Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Lee, S. C. , Hsiang, C. C. , Huang, H. and Ting, G.(1990) 'A Comparative Study of Gel-Type and Macroreticular Cation Exchange Resins for the Separation of Rare Earth Elements', Separation Science and Technology, 25: 13, 1857 — 1870

To link to this Article: DOI: 10.1080/01496399008050429

URL: http://dx.doi.org/10.1080/01496399008050429

SEPARATION SCIENCE AND TECHNOLOGY, 25(13-15), pp. 1857-1870 (1990)

A COMPARATIVE STUDY OF GEL-TYPE AND MACRORETICULAR CATION EXCHANGE RESINS FOR THE SEPARATION OF RARE EARTH ELEMENTS

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ABSTRACT

Owing to the macro- and micro- pores in the matrix , macroreticular resins have larger micro-void volume ratio in the ion exchange column chromatography . It is advantageous in the ion exchange kinetics resulting from the quicker mass transfer . By means of EDTA displacement column chromatography for the Pr-Nd separation study , we have found that macroreticular cation exchange resins have higher separation efficiency in HETP, single stage time, and the pure Pr production rate , e. g. for AG 50W-X8, 200~400 mesh resin (gel-type) and AG MP-50 , 200~400 mesh resin (macroreticular) , the HETP values are 0.40 cm and 0.24 cm ; the single stage times are 3.11 min and 1.30 min ; the pure Pr production rates are 0.19 and 0.68 m mole/hr , respectively . Because both types of resins contain the same functional group , the single stage separation factors for Pr-Nd separation have the same value of 2.0±0.1 at 92°C . The cation exchange resins which were prepared in our laboratory with higher micro-void volume ratio could improve the separation efficiency as well as reduce the pressure drop in the ion exchange column. It is suggested that new macroreticular cation exchange resins with high micro-void volume ratio and high degree of crosslinking can improve the rare earth separation efficiency which is an important design factor in the large-scale separation process for rare earth elements.

INTRODUCTION

Since the commercial introduction in 1959 of macroreticular (MR-type) ion exchange resin, Amberlite 200, the beginning of a new era in ion exchange was marked (1) . The differences in the morphology and texture of poly-styrene-divinylbenzene (PSD) copolymer matrix between the conventional gel-type and macroreticular resins have been clearly investigated . Their synthesis and structure are described in recent papers (2~4) . As shown in fig. 1., by conventional pearl polymerization techniques , a gel-type structure is obtained with pores of 10 Å and smaller . On the other hand , by using a special medium , a porous or macroreticular texture can be obtained . The porogenic agents for the latter preparation are solvents , non-solvents , polymer or cross-linking agents . Compared with the gel-type PSD resins , the macroreticular resins have much more complex morphology and texture. Typically , small nuclei (50~200 Å) are tightly grouped into microspheres (1000~2000 Å) which form agglomerates . This texture leads to the presence of two families of pores, small pores of some 10 to 100 Å , together with large pores ranging from 100 to 10,000 Å . Surface area can be as large as 800 m^2/g . These characteristics enhance greatly the chemical accessibility and the mass transfer of ions and large molecules . In the column chromatographic separation for rare earth elements , the important experimental parameters such as HETP , stage time and production rate reflect the differences of the separation efficiency of both types . Bio-Rad Lab's AG 50W (gel-type) resins , AG MP-50 (macroreticular) resins and self synthesized resins are compared by means of EDTA displacement column chromatography in Pr-Nd separation under the same experimental conditions.

EXPERIMENTAL

Apparatus

The experimental apparatus for the estimation of separation factor and the height equivalent to a theoretical plate (HETP) are self-fabricated glass columns with water jackets for temperature control . The dimension of the resin bed is 1.7 cm I.D. x 10 cm L for separation factor estimations and 1.7 cm I.D. x 50 cm L for HETP determinations . A corrosion-resistant metering pump is used to deliver various solutions and the Gilson's Model SC-30 fraction collectors are used to fractionate the effluents . Fig. 2. shows the experimental apparatus.

