

Recovering Americium and Curium from Mark-42 Target Materials— New Processing Approaches to Enhance Separations and Integrate Waste Stream Disposition—12228

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ABSTRACT

Oak Ridge National Laboratory (ORNL) is investigating flowsheets to enhance processing efficiencies and to address waste streams associated with recovery of americium (Am) and curium (Cm) from Mark-42 (Mk-42) target materials stored at ORNL. The objective of this work was to identify the most effective flowsheet with which to process the 104 Mk-42 oxide capsules holding a total of 80 g of plutonium (Pu), 190 g of Cm, 480 g of Am, and 5 kg of lanthanide (Ln) oxides for the recovery and purification of the Am/Cm for future use as feedstock for heavy actinide production. Studies were also conducted to solidify the process flowsheet waste streams for disposal.

INTRODUCTION

Mk-42 targets were fabricated from Pu-239 and irradiated to produce Pu-242, Am-243, and Cm-244 primarily for defense applications. They were irradiated at the Savannah River Site (SRS), and many of the targets were processed at SRS to recover Pu-242 and at ORNL to separate and recover Pu-242 and Am-243. Historically, the process shown in Fig. 1 was used to process Mk-42 segments to produce Pu, Am, and Cm products. In the later phases of the processing, Pu was the product of interest, and only the Pu separation and impurity removal processing steps were conducted. The time-consuming LiCl anion exchange processes being used to separate Am/Cm from the Ln fission products were not conducted. Of this original Mk-42 material, 28 unprocessed target segments and 104 capsules containing unseparated Am, Cm, and Ln fission product oxides (Am/Cm/Ln oxides) from processed targets remain in inventory at ORNL (Fig. 2). The Am and Cm in these targets are irreplaceable and are an attractive feedstock for the production of heavy actinides (Cf-252, Bk-249, etc.).

A study is under way to develop the most effective flowsheet to recover and purify the Am/Cm in the stored oxide capsules for future use as feedstock for heavy actinide production. To enhance the efficiency of separation, a series of batch and multistage liquid-liquid extraction processes were identified for testing to remove Pu and Ln with actual Am/Cm/Ln oxides. The process flowsheet proposed for testing is shown in Fig. 3. The flowsheet consists of an oxide dissolution step, a batch Pu extraction process, Ln partitioning steps, a step to remove complexants, an oxalate precipitation step, and a step to prepare the Am/Cm oxide for target fabrication. TALSPEAK (Trivalent Actinide-Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes)

