

PROGRESS IN CHEMICAL PROCESSING OF LEU TARGETS FOR ^{99}Mo PRODUCTION--1997

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ABSTRACT

Presented here are recent experimental results of our continuing development activities associated with converting current processes for producing fission-product ^{99}Mo from targets using high-enriched uranium (HEU) to low-enriched uranium (LEU). Studies were focused in four areas: (1) measuring the chemical behavior of iodine, rhodium, and silver in the LEU-modified Cintichem process, (2) performing experiments and calculations to assess the suitability of zinc fission barriers for LEU metal foil targets, (3) developing an actinide separations method for measuring alpha contamination of the purified ^{99}Mo product, and (4) developing a cooperation with Sandia National Laboratories and Los Alamos National Laboratory that will lead to approval by the U.S. Federal Drug Administration for production of ^{99}Mo from LEU targets. Experimental results continue to show the technical feasibility of converting current HEU processes to LEU.

INTRODUCTION

Most of the world's supply of ^{99}Mo is produced by the fissioning of ^{235}U in high-enriched uranium targets (HEU, generally 93% ^{235}U). To reduce nuclear-proliferation concerns, the U.S. Reduced Enrichment for Research and Test Reactors (RERTR) Program is working to convert the current HEU targets to low-enriched uranium (LEU, <20% ^{235}U). Switching to LEU targets also requires modifying the separation processes. Current HEU processes can be classified into two main groups based on whether the irradiated target is dissolved in acid or base. Our program has been working on both fronts, with development of acid-side processes being the furthest along. An LEU metal foil target may allow the facile replacement of HEU for both acid- and basic-dissolution processes. The irradiation and processing of the LEU metal-foil targets are being demonstrated in cooperation with researchers at the Indonesian PUSPIPTEK facility.

Currently, targets for the production of ^{99}Mo are generally either (1) miniature Al-clad fuel plates [1-9] or pins [10,11] containing U-Al alloy or UAl_x dispersion fuel similar to that used, at least in the past, to fuel a reactor or (2) a thin film of UO_2 coated on the inside of a stainless steel tube [12-14]. The

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⁹⁹Mo is extracted first by dissolving either the entire Al-clad fuel plate or pin or by dissolving the UO₂ and then performing a series of extraction and purification steps. Both acidic and basic dissolutions are used, and each producer has its own process. The highly competitive nature of the business and the stringent regulations governing the production of drugs make producers reluctant to change their processes.

To yield equivalent amounts of ⁹⁹Mo, the LEU targets must contain five to six times as much uranium as the HEU targets they replace. Substituting LEU for HEU in targets will require, in most cases, changes in both target design and chemical processing. Three major challenges have been identified: (1) to modify targets and processing as little as possible, (2) to assure continued high yield and purity of the ⁹⁹Mo product, and (3) to limit economic disadvantage. Keeping the target geometry the same, thereby minimizing the effects of LEU substitution on target irradiation, necessitates modifying the form of uranium used. Changing the amount and form of the uranium in the target necessitates modifying at least one or, possibly, two processing steps--dissolution and initial molybdenum recovery.

One of the issues raised in connection with using LEU to produce ⁹⁹Mo is the greater amount of ²³⁹Pu generated. The ²³⁹Pu is generated through neutron capture by the ²³⁸U. About 30 times more ²³⁹Pu is generated in an LEU target vs. an HEU target for an equivalent amount of ⁹⁹Mo. However, significantly more ²³⁴U is present in HEU than in LEU as a consequence of the enrichment process. Therefore, total alpha contamination of an irradiated LEU target is only ~20% higher than that of an equivalent HEU target.

Discussed below are four process-related issues that were studied this year. The first section reports our activities to better understand and predict the behavior of three fission products during molybdenum recovery and purification by the Cintichem process. These elements are iodine, rhodium, and silver. The next section reports progress on our studies to measure the effects of using zinc fission barriers for uranium-foil targets. The third section reports our development of a procedure to measure alpha contamination in the ⁹⁹Mo product. The fourth section discusses our initiatives with Sandia National Laboratories (SNL) and Los Alamos National Laboratory (LANL) to obtain U.S. Federal Drug Administration (FDA) approval for ⁹⁹Mo produced from LEU targets. Following these sections is a short Conclusions and Future Work section.

BEHAVIOR OF FISSION PRODUCTS IN THE LEU-MODIFIED CINTICHEM PROCESS

The Cintichem process currently uses HEU as U₃O₈ deposited on the inside of a cylindrical target [12-14]. After irradiation, the U₃O₈ in the target is dissolved in a mixture of sulfuric and nitric acid. Following dissolution and the addition of several reagents to the spent dissolver solution, molybdenum is precipitated by using α -benzoin oxime. Following this step, the precipitate is collected, washed, and redissolved. The redissolved molybdenum solution is then passed through two additional purification steps. It is our objective in switching to LEU to maintain the process for molybdenum recovery and separation from uranium (and its fission and absorption products) as close as possible to the current Cintichem process. It is also our goal to make improvements to the process that will alleviate any economic detriment to conversion to LEU. To this end, we are (1) developing an LEU metal-foil target and (2) have modified the dissolver solution to contain only nitric acid in place of the sulfuric and nitric acid mixture (sulfate in the high-activity waste complicates waste treatment and/or disposal [15]). Our past work in converting the Cintichem process has been discussed in earlier RERTR meetings [16-24].

Argonne National Laboratory is collaborating with the National Atomic Energy Agency (BATAN) of Indonesia and Sandia National Laboratories (SNL) to develop and demonstrate the use of LEU targets in the Cintichem process. The work described below was directed toward better understanding the chemical behavior of several radioisotopes that may be problematic to obtaining a pure ^{99}Mo product in the Cintichem process.

Radioiodine Decontamination

Most of the radioiodine in the Cintichem dissolver solution should be present as I_2 following dissolution by the nitric-acid/sulfuric-acid cocktail or by nitric acid alone. It will, therefore, be removed from the solution by evacuating the dissolver. The iodine is collected in an iodine trap. What passes through the iodine trap is held by the cold trap, which is maintained at liquid nitrogen temperatures. However, other iodine species (I^- , IO_3^- , and IO_4^-) may have formed during fissioning. The rate of isotopic exchange between I^- and I_2 is rapid, while isotopic exchange between either iodate or periodate and all other iodine species is slow [25]. Therefore, once radioiodine is in the form of iodate or periodate, addition of iodide or iodine carriers will have little effect on changing its oxidation state. For this reason, we studied the chemical behavior of iodate and periodate in molybdenum purification steps. All experiments were performed using carrier-free ^{125}I tracer purchased from Amersham Corp. The chemical form of the ^{125}I tracer was established by standard techniques [25].

In the Cintichem process, precipitation of silver iodide and sorption by activated charcoal (AC) and silver-coated activated charcoal (ACAC) are employed to remove radioiodine [14]. These methods would remove radioiodine in the form of molecular iodine (I_2) or iodide ion (I^-). We looked at the effectiveness of these steps at removing these species, as well as iodate (IO_3^-) and periodate (IO_4^-).