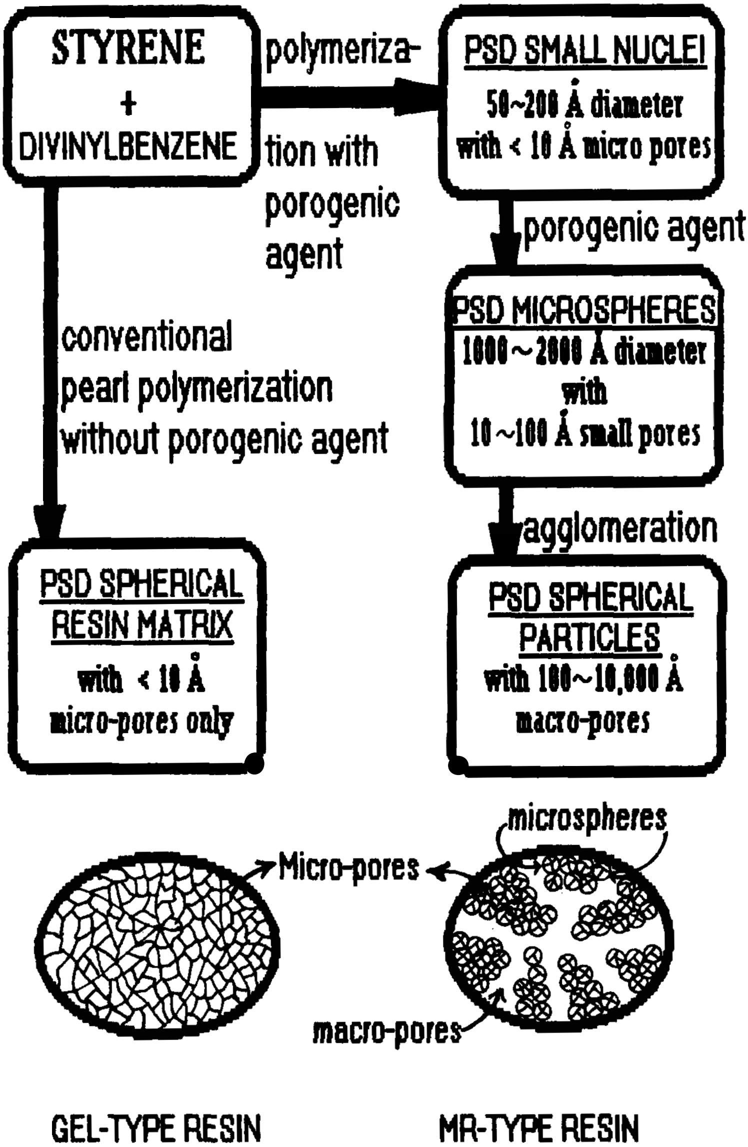
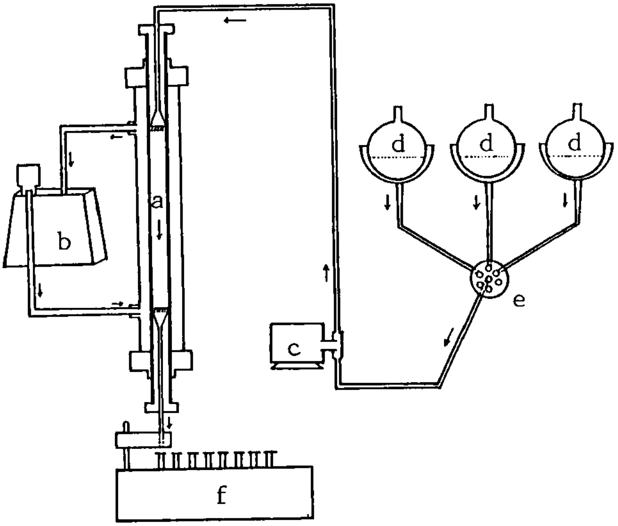


