*Extraction Chromatography of Neodymium
by an Organophosphorous Extractant
Supported on Various Polymeric Resins*

Doreen Y. Takigawa

Los Alamos
NATIONAL LABORATORY

Los Alamos, New Mexico 87545

MASTER

ds
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

EXTRACTION CHROMATOGRAPHY OF NEODYMIUM BY AN ORGANOPHOSPHOROUS EXTRACTANT SUPPORTED ON VARIOUS POLYMERIC RESINS

by

Doreen Y. Takigawa

ABSTRACT

Fifteen resins coated with dihexyl-N,N-diethylcarbamoylmethylphosphonate (CMP) were studied for their extraction of neodymium (Nd) in 4.0 and 7.0 M nitric acid. Resin properties, such as chemical composition and physical morphology, which can influence Nd extraction as well as subsequent resin regeneration (Nd stripping), were identified. Hydrophilic or polar resins coated with CMP efficiently extracted the Nd. Resins initially washed free of residual monomer and solvent before CMP coating outperformed their untreated counterparts. The macroporous styrene-divinylbenzene hydrophobic resins that were high in surface area were less effective supports compared with hydrophilic microporous Aurerez, polybenzimidazole (PBI) and macroporous Amberlite polyacrylic resins. Only one resin, Duolite C-467, showed no measurable improvement in Nd extraction with CMP coating. CMP-coated Aurerez PBI, a microporous and hydrophilic polymeric resin with an average surface area, showed the best overall efficiency for Nd removal and resin regeneration.

INTRODUCTION

Scientists at Los Alamos National Laboratory are investigating extraction chromatography as a viable method for recovering actinides from high-acid process effluents.¹ In this method synthetic resins act as polymeric adsorbents for a bidentate organophosphorous extractant specific for the removal of actinides. Extraction chromatography studies reported in the literature describe the removal of copper by LIX extractants.² Other reports describe the separation of americium from plutonium by a sequential procedure consisting of anion exchange and extraction chromatography.³ Navratil⁴ reports the use of non-ionic macroporous resins for the removal of dissolved extractants, such as organophosphorous compounds from aqueous waste streams.

The objective of the work reported here was to identify, by evaluating a variety of commercial resins coated with dihexyl-N,N-diethylcarbamoylmethylphosphonate (CMP), the effects of resin composition and physical morphology on neodymium (Nd) extraction. Nd served as an analog of americium, an actinide commonly found in acid waste streams. An understanding of the significant factors influencing the extraction behavior of the coated polymer resin is likely to lead to the development of a new generation of improved resins. Such resins will consist of extractants covalently bound on those polymer resins shown by experiment to be most suitable for this use.

EXPERIMENTAL METHOD

Reagents

All reagents were analytical grade products. CMP purchased from Industrial and Specialty Chemicals (Niagara Falls, New York) was used without further purification. Stock solutions of

2.0 g/l Nd were made from Nd nitrate hexahydrate (from the Aldrich Chemical Co.) in 4.0 M or 7.0 M nitric acid solutions. Buffer solutions for Nd analysis were prepared from sodium acetate and acetic and nitric acid and were stabilized at a pH of 3.3. Arsenazo III (also from the Aldrich Chemical Co.) in solution was used to obtain a color reaction with Nd to allow spectrophotometric determination of Nd at very low concentrations.

Polymeric Adsorbent Resins

- Aurorez polybenzimidazole (PBI) resin in two mesh sizes, 150 to 250 μm and 250 to 500 μm , were obtained from Celanese Corporation.
- Biobeads SM-2 and SM-7 were supplied by Biorad Laboratories.
- Amberlite IRC: 50S, 76, and 718; Amberlite XAD: 2, 4, 7, 8, and 16; and Duolite: C-467 and S-761 were obtained from Rohm and Haas Company.
- Lewatit OC A062 was obtained from Mobay Chemical Company.
- Dianex HP 20 was obtained from Dianex Systems.

Resin-Coating Procedure

A mixture of 5 ml of CMP and 2 g of resin was shaken at 350 rpm for 60 min in a temperature-controlled shaker bath at 55°C. The CMP was filtered from the resin, and the resin was rinsed and filtered repeatedly with a total of 500 ml of deionized water. This assured removal of any residual CMP adsorbed on the surface; CMP can adversely affect spectrophotometric evaluation of Nd.

Nd Extraction Experiment

The coated resin beads were divided by equal weights into two separate vials. To one vial, 5 ml of a Nd stock solution containing 2.0 g/l Nd in 4.0 M HNO_3 was added, and to the other vial, 5 ml of a stock solution containing 2.0 g/l Nd in 7.0 M HNO_3 was added. These vials were placed in a 40°C temperature-controlled bath and agitated for 10 min at 350 rpm. The 10-min batch contact time was selected to simulate a practical kinetic evaluation of the resin in a column.

