MANAGEMENT AND REPROCESSING OF
DISUSED NEUTRON SOURCES IN ATALANTE FACILITY

L. Donnet, C. Maillard, I. Solinhac, A. Millet, P. Bros,
V. Boyer Deslys, S. Paillard, M. Ranchoux
Actinides, Analysis and Experiments Office
CEA/Valrhô, BP 17171, 30207 Bagnols sur Cèze Cedex, France

ABSTRACT

The French Atomic Energy Commission (CEA), which supplies some radioactive sources both within and outside the CEA Group, is responsible for organizing and carrying out the disposal of the French sources at the end of their service lives. The ATALANTE facility is required to recover both neutron and gamma disused sources with activity levels exceeding 11 GBq (> 300 mCi).

This activity comprises two major facets in the ATALANTE facility:

- A management aspect : examining source retrieval requests and identifying sources to be recovered, reviewing inventories, enumerating sources, answering requests, organizing transportation, managing interim storage facilities, etc.,

- A technical and scientific aspect: destroying the disused sources using techniques suitable for high-activity media with the objective of recycling the materials after separation by qualified processes. The aspect includes also R&D for the separation of compounds (actinides and mainly beryllium).

A research program was undertaken to reduce the neutron yield of this mixture and recover the material with the following objectives:

- separate the americium from the beryllium and stabilize the americium as AmO_2;

- process the beryllium and effluent streams to obtain a Be chemical form and an Am concentration suitable for removal from the ATALANTE facility.

The treatment produces an actinide oxide (which is used later for R&D studies) and solid beryllium nitrate, which is considered as a waste and transferred to a surface interim storage site if the overall activity of the package after 300 years is less than 50 MBq (management for radioactive waste national agency ANDRA specifications). The Material Analysis and Metrology Laboratory of ATALANTE validate the residual alpha activity in the waste. The techniques used include alpha spectrometry and L line X ray fluorescence for alpha emitters, and plasma torch measurements (ICP-AES and ICP-MS) for beryllium analysis. Specific equipments for transport (B type cask), storage and treatment (hot shielded cells) are used for this activity.

INTRODUCTION

In 1990, French government decided that suppliers had to recover spent radioactive sources at the end of their use or within ten years after. In this frame, the ATALANTE facility is in charge

of the recovery of both gamma and neutron French sources with activity levels above 300 mCi (11 GBq). This task comprises two major parts. A management aspect consisting of:

- examine sources recovery requests,
- identify sources to be recovered from inventories,
- organize transports,
- manage small interim storage facilities.

A technical and scientific aspect concerning mainly:

- The development of specific devices to implement in hot cells,
- R&D studies to carry out actinides separation from beryllium.

The fabrication of sealed sources ended on 1992 at the FONTENAY AUX ROSES center and the activity was transferred to ATALANTE in MARCOULE where specific equipments have been implemented to keep on. This paper presents an overview of these equipments and gives the status on the R&D in progress concerning the recovery of spent high intensity neutron sources.

Management of Disused Neutron Sources

Neutron Sources to be Recovered

Most of the neutron sources comprise a mixture of beryllium (metal or oxide) and an alpha emitter such as ^{241}Am, ^{244}Cm, ^{238}Pu or ^{239}Pu. Neutrons are produced by reaction between alpha particles and beryllium as follows:
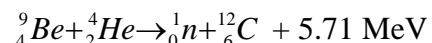
$$^{9}_{4}Be + ^{4}_{2}He \rightarrow ^{1}_{0}n + ^{12}_{6}C + 5.71 \text{ MeV}$$

Table I shows some neutron sources characteristics.