Fig. 1. Formation and Structure of Gel-Type And Macroreticular Resins.



a: resin bed, b: thermostat, c: pump
d: solutions, e: selector valve,
f: fraction collector

Fig. 2. Experimental Apparatus

Resins

Gel-type cation exchange resins : Bio-Rad Lab's analytical grade strongly acidic cation exchange resins were used . They consist of sulfonic acid functional groups attached to a styrene divinyl-benzene copolymer lattice , such as AG 50W-X4, AG 50W-X8, AG 50W-X10, AG 50W-X12, and AG 50W-X16, which are with 4%, 8%, 10%, 12%, and 16% crosslinkages, respectively . Because of the disappearing on drying of any pore structure that exists in the gel-type resins, the surface area are less than 0.1 square meters per gram and porosities are around 1 % (1).

Macroreticular cation exchange resins : Bio-Rad Lab's AG MP-50 resin is the macroporous equivalent of AG 50W-X8 resin. With uncollapsed macro- and micro- pores in the matrix , its effective surface area approximates 35 square meters per gram , porosity is 30~35 % , and the crosslinkage is 8 % (5) . ICE-1 , ICE-2 , ICE-3 and ICE-4 are laboratory synthesized macroreticular resins with similar chemical composition of AG MP-50 resin . The first three resins have the same degree of crosslinking of 20 % but have different porosities (54 % , 49 % , and 45 % , respectively) resulting from different porogenic agents used in the resin formation (6) . The degree of crosslinking of ICE-4 resin is 30 % and porosity is 47 % .

Micro-Void Volume Ratio Determination

The micro-void volume ratio (Rv) of a cation exchanger is represented by the following formula :

$$Rv = Pv/Sv \qquad (1)$$

Wherein Sv is the volume of the cation exchanger in the wet swollen state and Pv is the pore volume within the cation exchanger particles. The Pv and Sv are measured as follows :

Measurement of Pv:

(a) An aqueous solution containing 0.1 M/L of hydrogen ion and 0.1 M/L of $PrCl_3$ is supplied to a cation exchanger until equilibrium.

(b) The equilibrated cation exchanger is dehydrated by centrifugal force until the integrated amount of dehydration in the first stage becomes constant as the centrifugal force was increased . Generally the centrifugal force corresponds to about 500 to 9,000 r.p.m.

(c) The dehydrated cation exchanger is evaporated in a vacuum drier.

(d) The amount of water evaporated in (c) is that of water within pores and designated the pore volume within the cation exchanger particles.

Measurement of Sv :

Sv contains the true volume (Tv) of the dried cation exchanger and the pore volume within the cation exchange resin particles (Pv) . The true volume (Tv) of the dried cation exchanger was estimated by means of the measurements of the dry weight (Wt) and the true skeletal density (Dt) of the resin particles . Dt is measured with a multi-pycnometer.

Thus $$Sv \square Pv + Tv \qquad (2)$$

$$Rv = Pv / Sv \square Pv /(Pv + Tv) = \frac{Pv}{Pv + Wt/Dt} \qquad (3)$$

Chemical Analysis

The concentration of Pr or Nd in EDTA solution in the range of 10^{-1}~10^{-3} M/L was determined spectrophotometrically in the wave lengths of 446 nm and 800 nm , respectively . The absorption coefficients are 8.7 for Pr, and 11.2 for Nd . For lower concentration , the x-ray florometry was used.

