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# SEPARATION OF AMERICIUM, CURIUM, AND PLUTONIUM FROM IRRADIATED TARGETS

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## ABSTRACT

The Radiochemical Engineering Development Center (REDC) at Oak Ridge National Laboratory (ORNL) processes highly irradiated targets for the Mark 42 program to separate Am, Cm, and Pu. The target feed material for each assembly was 3.3 kg of plutonium (78% $^{239}$Pu) that was irradiated at the Savannah River Site to yield approximately 100 g each of $^{243}$Am and $^{244}$Cm, and 100-g quantities of $^{242}$Pu for special DOE projects. The REDC has plans to process ten of these target assemblies over the next few years. The first assembly has been dissolved, and approximately 1/4 of this material has been used to test the processing flowsheet. Various aqueous processes developed at the REDC over the past years were utilized to dissolve the target segments, separate the bulk of the impurities from the transuranics, separate the plutonium from the transplutonium actinides, and separate the rare earth fission products from the Am-Cm. The separation of the Am-Cm products to the desired purity levels presented new processing challenges for REDC operations. Through a combination of precipitation and cation-exchange operations, an Am product containing part-per-million levels of Cm was obtained. Standard REDC processing techniques were used to prepare the products as oxides for shipment. Future processing will focus on the reduction of waste solutions, improvement of yields, and application of new technologies for improved processing.

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## INTRODUCTION

In 1991, the Radiochemical Engineering Development Center (REDC) at Oak Ridge National Laboratory (ORNL) began processing highly irradiated Mark 42 target assemblies for the DOE Defense Production Program. The Mark 42 assemblies were fabricated and irradiated at the Savannah River Site (SRS) to produce Am, Cm, and Pu with unique compositions. It is this unique isotopic composition that makes the Mark 42 targets valuable to certain special DOE projects. A number of the assemblies, discharged in 1984, were processed at SRS to recover the plutonium content; however, the SRS did not have the capabilities to recover the americium and curium products at that time. Ten assemblies were reserved for processing at ORNL to recover the Am, Cm, and Pu products, since it is unlikely that any significant quantities of these materials will be produced in the near future.

The irradiated assemblies measure 14 ft in length, which posed a problem in handling in that no ORNL facility could handle the full-length assembly. The help of Pacific Northwest Laboratories (PNL) was enlisted to cut the active length of each assembly into eight 20-in. segments and repackage the individual segments. These segments could then be easily handled in the REDC hot cell facility. REDC is in the process of installing a dry-storage facility for the segmented assemblies so that the transportation/segmenting portion of the program can be accelerated and all the assemblies to be processed can be stored at the REDC.

The processing of the irradiated segments was accomplished using accepted aqueous processes employed in typical REDC operations for the dissolution of Mark 42 targets, separation of the impurities from the transuranics, separation of the plutonium from the transplutonium actinides, and separation of the rare earth fission products from the Am-Cm. The separation of the Am-Cm to produce a high-purity Am product (low ppm levels of Cm) and a Cm product (< 1% Am) at the desired impurity levels presented the greater processing challenge. The carbonate precipitation process proved to be the best choice for the bulk separation of the Am and Cm. A cation-exchange process was used for the final purification to obtain an acceptable Am product. Standard processing techniques used at the REDC were then employed to produce oxide products for shipment. Approximately one-fourth of the first assembly has been processed to test the flowsheet and techniques utilized in separating the Pu-Am-Cm. Further processing of the segmented assemblies will provide opportunities for process improvements as well as testing of new techniques and processes for accomplishing the desired separations.

