

SELECTIVE EXTRACTION OF LANTHANIDES AND ACTINIDES BY MAGNETIC SILICA PARTICLES WITH CMPO-MODIFIED CALIX[4]ARENES ON THE SURFACE

C. Grüttner¹, S. Rudershausen¹, S.E. Matthews², P. Wang², V.Böhmer², & J.-F.Dozol³

¹ *micromod Partikeltechnologie* GmbH, Friedrich-Barnewitz-Str.4, D-18119 Rostock, Germany

² Fachbereich Chemie und Pharmazie, Johannes-Gutenberg-Universität, Duesbergweg 10-14, Mainz, D-55099, Germany

³ CEA Cadarache, DCC/DESD/SEP/LPTE, St. Paul lez Durance, F-13108, France

INTRODUCTION:

The recovery of lanthanides and actinides from high level nuclear waste is an area of world-wide concern. Current approaches are based on the TRUEX process which utilizes the highly efficient, neutral, organophosphorous ligand; octyl phenyl *N,N*-diisobutyl carbamoylmethyl phosphine oxide (CMPO).¹ Previously, we have reported on calix[4]arene based extractants which incorporate CMPO moieties at the wide² or narrow rim. Such pre-organisation of the chelating ligands leads to a 100 fold increase² in extraction efficiency combined with an enhanced selectivity for actinides and lighter lanthanides.

Solvent extraction methods using either simple or calix[4]arene-based systems, despite being highly efficient, do not lead to a marked decrease in waste volume. Recent interest has been focused on the use of magnetic fluidised bed separation technology and the development of magnetically assisted chemical separation (MACS) systems for nuclear waste remediation. These combine the selectivity of a solvent exchange ligand system with improved separation, resulting in a system that can be used at low concentrations and provides only a small volume of high level waste. The magnetic particles can then be stripped, to enable re-use, or vitrified. Adsorption of CMPO to magnetic acrylicamide particles enhances extraction of americium and plutonium through a synergistic relationship between the extractant and magnetic particle.³

Here we report on magnetic silica particles with covalently attached CMPO derivatives on the surface, which allow for the evaluation of the pre-organisation effect of chelating ligands through direct comparison of calixarene and single ligand CMPO derivatives.

METHODS: As previously reported⁴ non-porous magnetic silica particles with a diameter of 6 μm and carboxylic acid functionalities on the surface were modified by covalent attachment of suitably amine derivatised ligands. The simple ligand (1) was easily synthesised by mono acylation of 1,7-

diaminoheptane with *p*-nitrophenyl(diphenylphosphoryl)acetate.² In contrast, a calix[4]arene-based system⁴ (2) was designed to allow chelation at the wide rim and attachment *via* a two-point interaction at the narrow rim (Figure 1).

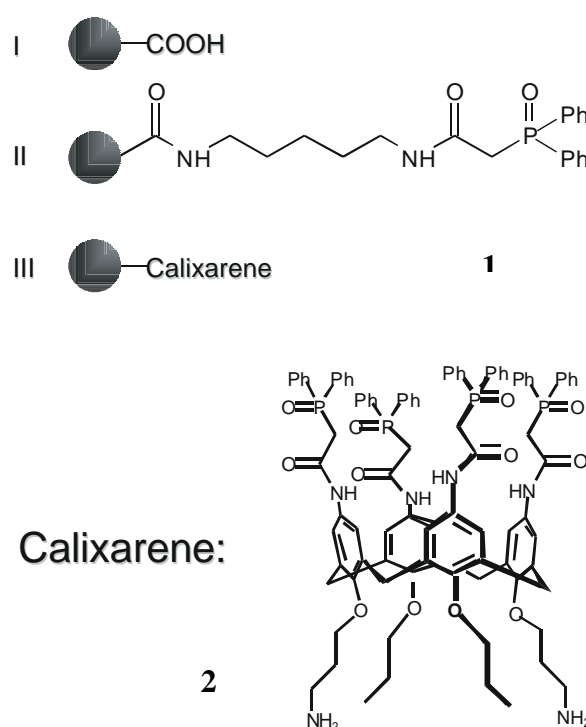


Fig. 1: Immobilization of the CMPO-derivative (1) and the CMPO-calix[4]arene (2) on the surface of non-porous magnetic silica particles (I).

