

# Selective dissolution of Am in basic media in the presence of ferricyanide ions: a mechanistic and structural study on Am(V) and Am(VI) compounds

By D. Meyer<sup>1,\*</sup>, S. Fouchard<sup>1</sup>, E. Simoni<sup>2</sup> and C. DenAuwer<sup>2</sup>

<sup>1</sup> CEA-DEN/MAR/DRCP/SCPS/LCAM, Atalante, BP 17171, F-30207 Bagnols/Cèze, France

<sup>2</sup> Institut de Physique Nucléaire, Université de Paris XI, Orsay, France

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**Summary.** Americium exhibits a soluble form in aqueous alkaline media in the presence of ferricyanide ions ( $\text{Fe}(\text{CN})_6^{3-}$ ), which is not the case for the other transplutonium elements (TPE). This soluble Am compound can be obtained by addition of a concentrated basic solution of ferricyanide ions on a trivalent americium hydroxide precipitate. Thus, this technique enables a complete and rapid extraction of americium through its soluble form in alkaline solutions whereas under these conditions, other TPE and the lanthanides remain in the solid state as trivalent hydroxides. In the case of dissolution involving large amounts of americium, the formation of the soluble americium species is followed by the appearance of a reddish precipitate in the basic solution. Dissolution of the reddish solid in NaOH or NaOH/ $\text{Fe}(\text{CN})_6^{3-}$  media demonstrated the existence of a media-dependent solubility of the precipitate, and therefore the existence of at least two forms of soluble Am.

Spectroscopic (UV-visible, EXAFS-XANES, Raman) and electrochemical investigations were carried out on the different forms of americium to determine the nature of the compounds. This study points out that the reddish solid Am compound is probably a  $\text{Am}(\text{V})$  hydroxide:  $\text{Na}_2\text{AmO}_2(\text{OH})_3 \cdot 3\text{H}_2\text{O}$  while the other Am species is a mixed americium–ferricyanide complex. This work demonstrates that this dissolution of  $\text{Am}(\text{III})$  solid compound is much more complex than a simple oxidation by the ferricyanide ions. The existence of a molecular interaction between  $\text{Am}(\text{V})\text{O}_2^+$  and ferricyanide ions is highly probable. This selective dissolution of americium by a basic ferricyanide solution can be used to define a separation process of Am from lanthanides and other transplutonium elements in the field of high level liquid waste treatment.

## Introduction

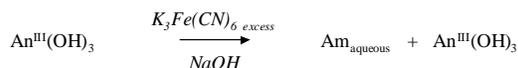
Americium chemistry received much attention recently since Am is one of the main radionuclide responsible for the long term radiotoxicity of nuclear waste. Common processes to separate americium from other transplutonium elements or lanthanides (Ln) are developed in acidic media. The chemical properties of the actinides in acidic media have been more extensively and more thoroughly investigated

than in basic media, no doubt because of their low solubility in basic media [1–9]. A previously unknown facet of americium chemistry was recently discovered, however: *i.e.* its unexpected behavior, compared with the other transplutonium elements [10–12]:  $\text{Am}(\text{III})$  is selectively dissolved by oxidation in the presence of ferricyanide ions in alkaline media, while the other transplutonium elements remain insoluble. This property lays the groundwork for separating Am from Cm and possibly from the lanthanides, in application of the radioactive waste treatment. This study was thus undertaken to extend our knowledge of the phenomenology and mechanism, as the first step toward understanding the dissolution process and developing a functional process.

The chemistry of the ferricyanide ion was extensively studied in different manners [13–17], but the results available today concerning its reactivity with the transuranium elements in nitric acid or basic media are essentially qualitative [10–12, 18–24]. The contact of solid Am, Cm, Cf and Bk species with a basic ferricyanide solution results in selective dissolution of americium by oxidation (Fig. 1).

The initial solid form of the actinides is usually an actinide hydroxide but some other compounds could be used, such as  $\text{Am}^{3+}_{\text{aq}}$ ,  $\text{Am}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{AmFe}(\text{CN})_6 \cdot n\text{H}_2\text{O}$ . Aging the oxidized Am dissolution solution leads to the formation of an  $\text{Am}(\text{V})$  precipitate.

In the present paper we expose the results of structural and mechanistical studies on the dissolution of americium hydroxide in basic ferricyanide solution. Investigating the dissolution mechanism provides a means for understanding the fundamental processes involved at the molecular level. All these aspects are the subjects of exploratory studies.



An: Am, Cm, Bk, Cf

An: Cm, Bk, Cf

**Fig. 1.** Transplutonium elements behaviour in the presence of ferricyanide ions in basic solutions.

## Experimental

All experiments were carried out using purified  $^{241}\text{Am}$  and  $^{244}\text{Cm}$  supplied by CEA from its own inventory.

\* Author for correspondence (E-mail: daniel.meyer@cea.fr).

$K_3Fe(CN)_6$ ,  $K_4Fe(CN)_6 \cdot 3H_2O$ , NaOH and  $HNO_3$  purchased from PROLABO was used without further purification. Mother solutions of different actinides were obtained by dissolution of the related oxide in analytical grade nitric acid. The actinide concentration in the mother solution ranged around 0.1 M.