Separation Factor Estimation

An excess of a known mixture of 0.0075M Pr/0.0075M Nd/0.015M EDTA solution, PH=3, was prepared, preheated and passed slowly (5 ml/min) through a H^+-form resin bed (1.7 cm I.D. x 10 cm L), maintained at 95°C, until the composition of the effluent solution coincides with that of the feed solution . Then the absorbed Pr-Nd mixture is stripped from the resin bed to determine the molar ratio of the components absorbed . The separation factors can be estimated by the following equation : (7)

$$\underset{Pr}{\overset{Nd}{\alpha}} = \frac{\text{ratio of Nd to Pr in solution}}{\text{ratio of Nd to Pr in resin bed}} \qquad (4)$$

HETP Estimation

The minimun displacement distances (L) required to achieve steady state conditions are estimated by Eq. (5).

$$L = \text{band length} \times V \qquad (5)$$

where V is the minimum number of band displacements required to resolve a mixture by displacement chromatography and depends solely on the mole fraction (No) of the component which elutes first in the original mixture and the separation factor (8,9), that is :

$$V = \frac{1 + (\alpha-1)No}{\alpha-1} \qquad (6)$$

In our case, No =0.5, α =2.0; so V =1.5,

$$L = 1.5 \times \text{band length} \qquad (7)$$

A band shorter than 30 cm of Pr-Nd mixture is formed by introducing a volume of 700 ml of the mixture solution of 0.0075 M Pr/0.0075 M Nd/0.015 M EDTA (PH=3.0) at constant flow rate of 15 ml/min into the cation exchange resin bed of 1.7 cm I.D. x 50 cm L, then the displacing solution of 0.015 MEDTA (PH=8.0) is used to displace out the sorbed Pr-Nd mixture band from the resin bed, all the inffluents and resin bed were preheated and maintained at 95'C and the effluent was fractionated and analysized for Pr & Nd ion concentration , a steady state displacement profile was obtained with the inherent overlap (ΔL) between pure Nd and Pr bands, then HETP were calculated by Eq.(8). :(7)

$$HETP = \frac{\Delta L}{4} \log \alpha^{Nd}_{Pr} \tag{8}$$

Single Stage Time (Ts) Estimation

Single stage time is calculated by means of dividing the HETP value by band velocity (Bv) which is measured in the band displacement experiment for the estimation of HETP, i.e..

$$Ts = \frac{HETP}{Bv} \tag{9}$$

Production Rate of Pure Pr (Rp)

Production rate of pure Pr is calculated by means of dividing the amount of 99 % pure Pr product (Mp) obtained in the single column band displacement chromatography by the time required for the over all separation operation (T) :

$$Rp = \frac{Mp}{T} \tag{10}$$

RESULTS AND DISCUSSION

EDTA Displacement Chromatograms (AG 50W-X8 vs AG MP-50)

According to the Bio-Rad Lab's product catalog (5), both AG 50W-X8 and AG MP-50 resins have the same chemical composition in the resin matrix, i.e. polystyrene divinyl benzene copolymer with 8 % crosslinkage and the same ion exchange functional group (sulfonyl group) . The only difference in their physical properties is that AG MP-50 has larger surface area and porosity than that of AG 50W-X8 . These two kinds of resins have been used in the single column band displacement chromatography . The chromatograms are shown in fig.3., with the same range of mesh size, AG MP-50 has smaller retention volumes and smaller inherent overlaps than that of AG 50W-X8 resins . The superiorities of AG MP-50 resins can as well be reflected from the key experimental parameters such as the HETP, stage time, and the production rate of pure Pr. These parameters are shown in table 1. From these data , we could see that the values of HETP, Ts , and Rp for AG MP-50 resin in the range of 200~400 mesh are 0.24 cm, 1.30 min, and 0.68 m mole of Pr/hr. Those for AG 50W-X8 resin with the same range of mesh size are only 0.4 cm, 3.11 min, and 0.19 m mole of Pr/hr, respectively.