## MARK 42 TARGET ASSEMBLY

The Mark 42 assemblies are a $PuO_2$-Al cermet extrusion with an aluminum cladding. They consist of three concentric cylinders 2.75, 3.25, and 4.0 in. in diameter. The active length is approximately 160 in. containing almost 30 kg of aluminum metal. The initial Pu loading of the assembly was 3.3 kg of $^{239}$Pu which was irradiated to >87 atom % fission. Core drill samples cut from the first target assembly received at the REDC showed both an axial and radial gradient in the irradiated assembly. For this reason, the nested cylinders were disassembled, and selected sections were dissolved to produce products with the higher isotopic purity (> $^{243}$Am and $^{242}$Pu content). The assemblies are also long cooled, so the only major fission product activities are the long-lived isotopes of Sr, Cs, and Eu. Table 1 gives the composition of the high-quality material recovered from the dissolution of the outer cylinders from five segments of the first assembly. Because of the axial gradient, the two end pieces of an assembly are of lower burnup and poorer quality. In order to keep the lower-quality material separate, these end pieces will not be included in the processing for product material.

## EXPERIMENTAL

Aqueous processes used at the REDC over the past several years were used in the processing of the Mark 42 materials. These processes form the framework for most of the separations work and product preparation work done at the REDC (1). Equipment racks contained in the shielded hot cells were designed and installed for specific process operations, and detailed procedures have been written to guide the operations. The mainline processing flowsheet for the Mark 42 materials is shown in Figure 1. Since most of these processes have been discussed in detail in various publications, a brief description of the individual processing steps will be given here and references made to the more detailed reports.

### Dissolution

The dissolution of the selected Mark 42 segment pieces was accomplished using a two-step process (2): caustic dissolution to remove the Al followed by an acid dissolution to dissolve the actinides and most of the fission products. This two-step process coupled with filtration produces a solids-free acid product solution suitable as feed material for subsequent chemical

TABLE 1. COMPOSITION OF FIRST MARK 42 MATERIAL PROCESSED

| Isotope | Mass (g) | Isotopic Purity % |
|---|---|---|
| $^{244}Cm$ | 15.3 | 91.6 |
| $^{243}Am$ | 15.9 | 98.6 |
| $^{239}Pu$ | 0.17 | 0.37 |
| $^{240}Pu$ | 5.24 | 11.4 |
| $^{242}Pu$ | 39.9 | 86.1 |
| Fission Products | (Ci) | |
| $^{106}Ru$ | 41 | |
| $^{125}Sb$ | 4.1 | |
| $^{134,137}Cs$ | 1980 | |
| $^{154,155}Eu$ | 70 | |

separation and purification steps. The caustic dissolution is accomplished by submerging the target segments in 2.25 M $NaNO_3$ solution, heating to 92 ± 2°C, and then metering in 10 M NaOH solution at a controlled rate to sustain the dissolution reaction. The overall chemical reaction occuring during this caustic-nitrate dissoluton step is given as follows:

$$Al + 0.63NaOH + 0.28NaNO_3 + 0.26H_2O \rightarrow NaAlO_2 + 0.37NH_3\uparrow + 0.01NaNO_2 + 0.02H_2\uparrow.$$

The use of the sodium nitrate solution significantly reduces the formation of hydrogen gas during the dissolution when compared to dissolution in sodium hydroxide alone. The caustic dissolves both the aluminum cladding and the aluminum in the cermet extrusion. The aluminum-bearing caustic solution is then pumped through a sintered stainless steel filter and discarded as waste. The filter is backflushed to the dissolver tank and the remaining solids are digested in 8 M $HNO_3$ which quantitatively dissolves the actinides and most of the remaining fission products. This solution is filtered through a 10 μm graded-density polypropylene filter to remove any remaining solids (primarily silica fission products) and produce an acid product for PUBEX extraction.