Dissolution experiments were performed using a tube supplied on its top with a removable  $0.45 \mu m$  filter compartment. The actinide hydroxides were obtained by adding 1 ml of 4 M NaOH solution to 1 ml of a 1 M  $HNO_3$  actinide solution in the top compartment. Centrifuged filtering isolated the resulting hydroxide precipitate. Alpha counting and spectroscopy on the initial solution and the filtrate determined the actinide amount in the solid precipitate. Usually no actinide remained in the filtrate. The basic ferricyanide solution, freshly prepared (in order to prevent the carbonation of the sodium hydroxide solution) was then added on the precipitate and after a determined contact time, typically 5 minutes, the solution was filtered. Actinide amount in the filtrate was determined by alpha counting and spectroscopy.

RAMAN spectra were acquired using a 532 nm He-Ne laser LABRAM spectrometer and a liquid cell especially designed for radioactive measurements.

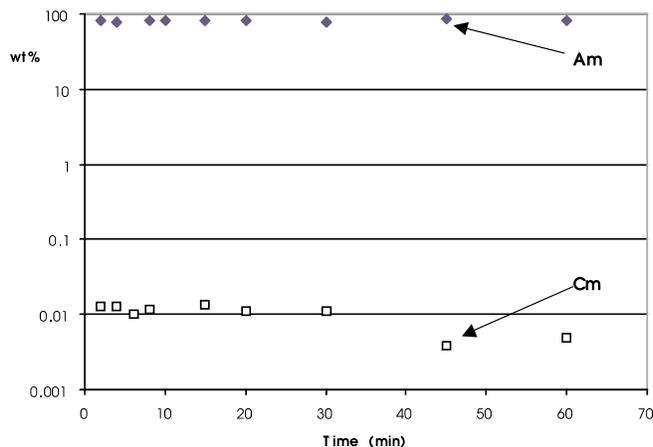
Electrochemical studies were carried out in using a EGG 273A radiometer potentiostat, a Hg/HgSO<sub>4</sub> reference electrode and a Pt working electrode.

A HP 8453 equipped with a diode detector was used for UV-visible spectroscopy. Alpha counting was done with a ZnS Canberra diode and the spectroscopy carried out on a Si Canberra spectrometer.

X-ray absorption spectras were measured at the LURE (Laboratoire pour l'utilisation de Rayonnement Electromagnétique) on the DCI ring (1.8 GeV,  $\lambda_c = 3.7$  keV) using the D44 experimental line. The radiologically nature of the measured compounds imposed the use of a special sample holder [25] to avoid any risk of radioactive material dispersion. A double crystal monochromator (Si 111) was used and X-ray absorption was measured in transmission mode. EXAFS and XANES spectra were measured at the  $L_{III}$  edge of Am (18 520 eV) using argon-filled ionization chambers. Energy resolution was around 7 eV and calibration was done using Zr K edge of a metallic Zr foil at 1814.0 eV [26]. EXAFS data were extracted from the raw absorption spectra by standard methods using in-house codes [27], and single scattering approximation was used for quantitative fitting procedure. The backscattering phases and amplitudes were extracted from the reference sample  $K_3AmO_2(CO_3)_2$ . The data simulation was performed following the classical fitting procedure by back-transformation of each peak of the pseudo-radial distribution function and fitting each Fourier-filtered EXAFS contribution using the reference phases and amplitudes.

## Results and discussion

Kinetic dissolution studies on an  $Am(OH)_3$  (96  $\mu g$ ),  $Cm(OH)_3$  (62  $\mu g$ ) solid mixture by a 4 M NaOH and 0.05 M  $K_3Fe(CN)_6$  solution were tried vainless. The laws governing the process kinetics could not be determined because of the velocity of the reaction: Am dissolution had al-



**Fig. 2.** Dissolution kinetics of Am and Cm (hydroxide forms) in the presence of ferricyanide ions in basic solutions.  $[NaOH] = 4$  M,  $[Fe(CN)_6] = 0.5$  M,  $V = 1$  ml,  $M(Am) = 96 \mu g$ ,  $M(Cm) = 62 \mu g$ .

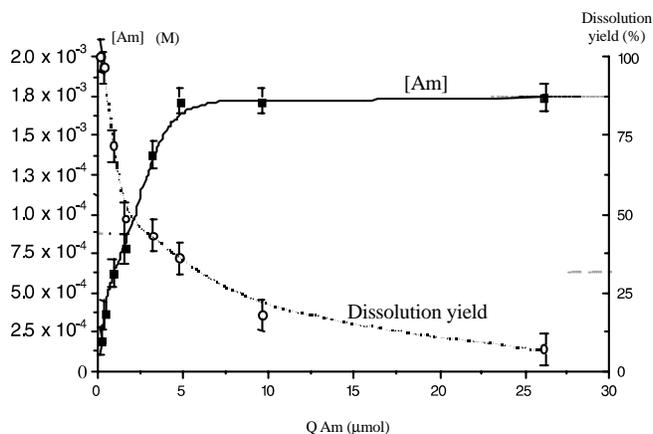
ready reached the maximum value at the initial sampling point (Fig. 2).