Precipitation of iodide ion by the addition of silver nitrate is considered quantitative; the solubility product of AgI is 8.3×10^{-17} [26]. Molecular iodine is not expected to precipitate with silver ion, but does react with silver metal to form the insoluble AgI . Silver iodate also has limited solubility, but its solubility product is significantly larger than that of AgI — 3.1×10^{-8} [26]. It is likely that silver periodate is more soluble than AgIO_3 . Because carrier precipitation is a likely mechanism for increasing the removal of ions to a greater extent than their solubility products predict, we looked at the coprecipitation of periodate on AgI and AgCl precipitates. Silver iodide was precipitated from a solution containing 4 mg of iodide ion, 1M HNO_3 , and the periodate- ^{125}I tracer by the addition of AgNO_3 solution. The amount of iodide ion was the same as used in the Cintichem process. The solution concentrations were calculated to be 0.005M I^- and 0.46M Ag^+ (assuming no precipitation). Silver chloride was precipitated from a solution containing HCl and the periodate- ^{125}I solution by adding AgNO_3 solution. Solution concentrations were calculated to be 0.017M Cl^- and 0.49M AgNO_3 (assuming no precipitation). After precipitation, the solutions (and precipitate) were allowed to stand 30 min with periodic mixing to give ample time for periodate pickup. The solutions were then centrifuged; the precipitates were washed twice with water and then dissolved in 4 mL of 2.6M sodium thiosulfate. Aliquots of the thiosulfate, supernatant, and wash solutions were analyzed for ^{125}I . The results shown in Table 1 confirm that coprecipitation is a likely mechanism for removal of the iodate and periodate forms. In both cases, the amount of periodate ion in solution was dropped by a factor of about twenty. None of the periodate ion would have precipitated without being carried by the AgCl or AgI , given the extremely low concentration of the tracer ($5 \times 10^{-11}\text{M}$).

We also studied the sorption of iodine species by AC and ACAC. The general trends of the data summarized in Table 2 are that (1) iodide is sorbed to a limited degree by AC and very well by ACAC, (2) iodine is sorbed to a limited degree by AC and very well by ACAC, and (3) neither iodate nor periodate is sorbed on AC or ACAC. For reference, a distribution coefficient (K_d) of ~ 10 mL/g will

allow the separation of a species from solution; however, it would not be an efficient process and would require large amounts of sorbent for high decontamination. On the other hand, a K_d of 1000 mL/g would provide an extremely efficient and effective decontamination process. Our results show that the ACAC sorbent provides such a process for I^- and I_2 removal.

Table 1. Coprecipitation of ^{125}I -Periodate with Silver Iodide and Silver Chloride from 1M HNO_3

Carrier	Fraction	Percent of ^{125}I Added
AgI	Precipitate	95
	Supernatant	7
	Wash Solution	0.2
AgCl	Precipitate	94
	Supernatant	1.0
	Wash Solution	<0.1

Table 2. Distribution Coefficients for Sorption of ^{125}I -Tracer, as Iodide, Iodine, Iodate, and Periodate, on Activated Charcoal (AC) and Silver-Coated Activated Charcoal (ACAC) from 0.2M NaOH Solution

Species	Distribution Coefficient ^a , mL/g	
	AC	ACAC
I^-	4	1,400
I_2	5	3,700
IO_3^-	<1	<1
IO_4^-	<1	<1

^aAverage values for contacts with different (1) ratios of mass of sorbent to volume of solution, (2) contact times, and (3) preparation of iodine species. Differences in K_d values for varying experimental conditions were indistinguishable. All measurements were done at room temperature with 2 mL of solution containing 0.2 g of solid.

Rhodium Decontamination

In the Cintichem process, columns of hydrated zirconium oxide (HZO), AC, and ACAC are used in the purification process. During 1997, we investigated the uptake of rhodium by these solids from

0.2M NaOH, the solution from which ^{99}Mo is purified during processing [14]. Rhodium isotopes from fission have half-lives ranging from <1 second to 35.4 hours. None is a suitable tracer. The best radioactive rhodium isotope for use as a tracer is ^{101}Rh , which decays by electron capture with a 3.3-year half-life and also emits several gamma rays. Ten microcuries of this nuclide was purchased from Isotope Products Laboratories (Burbank, CA) for use in these studies. The ^{101}Rh was carrier-free RhCl_3 in 5 mL of 6M HCl.

Measurements of distribution coefficients for rhodium between 0.2M NaOH and the three solid sorbents were complicated by the instability of the solutions. As the basic solution aged, the ^{101}Rh activity dropped. Initially, the 0.2M NaOH solutions were measured to contain between 93 and 103% of that pipetted from the stock ($5 \times 10^{-11}\text{M}$); Table 3 shows the decrease with time. The range of loss vs. time data is from a series of experiments where the degree of mixing and the material of the test tube were varied. No systematic trend was seen for either parameter; the ranges shown are more indicative of the difficulty in sampling a two-phase system. Because the tracer was initially in the form of RhCl_3 , it is likely that this effect is due to the conversion of Rh(III) from the soluble trichloride to an insoluble hydroxide form. The chemistry of Rh(III) is quite complex and generally not easily predictable [27]; however, one could infer from these data that the solubility of Rh(III) in 0.2M NaOH is $2 \times 10^{-12}\text{M}$ based on the amount still in solution after 13 days.

The loss of soluble rhodium with time complicates the measurement of its K_d for partitioning between 0.2M NaOH and the three solid sorbents. To deal with this problem, two K_d values are given for each sorbent at each mixing time. The first is based on the total concentration of rhodium added, and the second is based on the expected average amount of rhodium remaining in solution without the sorbent present (based on the data shown in Table 3). The data presented in Table 4 are better viewed qualitatively than quantitatively. The actual K_d is somewhere between the “remaining” and “added” values. All that can be inferred from these data is that (1) all three materials are effective sorbents for soluble and insoluble Rh(III)-Cl/OH species from 0.2M NaOH and (2) the order of sorbent effectiveness is as follows, ACAC better than AC better than HZO.

According to the calculations we presented in last year’s RERTR meeting [23], a typical 18-g LEU-foil target would contain 700 Ci of ^{99}Mo and 100 Ci of ^{105}Rh by 24 hours after the end of irradiation in the BATAN reactor. The volume of the 0.02M NaOH solution is ~40 mL. If one neglects all other rhodium that may be in solution as other fission-product isotopes and carrier, the rhodium concentration in this solution is calculated to be $3 \times 10^{-5}\text{M}$, a concentration $\sim 10^7$ higher than the above data allow. Adding to that factor is the high affinity for rhodium by the sorbents in the Mo-purification columns, which conservatively, may provide another decontamination factor of 100. To meet a specification of $0.05 \mu\text{Ci}/\text{mCi-}^{99}\text{Mo}$ would require a decontamination factor of ~ 3000 for the process. Based on the (1) low solubility of Rh(III) species in the process solution and (2) the effectiveness of the sorbents at removing rhodium from solution, attaining this decontamination should be no problem for the Cintichem process.

Silver Decontamination

Although the decontamination factors needed for silver fission products are small (2^{10}), their impurity levels in the ^{99}Mo are difficult to measure because they have no gamma peaks. Therefore, we measured the decontamination factors for irradiated-silver tracer in each step of the LEU-modified Cintichem process. The silver decontamination factors for the (1) initial molybdenum recovery step was >70 , (2) the first purification column was >40 , and the (3) second purification column was >40 . Multiplying the three decontamination factors would result in an overall decontamination factor of $>10^5$; silver should, therefore, not be a contamination problem in the Cintichem process.