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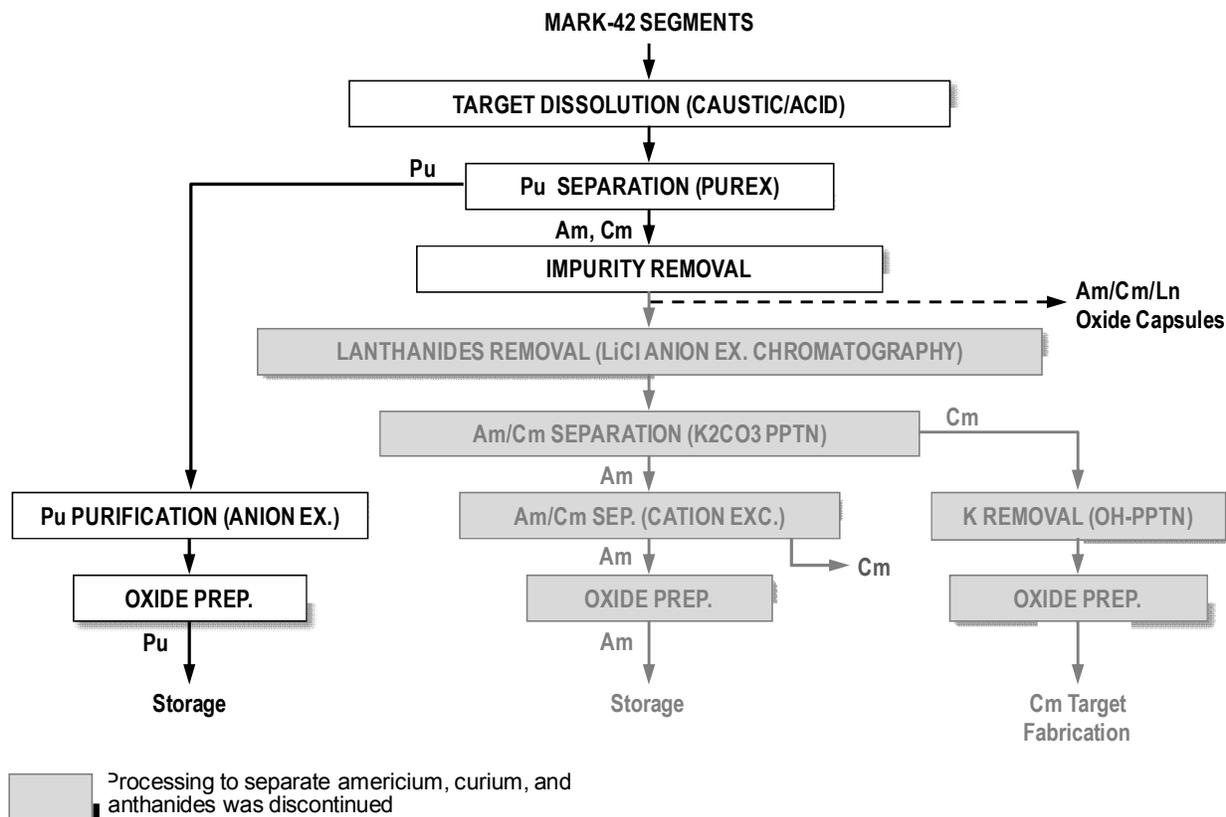


Fig. 1. Historic Mk-42 material separations flowsheet.



Mk-42 Segments Storage Canister



Am/Cm/Ln Oxide Capsule

Fig. 2. Mk-42 target segments and oxide capsules in storage.

flowsheet is used to separate the Ln from the Am/Cm elements [1, 2]. In the normal TALSPEAK process, the aqueous phase containing the complexing reagents plus the Ln and actinides is contacted with the organic phase to extract Ln.

In the Reverse TALSPEAK process, the organic phase is first loaded with the actinides and Ln and then contacted with the complexing aqueous phase to strip the actinides.

Each of the separations steps are described in more detail in the Separations Process section of this report.

A series of small runs is being conducted at the Radiochemical Engineering Development Center (REDC) at ORNL to demonstrate and refine the overall process shown in Fig. 3 to recover Am/Cm and to evaluate processing parameters to optimize the separations of Ln fission products from the Am/Cm constituents. Because of the large quantities of lanthanides and the extremely low disposal limit for Cm-244 (5.7×10^{-5} g/L) in the ORNL liquid waste system, multiple processing cycles may be needed to complete the required separations. Results from the first experimental runs and progress toward identifying the optimal flowsheet to process the Am/Cm/Ln oxides for recovery of Am/Cm, while addressing waste streams and process rework, are summarized below.

