

DEVELOPMENT OF THE SESAME PROCESS

L. Donnet, J. M. Adnet, N. Faure, P. Bros, Ph. Brossard, F. Josso
CE/Valrho/Marcoule, CEA/DCC/DRRV/SPHA, BP 171
30207 Bagnols-sur-Cèze Cedex
France

Abstract

The main goal of the SPIN program developed by CEA is to improve the management of high activity waste containing minor actinides and long-lived fission products. In that field, americium has been pointed out as the main hazardous element to be firstly recovered. With the aim to extract more than 99% of the americium contained in high level liquid waste (HLLW), the SESAME process, which consists in the selective extraction of oxidised Am, is foreseen as a promising way to succeed in Am management. Dealing with the americium selective recovery from HLLW, many studies concerning the electrochemical oxidation of Am to its hexavalent state in the presence of lacunary polyanionic ligands (LHPA) have been carried out. The main results of several laboratory scale tests of the SESAME process are presented and the further process development is discussed.

Introduction

As a part of the SPIN program launched by CEA, ACTINEX program is more precisely devoted to the definition of new processes for minor actinides and long-lived fission products recovery from HLLW. Among minor actinides, americium has been defined as the prior element to recover. In that field, SESAME process has been proposed to remove selectively americium from high activity liquid effluents. This process is based on the electrochemical oxidation of Am(III) to oxidation state (IV) or (VI) followed by the selective extraction of oxidised Am [1]. This process is especially interesting as it is not concerned with the actinide(III) to lanthanide(III) group separation.

Three possibilities exist to apply SESAME at the backend of the PUREX process. The simpler is the solution to treat, the easier the SESAME process is to implement. Thus, when going from SESAME A to SESAME C, the difficulty to remove Am from the solution increases. When dealing with SESAME C, many interfering elements have to be managed and Ru, Mo, Zr, Cs are the most troublesome ones for Am oxidation in the presence of LHPA.

If americium is coming from the stripping solution of DIAMEX process, many interfering elements have been removed and Am oxidation is easy to achieve.

This way corresponding to SESAME B, has been selected as the reference scheme and has been recently described². The main steps of that scheme are listed below:

- Concentration of the DIAMEX stripping solution to increase the acidity of the solution to ca $[\text{HNO}_3] = 5 \text{ M}$.
- Electrochemical oxidation of Ce(III) to Ce(IV) and extraction of Ce(IV) with TBP.
- Electrolysis of the solution after adjustment of the LHPA and AgNO_3 concentrations.
- Extraction of Am(VI) by TBP using a solvent extraction technique (centrifugal contactors).
- Recovery of the silver mediator using an electrodeposition technique (H_2O_2 is used as an antinitrite agent).

This paper is essentially focused on the R&D studies concerning the Am(III) to Am(VI) electrochemical oxidation mechanism and results dealing with the solvent extraction of Am(VI).

Electrochemical oxidation of Am(III) to Am(VI)

The electrochemical oxidation of Am(III) in nitric media is well known and has been described in several papers [1,5]. The quantitative oxidation can be carry out using complexants such as lacunary heteropolyanions which are specific for tetravalent species.

The stability constants of Am(III) and Am(IV) complexes with the relevant LHPA have been described by [6,8] and presented in Table 1.

Table 1. **Apparent stabilities of constants of 1:1 and 1:2 Am(III)/LHPA and Am(IV)/LHPA complexes in 1M nitric media**

Am + LHPA	$\log \beta_1$	$\log \beta_2$	$\log k_2 = \log \beta_2 - \log \beta_1$
Am(III) + $\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}^{10-}$	2.7±0.1	4.8*	2.1
Am(IV) + $\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}^{10-}$	19.3±0.2	22.9±0.2	3.6
Am(III) + $\alpha\text{-SiW}_{11}\text{O}_{39}^{8-}$	4.4±0.4	6.7±0.4	2.3
Am(IV) + $\alpha\text{-SiW}_{11}\text{O}_{39}^{8-}$	21.3±0.3	26.1±0.4	4.8

* extrapolate using estimated values in acid nitric concentration 2M from [4]

Those results show that Am(IV) is strongly complexed by LHPA, especially compared to Am(III). Another important result is that tungstosilicate is a stronger complexing agent towards Am than tungstophosphate. It is also of interest to note that the stability constants β_1 are much higher than constants k_2 . This fact can be explained taking into account electrostatic interactions which are important in such complexes. Indeed, constant β_1 characterises the interaction of one cation and one anion which is favourable, whereas constant k_2 characterises the interaction between two anions.