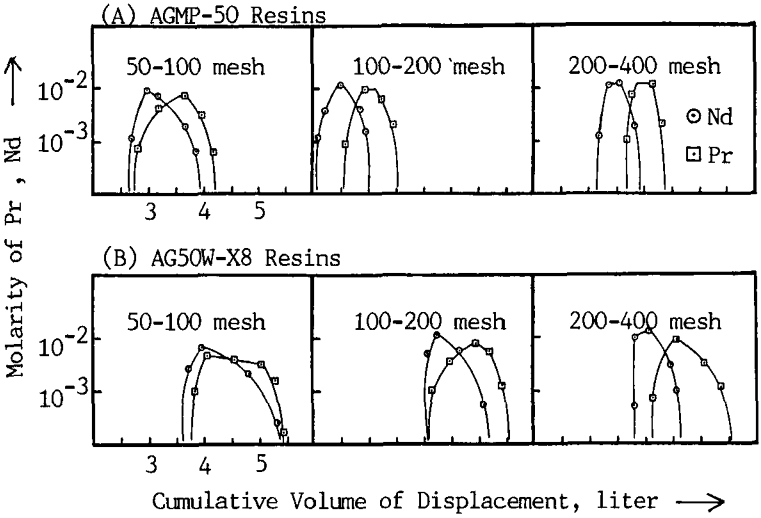


Fig. 3. EDTA Displacement Chromatograms for AGMP-50 and AG50W-X8 Resins.

Table 1. Chromatographic Parameters for Pr-Nd Separation with AG 50W-X8 and AG MP-50 Resins

	AG 50W-X8			AG MP-50		
	50-100 mesh	100-200 mesh	200-400 mesh	50-100 mesh	100-200 mesh	200-400 mesh
$\alpha_{\mathrm{Pr}}^{\mathrm{Nd}}$	2.0±0.1	2.0±0.1	2.0±0.1	2.0±0.1	2.0±0.1	2.0±0.1
HETP	1.19	0.79	0.40	1.06	0.48	0.24
Ts	8.85	5.91	3.11	6.26	2.58	1.30
Rp	0	0.21	0.19	0.19	0.55	0.68
Rv	0.48	0.47	0.49	0.51	0.52	0.51

It is suggested that the higher micro-void vloume ratio (Rv) of AG MP-50 resin which improves the kinetics of ion exchange process. This improvement reduces its value of HETP and stage time to about one-half of those of AG 50W-X8 resin , and raises up the production rate of Pr product to about three times of that of the latter . As for the separation factors , both types of resins are with the same value of 2.0 ± 0.1. Perhaps this is due to the fact that they have the same ion exchange functional group whereby have the same selectivity for Pr and Nd ions . Because the micro-void volume ratio is determined by the morphology and texture within the resin bead only , mesh size and shape show no effect on the Rv values of the same type of resins .

Effect of Degree of Crosslinking

In the band displacement experiments for gelular resins. AG 50W-X4, AG 50W-X8, and AG 50W-X12 with 4 % , 8 % , and 12 % degrees of crosslinking respectively were used . The single column band displacement experiments have been carried out under the same conditions for all the resins . The band displacement chromatograms are shown in fig. 4(B). The band retention volume is increased from 4.2 liters to 6.0 liters while the Pr-Nd inherent band overlap is reduced from 1.9 liters to 1.1 liters as the degree of crosslinking is increased from 4 % to 12 % .

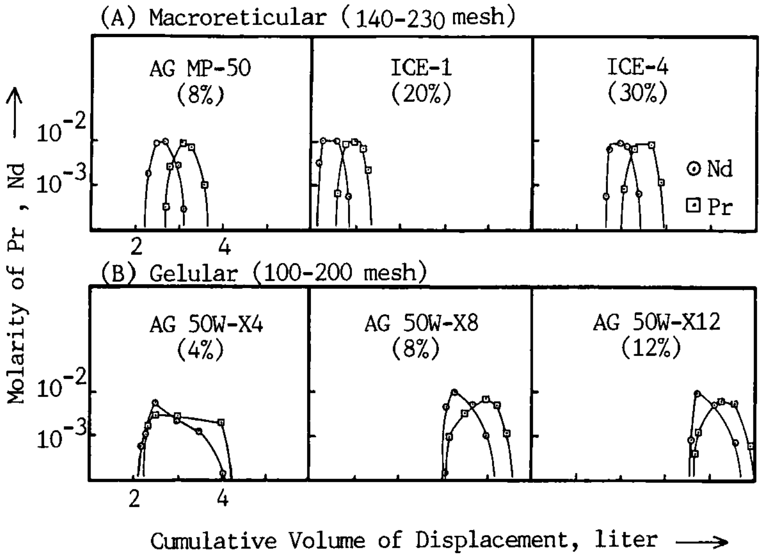


Fig. 4. EDTA Displacement Chromatograms for various Crosslinked Resins.

