PROCESSING OF LEU TARGETS FOR MO-99 PRODUCTION--DEMONSTRATION OF A MODIFIED CINTICHEM PROCESS*

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ABSTRACT

Two demonstrations of the use of the Cintichem process on simulated low enriched uranium (LEU, <20% ^{235}U) targets were run by personnel in the BATAN Isotope Production Facilities at PUSPIPTEK (Serpong, Indonesia). These demonstrations were done using a solution of either natural or depleted uranium spiked with irradiated high enriched uranium (HEU). The activity levels were low enough to perform the process in a fume hood. The volumes, equipment, and procedures used were the same as those used in the actual processing of irradiated HEU targets in a shielded cell. These results, when combined with data obtained at the University of Illinois and Argonne National Laboratory, show that substitution of LEU for HEU is possible for the Cintichem process, perhaps, with no modification.

INTRODUCTION

The Badan Tenaga Atom Nasional (BATAN) is currently producing ^{99}Mo from neutron irradiated HEU-UO_2 targets in the Isotope Production Facilities (PPR) at PUSPIPTEK, Serpong, Indonesia. The chemical procedure that is used to recover and purify the ^{99}Mo is part of the Cintichem process. Cintichem (a subsidiary of Medi-Physics Inc./Hofmann La-Roche) used the process until 1989 in the United States at their reactor facilities in Tuxedo, New York. Now, the proprietary rights for the process rest with the United States Department of Energy, and BATAN uses the process under a licensing agreement.

An active collaboration is underway between BATAN and Argonne National Laboratory (ANL) under the aegis of the RERTR program to carry out R&D work on the production of ^{99}Mo using LEU-metal foil targets. It is proposed to use the Cintichem process for the LEU targets

also, with appropriate modifications where needed. Work related to design and fabrication of a suitable LEU-metal foil target is also included in the R&D work [1, 2].

Two demonstrations were carried out at PPR this summer, using natural and depleted uranium (DU) solutions with spikes of irradiated HEU. Another demonstration was scheduled to be performed with a spike of irradiated LEU, but had to be delayed because of problems with the LEU-foil target [2]. The two demonstrations provided (1) basic information on the effectiveness of individual processing steps for purifying the ^{99}Mo product, (2) a better understanding of the Cintichem process to ANL personnel, and (3) the experience necessary to run an actual demonstration of LEU-target processing in 1996. This experience will be useful in improving the process for LEU targets.

EXPERIMENTAL

Mock demonstrations of the Cintichem processing of LEU metal foil targets were performed at PPR in June and July of 1995. Both demonstrations were run in a radioactive fume hood and employed the same volumes, equipment, and procedures that are used for irradiated HEU targets currently processed in the PPR. In the current Cintichem process [3, 4], the inside of cylindrical targets is electrochemically coated with UO_2. After irradiation, the target serves as the dissolver vessel. Following dissolution of the UO_2, the molybdenum is separated from other constituents by precipitation using a-benzoin oxime and then further purified. Specifics concerning the two demonstrations follow.

June-1995 Demonstration Using Natural Uranium Spiked with Irradiated HEU

The simulated dissolver solution was prepared by dissolving 15.8 g of natural uranium powder in 85 mL of the Cintichem cocktail solution at 90°C. Before processing was begun, a spike of dissolver solution from normal HEU processing was added to the natural-uranium solution. The solution was processed by the scheme described in Figure 1. Five samples were taken during processing, as shown in the figure, and counted by gamma spectroscopy and gross-alpha analysis.

July-1995 Demonstration Using Depleted Uranium Spiked with Irradiated LEU

The feed for processing was the dissolver solution (described elsewhere [5]) spiked with irradiated LEU. This solution was derived from dissolving an 18.1-g sample of depleted uranium metal foil (~125-µm thick) in an 80 mL solution of 3M nitric acid and 2M sulfuric acid. This dissolution was done at ~100°C in a closed system. Before processing was begun, a spike of dissolver solution from normal HEU processing was added to the depleted-uranium solution. The solution was processed by the scheme described in Figure 1. Five samples were taken during processing, as shown in the figure, and counted for alpha decay and by gamma spectroscopy.

After dissolution, this solution appeared to contain a substantial amount of dissolved nitrogen oxide gases and nitrite. This was identified by the large quantity of permanganate that reacted with the solution (40-50 times greater than expected). During normal processing of HEU targets, the target/dissolver is connected to an evacuated cold trap following dissolution, and only minor amounts of permanganate are necessary. Future demonstrations must include this step. Further investigations are needed in this area.

