

## Recycle of Am-241 Obtained from Long Term Stored Plutonium for Use in Radioisotope Power Systems - 15035

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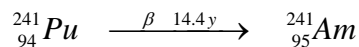
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### ABSTRACT

Pu-238 has been used as a power source for spacecraft since the early days of space exploration. It has proven to be an effective source of power where the use of solar generated power is impractical. Its application for use in spacecraft power systems was developed by the USA and Russia who have spent many \$100s of millions on its development and production. However, the original facilities for the production of Pu-238 are no longer in use and existing worldwide stockpiles have reduced to levels sufficient for only one or two further missions.

Production of Pu-238 requires considerable facilities including a nuclear reactor and reprocessing plants that are very expensive to build and operate. The European Space Agency (ESA) has assessed the options for post-launch power generation in future European space missions and has made the decision to pursue the use of Am-241 as an alternative isotope to power future European Radioisotope Power Systems (RPS). What makes Am-241 attractive for the European market is its 100% isotopically pure production from the decay of Pu-241 in separated civil plutonium stockpiles.

Historically, Europe has relied on collaborations with the USA or Russia to access these nuclear power sources. During 2009, the European Space Agency (ESA) funded a project to examine the cost and practicality of establishing a European source of material suitable for Radioisotope Power Systems (RPS). The study concluded that a small number of radioisotopes could be used in RPSs. On further review two leading candidates, Am-241 and Pu-238, were selected for further study. Whilst Pu-238 was recognized as the isotope of choice for use in RPSs, the costs of setting up a European based production facility was prohibitively expensive. Although Am-241 has a number of limitations compared to Pu-238, the much reduced production costs make Am-241 an attractive option for European based production of RPSs. Despite its lower power density of ~ 0.11 Wth/g, Am-241 is viewed as a potential alternative to Pu-238 because of its availability within the nuclear fuel cycle. During the reprocessing of spent nuclear fuel plutonium is separated as a chemically pure PuO<sub>2</sub> product, containing around 3-11% w/w of the Pu-241 isotope, and placed into storage. During storage the Pu-241 isotope beta decays to Am-241 with a half-life of 14.4 years.



This process has resulted in many 100 kgs of americium growing into the civil plutonium stockpile in the UK; material that is of value in generating heat sources and is able to be recycled.

The key benefit of Am-241 as a potential European RPS source isotope is the availability of feed material along with the facilities to process it. It is expected that aged civil PuO<sub>2</sub> will contain 25-50g Am-241 per kg PuO<sub>2</sub> depending on the source. A conceptual flowsheet using facilities for separating americium from plutonium is expected to produce on average 8.4kg Am/year.

ESA are now following their published roadmap of studies to develop flight ready RTGs and RHUs. This has included the development and testing of the flowsheet to be used for production of Am-241. The project has focused on underpinning the conceptual flowsheet, using aged plutonium in NNL's PuMA laboratory.

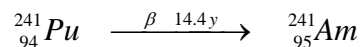
This has underpinned the design of a plant to produce a steady supply of Am-241. The scope of the overall project is “store to store” – the starting point is aged plutonium currently housed in existing Sellafield stores and the end point is the storage of separated plutonium and americium powders on the Sellafield site. The full scale process is planned to be housed within the NNL’s Central Laboratory in an existing facility designed for plutonium active operations.

## INTRODUCTION

Electrical power sources used in outer planet missions are a key enabling technology for data acquisition and communications. Pu-238 has been used as a power source for spacecraft since the early days of space exploration. It has proven to be an effective source of power where the use of solar generated power is impractical. The application of Pu-238 was developed by the USA and Russia who have spent many \$100s of millions on its development and production. However facilities for the production of Pu-238 in the USA shut down in 1988 and the stocks have been in decline ever since. Currently (2014) there is 17 kg Pu-238 within specification with a further 18 kg that can be brought into specification by blending with freshly produced Pu-238. A USA project to restart Pu-238 production is now underway to produce ~ 1.5 kg/year by the start of 2021 at a cost of \$85 – 125 million. Much of this remaining material is already allocated to future NASA missions [1]. With such a scarcity of supply and reliance on other nations there is an evident requirement for an independent and affordable European built radioisotope power system if planetary exploration is an ambition of the European space community.