The Nd remaining in the solution was evaluated by ultraviolet spectrophotometry, to determine, by difference, the amount of Nd adsorbed by the resin. Analysis of the Nd was performed by complexing the Nd with Arsenazo III (2:1 molar ratio Arsenazo:Nd) at a pH of 3.5. The solution containing Nd was diluted to concentrations in the 1×10^{-5} M to 5×10^{-5} M Nd concentration region, where Beer's law for Nd/Arsenazo complex was obeyed at $\lambda_{\text{max}} = 658$ nm. In every experiment, the Nd stock solution was also analyzed with the same dilution and Arsenazo complexation technique to establish the Nd standard base line.

Nd-Stripping Experiment

The resin tested for Nd extraction was filtered free from the Nd solution and placed in a vial. To this resin was added 3.5 ml of 0.1 M HNO_3 . This mixture was agitated for 1 min at 350 rpm in a temperature-controlled shaker bath at 40°C. The amount of Nd stripped from the resin was evaluated spectrophotometrically by the procedure described above.

RESULTS AND DISCUSSION

The 15 resins coated with CMP and tested for Nd extraction are listed in Table 1. The resins are ranked according to their overall performance for Nd extraction (in 4.0 and 7.0 M HNO_3) and their subsequent stripping and resin-regeneration ability. The ratings for each resin were assigned according to their comparative rankings on extraction and stripping abilities in Nd test solutions at 4.0 and 7.0 M HNO_3 . Tables 2 and 3 rank the resins according to their Nd extraction ability in 4.0 M HNO_3 and 7.0 M HNO_3 , respectively.

PBI

The Aurez PBI resin is a microporous spherical polymer having the following physical properties in the dry state⁵: bead size, 150 μm ; pore size, 80 $\text{\AA}$; specific surface area, 20 to 35 m^2/g ; and 5% to 10% swelling in water. The resin was supplied wet with a moisture content of approximately 80% (w/w). The PBI repeating unit structure,

has two tertiary nitrogens amenable to protonation, with a theoretical capacity of 6.5 meq/g. PBI is an acid-, temperature-, and radiation-resistant hydrophilic polymer that has been considered for use in ion exchange, in gas and liquid chromatography, and as an inert substrate for oxidizing and reducing agents. Although Aurez PBI without CMP coating extracted no Nd, when coated with CMP, it extracted very well (Tables 2 and 3). This finding suggests that PBI adsorbs CMP, which in turn creates a favorable environment for the sorption of Nd. The hydrophilic/polar nature of PBI resin appears to enhance the diffusion of metals in an aqueous environment.

The sorption of PBI for CMP is not surprising. PBI efficiently removes organic compounds such as phenols and carboxylic acids.⁶ Studies have found a sharp increase in the sorption capacity with the length of the carbon chain in a series of carboxylic acids. Thus, apolar (or hydrophobic) bonding interactions between the PBI and hydrocarbon components of the long-chain carboxylic acids enhances sorption. Hydrogen-bonding interactions also appear to play a role in the enhanced sorption of the phenols. Similar interactions have presumably occurred during the CMP sorption onto PBI observed in the work reported here.

Amberlite IRC-76

Unlike PBI, Amberlite IRC-76 is a weakly acidic macroporous resin supplied in the hydrogen form. It has carboxylic acid functional-exchange sites within a cross-linked polyacrylic matrix. The physical properties of Amberlite IRC-76 are as follows: bead size, 16 to 50 mesh (290 to 1000 μm); 54% to 58% moisture content; and macroporous. Because Amberlite IRC-76 is supplied in the hydrogen form, it is effective in removing ions associated with carbonate alkalinity as well as the adsorption of basic compounds such as CMP. Such macroreticular resins will adsorb significant quantities of compatible compounds, filling in the available voids. Also, the hydrophilic polyacrylic matrix of Amberlite IRC-76 is similar to that of Aurez PBI and may enhance the diffusion of metals in an aqueous environment. As indicated in Tables 2 and 3, Amberlite IRC-76/CMP behaves like Aurez PBI/CMP in its extraction capabilities at 4.0 and 7.0 M HNO_3 , but its stripping abilities are considerably better.