Table 3. Loss of ^{101}Rh Tracer from a 0.2M NaOH Solution vs. Time Over 13-Day Period^a

Time	Range of Remaining ^{101}Rh Activity, %
right after addition	93-103
15 min	82
30 min	47-89
1 hr	63
4 hr	17-71
2 d	28-41
5 d	10-22
13 d	1.8-2.2

^aOver the same 13-day period, the measured rhodium activity in a 6M HCl solution was constant.

Table 4. Distribution Coefficients vs. Mixing Time for Sorption of ^{101}Rh -Tracer^a on Hydrous Zirconium Oxide (HZO), Activated Charcoal (AC), and Silver-Coated Activated Charcoal (ACAC) from 0.2M NaOH Solution

Sorbent	Mixing Time, h	Distribution Coefficient ^a , mL/g	
		Added	Remaining
HZO	0.25	120	100
	0.5	270 ^b	120 ^b
	1	450	30
	2	305	<1
	4	280 ^b	<40 ^c
	24-26	40 ^b	2 ^b
AC	0.25	850	720
	0.5	3,400 ^b	1,500 ^b
	1	6,500 ^b	900
	2	2,000	20
	4	4,400 ^b	80 ^b
	24-26	1,600 ^b	40 ^b
ACAC	0.5	60,000	30,000
	24	4,700	180

^aAll measurements were done at room temperature in 2 mL of solution containing 0.2 g of solid. “Added” is calculated using the initial rhodium concentration in solution. “Remaining” is calculated based on an average value of how much rhodium would be left in solution with no sorbent present.

^bGeometric mean of two to five values. These values were generally within a factor of two.

^cOne value was -5; the other was 40.

EFFECTS OF A ZINC FISSION BARRIER ON PROCESSING OF LEU-FOIL TARGETS

Development of LEU metal-foil targets has led to the use of thin (10-15 μm) metal barriers between the uranium foil and the target walls [22]. Three metals (Cu, Fe, and Ni) were selected as primary candidates for the barrier material based on their physical, chemical, and nuclear properties. Physical characteristics are important to target fabrication and are discussed in reference 22. The effects of these three barrier materials on acid dissolution [24] and on the recovery and purity of ^{99}Mo and their nuclear properties [23] were also discussed last year.

Because the uranium foil target is now being developed as the primary LEU target for ^{99}Mo -production processes that begin by dissolving HEU-aluminide-dispersion targets in base, we needed to select and test the use of a base-soluble metal as a fission-recoil barrier. Neither Cu, Ni, nor Fe dissolves in base. Therefore, a challenging task in process development was identifying a suitable metal for a barrier material that could dissolve in alkaline solution and meet other mechanical and chemical criteria.

A literature survey found the following elements that dissolve in alkaline solutions: aluminum, zinc, beryllium, gallium, tin, arsenic, niobium, and tantalum. Aluminum dissolves at about the same rate as uranium metal in 5.0M H_2O_2 /1.5M NaOH solution at 70°C. However, there is a strong concern that uranium would react with aluminum during the target irradiation. Germanium and rhenium, although not amphoteric, are reported to dissolve readily in dilute hydrogen peroxide. The toxicity of beryllium metal and the low melting point of gallium (30°C) preclude their use. Arsenic is classified as a non-metal and may not have sufficient metallic properties to be made into a foil. Zinc is an active electropositive element and forms a strong anion with oxygen. It also dissolves readily in sodium-hydroxide/nitrate solution. Work on barrier materials for targets to be processed by dissolution in base has, therefore, focused on zinc. Because of the appeal of developing just one target for all processes, a zinc fission barrier is also being considered for the target in acid-side processing.

Three methods of forming the zinc barrier were considered: (1) pressing together zinc and uranium foils, (2) hot dipping the uranium target in molten zinc, and (3) electroplating the zinc onto the uranium foil. One of the most important constraints on the barrier is that it should be of relatively uniform thickness and not greater than 15 μm to minimize the material to be dissolved after irradiation. Use of pre-formed zinc foil pressed onto the uranium target was eliminated because of the high cost and porous nature of the zinc foils thinner than 20 μm . Hot dipping provides a coating of rather poorly controlled thickness, and thicknesses less than 20 μm are unlikely. Electroplating of zinc, on the other hand, seems to be a relatively simple and inexpensive process with good control over the thickness. Another paper being presented at this conference will discuss our progress in electrodepositing zinc barriers [28].

Nuclear Properties of Zinc Barriers

The ORIGEN2 code was used to calculate the neutron activation of zinc being used as a barrier material for irradiation of an LEU foil target in the BATAN RGS-GAS reactor. Table 5 presents the activity generated after 12 h of cooling for one gram of the 99.95% pure zinc. An 18-g LEU-foil target would require about 1.7 g of zinc for a double-sided 15- μm barrier. This target would produce about 700 Ci of ^{99}Mo for a 120-h irradiation. The documentation accompanying the zinc foil we purchased for use in earlier test targets listed the impurity content. The neutron activation products formed from the impurities were also examined. It was found that Zn has a lower neutron absorption than either Cu, Fe, or Ni. As expected, there is only a small amount of radioactivity produced from the impurities, and they

can be ignored for the zinc foil we purchased. However, the results in Table 5 show that the impurity levels of cadmium and copper should be carefully scrutinized in selecting zinc for barrier materials.

Table 5. The Activity Generated per Gram of Zinc Barrier Material during Target Irradiation

Irradiation conditions:				
Irradiation	120 hours		Thermal Flux:	1.90E+14 n/cm ² -s
Target Decay	12 hours		Epithermal Flux:	7.90E+13 n/cm ² -s
			Fast Flux:	6.90E+13 n/cm ² -s
Element	Content, g	Product	Half-Life	Activity
Zn	0.9995	Zn-65	243.9 d	0.43 Ci
		Zn-69m	13.76 h	0.79 Ci
		Cu-64	12.7 h	0.13 Ci
Ca	0.000001	Ca-44	165 d	0.1 μCi
Cd	0.000020	Cd-115	53.46 d	0.41 Ci
Cu	0.000015	Cu-64	12.7 h	1.65 Ci
Fe	0.000010	Fe-55	2.73 y	0.31 μCi
		Fe-59	44.5 d	0.21 μCi
In	0.000010	In-114m	49.51 d	79 μCi
Mg	0.000001	Na-24	14.96 h	0.03 μCi
Na	0.000002	Na-24	14.96 h	98 μCi
Ni	0.000001	Co-59	70.92 h	0.07 μCi
Pb	0.000100	Pb-208	3.25 h	0.26 μCi
Si	0.000002	Si-31	2.62 h	0.04 μCi
Sn	0.000008	Sn-119m	245 d	2.1 μCi

Dissolution in Base

Three types of solutions for dissolving zinc were studied: NaOH, NaOH/H₂O₂, and NaOH/NaNO₃. A variety of solutions containing NaOH or NaOH/H₂O₂ showed dissolution rates less than the desired 2 mg/(cm²•min). On the other hand, a variety of solutions containing NaOH and NaNO₃ gave dissolution rates well above that. A solution of 2.5M NaOH/1M NaNO₃ at 70°C is our standard for rapid dissolution of pure zinc metal. Experiments have confirmed that a zinc coating electroplated onto the uranium-foil surface is also dissolved rapidly by this solution. Analysis by energy dispersive spectroscopy (EDS) of the foils left after dissolution showed that all of the zinc plate was dissolved from

the uranium. Liquid scintillation counting of the dissolution solution showed that virtually none of the uranium foil was dissolved with the zinc.

