Processing and Disposition of Special Actinide Target Materials - 17071

Brad Patton*, Miting Du*, Sharon Robinson*, Nicholas Bridges**, and Nicholas Quintero***
*Oak Ridge National Laboratory, P. O. Box 2008, Oak Ridge, TN 37831
**Savannah River National Laboratory
***US Department of Energy

ABSTRACT

The DOE manages an inventory of materials that contain a range of long-lived radioisotopes that were produced from the 1960s through the 1980s by irradiating targets in high-flux reactors at the SRS to produce special heavy isotopes for DOE programmatic use, scientific research, and industrial and medical applications. Among the products were Cf-249, -250, -251, and -252; heavy curium (≥50% Cm-246); and Pu-242 and -244. The irradiation of the Mark-18A (Mk-18A) targets at extremely high fluxes produced the world's supply of heavy curium and Pu-244. Approximately one fourth of the Mk-18A targets were processed in the 1970s to recover and enrich the material that has been used as the global source of Pu-244 and heavy curium by industry and researchers. These isotopes are still in demand, and the available supply of purified material is dwindling. A program has been initiated to recover heavy curium and Pu-244 from the remaining stored unprocessed Mk-18A targets. Improved flowsheets to process the materials to recover Pu-244 and heavy curium are being developed. Evaluations are also underway to determine whether additional materials present in the targets in much smaller quantities, such as long-lived fission product (LLFP) isotopes, can be recovered for research and development applications.

INTRODUCTION

Eighty-six Mk-18A targets were irradiated in a high-neutron-flux mode in the K-Reactor at SRS from August 1969 to November 1970 and then irradiated in a low-flux mode until 1979. Upon removal from the reactor, 21 targets were processed at ORNL in 1972–73 to recover Cf-252, Bk-249, Es-253, heavy curium, and plutonium. The plutonium by-product recovered from processing the Mk-18A targets contained the rare plutonium isotope Pu-244. The plutonium was purified and transported to the ORNL Actinide Calutron Facility where the plutonium isotopes were electromagnetically separated and the Pu-244 was enriched to >97% isotopic purity. This high-purity sample of Pu-244 was portioned out to scientists for basic research and for safeguards programs. The

processing of these 21 Mk-18A targets provided the current source of the world's supply of separated Pu-244 and heavy curium.

The 65 unprocessed targets contain the world's supply of unseparated Pu-244 and significant amounts of heavy curium needed for heavy-actinide production. These targets were placed in water basin storage in the Receiving Basin for Offsite Fuels until 2001 when they were moved to their present storage location in L-Basin at SRS. The targets have been stored in their original irradiated form doubly contained in aluminum J-cans in the L-Basin at SRS since 2001.

The majority (>80%) of the existing global inventory of Pu-244 is contained in the 65 Mk-18A targets stored at SRS. Plutonium-244 is not present in nature and is not produced in defense production or the commercial market place. Its characteristics make it irreplaceable for quantitative nuclear forensic analysis if enriched to the required purity. It provides the capability to perform high-precision analysis in support of U.S. nonproliferation objectives. The Mk-18A targets also contain ~80% of the nation's heavy curium inventory. The heavy curium in the Mk-18A targets is an attractive long-term feedstock for the production of Cf-252 and other heavy elements. Although alternative feedstocks for heavy element production are available, they are much less attractive than heavy curium contained in the Mk-18A targets.

The Mk-18A targets also contain other valuable high-Z isotopes and long-half-life fission product isotopes. Radioisotopes of Pu, minor actinides like neptunium, Am and Cm and LLFP (those with half lives in millions of years) constitute the main waste burden from a power reactor. Long-lived fission products will have a significant impact on the long-term dose associated with radionuclide release from a high-level waste geologic repository. An option that is being considered to reduce the toxicity of high-level waste requiring geologic disposal is to transmute the LLFP into stable or short-lived isotopes. Accurate neutron cross-section data for minor actinides and LLFP are necessary to estimate their production and transmutation rates in advanced nuclear reactor systems.