The tests also showed that while 80–90 wt % of the initial Am was dissolved, the Cm pollution remained below 0.01 wt % of the initial curium content (in the order of magnitude of the Cm contamination of the experimental glovebox). The same behavior was observed in the presence of lanthanide hydroxides, which were also insoluble. Americium dissolution is thus possible with remarkable selectivity from a solid mixture of Am, Cm and lanthanides.

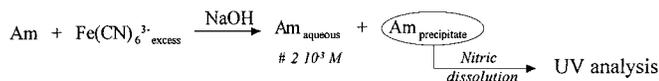
Monitoring the Am dissolution percentage versus the NaOH concentration revealed that the Am concentration in solution leveled off at sodium hydroxide concentrations above 4 M, and that the quantity of dissolved Am diminished at lower NaOH concentrations. This may be attributable to variations in the solubility of the oxidized Am species according to the alkali concentration.

A solubility of  $1.8 \times 10^{-3}$  M was determined for the total amount of americium dissolved by ferricyanide ions in the basic solution (Fig. 3).

For a given volume, exceeding this quantity of soluble Am in the initial hydroxide form does not result in  $Am(OH)_3$  insolubility, but rather in the formation of a different reddish-brown precipitate (Scheme 1). Various disso-



**Fig. 3.** Dissolution yield of Am in basic media as a function of initial Am amount.



**Scheme 1.** Formation of reddish precipitate in the presence of Ferricyanide excess.

lutions performed on different chemical forms of americium emphasize the importance of the interface reactions between the Am species and the oxidant agent  $\text{Fe}(\text{CN})_6^{3-}$ , through the final concentration of Am in solution or the oxidation degree of the residual precipitate.

These observations enable us to conclude about the nature of the compounds observed during the dissolution reaction and the mechanism. Firstly the minor dissolution and the uncompleted oxidation of  $\text{Am}(\text{OH})_3$  compared with the free form of  $\text{Am}^{3+}$  mentioned in the Table 1 show that the reactions at the interface were clearly involved. Thus, dissolutions carried out on free forms of Am ( $\text{Am}^{3+}$  and  $\text{AmO}_2^+$ ) confirmed that the oxidation degree of the residual solid is Am(V) (with its own solubility about  $2.3 \times 10^{-4} \text{ M}$  in a 4 M NaOH medium) and dissolutions performed on this pentavalent precipitate revealed that at least two Am species are present in the dissolution process.

In order to extend our knowledge of the dissolution mechanism, the nature of the observed Am compounds must be determined, particularly for the final soluble form and the reddish-brown precipitate.

The solid compound can be obtained in larger quantities and isolated by filtration. This solid species is soluble in acid media, and the UV-visible spectrum shows that the Am in solution is at oxidation state V, which is coherent with the redox potential of Am(V) complex in basic ferricyanide aqueous solution (Table 2).

In order to avoid any ambiguity concerning a possible reaction when this compound is dissolved in acid solution, we analyzed the solid compound by X-ray absorption (Am  $L_{\text{III}}$ -edge) spectroscopy.

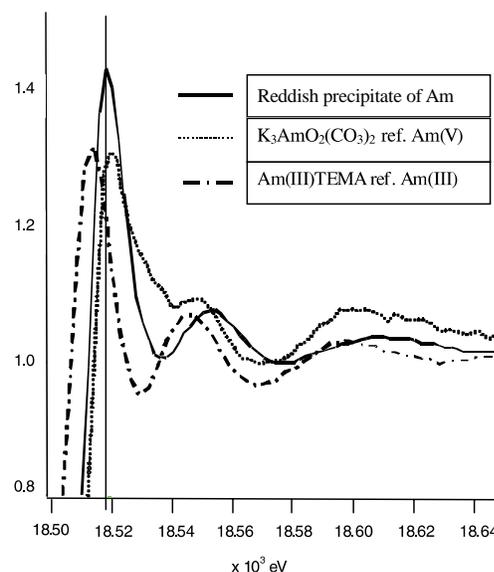
Reference compounds must be available both for the XANES (edge comparison) and EXAFS (phase and amplitude corrections) aspects of this type of spectroscopic examination. Although data are available for Am(III) [32], no Am(V) spectrum has been published to date. The  $\text{K}_3\text{AmO}_2(\text{CO}_3)_2$  compound was therefore synthesized ac-

**Table 2.** Redox potential of ferricyanide ion and Am compound in basic aqueous media.

Couples	Potentials $V_{\text{NHE}}$	Reference
$\text{Am}^{\text{VI}}\text{O}_2(\text{OH})_4^{2-} / \text{Am}^{\text{V}}\text{O}_2(\text{OH})_3^{2-}$	0.65	[4,6,28]
$\text{Am}^{\text{V}}\text{O}_2(\text{OH})_3^{2-} / \text{Am}(\text{OH})_{4\text{aq}}$	0.2	[29]
$\text{Am}(\text{OH})_{4\text{aq}} / \text{Am}(\text{OH})_{3\text{aq}}$	< 0.5	[30]
$\text{Am}(\text{OH})_{4\text{aq}} / \text{Am}(\text{OH})_{3\text{aq}}$	-0.4	[31]
$\text{Fe}(\text{CN})_6^{3-} / \text{Fe}(\text{CN})_6^{4-}$	0.4	[6,7,10,29]

cording to classical methods [33] and its X-ray absorption spectrum was recorded.

