THE SEPARATION OF ^{241}Am FROM AGED PLUTONIUM DIOXIDE FOR USE IN RADIOISOTOPE POWER SYSTEMS

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ABSTRACT

Electrical power sources used in outer planet missions are a key enabling technology for data acquisition and communications. State-of-the-art power sources generate electricity from alpha decay of ^{238}Pu via thermoelectric conversion. However, production of ^{238}Pu requires specialist facilities including a nuclear reactor, a source of ^{237}Np for target irradiation and hotcells to chemically separate neptunium and plutonium within the irradiated targets. These specialist facilities are expensive to build and operate, so naturally, a more economical alternative is attractive to the industry. Within Europe ^{241}Am is considered a promising alternative heat source for radioisotope thermoelectric generators (RTGs) and radioisotope heating units (RHUs). As a daughter product of ^{241}Pu decay, ^{241}Am exists in 1000 kgs quantities within the UK civil plutonium stockpile.

A chemical separation process is required to extract the ^{241}Am in a pure form and this paper describes the AMPPEX process (Americium and Plutonium Purification by Extraction), successfully developed over the past five years to isolate ^{241}Am in high yield (> 99%) and to a high purity (> 99%).

The process starts by dissolving plutonium dioxide in nitric acid with the aid of a silver(II) catalyst, which is generated electrochemically. The solution is then conditioned and fed to a PUREX type solvent extraction process, where the plutonium is separated from the americium and silver. The plutonium is converted back to plutonium dioxide and the americium is fed forward to a second solvent extraction step. Here the americium is selectively extracted leaving the silver in the aqueous phase. The americium is stripped from the solvent and recovered from solution as americium oxalate, which is calcined to give americium dioxide as the final product. This paper will describe the development of the separation process over a series of six solvent extraction separation trials using centrifugal contactors. The material produced (~ 4g ^{241}Am) was used to make ceramic pellets to establish the behaviour of americium oxide material under high temperature (1450°C) sintering conditions.

The chemical separation process is now demonstrated at concentrations expected on the full scale facility taking this process to TRL 4-5.

1. INTRODUCTION

Over the last few years there has been an interest by the European Space Agency (ESA) to develop power systems for space missions within Europe [1] and a study was initiated to explore the development of radioisotope powered systems suitable for producing heat and electrical power. A wide range of isotopes were considered and while ^{238}Pu was the most attractive from a performance perspective, the most accessible and economically viable isotope in Europe proved to be ^{241}Am with a half-life of 432.7 years and a specific thermal power output of 0.1146 W_{th}/g. The radioisotope ^{241}Am is a by-product of the civil nuclear energy industry. Over the last few decades France and the UK have provided a service to reprocess spent nuclear fuel from nuclear reactor sites, separating the uranium and plutonium and storing these products as the oxides ready for reuse in new fuel. Some of the plutonium has been stored for many decades and one of the isotopes (^{241}Pu), present within the plutonium, has beta decayed to the isotopically pure ^{241}Am . A programme of work was initiated by ESA in 2009 to develop a process to isolate ^{241}Am from plutonium dioxide (PuO_2) [2, 3], while separate parallel studies established how the isotope would be incorporated in to power systems [4]. This paper provides an overview of the radioisotope production aspects of the programme.

2. CHEMICAL SEPARATION

The outline process to separate americium from plutonium dioxide powder is shown in Fig. 1. The process involves dissolving the plutonium dioxide using a silver catalyst and then separating the plutonium from americium and silver by solvent extraction. Next the silver is removed in a second solvent extraction process and the purified americium nitrate solution is treated with oxalic acid to precipitate americium oxalate. This oxalate solid is heated and decomposed converting to an

americium dioxide product ready for making ceramic pellets. The ultimate aim of the radioisotope production project is to demonstrate a feasible method of producing a pure product that can be made into a ceramic heat source.

Figure 1. Outline of the chemical separation process.

