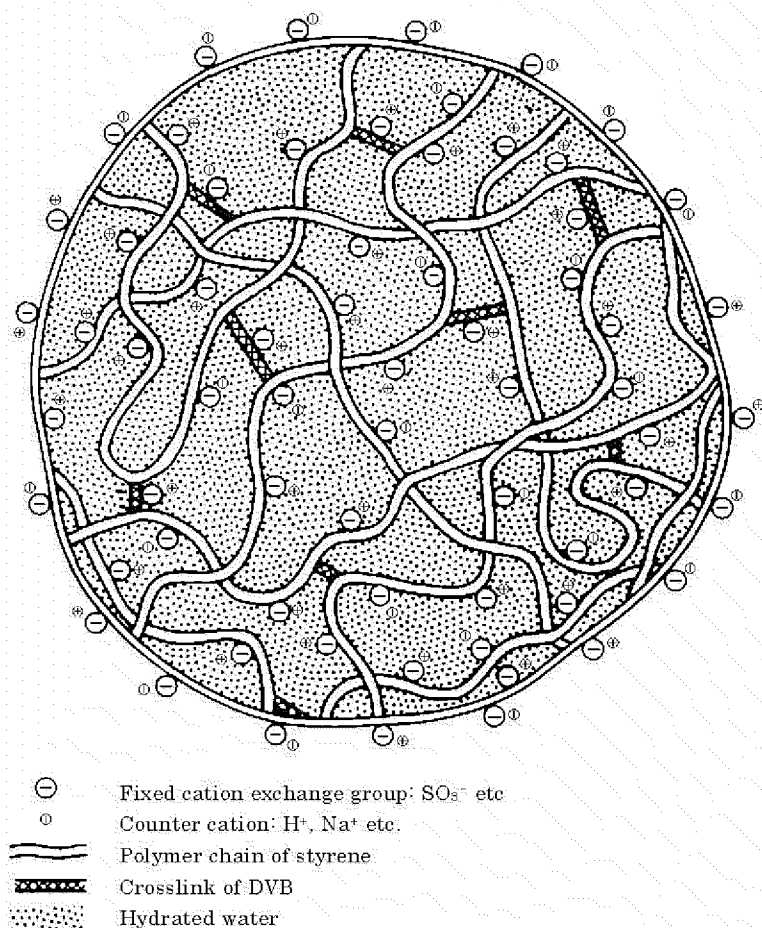
1. Basic Structures of Ion Exchange Resins

Ion Exchange Resin (IER) is a kind of synthetic resins that is manufactured by introducing functional groups such as sulfonic acid and quaternary ammonium into three-dimensionally crosslinked polymer matrix. The typical polymer matrix is a co-polymer made from two kinds of monomers, one is styrene and the other is divinylbenzene (DVB) and the standard industrial products are spherical shaped, the diameters of which are $300\sim 1,180\ \mu\text{m}$ (50~14 mesh). These crosslinked polymers are synthesized from styrene and DVB that has two vinyl groups at the same benzene ring through suspension polymerization in water, as shown in Fig. I-1-1



[Fig. I-1-1] Chemical structure of styrene-divinylbenzene copolymer

IERs are manufactured by introducing ion-exchangeable functional groups to these crosslinked polymer structures. The ion-exchangeable functional groups such as sulfonic acid groups, $-\text{SO}_3^-$, or quaternary ammonium groups, $\equiv\text{N}^+$, are called "fixed ions" because they are chemically bonded to the polymer structure. On the contrary, the mobile ions that are electrically neutralized with such fixed ions, H^+ in the case of $-\text{SO}_3^-$, are called "counter ions."



[Fig.I-1-2] Structural model of ion-exchange resin

Fig.I-1-2 shows a structural model of a typical IER particle. Although the polymer matrix of IERs looks like some simple planar structure in Fig.I-1-1, its actual structure is thought to be a complicated three-dimensional structure of crosslinked elastic polystyrene chains by DVB in some irregular lengths and irregular intervals.

The density of such crosslinks varies in accordance with the ratio of

DVB versus styrene. That is, when we increase the amount of DVB, bi-functional monomer, in the copolymerization, the chain branching increases in the polymer matrix of the IER and thus it has a dense network. When we decrease the amount of DVB, on the other hand, the network becomes sparse. In this way, DVB play the connecting knots of the styrene polymer chains and so they are called "crosslinking agent." We can estimate the concentration of the crosslinks in the networks of the polymer matrix by the DVB's amount in the copolymerization. Thus, we call DVB%, DVB versus total monomers in weight/ weight (%), "crosslinkage."