Table I. Neutron Sources Characteristics

Source type	Half life (year)	Alpha emission energy (MeV)	Neutron yield	
			($\times 10^6$ n/s/Ci)	($\times 10^6$ n/s/g)
^{241}AmBe	432	5.4	2.2	7.7
^{239}PuBe	24400	5.1	1.5	0.09
^{244}CmBe	18.1	5.8	2.6	200

PuBe sources are often used as standards for neutron counters because of their stability. AmBe sources are used in numerous fields: petroleum industry (well logging), soil science (density and moisture content determinations), activation analysis…

The inventory of the neutron sources manufactured in FONTENAY AUX ROSES and then in MARCOULE has been done (cf. Table II). It allows identifying disused sources to be recovered which are stored in or out of ATALANTE.

Table II. Neutrons Sources Inventory

Source Type	Actinide mass stored in ATALANTE		Actinide mass stored out of ATALANTE		TOTAL (g)
	sources	G	sources	g	
^{241}AmBe	207	80	919	590	670
^{239}PuBe	4	432	26	713	1145
^{244}CmBe	10	0.37	30	3	17

Most of the plutonium beryllium neutron sources are Pu-Be alloy that have been prepared by reduction of plutonium dioxide or fluoride by beryllium and described by several authors [1][2][3][4]. The AmBe neutrons sources have been prepared by mixing of americium dioxide and beryllium powder. ^{241}AmBe and ^{239}PuBe represent significant masses which could be used for other applications (R&D studies, …) and require some R&D for reprocessing.

Main equipments used for the neutron sources recovery

A specific cask (photo n°1) has been developed by the CEA for high activity sources transport. The pending renewal of approval by the French safety authority is scheduled for 2005. This shipping container allows transporting a large variety of actinides as shown in table III.

Table III. CTB Cask Contents

Element	Isotopes	Weight (g)	Element	Isotopes	Weight (g)
Tc	99	100	Am	241- 243	30
Th	228	10^{-2}		242	$2\ 10^{-2}$
	229	250	Cm	244	6
	Natural	1000		248	10^{-3}
U	232	2	Cf (special form)	252	$5\ 10^{-5}$
	233-234-235	30	Alpha emitters and	^{238}Pu	2.92
	237	250	light element (Be, B,	^{239}Pu	250
Np	238	30	F, C, or Li) mixtures	^{241}Am	14.5
	239	10^{-3}	in special form	^{244}Cm	0.617
Pu	238	30			
	239-240-241-242	250			

In the ATALANTE facility, the RESO room is devoted to the low activity radioactive sources storage. In the case of actinide beryllium sources, it cannot be used because of the intense neutron emission. So, sources are directly introduced into the C10 hot cell (cf. photo n°2), which has a biological shield suitable for high neutron emissions.

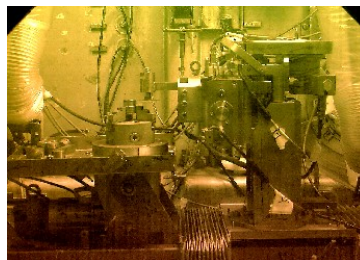Photo n°1: CTB Cask

Photo n°2: C10 Hot cell – General view

Photo n°3: Sources opening machine

After their introduction, the sources are opened with a specific device (photo n°3). Since 1997, about 160 [241]AmBe sources have been opened, leading to the recovery of about 600 g of material (Am + Be). R&D studies are now in progress at the L6 laboratory to perform Am/Be separation. Specific analytical developments are also needed, in particular to characterize the waste containing the beryllium. These tasks are carried out in laboratories L19 (ICP measurements) and L27 (radiometric determinations). The R&D results will be used to perform the chemical operations in hot cells.

REPROCESSING OF THE AmO_2/Be SOURCES

Studies have been undertaken to reduce the neutron yield of the mixture (Am/Be) and to recover the material with the following objectives:

- separate the americium from the beryllium and stabilize the americium as AmO_2;
- process the beryllium and effluent streams to obtain a Be chemical form and an Am concentration suitable for removal from the ATALANTE facility.

Different steps have been studied:

- to dissolve the AmO2/Be mixture,
- to perform the Am/Be separation,
- to obtain pure americium,
- to produce Be nitrate at an activity level suitable for a waste surface site disposal.

The obtained results allow proposing a diagram of the reprocessing that will have to be validated with actual material.

