Available online at www.sciencedirect.com
ScienceDirect
C. R. Chimie 10 (2007) 1001–1009
COMPTES RENDUS CHIMIE
http://france.elsevier.com/direct/CRAS2C/

Full paper / Mémoire

# Extraction of plutonium and americium using silica hybrid materials

Daniel J.M. Meyer [a,*], Stéphane Bourg [b], Olivier Conocar [b], Jean-Charles Broudic [b], Joël J.E. Moreau [c], Michel Wong Chi Man [c]

[a] *Institut de chimie séparative de Marcoule, UMR 5257, BP 17171, 30207 Bagnols-sur-Cèze, France*
[b] *CEA–DEN/DRCP/SSCPS, BP 17171, 30207 Bagnols-sur-Cèze, France*
[c] *Laboratoire "Architectures moléculaires et matériaux nanostructurés", UMR 5253, CNRS–ENSCM–UMII–UMI, Institut Charles-Gerhardt de Montpellier, École nationale supérieure de chimie de Montpellier, 8, rue de l'École-Normale, 34296 Montpellier cedex 5, France*

Received 7 November 2006; accepted after revision 23 April 2007
Available online 20 June 2007

**Abstract**

These studies are related to the development of an innovative solution for the extraction of transuranium elements from high radioactive level acid solutions. In this frame, advanced silica hybrid materials were developed by hydrolysis and condensation of molecular species functionalised with complexing functions, leading to the improvement of solid–liquid extraction techniques.

The influence of the nature of the complexing organic groups, of the microstructure and of the extractant loading in the condensed matter on the distribution coefficient is determined in the case of americium and plutonium extractions from nitric acid media. Preliminary studies on the americium–europium separation using these materials were also tackled. ***To cite this article: Daniel J.M. Meyer et al., C. R. Chimie 10 (2007).***
© 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

**Résumé**

Ces études se placent dans le contexte du développement de solutions innovantes pour l'extraction d'éléments transuraniens de solutions d'acide nitrique fortement radioactive. Ainsi, des matériaux avancés, de type silices hybrides, obtenus par hydrolyse puis condensation d'espèces moléculaires contenant des fonctions complexantes, ont été développés afin d'améliorer les techniques d'extraction par voie solide–liquide.

L'influence de la nature du groupe extractant, de la microstructure et de la concentration en fonction complexante dans le solide sur le coefficient de partage solide–liquide a été déterminée dans le cas de l'extraction de l'américium et du plutonium d'une solution d'acide nitrique. Des essais préliminaires portant sur la séparation américium–europium par ces matériaux a également ont été abordés. ***Pour citer cet article : Daniel J.M. Meyer et al., C. R. Chimie 10 (2007).***
© 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

* Corresponding author.
*E-mail address:* daniel.meyer@cea.fr (D.J.M. Meyer).

1631-0748/$ - see front matter © 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.crci.2007.04.013

*Keywords:* Actinides; Extraction; Hybrid material; Sol–gel; Silica

*Mots-clés :* Actinides ; Extraction ; Matériau hybride ; Sol-gel ; Silice

## 1. Introduction

The nuclear industry and the progress in the related research and development programs produces high-level liquid wastes containing radionuclides such as actinides and fission products, causing long-term storage problems. One interesting treatment route to solve the actinide question consists in implementing a solid–liquid extraction step followed by an actinide recovery stage or an actinide immobilisation stage (Fig. 1). In this frame, hybrid silica gels obtained by sol–gel techniques [1] under mild conditions are suitable candidates as solid extractants.

This versatile synthetic approach allows us to take advantage of molecular engineering to modify the silica skeleton by introducing organic functions (such as ligands or extractants) and structural blocks during the synthesis to control the overall reactivity, the texture and the structure of the hybrid material [2]. By this way a wide variety of materials can be produced according to the intrinsic properties of the organic function [2a,j,k]. The incorporation of functionalised ligands opens interesting possibilities for metal complexation or extraction [3].

The mild conditions of the sol–gel approach also allow the tuning of the material properties by the loading of the complexing moieties. Finally, imprinting techniques can also be used in this frame for overall structure–properties relation adjustments [2g,3d,4]. In such a way, actinide extraction as well as catalyst support enhancement has been described [3d,e,5].

In this work we report the synthesis of polyamine-polyether- and pyridine-functionalised hybrid silica materials and their extraction properties for plutonium and americium from nitric acid solutions, with highlights on the influence of the chemical pattern, the textural aspects and the extractant loading on the extraction properties.

The synthetic route leading to the materials consists of the hydrolysis and the condensation between $Si(OEt)_4$ and the functionalised $LSi(OEt)_n$ (Fig. 2) where the organic functions L (Fig. 3) were chosen for their ability to complex several metallic cations [6].