3. DEVELOPMENT OF THE SEPARATION PROCESS

The development work required to underpin the concept design of the plant focused on the dissolution, solvent extraction and americium finishing processes as the most technically immature aspects that needed to be demonstrated. This demonstration was performed in three experimental runs. Run 1 demonstrated the proof of concept at low americium concentrations with relatively small total amounts of plutonium dioxide. Runs 2 and 3 demonstrated that the process could work at normal operating concentrations (Run 2) as well as beyond the bounding case concentrations (Run 3) of americium whilst maintaining the product quality and minimising wastes. In all of our solvent extraction development runs a 32 stage centrifugal contactor rig was used with counter-current solvent and aqueous feeds into banks of 2 or 4 contactors with 1cm rotors the operational details of which can be found elsewhere [5]. The development results are discussed in more detail in the following sections.

3.1. PLUTONIUM DIOXIDE DISSOLUTION

This process allowed the very insoluble plutonium dioxide powder to be dissolved ready for the next stage in the process.

In Run 1 of the development work a 100 mL electrochemical cell (Fig. 2) based on the CEPD design [6] was used producing a range of plutonium concentrations from 5 – 200 gPu/L all within a 2 hour reaction period. The cell consisted of an outer platinum anode and titanium or tantalum cathode separated by a porous alumina membrane. Variables such as the current, anode surface area, anode design, stirrer speed, silver nitrate and nitric acid concentration were explored. The current efficiency was generally between 70–80%. In Runs 2 and 3 a 500 mL cell (Fig. 2) was employed that contained similar anode and cathode design but also had space for a UV/vis fibre optic probe that allowed progress

of the reaction to be measured in-situ, thus reducing the manual operations required.

Figure 2. The two sizes of dissolution cell used; left) 100 mL cell; right 500 mL cell with UV/vis dip probe.

The 500 mL cell performed less efficiently (60-70% current utilised) but 80 g of plutonium dioxide was completely dissolved within 140 minutes using 0.1 mol/L silver in nitric acid. During dissolution the UV/vis signal for silver(II) (600 nm; shoulder) is reduced while PuO₂ is dissolving and the Pu(VI) peak at 830 nm grows until the dissolution is complete. Once complete, the silver(II) concentration rapidly increases to a steady state providing an excellent indication of a completed reaction. Next NO_x gas is passed through the liquor at 50°C for around 30 minutes and the UV/vis spectrum is monitored until the Pu(VI) signal at 830 nm is replaced by the characteristic Pu(IV) spectrum (Fig 3). Once conditioned, the solution is filtered and analysed for nitric acid and plutonium concentrations. The liquor is then made up to ~100 gPu/L and 4.5 mol/L nitric acid ready to be fed to the solvent extraction stage. It was at this point additional uranium and neptunium was added to increase their concentrations to that representative of fully aged plutonium dioxide. Neptunium is generated from the radioactive decay of americium and uranium from the decay of plutonium isotopes.

Figure 3. The UV/vis spectrum of the plutonium nitrate solution during NO_x conditioning as it changes from Pu(VI) to Pu(IV).

3.2 SEPARATION OF PLUTONIUM FROM

AMERICIUM

In this part of the process a flowsheet was designed based on well established PUREX technology. In Run 1 of the development work the objective was to assess how all of the main elements behaved during extraction into 30% TBP/OK solvent followed by stripping of the plutonium using a hydroxylamine nitrate solution to reduce the extractable Pu(IV) to the poorly extracted Pu(III). At this stage it is important to ensure as much of the plutonium, neptunium and uranium as possible is removed from the americium stream. This is to ensure a pure product because the next solvent extraction stage does not provide such a good decontamination factor for these elements. Another concern was whether the acidity carried over within the solvent would slow the kinetics of plutonium reduction [7].