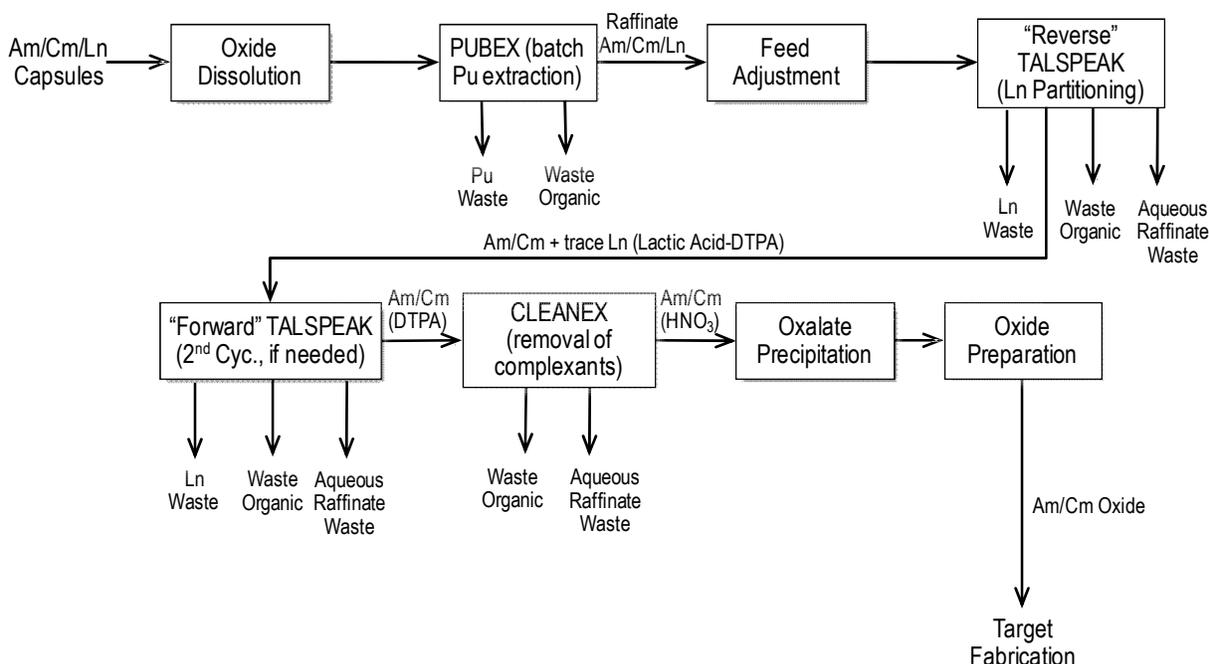


Fig. 3. Proposed separations flowsheet.

THE SEPARATIONS PROCESS

The first in a series of small runs has been completed using the flowsheet shown in Fig. 4. Figure 4(a) shows the overall flowsheet, and Figs. 4(b) and 4(c) show the details of the Reverse TAL SPEAK and CLEANEX processing steps, respectively. The purpose of the run was to demonstrate the overall process to recover Am/Cm and to optimize the separations of Ln fission products in storage at ORNL. Figure 4 is a simplified version of the proposed separations flowsheet shown in Fig. 3. Only one Ln partitioning step was performed, and the aqueous Am/Cm stream was not converted to an oxide [steps shown “grayed out” in Fig. 4(a)]. The results of the demonstration runs are described below, and the stream compositions are shown in Table I.