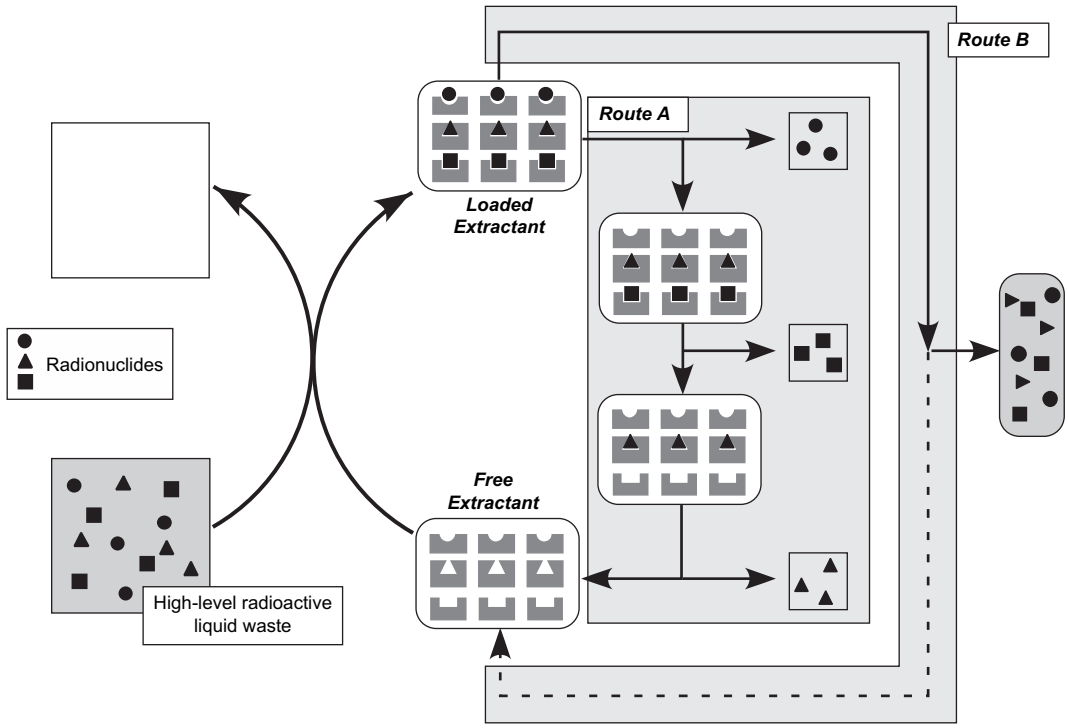



Fig. 1. HLLW Treatment: route A leads to a radionuclide recycling, while route B leads to the confinement of the radionuclide in a solid matrix with possible recycling of the solid extractant.

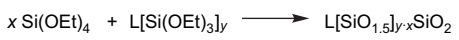



Fig. 2. Hybrid silica synthetic route.

All the materials obtained by this technique are given in Table 1.

A first series of solid–liquid extraction tests were done to establish the best organic function for the actinide extraction, then further studies on the most efficient remaining best-functionalised material were carried out to determine the importance of the loading and the insertion mode of the coordinating organic function on the extraction of Am(III), Pu(IV) and Eu(III) from nitric acid solutions.

## 2. Results and discussions

These studies are essentially focused on the determination of the distribution coefficients for selected functionalised hybrid materials and will be discussed on a qualitative level.

Owing to the nature of the americium and plutonium species in nitric acid media [7] and the basic nature of the ligands, in particular the amine and the pyridine group, the extraction studies were performed over a large range of nitric acid concentration, usually [$HNO_3$] varying from $10^{-3}$ M up to 4 or 6 M. In these operating conditions, americium will be found in oxidation state (III) and plutonium in oxidation state (IV).

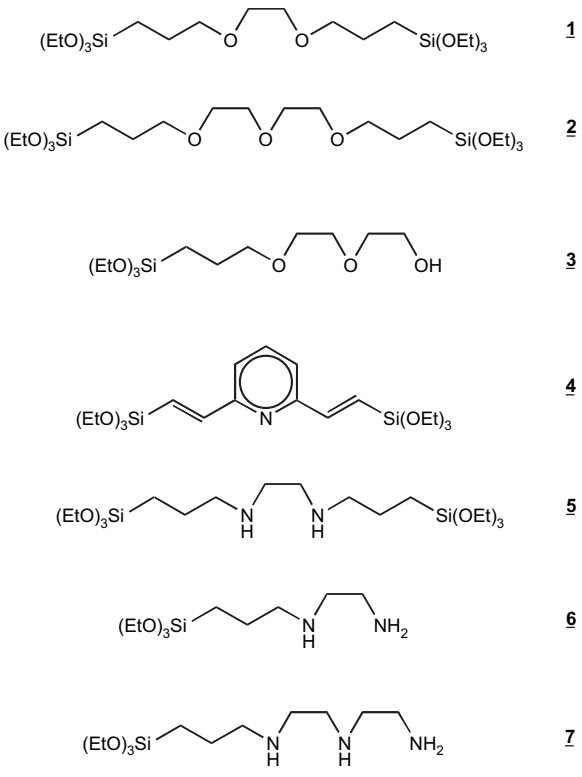



Fig. 3. Triethoxysilylated ligands used to build hybrid silicas.

### 2.1. Preliminary scanning for Am(III) extraction

Preliminary experiments were performed to determine the distribution coefficient for a first series of hybrid materials functionalised with polyether, pyridine and diaminoethylene groups with 0.018 M nitric acid solution. The results show that only some diaminoethylene gels extract americium with $K_d$(Am) values ranging from some hundreds to some thousands mL/g (Table 2a).

Polyether and pyridine, usually known for their complexing properties for several metals at low acidity do not extract americium in our conditions. The low $K_d$(Am) values usually point out a very low affinity of the functionalised material for the americium. The structural organisation of the potential complexing sites inside the condensed matter is not favourable to the coordination of the americium species, despite a high number of coordination functions introduced in the silica skeleton, such as in gel **G4a**. The source of this inefficient organisation of the extractant sites in the polyether and pyridine hybrid materials is probably due to an inadequate self-assembling of the functionalised precursor in the solution during the condensation process, producing a negative template effect leading to non-coordinating sites for americium.