Historically, Europe has relied on collaborations with the USA or Russia to access these nuclear power sources. During 2009, the European Space Agency (ESA) funded a project to examine the cost and practicality of establishing a European source of material suitable for Radioisotope Power Systems (RPS). The study concluded that a small number of radioisotopes could be used in RPSs. On further review two leading candidates, Am-241 and Pu-238, were selected for further study. Whilst Pu-238 was recognized as the isotope of choice for use in RPSs, the costs of setting up a European based production facility was prohibitively expensive.

Despite its lower power density of ~ 0.11 Wth/g compared to Pu-238’s ~0.41 Wth/g, Am-241 is viewed as a potential alternative to Pu-238 because of its availability within the nuclear fuel cycle. During the reprocessing of spent nuclear fuel plutonium is separated as a chemically pure plutonium dioxide (PuO<sub>2</sub>) product, containing around 3-11 % w/w of the Pu-241 isotope, and placed into storage. During storage the Pu-241 isotope beta decays to Am-241 with a half-life of 14.4 years.



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As part of this study both radioisotope thermoelectric generators (RTGs) (5 – 50 We) and Stirling engine technology (~100 - 150 We) are feasible with Wth – We conversion efficiencies of 4 to >25 % respectively. Small <5 Wth radioisotope heating units (RHUs) have also been designed that can keep spacecraft instrumentation warm. In order to realize the use of Am-241 as a power source a production route must first be established. The following sections describe the chemical separation process that is part of an overall store to store process of taking aged PuO<sub>2</sub> from Sellafield stores, removing the americium and returning pure plutonium and americium products back to the store ready for use.

## DESCRIPTION

Over the past two years a process for separating Am-241 from the PuO<sub>2</sub> to enable recycle has been defined and a concept flowsheet for the process of separation and buffer storage of Am-241 has been developed (Figure 1):

- Removal of Pu cans from the store
- Transport of the cans to the Central Laboratory import facility
- Dispensing the plutonium
- Ag<sup>2+</sup> catalytic dissolution of PuO<sub>2</sub> in nitric acid
- Am/Pu separation using solvent extraction
- Am/Ag separation using solvent extraction
- Formation (Oxalate precipitation) and packing of a plutonium oxide product
- Formation (Oxalate precipitation) and packing of an americium oxide product
- Ag and solvents recycled
- Storage of the americium oxide product
- Returning purified plutonium oxide back to the store

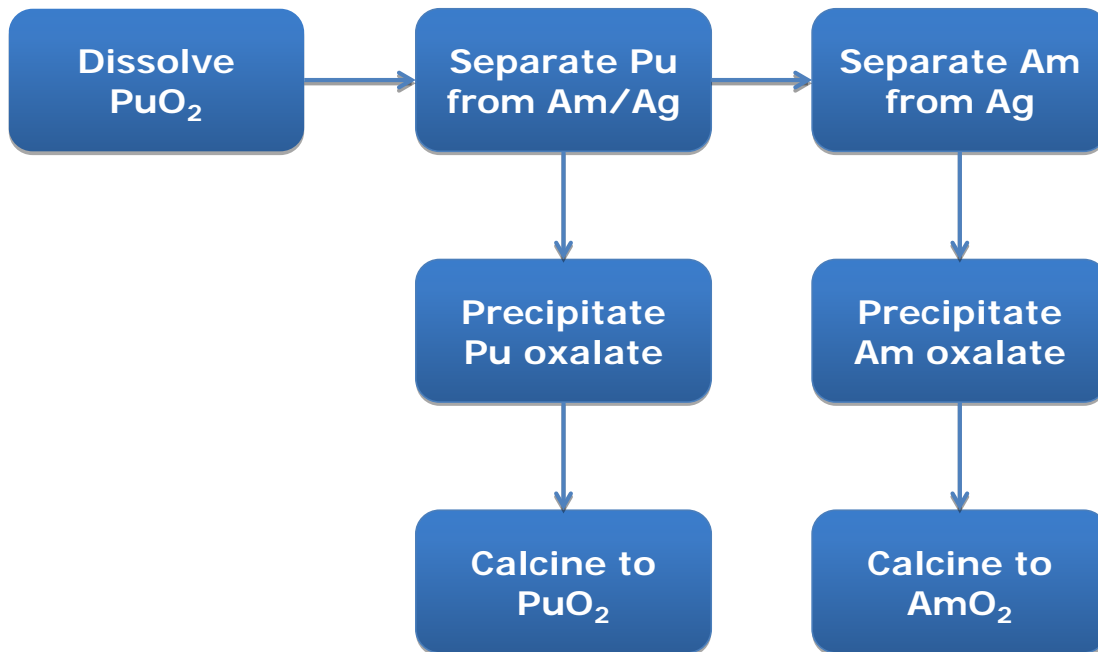


Figure 1. Outline of the process for isolating Am-241 from PuO<sub>2</sub>.