Because radioactive-decay heat is generated within the irradiated LEU, we were concerned that a zinc barrier might melt during transport of the target from the reactor pool to the processing hot cell. The biggest hindrance to the transfer of heat from the target during transport is the relatively small surface area from which heat can be transferred. Simple calculations were made for natural convection in the air immediately after the target leaves the cooling pool and for the possibility that the target will be placed in a cask and shipped over a 24-h time frame. Although exact temperatures to be experienced by the zinc barriers cannot be predicted, calculations show that temperatures in the range of 300-400°C are likely. Although this is very close to zinc's melting point (420°C), it is expected that the zinc will not melt. However, when a zinc-plated uranium foil was heat treated at 375°C overnight in an evacuated glass tube, an intermetallic U/Zn compound was formed. The intermetallic U/Zn compound is visually distinct from the unheated zinc-plated uranium foil when viewed through a microscope with a magnification of about 440X. Figures 1a and b are micrographs of a zinc-plated depleted-uranium (DU) foil after heat treatment. Figure 2 is a micrograph of another section of the foil before this heat treatment. With this intermetallic compound, the interface between the zinc and the uranium is almost indistinguishable (Fig. 1), whereas it had been pronounced before (Fig. 2). Notice the dendrite formations along the edge of the foil in Fig. 1a. Even if the target is held at low overall temperatures during transport, it is likely that ion mixing resulting from stopping the fission fragments during irradiation will likely cause the formation of this intermetallic compound at the U/Zn interface.

We have been unsuccessful in trying to duplicate the effect of this heat treatment. In the sample shown in Fig. 2, the uranium was severely overetched during surface preparation for electrodeposition; however, the adhesion of the zinc to the uranium was excellent. (Details on surface preparation for electrodeposition can be found in reference 28.) The obvious difference between the "successfully" heat-treated foil and the "unsuccessful" attempts is the quality of the zinc plate. In the successful foil, the zinc plate was even, continuous, and non-nodular. In the unsuccessful foils, the zinc plate was nodular and porous. The unsuccessful foils show severe oxidation and separation of the zinc plate from the foil in a scaly pattern. In fact, it appears that holes have been "blown" all the way through the uranium foil. One possible explanation is that the zinc plate on the unsuccessful foils retains water because of its nodular, porous nature. This water expands tremendously when it is converted to steam and becomes extremely corrosive to uranium. The successful foil was not porous and should not have retained much water in its matrix. Future experiments are planned to test this hypothesis.

Solutions suitable for dissolving the intermetallic U/Zn compound were investigated. Attempts to dissolve the zinc from the heated foil showed that this intermetallic would not dissolve as the zinc plate had from the unheated foils (at 70°C with a solution of 2.5M NaOH and 1M NaNO₃). On the other hand, a solution of 1.5M NaOH/5M H₂O₂ appeared to dissolve the intermetallic compound faster than it did pure zinc or pure uranium. Additional experimental work is necessary to clarify the rate of dissolution.

Dissolution of Zinc in Nitric Acid

Researchers at PUSPIPTEK attempted to dissolve a Zn-barrier LEU foil that was successfully removed from an irradiated target. They used conditions that should have completely dissolved the foil in 30 min. The gas pressure generated during dissolution and the radioactivity levels in the spent dissolver solution both were far lower than expected. This may be due to (1) the formation of the U/Zn compound at the Zn-foil/U-foil interface during irradiation and (2) this compound dissolving at a lower rate than either uranium or zinc. To test this hypothesis, a piece of the zinc-plated uranium foil that formed the U/Zn intermetallic was dissolved in 8M HNO₃ at 80°C. It did dissolve at a rate substantially

lower than either metal alone. (Zinc dissolves almost instantaneously in 8M HNO₃ at 80°C.) During 1998, we will undertake a series of experiments to quantitate the rate of dissolution for this compound and develop conditions for dissolving zinc-barrier uranium-foil targets in nitric acid.

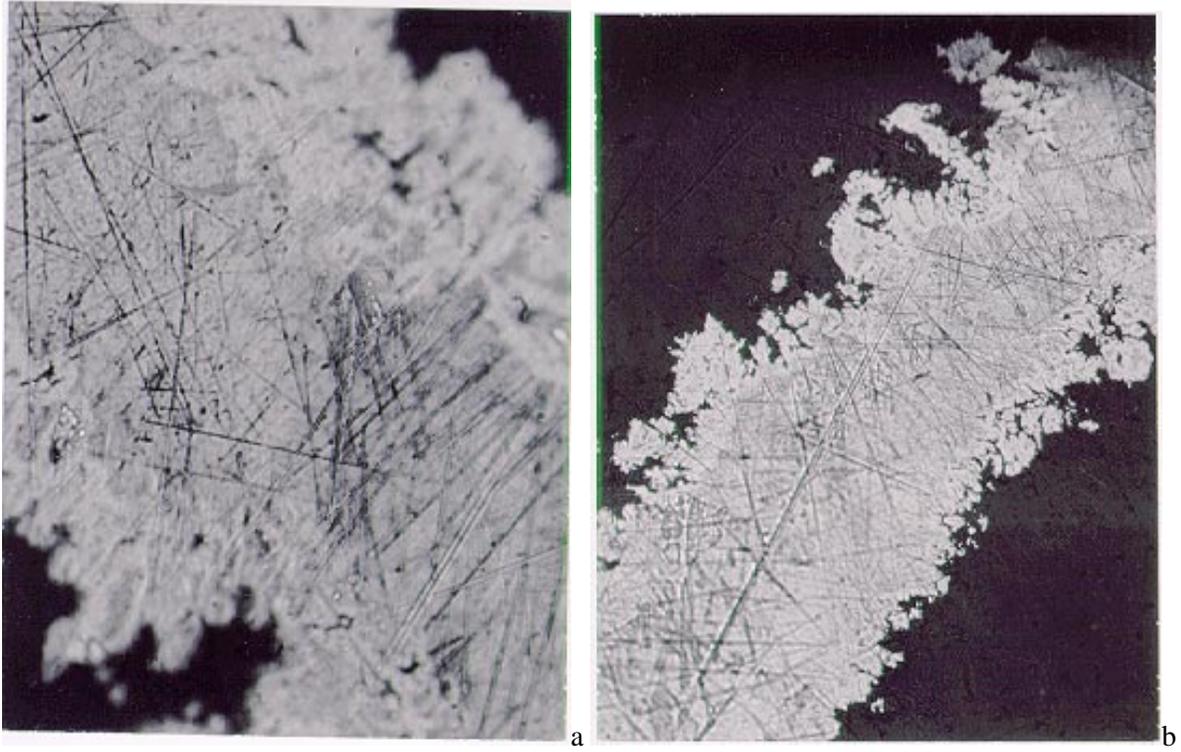


Figure 1. Two Sections of Zn-plated Uranium Foil after Heating at 375°C Overnight (Compare to Figure 2).