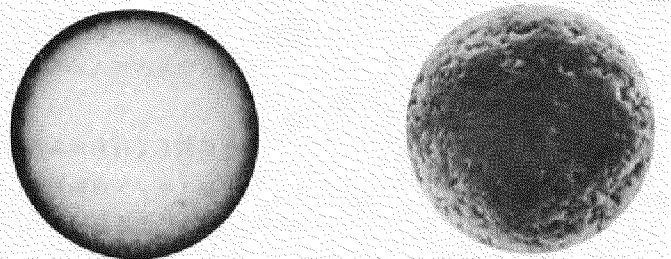
There exist "micropores" in the wet IERs and ion exchanges do occur within such micropores where ions could diffuse. The micropores become smaller in accordance with the higher crosslinkage, and it becomes more difficult for ions to diffuse in the micropores. Although ion diffusion becomes easy in the low crosslinkage IERs, micropores of which are large, it becomes hard to handle them because of their softness and weakness as resin-materials when their crosslinkage is too low. The standard crosslinkage might be, thus, around 8%.

Ion exchange initiates by the diffusion of counter ions as we have explained, and such diffusion is affected by the network structures of the IER polymer matrix, so the crosslinkage of IERs is one of the important factors that decide the properties of IERs. Since other crosslinking reactions than that by DVB occur as side-reactions in the process of introducing ion-exchangeable function groups into the polymer matrix, it is not correct, in the strict meanings, to define the crosslinks in the IERs only by the crosslinkage. However, there may be no problems to use DVB% as a measure of the crosslinks in IERs, because the side-reactions to form the other crosslinks are usually rather little and negligible compared to the main crosslink reactions by DVB.

The copolymers of styrene and DVB have no water absorbability, and they gain such strong water absorbability after they are introduced ion-exchangeable functional groups. These polymers with ion-exchangeable functional groups have swelling property when dipped in water. Such high water absorbability and swelling property are said to be derived from the hydration reactions of both their fixed ions and counter ions and from their osmotic pressures. Though the polymer matrix extends its length and enlarges its volume by such hydration reactions and osmotic pressures, such levels of hydration or swelling become stable at the balanced point between the expansion force and the contracting one of the polymer chains. In other words, the high crosslinkage resins absorb less water and swell less than the low crosslinkage ones. In any cases, IERs swell and have micropores within their own polymer matrices when they

are dipped in water.

The simple copolymers that are manufactured from styrene and DVB have transparent appearance and have gel structures, so they are called "gel"-type IERs. We can also produce porous IERs by specialized polymerizations. We have two types of such porous resins: one is "porous"-type resin and the other is "highly porous"-type one, which we will explain further in the next section. The basic structures of these two types are the same as the gel-type, and they have a lot of macropores in the polymer matrices and much larger specific areas of the active surface than the gel-type.



[Fig I-1-3] Photomicrographs of gel-type and porous-type IERs

2. Types and Groupings of Ion Exchange Resins

Ion Exchange Resin (IER) is a kind of synthetic resins that is manufactured by introducing functional groups of ion exchange into three-dimensionally crosslinked polymer matrix, as we have already explained in the previous section. The typical functional groups of ion exchange are sulfonic acids and quaternary ammoniums, and such IERs are roughly classified by their functions into the cation exchange resins (CERs) that can exchange cations and the anion exchange resins (AERs) that can exchange anions.

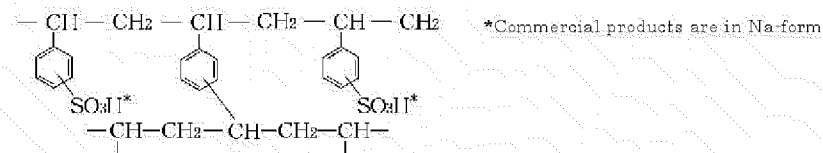
There are also the amphoteric IERs that have cation exchange groups and anion exchange ones in the anion exchange group and the cation exchange group coexist on the same functional group chain, the chelating resins that can trap ions through forming chelates, and the specialized resins such as synthetic adsorbents with no ion exchange functional groups. We explain the properties of these resins individually in this section.