The Office of Nuclear Materials Integration (ONMI) established the Mk-18A Target Material Recovery Program (MTMRP) in 2015 to preserve the Pu-244 and heavy curium in these targets [1]. Evaluations are now underway to determine whether additional rare isotopes present in the targets in much smaller quantities than plutonium and heavy curium can be recovered for research and development applications.

DESCRIPTION

The high neutron irradiation of Pu-242 in the Mk-18A targets in the K Reactor at SRS resulted in unique contents, generating significant quantities of Pu-244, heavy curium, high-Z isotopes, and LLFP isotopes. The isotopic composition of the 65 Mk-18A targets in storage at SRS is shown in TABLE I [2].

TABLE I. Composition of Mk-18A Targets (decayed to 10-1-2022)

Isotope	Mass (g/target)	Activity (Ci/target)
Actinides		
Pu-238	1.03E-02	1.75E-01
Pu-239	5.99E-03	3.71E-04
Pu-240	7.95E+00	1.83E+00
Pu-241	5.42E-02	5.96E+00
Pu-242	8.45E-01	3.30E-03
Pu-244	3.69E-01	6.64E-06
Am-241	3.48E-01	1.11E+00
Am-243	6.35E-01	1.21E-01
Cm-244	1.87E+00	1.53E+02
Cm-245	4.25E-01	7.23E-02
Cm-246	6.81E+00	2.11E+00
Cm-247	3.75E-01	3.49E-05
Cm-248	5.40E-01	2.27E-03
Bk-249	2.04E-16	3.26E-13
Cf-249	8.91E-03	3.65E-02
Cf-250	5.94E-04	6.54E-02
Cf-251	1.91E-03	3.06E-03
Cf-252	5.46E-07	2.95E-04
Total actinides	2.03E+04	4.63E+03

Isotope	Mass (g/target)	Activity (Ci/target)
Primary Fission Products		
Cs-137	7.72E-01	6.69E+01
Ba-137m	1.17E-07	6.32E+01
Y-90	5.34E-05	1.19E+01
Sr-90	8.67E-02	1.19E+01
Eu-154	1.77E-03	4.77E-01
Kr-85	6.98E-04	2.79E-01
Sm-151	2.46E-03	6.48E-02
Eu-155	3.36E-05	1.65E-02
Sn-121m	2.32E-04	1.56E-02
Sn-121	3.08E-08	1.21E-02
Tc-99	4.01E-01	6.86E-03
Cs-134	1.19E-06	1.54E-03
Transition Metals of Interest		
Se-79	1.91E-03	2.94E-05
Zr-93	4.32E-01	1.08E-03
Tc-99	4.01E-01	6.86E-03
Pd-107	1.16E+00	5.89E-04
Sn-126	5.29E-02	6.53E-04
I-129	1.74E-01	3.07E-05

Of particular interest are the Pu-244 and heavy curium. The total inventory in the Mk-18A targets is about 24 g of Pu-244 in several hundred grams of plutonium, primarily Pu-240. The Mk-18A targets also contain ~650 g of heavy curium, which is the majority of the nation's heavy curium inventory. They also contain other valuable high-Z isotopes (e.g., Cf-249, Cf-251, Am-243) and LLFP isotopes (e.g., Se-79, Zr-93, Tc-99, Pd-107, Sn-126, and I-129.

The flowsheet used to process the 21 Mk-18A targets at ORNL in the 1970s is shown in Fig. 1 [3]. The unit operations included caustic dissolution of aluminum cladding to remove the caustic-soluble aluminum and caustic-soluble fission products such as cesium. The actinides and remaining fission product solids were then dissolved in nitric acid. Each batch of acidic dissolver solution was processed through a Plutonium Batch Extraction (Pubex) process to recover the plutonium. The recovered plutonium was further purified by ion exchange and then converted to an oxide product. The transplutonium stream from the Pubex extraction of three Mk-18A targets was then combined for subsequent processing steps. The Cleanup Extraction (Cleanex) batch process was used to remove non-lanthanide fission products and convert the transplutonium stream to a chloride solution.