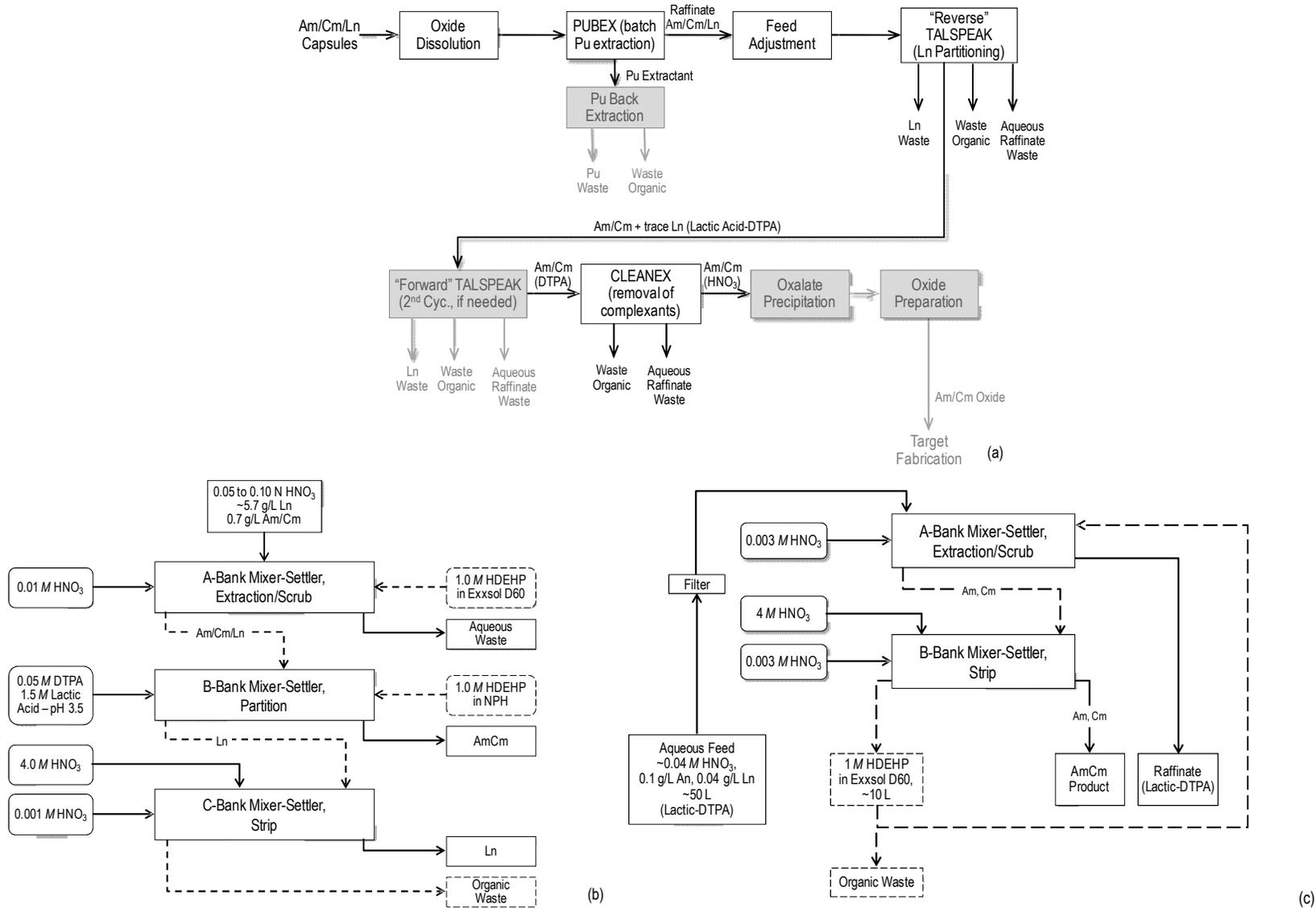


Fig. 4. (a) Demonstrated overall processing flowsheet; (b) Reverse TALSPEAK flowsheet; (c) CLEANEX flowsheet.

Table I. Measured Feed and Outlet Stream Compositions.

Stream	Am, g	Cm, g	Pu, g	Ln, g
Feed material				
Feed (Am/Cm/Ln capsule dissolved oxide)	4.62	1.79	1.25	50.3
Outlet streams				
PUBEX outlet streams				
PUBEX extractant	<9E-4	6E-5	0.94	0.008
Reverse TALSPEAK outlet streams				
Reverse TALSPEAK Ln waste	0.063	0.024	0.004	50.5
Reverse TALSPEAK aqueous raffinate waste	<3E-3	3E-5	0.006	0.005
Reverse TALSPEAK waste organic	<7E-4	4E-6	0.020	0.002
CLEANEX outlet streams				
CLEANEX Am/Cm product	4.27	1.83		1.1
CLEANEX aqueous raffinate waste (lactic acid)	0.004	2E-4	0.18	0.007
CLEANEX waste organic	<2E-4	2E-6	0.002	3E-4
Sum of outlet streams	4.33	1.85	1.12	51.6

PUBEX separations step

The oxide feed for the demonstration test was dissolved in strong nitric acid; the amounts recovered are listed in Table I as “Feed.” The first separation was a batch solvent extraction step (PUBEX process) [3] to remove the Pu-240 that had grown from the decay of Cm-244. The acidity of the aqueous feed was first reduced to ~0.5 M by extended evaporation and dilution with water.