The carboxylic acid groups of the particles were first activated by treatment with DCC, then washed by magnetic separation before being treated with the amino CMPO derivatives (1) and (2). The concentration of carboxylic acid groups (50 $\mu\text{mol/g}$) on the surface of the particles was determined by polyelectrolyte titrations. A 50 $\mu\text{mol/g}$ concentration of CMPO ligands on the surface was achieved through stoichiometric treatment of the particles with either 50 $\mu\text{mol/g}$ of (1) or 12.5 $\mu\text{mol/g}$ of (2).

Highly porous magnetic silica particles with a diameter of 100 μm have a larger area for the immobilization of chelators per g of particles than corresponding non-porous particles. The density of functional groups on the surface of porous magnetic silica particles increases to about 800 μmol per g of particles in comparison to about 50 μmol per g of non-porous particles. The calix[4]-arenes (**3**) and (**4**) were covalently attached on the surface of highly porous magnetic silica particles to study the influence of the effective area for chelator binding on the surface of magnetic particles (Figure 2).

Furthermore, the very important influence of the spacer length between the calixarene moiety and the particle surface was studied. This spacer length increases from three carbon atoms in calixarene (**2**) to 5 in calixarene (**3**) and to 10 carbon atoms in (**4**).

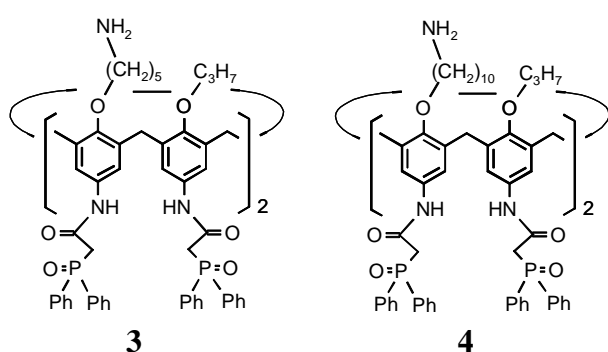


Fig. 2: CMPO-calix[4]arenes (**3**) and (**4**)

Solid-liquid extraction experiments were performed under conditions that simulate European nuclear waste streams (4M NaNO_3 , 1M HNO_3). Separation of europium or americium as representatives of the early lanthanides and actinides, was initially evaluated. γ -Ray spectroscopic measurements of the initial nuclide activity in the aqueous phase and the activity after shaking with the particles were used to calculate the percentage extraction.

The covalent binding of the CMPO-calix[4]arenes (**3**) and (**4**) on the surface of the porous magnetic silica particles was followed by spectrophotometric determination of the decrease of the calix[4]arene concentration in the supernatant after magnetic separation of the particles. In contrast to the high density of functional binding sites on the particle surface of about 800 μmol per g of particle, a calix[4]arene binding capacity of about 25 μmol per g of particles was obtained. This is due to the corresponding space requirement of the large calix[4]arene molecules.

Solid-liquid extraction experiments were carried out to determine the percentage extraction and

distribution coefficients K_D of europium and americium separation with the highly porous magnetic silica particles. The porous particles (**IV**) have the CMPO-calix[4]arene (**3**) on the surface, and the particles (**V**) the CMPO-calix[4]arene (**4**). For comparison of different solid-liquid extraction experiments, the volume of the aqueous phase and the mass of particles were included in the calculation of the distribution coefficient K_D .

