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Recent Studies on Ca Isotope Separation by Crown-Ether Resin Chromatography**Shin Okumura^a, Saori Umehara^b, Tadafumi Kishimoto^b, Masao Nomura^a,
Yasuhiko Fujii^{a,*}, Tatsuya Suzuki^c, Masaki Ozawa^a**^aLaboratory for Advanced Nuclear Energy, Tokyo Institute of Technology^bResearch Center for Nuclear Physics, Osaka University^cGraduate School of Engineering, Nagaoka University of Technology**Received March 15, 2016; Accepted October 11, 2016**

Benzo-18-crown-6 ether resin was synthesized with the carrier of porous fine silica beads. By using synthesized crown ether resin packed in glass columns, ⁴⁸Ca enrichment was studied. A high speed chromatography experiment was conducted at the band migration speed of 48 m day⁻¹. In spite of the high speed of migration, enrichment of ⁴⁸Ca was observed at the front boundary of the displacement type chromatography. Comparing with previously reported experiments of 1 m 3 m and 200 m migrations, we confirmed that separation coefficient ϵ slightly decreases with increase in the band velocity. In addition, the enriched zone was found to increase with increase in the migration length. The observed relation shows that the width of the enriched zone is proportional to square root of the migration length.

1. Introduction

Chromatography is an effective chemical separation technique and has been broadly applied for chemical analysis, purification of materials, etc. In particular, chromatography using ion exchange resin has been applied in broad area of chemistry as a powerful technique of separation. This technique is applicable even for isotope separation.

For many years, Research Laboratory for Nuclear Reactors (Presently, Laboratory for Advanced Nuclear Energy) has conducted the study on isotope effects and isotope separation of a number of elements including uranium by using ion-exchange chromatography. The ion-exchange uranium enrichment is characterized as high proliferation resistant technology. In the course of the study on the ion exchange uranium enrichment, organic resin embedded in porous silica beads was synthesized. This technique has been applied to synthesis of crown-ether resin and used for isotope separation of zinc and calcium.

Isotope separation developed for nuclear engineering has expanded its application to various fields. Research into double β decay is a typical area where isotope separation is anticipated. The isotope ⁴⁸Ca is a double β nuclide with the natural abundance of 0.187 %. Development of ⁴⁸Ca enrichment technology is anticipated. Usual isotope separation techniques of gaseous diffusion and centrifuge are not applicable for ⁴⁸Ca, because there is no gaseous compound usable as the working medium. Chemical exchange methods, utilizing functional materials like crown-ether and cryptand, are more appropriate than the physical isotope separation methods.

Calcium isotope separation by using crown-ether was reported by Heumann and Jepson. Heumann studied calcium isotope separation using strongly acidic cation exchange resin, dibenzo-18-crown-6 ether resin, and [2_B.2.2] cryptand [1]. Jepson reported calcium isotope separation using synthesized crown-ether resin packed in a column [2]. Synthesis of crown ether resin is possible but synthesis of large amount of fine resin is very difficult. In our laboratory, benzo-18-crown-6

ether resin has been synthesized by condensation process. Production of fine particle resin is very difficult by condensation reactions. In spite of the difficulty, we have developed production technology of fine particle crown-ether resin embedded in porous silica beads. By using this resin, chromatographic experiments have been conducted at different operational conditions by the researchers including the present authors to study ⁴⁸Ca isotope separation [3-8]. In the present paper, attention has been placed on the high speed chromatography.

2. Experimental

Benzo-18-crown-6 ether resin embedded in porous silica beads was synthesized in our laboratory and packed in 10 units of glass columns; the diameter was 8 mm and the length was 100 cm each. The packed resin was pretreated with 500cm³ of deionized water and rinsed with 500 cm³ of 9M HCl solution. Then the first six columns, connected in series, were charged with Ca solution; 0.1 M (mol dm⁻³) Ca in 9M HCl. The flow rate was 2 cm³ min⁻¹. The column temperature was kept constant at 35 °C by circulating thermostated water.