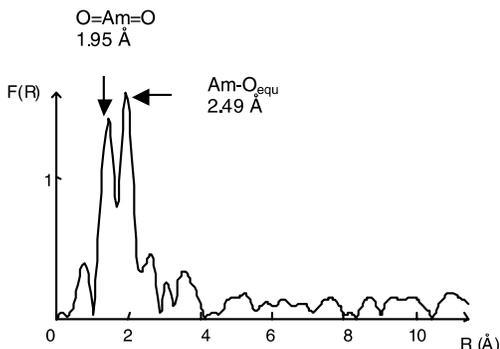
The XANES region of the absorption spectrum shows an  $L_{\text{III}}$ -edge energy of 18518.6 eV for the reddish-brown compound (Fig. 4); values were measured for an Am(III) (TEMA) compound (18517.2 eV) and for  $\text{K}_3\text{AmO}_2(\text{CO}_3)_2$  (18520.0 eV). These findings indicate that the americium in the unknown species is most likely at a higher oxidation state (IV or V). Analysis of the EXAFS oscillation revealed two types of bonds around Am.



**Fig. 4.** XANES spectroscopies of americium compounds at the  $L_{\text{III}}$  edge.

**Table 1.** Results of different interactions of americium species with basic ferricyanide solution.

Americium SPECIES	Reagents	$[\text{Am}_{\text{aqueous}}] \text{ (M)}$	UV analysis in nitric solution
$\text{Am}(\text{OH})_3$	$[\text{Fe}(\text{CN})_6^{3-}] = 0.5 \text{ M}$ $[\text{NaOH}] = 4 \text{ M}$	$1.8 \times 10^{-3} \text{ M}$	$\text{Am}^{3+} + \text{AmO}_2^+$ $\Rightarrow$ mixture of oxidation degree in the $\text{Am}_{\text{precipitate}}$
$\text{Am}^{3+}$ in $\text{HNO}_3$	$[\text{Fe}(\text{CN})_6^{3-}] = 0.5 \text{ M}$ $[\text{NaOH}] = 4.5 \text{ M}$	$2.5 \times 10^{-3} \text{ M}$	$\text{AmO}_2^+$ $\Rightarrow$ <b>only one oxidation degree in the <math>\text{Am}_{\text{precipitate}}</math></b>
$\text{Am}_{\text{precipitate}}$	$[\text{Fe}(\text{CN})_6^{3-}] = 0.5 \text{ M}$ $[\text{NaOH}] = 4 \text{ M}$	$2.3 \times 10^{-4} \text{ M}$	$\text{AmO}_2^+$ $\Rightarrow$ only one oxidation degree in the $\text{Am}_{\text{precipitate}}$
$\text{AmO}_2^+$ in $\text{HNO}_3$	$[\text{Fe}(\text{CN})_6^{3-}] = 0.5 \text{ M}$ $[\text{NaOH}] = 4.5 \text{ M}$	$2.5 \times 10^{-3} \text{ M}$	$\text{AmO}_2^+$ $\Rightarrow$ only one oxidation degree in the $\text{Am}_{\text{precipitate}}$



**Fig. 5.** Modulus of the PRDF of the EXAFS oscillation for the reddish complex with a coordination number of 6 (phase corrected).

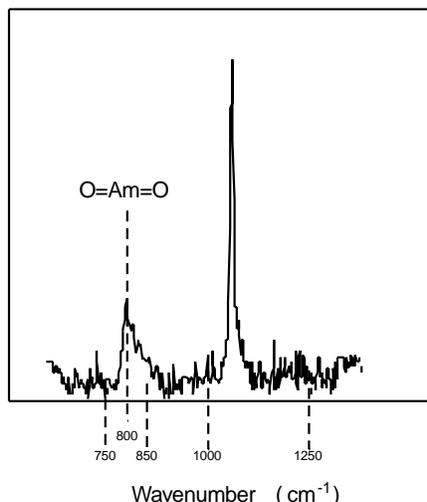
The EXAFS data from the  $\text{K}_3\text{AmO}_2(\text{CO}_3)_2$  spectrum can be used to evaluate the experimental phases and amplitudes, and to determine the bond lengths more accurately and the coordination number of Am in the reddish-brown compound (Fig. 5). A short (1.95 Å) bond was thus attributed to the Am=O bonds of the americyl group, and a long (2.49 Å) bond to the Am–O bonds in the equatorial Am–OH groups. The best fit of the experimental data was obtained with a coordination number of 6. These results suggest that the reddish-brown precipitate can be a hydroxide  $\text{Na}_{6-x}\text{AmO}_2(\text{OH})_x(\text{H}_2\text{O})_{4-x} \cdot n\text{H}_2\text{O}$  ( $x = 3, 4$ ).