(1) Cation exchange resins (CERs)

CERs can exchange positive ions such as Na^+ and Ca^{2+} and are classified into two groups, strongly acidic and weakly acidic, in accordance with their acidities.

1) Strongly acidic cation exchange resins

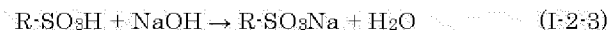
The resins with sulfonic acids as their functional groups, Fig.I-2-1, are called strongly acidic cation exchange resins, since their acidity is strong as hydrochloric acid or sulfuric acid. DIAION® SK, PK, and HPK Series belong to this classification.



[Fig I-2-1] Chemical structure of Strongly acidic Cation Exchange Resin

The sulfonic acid groups ($-\text{SO}_3\text{H}$), active groups in these resins, are strongly acidic and they dissociate not only in alkaline solutions but also in acidic solutions to $-\text{SO}_3^-\text{H}^+$ form. We have explained that we call $-\text{SO}_3^-$ as a fixed ion and H^+ as a counter ion in the previous section, and the ion exchange reactions are the exchange reactions of counter ions. SACERs can exchange their counter ions even with neutral salts as with bases; Equations I-2-1 ~ I-2-3.

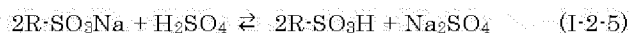
Thus, the strongly acidic cation exchange resins can exchange cations in the all pH range and they are most widely used.



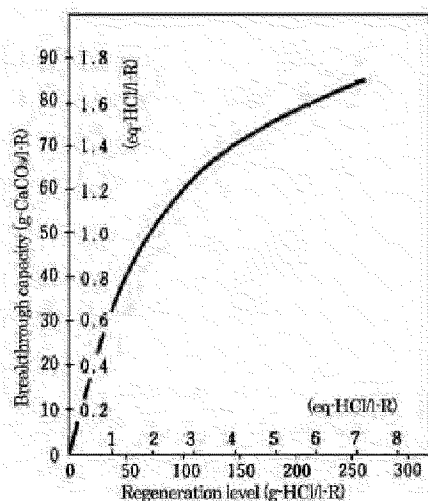
The reactions in Eq. I-2-1 and Eq. I-2-2 are reversible, and thus there exists equilibrium in the batch operations. However, we can exchange cations effectively when we pass the objective solution through the resin tower, the column that is packed with the resins, because the equilibrium shifts the right direction. We call such procedure with the resin tower as the dynamic ion exchange method or the column ion exchange method.

On the other hand, we can easily exchange cations even in the batch operations when we exchange cations with bases as in Eq.I-2-3, since there is no equilibrium as in Eqs.I-2-1 and I-2-2.

We have to regenerate the cation exchange resins to their original R-SO₃H forms after they are used for the exchange with other cations. Such regeneration is normally performed with hydrochloric acid aqueous solutions or sulfuric acid aqueous solutions, as shown in Eqs.I-2-4 and I-2-5, in these cases the counter cation is Na⁺.



It needs, unfortunately, much more regenerants than the theoretical amount when we regenerate the strongly acidic cation exchange resin (SACER), since SACER is strongly acidic. Eq.I-2-2 shows the relation between the regeneration level and the breakthrough exchange capacity of DIAION® SK1B; the regeneration level is the ratio of the regenerant versus the treated resin and the breakthrough exchange capacity is the exchange capacity when the ions leakage exceeds the maximum tolerance.



[Fig.I-2-2] Regeneration level and Breakthrough Exchange Capacity of DIAION® SK1B; by 15% HCl aq.

[Table I-2-1] Comparison of strongly acidic cation exchange resins and weakly acidic cation exchange resins