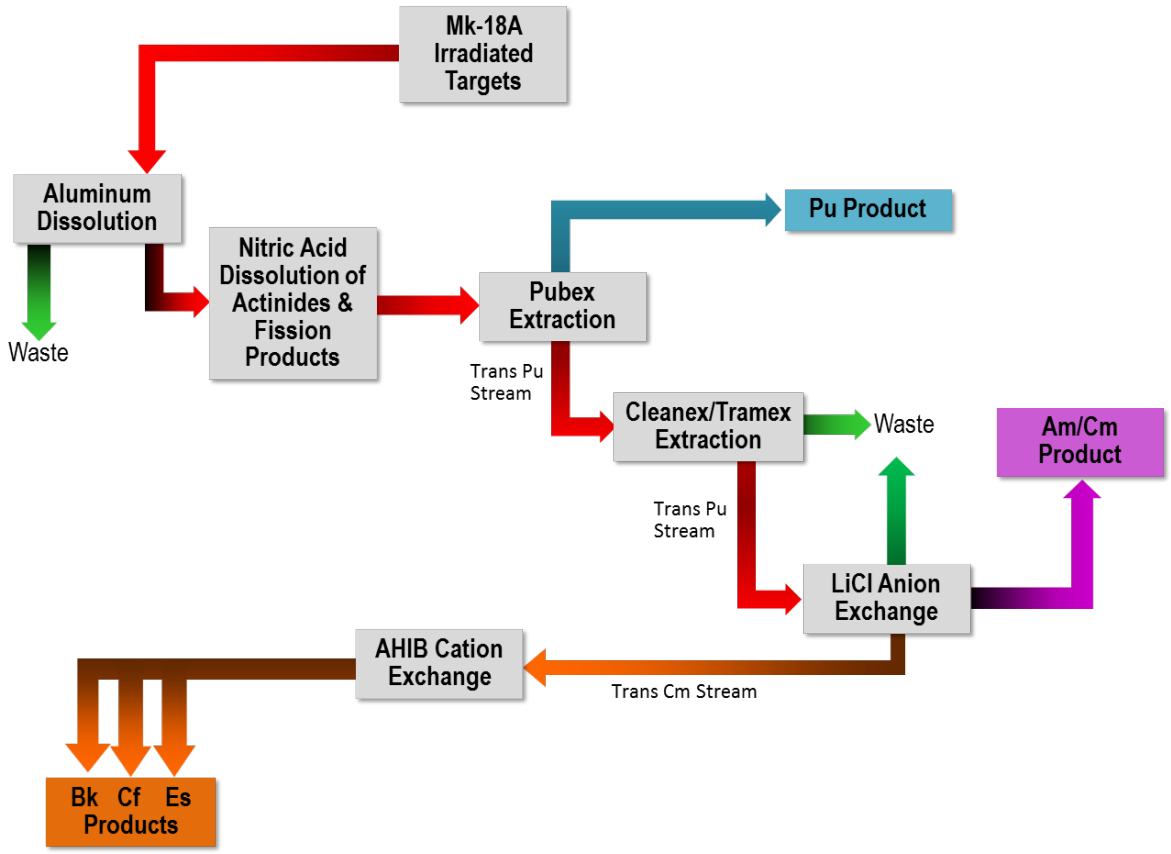

Fig. 1. Mk-18A processing flowsheet used in the 1970s.

Lithium chloride (LiCl) was added to the Cleanex product and the bulk of the lanthanide fission products were removed using a batch transuranium amine extraction (Tramex) process. A LiCl anion exchange chromatography process was then used to remove residual lanthanides and separate the Am/Cm product from the transcurium elements. After conversion of the transcurium stream back to nitric acid media, the alpha-hydroxyisobutyrate (AHIB) cation exchange chromatographic process was used to separate the heavy-actinide transcurium elements: Bk, Cf, and Es.