By comparing the bond lengths of the two Am(V) compounds, the electron overlap on the equatorial plane of the hydroxide was found to be greater for the carbonate (Table 3).

The two free electron doublets on the oxygen atom of the –OH ligand can stabilize the high oxidation states by  $\pi$  donation to empty metal  $d$  or  $f$  orbitals. This overlap results in a contraction of the ligand-metal bond. In the case of the carbonate ligand, the oxygen atom doublets are also committed to the ligand  $\pi$  system, making the ligand-metal contraction weaker. The increased equatorial overlap in the hydroxide compound tends to extend the axial Am=O bond. This implies that stabilization by axial and equatorial  $\pi$  donation occurs with the same orbitals in the metal. Amplifying the equatorial orbital overlap in the hydroxide increases the electron density around the Am atom with respect to the Am(V) carbonates. This increase accounts for the energy shift of the XANES emission edge when passing from the carbonate to the hydroxide.

While the solid compound was successfully analyzed, determining the Am species in solution was more difficult. The low solubility of the complex prevented interpretation of the UV-visible signature, and the X-ray absorption spectrum acquisition was unsuccessful because of the minute quantity of Am in the solution.

Despite the drastic low concentration of Am, we were able to measure a Raman diffusion spectrum for the compound in solution (Fig. 6). A diffusion line at  $790\text{ cm}^{-1}$



**Fig. 6.** Raman diffusion spectra of dissolved Am.

was attributed to the polarizability variation due to the symmetric O=Am=O vibration. Except for americium carbonate, this line is situated around  $750\text{ cm}^{-1}$  in the case of an O=An(V)=O group, and near  $800\text{ cm}^{-1}$  for an O=An(VI)=O group [34, 35] (An = Np, Pu, Am). In the case of Am, the delocalized  $\pi$  electrons of the carbonate ligand stabilized the electron deficiency at the metal core more efficiently than the oxo axial ligands. This will minimize the bonding effects in the axial field when changing the oxidation state of Am complexed by carbonate type ligands.

In the absence of this type of equatorial ligands, the observed  $40\text{ cm}^{-1}$  shift toward the higher energy region indicates that this Am compound has shorter Am=O bonds than the Am(V)=O bond. This contraction is due to greater  $\pi$  donation by the oxygen atom to the Am atom, and is characteristic of a lower electron density in the metal. The americium in this compound is probably closer to an oxidation state VI.

The effect of the quantity of ferricyanide ions versus dissolved Am concentration on the dissolution performance seems to confirm this result since a minimum  $\text{Fe}(\text{CN})_6^{3-}/\text{Am}$  ratio of 3 : 1 must be applied in order to reach the maximum of the dissolution (Fig. 7).

With an initial  $\text{Fe}(\text{CN})_6^{3-}/\text{Am}$  ratio of 3 : 1, an electrochemical potential measurement of a dissolution solution at equilibrium gives a value below that of the Fe(III)/Fe(II) couple in this medium.

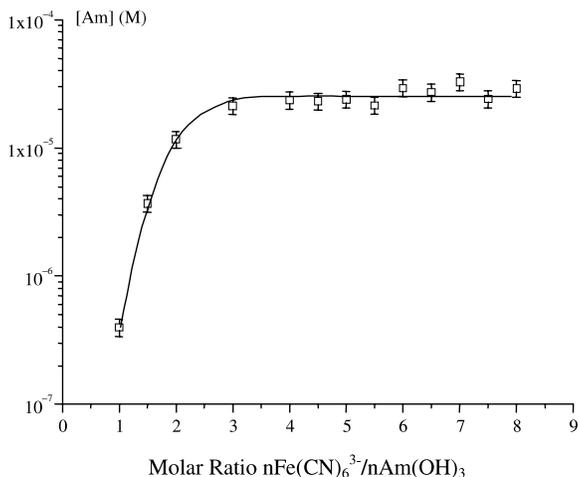
$$E_{\text{eq}} = 0.32V_{\text{NHE}}$$

$$E'_{\text{o}} = 0.4V_{\text{NHE}} \text{ for } \text{Fe}(\text{III})(\text{CN})_6^{3-}/\text{Fe}(\text{II})(\text{CN})_6^{3-}$$

This result implies that most of the Fe is reduced to oxidation state II, and that 3 electrons per Am are therefore necessary to reduce all the Fe(III) to Fe(II), as indicated in

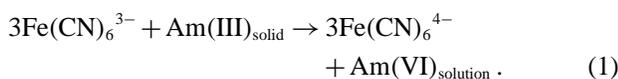
**Table 3.** Am bond lengths for  $\text{Na}_{6-x}\text{AmO}_2(\text{OH})_x(\text{H}_2\text{O})_{4-x} \cdot n\text{H}_2\text{O}$  ( $x = 3, 4$ ) and  $\text{K}_3\text{AmO}_2(\text{CO}_3)_2$  with a coordination number of 6.

