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REACTOR PRODUCTION OF ^{252}Cf AND TRANSCURIUM ISOTOPES

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ABSTRACT

Berkelium, californium, einsteinium, and fermium are currently produced in the High Flux Isotope Reactor (HFIR) and recovered in the Radiochemical Engineering Development Center (REDC) at the Oak Ridge National Laboratory (ORNL). All the isotopes are used for research. In addition, ^{252}Cf, ^{253}Es, and ^{255}Fm have been considered or are used for industrial or medical applications. ORNL is the sole producer of these transcurium isotopes in the western world.

A wide range of actinide samples were irradiated in special test assemblies at the Fast Flux Test Facility (FFTF) at Hanford, Washington. The purpose of the experiments was to evaluate the usefulness of the two-group flux model for transmutations in the special assemblies with an eventual goal of determining the feasibility of producing macro amounts of transcurium isotopes in the FFTF. Preliminary results from the production of ^{254g}Es from ^{252}Cf will be discussed.

1. INTRODUCTION

Transcurium elements are of continuing interest to scientists for a variety of reasons involving both fundamental research and practical applications. These elements include berkelium ($_{97}$Bk), californium ($_{98}$Cf), einsteinium ($_{99}$Es), and fermium ($_{100}$Fm). Fermium is the heaviest element that can be produced in nuclear reactors; heavier nuclides ($Z > 100$) must be produced in particle accelerators. Berkelium and californium were first discovered in 1949[1] and 1950[2] in the reaction products from accelerator bombardments on americium and curium targets. Other, heavier berkelium and californium isotopes and einsteinium and fermium were discovered in 1952 in the debris from a thermonuclear test explosion.[3]

2. BACKGROUND

A sustained effort to produce the heavier actinides started in the late-1950s with the irradiation of ^{239}Pu at the Materials Test Reactor at Idaho National Engineering Laboratory and subsequent recovery of the purified ^{252}Cf at Lawrence Berkeley Laboratory, and continued into the late-1960s with a large-scale evaluation program at the Savannah River Site and a smaller effort at ORNL. Since 1973, though, the entire supply of ^{252}Cf and other transcurium elements in the western world has been produced in the HFIR and recovered at the REDC at ORNL as part of the National Transplutonium Element Production Program, aimed at supplying heavy elements for research and applied purposes.

Production of the transcurium elements is generally based on a long series of neutron captures and beta decays (see Fig. 1). Competing destructive reactions are neutron-induced fission, alpha decay, and spontaneous fission. Heavy element yields are particularly dependent on neutron fluxes, irradiation times, and the composition of target or starting material.

3. PRODUCTION AND RECOVERY

Four generations of targets have been fabricated to produce transcurium elements. Initially, the target material was ^{239}Pu and evolved through ^{242}Pu to $^{244\text{-}248}Cm$. The current generation of curium targets are remotely fabricated at the REDC. Pure aluminum powder and actinide oxide powders are cold-pressed into pellets ~1.45 cm in length and 0.633 cm in diameter. A single target consists of 35 pellets with an active length of 50.8 cm and an overall target length of 88.9 cm. Total actinide loading is on the order of 9-10 g/target.[4]

Targets are irradiated for 12-15 months in the target island of the HFIR. The HFIR produces a very high thermal flux of $\sim 2 \times 10^{15}$ n/cm^2-s in the target island with a thermal-to-epithermal flux ratio of ~23. Typical charge and discharge compositions are shown in Tables 1 and 2. The targets are allowed to decay for 2-4 weeks before beginning processing. All processing takes place inside heavily-shielded hot cells and shielded glove boxes.

Processing of the targets involves a series of chemical operations.[5] The targets are dissolved in a caustic-nitrate solution and then undergo batch extractions, anion exchange, and cation exchange chromatography. Einsteinium and fermium undergo additional cation exchange chromatography to produce highly-separated and purified products. Berkelium and californium are separated from each other using batch extraction followed by cation exchange chromatography. Americium and curium undergo oxalate precipitation and calcination and are recycled back into target fabrication. Californium-252 is transferred to a dedicated hot-cell facility where residual ^{244}Cm is removed by cation exchange and the ^{252}Cf is fabricated into neutron sources[6] or is "milked" for ^{248}Cm, the alpha decay daughter of ^{252}Cf. A normal production and recovery campaign consists of 12-15 targets/yr with the capability to increase to ~45 targets/yr. A processing campaign normally requires 3-5 months to complete and yields are typically greater than 95%.