Strongly acidic cation exchange resins	Weakly acidic cation exchange resins
<ul style="list-style-type: none"> • Insoluble in water, strongly acidic as mineral acids 	<ul style="list-style-type: none"> • Insoluble in water, weakly acidic as organic acids
<ul style="list-style-type: none"> • Dissociate in aqueous solutions of all pH range $\text{RSO}_3\text{H} \rightarrow \text{RSO}_3^- + \text{H}^+$ (fixed ion) (mobile ion) 	<ul style="list-style-type: none"> • Dissociate in neutral ~ alkaline aqueous solutions $\text{RCOOH} \rightarrow \text{RCOO}^- + \text{H}^+$ (fixed ion) (mobile ion)
<ul style="list-style-type: none"> • Exchange cations even with neutral salts $\text{RSO}_3\text{H} + \text{NaOH} \rightarrow \text{RSO}_3\text{Na} + \text{H}_2\text{O}$ $2\text{RSO}_3\text{H} + \text{Ca}(\text{HCO}_3)_2 \rightarrow (\text{RSO}_3)_2\text{Ca} + \text{H}_2\text{CO}_3$ $\text{RSO}_3\text{H} + \text{NaCl} \rightleftharpoons \text{RSO}_3\text{Na} + \text{HCl}$ 	<ul style="list-style-type: none"> • Exchange cations with bases such as NaOH and with basic salts as $\text{Ca}(\text{HCO}_3)_2$, but not with neutral salts in the ordinary conditions $\text{RCOOH} + \text{NaOH} \rightarrow \text{RCOONa} + \text{H}_2\text{O}$ $2\text{RCOOH} + \text{Ca}(\text{HCO}_3)_2 \rightleftharpoons (\text{RCOO})_2\text{Ca} + 2\text{H}_2\text{CO}_3$
<ul style="list-style-type: none"> • Selectivity of cations in solutions at low concentration $[\text{Ba}^{2+}] > \text{Ca}^{2+} > \text{Mg}^{2+}$ $[\text{K}^+] > \text{NH}_4^+ > \text{Na}^+ > \text{H}^+$ 	<ul style="list-style-type: none"> • Almost the same as SACER, but the selectivity of H⁺ is higher than of divalent cations
<ul style="list-style-type: none"> • Selectivity decreases and sometimes reverses in solutions at high concentration 	
<ul style="list-style-type: none"> • The exchanged cation hydrolyzed slightly but we can ordinarily ignore. 	<ul style="list-style-type: none"> • The exchanged cation is easy to hydrolyze $\text{RCOONa} + \text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{NaOH}$
<ul style="list-style-type: none"> • The exhausted resin can be regenerated by HCl or H₂SO₄ $(\text{RSO}_3)_2\text{Ca} + 2\text{HCl} \rightleftharpoons 2\text{RSO}_3\text{H} + \text{CaCl}_2$ 	<ul style="list-style-type: none"> • The exhausted resin can be regenerated by HCl or H₂SO₄ $(\text{RCOO})_2\text{Ca} + 2\text{HCl} \rightarrow 2\text{RCOOH} + \text{CaCl}_2$
<ul style="list-style-type: none"> • Difficult to be regenerated. Much more regenerants are necessary than the theoretical amount. 	<ul style="list-style-type: none"> • Easy to be regenerated with a little more regenerants than the theoretical amount.
<ul style="list-style-type: none"> • Reaction rate is high. 	<ul style="list-style-type: none"> • Reaction rate is slower than SACER.
<ul style="list-style-type: none"> • Na-form resins, regenerated with NaCl solutions, can be used for softening of water. $2\text{RSO}_3\text{Na} + \text{CaCl}_2 \rightleftharpoons (\text{RSO}_3)_2\text{Ca} + 2\text{NaCl}$ 	<ul style="list-style-type: none"> • Na-form resins can sometimes exchange with metal cations: $2\text{RCOONa} + \text{CaCl}_2 \rightarrow (\text{RCOO})_2\text{Ca} + 2\text{NaCl}$ Regeneration must be made by mineral acids and then by NaOH.
<ul style="list-style-type: none"> • The volume of the loaded form is larger than the regenerated form: H-form. 	<ul style="list-style-type: none"> • The volume of the loaded form is very much larger than the regenerated form: H-form.

This DIAION® SK1B is relatively stable at high temperatures and it is actually stable at 100 ~ 120°C and thus is used widely as acidic catalysts in various reactions. It is, however, weak against oxidizing agents. Thus, care must be taken about the oxidizing agents, since the main matrix chain is fragmented by oxidation and the resin itself swells irreversibly, which we explain in the latter section.

More attention will be paid in the low crosslinked resins, because such irreversible swelling is easy to happen in such resins.