AmO$_2$/Be dissolution

Different media has been tested for AmBe sources dissolution:

- Highly concentrated nitric acid, which enables a selective dissolution of Am. Indeed, from 5, the beryllium metal is insoluble in highly concentrated nitric acid due to passivated layer formation.

- Sodium hydroxide, which enables a selective dissolution of Be 5.

- Nitric acid between 6 to 7 M, which enables a total dissolution of Am and Be. At high temperature the dissolution kinetics should be increased compared to those observed by 6.

The study involved about 50 mg of powder (5 mg Am, 45 mg Be), and yielded the following results:

- Dissolving AmO2/Be in 15 M HNO3 at room temperature results in complete and rapid dissolution of Am (2 hours) and virtually complete but slow dissolution of beryllium (48 hours).

- Dissolving AmO2/Be in 7 M boiling NaOH results in partial dissolution of Am (60% in 6 hours). Be metal fully and rapidly (<30 min) dissolves, but then precipitates as a white (Be(OH)2) powder.

- Dissolving AmO2/Be in boiling 7 M HNO3 results in complete and rapid dissolution of Am (<30 min) as expected.

The third method was selected to reprocess the sources.

Am^{3+}/Be^{2+} separation by Am oxalate precipitation

The separation AmBe by oxalate precipitation is based on the difference of solubility of each element in a low acid concentration solution. In fact the solubility of oxalate beryllium is around 750g/1000g in 0.1 M oxalic acid solution 7, whereas the americium solubility is around 1 mg.L^{-1} in 0.1 M oxalic acid solution 8. The process is used for conversion or co conversion of actinide in oxide 9.

Am/Be separation was performed under standard Am^{3+} oxalate precipitation conditions using AmO$_2$/Be dissolution solutions (pH=1, [H$_2$C$_2$O$_4$]$_{excess}$ = 0.1 M). The Am/Be separation was very efficient. The Am decontamination factor with respect to Be, DF$_{Am/Be}$, was better than 700. The americium oxalate precipitate contained less than 1 wt% beryllium and was suitable for reconditioning as an oxide for other applications. Conversely, the americium content ([Am] > 3 mg.L^{-1}) of the beryllium solution (filtrate) still exceeded the limit for removal of Be waste from the ATALANTE facility (maximum permissible limit: 12.7 µg Am.g^{-1} of waste). An additional Be decontamination step with a (Be/Am) decontamination factor of about 300 was necessary.

Enhanced Be/Am decontamination by chromatography

Three chromatography media (CMPO(13%) + TBP(27%) + GC-71, Dowex 50WX8 cation exchange resin, TBPDMDBTDMA(30%) + SiO_2) were tested on the basis of published findings that Am/Be separation is possible in nitric acid without requiring a salting-out or complexing additive 10. Based on the Kd values determined from a synthetic Am solution and synthetic Be solutions, we continued these studies with the cation exchange resin (Table IV).

Table IV. Am Distribution Factor

	$[HNO_3]$ (M)	Kd_{Am} $(mL.g^{-1})$	Kd_{Be} $(mL.g^{-1})$
DOWEX 50WX8 cation exchange resin	0.25	11393	35.4
	7	0.89	0.23
DMDBTDMA(30%) + SiO_2	0.01	1.74	Low*
	3	13.2	Low*
	5	16.8	Low*
CMPO(13%) + TBP(27%) + Amberchrom CG-71 polymer	0.01	2.6	Low*
	2	115.8	Low*
	3	105	Low*

*Poor sensitivity of the absorption spectrophotometry determination method: $[Be]_{before} = [Be]_{after}$

The studies showed that the apparent Am distribution factor is highly dependent on the cation concentration of the feed solution: $Kd_{Am} > 1000$ if $[Be^{2+}] < 1$ g.L^{-1}, $Kd_{Am} < 4$ with $[Na^+] = 4$ mol.L^{-1} (filtrate).