4. APPLICATIONS

The mainline products are ^{249}Bk, ^{252}Cf, ^{253}Es, and ^{257}Fm, along with the derived products of ^{248}Cm, ^{249}Cf, ^{254}Es, and ^{255}Fm. Most of these isotopes are used for research in nuclear reactions and for synthesis of new species and in the studies of nuclear, chemical, and solid state properties,

and spectroscopy. The three isotopes that have been considered or used for applied purposes (industrial and/or medical) are ^{252}Cf, ^{253}Es, and ^{255}Fm.

Californium-252 is used for neutron radiography, neutron gauging, activation analysis, transuranic waste assay, neutron damage studies, dosimetry standards, and reactor startup sources. From 1987 through 1989, ~380 mg of ^{252}Cf were sold or loaned for these types of applications. In addition, ^{252}Cf is showing particular promise for the treatment of cervical cancers and gliomas.[7] It also has potential as a source of neutrons for external beam and implant-based boron neutron capture therapy. Einsteinium-253 and ^{255}Fm are currently being investigated for radiolabeling tumor-specific antibodies for radioimmunotherapy.[8]

5. MULTI-ISOTOPE PRODUCTION TEST

In 1989, a Multi-Isotope Production (MIP) test was conducted at the FFTF at Hanford, Washington, in conjunction with the Space Isotope Production (SIP) test.[9] The tests were unique in that the normally fast neutron flux in the FFTF was moderated by yttrium hydride test assemblies in order to enhance the thermal and epithermal flux in a region of the reactor for test samples. Interest in developing a backup capability to the HFIR and the potential impact of a much smaller thermal-to-epithermal flux ratio on transcurium isotopic compositions and yields led to ORNL's participation in the MIP test.

The principal goal was to try to evaluate the usefulness of the two-group flux model, normally quite satisfactory for well-moderated reactors such as HFIR, specific to transmutations in the special assemblies. Toward this goal, multi-nanogram samples of high-isotopic purity ^{240}Pu, ^{242}Pu, ^{243}Am, ^{249}Cf, as well as light- and heavy-mixtures of curium isotopes, and ^{252}Cf-rich samples

were irradiated. A total of 18 samples in three capsules were irradiated with flux monitors. Incorporated in each capsule was a gadolinium-filtered packet of samples and monitors to allow a direct measurement of epithermal fluxes and resonance integrals. A typical experimental package is shown in Fig. 2. The samples were irradiated at the FFTF for ~10.5 effective full power days and, in due course, returned to ORNL for analyses and evaluation.

The two-group flux model depends on a description of the reactor neutron flux spectrum in which a thermal component is approximated by a Maxwellian distribution (characterized by temperature) and a "1/E" distribution extending from energies just above thermal to near fission neutron energies (an energy span of $\sim 10^5$). In special cases, it is also necessary to take into account the fast neutron component of the flux spectrum ($E_n \geq 0.1$ MeV). For low temperature, well-moderated reactors, predictions of the two-group model have been found to agree very well with experiment. However, the application of the model has been less thoroughly tested for reactors operating at high temperatures with fuel primarily undergoing fission with fast neutrons. Full-core Monte Carlo modeling of the FFTF neutron flux had indicated that this two-component characterization required by the model would be nearly satisfied in the test assemblies.[10] The two components of the flux spectrum (i.e., the thermal flux and the resonance flux per unit lethargy) can be individually evaluated with the use of neutron filters. Gadolinium filters were substituted for the more usual cadmium filters because of the high temperature of the assemblies. Thus, in principle, it becomes possible to evaluate both thermal cross sections and resonance integrals. In this irradiation, the estimation of the neutron temperature of ~0.06 eV characterizing the thermal flux was made from calculations of assembly temperatures.[11] The gadolinium filter cutoff energy was then taken to be ~0.44 eV from the calculations of Stoughton et al.[12] Standard resonance integrals, normally defined with a lower limit of 0.50 eV, were corrected to this limit appropriate to the current irradiation. Thermal neutron cross sections and resonance integrals

were taken from the compilation of Mughabghab et al.[13] The temperature-dependent Westcott g-factors [which corrects for the deviation from (1/V)-dependence of cross sections in the thermal region] are due to N. Holden et al. of the National Nuclear Data Center at Brookhaven National Laboratory.[14] Calculations of the yields of several nuclides in the production chains have now been compared with preliminary experimental measurements.

6. RESULTS

One sequence of nuclides of special interest involves the production of the 276-day ^{254g}Es from the irradiation of ^{252}Cf (see Fig. 3). Approximately 10 ng of ^{252}Cf were irradiated in both the filtered and unfiltered positions. The irradiated ^{252}Cf was analyzed by mass spectroscopy for the californium isotopes and by alpha spectroscopy for ^{252}Cf, $^{253\text{-}254g}$Es, and ^{255}Fm. Two-group fluxes were determined from the activation of cobalt flux wires. The initial composition of the californium samples is given in Table 3. The entire sequence was accounted for in the transmutation calculations. However, the impact of the ^{248}Cm and the lighter californium isotopes on the final amount of ^{252}Cf is small (<1% for the filtered sample and <2% for the unfiltered sample) and, therefore, ratios of ^{253}Es and ^{254g}Es to ^{252}Cf should be essentially unaffected by any uncertainties in the transmutation rates of the lighter californium isotopes.