**Table 1. Overall Rating of
CMP-Coated Resins**

Resin	Rating
Aurorez PBI	4.5
Amberlite IRC-76	5.83
SM-7	6.00
Lewatit OC A062	7.00
XAD-8	7.17
Dianex HP 20	7.17
XAD-7	7.5
Duolite S761	7.67
XAD-16	11.33
XAD-4	11.67
XAD-2	12.0
Amberlite IRC-718	12.34

**Table 2. Nd Extraction/Stripping from CMP-
Coated Resins at 4.0 M HNO₃**

Resin	Extraction (%)	Stripping (%)
Duolite C-467	88.4	8.3
SM-7	87.1	28.9
Aurorez PBI	83.2	45.3
XAD-7	83.1	17.1
Amberlite IRC-76	82.3	52.6
Dianex HP 20	81.7	36.9
XAD-8	78.0	51.2
Duolite S-761	76.7	37.3
IRC 50-S	75.4	61.2
Lewatit OC A062	71.4	50.8
XAD-4	71.1	27.2
XAD-16	66.3	41.4
SM-2	60.1	58.5
XAD-2	46.3	50.6
Amberlite IRC-718	32.3	63.1

**Table 3. Nd Extraction/Stripping from CMP-
Coated Resins at 7.0 M HNO₃**

Resin	Extraction (%)	Stripping (%)
SM-7	92.4	20.9
Aurorez PBI	88.5	37.7
Lewatit OC A062	86.2	39.0
Duolite S-761	86.0	31.9
XAD-7	85.8	12.0
Duolite C-467	85.8	10.2
IRC-76	85.5	50.6
XAD-8	84.5	36.1
Dianex HP 20	80.0	34.3
XAD-16	79.3	41.4
Amberlite IRC-50S	78.8	75.8
XAD-4	75.5	26.5
SM-2	58.8	46.6
XAD-2	57.8	40.9
Amberlite IRC-718	33.7	72.0

SM-7, XAD-7, and XAD-8

The chemical composition of the three macroporous resins, SM-7, XAD-7, and XAD-8, is the same as that of an acrylic, nonfunctionalized polymer matrix. In fact, SM-7 and XAD-7 are the same resin (20 to 50 mesh, 90-Å pore size, and 450-m²/g surface area). Biorad Laboratories, which supplies SM-7, acknowledged that the XAD-7 resin they purchase from Rohm and Haas is rigorously washed with a mixture of hot water, 70% isopropanol, and 100% methanol. This technique presumably washes the beads free of excess toluene, cyclohexanol, methyl methacrylate, and ethylene dimethacrylate, which are left as surface residue from the polymerization. As indicated in Tables 1 through 3, SM-7/CMP and XAD-7/CMP behave differently. SM-7/CMP outperforms XAD-7/CMP in Nd extraction and stripping in 4.0 and 7.0 M HNO₃ test solutions. XAD-8, which is lower in surface area—160 m²/g—but larger in pore size—225 Å—performs similarly to the XAD-7 in extraction of Nd but better in stripping.

Duolite C-467

The Duolite C-467 resin is a macroporous, divinylbenzene cross-linked polystyrene with aminophosphonic functional groups. The bead size is 0.3 to 1 mm (18 to 50 mesh size). The Nd extraction and stripping properties before and after coating with CMP are the same. Duolite C-467 is the only resin tested that extracted Nd in 4.0 M and 7.0 M HNO₃ to the same degree, regardless of whether it was coated with CMP. Although the polymer matrix remained the same, the aminophosphonic functionality enhanced the adsorption of Nd considerably more than did the nonfunctionalized polystyrene. Because this resin is such a strong complexant for Nd, however, its stripping property is very poor (Tables 2 and 3).

Lewatit OC A062 and Dianex HP 20

Both Lewatit OC A062 and Dianex HP 20 are macroporous and macroreticular polystyrene divinylbenzene. Lewatit OC A062 has the following properties: 40 mesh size, 110-Å pore size, and 500-m²/g surface area. Dianex HP 20 has a mesh size of 20 to 50 and a surface area of 511 m²/g. These two macroporous resins are prepared differently from the polystyrene divinylbenzene XAD-2, -4, and -16 series described below.⁷ The resin synthesis involves copolymerization of styrene and divinylbenzene in the presence of an inert polymer. When the polymerization is complete, the occluded polymer is extracted, resulting in a resin with a uniform pore-size distribution. Macroreticular resins have a definitive and permanent internal porous structure that can absorb significant quantities of solvent, filling the available void space. Comparison of the Nd extraction results for these resins over the XAD series suggests that macroporous and macroreticular resins may adsorb more CMP, resulting in enhanced adsorption for Nd.

Duolite S-761

The physical properties of Duolite S-761 resin are as follows: 16 to 50 mesh size, 600-Å pore size, and 300-m²/g surface area. The phenolic composition of this resin would make it intermediate in polarity between the polar acrylic XAD-7 and the apolar styrene XAD-2, -4, and -16 series adsorbents. Accordingly, the effect of this composition is reflected in Table 1, where the overall performance falls between those of the acrylic and the styrene resins.