Americium distribution coefficient measurements for gels **G1a–G4c** over a range of nitric acid concentration from 0.018 M to 1 M show no significant changes in the extraction behaviour (Table 2b).

These observations show clearly that the change of the speciation for americium does not affect the magnitudes of the distribution coefficients. In any case, this means that americium will be never coordinated.

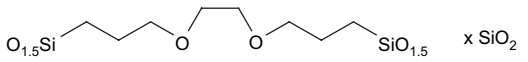
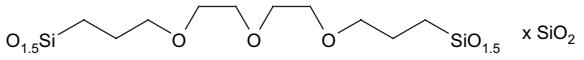
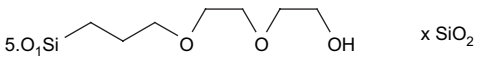
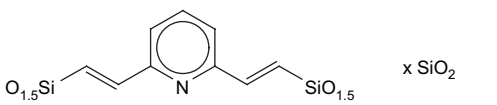
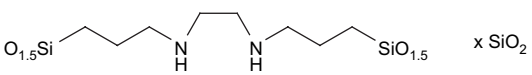
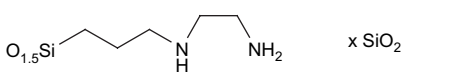
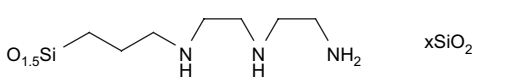
Further studies were essentially carried out on polyamine-functionalised hybrid materials to determine the influence of structural and extractant loading aspects on the extraction properties of americium and plutonium.

### 2.2. Am(III) extraction by polyamines

#### 2.2.1. Influence of the polyamine pattern

Gels **G6b** and **G7d** show very high coefficient distribution, respectively, around $3 \times 10^5$ mL/g and $7 \times 10^4$ mL/g, for a nitric acid concentration less than 0.01 M (Fig. 4). This value drops drastically to less than 10 mL/g for [$HNO_3$] higher than 0.1 M.

Table 1
Synthesised hybrid materials

| Hybrid silica material | *X* | Gel reference |
|---|---|---|
|  | 5<br>10 | **G1a**<br>**G1b** |
|  | 5<br>10 | **G2a**<br>**G2b** |
|  | 10 | **G3** |
|  | 0<br>5<br>10 | **G4a**<br>**G4b**<br>**G4c** |
|  | 0<br>5<br>10 | **G5a**<br>**G5b**<br>**G5c** |
|  | 2<br>5<br>10 | **G6a**<br>**G6b**<br>**G6c** |
|  | 2<br>3<br>4<br>5<br>6<br>10 | **G7a**<br>**G7b**<br>**G7c**<br>**G7d**<br>**G7e**<br>**G7f** |

$X = Si(OEt)_4/Si(OR)_3L$ initial ratio during synthesis.

The same behaviour is observed for gel **G5a** with much lower $K_d$ values. This type of results is usually observed in the case of a typical metallic complexation behaviour. In fact, at low acidity, the non-protonated amino functions are able to coordinate the americium core with high affinity, leading to a high value of the distribution coefficient. At higher $[HNO_3]$ concentration, the competitive extraction of $H^+$ by the amino group as well as the complexation of the Am(III) cation by the nitrate anion in the solution, is more efficient than the complexation of the Am(III) by diaminoethylene moieties, decreasing the distribution coefficients.

Table 2a
Results of preliminary Am(III) distribution coefficient scanning for different functionalised hybrid materials; $[HNO_3] = 0.018$ M

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Polyether | Gel | **G1a** | **G1b** | **G2a** | **G2b** | **G3** | |
| | $K_d$ (mL/g) | 1.1 | 1.8 | 0.8 | 1.6 | 2.7 | |
| Pyridine | Gel | **G4a** | **G4b** | **G4c** | | | |
| | $K_d$ (mL/g) | 2.0 | 0.9 | 2 | | | |
| Polyamine | Gel | **G5a** | **G5b** | **G6b** | **G6c** | **G7d** | **G7f** |
| | $K_d$ (mL/g) | **338** | 3.3 | **2822** | 2.3 | **2226** | 0.9 |

It means that Am(III) is extracted as neutral complex. Preliminary comparative EXAFS studies on $Nd(NO_3)_3 \cdot 6H_2O$ and $Nd(NO_3)_3$(ethylenediamine) extracted by the gels **G5a**, **G6b**, **G6c**, **G7a** and **G7b**[1] and the speciation of americium in this nitric acid range let us expect that for the extracted complex, one nitrate remains probably in the first coordination sphere, while hydroxide ligands guarantee neutrality and the ethylenediamine pattern coordinate as chelate Am(III). The fact that the gels **G5a** and **G6b** show high $K_d$(Am) means that the ethylenediamine pattern is sufficient for extraction of Am(III) compared with the triaminodiethylene moiety. No significant differences are observed between

[1] Unpublished work under progress.