## Pubex Batch Solvent Extraction

The objective of this process (3) step is to separate the Pu from the Am, Cm, and fission products. This separation is accomplished by extracting the Pu into 1.0 M di(2-ethylhexyl)

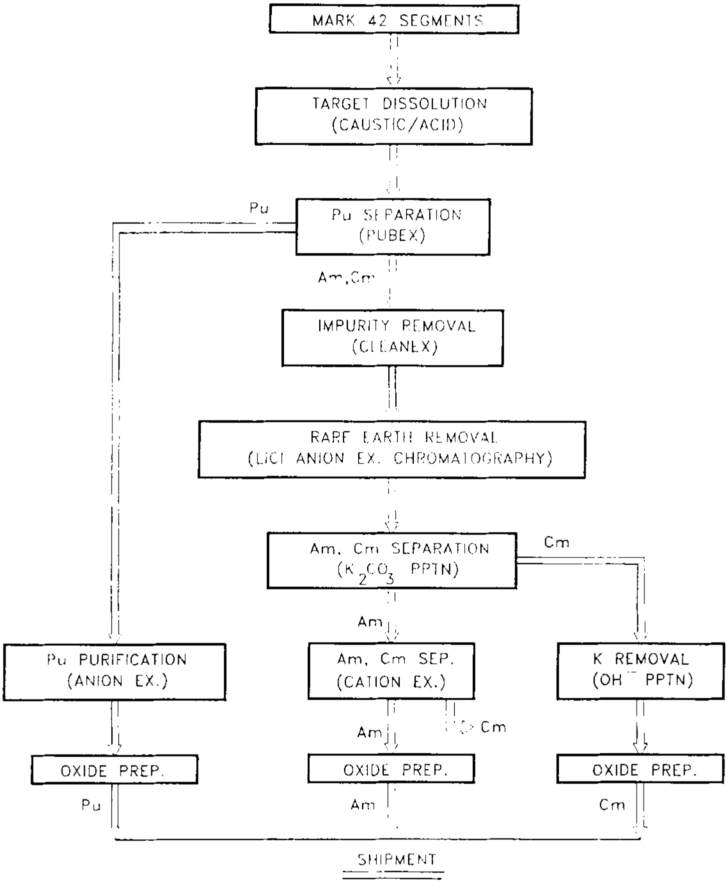

FIGURE 1. Mainline processing flowsheet for the Mark 42 materials.

phosphoric acid (HDEHP) in diethylbenzene diluent. For the extraction, the feed solution is sparged with nitric oxide to oxidze the Pu to the higher Pu(IV) valence for extraction. The plutonium and other high-valent elements, such as Zr and Mo, are extracted at high acid (~2.0 M $HNO_3$), while the Am, Cm, and other fission and corrosion products remain unextracted in the raffinate solution, thus yielding the desired separation. An organic soluble reductant, dibutylhydroquinone, which reduces the Pu to the Pu(III) valence, is added as an organic-phase modifier. The Pu is then stripped in higher acid (~6.0 M HCl) which contains a holding reductant. The Pu product solution is then further purified using anion exchange and Ionac A-580 resin followed by oxalate precipitation and calcination of the precipitate to an oxide product for shipment. The extraction raffinate containing the Am-Cm is the feed solution for a Cleanex batch extraction.

### Cleanex Batch Solvent Extraction

The objective of the Cleanex solvent extraction process (4) is to separate the trivalent actinides and rare earth fission products from the other impurities. The extractant for the Cleanex process is 1.0 M HDEHP in an n-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 in the extraction raffinate which is discarded. The trivalent actinides and rare earths are then easily stripped with several contacts with strong HCl (~6.0 M). This strip solution is then processed to separate the Am-Cm from the rare earths.

### LiCl Chromatographic Anion Exchange

The rare earth content of the Cleanex strip solution is about eight times higher by mass than the trivalent actinides. The separation of these rare earths from the Am-Cm is the objective of the LiCl chromatographic anion-exchange process (5). The feed for this process is adjusted to 11 to 12 M LiCl so that the anion complexes that are formed will preferentially load on the anion-exchange resin. Dowex-1 is the resin of choice for these operations. As the high-chloride solution is passed through the resin bed, the rare earth complexes load less strongly and will migrate ahead of the Am-Cm complexes. A 10 M LiCl solution is used to elute and flush the rare earth complexes off the resin followed by a 1 M HCl strip solution to remove the Am-Cm. The capacity of the resin column (~ 1.3 L of resin) allows for about 150 g of rare earths and 10 to 20 g of actinides, thus requiring multiple runs for the full separation. The first runs are typically for a coarse separation followed by second-cycle runs to get a more complete separation of the Am-Cm from the rare earths. In-line alpha monitoring of the exit stream from the column is used in making the proper separations. Sodium hydroxide is added to the Am-Cm product from the LiCl anion exchange runs to precipitate the Am-Cm as hydroxides. This precipitate is washed with dilute sodium hydroxide and water to remove the excess LiCl and dissolved in $HNO_3$ to provide a feed material for the Am-Cm separation operations.