DOWEX 50WX8 resin is therefore unsuitable for processing large quantities of AmO_2/Be sources: a 600 g batch of AmO_2/Be would require 600 liters of solution and probably several kilograms of resin.

However chromatographic extraction using cationic resin could probably be used to enhance Am decontamination after the Am oxalate precipitation. This step will be tested soon.

Other AmO_2/Be separation routes

Am^{3+}/Be^{2+} separation by selective Be hydroxide precipitation has been examined. pH ranges corresponding to the formation of solid $Be(OH)_2$ and $Am(OH)_3$ compounds are really distant ($Be(OH)_2$: $5 < pH < 811$; $Am(OH)_3$: $pH > 8$ 8). The first run at pH 7.9 leads to a Be/Am separation factor close to 2. Be is almost quantitatively precipitated with 50 percent of americium. In the second run done at pH 7.0 precipitation Be yield is only 78 percent. The Be/Am separation factor is higher than that obtained for the previous experiment but is still too low (3). This route is not efficient enough and has been given up.

Am^{3+}/Be^{2+} separation by selective Am hydroxide precipitation may also be possible based on published findings 11. $Be(OH)_2$ dissolves at pH>12, forming the soluble species $Be_2(OH)^{3+}$ and $Be_3(OH)_3^{3+}$. Am remains as a solid hydroxide. The solubility of $Am(OH)_3$ in 0.3 M $NaNO_2$ / 2

M NaOH is equal to 0.01 mg•L^{-1} 8. The experiments have consisted of addition of concentrated sodium hydroxide into an Am/Be solution until it reached a final sodium hydroxide concentration of 2 M. The gel formation (probably amorphous Be(OH)$_2$) has been observed to start at pH around 5. At pH higher than 8 the solution become clear. After 24h digestion, the supernatant contains 96 percent of Be. Be/Am separation factor (23) depends highly on the Am content (0.3 mg.L^{-1}), which is very high compared to literature. The presence of Am colloid is suspected to explain this phenomenon. Therefore the treatment consisting of heating the solution at 50°C for 5h followed by filtration (porosity 0.2 µm) has allowed decreasing the Am content to 0.01 mg.L^{-1}. The Be/Am separation factor is 43 for this step and around 1000 for this global route. The Am content in the Be is lower than 5 µg/g of Be which is compatible for Be storage.
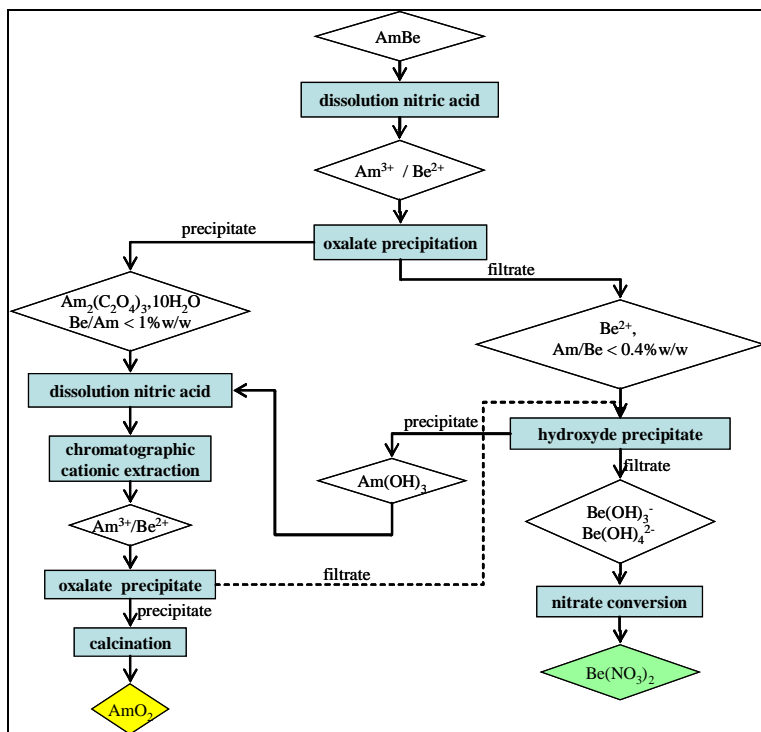