Table 2b
Distribution coefficient $K_d$ (mL/g) for Am(III) extraction from nitric acid for polyether (**G1a–G3**) and pyridine (**G4a–c**) functionalised materials

| $[HNO_3]$ (M) | Polyether | | | | | Pyridine | | |
|---|---|---|---|---|---|---|---|---|
| | **G1a** | **G1b** | **G2a** | **G2b** | **G3** | **G4a** | **G4b** | **G4c** |
| 0.0188 | 1.1 | 1.8 | 0.8 | 1.6 | 2.7 | 2.0 | 0.9 | 2.0 |
| 0.05 | 1.2 | 2.3 | 1.1 | 1.8 | 1.8 | 2.2 | 2.8 | 2.4 |
| 0.075 | 1.1 | 1.8 | 0.3 | 1.9 | 1.9 | 1.8 | 1.3 | 2.6 |
| 0.1 | 1.7 | 1.2 | 0.8 | 1.4 | 1.4 | 1.8 | 1.6 | 2.3 |
| 0.5 | 1.3 | 1.1 | 1.1 | 1.3 | 1.3 | 1.5 | 1.7 | 2.4 |
| 1 | 1.2 | 1.2 | 0.9 | 1.6 | 1.6 | 1.8 | 1.3 | 2.8 |

hybrids **G6b** and **G7d**. The low $K_d$(Am) for gel **G5a** compared with hybrids **G6b** and **G7d** lets us assume that the complexing pattern needs to be cleared of some conformational restrictions for efficient extraction. In gel **G5a**, the doubly bonded ligand to the silica skeleton is probably too structurally constrained for effective coordination showing lower affinity for Am(III), while in the case of the **G6b** and **G7d** prepared from the monosilylated diamino and triamino ligands, these pendant ligands are more flexible in the hybrid material.

### 2.2.2. *Influence of the ligand loadings*

The influence of the extractant loading on the americium distribution coefficient from dilute nitric acid media was studied for the free diaminoethylene-functionalised hybrid materials **G6a–c**, **G7a** and **G7c–f** (Fig. 5).

In these experiments, the initial ratio between the functionalised molecular precursor, $LSi(OEt)_3$, and the tetraethoxysilane $Si(OEt)_4$ is modulated, producing hybrid silica gels with varying extractant loading with Si/L from 3 to 11.

The measurement of the $K_d$(Am) shows high values for hybrids **G6b**, **G7c**, **G7d** and **G7e**. This corresponds

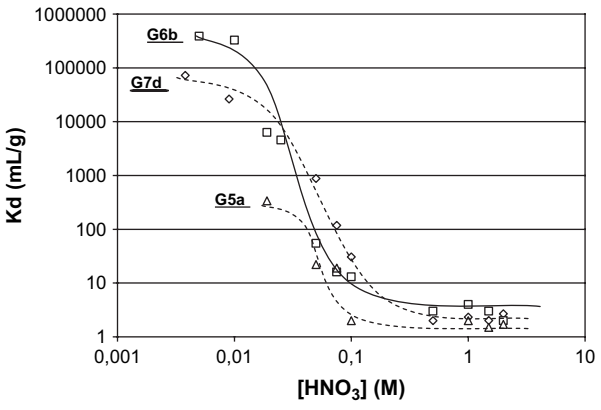



Fig. 4. $K_d$(Am) for gels **G5a**, **G6b** and **G7d** for $[HNO_3]$ ranging from 0.0038 M to 2 M.

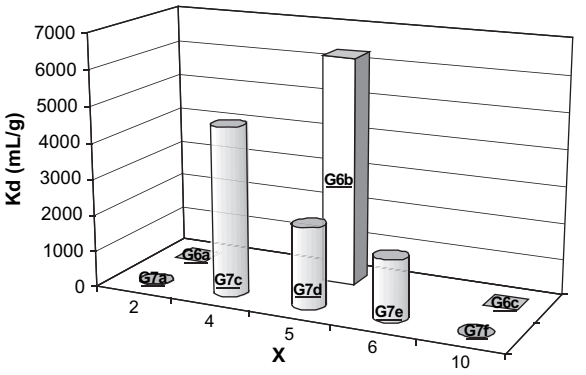



Fig. 5. Effect of the extractant loading on the Am(III) distribution coefficient. $X$ is the ratio $Si(OEt)_4/Si(OEt)_3L$/expected after synthesis. $[HNO_3] = 0.018$ M.

to the gel with observed Si/L ratios of 5, 6 and 7. A low $K_d$(Am) value for the high Si/L ratio is somewhere expected owing to the dilution of the extraction function during the condensation process in the material, although a value around 2 is a surprisingly very low value. Also for the material with a high extractant loading such as hybrids **G6a** and **G7a**, the $K_d$(Am) value is less than 3.

These strong differences for the $K_d$(Am) values are usually characteristic of a strong affinity variation for the americium. The structural organisation of the complexing site inside the materials will be probably at the origin of this observation. The structure of the site in the final material is greatly dependent on the organisation in solution of the molecular silicon species during the condensation process as well as the collapse process which occurs during the drying stage. Most likely, the heavy extractant loading materials **G6a** and **G7a** have a strong organic nature which will be easily reorganised during the drying period, leading to non-complexing sites, even when the high Si/L ratio for the light extractant loading **G6c** and **G7f** materials is favourable to a surrounding of the autoassembled organic function by a silica layer, shielding the complexing sites. The medium extractant loaded materials **G6b** and **G7c–e** will probably have a rigid enough mineral character avoiding a site collapse as well as a Si/L ratio capable of generating surface accessible complexing sites.