When the front edge of the Ca adsorption zone reached the bottom of the fifth column, the outlet of the sixth column was connected to the top of the seventh column by using a flexible tube. Then the first column was disconnected from the line, and the Ca feed solution was charged into the line from the inlet of the 2nd column. In the same way, when the adsorption band reached the bottom of the sixth column, the feed solution was charged into the third column. In this manner, chromatographic operation was continued maintaining the connection of six columns in series for formation of the Ca adsorption band. At the initial stage of the chromatography before the sampling of the fractions of effluent, as seen in Figure 1, the effluent volume 304 cm³ was collected from the bottom of the sixth column, and then 25 cm³ of effluent was collected from the seventh, the eighth and the ninth columns. From the 10th column 80 cm³ of effluent was collected. The total volume of effluent collected by the graduated cylinders was 459 cm³. Thereafter the effluent taken from the outlet of the 10th column

*1Corresponding author. E-mail: fujiiyxyz@road.ocn.ne.jp, fax; +81 445558271

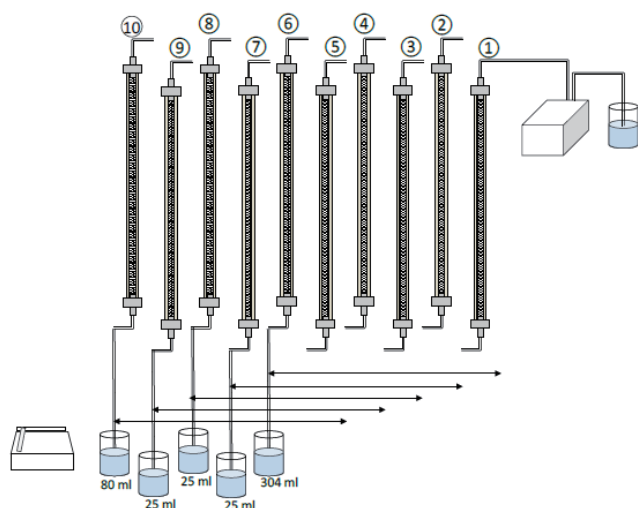


Figure 1. The experimental apparatus for 10 m migration chromatography.

was collected in fraction by a fraction collector; the volume of each fraction was 4 cm³.

The concentrations of calcium in the collected fractions were measured by flame photometry at the wave length of 622 nm using a spectrophotometer ANA-182F (Tokyo Photoelectric Co. Ltd). From the collected fractions of effluent, a portion of the fraction was sampled and added with HI solution, then heated to dryness. The sampled CaCl₂ was converted to CaI₂ and subjected to isotope analysis. The calcium isotopic abundance ratio of [⁴⁸Ca]/[⁴⁰Ca] in each collected fraction was determined by a thermal-ionization mass spectrometry using a mass spectrometer Finnigan MAT 261. More detailed description was made on the mass spectrometric isotope analysis in a previous work [4].

3. Results and discussion

3.1. Separation Coefficient. The aim of the present work is to evaluate the effects of migration speed on the enrichment of calcium isotope. The migration speed of the adsorption band is considered to affect the separation process. High speed migration can enhance the productivity of separation. However it is believed that the HETP is increased when the band speed is increased. The separation coefficient is theoretically independent of the band speed. However we have to verify if this is true or not in the practical case of high speed migration.

In the previous work, we have conducted the experimental work at the band speed up to ca. 20 m d⁻¹ using this type of resin embedded in the porous beads of MST-8 produced by Mizusawa Chemical Co. In the present work, the calcium adsorptive chromatography was conducted at the feed flow rate of 2 ml/min. The observed band velocity at the feed flow rate was 48 m d⁻¹. Chromatographic profile of calcium elution in effluent is shown in Figure 2. The front boundary is very sharp. This fact suggests that the adsorption of calcium ions on benzo-18-crown-6 ether resin is very fast. The determined isotopic abundance ratios of [⁴⁸Ca]/[⁴⁰Ca] of the front part of the adsorption band are plotted also in Figure 2. It is clearly seen that the heavier isotope ⁴⁸Ca is accumulated in the front region of the Ca adsorption band. This enrichment tendency of heavy isotope at the front boundary is the same as ones observed in the previous work on calcium isotope separation by crown ether resin [3-7]. In spite of the high speed of the band migration, the enrichment of ⁴⁸Ca was successfully realized at the front band boundary.