The porous magnetic silica particles with the highest percentage extraction (**IV**) of europium were used to study the possibility of recycling the magnetic particles by back extraction of the europium from the particle surface. Therefore 5 mg of magnetic particles (**IV**) were incubated for one hour with 5 ml europium nitrate solution (10^{-4} mol/l, 1 mol/l HNO_3). After magnetic separation the supernatant was removed and stored. The particles were incubated for 30 min with HEDPA solution (1-hydroxyethane-1,1-diphosphonic acid, 10^{-3} mol/l). Then the particles were washed with water for three times and again incubated with 5 ml europium nitrate solution (10^{-4} mol/l, 1 mol/l HNO_3) for one hour. The complexation – back extraction – washing cycle was repeated for three times. The europium concentration remaining in the supernatants after the complexation process was monitored spectrophotometrically using Arsenazo III as reagent (Figure 3).

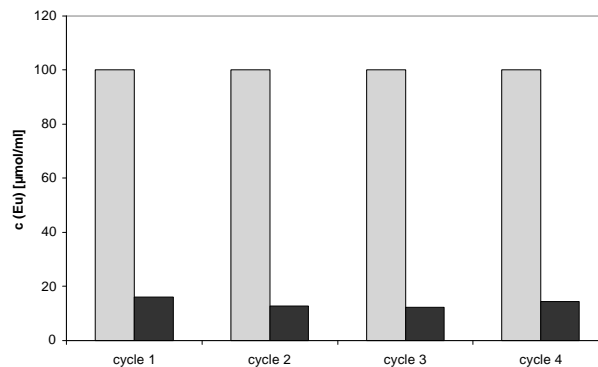


Fig. 3: Complexation of europium cations on the surface of porous magnetic silica particles with CMPO-calix[4]arene (**4**) on the surface. The initial europium concentration in each cycle is 100 $\mu\text{mol/l}$ (light columns). The europium concentration in the supernatant after incubation with particles (cycle 1), after complexation – back extraction – complexation (cycle 2) etc. is shown as dark columns.

RESULTS: Attachment of the simple CMPO ligand (**I**) directly onto the surface of magnetic particles (**II**) enables extraction of europium and americium albeit at a low level. However, with the calix[4]arene(**2**)-based particles (**III**) there is significant enhancement in extraction, with a preference for americium (Table 1) as previously seen with non-particulate calixarene systems.² Comparable partition coefficients for europium extraction to the chemically sorbed systems are obtained. However, larger K_D values per mass of ligating function are found for americium. Thus covalently bound ligand particles show greatly enhanced extraction of americium over europium and offer the potential of selective extraction systems. Interestingly, preliminary results on the extraction of ^{139}Ce are in marked contrast to those found previously for the flexible wide rim CMPO-calix[4]arenes. The minimal extraction of cerium, by CMPO-calix[4]arenes, has been rationalised by the oxidation of Ce^{3+} to the smaller radius Ce^{4+} in the extremely acidic conditions used. However, with the solid-liquid extraction conditions reported here, 90% extraction of cerium is achieved within 19 hours of shaking, offering an opportunity for effective and selective separation.

Table 1. Percentage extraction (%E) of lanthanides and actinides by CMPO and CMPO-calix[4]arene non-porous magnetic silica particles after 19 h shaking (**I-III**, figure 1). ($\%E = 100(A_0 - A) / A_0$ where A_0 and A symbolise the initial and final activity of the aqueous phase)

Magnetic particles	% E		
	^{152}Eu	^{241}Am	^{139}Ce
I	4	0	9
II	2	1	9
III	78	82	92

The highly porous magnetic silica particles have a higher density of CMPO-calix[4]arenes (**3**) or (**4**) on their surface (25 μmol per g of particles) than the non-porous particles (12.5 μmol / g). The percentage extraction of europium and americium with particles (**IV**) and (**V**) demonstrates the very high separation level for both cations in connection with a high selectivity for americium over europium (Table 2). The distribution coefficients K_D for

europium and americium are dependent on the length of the spacer between the particle surface and the calixarene moiety. A prolongation of the spacer length from 3 to 10 carbon atoms decreases the K_D values for both cations (Table 3).