Approximately 400 g of Cm-244, 0.05 g of Bk-249, 0.4 g Cf-252, and 8×10^{-5} g Es-253 were recovered from processing the 21 Mk-18A targets. A total of 37 g of plutonium was also recovered with at least 8.88 g of the plutonium material being Pu-244. The Bk-249, Cf-252, and Es-253 were distributed to customers. The plutonium was isotopically purified in the ORNL Calutrons to obtain 4.33 g of highly enriched (>97%) Pu-244, which was distributed to users. The Am/Cm product has primarily been used as feedstock for production of heavy actinides at ORNL.

Minor actinides and LLFP were not recovered during the Mk-18A processing campaigns. However, ORNL has experience with recovering these materials from Mark-42 (Mk-42) targets which were fabricated from Pu-239 and highly irradiated at SRS to produce material for the DOE Defense Production Program in the 1980s.

In 1991, ORNL began processing the targets to recover Am, Cm, and Pu [4]. The process flowsheet used to recover Pu and Am/Cm products is similar that shown in Fig.1 without the last transcurium processing step to separate the heavy actinides since they were not present in recoverable quantities. The organic waste stream from the Cleanex extraction step in one of the production campaigns was further processed to recover Zr-93 for research purposes.

The objective of the Cleanex solvent extraction process is to separate the trivalent actinides and rare earth fission products from other impurities. The extractant for the Cleanex process is 1.0 *M* di(2-ethylhexyl)phosphoric acid (HDEHP) in a normal paraffin hydrocarbon diluent. When the acidity is adjusted to a few hundredths molar, the trivalent actinides and rare earths are strongly extracted leaving most of the impurities, such as iron, molybdenum, and zirconium, if present, in the organic extractant, which is normally discarded as waste. In this case, the Zr-93 was extracted from the HDEHP waste stream by stripping with 0.6 *M* oxalic acid in <0.55 *M* nitric acid and drying to drive off the oxalic acid. The precipitates were dissolved in hydrochloric acid for additional purification of the zirconium by ion exchange using MP-50 cation exchange resin, MP-1 anion exchange resin, and DGA resin followed by oxalate precipitation and calcination to obtain a ZrO_2 product. A total of 3.5 g of ZrO_2 containing ~500 mg Zr-93 was recovered and shipped to the Kyoto University Research Reactor Institute to determine the neutron-capture cross section at the Japan Proton Accelerator Research Center. The atomic abundance of Zr-93 in the samples was determined to be 18.86% [5].

DISCUSSION

The DOE ONMI established the MTMRP in 2015 to preserve the world's supply of Pu-244 and heavy curium. Under the MTMRP, the Mk-18A targets will be retrieved from wet storage at SRS and processed in the Shielded Cells facility at SRNL to produce two products: a plutonium-rich oxide stream and an oxide material, which will contain the americium, curium, and lanthanides. These materials will be shipped to ORNL for storage and any additional processing required to prepare them for future beneficial use.

The processing flowsheet for the remaining Mk-18A targets is presently under development. The processes developed at ORNL in the 1970s are being used as the baseline for the dissolution and filtration steps in the proposed flowsheet, but they may be modified as the flowsheet is further developed. Anion exchange is being considered to separate the plutonium from the Am/Cm stream and a purification step, such as oxalate precipitation, is being considered to remove fission products and residual aluminum and silica from the Am/Cm product before shipment to ORNL. The proposed MTMRP processing flowsheet is shown in Fig. 2. The MTMRP Am/Cm product could be used as feedstock in the current Cf-252 production flowsheet as shown in Fig. 3.