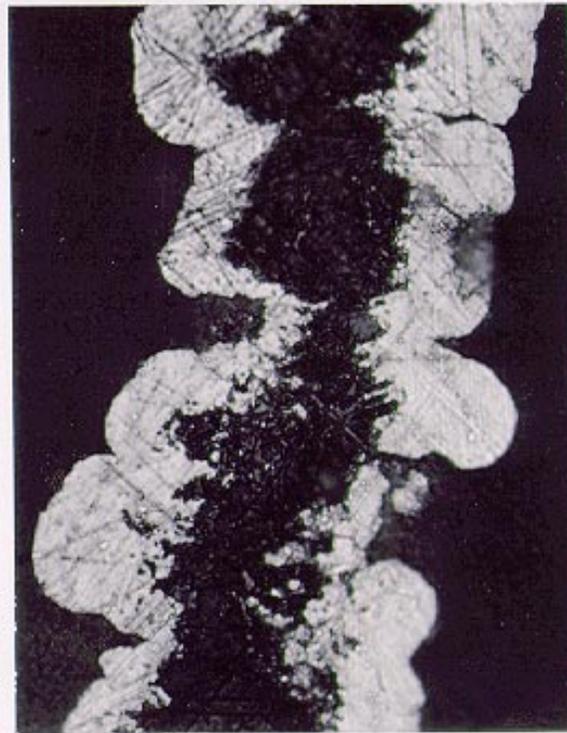


Figure 2. Early Zn-Plated Uranium Foil Showing Considerable Loss of Uranium during Etching

PROCEDURE TO QUANTITATE ALPHA CONTAMINATION OF THE ^{99}Mo PRODUCT

Irradiation of an LEU target will produce about 30 times more ^{239}Pu than an HEU target producing the same quantity of ^{99}Mo . However, a typical HEU target is substantially more enriched in ^{234}U than a typical LEU target. For a list of isotopic analyses from seven LEU batches we had available, the ratio of $^{235}\text{U}/^{234}\text{U}$ was 140 ± 30 ; for a list of five HEU analyses, the $^{235}\text{U}/^{234}\text{U}$ ratio was 92 ± 6 . (The $^{235}\text{U}/^{234}\text{U}$ ratio for natural uranium is 126.) A typical LEU target with the same amount of ^{235}U as an HEU target will have only 2/3 of the short-lived ^{234}U . Therefore, even with substantially greater production of ^{239}Pu , the total alpha activity of an irradiated LEU target is only about 20% higher than an equivalent HEU target.

Although the total alpha activity in an irradiated LEU sample is not far different from that in a comparable HEU target, the great concern over plutonium has made the measurement of alpha contamination an essential component of our efforts to convert ^{99}Mo production to LEU. We are in the process of developing and testing a procedure for separating and recovering actinide elements from the ^{99}Mo product that will allow easy and effective measurement of alpha contamination of $<10^{-7}$ $\mu\text{Ci-}\alpha/\text{mCi-}^{99}\text{Mo}$. This technique is a modification of a procedure developed by Eichrom Industries (Darien, IL, USA) for measuring dilute concentrations of actinides in urine and fecal samples. We are investigating the use of Eichrom prepackaged TRU-Select columns to extract the actinides from the molybdenum.

The stringent alpha-contamination limit for the ^{99}Mo product necessitates removal of the alpha emitters from the ^{99}Mo . A typical sample for analysis would contain ~ 180 mCi of ^{99}Mo and, therefore, must contain less than 2×10^{-5} μCi (41 dpm) of α emitters to meet the alpha purity specifications. Without separation from the molybdenum, interference from the ^{99}Mo beta/gamma makes counting this low level of alpha nearly impossible. Also, handling the counting plate would give a high dose to analytical personnel. We are developing the use of TRU-Select columns to separate the alpha-emitting isotopes (i.e., U, Np, Pu) from the ^{99}Mo by determining the chromatographic behavior of molybdenum and the three actinide species--Pu(IV), Np(V), and U(VI). Based on the known chemical properties of this column and the feed solution being used, actinides in the III, IV, and VI oxidation states should all be strongly sorbed by the column, and Mo(VI) should pass through. Conditions in the feed solution are set to reduce Np(V) or Pu(V) to the strongly sorbed IV oxidation state.

In our experiments on actinide behavior, equivalent masses of short-lived isotopes were substituted for ^{239}Pu and ^{234}U to increase the amount of activity. In doing so, 41 dpm due to a mixture of 1.0 wt% ^{234}U , 93 wt% ^{235}U , 0.43 wt% ^{236}U , and 5.57 wt% ^{238}U became 610 cpm of ^{233}U , and 41 dpm of ^{239}Pu became 6,200 dpm of a mixture of 54 wt% ^{238}Pu and 46 wt% ^{239}Pu . The neptunium solution was prepared by adding 10,000 dpm of ^{239}Np to 41 dpm of ^{237}Np . A solution simulating the ^{99}Mo product was prepared by spiking the equivalent mass of actinide into a solution containing 0.25 g/L molybdenum (as MoO_4^-) in 0.2M NaOH. After spiking each solution with either $^{233}\text{U(VI)}$, $^{238+239}\text{Pu(IV)}$, or $^{237+239}\text{Np(V)}$, the solution was stirred for several days to allow the isotopes to equilibrate. Significantly, $\sim 90\%$ of the Pu(IV), $\sim 10\%$ of the U(VI), and almost none of the Np(V) precipitated after addition to the basic solution. The significance of this finding is that, if plutonium were maintained in the IV oxidation state, it would not be a contamination problem. However, plutonium in the V oxidation state would be soluble enough to be of concern.

Briefly, the chromatographic procedure calls for addition of a small aliquot (e.g., 10 μL) of the ^{99}Mo product solution to 10 mL of a feed containing 3M HNO_3 and 1M $\text{Al(NO}_3)_3$ and a yet-to-be-determined concentration of oxalic acid. The feed solution may also contain ascorbic acid and ferrous sulfamate. [Oxalic acid is added to complex MoO_4^{2-} and prevent it from being sorbed on the

column. It also forces Np(V) into the IV oxidation state. The two reductants, ascorbic acid and ferrous sulfamate, hold plutonium in the III and Np in the IV oxidation states.] The feed is passed through the column and followed by a 5- to 15-mL wash of 2M HNO₃. (At this point, “all” the molybdenum should be removed from the column. However, at the time of writing this paper, we have yet to find the proper conditions for complete molybdenum separation.) The actinides are stripped from the column with 10 mL of 0.1M NH₄(HC₂O₄). The actinides can then be electrodeposited on a plate for alpha counting.

Shown in Figs. 3 through 5 are results of five column runs where samples of the effluent were taken approximately every milliliter. The feeds for all three actinides contained the reductants. All three actinides were tested with 0.1M oxalic acid in the feed; Np (V) was also tested with 0.03 and 0.01M oxalic acid. The results are very encouraging. Figure 3 shows that uranium in the feed was sorbed by the column and not released until stripped. Likewise, Fig. 4 shows similar behavior for Pu(IV). Figure 5 shows that all of the neptunium in the feed was sorbed by the column and remained on the column during washing for all three oxalic acid concentrations. The only difference was more tailing in the strip for solutions with lower amounts of oxalic acid in the feed. However, in all cases, stripping was essentially complete.