This phenomenon may imply that the mass transfer rate within the resinous matrix is decreased while the chemical accessibility is increased , for Rv value is reduced from 0.57 to 0.37 but the total exchange capacity is raised from 1.1 to 2.1 meq/ml as shown in table 2 .

The chromatographic parameters have been estimated as in table 2. The values of HETP are determined to be 1.9 cm, 0.79 cm, and 0.67 cm while the stage times are 10.7 min, 6.0 min, and 5.5 min for 4%, 8% and 12% crosslinked resins , respectively . With the smallest value of HETP and stage time, the 12 % crosslinked resin possesses the highest efficiency for the separation of Pr-Nd mixture . The pure Pr production rate as shown in table 2. could prove this fact. For further comparison, more basic properties of the resins were studied, as shown in table 3. e. g., the true sorption capacities were 0.18, 0.35, and 0.38 mmole/ml of resin bed, the true densities were 1.694, 1.675 and 1.641 g/ml for 4 % , 8 % , and 12 % crosslinked gel-type resin with the particle size of 100~200 mesh .

Table 2. Effects of Degree of Crosslinking in Gel-Type Cation Exchange Resins (100~200 mesh)

	AG 50W-X4	AG 50W-X8	AG 50W-X12
Crosslinkage	4%	8%	12%
α^{Nd}_{Pr}	2.0±0.1	2.0±0.1	2.0±0.1
HETP (cm)	1.90	0.79	0.67
Ts (min)	10.70	5.91	5.50
* Tatal Exchange Capacity(meq/ml)	1.1	1.7	2.1
Rp	0.02	0.21	0.23
Rv	0.57	0.47	0.37

* data from ref. (5).

Table 3. Comparison for Properties of Gelular and Macroreticular Cation Exchange Resins

Resins			Type	Pv/Wt (ml/g)	Dt (g/ml)	Rv (ml/ml)	Total Exchange Capacity (meq/ml)	Sorption capacity for Pr (m mole/ml)	Pressure Drop $\frac{(Kg/cm^3)}{cm}$
Code	ASTM mesh size	cross-linkage							
AG 50W-X4	100~200	4%	Gel	0.7667	1.6940	0.565	1.1	0.18	0.018
AG 50W-X8	100~200	8%	"	0.5267	1.6746	0.469	1.7	0.35	0.018
AG 50W-X8	200~400	8%	"	0.5173	1.6730	0.489	1.7	0.36	0.030
AG 50W-X12	100~200	12%	"	0.3563	1.6406	0.369	2.1	0.38	0.021
AG MP-50	100~200	8%	MR	0.6448	1.6706	0.519	1.5	0.23	0.014
AG MP-50	200~400	8%	"	0.6242	1.6756	0.511	1.5	0.29	0.032
ICE-1	140~230	20%	"	0.9588	1.5307	0.595	1.1	0.21	0.009
ICE-2	"	20%	"	0.7891	1.5412	0.549	1.5	0.19	0.010
ICE-3	"	20%	"	0.6824	1.4565	0.499	1.4	0.15	0.012
ICE-4	"	30%	"	0.7218	1.5902	0.534	1.6	0.29	0.011