Current work is now focused on underpinning the conceptual flowsheet, using aged plutonium in NNL's PuMA laboratory and progress so far is discussed in the following section.

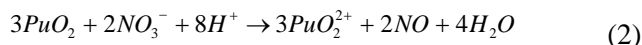
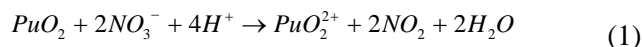
## DISCUSSION

### Plutonium Dioxide (PuO<sub>2</sub>) Dissolution

For many years there has been an interest in the dissolution of PuO<sub>2</sub> to recover plutonium from wastes and scraps. The dissolution of PuO<sub>2</sub> in nitric acid is difficult and hence the method of choice for dissolution of PuO<sub>2</sub> and MOx residues is through the use of strong oxidants such as Ce<sup>4+</sup> or Ag<sup>2+</sup>. The advantage of these oxidants over others is that they are effective at catalytic concentrations and can be regenerated by electrochemical means. To date only the Ag<sup>2+</sup> process has been implemented on an industrial scale.

For this flowsheet, oxidative dissolution is carried out by Ag<sup>2+</sup>, which is generated by passing current through the dissolver solution containing silver nitrate (Ag<sup>+</sup>). The electrodes are separated by housing the cathode in a separate compartment and a membrane is used to allow charge transfer. Due to the highly oxidizing nature of Ag<sup>2+</sup> the dissolver is generally made from highly resistant materials such as titanium, whilst the electrodes are manufactured from similarly resistant materials such as titanium/platinum and tantalum.

The overall reaction chemistry for the dissolution of PuO<sub>2</sub> is shown in Eq1 and Eq2 with the dissolution driven by the oxidation to the more soluble PuO<sub>2</sub><sup>2+</sup> species. The production of PuO<sub>2</sub><sup>2+</sup> is monitored using UV/visible electronic absorption spectroscopy following the 830 nm signal, which provides a quantitative measure of how much of the PuO<sub>2</sub> has dissolved and when the dissolution is complete.



Side reactions, such as oxidation of water can be significant at high temperatures, so the dissolution is generally carried out at just above ambient temperature. Reduction of nitric acid occurs at the cathode producing NO<sub>2</sub> and NO. As NO<sub>2</sub> and NO would rapidly react with Ag<sup>2+</sup> a membrane separates the anode and cathode compartments. An example of the experimental setup is shown in Figure 2 together with an example of the dissolution of PuO<sub>2</sub> showing the production of PuO<sub>2</sub><sup>2+</sup> over time, Figure 3. Experiments have been performed to demonstrate that up to 200g/l Pu solutions can be generated within 2 hrs. These solutions are then conditioned by bubbling NO<sub>x</sub> gases through to convert PuO<sub>2</sub><sup>2+</sup> to Pu<sup>4+</sup>, which is more extractable during the first solvent extraction process.



Figure 2. Experimental setup for 100 ml dissolutions using electrochemically generated Ag<sup>2+</sup>