Compound	Am=O (Å)	Am–O equatorial (Å)
$\text{Na}_{6-x}\text{AmO}_2(\text{OH})_x(\text{H}_2\text{O})_{4-x} \cdot n\text{H}_2\text{O}$ ( $x = 3, 4$ )	1.95	2.49
$\text{K}_3\text{AmO}_2(\text{CO}_3)_2$	1.93	2.55



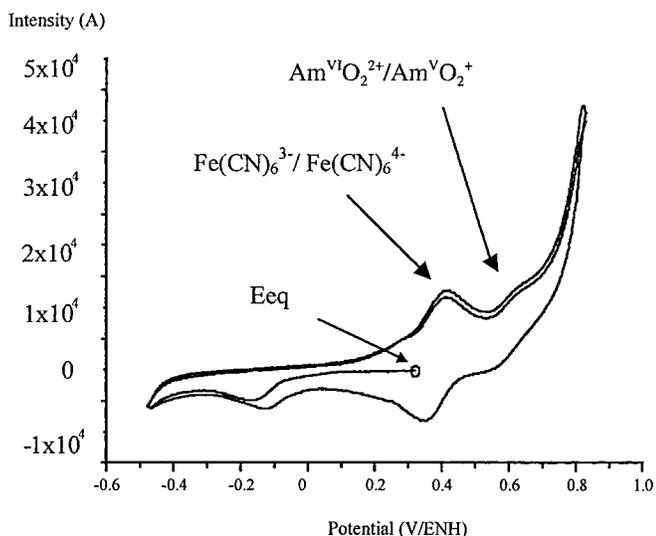
**Fig. 7.** Dissolved Am quantity versus  $\text{Fe}(\text{CN})_6^{3-}/\text{Am}$  ratio  $[\text{NaOH}] = 4 \text{ M}$ ,  $V = 1 \text{ ml}$ , Time = 30 min.

Eq. (1):



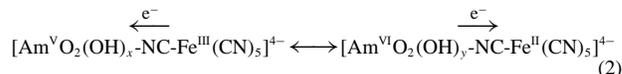
This result was confirmed by the direct measurement of the ferricyanide ions concentration along the dissolution of the trivalent Am: finally in the basic solution, all the initial  $\text{Fe}(\text{CN})_6^{3-}$  ions were reduced in order to oxidize and solubilize the americium. Cyclic voltammetry analysis showed that the potential of the  $\text{Am}(\text{VI})/\text{Am}(\text{V})$  couple is higher than for the  $\text{Fe}(\text{III})/\text{Fe}(\text{II})$  couple under the same experimental conditions (Table 2 and Fig. 8). This observation means that it is impossible for  $\text{Fe}(\text{III})$  to oxidize  $\text{Am}(\text{V})$  by an **intermolecular** electron transport mechanism in aqueous solution.

However, the differences in the amount of dissolved Am between a complexed form of pentavalent Am (such as  $\text{Na}_{6-x}\text{AmO}_2(\text{OH})_x(\text{H}_2\text{O})_{4-x} \cdot n\text{H}_2\text{O}$ ,  $x = 3, 4$ ) and a free aqueous complex of  $\text{Am}(\text{V})$  (*i.e.*  $\text{AmO}^+$ ) as shown in Table 1



**Fig. 8.** Cyclic voltammogram of an Am solution after dissolution by  $\text{Fe}(\text{CN})_6^{3-}$  in  $\text{NaOH}$  medium.  $[\text{Am}] = 2.2 \times 10^{-3} \text{ M}$ ,  $[\text{NaOH}] = 4 \text{ M}$ ,  $\text{Fe}/\text{Am}^{\text{III}} = 3$ ,  $S = 0.2 \text{ cm}^2$ , Ref:  $\text{Hg}/\text{Hg}_2\text{SO}_4$ .

line 3 and 4, in the presence of a stoichiometric solution of  $\text{Fe}(\text{CN})_6^{3-}$  enable us to approach a new way to explain the oxidative dissolution of  $\text{Am}(\text{V})$ . Assuming the Am in solution is at oxidation state VI, the  $\text{Am}(\text{V})_{\text{aq}}$  can be oxidized only by **intramolecular** transport after the formation of an  $\text{Am}(\text{V})\text{-Fe}(\text{CN})_6^{3-}$  complex (Eq. (2)). The hydroxide type  $\text{Na}_{6-x}\text{AmO}_2(\text{OH})_x(\text{H}_2\text{O})_{4-x} \cdot n\text{H}_2\text{O}$  ( $x = 3, 4$ ) in the same conditions is not able to form a ferricyanide complex.

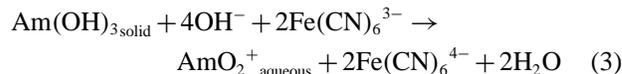


On the basis of these results we were able to define the broad outlines of a hypothesis to account for the mechanism by which Am solid compound or its soluble form, is transferred to a basic ferricyanide solution.

The initial approach consists in dividing the process into two main steps. During the first step  $\text{Am}(\text{III})$  is dissolved, and the electron transfers between Fe and Am are intermolecular. During the second step,  $\text{Am}(\text{V})_{\text{aq}}$  interacts with the  $\text{Fe}(\text{CN})_6^{3-}$  ion in the INNER sphere, and electron transfers are intramolecular.