Evaluations are underway to determine whether additional rare fission product isotopes present in the targets in much smaller quantities can be recovered. These

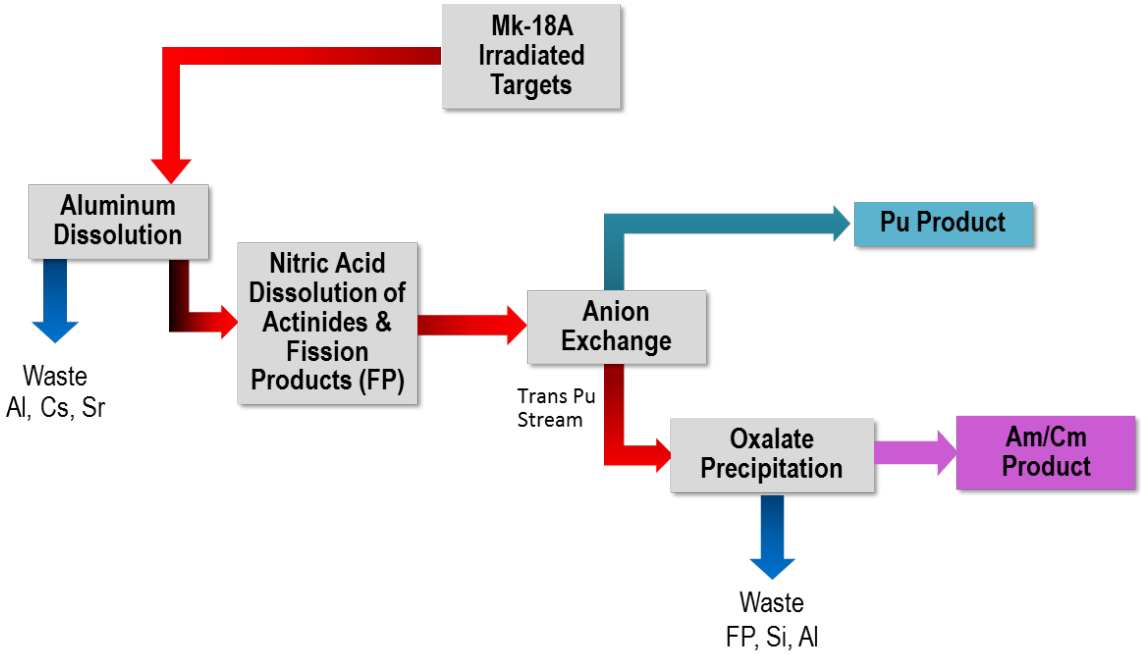

Fig. 2. Conceptual Mk-18A processing flowsheet.

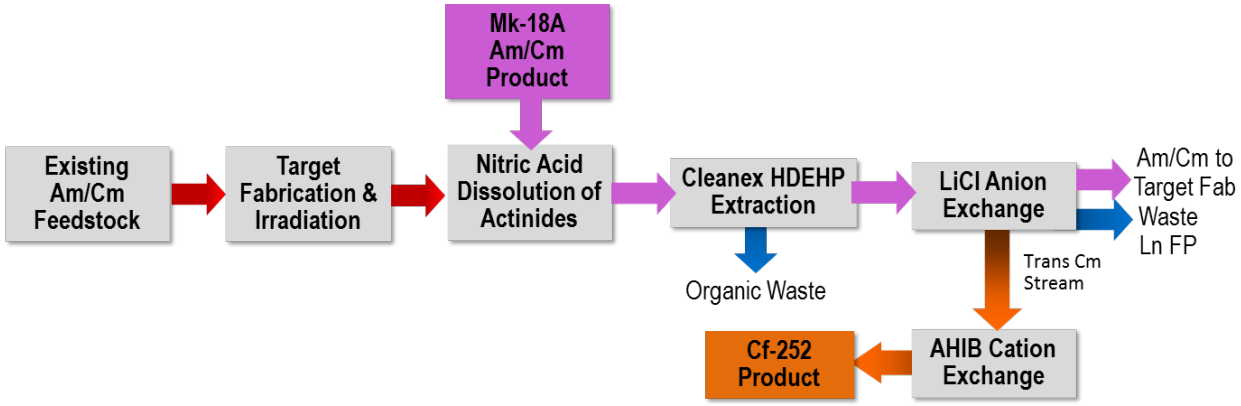

Fig. 3. Utilization of Mk-18A Am/Cm product for Cf-252 production

evaluations include assessment of the quality, value and demand for the materials; process modifications required to facilitate recovery; the incremental costs for their recovery; and the reduction of the waste load associated with treatment of the waste streams generated from these recovery operations.