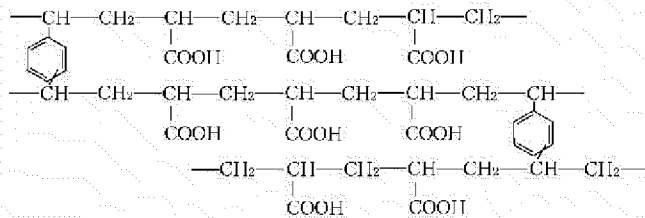
The product names of the standard strongly acidic cation exchange resins of DIAION® are as follows:

Gel-type (SK Series):	SK104, SK1B, SK110, SK112, SK116
Porous-type (PK Series):	PK208, PK212, PK216, PK218, PK220, PK228
Highly porous-type (HPK Series):	HPK25

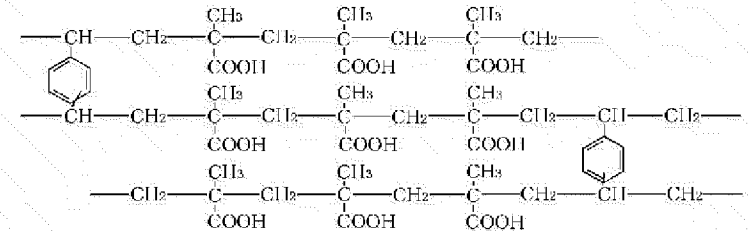
2) Weakly acidic cation exchange resins

Weakly acidic cation exchange resins (WACERs) are weakly acidic IERs that have carboxylic acid groups (-COOH) as ion-exchangeable groups, as in Figs. I-2-3 and I-2-4. DIAION® WK10, made from methacrylic acid, and DIAION® WK40, made from acrylic acid, are our products in this grouping.

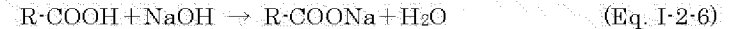
Because carboxylic acid groups in WACERs are weakly acidic, WACERs can neither dissociate nor exchange ions in the acidic solutions they cannot split neutral salts, such as NaCl and Na₂SO₄. However, they can exchange cations with bases like NaOH and with salt of weakly acids like NaHCO₃, as shown in Eqs. I-2-6 and I-2-7.



[Fig. I-2-3] Chemical structure of Acrylic acid type WACERs



[Fig. I-2-4] Chemical structure of Methacrylic acid type WACERs



Though the selectivity of WACERs toward each cation is almost the same as the one of SACERs, the selectivity to H⁺ ion is one of the exceptions and is located on the top level among monovalent ions. Thus, that WACERs are easily regenerated to H-forms is one of their properties.

We have already explained that SACERs can exchange their counter ions even with neutral salts as with bases and so they are most widely used in various fields. From the point of regeneration, however, they are more difficult to be regenerated than WACERs and it needs larger amount of regenerants than the theoretical one to regenerate WACERs.

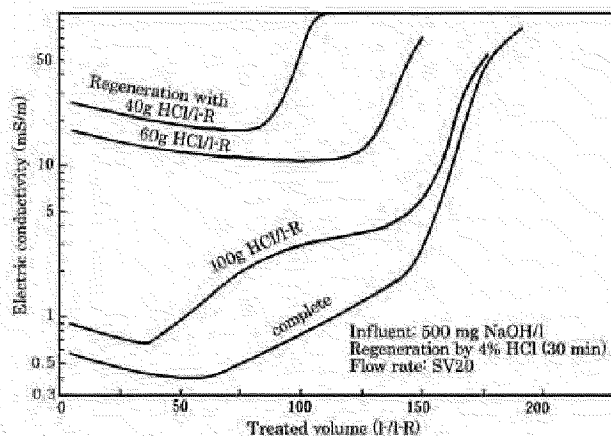
WACERs, on the contrary to SACERs, are economical because they are easy to be regenerated and slightly excess of regenerants are enough for regeneration, though WACERs have the disadvantage that they can be used in the limited pH range. WACERs can be regenerated by the spent regeneration effluents of SACERs. So that, combined operations with SACERs and WACERs could often reduce regenerants totally. Still, WACERs have another disadvantage that they tend to be hydrolyzed and to release the captured cations into the treated water only if they contact a flow of water.