### Step 1

The overall balance for this step is expressed by the dissolution and oxidation of  $\text{Am}(\text{III})$  to  $\text{Am}(\text{V})$  hydroxide by the ferricyanide ion (Eq. (3)):



The manner in which each elementary process occurs has not been precisely established. Oxidation may occur entirely in solution by reaction of the small quantity of dissolved  $\text{Am}(\text{OH})_3$  with the ferricyanide ions, in which case the reactions would shift the  $\text{Am}(\text{OH})_3$  dissolution equilibrium as in Eq. (3). At this stage the free form of  $\text{Am}(\text{V})$  can react with another  $\text{Fe}(\text{CN})_6^{3-}$  molecule (solubilization) or precipitate to form  $\text{Na}_{6-x}\text{AmO}_2(\text{OH})_x(\text{H}_2\text{O})_{4-x} \cdot n\text{H}_2\text{O}$  ( $x = 3, 4$ ) (hydrolysis of the excess of Am, over  $2.5 \times 10^{-3} \text{ M}$ ).

### Step 2

In the second step, the aqueous form of  $\text{Am}(\text{V})$  combines with the third  $\text{Fe}(\text{CN})_6^{3-}$  molecule to form an  $\text{Am}(\text{VI})$  complex of the following type:  $[\text{Am}^{\text{VI}}\text{O}_2\text{-NC-Fe}(\text{CN})_5]$ , as shown in Eq. (2).

The reaction between a dissociated form of  $\text{Am}(\text{V})$  with a ferricyanide ion leading to the formation of an  $\text{Am}(\text{V})\text{-Fe}(\text{III})$  compound is a possible hypothesis. An interaction between the metallic centers by a delocalized  $\pi$  system (*e.g.*  $\text{Am-N-C-Fe}$ ) could be considered. The  $\text{Am}(\text{VI})\text{-Fe}(\text{II})$  compound would then be a resonant form of the  $\text{Am}(\text{V})\text{-Fe}(\text{III})$  species through reversible intramolecular electron transfer along the  $\pi$  system. These resonant forms are only extreme forms of reality. If the “ $\text{Am}(\text{VI})\text{-ferricyanide}$ ” compound exists, only a fraction of the electron density and not the entire electron is transferred

from the Am to the Fe. This  $[\text{AmO}_2\text{Fe}(\text{CN})_6]^{4-}$  compound could precipitate as  $\text{Na}_{6-x}\text{AmO}_2(\text{OH})_x(\text{H}_2\text{O})_{4-x} \cdot n\text{H}_2\text{O}$  ( $x = 3, 4$ ) by reduction of the actinide (radiolysis) and dissociation of the bimolecular complex (no more electron delocalized).

## Conclusion

This work demonstrates that selective dissolution of americium by a basic ferricyanide solution could lay the foundations for a process by which Am is separated from the other transplutonium elements and from the lanthanides. The dissolved Am is highly pure. Although the low solubility of Am constitutes a limitation this obstacle to industrial development might be eliminated by modifying the reaction medium, or mitigated by using the basic medium as a transfer vector toward another medium.

At a more fundamental level, X-ray absorption analyses were carried out for the first time on Am(V) compounds. The axial Am=O and equatorial Am–O bond lengths in the  $\text{Na}_{6-x}\text{AmO}_2(\text{OH})_x(\text{H}_2\text{O})_{4-x} \cdot n\text{H}_2\text{O}$  ( $x = 3, 4$ ) and  $\text{K}_3\text{AmO}_2(\text{CO}_3)_2$  compounds have been determined in the solid state. The postulated existence of an electrodeficient Am compound ( $[\text{AmO}_2\text{Fe}(\text{CN})_6]^{2-}$ ) accounts for the overall electron balance of the dissolution process, and for the shifted O=Am=O line of the Raman spectrum.

The broad outlines of a mechanism accounting for Am dissolution by ferricyanide ions in basic media were given from the experimental data. An oxidizing dissolution phase characterized by intermolecular electron transfer and a complexation phase accompanied by intramolecular electron density transfer were considered.

A more detailed analysis of the solid/liquid interface will be necessary to localize and identify the sequence of the initial steps. It will be indispensable to verify the hypothesis of an Am-Fe interaction via a cyanide ligand before progressing with the study of the dissolution mechanism. Finally, determining the exact nature of the Am-ferricyanide compound is crucial to understanding the intramolecular electron transfer.