A review of the actinides listed in Table I indicate that in addition to the Pu, Am, and Cm, the mixed Cf (Cf-249, 250, and 251) contained in the Mk-18A targets could potentially be recovered for use by super heavy element research programs. A concept for recovering the decayed mixed Cf and using the purified Am/Cm from the Mk-18A material for Cf-252 feedstock is shown in Fig. 4. The Am/Cm product from the material being produced by the MTMRP could be processed by the same procedures previously used in the 1970s to recover Cf, Bk, and Es from the Mk-18A targets. This may be advantageous for Cf-252 production, because if the mixed Cf

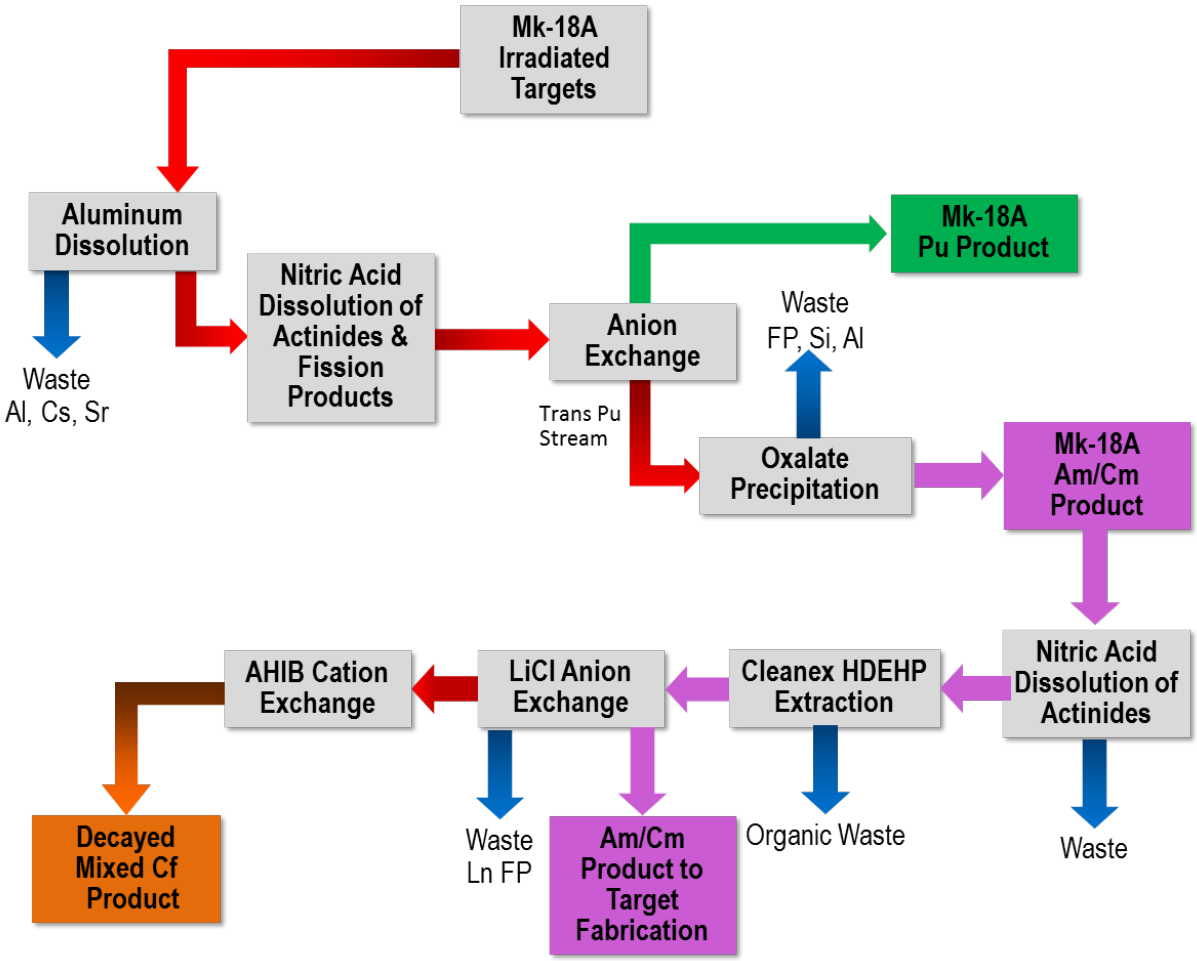

Fig. 4. Conceptual flowsheet for recovering mixed californium from Mk-18A targets

is left in the Am/Cm material being used as Cf-252 production feedstock, the final Cf-252 product will contain newly produced Cf-252 that could be isotopically diluted with the residual mixed Cf remaining after transmutation and potentially result in a less desirable material for the Cf-252 end users. In addition, if the mixed Cf is not separated it would not be available for use in super heavy element research programs.

The management of long-lived nuclear waste is a critical part of advanced fuel cycles, and LLFP are being considered for nuclear transmutation. For this to be feasible, the nuclear cross-section for the proposed transmutation reactions has to be as high as possible. In general, while the nuclear cross-sections of interest for transmutation of LLFP are available for stable isotopes, the required data for the radioactive LLFP are rather sparse. More accurate neutron cross-section data are necessary to estimate the production and transmutation rates in advanced nuclear reactor systems. Of particular interest are Se-79, Zr-93, Tc-99, Pd-107, Sn-126, I-129 and Cs-135. The amounts of these isotopes in the Mk-18A targets are shown in Table II. Of these, the neutron cross-sections have only been measured for I-129, Tc-99, and Zr-93 [5,6].

Table II. Long-lived Fission Products in Mk-18A Targets

Isotope	Half-life (y)	Total Mass (g)	Isotopic Weight %
Se-79	2.9×10^5	0.124	5.3
Zr-93	1.5×10^6	28.1	19.1
Tc-99	2.13×10^5	26.0	100.0
Pd-107	6.5×10^6	75.1	14.5
Sn-126	2.3×10^5	3.44	17.9
I-129	1.57×10^7	2.54	37.4