Two metered additions of 30 vol % H₂O₂ were then made to adjust Pu valence to the tetravalent state. The adjusted feed was contacted with a batch of 1.0 M di(2-ethyl hexyl) phosphoric acid (HDEHP) in Exxsol D60 diluent to extract the Pu. The raffinate containing the trivalent Am, Cm, and Ln elements was phase separated and transferred to a separate collection tank to become the feed stream for the Reverse TALSPEAK separations step. The solvent was washed with several batches of 4.0 M HNO₃, and

the wash solutions were combined with the raffinate. The amounts of Am, Cm, Pu, and Ln measured in the organic extractant are listed in Table I under the title “PUBEX extractant.” In the future, this stream will be further processed to back extract the Pu from the solvent into strong hydrochloric acid, and the resulting Pu aqueous stream and stripped organic will be disposed of as wastes.

Reverse TALSPEAK separations step

The next processing step used three 16-stage mixer-settler contactors to run a Reverse TALSPEAK flowsheet [Fig. 4(b)] to separate the Ln from Am/Cm [4, 5]. The raffinate from the PUBEX run was adjusted to low acid conditions by extended evaporations and additions of NH_4OH solutions. Once the proper acid conditions were reached, the solution was diluted with water to make a final feed solution of $\sim 0.04 \text{ N H}^+$, $\sim 5.7 \text{ g/L}$ of Ln, and 0.7 g/L of Am/Cm.

In this process, the first contactor bank was used to extract the Ln and actinides into an organic extractant, 1.0 M HDEHP in Exxsol D60. The second contactor was used to partition the Am and Cm from the Ln, and the third was used to strip the Ln from the extractant. The partitioning of the Am/Cm in the second contactor was accomplished with a 1.5 M lactic acid— 0.05 M diethylenetriaminepentaacetic acid (DTPA) strip solution adjusted to pH 3.5 and a scrub of 1.0 M HDEHP . The actinides are more strongly complexed with the DTPA than the Ln; consequently, if proper conditions are set in the contactor (flow ratios, number of strip to back-scrub stages, etc.), the actinides can be stripped from the extractant while leaving the Ln in the solvent (partitioned). An organic back-scrub of the actinide stream is needed to re-extract small amounts of Ln that are stripped and improve the overall separation. The Ln is finally stripped with $\sim 4 \text{ M HNO}_3$.

The Am/Cm stream becomes the feed for the CLEANEX process, and three waste streams are produced (i.e., the Ln waste, aqueous raffinate waste, and the organic extractant). The measured results for each stream are shown in Table I. The measured Ln and actinide content in both the aqueous raffinate and waste organic was very low. The Ln/actinide ratio in the Am/Cm product was lowered from 7.8 to 0.18 with a decontamination factor (DF) of ~ 40 and a measured Am/Cm loss to the Ln waste of $\sim 1\%$. The amount of Am/Cm losses measured may be partially due to residual contamination in the collection tanks in the processing facility. Future larger-scale tests will better quantify these losses.

CLEANEX separations step

The next step was the recovery of the actinides from the TALSPEAK reagent, 1.5 M lactic acid—DTPA. This was accomplished by running a CLEANEX-type flowsheet [Fig. 4(c)] in two mixer-settler contactors [6]. The name CLEANEX was coined because the process was initially developed to “clean up” solutions containing a wide variety of contaminants.

The first contactor extracted the actinides into 1.0 M HDEHP in Exxsol D60, and the second contactor stripped the actinides with 4.0 M HNO₃. To efficiently extract the actinides, the aqueous feed is acidified (pH <2) with nitric acid to break the DTPA complex. The measured results from the Am/Cm actinide product and the aqueous raffinate waste and waste organic streams are listed in Table I.