Once proof of concept was established the amounts of americium in the feed were increased (Tab. 1). The americium concentration in Run 3 was increased to 5.2 g/L by adding the americium produced in Run 2 (~1.7 gAm) to the dissolved aged plutonium dioxide in Run 3.

Table 1. Feed concentrations to the first solvent extraction process

	Full scale process	Run 1	Run 2	Run 3
	g/L	g/L	g/L	g/L
Np	0.27	0.23	0.10	0.26
U	0.39	0.33	0.58	0.42
Pu	95	89	98	97.7
Am	4.80	0.92	2.94	5.20
Ag	10.79	10.79	7.90	9.58
Volume (mL)	3000	500	633	727
Nitric acid (mol/L)	3.5	3.5	4.5	4.2

Plutonium was effectively extracted in Run 1 with only 0.008 gPu/L following the americium product (Tab. 2). The stripping was successfully demonstrated at ambient glovebox temperatures (20-30°C) with > 99.9% of the plutonium recovered. After modelling the plutonium and nitric acid behaviour in the extract and stripping stages of the flowsheet, the feed nitric acid concentration was increased (Tab. 1) to aid extraction and increase the acidity of the americium/silver product. These improvements gave a reduction in the amount of impurities in the americium product (Tab. 2) and ultimately reduced the amount of radioactivity in the

waste streams. With an increase in feed acidity the amount of plutonium that followed the americium dropped by nearly two orders of magnitude by %w/w (Tab. 2). The plutonium was sufficiently free of silver to meet the product specifications required, providing a fresh plutonium product free of americium. Most of the uranium was extracted, 90% of which remained in the solvent during the stripping stage. As expected [8], the neptunium was split between the plutonium product (55%) and the americium product (41%) with the remainder left in the solvent.

Table 2. Relative concentrations of key elements in the americium/silver product.

	Run 1 %w/w	Run 2 %w/w	Run 3 %w/w
Np	9.50%	1.04%	2.13%
U	0.10%	0.03%	0.03%
Pu	1.70%	0.05%	0.02%
Am	89%	98.90%	97.8%

The main impurity in the americium product, other than silver (~5g/L), is neptunium. The amount of neptunium extracted with the plutonium could be increased further by increasing the acidity and temperature and controlling the nitrous acid concentration to generate more extractable Np(VI) [8], however it was decided that the decontamination factors downstream were sufficient to not warrant further development in this area.

3.3 SEPARATION OF AMERICIUM FROM SILVER

The strategy used for separating americium from silver was solvent extraction using a chelating nitrogen donor ligand TODGA (Fig. 4) that is known to extract americium very well but tends to form a third phase quite readily in hydrocarbon diluents [9]. Third phase formation can cause difficulties during the extraction process and needs to be avoided. An additive, DHOA (Fig. 4), was used to mitigate this third phase effect and allow sufficient americium loading of the solvent. The solvent formulation was optimised to provide good extraction at 2-3 mol/L nitric acid ($D_{Am} \sim 50$) while allowing efficient stripping at low (~ 0.01 mol/L) nitric acid concentration ($D_{Am} < 0.1$).

During the development of this part of the flowsheet one objective was to minimise the volume of solvent used and increase the concentration of americium in the final product, from 0.4 gAm/L in Run 1 to 6 gAm/L in Run 3. This enabled the product americium nitrate solution could be used directly in the oxalate precipitation stage, avoiding an evaporation step and reducing process costs.

Figure 4. Reagents used in the solvent formulation used for the americium silver separation

Analysis of the products from this second solvent extraction stage demonstrated that extraction of americium is excellent and the amount that is lost to the silver stream is low, typically 1×10^{-6} g/L, which is approaching the practical levels of unavoidable cross contamination within our centrifugal contactor rig. The decontamination of silver from the americium product was excellent with typically less than 0.1 mg/L in the americium product (Tab. 3). The main contaminant is again neptunium but this is significantly reduced because most of what is extracted remains within the solvent. Only around 15% of the original neptunium with a decontamination factor of 6.7 to 11.6 times less neptunium in the americium product compared to the feed solution. The final purity of the americium as a percentage of the key elements analysed is > 99% (Tab. 3).