The most important factor to evaluate the chromatographic

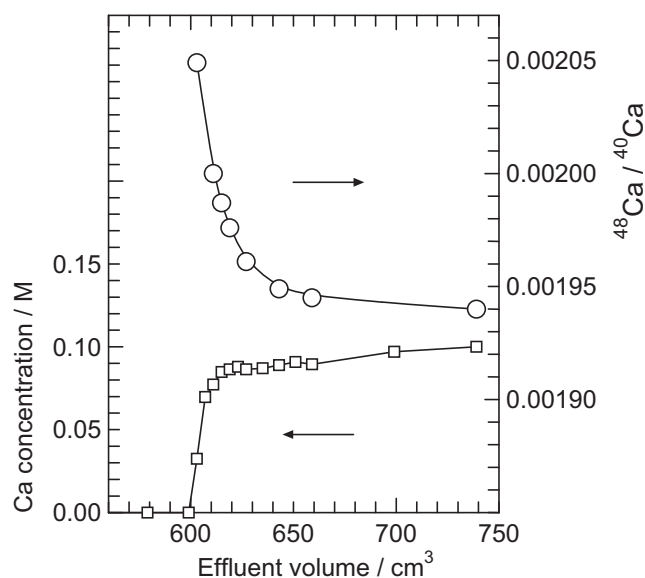


Figure 2. Calcium concentration profile and ⁴⁸Ca enrichment at the front boundary of 10 m migration breakthrough chromatography.

isotope separation process is the separation coefficient ε . The separation coefficient of this system is calculated by the following equation using the experimentally observed data of the calcium concentration and the isotopic abundance ratios in the fractions collected from the effluent,

$$\varepsilon = S q_i (r_i / r_o - 1) / Q \quad (1)$$

where r_o and r_i are isotopic abundance ratio [⁴⁸Ca]/[⁴⁰Ca] of calcium in the feed and in the effluent fraction i , respectively. The measured value of r_o in the present work is 0.001935. The adsorption capacity of Q is calculated as,

$$Q = C_o (V_B - V_D), \quad (2)$$

where C_o is the concentration of calcium in the feed solution, V_B is the effluent volume of the break through point and V_D is the total dead volume of the columns connected in series. Based on eq 1 and using the experimentally observed data, the separation coefficient ε of the present system is calculated as 0.0026 and presented in Table 1. In the present work the error of the observed ε consists of uncertainties in Ca concentration analysis (about 5%) and the isotopic abundance ratio analysis (about 7%). The range of error indicates 1 σ .

Previously observed separation coefficients are presented also in TABLE 1. The value of ε is 0.0036 and 0.0032 for the migration 1m and 3m, respectively. Although the error ranges are large, apparently ε is decreased in the cases of chromatographic experiments at high migration velocity. Probably it is difficult to fully attain the isotopic exchange equilibrium between two phases within the short contact time, when the flow rate is very fast.

3.2. HETP. Another important factor of the chromatographic separation process is the height equivalent to a theoretical plate (HETP). HETP is a kinetic factor and reduced when the isotopic exchange rate is fast between the solution phase and the resin phase. The smaller HETP means the better separation efficiency.

The HETP is defined as the slope of the enrichment profile created in the adsorption band after the isotopically steady state is attained. Such a state is attained only in the case of long migration and narrow adsorption band. In the usual cases of migration, isotopic enrichment process is not steady state. In the isotopically non-steady state, the slope varies depending

TABLE 1: Experimental results of calcium isotope separation by chromatographic migration conducted using the eluent of 9M HCl at 35°C

Migration length, m	Migration Velocity, m d ⁻¹	Separation coefficient, $\varepsilon \times 10^3$	HETP, mm	Enriched zone width, cm	Remarks
1	6.5	3.6±1.4	3.7	17	Ref. [5]
3	22.5	3.2±0.6	4	20	Ref. [10]
10	48	2.6±0.3	6	54	Present work
200	20	3.0±0.1	8.3	238	Ref. [5]

The errors of separation coefficient show 1σ .
The error range of HETP is approximately ± 1 mm in each run.

on the position in the band, from the maximum value at the band front to practically zero at the far inside the band. The HETP of the chromatographic enrichment process in the non-steady state is very difficult to obtain by theoretical calculation. However, using the very simple assumption of the single phase migration, the theory of HETP for displacement-type isotope enrichment has been developed [8, 9]. According to the theory, HETP of the experimental separation system is calculated by the following equations,

$$\ln(r_i - r_o) = k(X_i - L) + \ln(r_L - r_o) \quad (3)$$

$$H = \varepsilon / k + 1 / Lk^2 \quad (4)$$

where k is an experimentally determined gradient of enrichment curve, H is a height equivalent to a theoretical plate, L is the total length of the resin bed of the columns. In this theory, the volume of effluent fraction, or the volume of moving-phase, is converted to the location of the stationary phase. The volume difference between the effluent volume of breakthrough point and the effluent volume of fraction i is converted to $|X_i - L|$. The conversion factor C_F is given as,