## Am-Cm Separation

In most REDC processing, no further separation of the Am-Cm is necessary; however, for the Mark 42 materials, a separation of the Am-Cm was required. In addition, the final product specifications (<1% Am in the Cm product and <100 ppm Cm in the Am product) required a very high Cm decontamination factor (DF) from the Am product. Several methods for the Am-Cm separation were investigated including oxidation of the Am to Am(V) and cation exchange to effect the separation. Both organic and inorganic cation exchangers were investigated. The radiolysis effects of the Cm on the oxidized Am were so great that the desired separation could not be achieved in the short time period that the Am(V) was present. Attention was then focused on a bulk separation of the Cm from the Am to reduce the radiolysis effects followed by a more complete separation using cation exchange to obtain the desired separation levels. The flowsheet for the Am-Cm separation is shown in Figure 2.

## Potassium Carbonate Precipitation Process

A potassium carbonate precipitation process (6) that was developed in 1968 was chosen as the most appropriate option for a bulk separation of the Am-Cm products at the REDC since this process could be adapted for use with the existing equipment. Potassium carbonate was added to the Am-Cm product recovered from the hydroxide precipitation step to make a 3.5 M $K_2CO_3$ solution. The resulting solution was sparged with a 3% ozone/oxygen mixture to oxidize Am to Am(V) and form the insoluble $K_3AmO_2(CO_3)_2$ complex, which was easily filtered to yield the Cm product solution. The Am precipitate was dissolved in nitric acid and treated with hydroxylamine nitrate to reduce the Am(V) to Am(III). The entire process was repeated for two more cycles. Each cycle became less and less effective, and the Cm specification in the Am product was not met. A cation-exchange column was then employed for the final purification.

## Cation Exchange

After the third-cycle precipitation, the Am product was dissolved in nitric acid without the addition of hydroxylamine nitrate. The Am remained as Am(V) in the acid solution. This solution was passed through Dowex 50W-X8 cation-exchange resin, which removed the residual Cm, while the Am(V) passed through the resin, reporting to the column raffinate. The

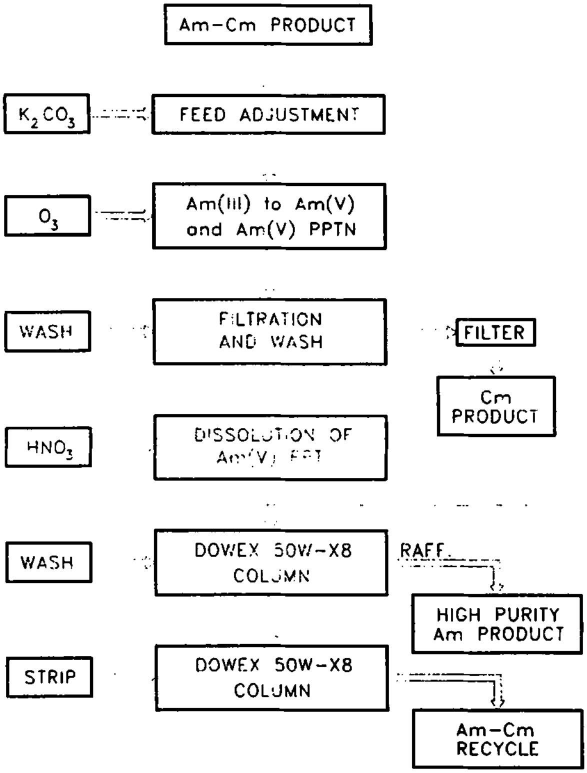

FIGURE 2. Flowsheet for the Am-Cm separation.