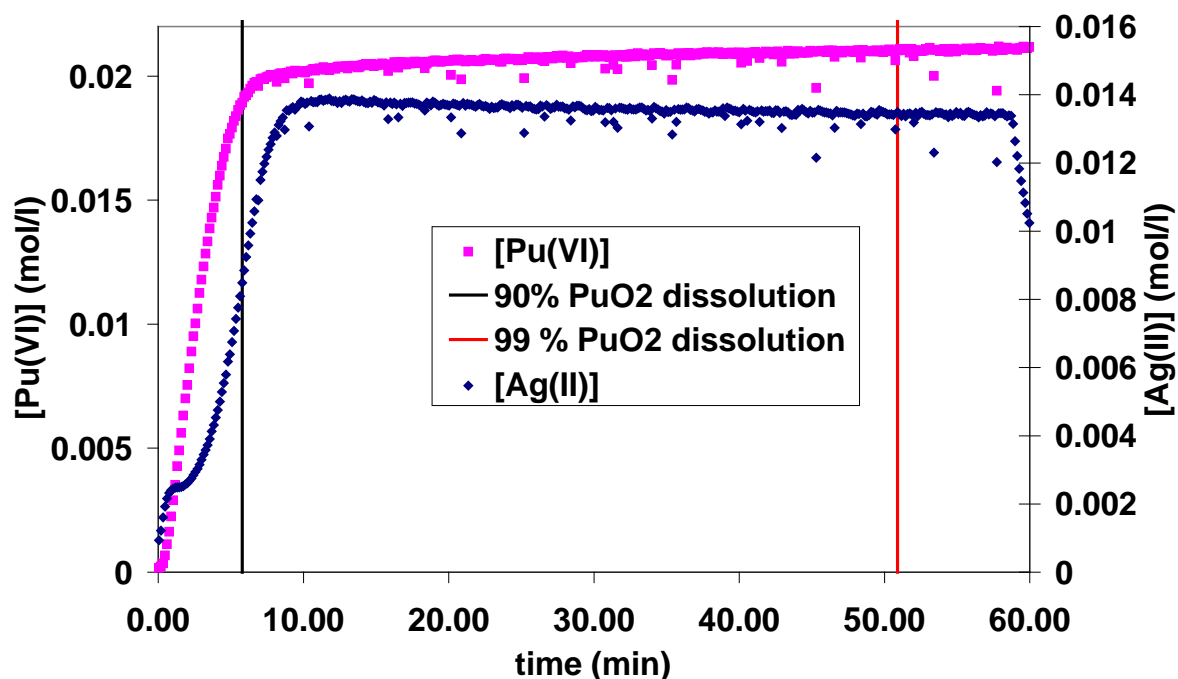


Figure 3. an example of the formation of PuO<sub>2</sub><sup>2+</sup> ([Pu(VI)]) over time (5A; 40°C; 4M HNO<sub>3</sub>; 5 g PuO<sub>2</sub> in 100ml).

### Plutonium Separation from Americium and Silver

A simple solvent extraction process using centrifugal contactors is used to separate the plutonium from the americium rich stream, Figure 4. This first solvent extraction process uses tributyl phosphate (TBP) in odourless kerosene (OK) to extract the plutonium into an immiscible solvent phase while leaving the americium and silver in the aqueous phase. The plutonium is then recovered from the solvent by reducing with hydroxylamine nitrate to plutonium (III) nitrate, which has low extractability in TBP/OK. The plutonium is recovered in > 99.9% yield and ~ 99.8% purity, which is important when complying with the strict requirements for returning the material back to storage.

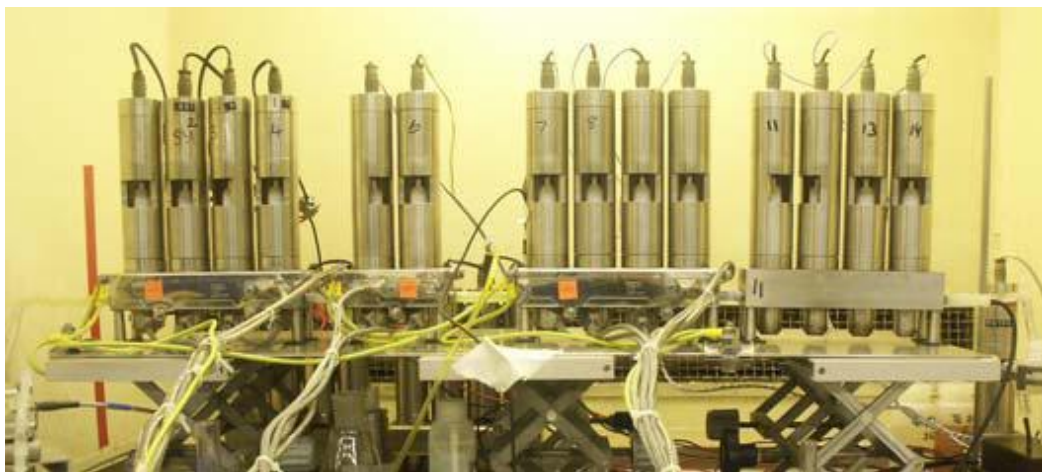


Figure 4. A bank of centrifugal contactors used to perform solvent extraction.