## References

- Cohen, D.: *Inorg. Nucl. Chem. Lett.* **8**, 533 (1972).
- Tananaev, I. G.: *Radiokhim.* **31**(3), 46 (1989).
- Penneman, R. A., Coleman, J. S., Keenan, T. K. J.: *Inorg. Nucl. Chem.* **17**, 138 (1961).
- Nikolaevskii, V. B., Shilov, V. P., Krot, N. N.: *Radiokhim.* **16**(1), 122 (1974).
- Nikolaevskii, V. B., Shilov, V. P., Krot, N. N., Peretruckhin, V. F.: *Radiokhim.* **17**(3), 431 (1975); Nikolaevskii, V. B., Shilov, V. P., Krot, N. N., Peretruckhin, V. F.: *Radiokhim.* **17**(3), 426 (1975).
- Peretruckhin, V. F., Krot, N. N., Gel'man, A. D.: *Radiokhim.* **14**(1), 72 (1972); Peretruckhin, V. F., Nikolaevskii, V. B., Shilov, V. P.: *Radiokhim.* **16**(6), 833 (1974); Peretruckhin, V. F., Alekseeva, D. P.: *Radiokhim.* **16**(6), 836 (1974); Peretruckhin, V. F., Alekseeva, D. P.: *Radiokhim.* **16**(6), 843 (1974).
- Shilov, V. P.: *Radiokhim.* **18**(4), 659 (1976); Shilov, V. P., Gargov, A. Yu., Krot, N. N., Yusov, A. B.: *Radiokhim.* **39**(6), 515 (1997).
- Simakin, G. A., Matyaschchuk, I. V., Vladimirova, N. A.: *Radiokhim.* **15**(1), 98 (1973).
- Tananaev, I. G.: *Radiokhim.* **32**(5), 53 (1990); Tananaev, I. G.: *Radiokhim.* **32**(4), 4 (1990); Tananaev, I. G.: *Radiokhim.* **33**(3), 24 (1991).
- Kulyako, Y. M., Trofimov, T. I., Malikov, D. A., Lebedev, I. A., Myasoedov, B. F.: *Radiokhim.* **35**(5), 68 (1993) [*Russ. Radiochem. (Engl. Transl.)* **35**, 549 (1993)].
- Kulyako, Y. M., Trofimov, T. I., Malikov, D. A., Lebedev, I. A., Myasoedov, B. F.: *Radiokhim.* **35**(4), 38 (1993) [*Russ. Radiochem. (Engl. Transl.)* **35**, 25 (1993)].
- Kulyako, Y. M., Trofimov, T. I., Malikov, D. A., Myasoedov, B. F.: *Mendeleev Comm.* **5**, 173 (1996).
- Bellomo, A., De Marco, D., Casale, A.: *Talanta* **22**, 197 (1975).
- Griffith, W. P.: *Coord. Chem. Rev.* **17**, 177 (1975) and references cited therein.
- Jones, L. H.: *Inorg. Chem.* **2**(4), 777 (1963).
- Lanjewar, R. B., Garg, A. N.: *Ind. Journ. Chem.* **32A**(11), 969 (1993).
- Vannerberg, N. G.: *Acta Chem. Scand.* **26**(7), 2863 (1972).
- Hassan, R. M., Kojima, T., Kikutomi, H.: *Bull. Res. Lab. Nucl. React.* **5**, 41 (1980).
- Jiang, M., Wang, M., Zhou, X.: *Chem. Lett.* **3**, 1709 (1992).
- Kourim, V., Laznicek, M., Dolezal, J.: *J. Radioanal. Chem.* **21**, 355 (1974).
- Krot, N. N., Mefodieva, M. P., Afanasieva, T. V.: *Radiokhim.* **19**(2), 230 (1977).
- Krtil, J.: *Radiochim. Acta* **7**, 30 (1967).
- Rizvi, G. H.: *J. Radioanal. Nucl. Chem.* **125**(2), 333 (1988).
- Sullivan, J. C., Brown, W., Nash, K., Thompson, M.: *Radiochim. Acta* **30**, 45 (1982).
- Chabane, A.: PhD Thesis. Université Paris XI, Orsay, France (1997).
- Reference X-ray spectra of metal foils, EXAFS MATERIALS, 871, El Cerro Blvd, Danville, CA 94526, USA.
- Michalowicz, A.: PhD Thesis. Université du Val-de-Marne, France, (1990); Michalowicz, A.: *J. Phys. IV* **7**, 2 (1997).
- Peretruckhin, V. F., David, F., Maslennikov, A. G.: *Electrochemical Properties and Thermodynamics Stability of Plutonium and Neighbour Actinides in the Oxidation States (V)-(VI) in Aqueous Alkaline Solutions. Abstract Journée des Actinides, Méribel France* (1992).
- Bard, A. J., Parson, R., Jorda, J.: *Standart Potentials in Aqueous Solution*. Ed. Dekker IUPAC (1985).
- Penneman, R. A., Coleman, J. S., Keenan, T. K.: *J. Inorg. Nucl. Chem.* **17**, 138 (1961).
- Latimer, W.: *Oxydation State of the Elements and their Potentials in Aqueous Solution*. UL Moscow 318 (1953).
- DenAuwer, C. *et al.*: *Inorg. Chem.* **39**, 1487 (2000).
- Burney, G. A.: *Nucl. Appl.* **4**, 217 (1968).
- Madic, C., Hobart, D. E., Begun, G. M.: *Inorg. Chem.* **22**, 1424 (1983).
- Basile, L. J., Sullivan, J. C., Ferraro, J. R., LaBonville, P.: *Appl. Spectrosc.* **28**, 142 (1974).