$$C_F = L / V_B \quad (5)$$

$$X_i - L = -C_F(V_i - V_B) \quad (6)$$

To apply this theory to the actual systems, it is noted that the isotopic ratio in the solution phase is in equilibrium with the isotopic ratio in the adsorption phase. If the isotopic abundance ratio of adsorbed Ca is natural r_o , the isotopic abundance ratio in the solution phase becomes $r_o a$. Therefore the practical value of the original isotopic ratio in the solution phase is $r_o(1+\varepsilon)$ rather than r_o . For the convenience, $r_o(1+\varepsilon)$ is expressed as r_o^* and above mentioned eq 3 can be written as,

$$\ln(r_i - r_o^*) = -k(L / V_B)(V_i - V_B) + c \quad (7)$$

where c is $\ln(r_L - r_o)$. According to eq 7, the experimental data, $(r_i - r_o^*)$, of the cases of migration 10 m and 200 m are plotted in Fig. 3 as a function of $(V_i - V_B)$ of each fraction i . The plots of $(r_i - r_o^*)$ of migration 200m in Figure 3 gave HETP of 8 mm.

By using eqs. 4 and 7, HETP of the present system was calculated as 6 mm for the migration of 10 m. Separation coefficient and HETP of the present work are listed in Table 1 along with those of the other experimental runs previously conducted. It is seen that HETP is increased with increase in the migration speed among the chromatographic migrations of 1m, 3m and 10m. In the case of 200m migration, HETP was enlarged, which is probably due to the large number of connections between the columns.

3.3. Width of enriched zone. So far, in our previous work,

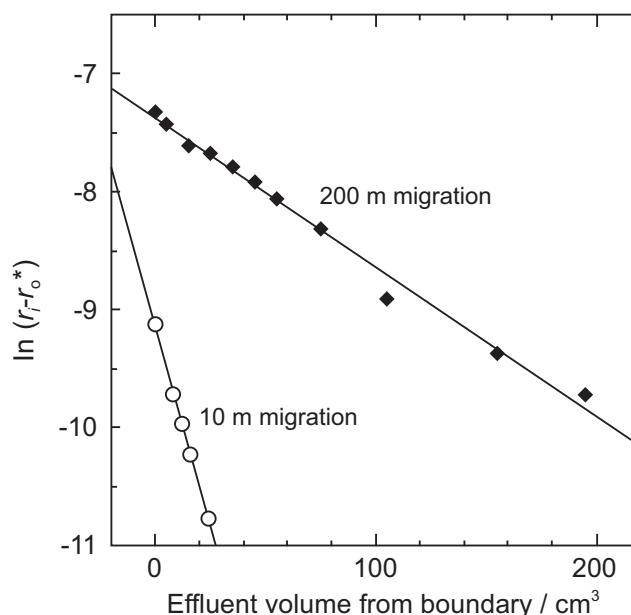


Figure 3. Increment of $^{48}\text{Ca}/^{40}\text{Ca}$ isotopic ratio of calcium in the effluent; two cases of the migration lengths of 10 m and 200 m. ($r_o^* = 0.001940$)

we have not yet discussed details about the length of the enriched zone developed in the chromatographic band. To design the enrichment plant, an important factor is the length of the adsorption band created in the packed separation column. Sufficiently long adsorption band is necessary to reach the desired enrichment at the front boundary. On the other hand, the length of the band should be short, as short as possible, from the view point of column utilization efficiency. To limit the length of the adsorption band, we have to know the width of the enriched zone. From the practical view point, we define the enrichment zone as the area where the increment of enrichment degree of calcium in fraction i , $(r_i - r_o)$, is larger than 10 % of the front maximum value $(r_L - r_o)$. This means the enrichment zone is holding 90% of the enriched isotope accumulated in the front boundary region, and therefore 10% of the enrichment capacity is left in the latter part of the adsorption band during the migration. The enriched isotope in the latter part can not be recovered and regarded as being lost. The width of the enriched zone defined by the criteria mentioned above was calculated for each chromatographic experiment and listed in TABLE 1. The calculated enriched zone width for each chromatographic run is plotted against the square root of migration distance in Figure 4. It is seen the enriched zone width is linearly proportional to the square root of migration distance. The results indicate the following empirical relation,