### Americium Separation from Silver

The separated americium left in the nitric acid stream is contaminated with silver from the dissolution process and needs to be removed. A second solvent system is required for the Ag/Am separation and experiments have been performed to select a suitable solvent system based on the following criteria:

- An appropriate solvent system that can deal with the proposed Am solvent concentrations (up to 5g/l; 0.021 M) without forming a third phase
- The solvent must also extract Am with a high enough D value (>50) under expected acid conditions (~2-3 M HNO<sub>3</sub>)
- The solvent must also enable the backwashing of Am with a low enough D value (< 0.1) under low acid conditions (~0.1-0.01 M HNO<sub>3</sub>)
- A recycle and disposal route must be feasible
- The solvent must be able to withstand the anticipated radiation levels

Using these selection criteria NNL has developed a solvent system that can achieve near full recovery of americium.

In the extraction section > 99.99% of the americium is extracted with only  $\sim 1 \times 10^{-6}$  g/L left in the aqueous phase, Figure 5. More than 99.99% of the silver and around 60% of the neptunium is left in the aqueous phase. A silver recovery process is designed into the full scale facility that will remove 99% of the silver from the effluent stream. The silver is recovered and recycled to the start of the process by dissolving in nitric acid. The americium loaded solvent is then treated with fresh dilute nitric acid to recover the extracted americium (backwashed). More than 99.99% of the americium is recovered from the solvent, Figure 6. In the full scale facility the solvent will be washed and recycled.

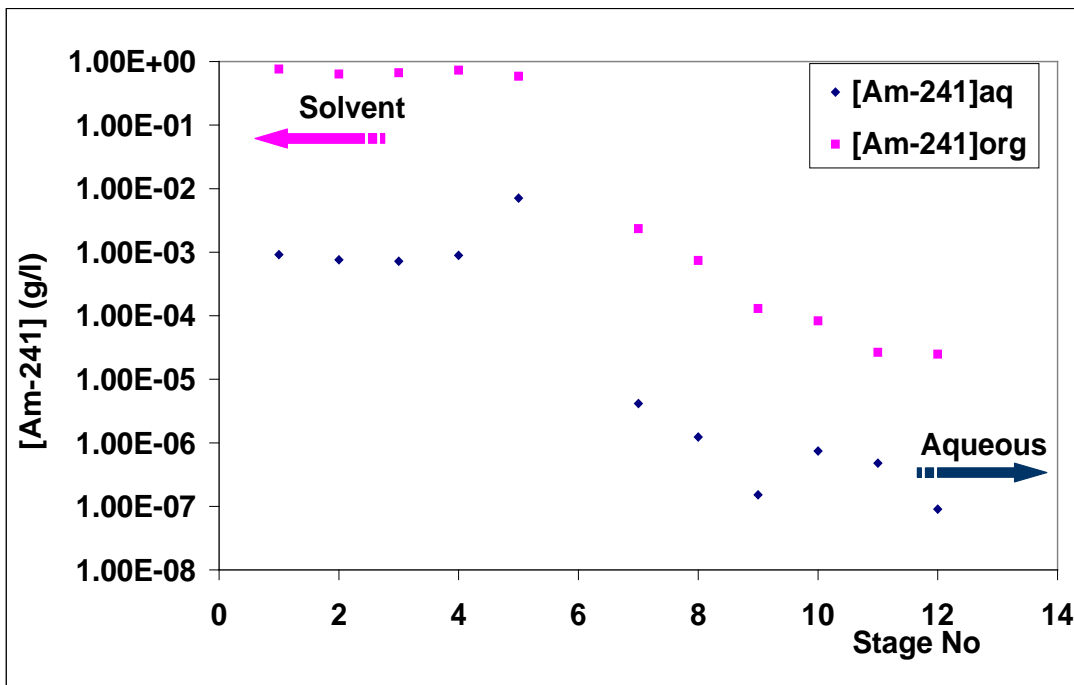


Figure 5. The concentration of americium in each of the centrifugal contactor stages at the end of the trial for the extract and scrub stages (org = organic phase; aq = aqueous phase).