The raffinate and waste organic streams contained very low levels of Ln and actinides. The resulting actinide product was in a clean nitric acid solution. In the full flowsheet shown in Fig. 3, this material would be converted to an oxide using oxalate precipitation for storage or loaded on resin and calcined for heavy-actinide target production. Since CLEANEX does not separate Ln from actinides, all of the Ln measured in this product was from the Reverse-TALSPEAK effluent. An additional Ln separations step may be performed in the future.

WASTE TREATMENT

Several waste streams will be generated from the Am/Cm recovery processes as shown in Fig. 3 and 4 and Table I. Scoping studies were performed with simulated materials to represent the waste streams, and formulations were developed for solidifying the waste to meet Waste Isolation Pilot Plant (WIPP) waste acceptance criteria (WAC) and be acceptable for performing the solidification operations remotely in hot cells. If a solidified material met the WIPP WAC for having less than 1% freestanding liquid, the formulation was then evaluated further based on other factors such as volume increase, the workability of the materials, and the length of time the material remained plastic before hardening.

The materials tested are shown in Table II, and the results of the most promising solidification formulations are given in Tables III and are described below.

An organic waste simulant consisting of a mixture of Exxsol D60 and HDEHP was tested. Sorbents tested for solidifying this organic stream included (1) Petroset II, (2) Organoclay BM-Qt-199, (3) MCM-830P, (4) HS300, (5) Aqua ET-1, (6) EC-199, and (7) Purina Tidy Cat kitty litter. Both Petroset II and Biomin EC-199 satisfactorily solidified this simulate waste stream under the test conditions. However, the Biomin EC-199 required three times more adsorbent to solidify the waste and resulted in a 50% larger volume increase. Therefore, Petroset II was selected as the most promising adsorbent for inclusion in Table III.

Three aqueous wastes were tested: (1) a mixture of 1 M DTPA and 3 M lactic acid to represent an aqueous raffinate waste, (2) a Ln/HNO₃ waste simulant containing 1 M Ln in a 6 M HNO₃ solution, and (3) a 80 g/L Pu/HNO₃ waste simulated with thorium nitrate in a 6 M HNO₃ solution. Sorbents tested for solidification of these aqueous streams included (1) Type I/II ordinary Portland cement, (2) blended ternary cement TERCEM 3000[®], (3) Ciment FONDU[®], (4) vermiculite, (5) a lightweight aggregate, (6) Class C fly ash, and (7) sodium silicate. The most promising formulations for each aqueous waste stream are shown in Table III. Each of these formulations resulted in workable mixing

Table II. Materials Tested for Solidification of Waste Streams.

Solidification Material	Manufacturer
Waste Organic Stream	
Petroset II	IMPACT – Fluid Tech
Organoclay BM-Qt-199	M2 Polymer
MCM-830P	Ecologix Environmental Systems
HS300	M2 Polymer
Aqua ET-1	Aqua Technologies
EC-199	Biomin
Tidy Cat kitty liter	Purina
Aqueous Waste Streams	
Ordinary Portland cement Type I/II	Lafarge
Blended Ternary cement TERCEM 3000 [®]	Lafarge
Ciment FONDU [®]	Kerneos
Vermiculite	Sungro Horticulture
Lightweight aggregate	Big River Industries, Inc.
Class C fly ash	Boral Material Technologies
Sodium Silicate N	PQ Corporation

Table III. Example Waste Solidification Formulations.

Waste Formulation Components	Weight Percent
Waste Organic Stream	
Waste simulant	67
Petroset II	33
Pu Waste Stream	
Waste simulant	41
TERCEM 3000 [®]	41
Vermiculite	2
Lightweight aggregate	16
Ln Waste Stream	
Waste simulant	42
Portland cement	41
Vermiculite	2
Lightweight aggregate	15
Aqueous Raffinate Waste Stream	
Waste simulant	40
Ciment FONDU [®]	35
Vermiculite	5
Lightweight aggregate	20

times of 5–6 hours and required approximately 20–21 hours for the mixtures to harden.