$$We = 0.17 L^{1/2} \quad (8)$$

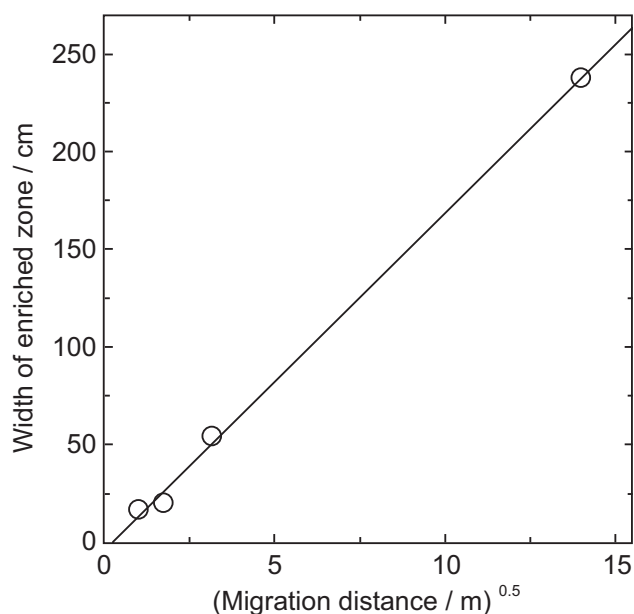


Figure 4. An empirical relation between the migration distance and the width of enriched zone.

where W_e is the enriched zone width. If we use this eq 8, it is suggested that after the 3000m migration the enrichment zone will reach the length of ca. 9 m. The length of 9 m is quite long but may be within the acceptable length from the view point of the column size, if the actual plant can be composed of columns whose height is approximately 10 m. Improvement in the HETP could make the enrichment plant more compact.

4. Conclusions

Calcium isotope separation was studied by using synthesized benzo-18-crown-6-ether resin in porous fine silica beads. High speed chromatography was conducted at the band migration speed of 48 m/day using 10 units of 1m glass columns connected in series. In spite of the high speed of migration, enrichment of ^{48}Ca was observed at the front boundary of the adsorption band. Observed separation coefficient was 2.6×10^{-3} , and the value of HETP is 6 mm. By comparing with previously reported data, it is seen that ϵ slightly decreases with increase in the band velocity. It is also seen that HETP

increases with increase in the band velocity among the migration distances of 1m, 3m and 10m. Concerning the width of the enriched zone, it was observed that the enriched zone width is proportional to the square root of migration distance.

Acknowledgements

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References

- (1) *Stable Isotope*, edited by H.L. Schmidt, H. Foerstel, and K. Heinzinger (Elsevier, Amsterdam, 1982).
- (2) B.E. Jepson, W.F. Evans, MLM-3654, pp.4-26 (1990).
- (3) Y. Fujii, M. Nomura, T. Kaneshiki, Y. Sakuma, T. Suzuki, S. Umehara, et al. Mass dependence of calcium isotope fractionations in crown-ether resin chromatography. *Isotopes in Environmental and Health Studies* 46, 233-241 (2010).
- (4) S. Okumura, S. Umehara, Y. Fujii, M. Nomura, T. Kaneshiki, M. Ozawa, T. Kishimoto, *J. Chromatogr. A* 1415, 67 (2015).
- (5) S. Umehara, T. Kishimoto, H. Kakubata, M. Nomura, T. Kaneshiki, T. Suzuki, Y. Fujii, S. Nemoto, *Prog. Theor. Exp. Phys.* 053C03, doi: 10.1093/ptep/ptv063 (2015).
- (6) Y. Fujii, T. Kaneshiki, M. Nomura, T. Suzuki, S. Umehara, T. Kishimoto, *Proceedings of 12th Intern. Workshop on Separation Phenomena in Liquids and Gases* (SPLG, June 2012, Paris) 44-49.
- (7) S. Nemoto, K. Suga, Y. Fukuda, M. Nomura, T. Suzuki, T. Oi, *J. Nucl. Sci. Technol.* 49, 425 (2012).
- (8) Y. Fujii, M. Aida, M. Okamoto, T. Oi. *Sep. Sci. Technol.* 20, 377, (1985).
- (9) M. Aida, Y. Fujii, M. Okamoto, *Sep. Sci. Technol.* 21, 643 (1986).
- (10) S. Umehara, S. Okumura, M. Nomura, T. Kaneshiki, Y. Fujii, T. Kishimoto, *13th Workshop on Separation Phenomena in Liquids and Gases*, Talk 5 (SPLG, June 2015, Bariloche, Argentina).