Fig. I-2-5 shows the quality change of the water treated by DIAION® WK10, one of methacrylic acid type WACERs, during a 500 mg/L NaOH aqueous solution passes through it; there are four curved lines at different regeneration levels. As the regeneration level declines, i.e. the decrease of the regenerant of HCl, the unregenerated resins increase in the bottom part of the column, and thus the quality of the treated water

becomes worse, the electrical conductivity of which becomes higher, due to the elution of the remaining captured ions in the bottom.

Another weak point of WACERs is the drastic volume increase when they exchange other cations from the original H^+ ions. Some WACERs double the volumes, and such volume expansion may increase the head loss of the columns, small columns particularly, and may destroy the columns in some cases. One has to be careful in such operations.

We have two types of WACER products; acrylic acid type and methacrylic acid type in Fig.I-2-3 and Fig.I-2-4 respectively. The acrylic acid type is more acidic, the pKa of carboxylic acid groups in which is around 5.3, than the methacrylic acid one, and so it is widely used in the treatment of the hard water of high bicarbonates concentration. The methacrylic acid type of WACERs, less acidic and pKa is around 6, is used in other specialized fields.



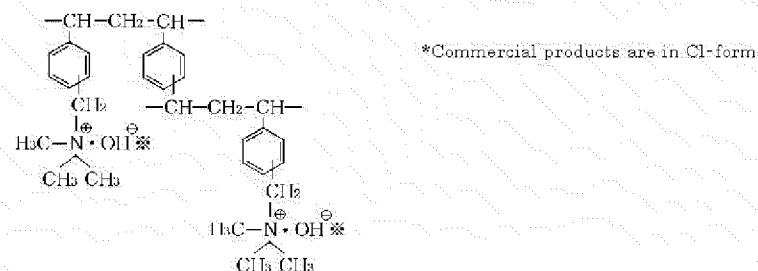
[Fig.I-2-5] The quality change of 500 mg/L NaOH water treated by WK10

(2) Anion exchange resins (AERs)

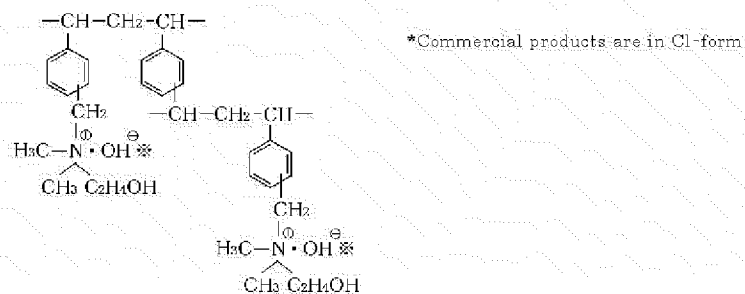
AERs are IERs that can exchange anions such as Cl^- and SO_4^{2-} and are classified into two groups; one is the group of strongly basic anion exchange resins, SBAERs, and the other is of weakly basic anion exchange resins, WBAERs.

1) Strongly basic anion exchange resins (SBAERs)

Fig.I-2-6 and Fig.I-2-7 show the resins with quaternary ammonium groups ($\equiv N^+$) as their functional groups, such resins dissociate and show as strong basicity as inorganic bases like NaOH or KOH. Accordingly, they are called strong basic anion exchange resins (SBAERs). DIAION® SA, PA, and HPA Series belong to this classification.