Three column experiments were run to study the behavior of molybdenum for oxalic acid concentrations in the feed of 0.01, 0.03, and 0.1M. Although the activity of ⁹⁹Mo was too low for accurate analyses, the results in Fig. 6 indicate that molybdenum does not move unhindered through the column. As expected, the higher concentrations of oxalic acid show more ability to hold back the molybdenum from extracting onto the column. We are in the process of (1) repeating these experiments using much higher ⁹⁹Mo activities in the feed and (2) running a series of experiments where no reducing agents are added to the feed, the oxalic acid concentration is varied over a wider range, and the volume of the column wash solution is increased. We are confident that this technique will work; it is just a matter of finding the proper conditions for maximum separation of the actinides from the ⁹⁹Mo.

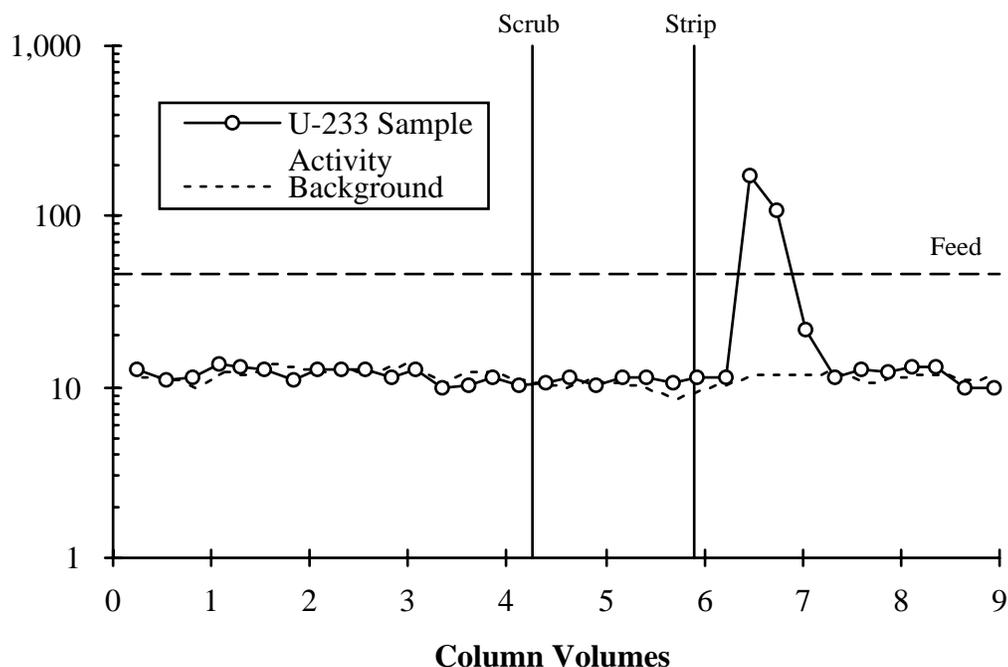


Figure 3. Elution Profile of Uranium on TRU-Select Column (0.1M H₂C₂O₄)

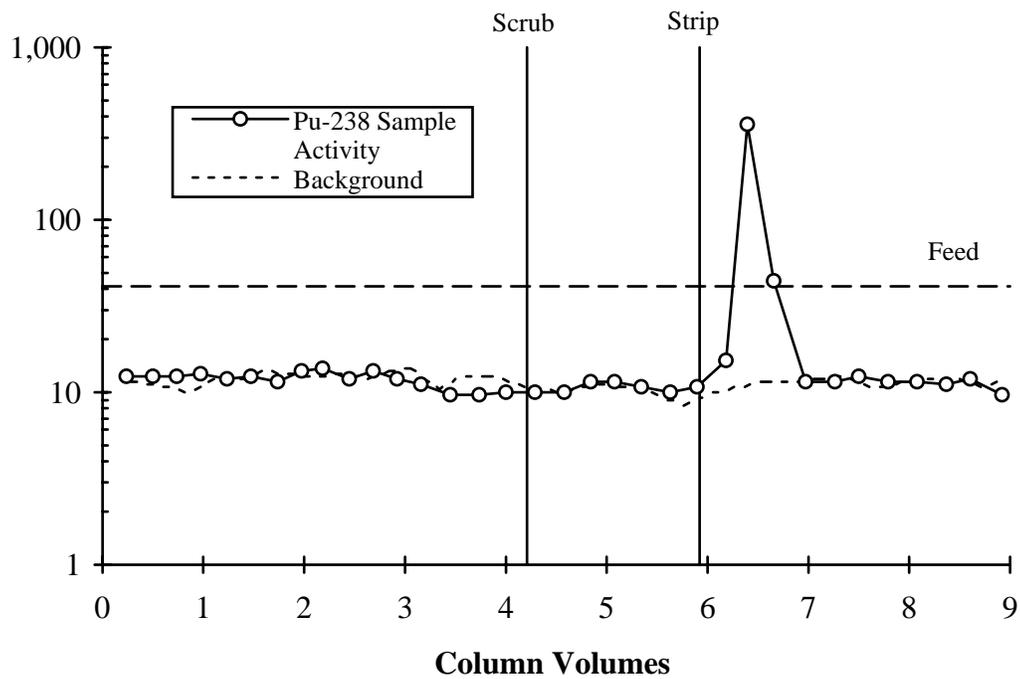


Figure 4. Elution Profile of Plutonium on TRU-Select Column (0.1M H₂C₂O₄)

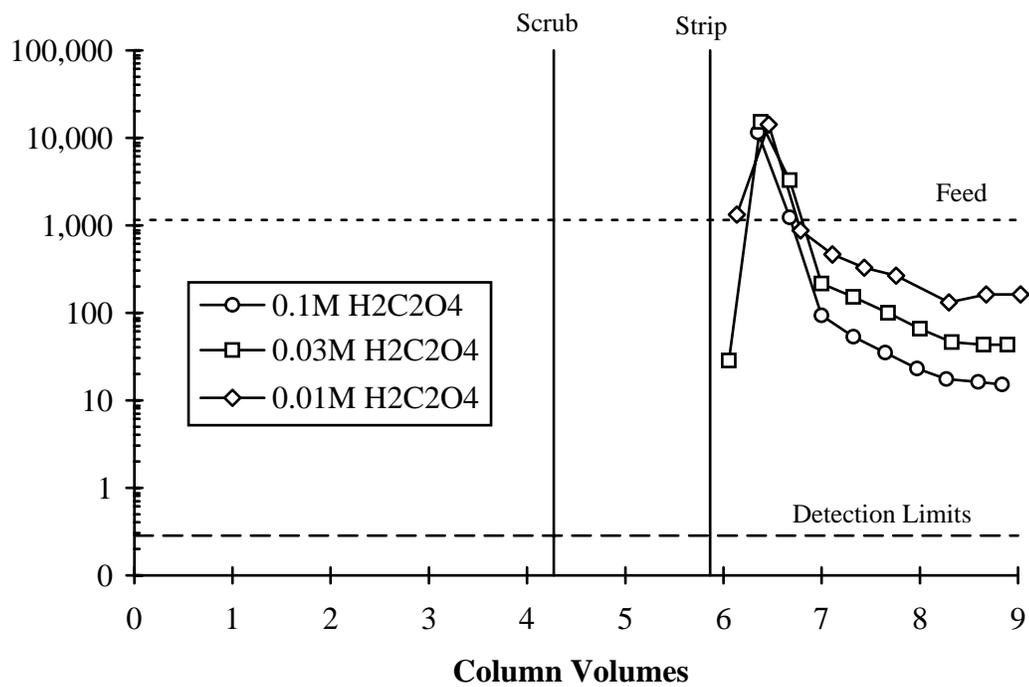


Figure 5. Elution Profile of Neptunium on TRU-Select Column (Various Concentrations of H₂C₂O₄)