Table 3. Relative concentrations of key elements in the americium product stream after the americium/silver separation

	Run 1 %w/w	Run 2 %w/w	Run 3 %w/w
Np	1.14%	0.21%	0.34%
U	0.10%	0.02%	0.03%
Pu	0.53%	0.11%	0.04%
Am	98.21%	99.63%	99.59%
Ag	0.02%	0.03%	0.001%

4. AMERICIUM OXALATE PRECIPITATION

In order to obtain an americium oxide powder the americium nitrate solution in Tab. 3 needs to be converted to a suitable. Americium oxalate is a good precursor to the formation of an americium oxide because the powder formed is easily filtered and readily decomposes to the oxide. A system was developed for continuous precipitation using a vessel with a spout that overflowed onto a simple filtration bed (Fig. 5). The americium nitrate and oxalic acid stocks were pumped into the precipitator at a set flowrate that gave a steady state average residence time within the vessel of around 14 mins. This design helped to minimise the extremity dose to operators with very little manual intervention required. Around 3.5 g of americium were recovered in one run and the pale yellow precipitate (Fig. 6) was easily collected from the filter membrane after washing the

solid free of oxalic and nitric acids with demineralised water. The americium nitrate feed contains 0.25 – 0.3 mol/L nitric acid and the amount of americium lost to the filtrate is typically 1 mgAm/L giving an americium recovery of > 99.9%.

Figure 5. Experimental setup for the precipitation of americium oxalate.

Another benefit of the oxalate precipitation step is an additional decontamination factor for neptunium of around 5. The solubility of americium in the filtrate is consistent with published literature values [10] at ambient temperatures (23-25°C), the final nitric acid (0.23 mol/L) and oxalic acid (0.1 mol/L) concentrations. Increasing the precipitation temperature to 60°C leads to an increase in americium losses to around 10 mg/L, which is also acceptable from a recovery viewpoint and provides the option of influencing the americium oxalate particle size distribution and morphology. It is expected, from the behaviour of plutonium oxalate, that the size and morphology of the americium oxide will be similar to the parent oxalate, which may be important when making ceramic heat source pellets.

5. AMERICIUM OXIDE FORMATION

The americium oxalate needs to be converted from the americium oxalate to the oxide, which will be the feed material for making the ceramic heat source. A comprehensive study on the behaviour of cerium oxalate formation and conversion to the oxide was performed to establish how the change in powder properties changed as the precipitation and calcination conditions were altered. These surrogate oxide powders were then pressed into pellets and sintered at temperatures up to 1600°C. The objective of this study was to establish whether by altering the precipitation and calcination conditions optimal powder properties could be established that would provide suitable ceramic material without the need for milling of the powder. The details

of this study will be published elsewhere; suffice to say that the optimal conditions decided were a precipitation at 25°C and decomposition of the oxalate at 650°C. This turned the oxalate from pale yellow to a black oxide powder (Fig. 6).

Figure 6. Americium oxalate before (left) and after (right) decomposing to the oxide.

For each of the development runs a sample of the oxide was analysed to establish the concentration of the key elements as impurities in the sample. An example of the final purity of the americium with respect to the other key elements analysed is compared against the americium nitrate product for development Run 3 (Tab. 4).

The analytical results demonstrate that the relative amount of neptunium has decreased, consistent with the analysis of the filtrate liquors from the americium oxalate precipitation experiments. The purity of the americium appears to be very good (> 99%), however, these results are preliminary and do not establish whether there are any volatile species such as carbon remaining within the material.

Table 4. Concentrations of key elements in the americium nitrate solution and americium dioxide for development Run 3.