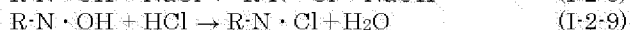


[Fig. I-2-6] Chemical structure of Strongly Basic Anion Exchange Resins type I

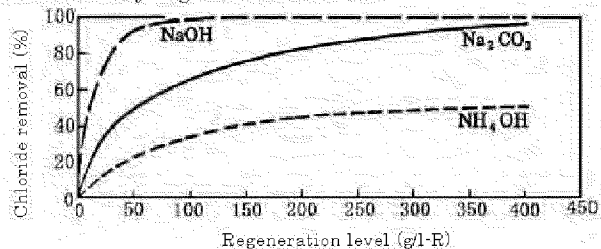


[Fig.I-2-7] Chemical structure of Strongly Basic Anion Exchange Resins type II

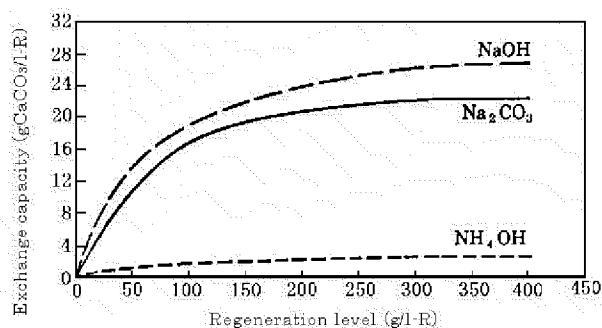
The quaternary ammonium groups ($\equiv N^+$), active groups in these resins, are strongly basic and they dissociate not only in acidic solutions but also in alkaline solutions to $\equiv N^+ OH^-$ form. SBAERs can exchange their counter ions even with neutral salts as with inorganic acids, as shown in Equations I-2-8 and I-2-9. They can exchange anions with weak acids such as silicic acids and carbonic acids. SBAERs are ion-exchangeable in all pH range.



SBAERs are usually regenerated with NaOH aqueous solutions. Eq.I-2-10 shows the regeneration reaction of Cl-form SBAER. The reactions in Eqs.I-2-8 and I-2-10 are reversible, so we emphasize again that we can exchange anions effectively when we pass the objective influent through the resin tower. Fig.I-2-7 and Fig.I-2-8 show the differences in the regeneration process due to the regenerant of different basicity. Highly basic NaOH is the most effective, both the regeneration rate and the exchange capacity decline in the case of Na_2CO_3 and weakly basic NH_4OH can hardly regenerate SBAERs.



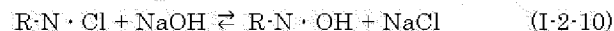
[Fig.I-2-8] Regeneration Level and Regeneration Rate of Strong Basic Anion Exchange Resins (2)
Exhaustant: NaCl, 500mg $CaCO_3$ /l



[Fig.I-2-9] Regeneration Level and Exchange Capacity of Strong Basic Anion Exchange Resins (2)
Exhaustant: NaCl, 500mg $CaCO_3$ /l

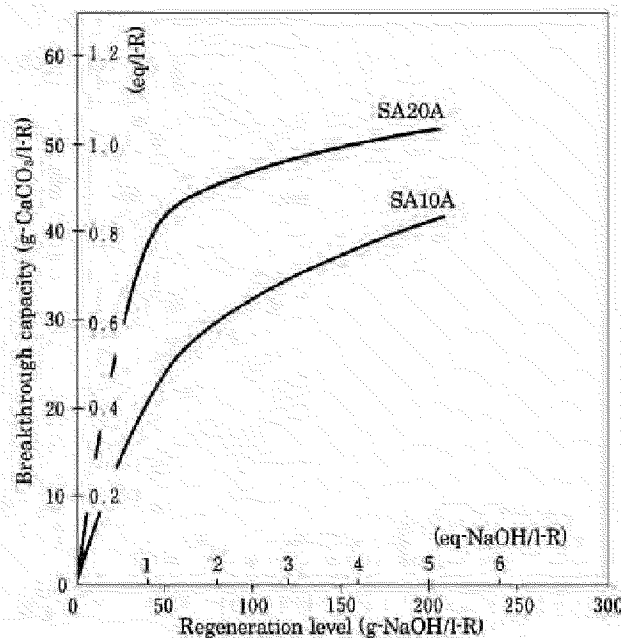
Eq.I-2-10 shows the regeneration reaction of Cl-form SBAER. The reactions in Eqs.I-2-8 and I-2-10 are reversible, so we emphasize again that we can exchange anions effectively when we pass the objective

influent through the resin tower.



It needs much more regenerants than the theoretical amount to regenerate SBAERs, since SBAER is strongly basic. This is the same phenomenon as in the strongly acidic cation exchange resins.

There are two types of SBAERs; type I has trimethylammonium groups, $R \cdot N^+(CH_3)_3$, as ion exchange groups and type II has dimethylethanolammonium groups, $R \cdot N^+(CH_3)_2 \cdot CH_2CH_2OH$. Both types I and II are strongly basic, type II is slightly weak in basicity and thus somewhat easy to be regenerated. Fig.I-2-10 shows the comparison of DIAION® SA10A and SA20A, the typical products of type I and type II respectively, on the relation between the regeneration level and the breakthrough exchange capacity.



[Fig.I-2-10] Regeneration Level and Breakthrough Exchange Capacity of DIAION® SA10A and SA20A