The determination of the formation constant of the complexes has permitted to determine the variation of standard conditional potential of Am pair involved as function of logarithm of LHPA concentration. According to the Nernst formula, in the case of same total concentration for both Am(IV) and Am(III), the equilibrium potential of the solution is expressed by the Eq. 1):

$$E_{eq}^{IV/III} = 2.62 + \frac{2.3.R.T}{F} \log \left(\frac{1 + \beta_1^{III} [LHPA] + \beta_2^{III} [LHPA]^2}{1 + \beta_1^{IV} [LHPA] + \beta_2^{IV} [LHPA]^2} \right) \quad (1)$$

For the Am(VI)/Am(IV) pair, same formula can be written as Eq (2):

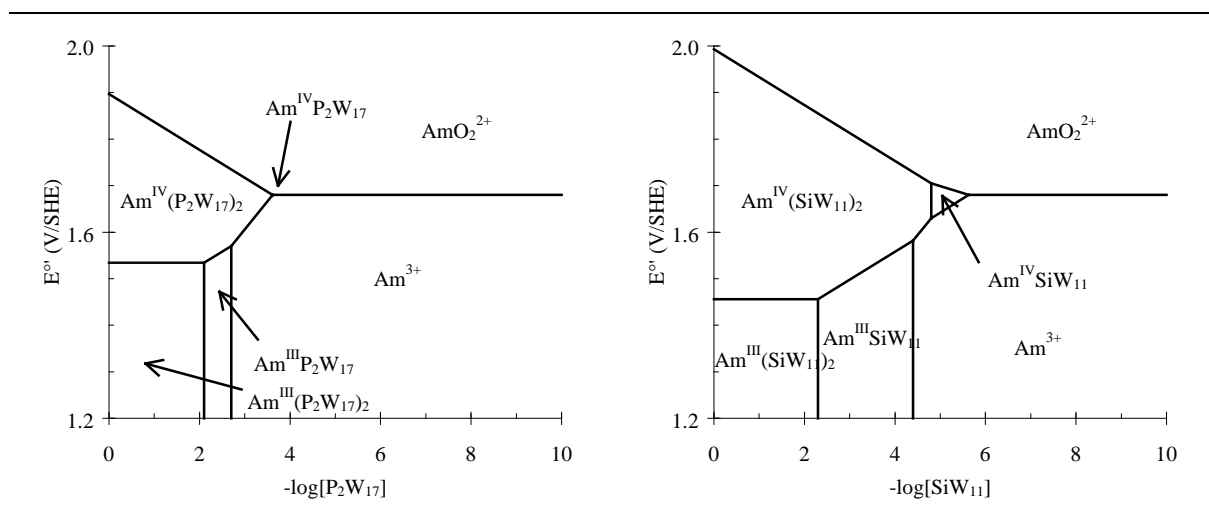
$$E_{eq}^{VI/IV} = 1.21 + \frac{2.3 RT}{2 F} \log \left(\frac{1 + \beta_1^{IV} [LHPA] + \beta_2^{IV} [LHPA]^2}{1} \right) \quad (2)$$

The potential diagram shows that the potential of $\text{Am(LHPA)}_2/\text{AmO}_2^+$ pair with $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$ is lower than in the presence of $\text{SiW}_{11}\text{O}_{39}^{8-}$ and explains that in the case of $\text{SiW}_{11}\text{O}_{39}^{8-}$ it is impossible to get Am(VI) for polyanion/Am ratio higher than two. As it has been observed, the final oxidation state of Am depends on the $[\text{LHPA}(\text{total})]/[\text{Am}]$ ratio and on the oxidation potential.