Although a cross-section for Zr-93 has already been measured, this isotope does not exist in nature. Large amounts of irradiated fissionable material are required to produce gram quantities of Zr-93. It was produced in these quantities by high neutron-flux irradiation of the Mk-18A and Mk-42 targets in the shutdown reactors at SRS and may be worth further consideration for recovery. In addition, the recovery of Se-79, Pd-107, and Sn-126 may also be needed for use in the transmutation studies described above.

Evaluation of the lanthanides indicates that for the most part they are mixed stable isotopes; recovery would not be worth pursuing. A similar conclusion was made for the transition metal fission products.

The next steps in these evaluations will be to determine how the LLFP isotopes partition throughout the Mk-18A processing flowsheet as it is developed further. It may be possible that slight changes in the planned processing flowsheet could isolate the materials of interest and make them available for further processing to meet user needs. The additional steps required to recover and purify these materials need to be defined. The incremental costs for their recovery from the Mk-18A targets and the reduction of the waste load associated with treatment of the waste streams generated from these recovery operations need to be developed.

CONCLUSIONS

The MTMRP has been initiated to recover heavy curium and Pu-244 from the Mk-18A targets stored at SRS which contain >80% of the global supply of these materials. Flowsheets to process the materials to recover Pu-244 and heavy curium are being developed based on the flowsheets used to process a subset of the targets at ORNL in the 1970s.

Recovery of mixed Cf is being considered to potentially improve the Cf-252 product and provide Cf for super heavy element research. Evaluations are underway to determine whether additional rare LLFP isotopes present in the targets in much smaller quantities can be recovered. These evaluations include assessment of the quality, value, and demand of the materials; process modifications required to facilitate recovery; the incremental costs for their recovery from the Mk-18A targets; and the reduction of the waste load associated with treatment of the waste streams generated from these recovery operations.

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