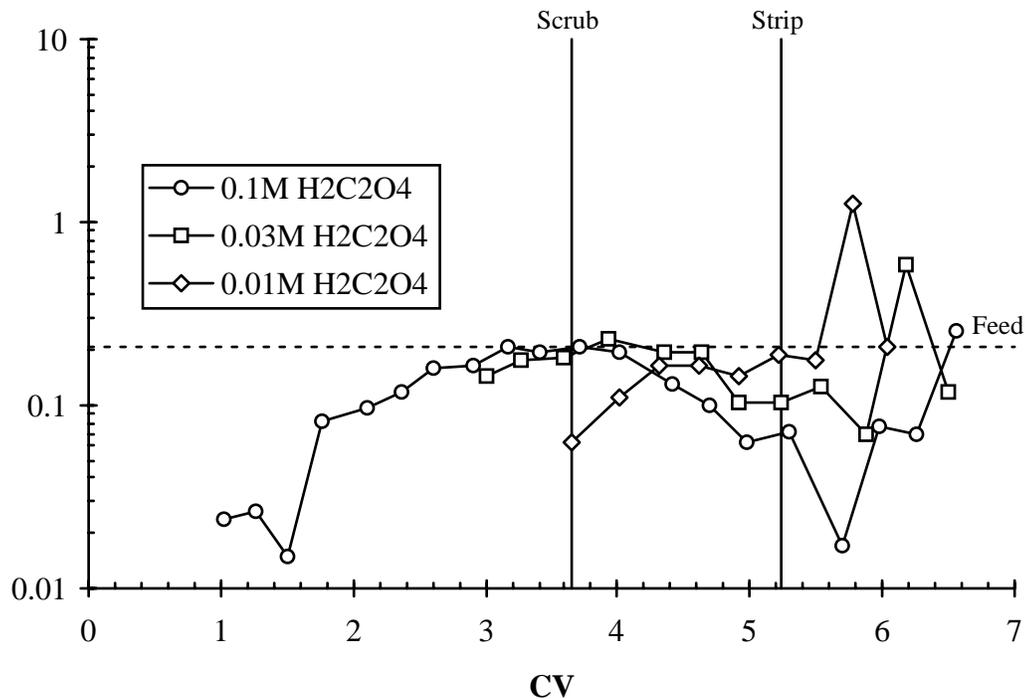


Figure 6. Concentration Profile of Molybdenum in the Effluent of the TRU-Select Column (Various Concentrations of H₂C₂O₄)

CERTIFICATION OF LEU OXIDE TARGETS FOR ⁹⁹Mo PRODUCTION

Los Alamos National Laboratory is fabricating LEU-oxide Cintichem targets that will be irradiated in the SNL ACRR (Annular Core Research Reactor) and processed to recover and purify ⁹⁹Mo. Targets will be fabricated with up to 60 g of U₃O₈ electroplated onto the inner surface of the Cintichem target. Use of LEU will be part of the process validation activities that SNL will perform to become an approved supplier to one or more radiopharmaceutical companies. Amended Drug Master Files will be submitted by the radiopharmaceutical companies to the U.S. FDA for approval of the ⁹⁹Mo products. Process validation challenges production parameters to the limits of what could be expected during operation; for example, the ²³⁵U-enrichment lower limit will be 18 wt%. Samples of ⁹⁹Mo produced during process validation will be sent to one or more radiopharmaceutical companies for purity verification. The approval of the SNL product by the FDA is a major milestone in the acceptability of LEU for ⁹⁹Mo production. In the future, only the U-metal target will need to be proven, not the isotopic composition of the uranium.

CONCLUSIONS AND FUTURE WORK

Testing and development activities are continuing to support modification of the Cintichem process for use with LEU targets and to assist BATAN researchers at the PUSPIPTEK Radioisotope Production Centre who are preparing to demonstrate this process on a fully irradiated LEU target. Our collaboration with BATAN is vital to developing and validating this process--as is our new cooperation with Sandia National Laboratories and Los Alamos National Laboratory. All is still in place for demonstration of the process at PUSPIPTEK. A new set of targets is being prepared at Argonne, and we

are planning the irradiations and full-scale process demonstration in February/March 1998. These targets will include foils electroplated with fission barriers of zinc and nickel. We are also planning to measure alpha contamination of the ^{99}Mo product with the method now under development.

Efforts will be made to secure a commercial partner for base-side processing during 1998. With the help of that partner, we will set our priorities on developing the zinc-barrier foil target or the UO_2/Al dispersion-fuel target, which is also discussed during this symposium [29]. The partner will assist in (1) refining our design of the dissolution system, (2) focusing our development activities, and (3) demonstrating processing of irradiated full-scale targets.

The RERTR Program wishes to work with all current and future producers of ^{99}Mo to assure that, ultimately, no HEU is needed for ^{99}Mo production.

REFERENCES

- [1] J. Konrad, "Facilities for the Irradiation of ^{235}U for the Production of ^{99}Mo at the HFR Petten," Irradiation Technology, Proc. of the Int. Topical Mtg., Grenoble, France (1982) 677-683.
- [2] J. Salacz, "Production of Fission Mo-99, I-131 and Xe-133," Revue IRE Tijdschrift, Vol. 9, No. 3 (1985).
- [3] C. J. Fallais, A. Morel De Westgaver, L. Heeren, J. M. Baugnet, J. M. Gandolfo, and W. Boeykens, "Production of Radioisotopes with BR2 Facilities," BR2 Reactor Mtg., Mol, Belgium, INIS MF 4426, pp. IX-1 to -11 (1978).
- [4] A. A. Sameh and H. J. Ache, "Production Techniques of Fission Molybdenum-99," Radiochimica Acta 41 (1987) 65-72.
- [5] R. O. Marques, P. R. Cristini, H. Fernandez, and D. Marziale, "Operation and Installation for Fission ^{99}Mo Production in Argentina," Fission Molybdenum for Medical Use, Proc. of Technical Committee Mtg. Organized by the International Atomic Energy Agency, Karlsruhe, October 13-16, 1987, IAEA-TECDOC-515 (1989) 23-33.
- [6] A. A. Sameh and H. J. Ache, "Production Techniques of Fission ^{99}Mo ," Fission Molybdenum for Medical Use, Proc. of Technical Committee Mtg. Organized by the International Atomic Energy Agency, Karlsruhe, October 13-16, 1987, IAEA-TECDOC-515 (1989) 47-64.
- [7] J. Salacz, "Processing of Irradiated ^{235}U for the Production of ^{99}Mo , ^{131}I , and ^{133}Xe Radioisotopes," Fission Molybdenum for Medical Use, Proc. of Technical Committee Mtg. Organized by the International Atomic Energy Agency, Karlsruhe, October 13-16, 1987, IAEA-TECDOC-515 (1989) 149-154.
- [8] A. A. Sameh and A. Bertram-Berg, "HEU and LEU MTR Fuel Elements as Target Materials for the Production of Fission Molybdenum," Proc. of the 1992 International Meeting on Reduced Enrichment for Research and Test Reactors, Roskilde, Denmark, September 27-October 1, 1992, Argonne National Laboratory Report, ANL/RERTR/TM19, CONF-9209266 (1993) 313-333.
- [9] H. Cols, P. R. Cristini, and R. O. Marques, "Preliminary Investigations on the Use of Uranium Silicide Targets for Fission Mo-99 Production," Proc. of 1994 International Meeting on Reduced