If this ratio exceeds two, quantitative and rapid oxidation of Am(III) to $\text{Am}^{\text{IV}}(\text{LHPA})_2$ is observed and, as those complexes don't get oxidised at an anode potential of less than 2.2 V/SHE, no Am(VI) is observed. For ratios below two, the final oxidation products are Am(VI) and $\text{Am}^{\text{IV}}(\text{LHPA})_2$; such oxidation was obtained with a ratio R of 0.5. The evolution of the UV-visible spectrum of the solution during the oxidation process was recorded and used to estimate the evolution of Am oxidation. From these data and the balance and equilibrium equations, it was then possible to compute the speciation of Am throughout the oxidation process as shown on Figure 3.

Initial rapid oxidation of Am(III) to Am(IV)-LHPA complexes occurs, and then Am(VI) is generated. The calculated transient formation of 1:1 Am(IV) complexes was confirmed by a small peak at 560 nm in the UV-visible spectra [6]. The slow oxidation rate can be explained by the great structural change between complexed Am(IV) and the americium ion.

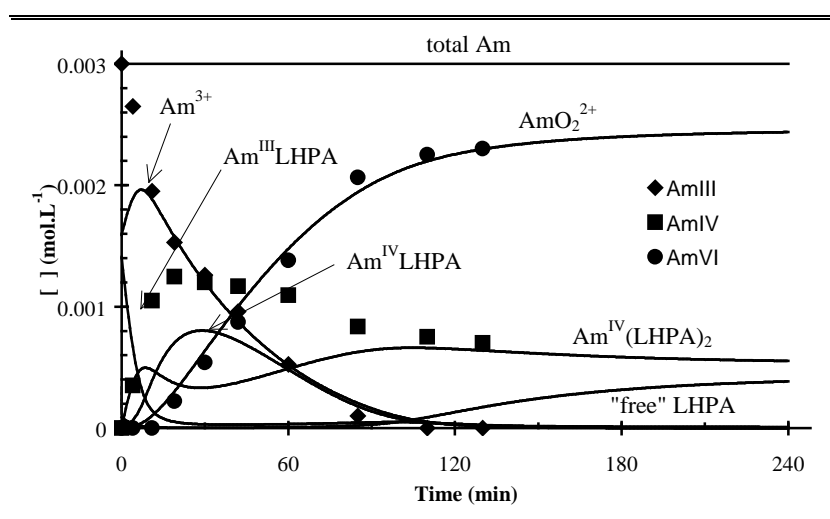
Figure 1. E-pL diagram of the standard conditional potential of Am as function of -log(LHPA) with the two LHPA : $P_2W_{17}O_{61}^{10-}$ and $SiW_{11}O_{39}^{8-}$ in 1M nitric acid



As a conclusion, quantitative Am(VI) generation is possible with both polyanions. Nevertheless, it is easier to obtain Am(IV) with the tungstosilicate and easier to reach Am(VI) with tungstophosphate.

Figure 2. Evolution of Am species during electrochemical oxidation of Am(III) with tungstosilicate and silver nitrate. ■ experimental data, — computed data.

conditions: $[Am] = 3 \times 10^{-3}$ M, $[SiW_{11}O_{39}^{8-}]/[Am] = 0.5$, $[HNO_3] = 1$ M, $j = 0.38$ mA.cm $^{-2}$, $E = 1.92$ V/SHE, $[AgNO_3] = 0.01$ M,



Solvent extraction of Am(VI)

As the process to develop is supposed to work in a continuous way, oxidised Am will essentially be recovered using a solvent extraction technique. Among the two Am oxidation states suitable for that process (Am(IV) or Am(VI)), Am(VI) is of first interest as it exists in the aqueous phase as the AmO_2^{2+} species which is not complexed with LHPA ligand in the operating conditions. So, in the case of Am(VI) recovery, a selective extraction actually occurs. Concerning Am(IV) extraction, Am has to be extracted in the form of the $\text{Am}^{\text{IV}}(\text{LHPA})_2$ complex which requires a further Am / LHPA separation steps.