	Americium nitrate	Americium dioxide
	%w/w	%w/w
Np	0.34%	0.07%
U	0.03%	0.03%
Pu	0.04%	0.02%
Am	99.59%	99.88%
Ag	0.001%	0.001%

After heat treating this material to 1450°C in a reducing atmosphere (5% H_2 /Argon) for 4 hours followed by oxidising at 800°C for 4 hours the resulting AmO_2 material was tested for americium assay by calorimetry to determine the power output per gram of material. The results showed an assay of 100.4% $\pm$ 0.43 % confirming the high purity of the sample.

6. AMERICIUM OXIDE PELLET FORMATION

The americium oxide powder was then used in a small number of experiments to produce a sintered ceramic pellet. The powder morphology is consistent with particle size and shape of surrogate cerium dioxide

material produced using identical oxalate precipitation methods. In our studies on cerium dioxide, made from the decomposition of cerium oxalate, particle morphology is retained upon decomposition to the oxide. The similarity of the particle shapes (Fig. 7) would suggest that this also occurs when americium oxalate is decomposed to americium dioxide, suggesting that cerium oxalate and oxide is a good surrogate for americium oxide powders.

Figure 7. Comparison of cerium oxide (left) and americium oxide (right) powder morphology. Powders produced under the same oxalate precipitation conditions of continuous precipitation at 25°C.

When making ceramic pellets the chemical behaviour of americium oxides needs consideration. It is well documented that americium dioxide loses oxygen when heated to beyond 800°C to form an oxide with a lower oxygen to americium ratio AmO_{2-x} (where $x = 0 - 0.5$) and can occur at even lower temperatures in a reducing atmosphere [11, 12]. This is an important safety consideration because in launch accident scenarios it is possible for the heat source material to reach high temperatures (< 1800°C). The loss of oxygen at relatively low temperatures means the cladding that encapsulates the heat source needs to be designed to deal with such gas losses. If it is not possible to manage such gas releases safely then the use of AmO_2 may be excluded. It is then also important to understand the conditions under which ceramic Am_2O_3 can be made and stored.

There is also the potential for americium to volatilise either as $\text{AmO}_2(\text{g})$, $\text{AmO}(\text{g})$ or $\text{Am}(\text{g})$ and so tests were performed to establish how the oxide stoichiometry changes under different sintering atmospheres and whether significant mass loss of material occurs.

In order to explore some of these expected difficulties a series of pelleting trials were performed within shielded hot cells where the powder was manipulated using remotely operated mechanical arms to minimise the radiation dose to the operators. Around 400 mg of as received americium dioxide powder was pressed into a “green pellet” that and then sintered in a high temperature furnace. The pellets were sintered at 1450°C under varying atmospheres (Tab. 5) to give a sintered pellet. The sintered pellets produced were analysed for geometric dimensions and mass to calculate the density

of the pellets. The densities and % of theoretical Density (TD) are shown in Tab. 6.

No detectable levels of americium were lost from any of the sintering trials all of which were performed at 1450°C, consistent with previous literature reports [13, 14].

Table 5 Sintering atmospheres and pressing pressure of the americium oxide pellets made.

Pellet No.	Sintering Atmosphere	Die diameter (mm)	Press. (MPa)
1	Ar/H ₂ /2000 ppm H ₂ O	5.40	480
2	Ar/H ₂ /2000 ppm H ₂ O	5.40	480
3	Ar/H ₂	5.40	480
4	Air	5.40	480
5	Argon	5.40	480
6	Ar/H ₂	5.40	480
7	Ar/H ₂	5.25	508
8	Ar/H ₂	5.25	323

In most cases, where a reducing atmosphere is employed, sufficiently high pellet densities were obtained (~ 90% TD), although cracking of the pellet around the circumference (Fig. 8) occurred (with the exception of pellet 3). While it is not clear why cracking occurs there are a number of possible contributing factors:

- The mechanism may be end-capping where the pellet expands as it comes out of the die as the stress is relieved there is radial expansion. There are many factors that influence the likelihood of end-capping [15] such as powder characteristics, pressing pressure, tapering of the die, material of fabrication of the die and lubrication of the die. Given the small size of the discs this mechanism seems less likely.
- The loss of oxygen upon sintering of the sample could cause high porosity leading to weakened pellets and linked pores leading to cracks.
- The changes in phases from face centred cubic (fcc) AmO₂ phase to body centred cubic (bcc) Am₂O_{3+y} phase to hexagonal Am₂O₃ phase may result in stresses within the material as the pellet heats, loses oxygen and cools down [12].
- Thermal expansion of the hexagonal Am₂O₃ phase is higher than fcc AmO₂ phase and may result in stresses during thermal cycling.

- The volatile impurity found within the material could also be causing high porosity and cracks as it is released during pre-treatment.

Table 6. Density and theoretical density of the americium oxide pellets made before (green) and after (sintered) sintering at 1450°C.

Pellet No.	Green Pellet		Sintered Pellet		Am-O form
	Density (g/cm ³)	TD* (%)	Density (g/cm ³)	TD* (%)	
1	6.61	56.2	9.36	80	Am ₂ O ₃
2	6.85	58.2	8.5	72	Am ₂ O ₃
3	6.78	57.6	10.71	91	Am ₂ O ₃
4	6.69	57.3	9.58	82	AmO ₂
5	6.62	56.2	N/A	N/A	Am ₂ O ₃
6	6.56	55.7	N/A	N/A	Am ₂ O ₃
7	6.63	56.3	10.71	91	Am ₂ O ₃
8	5.89	50.0	10.57	90	Am ₂ O ₃

*TD for AmO₂ = 11.68 g/cm³; for Am₂O₃ = 11.77 g/cm³ [16].

Pre-treatment of the green pellet performed at 1050°C for 10 hours under the sintering atmosphere to drive off any impurities did not prevent this cracking.

Figure 8. Americium oxide pellet after sintering showing cracking around the circumference (Pellet 7).

When forming pellets 1-6 a small sample of americium oxide powder was sintered by the side of the pellet and then analysed to determine the crystal form of the material post sintering. The powders were analysed using Raman spectroscopy and powder X-Ray diffraction (PXRD).

The reduced form of americium oxide tends to form and this is identified by the A-type hexagonal Am₂O₃ seen in the PXRD diffractogram (Fig. 9) and the characteristic Raman spectrum (Fig. 10). Even without a reducing atmosphere (Argon, only pellet 5) complete reduction occurs.

An AmO₂ pellet could only be produced if sintering is performed in air and the temperature is held at 800°C for

a period to ensure a stoichiometry of $\text{AmO}_{2.00}$.

Figure 9. Examples of the PXR D results for a reduced Am_2O_3 (left) and oxidised AmO_2 (right) pellet.

Figure 10. Examples of the Raman results for a reduced Am_2O_3 (left) and oxidised AmO_2 (right) pellet.

Note the Raman spectrum of the hexagonal A-type Am_2O_3 is the first time a clean spectrum with low contamination from other phases has been reported [17].

The purity of the Am_2O_3 PXR D samples and lack of re-oxidation in the manipulation of the sample between analytical facilities demonstrates that the reduced form of americium oxide can be handled albeit in environments that are nominally inert atmospheres ($< 1\% \text{O}_2$). This provides confidence that this material can be controlled to avoid oxidation using standard inert systems if this was to be the final chemical form.

7. CONCLUSIONS

The separation process to extract americium from aged plutonium dioxide is mature and demonstrated at actual americium concentration levels with no detriment to the recovery ($> 99\%$) or purity ($> 99\%$) of the americium produced. This takes the TRL level from 3 to 4-5. The requirements for building a full scale facility and dealing with the radioactive waste streams generated are now fully understood. Investment is now required to build the full scale facility to establish a throughput high enough to support the ESA mission.