Fig. 1. AmO$_2$/Be neutron source reprocessing flowsheet

Current flowsheet

The results obtained up to now allow proposing a reprocessing flowsheet for the AmBe neutron sources (Figure 1). Before the reprocessing of real sources in hot cells two unitary steps (Am purification by cationic chromatographic extraction and conversion of Be in nitrate form) and the global flowsheet have to be validated.

ANALYTICAL STUDIES

In collaboration with ANDRA (the French National Radioactive Waste Management Agency), the beryllium arising from source processing is placed in interim storage at a surface site. The

resulting waste package must only contain beryllium nitrate, and its activity after 300 years must not exceed 50 MBq.

In the ATALANTE facility, the waste drums destined for an ANDRA site are measured by passive neutron counting in addition to gamma spectrometry measurements. These techniques are unreliable in the case of waste arising from the destruction of neutron sources; it was therefore decided that the waste activity would be determined prior to conditioning. Specific protocols have been developed for this purpose.

Determination of the Be concentration in the Be nitrate solution

After the beryllium nitrate conversion in hot cell, a sample is then dissolved in nitric acid and transferred to the Analysis Laboratory. The quantity of beryllium in the dissolution solution is determined by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) and by (Inductively Coupled Plasma – Quadrupolar Mass Spectrometry (ICP-QMS). In both techniques, plasma is used to excite the atoms initially present in the liquid sample. ICP-AES detects the photon radiation emitted during the atom relaxation processes and the excited ions (emission spectrometry), while in ICP-QMS the ions formed in the plasma are collected and counted (mass spectrometry). ICP-AES is capable of measuring each element by its particular wavelengths, while ICP-QMS discriminates among the elements according to the ion mass/charge ratio.

The determination was performed with the equipment in laboratory L19 using Beryllium analysis by ICP-AES and ICP-MS. ICP analyses are carried out on a highly diluted sample. An internal measurement standard is added to the ICP measurement sample to correct for the matrix effects. The nature of the standard depends on the element being assayed and the technique used. Holmium (Ho) was used for ICP-AES measurements and indium (^{115}In) for ICP-QMS. In these conditions, both techniques are very sensitive and the quantification limits are respectively equal to 0.2 mg.L^{-1} and 0.01 mg.L^{-1} for ICP/AES and ICP/MS.

Determination of the alpha activity in the residual beryllium nitrate

The alpha activity was determined for a surrogate solution containing beryllium (50 g/L) and ^{239}plutonium (11 mg/L) using a semiconductor detection system. The dilution factor and the quantity deposited for source preparation allowed usable spectra to be recorded in a reasonable time with an activity of about 5 Bq.

The plutonium concentration determined from the alpha activity was consistent with the value obtained by X ray fluorescence. The system is capable of determining trace quantities of uranium and plutonium in aqueous or organic solutions arising from spent nuclear fuel reprocessing.

CONCLUSION

The numbers of neutron sources produced by CEA during the past 30 years and the quantity of each element involved have been evaluated.

The management of recovery, transportation and mechanical destruction of neutron sources in the ATALANTE facility has been detailed.

The studies relative to the reprocessing of AmBe neutron sources are almost achieved. The specified of Be concentrations in the Am product have been reached and are lower than 12.7 µg Be g^{-1} Am. A flowsheet has been proposed and has to be validated by reprocessing AmBe sources in the hot cell.

Concerning analysis of Be waste, the results obtained show that the selected techniques and operating procedures correctly characterize beryllium waste. No interference was observed for analysis of beryllium by ICP-MS or by ICP-AES. For activity measurement, we demonstrated that sample dilution followed by semiconductor alpha spectrometry measurements yielded usable count rates and dead time values, avoiding performing difficult chemical separation steps.

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