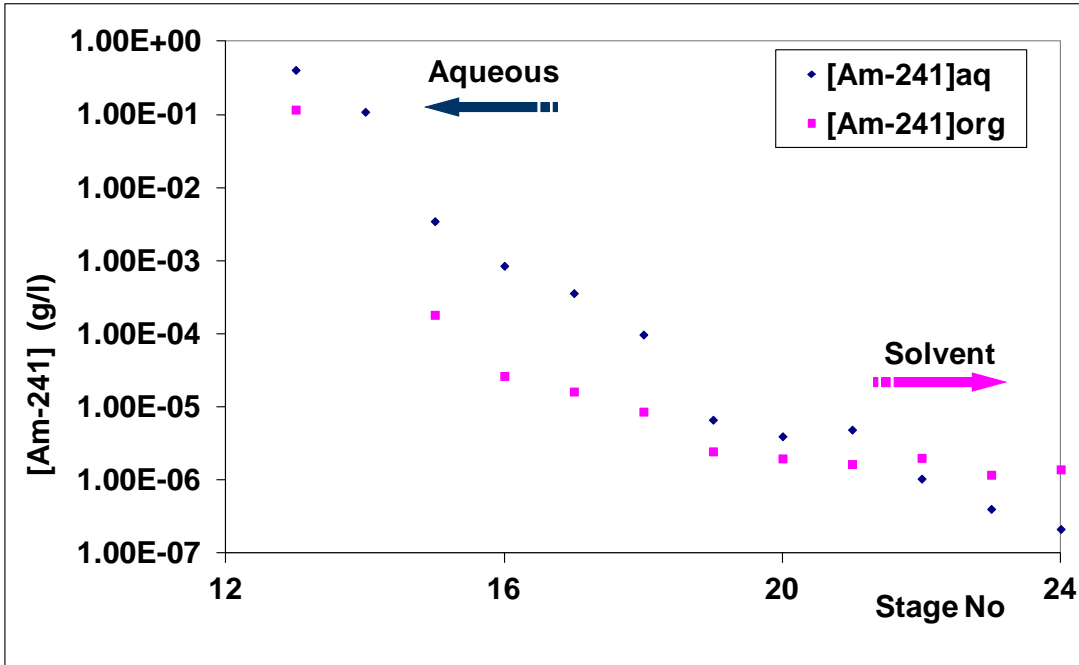


Figure 6. The concentration of americium in each of the centrifugal contactor stages at the end of the trial for the backwashing stages (org = organic phase; aq = aqueous phase).

### Americium Precipitation and Calcination

The americium is recovered by americium oxalate precipitation  $[\text{Am}_2(\text{C}_2\text{O}_4)_3 \cdot x\text{H}_2\text{O}]$  ( $x \sim 10$ ). During precipitation, filtration and washing some of the americium will inevitably be lost to the oxalate mother liquor. Optimization of the process to achieve a particular particle size range / morphology will be performed to generate baseline data for future pellet forming studies. It is expected that, as with plutonium oxalate calcinations, the particle morphology will be retained but with a 20% decrease in volume. However, it should be stressed that the information generated is very dependent on the stirring speed, impurity levels, residence time, digestion time, temperature and chemical composition of the liquor and may not be representative of the particle size and morphology when implemented on a full scale process. Calcination to  $\text{AmO}_2$  under an oxidizing atmosphere followed by heating to  $950^\circ\text{C}$  under a reducing atmosphere ( $\text{H}_2/\text{Ar}$ ) will give  $\text{AmO}_{2-x}$ . The optimum value of  $x$  remains to be established.

### Concept Plant Design

The processing of americium, with its associated gamma and neutron hazards, requires the use of containment to prevent internal dose to operators, shielding to minimize the external dose to operators, and remote or automatic operations to minimize the contact dose to operators. In addition, the presence of fissile and fissionable materials requires strict criticality control to ensure a failsafe process. Based on the above flowsheet each of the process steps requires alpha active gloveboxes (Figure 7) with all the required criticality and radiological controls in addition to support operations such as analysis, waste treatment steps, off-gas abatement and buffer storage.



Figure 7. An example of the alpha active containment boxes at NNL.