Am product was precipitated using oxalate precipitation techniques and fired to an oxide product for shipment. The curium product from the carbonate precipitation operations was stored for hydroxide precipitation to remove the potassium carbonate at a later time.

## RESULTS AND DISCUSSION

The focus of this section will be on the result of the various separation processes used in the initial processing of the Mark 42 material following the dissolution of outer cylinders from five segments of the first assembly. The dissolution step yielded the first fission product separation where about 95% of the cesium as well as other caustic-soluble fission products were contained in the dejacketing solution.

The first actinide product separation occurred during the PUBEX solvent extraction. The Pu(IV) was highly extractable in 1.0 M HDEHP (D values >3000), while the other actinides remain inextractable (Cm $D=10^{-4}$). Pu recoveries were >99% for this process with DFs of $10^3$ for both Am-Cm and the remaining $^{134,137}Cs$. The DFs for ruthenium and antimony were 19 and 6, respectively, but these impurities should be removed by subsequent Pu anion-exchange purification.

In the Cleanex solvent extraction, the only measurable DFs that can be calculated from the analytical data were for the remaining Cs (DF=140) and Ru (DF=11). However, from past experience, this process also removes most of the corrosion product and fission product impurities except for the trivalent rare earths which follow the Am-Cm in this extraction process. The Cleanex solvent extraction will remove all the remaining Al carried over from the caustic dissolution and the sodium added from the acid adjustment to effect the extraction of the actinides. The recoveries of Am-Cm from this Cleanex extraction were >98% with the remaining actinides recovered in waste solution processing (a second stage of Cleanex solvent extraction) operations and recycled into future processing operations.

One-half of the feed solution was processed in each of two LiCl chromatographic anion-exchange runs for the bulk separation of the Am-Cm product from the rare earths. Both of these runs gave Am-Cm product DFs from the rare earths of slightly over 10. One-fourth of the product recovered in the first-cycle runs was processed in each of four second-cycle runs for a more complete separation of the Am-Cm product from the rare earths resulted in DFs of $10^2$ - $10^3$, thus yielding overall DFs of $10^3$ - $10^4$. Hydroxide precipitation techniques were used to remove the bulk of the LiCl from the Am-Cm product and to prepare the feed for the carbonate precipitation operations.

Three carbonate precipitation runs were made to effect the separation of the Am and Cm. The first-cycle precipitation yielded a Cm DF of 46 (2.1% Cm) in the Am product and a Cm product containing 1% Am. The Cm product from this run was acceptable for its intended use, and no further purification was necessary. The Am product was recycled for the second carbonate precipitation run yielding an additional Cm DF of 10 (0.2% Cm). Following a third carbonate precipitation run, which yielded little improvement in the Am product (0.1% Cm), the specifications were still not met.

The cation-exchange run did give the desire product specifications with an additional Cm DF of 200 (5 ppm Cm in Am product), thus giving an overall DF of $2 \times 10^5$ for the combined carbonate precipitation/cation-exchange runs. The major drawback to this operation was that only 80% of the Am was recovered in the Am product with the remaining 20% being stripped with the Cm impurity for recycle.

## CONCLUSIONS

The REDC has demonstrated the successful processing of an irradiated Mark 42 assembly to separate the Pu, Am, and Cm products to the desired purity levels. Various processes that are common in REDC operations were used to effect these separations. The separation of the Am-Cm products and the production of a very high purity Am product was accomplished using a combination of a reliable process operation (carbonate precipitation) coupled with standard cation-exchange techniques to yield products with the desired specifications. Other processing techniques could be used to obtain the desired separations. These would include the application of PUREX technology for Pu separation and TRUEX technology for Pu and Am-Cm product separation. Other technologies for the reduction of waste solutions and management of wastes in forms suitable for more direct disposal could also be applied to the Mark 42 processing.

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