To check the possibility to recover oxidised Am from fission products solution, extraction tests using a chromatographic extraction technique have been run on simulated mixtures of Am, Cm and lanthanides. The possibility to selectively recover Am(VI) from solutions with acidity ranging from 1 M to 3 M, has been validated with columns packed with silica gel loaded with HD(DiBM)P (27% wt). The treated solution was previously electrolysed in the presence of the $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$ polyanion and silver nitrate.

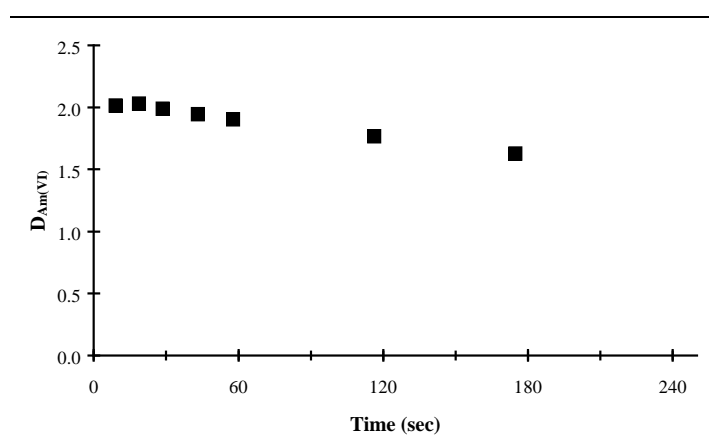
As satisfactory results have been obtained, R&D studies on Am(VI) solvent extraction have been launched.

Batch tests experiments

As our main purpose is to develop the reference process described above, Am has to be extracted from highly acidic solutions ($[\text{HNO}_3] \sim 5 \text{ M}$). In that field TBP is the most suitable molecule for the extraction of hexavalent species. In addition it is an industrially used extractant showing good stability towards radiolysis and acidic hydrolysis.

Figure 3. Kinetics of extraction of Am(VI) by TBP in 5M nitric acid

conditions: $[\text{Am}] = 3 \times 10^{-3} \text{ M}$, $[\text{HNO}_3] = 5 \text{ M}$, 30% TBP in Dodecane, $[\text{AgNO}_3] = 0.01 \text{ M}$, room temperature

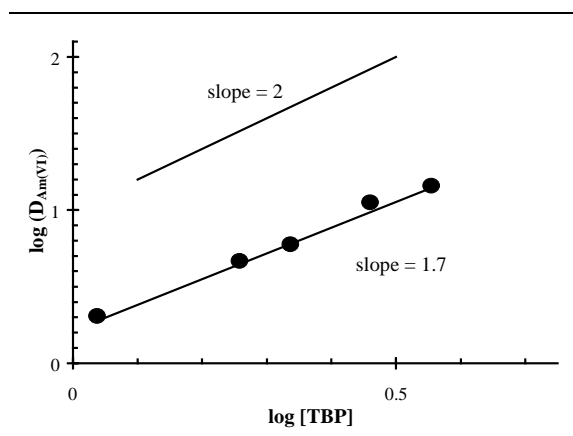


Distribution coefficients of Am(VI) have been determined in 5 M nitric acid solution for different contacting time. As shown on Figure 3, the equilibrium time is reached quickly but after 30 sec decreases slowly. This decrease is not only due to the self reduction of Am(VI) but due to the direct reduction with the solvent. These results have been confirmed during the measurement of distribution coefficient as function of TBP concentration. The logarithm representation: $\log(D_{\text{Am(VI)}}) = f(\log([\text{TBP}]))$, gives a slope of 1.7 compared to the expected slope 2 as shown on Figure 4.