From these preliminary pelleting trials it is clear that the reduced Am_2O_3 form is readily generated even in the absence of a reducing hydrogen atmosphere, consistent with reported thermodynamic data. Pellets containing Am_2O_3 are sufficiently densified but further development work on the sintering conditions and how they relate to the particle morphology remains. If Am_2O_3 is the preferred chemical form then the next development stage will also need to assess chemical interactions with potential cladding materials. Further studies are aimed at producing a Radioisotope Heat Source prototype using 10s g of americium oxide material.

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9. REFERENCES

1. Summerer, L. & Stephenson, K. (2011). Proc. IMechE G: J. Aero. Eng. 225, 129–143.
2. Cordingley, L. Rice, T. Sarsfield, M. J. Stephenson, K. & Tinsley T. (2011). Paper s27_4cordi, Proc. '9th European Space Power Conference', Saint Raphaël, France, 6–10 June, (ESA SP-690, October, 2011).
3. Baker, S.R. Bell, K.J. Brown, J. Carrigan, C. Carrott, M.J. Gregson, C. Clough, M. Maher, C.J. Mason, C. Rhodes, C.J. Rice, T.G. Sarsfield, M.J. Stephenson, K. Taylor, R.J. Tinsley, T.P. Woodhead, D.A. & Wiss, T. (2014). Paper nps5_sarsfield, Proc. '10th European Space Power Conference', Noordwijkerhout, The Netherlands, 15–17 April, (ESA SP-719, May 2014).
4. Williams, H. R. Ambrosi, R. M. Bannister, N. P. Samara-Ratna, & P. Sykes, (2012). J. Int. J. Energy Res., 36, 1192.
5. Carrott, M.J. Bell, K. Brown, J. Geist, A. Gregson, C.R. Heres, X. Maher, C.J. Malmbeck, R. Mason, C. Modolo, G. Muellich, U. Sarsfield, M.J. Wilden, A. & Taylor R.J., (2014). Solv. Extr. Ion Exch. 32, 447.
6. Ryan, J.L. Bray, L.A. & Boldt, A.L. (1987). "Dissolution of PuO_2 or NpO_2 using electrolytically regenerated reagents", United States Patent 4686019.
7. Koltunov, V.S. & Zhuravleva, G.I. (1978). Radiokhim. 20, 94.
8. Taylor, R.J. Gregson, C.R. Carrott, M.J. Mason, C. & Sarsfield, M.J. (2013). Solv. Extr. Ion Exch. 31, 442.
9. Sasaki, Y. Sugo, Y. Suzuki, S. & Kimura, T. (2005). Anal. Chim. Acta, 543, 31.
10. Burney, G.A. & Porter, J.A. (1967). Inorg. Nucl. Chem. Letts., 3, 79.

11. Chikalla, T.D. & Eyring, L. (1968). *J. Inorg. Nucl. Chem.*, 30, 133.
12. Lebreton, F. Belin, R.C. Delahaye, T. & Blanchart, P. (2012). *J. Solid State Chem.*, 196, 217.
13. Nishi, T. Takano, M. Itoh, A. Akabori, M. Arai, Y. Minato, K. & Numata, M. (2008). *J. Nucl. Mats.*, 373, 295.
14. Nishi, T. Itoh, A. Ichise, K. & Arai, Y. (2011). *J. Nucl. Mats.*, 414, 109.
15. Balakrishna, P. Chakraborty, K.P. & Singh, A. (1996). *Ind. J. Engin. Mats. Sci.*, 3, 196.
16. D.R. Lide, “Handbook of Chemistry and Physics”, 81st Ed., pp 4-40, (2000-2001).
17. Horlait, D. Caraballo, R. Lebreton, F. Jégou, C. Roussel, P. & Delahaye, T. (2014). *J. Solid State Chem.*, 217, 159.