However, the measured textural parameters (pore mean diameter, pore volume and specific surface areas) show clearly no influence on the distribution coefficient for Am(III) (Table 3).

Hybrid **G5a** has a specific surface area of 3 $m^2/g$ with a $K_d$(Am) of 338 mL/g, whereas gels **G5b** and **G5b**, which are not able to extract Am, exhibit high specific surface areas, respectively, 382 $m^2/g$ and 287 $m^2/g$. For the gels **G6b** and **G7d**, the specific surface areas

Table 3
Pore volume ($V_p$), specific surface areas ($S$) and pore diameter ($Ø_p$) for diaminoethylene based hybrid materials by BET calculation and the $K_d$(Am) for $[HNO_3] = 0.018$ M

| Gel | $V_p$ (mL/g) | $S$ ($m^2$/g) | $Ø_p$ (Å) | $K_d$(Am) (mL/g) |
|---|---|---|---|---|
| **G5a** | – | 4 | – | 338 |
| **G5b** | 0.84 | 382 | 87 | 3.3 |
| **G5c** | 1.04 | 287 | 144[a] | 0.5 |
| **G6a** | – | 9.6 | – | 2.0 |
| **G6b** | 0.97 | 269 | 145 | 6291 |
| **G6c** | 1.32 | 354 | 148 | 2.3 |
| **G7a** | – | 9.2 | – | 3.1 |
| **G7d** | 0.39 | 110 | 142[a] | 2226 |
| **G7f** | 0.32 | 109 | 118 | 2.0 |

[a] macroporous.

are, respectively, 269 $m^2$/g and 110 $m^2$/g and the $K_d$(Am) of 6291 mL/g and 2226 mL/g. From the same family, the hybrids **G6c** and **G7f** have a specific surface area of the same order of magnitude, respectively, 353 $m^2$/g and 109 $m^2$/g with a $K_d$(Am) of 2.3 mL/g and 2.0 mL/g. It looks likely that the Si/L ratio plays an important role in the extracting properties of the solids.

### 2.3. Am(III) and Eu(III) concomitant extractions

Aiming Am(III)/Eu(III) separation, distribution coefficient measurements for these two elements were done for hybrid material **G7d**, which shows a good extraction behaviour for Am(III). A solution containing a mixture of Am(III) and Eu(III) (see Section 4) was used for all extraction experiments (Fig. 6).

Unfortunately, no significant differences for the distribution coefficient values were observed whichever the $HNO_3$ concentration may be. In these conditions the behaviour of both elements is identical, preventing an efficient separation. The material needs to be improved in order to increase the separation factor between Am and Eu. This can be envisaged by the use of template effects like the imprinting techniques using metal complexes, successfully undertaken for diamide hybrid material to increase not only the overall extraction performance, but also the separation factor between Eu, Nd and Am [3d].

### 2.4. Pu(IV) extraction by polyamines functionalised materials

The distribution coefficient for Pu(IV) in nitric acid for hybrid material **G7d** was measured to determine fundamental differences between two actinides, such as Pu(IV) and Am(III), showing different speciation along a nitric acid concentration range [7]. To avoid plutonium hydrolysis problems, the study has to be limited to a nitric acid concentration ranging from 0.5 M to 6 M.

For gel **G7d**, the plutonium experiments show a maximum distribution coefficient around 66 mL/g, which is very low compared with the americium experiments where the maximum distribution coefficient is between $10^4$ mL/g and $10^5$ mL/g (Fig. 7). This value of 66 mL/g is observed for $[HNO_3]$ from 4 M to 6 M. At these acidities, Pu(IV) nitrate species exist as $Pu(NO_3)_5^-$ and $Pu(NO_3)_6^{2-}$ anions, while the ethylenediamine functions form protonated cationic entities. Under these conditions, the extraction mechanism of Pu(IV) is certainly an anion exchange process. This is confirmed by the low $[HNO_3]$ back extraction conditions where Pu(IV) forms a neutral tetranitrate complex.

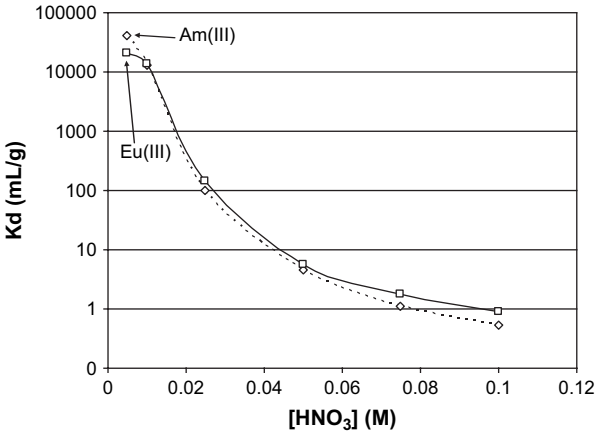



Fig. 6. Distribution coefficients of Am(III) and Eu(III) vs nitric acid concentration for gel **G7d**.