The above test results are based on scoping studies using simulated waste streams. Additional tests are recommended with actual waste materials under hot-cell-facility operating conditions to confirm the final waste treatment formulations.

CONCLUSIONS

ORNL is investigating flowsheets to enhance processing efficiencies and address waste streams associated with recovery of Am and Cm from Mk-42 target materials stored at ORNL. A series of small-scale runs are being performed to demonstrate an improved process to recover Am/Cm and to optimize the separations of Ln fission products from the Am/Cm constituents. The first of these runs has been completed using one of the Am/Cm/Ln oxide capsules stored at ORNL.

The demonstration run showed promising results with a Ln DF of 40 for the Am/Cm product and an Am/Cm DF of 75 for the Ln product. In addition, the total losses of Am, Cm, and Ln to the waste solvents and raffinates were very low at <0.2%, 0.02%, and 0.04%, respectively. However, the Ln-actinide separation was less than desired. For future Reverse TALSPEAK demonstration runs, several parameters will be adjusted (flow rates, the ratio of scrub to strip stages, etc.) to improve the removal of Ln from the actinides. The next step will also include scale-up of the processing flowsheet to use more concentrated solutions (15 g/L Ln versus 5g/L) and larger volumes and to recycle the HDEHP solvent. This should improve the overall processing efficiency and further reduce losses to waste streams.

Studies have been performed with simulated wastes to develop solidification processes for disposal of the secondary waste streams generated by this flowsheet. Formulations were successfully developed for all the waste simulants. Additional tests with actual waste will be the next step in this effort.

Future plans are to process all of the remaining 103 capsules in storage at ORNL. A nine-capsule test is now under way to provide additional information to scale-up the process to a target 20-capsule batch size for future processing runs.

ACKNOWLEDGMENTS

This work was funded by the Department of Energy National Nuclear Security Administration NA-73 Office of Nuclear Materials Integration. The separations processes were performed by ORNL's REDC staff.

REFERENCES

1. Weaver, B.S., and Kappelmann, F.A. (1968). Preferential Extraction of Lanthanides over Trivalent Actinides by Monoacidic Organophosphates from Carboxylic Acids and from Mixtures of Carboxylic Acids and Aminopolyacetic Acids. *J. Inorg. Nucl. Chem.*, 30, 263–272.
2. Del Cul, D.G., Bond, W.D., Toth, L.M., Davis, G.D., Dai, S., and Metcalf, D.H. (1994). Citrate Based “TALSPEAK” Lanthanide-Actinide Separation Process. ORNL/TM-12785, Oak Ridge National Laboratory, Oak Ridge, TN
3. Faraday, J.J. and Chilton, J.M. (1969). Isolation of Plutonium in Chloride Media—II. *J. Inorg. Nucl. Chem.*, 31, 3247–3254.
4. Persson, G., Svantesson, I., Wingefors, S., and Liljenzin, J.O. (1984). Hot Test of a Talspeak Procedure for Separation of Actinides and Lanthanides Using Recirculating DTPA-Lactic Acid Solution. *Solvent Extraction and Ion Exchange*, 2(1), 89–113.
5. Koch, G., Kolarik, Z., and Haug, H. (1976). A Solvent Extraction – Ion Exchange Process for the Recovery of Transplutonium Elements from Power Reactor Fuels. *J. Inorg. Nucl. Chem. Supplement*, 165–170.
6. Bigelow, J.E., Collins, E.D., and King, L.J. (1980). “The Cleanex” Process: A Versatile Solvent Extraction Process for Recovery and Purification of Lanthanides, Americium, and Curium. ACS Symposium Series, No. 117 Actinide Separations.