Alpha spectroscopy of ^{253}Es was carried out at a number of different times after discharge from the FFTF. This allowed for positive identification of ^{253}Es (coupled with its alpha particle energies) and also allowed for the determination of ^{253}Cf, its ß-decay precursor. Einsteinium-254 was also measured concurrently with the ^{253}Es. However, the definitive measurements were made

at times greater than six months after discharge in order to allow the ^{253}Es to decay to levels that would not interfere with the measurement of ^{254}Es. Counting statistics were generally no poorer than 4% for all californium samples.

Calculations were based on the cross sections given in Table 4. Both calculated and experimentally measured isotopic values were compared to the amount of ^{252}Cf remaining after irradiation. The use of ratios (e.g., $^{254}Es/^{252}Cf$), rather than evaluating individual nuclides, eliminated the need for precise quantitative chemical recoveries or yield evaluations leading to higher precision. These ratios were used to construct a calculated/experimental ratio (C/E) which would be indicative of the usefulness of the two-group flux model. The C/E results for both the filtered and unfiltered samples are given in Table 5.

TABLE 1. Typical Transplutonium Charge Composition

Isotope	Quantity (g/target)
^{238}Pu	8.10×10^{-4}
^{239}Pu	1.00×10^{-3}
^{240}Pu	2.30×10^{-1}
^{241}Pu	1.40×10^{-4}
^{242}Pu	8.70×10^{-4}
^{241}Am	1.46×10^{-1}
^{243}Am	3.24×10^{-1}
^{242}Cm	7.00×10^{-5}
^{243}Cm	1.60×10^{-3}
^{244}Cm	3.83×10^{0}
^{245}Cm	5.36×10^{-2}
^{246}Cm	3.60×10^{0}
^{247}Cm	1.02×10^{-1}
^{248}Cm	6.30×10^{-1}

TABLE 2. Typical Annual Yields from Transplutonium Targets[a]

Isotope	Quantity
^{249}Bk	60-70 mg
^{249}Cf	b
^{252}Cf	~500 mg
^{253}Es	2-3 mg
^{254}Es[c]	4 μg
^{255}Fm	4-8 ng
^{257}Fm	1-2 pg

[a]Based on 13 $^{244-248}$Cm targets.
[b]Californium-249 is the daughter of ^{249}Bk. Yield is dependent on time of berkelium/californium separation.
[c]Nine months after discharge.

TABLE 3. Initial Californium Composition

Isotope	Atom Percent (%)
^{248}Cm	28
^{249}Cf	10.37
^{250}Cf	8.43
^{251}Cf	2.92
^{252}Cf	50.28
^{254}Es	0.0056

TABLE 4. Thermal Cross Sections and Resonance Integrals[12]

Isotope	Half Life	σ_γ (b)	σ_f (b)	I_γ (b)[c]	I_f (b)[c]
^{252}Cf	2.645 y	19.5[a]	30.6[b]	44.1	110.9
^{253}Cf	17.81 d	17.6	1300.0	13.5	2036.5
^{253}Es	20.47 d	5.8 (^{254g}Es)	0.0	114.2 (^{254g}Es)	0.0
		178 (^{254m}Es)	0.0	3755 (^{254m}Es)	0.0
^{254g}Es	275.7 d	28.3	1970	19.0	1255.2

[a] σ_γ (^{252}Cf) = g_γ (T°)·σ°_γ.
g_γ = 0.9544 at 0.06 eV.[13]

[b] σ_f (^{252}Cf) = g_f (T°)·σ°_f.
g_f = 0.9554 at 0.06 eV.[13]

[c] Lower energy limit for resonance integrals =0.44 eV (based on gadolinium cutoff energy at 0.06 eV).[11]

TABLE 5. C/E Values for the Production of ^{254g}Es from ^{252}Cf

Isotope	C/E[a]	
	Filtered[b]	Unfiltered[c]
^{253}Cf		
^{253}Es		
^{254g}Es		

[a] $C/E = \frac{(N_i/^{252}Cf)_{calc}}{(N_i/^{252}Cf)_{exp}}$ where $N_i = {}^{253}Cf$, ^{253}Es, or ^{254g}Es

[b] Filtered: epithermal flux.

[c] Unfiltered: epithermal + thermal flux.

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