In the experiments with macroreticular resins. AG MP-50 , ICE-1 , ICE-2, ICE-3 and ICE-4 with 8 % , 20 % , 20 % , 20 % and 30 % of degree of crosslinking were used. There is no apparent regular trend parallel with the degree of crosslinking from the experimental parameters as shown in fig. 4(A)., or from the experimental parameters as shown in table 4. With the highest value of Rv among this group of samples, ICE-1 resin has the smallest band retention volume , inherent band overlap, HETP , as well as Ts , and shows a uniquely high pure Pr production rate which represents the best separation efficiency among the samples. In the comparison of their performances at the same degree of crosslinking which is 20 % (see table 3 & 4) , ICE-1 , ICE-2 and ICE-3 resins show the apparent trends of variation of HETP , Ts and Rp parrallel to the values of Rv and true sorption capacities . This result may be construed to mean that the higher values of Rv and true sorption capacities represent quicker mass transfer and easier chemical accessibility . As far as the separation factors are concerned , both types of resins are with the same values at 2.0 ± 0.1 as the degree of crosslinking are between 4 % and 30 % . These results have revealed the fact that the degree of crosslinking in both types of resin has no effect on the ion exchange selectivity for Nd and Pr ions (4). The modification of ion exchange functional groups would be necessary for the improvement of the ion exchange selectivity (10~13) . In the macroreticular matrix the morphology and texture are complex , the porosity is determined by porogenic agent in the process of particle

Table 4. Effects of Degree of Crosslinking in Macroreticular Ion Exchange Resin (140~230 mesh)

	AG MP-50	ICE-1	ICE-2	ICE-3	ICE-4
Crosslinkage	8%	20%	20%	20%	30%
α^{Nd}_{Pr}	2.0±0.1	2.0±0.1	2.0±0.1	2.0±0.1	2.0±0.1
HETP (cm)	0.45	0.36	0.38	0.83	0.44
Ts (min)	2.50	1.24	1.44	3.00	2.40
Rp $(\frac{m\ mole}{hr})$	0.57	1.03	0.96	0.91	0.94
Rv (ml/ml)	0.51	0.60	0.55	0.50	0.54

formation and not be controlled by the degree of crosslinking of the PSD copolymer . According to the opinion of Miyake and coworkers (6) , in order to maintain a high ion exchange rate with an increased degree of crosslinking , it is preferred that the cation exchanger having the Rv value of 0.55 to 0.82 , has a degree of crosslinking of 17 to 80 % . Since the change in volume of cation exchange resin bed in the development of rare earth band in the chromatography and in the regeneration of the cation exchanger is small , and also the pressure drop through this resin bed is small . For instance , the pressure drop is only 0.009 kg/cm^2 per centimeter for ICE-1 resin with particle size at 140~230 mesh , that is one half of AG 50W-X8 at 100~200 mesh . The superiosities mentioned above accompanied with their remarkable separation efficiency make MR- type ion exchange resins an excellent material for large-scale rare earth elements separation . The data which are shown in table 2~4. strongly support this point of view . Take the gelular AG 50W-X4 resin and the macroreticular ICE-1 resin as an example : both types of resins possess quite similar values of micro-void volume ratios and total exchange capacities , however , they perform in quite different manner in the chromatographic separation. As shown in fig. 4 . the band retention volumes are 4.2 liters for the former (gelular type) and 2.3 liters for the latter (MR type) , the inherent band overlap is 1.9 liters for the former and 0.3 liters for the latter . The superiorities of ICE-1 MR type resin over AG 50W-X4 gelular resin can further be reflected in HETP , Ts , Rp , sorption capacity and pressure drop (see table 2. to table 4.) . It is believed that these superiorities of ICE-1 resin are due to its high degree of crosslinking in the high porous macroreticular resinous matrix.

CONCLUSION

From the experimental results , we obtain the conclusion that gel-type and MR type cation exchange resins of PSD matrix with sulfonyl ion exchange groups possess the same ion exchange selectivity for the rare earth metal ions . However , owing to the differences in the morphology and texture in the matrix structure , MR type resins have superior characteristics including high micro-void volume ratio, rapid ion exchange kinetics , easily accessible sites , low pressure drop. So , in the EDTA displacement column chromatography , MR type resins have shown the smaller band overlap , smaller HETP and Ts values, smaller pressure drop of resin bed but make higher production rate of pure Pr product.

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