Table 2. Percentage extraction (%E) of lanthanides and actinides by CMPO-calix[4]arene porous magnetic silica particles after 1 h shaking.

Magnetic particles	^{152}Eu	^{241}Am
IV	80	90
V	63	80

Table 3. Distribution coefficients for lanthanides and actinides by CMPO-calix[4]arene magnetic silica particles (**III-V**). ($KD = 100(A_0 - A) \times V / A \times m$ where A_0 and A symbolise the initial and final activity of the aqueous phase, V the volume of aqueous phase and m the mass of magnetic particles).

Magnetic Particles	K_D [ml / g]	
	^{152}Eu	^{241}Am
III (nonporous)	261	335
IV (porous)	129	310
V (porous)	57	132

The possibility of re-using the magnetic particles after the primary cation separation is very important for the cost reduction of a magnetic particle based separation process of lanthanides and actinides.

The back extraction experiment of europium from magnetic particles (**IV**) with HEDPA has shown that there is no significant loss of separation capacity for europium after stripping (Figure 3). This enables the re-use of the CMPO-calix[4]arene modified magnetic silica particles.

DISCUSSION & CONCLUSIONS: The importance of pre-organisation of chelating ligands onto a calix[4]arene scaffold was demonstrated by

experiments on magnetic particles (Table 1 and 2). We have developed a magnetic particle based process which applies a pre-organized calix[4]arene-CMPO ligand covalently attached on the particle surface. Efficient extraction of americium and europium from simulated nuclear waste conditions has been achieved together with surprisingly high levels of cerium extraction.

Highly porous magnetic silica particles allow for a higher density of CMPO-calix[4]arenes than do corresponding non-porous particles. In combination with the optimal spacer length between the particle surface and the calixarene moiety, the extraction properties of these particles can be further increased. Initial studies have shown that spacer lengths of 3 to 5 carbon atoms lead to a more effective extraction of europium and americium than the highly flexible C10 spacer. This can be explained by additional intermolecular interactions between the CMPO units of neighboring calixarenes. But the increasing spacer length to C5 and C10 results in an increasing selectivity of the particles for americium over europium (K_D (Am) / K_D (Eu)) from 1.28 for the C3 spacer to 2.3 – 2.4 for the longer C5 and C10 spacers. This higher selectivity is due to the complex formation of europium or americium cations with CMPO units from single calixarenes. Thus the optimal spacer length for calixarene attachment on a particle surface must prevent interactions between the CMPO units of different calixarenes for a complete exploitation of the pre-organisation effect of chelating CMPO ligands onto a calix[4]arene scaffold. This is the crucial factor for a high complexation capacity and selectivity of cation binding.

The possibility of recycling the magnetic particles was demonstrated by back extraction of europium from the particle surface. The complexation capacity of the particles did not change within four complexation – back extraction cycles. This allows for the use of magnetic particles with CMPO-calix[4]arenes on the surface in industrial applications.

REFERENCES: ¹ E. P. Horwitz, D. G. Kalina, H. Diamond, D. G. Vandegrift, W. W. Schultz (1985) *Solv Extr Ion Exch* 75:3. ² F. Arnaud-Neu, V. Böhmer, J-F. Dozol, C. Grüttner, R. A. Jakobi, D. Kraft, O. Mauprivez, H. Rouquette, M-J. Schwing-Weill, N. Simon, W. Vogt (1996) *J Chem Soc, Perkin Trans 2*: 1175-1182. ³ L. Nuñez, B. A. Buchholz, G. F. Vandegrift (1995) *Sep. Sci. Tech.*

30, 1455-1471. ⁴ S. E. Matthews, P. Parzuchowski, A. Garcia-Carrera, C. Grüttner, J-F. Dozol, V. Böhmer (2001) *Chem Commun*: 417-418.

ACKNOWLEDGEMENTS: This work is financially supported by the European Commission in the framework of the research program “Selective extraction of minor actinides from high activity liquid waste by organized matrices”, CONTRACT N° FIKW-CT2000-00088.