Amberlite IRC-50S

Amberlite IRC-50S, a weakly acidic, macroporous, cation-exchange resin is prepared from methacrylic acid and divinylbenzene. The carboxylic functionality has an affinity for basic compounds, hence the adsorption for CMP. As observed in Tables 2 and 3, its Nd extraction ability in 4.0 M and 7.0 M HNO₃ was lower than that of IRC-76, which is the strictly hydrophilic cation-exchange resin (with hydrophilic cross links) composed of a polyacrylic ester matrix. Amberlite IRC-50S, however, outperformed the nonfunctionalized polystyrene divinylbenzene series XAD-2, -4, and -16 in Nd extraction and, more significantly, in its efficient stripping ability.

SM-2 and XAD-2, -4, and -16

The SM-2 and XAD-2, -4, and -16 resins are all polystyrene divinylbenzene in composition. The SM-2 resin is exactly the same as the XAD-2 resin in physical structure: 20 to 60 mesh, 90-Å pore size, and 300-m²/g surface area. The SM-2 resin, however, outperforms the XAD-2 resin, most likely for the same reason that SM-7 outperforms XAD-7. The superior performance of SM-2 and SM-7 is attributed to the cleaning of surface residue left over from the polymerization. As indicated in Table 1, XAD-16 performs better than XAD-4, which performs better than XAD-2. This performance order corresponds to increases in respective surface areas: XAD-16, -4, and -2 have surface areas of 800, 725, and 300 m²/g, respectively.

Amberlite IRC-718

Amberlite IRC-718 is a cation-exchange resin with iminodiacetic acid functionality bonded to a styrene divinylbenzene matrix. This resin has high affinity for heavy-metal ions at pH greater than 1.5. However, in most cases, the resin's capacity for metal ions falls off sharply at low pH. The adsorption of CMP and the concomitant extraction of Nd onto IRC-718 may be small because of the hydrophobic matrix. As with the other carboxylic functionalities, the Nd stripping ability is relatively high compared with that of nonfunctionalized or aminophosphonic-functionalized resins.

CONCLUSIONS

Hydrophilic and polar resins coated with CMP exhibited the best extraction behavior for Nd. Biobeads SM-2 and SM-7 showed that resins that are extensively washed free of residual monomer and solvent before CMP coating outperform their unwashed counterparts XAD-2 and XAD-7 obtained from Rohm and Haas. Although hydrophobic polystyrene divinylbenzene nonfunctionalized adsorbents do not perform nearly as well as hydrophilic resins, when compared with each other, the more macroporous and higher-surface-area polystyrene-based resin performed better. Duolite C-467, a polystyrene-based resin with aminophosphonic functional groups, extracted Nd well by itself and showed no enhanced Nd extraction with CMP coating. Duolite C-467 is such a strong complexant, however, that its Nd-stripping ability is very poor. Aurorez PBI, a microporous resin prepared from a hydrophilic, linear aromatic polymer performed the best when coated with CMP. As an acid- and radiation-resistant polymer, PBI is well suited for its use in actinide recovery operations. Because PBI has two secondary nitrogens, which can become functionalized, it may be developed into an exceptional resin bearing covalently bound, actinide-specific extractants. Work is currently being pursued in this area, with the attachment of malonamide extractants to PBI.

ACKNOWLEDGMENTS

The author gratefully acknowledges the contributions of Harry Bush and A. James Gray.

REFERENCES

1. S. L. Yarbrow, S. L. Dunn, and S. B. Shreiber, "Processing Low Level Radioactive Solutions using Extraction Chromatography," 1989 AIChE Annual Meeting, San Francisco, California, 1989.
2. M. Hemmes and J. R. Parrish, "Extraction Chromatography of Copper by LIX-64N and LIX-65N Supported on the Macroporous Resin, XAD-7," *Analytica Chimica Acta* **94**, 307 (1977).
3. M. Yamamoto, K. Komura, and N. Sakanoue, "A Simple Sequential Separation Method of Pu and Am by Anion Exchange and Extraction Chromatography," *Radiochimica Acta* **29**, 205 (1981).
4. J. D. Navratil, "Removal of Solubilized Solvent Extractants from Aqueous Waste Streams," *J. Nuc. Sci. and Tech.* **18**(7), 561 (1981).
5. A. Buckley, D. E. Stuetz, and G. A. Serad, "Polybenzimidazoles," *Encyclopedia of Polym. Sci. and Eng.*, Vol. 11, p. 572, (John Wiley & Sons, Inc., New York, 1988).
6. M. Chanda, K. F. O'Driscoll, and G. L. Rempel, "Sorption of Phenolics and Carboxylic Acids on Polybenzimidazole," *Reactive Polymers* **4**, 39 (1985).
7. J. Ungar, Dianex Systems, personal communication, November 1990.

END

**DATE
FILMED**

4 / 20 / 93