By generating a 3D virtual image of the plant layout we have established the footprint and relative positions of vent systems with utility supplies and waste routes to ensure that the available space within the National Nuclear Laboratory, Central Lab, can accommodate a full scale production facility that is capable of producing around 8.4kg of Am-241 per year, Figure 8.

An important support facility for the development of a production scale Am-241 processing capability is the NNL's Plutonium and Minor Actinides ("PuMA") laboratory located at Sellafield. This is a civil plutonium research facility housing a range of cutting edge gloveboxes and other equipment such as miniature centrifugal contactors for solvent extraction. Within this facility NNL has the capability to run experiments with more civil plutonium than any other research laboratory in the UK.

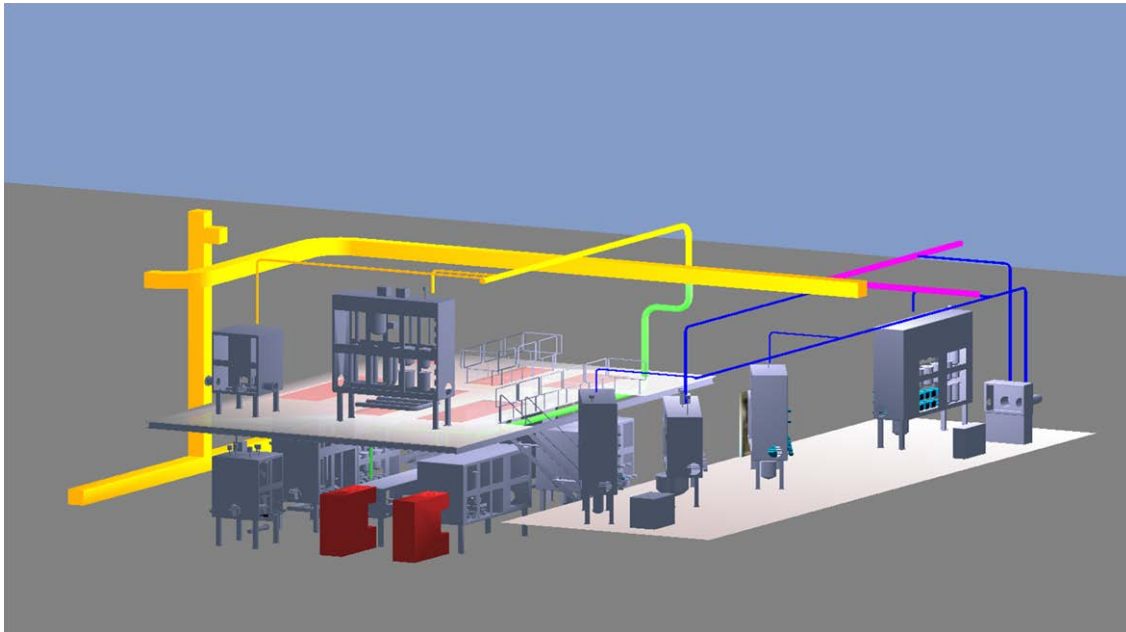


Figure 8. A still from the 3D immersion suite used to visualize the layout of the plant.



Using this facility, the development of a flowsheet for the extraction of Am-241 from aged civil plutonium will continue over the next 2 years. The flowsheet will be tested at an order of magnitude higher feed level and will provide enough material to make a light weight radioisotope heating unit. This material will be pressed into americium oxide and sintered to make dense pellets.

## **CONCLUSION**

A conceptual flowsheet for the separation of Am-241 from civil PuO<sub>2</sub> stocks has been prepared and is in the process of validation. Based on this flowsheet a concept plant layout has been designed and the construction costs established to be significantly less than building a new plant. The process is designed not only to provide a new heat source that can be used in power systems by recycle of a waste material, but has the added benefit of making a PuO<sub>2</sub> product that is easier to handle and fabricate into new nuclear fuel.

## **REFERENCES**

1) Dudzinski, L. Radioisotope power systems and planetary technologies, NASA, November 2013, [http://www.lpi.usra.edu/vexag/meetings/archive/vexag\\_11/presentations/1119-1130-Dudzinski.pdf](http://www.lpi.usra.edu/vexag/meetings/archive/vexag_11/presentations/1119-1130-Dudzinski.pdf).

## **ACKNOWLEDGMENT**

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