The mechanism extraction of trivalent lanthanides involves three molecules of TBP per molecule of lanthanides. Therefore, as the TBP concentration increases, a diminution of the separation factor between Am and Ln(III) occurs. Thus, for the further continuous experiments a 30% v/v of TBP concentration has been chosen.

Figure 4. **Influence on the TBP concentration on distribution coefficient of Am(VI) in 5M nitric acid.**

conditions: $[Am] = 3 \times 10^{-3}$ M, $[HNO_3] = 5$ M, $[AgNO_3] = 0.01$ M, contacting time = 30 sec, room temperature



Extraction using centrifugal contactors

To confirm the possibility to extract selectively oxidised americium, a hot test has been run on a simulated Am-Cm-Ln mixture representative of a DIAMEX stripping solution [9]. During that test called SESAME 3, Am was oxidised in an electrolysis cell (both LHPA : PW and SiW have been tested) which was connected to a set of two centrifugal contactors. Once Am(III) is quantitatively oxidised to Am(VI), the solution is contacted with the organic phase (HD(DiBM)P 0.5 M or TBP 30% vol in dodecane). After two extraction stages, the aqueous phase was sent back to the electrolysis cell (the electrolysis current is not switched off during the extraction). This test was mainly performed to check the Am(VI) extraction with a liquid organic phase, so no scrubbing and stripping stages were added to the experimental set-up.

During these experimentations, the influence of the following parameters has been studied; nature of LHPA, americium concentration, nature of the extracting molecule, organic to aqueous ratio (O/A).

These tests have proved the possibility to produce Am(VI) using either PW or SiW polyanions whatever is the starting solution. Concerning the use of SiW, the oxidation kinetics of Am(III) to Am(VI) is generally slower than in the presence of PW. This confirms previous laboratory scale experiments. If americium concentration is increased (about ten times), a quantitative oxidation is still obtained. This corresponds to the treatment of a DIAMEX solution which has been concentrated as proposed in the SESAME reference scheme.

Extraction tests have demonstrated that Am(VI) extraction can be done with both selected extractants. With HD(DiBM)P the extraction kinetics of Am(VI) is much slower than with TBP, however, better separations factors between Am and Cm and trivalent lanthanides are obtained.

Concerning TBP, americium recovery yields close to 90% were reached, but due to the configuration of the set-up (no scrubbing of organic phase) an important amount of Cm(III) and Ln(III) (about 20% of initial amount) has been co-extracted with Am. This configuration of the extracting device has also brought some drawbacks such as the solubilization of organic species in the electrolyzer which prevents the americium oxidation.

Figure 5. **Extraction of Am(VI) with TBP**

conditions: *oxidation* : $[Am] = 2.6 \times 10^{-3} M$, $[HNO_3] = 4 M$, $[Ag] = 5 \times 10^{-3} M$,
 $[PW]_{free}/[Am] = 0.5T = 305 K$, $V = 250 ml$, $I = 0.5 A$, $S = 12.5 cm^2$ Pt anode (10% Ir).
extraction : TBP (30 %) / dodecane, $O = 0.8 l/h$, $A = 0.3 l/h$, $I = 2 A$ during extraction