- Enrichment for Research and Test Reactors, Williamsburg, Virginia, September 18-23, 1994, Argonne National Laboratory Report, ANL/RERTR/TM-20 (in press).
- [10] R. T. Jones, "AEC-2 Experiments in Support of ^{99}Mo Production in NRU," Atomic Energy of Canada Limited, AECL-7335 (1982).
- [11] K. A. Burril and R. J. Harrison, "Development of the ^{99}Mo Process at CRNL," Fission Molybdenum for Medical Use, Proc. of Technical Committee Mtg. Organized by the International Atomic Energy Agency, Karlsruhe, October 13-16, 1987, IAEA-TECDOC-515 (1989) 35-46.
- [12] H. Arino, H. H. Kramer, J. J. McGovern, and A. K. Thornton, "Production of High Purity Fission Product Molybdenum-99," U.S. Patent 3,799,883 (1974).
- [13] H. Arino, F. J. Cosolito, K. D. George, and A. K. Thornton, "Preparation of a Primary Target for the Production of Fission Products in a Nuclear Reactor," U.S. Patent 3,940,318 (1976).
- [14] C. D. Massey, D. L. Miller, S. D. Carson, T. A. Wheeler, S. W. Longley, R. L. Coats, E. J. Parma, M. McDonald, M. E. Vernon, S. C. Bourcier, S. G. Mills, A. J. Trennel, and K. R. Boldt, "Feasibility Study of Medical Isotope Production at Sandia National Laboratories," SAND95-2703 Rev. O, Sandia National Laboratories (1995).
- [15] E. P. Gause, L. G. Stang, D. R. Dougherty, E. Veakis, and J. Smalley, "Characterization of the Radioactive Large Quantity Waste Package of the Union Carbide Corporation," BNL-NUREG-30247R Nuclear Waste Management Division, Department of Nuclear Energy, Brookhaven National Laboratory Informal Report, Upton, New York (July 1982).
- [16] G. F. Vandegrift, D. J. Chaiko, R. R. Heinrich, E. T. Kucera, K. J. Jensen, D. S. Poa, R. Varma, and D. R. Vissers, "Preliminary Investigations for Technology Assessment of ^{99}Mo Production from LEU Targets," 1986 International Meeting on Reduced Enrichment for Research and Test Reactors (RERTR), November 3-6, 1986, Gatlinburg, Tennessee, ANL/RERTR/TM-9,CONF-861185 (1988) 64-79.
- [17] T. C. Wiencek, G. L. Hofman, E. L. Wood, C. T. Wu, and J. L. Snelgrove, "LEU ^{99}Mo Target Fabrication and Testing: Overview, Status, and Plans," Proceedings of the 1994 International Meeting on Reduced Enrichment for Research and Test Reactors, Williamsburg, Virginia, September 18-23, 1994, Argonne National Laboratory Report, ANL/RERTR/TM-20 (in press).
- [18] B. Srinivasan, J. C. Hutter, G. K. Johnson, and G. F. Vandegrift, "Development of Dissolution Process for Metal Foil Target Containing Low Enriched Uranium," Proceedings of the 1994 International Meeting on Reduced Enrichment for Research and Test Reactors, Williamsburg, Virginia, September 18-23, 1994, Argonne National Laboratory Report, ANL/RERTR/TM-20 (in press).
- [19] B. Srinivasan, R. A. Leonard, S. Aase, G. F. Vandegrift, Moeridun, A. A. Rauf, H. Lubis, A. Hardi, S. Amini, and Y. Nampira, "Processing of LEU Targets for ^{99}Mo Production--Dissolution of Metal Foils by Nitric-Acid/Sulfuric-Acid Mixtures," Proceedings of the XVIII International Meeting on Reduced Enrichment for Research and Test Reactors, Paris, France, September 17-21, 1995, paper no. 3-2 (1996).

- [20] D. Wu, B. A. Buchholz, S. Landsberger, and G. F. Vandegrift, "Processing of LEU Targets for Mo Production--Testing and Modification of the Cintichem Process," Proceedings of the XVIII International Meeting on Reduced Enrichment for Research and Test Reactors, Paris, France, September 17-21, 1995, paper no. 3-3 (1996).
- [21] S. Aliludin, A. Mutalib, A. Sukmana, Kadarisman, A. H. Gunwan, G. F. Vandegrift, B. Srinivasan, J. L. Snelgrove, and D. Wu, "Processing of LEU Targets for ⁹⁹Mo Production--Demonstration of a Modified Cintichem Process," Proceedings of the XVIII International Meeting on Reduced Enrichment for Research and Test Reactors, Paris, France, September 17-21, 1995, paper no. 3-4 (1996).
- [22] G. L. Hofman, T. C. Wiencek, E. L. Wood, and J. L. Snelgrove, "Irradiation Tests of ⁹⁹Mo Isotope Production Employing Uranium Metal Foils," presented at the 19th International Meeting on Reduced Enrichment for Research and Test Reactors, October 7-10, 1996, Seoul, Korea (1996).
- [23] D. Wu, S. Landsberger, and G. F. Vandegrift, "Progress in Chemical Treatment of LEU Targets by the Modified Cintichem Process," 19th International Meeting on Reduced Enrichment for Research and Test Reactors, Seoul, Korea, October 6-10, 1996 (1996) 172-179.
- [24] R. A. Leonard, L. Chen, C. J. Mertz, and G. F. Vandegrift, "Progress in Dissolving Modified LEU Cintichem Targets," Proceedings of the 19th International Meeting on Reduced Enrichment for Research and Test Reactors, Seoul, Korea, October 7-10, 1996 (1997) 189-197.
- [25] M. Kahn and J. Kleinberg, "The Radiochemistry of Iodine," National Academy of Sciences, National Research Council, NTIS, Springfield, VA (1977).
- [26] D. A. Skoog and D. M. West, "Fundamentals of Analytical Chemistry," Holt, Rinehart, and Winston, New York (1963) 770.
- [27] G. R. Choppin, "The Radiochemistry of Rhodium," National Academy of Sciences, National Research Council, NTIS, Springfield, VA (1960).
- [28] J. A. Smaga, J. Sedlet, C. Conner, M. W. Liberatore, D. E. Walker, D. G. Wygmans, and G. F. Vandegrift, "Electroplating Fission-Recoil Barriers onto LEU-Metal Foils for ⁹⁹Mo-Production Targets," 1997 International Meeting on Reduced Enrichment for Research and Test Reactors, Jackson Hole, Wyoming, October 5-10, 1997, this meeting.
- [29] C. Conner, S. Aase, D. G. Wygmans, G. F. Vandegrift, D. Wu, S. Landsberger, "Dissolution of Low-Enriched UO₂/Al Dispersion Plates in Alkaline Peroxide Solution," 1997 International Meeting on Reduced Enrichment for Research and Test Reactors, Jackson Hole, Wyoming, October 5-10, 1997, this meeting.