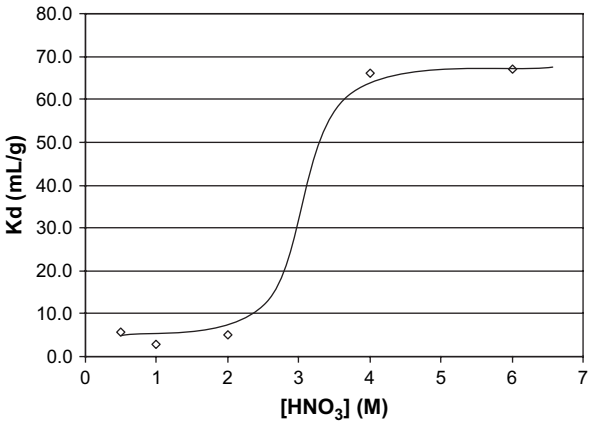



Fig. 7. Distribution coefficient for gel **G7d** for P(IV).

## 3. Conclusions

In this work it is shown that the synthesis of hybrid materials using sol–gel techniques is suitable to obtain high-performance solid material to extract americium from low-concentrated nitric acid solutions. A first tuning of the extraction properties can be done by the use of different chemical patterns and through the control of the extractant loading in the material. Extended control of the extraction behaviour can be considered by the use of molecular engineering such as template techniques.

We have also synthesised hybrid materials having two extraction mechanisms for two different actinides:

- metal complexation at low acidity for Am(III);
- anion exchange at high acidity for Pu(IV).

## 4. Experimental

All experiments related to the synthesis of the hybrid material were carried out under nitrogen atmosphere. Ethanol was dried by distillation over magnesium and under nitrogen atmosphere before use. All reagents and functionalised triethoxysilane (**1**–**7**) were available commercially from Gelest™ or Sigma-Aldrich™ and used without further purification.

$^{241}$Am, $^{152}$Eu and Pu were provided by CEA (France) and, after purification by chromatographic methods [8], starting solutions were prepared. The americium experiments were performed using a solution with [Am] = 0.0261 g/L and [$HNO_3$] = 0.037 M. The plutonium experiments were realised using a solution with [Pu] = 0.323 g/L and [$HNO_3$] = 0.111 M. For the americium–europium experiments, the $^{152}$Eu tracer was added to an Am/Eu solution with [Am] = 0.029 g/L, [Eu] = 0.016 g/L and [$HNO_3$] = 0.01 M.

Infrared spectra were recorded on a PerkinElmer FT 1000. Solid-state NMR was performed on a FTAM 300, with a $^{29}$Si frequency of 59.62 MHz, an acquisition delay of 10 s, a rotation speed of 5000 Hz and from 300 up to 18,000 scans. Chemical shifts $\delta$ were in ppm with TMS as internal reference. Specific surface, pore volume and mean pore diameter were determined by BET calculation after nitrogen adsorption–desorption measurements on a Micrometrics 2375 or a Coulter SA 3100 apparatus. Alpha activity was determined on a Camberra model 7401 and gamma counting was performed on a Cobra II counter, 59 keV for $^{241}$Am and 122 keV for $^{152}$Eu.

All batch distribution coefficient measurements' experiments were realised in 2-mL microtubes. A mixture of 1 mL of the metallic solution and 50–100 mg of hybrid material was shaken for 15 min. After filtration by centrifugation over a 45-μm filter, the filtrate was analysed by alpha or gamma counting. Before all extraction experiments, the material was contacted with a solution showing the same $HNO_3$ concentration.

In solid–liquid extraction, the distribution coefficient for a given metal ($K_d$) is defined as the ratio of the amount of the metal in the solid to the amount of the metal in the solution at equilibrium, if the amount of the extracting group in the solid is assumed to be constant. This is achieved by using initial concentrations of metal around 0.1% of the total amount of extracting group in the solid. The initial and final concentrations of metal in solution were determined by alpha counting for the Am and Pu experiments and gamma counting for the Am and Eu experiments. $K_d$ is given by the formula:

$$K_d(\mathrm{mL/g}) = \frac{(A_0 - A)}{A} \bullet \frac{v_{\mathrm{solution}}(\mathrm{mL})}{m_{\mathrm{gel}}(\mathrm{g})}$$

where $A_0$ and $A$ are the activities (alpha or gamma) of the solution before and after extraction. Usually from 3 up to 5 batch experiments were done for one $K_d$ measurement. Overall uncertainties on the values of the $K_d$'s less than 10,000 are estimated at less than 20% and come essentially from the dilution of the samples and the preparation of the samples (disk coating and heating) for alpha counting. For higher $K_d$ values, the residual amount of radionuclide in the filtrate is of the same order of magnitude as the background composition of the glove box, and uncertainties can reach 50%.

The hybrid silicas were obtained according to the same general procedure [3f]: in a Schlenck tube, the chosen precursor (from **1** to **7**) and $Si(OEt)_4$ are added (in the desired ratio) to dry ethanol, with a concentration of Si around 1 M. Under magnetic stirring, the corresponding amount of water is added (0.5 mole equivalent/mole of ethoxy group). The condensation process stars in less than 12 h. After an aging period of one week, the solid is dried under vacuum at 80 °C, washed with acetone and diethylether and dried again under vacuum at 80 °C for 24 h.

### *4.1. Selected experimental data for some polyamines functionalised materials*

#### *4.1.1. Hybrid **G5a***

White powder; IR (KBr, $cm^{-1}$): $\nu_{Si-O} = 1086$; $\nu_{C-H} = 2939$; NMR $^{29}$Si CP-MAS ($\delta$, ppm): −58.9 ($T_2$), −66.1 ($T_3$); BET $S = 4\ m^2/g$.