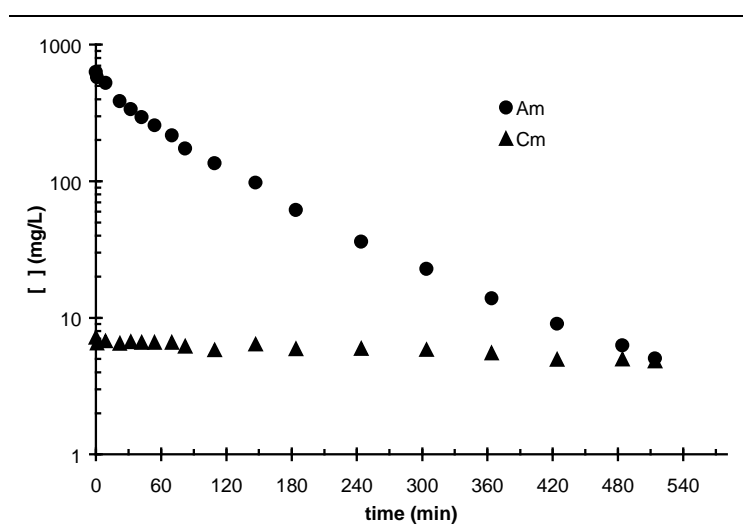


Figure 5 shows the variations of americium and curium concentrations versus time during an extraction test with TBP run on a concentrated americium solution. Am is gradually extracted from aqueous solution but the overall processing time is quite long.

Preliminary tests have confirmed the improvement of americium decontamination factor towards Cm and Ln when the loaded organic phase is scrubbed with nitric acid solution containing AgO. It was also checked that Am(VI) stripping with a reducing solution ($HNO_3 + H_2O_2$) was quite easy to achieve. Through the SESAME 3 test, the solvent extraction of Am(VI) from acidic nitric acid solutions was validated. However the tested experimental set-up did not permit to achieve the required americium recovery yields (greater than 99%). Further tests including scrubbing stages of organic and aqueous phases are planned to improve recovery yields and decontamination factors of Am. The diluent scrubbing of the aqueous phase which removes solubilized organic species coming from extraction stages is necessary to build a multistage scheme including several consecutive extraction and oxidation steps.

Further R&D Studies

Following these demonstration tests of SESAME process, more basic studies are still underway. They concern americium oxidation and extraction, LHPA removal and recycling, oxidised Am and LHPA on-line measurement, degradation and recycling of extracting molecules, recovery of silver from Am extraction raffinates. The extraction of Ce(IV) by TBP using centrifugal contactors has also been defined and successfully tested.

A new hot cell experiment using benches of centrifugal contactors is planned in the beginning of next year. It consists in the test of separation scheme including extraction, scrubbing and stripping steps. A diluent scrubbing of the raffinate will be added to enhance the electrochemical oxidation efficiency of further stages. Results of these experiments will allow to implement the separation flowsheet achieving the required performances.

Conclusion

The feasibility demonstration of SESAME principle is now achieved. Much attention is still to be paid on the extraction of Am(VI) which needs to be improved. Next hot tests should involve a more complete separation scheme as proposed in the reference scheme and take into account the main observations of SESAME 3 test. Especially, no extraction loop is expected to be used. Other studies concerning the alternative route (extraction of Am(IV)) are also underway but to a lesser extent.

REFERENCES

- [1] J.M. Adnet, L. Donnet, Ph. Brossard and J. Bourges, US Patent N°5609, 11 March 1997.
- [2] J.M. Adnet, L. Donnet, N. Faure, P. Bros, Ph. Brossard and F. Josso, Proceedings of RECOD'98, Nice, 1998.
- [3] M.S. Milyukova, M.N. Litvina, B.F. Myasoedov, *Radiokhimiya*, **25**, 1983.
- [4] J.M. Adnet, Thesis, Rapport CEA-R-5615, 1992.
- [5] A.S. Saprykin, V.P. Shilov, V.I. Spitsyn, N.N. Krot, *Dokl. Akad. Nauk SSSR*, **226**(4), 1976.
- [6] J.M. Adnet, L. Donnet, D. Chartier, N. Faure, P. Bros, Ph. Brossard, Proceedings of OECD NEA workshop, Villeneuve-lès-Avignon, 1996.
- [7] D. Chartier, L. Donnet and J.M. Adnet, submitted.
- [8] D. Chartier, L. Donnet and J.M. Adnet, *Radiochimica Acta*, accepted NS-122.
- [9] C. Madic, P. Blanc, N. Condamines, P. Baron, L. Berthon, C. Nicol, C. Pozzo, M. Lecomte, M. Philippe, M. Masson, C. Hecquet, M.J. Hudson, Proceedings of RECOD'94, London, 1994.