*4.1.2. Hybrid **G5b***

Yellow powder; IR (KBr, $cm^{-1}$): $\nu_{Si-O} = 1119$; $\nu_{C-H} = 2957$ and 2854; NMR $^{13}C$ CP-MAS ($\delta$, ppm): 9.5 ($CH_2Si$), 22.4 ($CH_2CH_2CH_2$), 50.4 ($CH_2N$); NMR $^{29}Si$ CP-MAS ($\delta$, ppm): −57.2 ($T^2$), −63.1 ($T_3$), −100.9 ($Q_3$), −108.3 ($Q_4$); BET $S = 382\ m^2/g$, $V_p = 0.84\ cm^3/g$, $\emptyset_p = 87$ Å.

*4.1.3. Hybrid **G5c***

White powder; IR (KBr, $cm^{-1}$): $\nu_{Si-O} = 1109$; $\nu_{C-H} = 2953$ and 2851; NMR $^{13}C$ CP-MAS ($\delta$, ppm): 9.5 ($CH_2Si$), 22.4 ($CH_2CH_2CH_2$), 48.9 ($CH_2N$); NMR $^{29}Si$ CP-MAS ($\delta$, ppm): −57.9 ($T^2$), −64.3 ($T_3$), −101.1 ($Q_3$), −108.4 ($Q_4$); BET $S = 287\ m^2/g$, $V_p = 1.04\ cm^3/g$, $\emptyset_p = 144$ Å.

*4.1.4. Hybrid **G6a***

White powder; IR (KBr, $cm^{-1}$): $\nu_{Si-O} = 1095$; $\nu_{C-H} = 2940$; NMR $^{29}Si$ CP-MAS ($\delta$, ppm): −65.8 ($T_3$), −101.3 ($Q_3$), −109.6 ($Q_4$); BET $S = 9.6\ m^2/g$.

*4.1.5. Hybrid **G6b***

White powder; IR (KBr, $cm^{-1}$): $\nu_{Si-O} = 1120$; NMR $^{13}C$ CP-MAS ($\delta$, ppm): 9.5 ($CH_2Si$), 21.4 ($CH_2CH_2CH_2$), 40.3 ($CH_2N$), 50.6 ($OCH_3$); NMR $^{29}Si$ CP-MAS ($\delta$, ppm): −66.4 ($T_3$), −101.4 ($Q_3$), −108.4 ($Q_4$); BET $S = 269\ m^2/g$, $V_p = 0.97\ cm^3/g$, $\emptyset_p = 145$ Å.

*4.1.6. $_3$Hybrid **G6c***

White powder; IR (KBr, $cm^{-1}$): $\nu_{Si-O} = 1115$; NMR $^{13}C$ CP-MAS ($\delta$, ppm): 9.5 ($CH_2Si$), 21.4 ($CH_2CH_2CH_2$), 50 ($CH_2N$); NMR $^{29}Si$ CP-MAS (δ, ppm): −64.0 ($T_3$), −101.0 ($Q_3$), −106.9 ($Q_4$); BET $S = 354\ m^2/g$, $V_p = 1.32\ cm^3/g$, $\emptyset_p = 148$ Å.

*4.1.7. Hybrid **G7a***

White powder; NMR $^{13}C$ CP-MAS ($\delta$, ppm): 8.9 ($CH_2Si$), 25.4 ($CH_2CH_2CH_2$), 49.4 ($CH_2N$); NMR $^{29}Si$ CP-MAS ($\delta$, ppm): −66.9 ($T_3$), −102.1 ($Q_3$), −110.7 ($Q_4$); BET $S = 9{,}2\ m^2/g$.

*4.1.8. Hybrid **G7b***

White powder; IR (KBr, $cm^{-1}$): $\nu_{Si-O} = 1054$; $\nu_{C-H} = 2948$; NMR $^{29}Si$ CP-MAS ($\delta$, ppm): −68.4 ($T_3$), −101.1 ($Q_3$), −109.6 ($Q_4$); BET $S = 98\ m^2/g$; $V_p = 0.25\ cm^3/g$, $\emptyset_p = 103$ Å.

## References


[1] (a) C.J. Brinker, G.W. Scherer, Sol–Gel Science, the Physics and Chemistry of Sol–Gel Processing, Academic Press, San Diego, CA, 1989;
(b) C.J. Brinker, G.W. Scherer, Sol–Gel Science, Academic Press, London, 1990;
(c) K.J. Shea, D.A. Loy, Chem. Mater. 13 (2001) 3306;
(d) G. Cerveau, R.J.P. Corriu, E. Framery, Chem. Mater. 13 (2001) 3373;
(e) K.J. Shea, J.J.E. Moreau, D.A. Loy, R.J.P. Corriu, B. Boury, in: P. Gomez-Romero, C. Sanchez (Eds.), Functional Hybrid Materials, Wiley, Weinheim, 2004, p. 50.

[2] (a) H. Schmidt, Mater. Res. Soc. Symp. Proc. 180 (1990) 961 and references therein;
(b) C. Sanchez, F. Ribot, New J. Chem. 18 (1994) 1007 and references therein;
(c) D.A. Loy, K.J. Shea, Chem. Rev. 95 (1995) 1431 and references therein;
(d) R.H. Baney, M. Itoh, A. Sakakibara, T. Suzuki, Chem. Rev. 95 (1995) 1409;
(e) R. Corriu, J.J.E. Moreau, P. Thépot, M. Wong Chi Man, Chem. Mater. 4 (1992) 1217;
(f) R. Corriu, D. Leclercq, Angew. Chem. Int. Ed. Engl. 35 (1996) 1420 and references therein;
(g) Special issue, in: C. Sanchez (Ed.), Functional Hybrid Materials, J. Mater. Chem. 15 (35–36) (2005) 3541;
(h) P.M. Chevalier, R.J.P. Corriu, J.J.E. Moreau, M. Wong Chi Man, J. Sol–Gel Sci. Technol. 8 (1997) 603;
(i) P.M. Chevalier, R.J.P. Corriu, P. Delors, J.J.E. Moreau, M. Wong Chi Man, New J. Chem. 22 (1998) 423;
(j) A.C. Franville, D. Zambon, R. Mahiou, Y. Troin, Chem. Mater. 12 (2000) 428;
(k) B. Lebeau, S. Brasselet, J. Zyss, C. Sanchez, Chem. Mater. 9 (1997) 1012.

[3] (a) U. Schubert, N. Husing, A. Lorenz, Chem. Mater. 7 (1995) 2010;
(b) U. Schubert, New J. Chem. 18 (1994) 1049 and references therein;
(c) M.G. Voronkov, N.N. Vlasova, Y.N. Pozhidaev, A.E. Pestunovich, A.I. Kirillov, Dokl. Akad. Nauk SSSR 320 (1991) 658;
N.N. Vlasova, G.Y. Zhila, A.I. Kirillov, M.G. Voronkov, Heteroat. Chem. 6 (1995) 311;
(d) J.C. Broudic, O. Conocar, J.J.E. Moreau, D. Meyer, M. Wong Chi Man, J. Mater. Chem. 9 (1999) 2283;
(e) S. Bourg, J.C. Broudic, O. Conocar, J.J.E. Moreau, D. Meyer, M. Wong Chi Man, Chem. Mater. 13 (2000) 491;
(f) O. Conocar, Thèse de doctorat, Université Montpellier-2, France, 22 octobre 1998;
(g) A.G.S. Prado, L.N.H. Arakaki, C. Airoldi, J. Chem. Soc. Dalton Trans. (2001) 2206;
(h) H.J. Im, Y. Yang, L.R. Alain, C.E. Barnes, S. Dai, Z. Xue, Environ. Sci. Technol. 34 (2000) 2209.

[4] (a) F.H. Dickey, Proc. Natl Acad. Sci. USA 35 (1949) 227;
(b) N.K. Raman, M.T. Anderson, C.J. Brinker, Chem. Mater. 8 (1996) 1682 and references therein;
(c) J.J.E. Moreau, M. Wong Chi Man, Coord. Chem. Rev. 178–180 (1998) 1073 and references therein;
(d) T.J. Barton, T.L.M. Bull, W.G. Klemperer, D.A. Loy, B. McEnaney, M. Misono, P.A. Monson, G. Pez, G.W. Scherer, J.C. Vartuli, O.M. Yaghi, Chem. Mater. 11 (1999) 2633 and references therein;
(e) S. Mann, S.L. Burkett, S.A. Davis, C.E. Fowler, N.H. Mendelson, S.D. Sims, D. Walsh, N. Whilton, Chem. Mater. 9 (1997) 2300;

(f) C. Pinel, P. Loisil, P. Gallezot, Adv. Mater. 9 (1997) 582;
(g) R. Makote, M.M. Collinson, Chem. Mater. 10 (1998) 2440.
[5] (a) S. Dai, Y.S. Shin, C.E. Barnes, L.M. Toth, Chem. Mater. 9 (1997) 2521;
(b) S. Dai, Y.S. Shin, L.M. Toth, C.E. Barnes, J. Phys. Chem. B 101 (1997) 5521;
(c) A. Adima, J.J.E. Moreau, M. Wong Chi Man, J. Mater. Chem. 7 (1997) 2331;
(d) A. Brethon, J.J.E. Moreau, M. Wong Chi Man, Tetrahedron: Asymmetry 15 (2004) 495;
(e) X. Elias, R. Pleixats, M. Wong Chi Man, J.J.E. Moreau, Adv. Synth. Catal. 348 (2006) 751;
(f) M. Trilla, R. Pleixats, M. Wong Chi Man, C. Bied, J.J.E. Moreau, Tetrahedron Lett. 47 (2006) 2399;
(g) A. Adima, J.J.E. Moreau, M. Wong Chi Man, Chirality 12 (2000) 411.
[6] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, fifth ed. Wiley Intescience, New York, Chichester, Brisbane, Toronto, Singapore, 1988;
G.B. Kauffman (Ed.), Coordination Chemistry, A Century of Progress 1893–1993, ACS Symposium Series 565, American Chemical Society, Washington DC, 1994.
[7] (a) A. Bercernil-Vilchis, Y. Meas, A. Rojas-Hernandez, Radiochim. Acta 64 (1994) 99;
(b) Y.S. Korotkin, Radiokhimiya 16 (1974) 221;
(c) L.V. Lipis, B.G. Pozharrskii, V.V. Fomin, J. Struct. USSR 1 (1960) 125;
(d) B.G. Posharzskij, I.A. Fedorov, V.B. Shevchenko, Russian J. Inorg. Chem. 9 (1964) 154.
[8] J. Korkisch, Handbook of Ion Exchange Resins and their Application to Inorganic Analytical Chemistry, Volume II: Actinides, CRC Press, Florida, 1989.