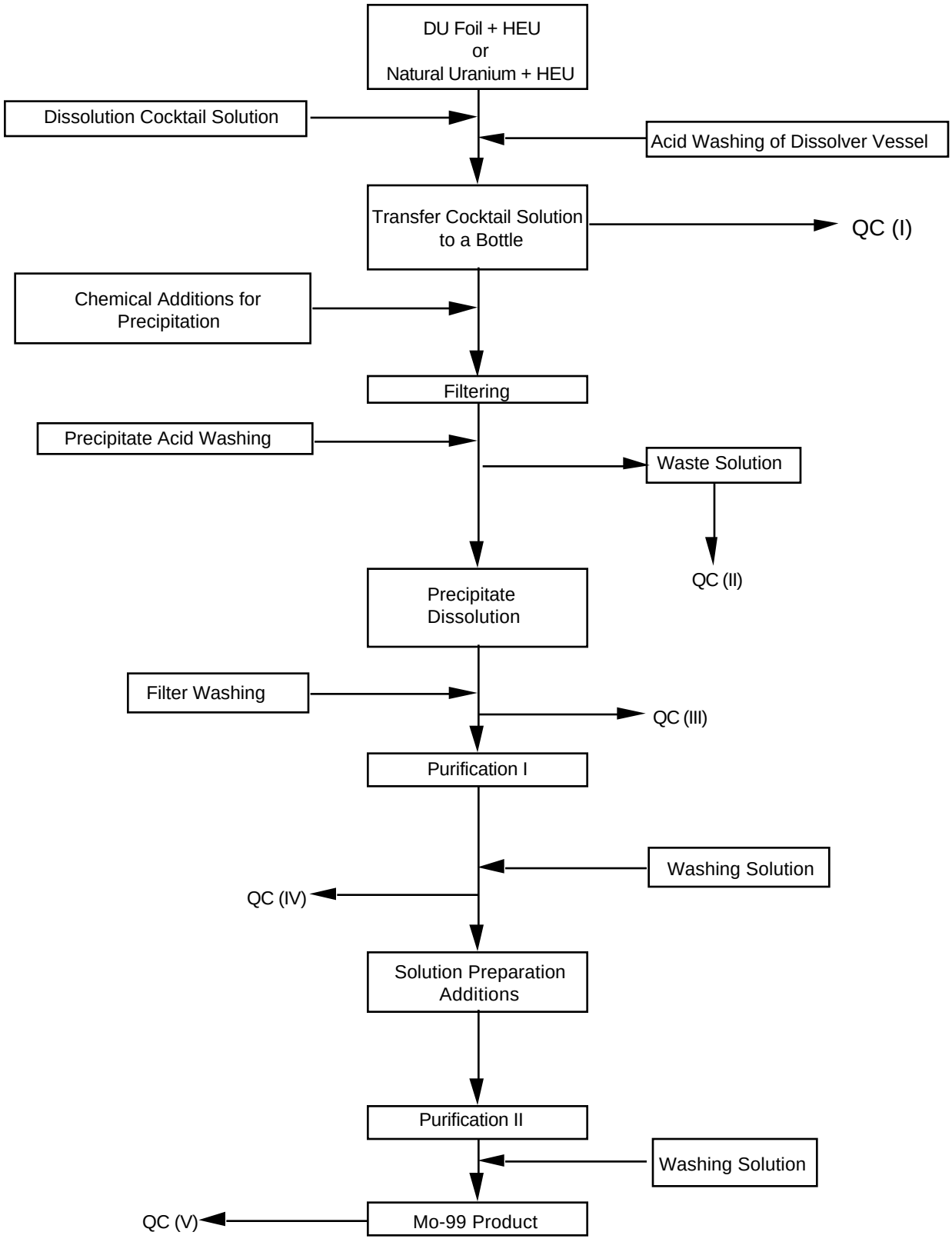

Figure 1. Flowsheet for Separation of Molybdenum-99 Using Cintichem Process

RESULTS

There are two major differences between HEU and LEU targets:

1. Approximately five times the amount of uranium is needed in the LEU target to produce the equivalent of ^{99}Mo.

2. Approximately 50 times more ^{239}Pu is generated from the irradiation of LEU.

Both of these differences are due to ^{235}U enrichment in the uranium target material. In HEU, approximately 93% of the uranium is ^{235}U; the ^{235}U enrichment is ≤20% in LEU. Fissioning of ^{235}U produces ^{99}Mo and other fission products; activation of ^{238}U produces ^{239}Np and other transuranic elements. In the mock demonstrations performed at the PPR, the uranium concentration was equivalent to processing an LEU metal target; however, the spike came from an irradiated HEU target. Using an HEU spike provided all fission products produced by LEU targets but did not allow us to measure the decontamination of molybdenum from ^{239}Np, which decays to the alpha-decaying ^{239}Pu. Also, the HEU spike was several days old before the demonstrations were started, which means that several short half-life fission products were not measurable. Even with these problems, the demonstration runs produced important information on fission-product decontamination, gave ANL first-hand experience in the Cintichem process, and will be useful in planning future development work.

An abbreviated version of the flowsheet for the Cintichem process that was used to recover ^{99}Mo in these demonstrations is shown in Figure 1. (Many details of the process are considered proprietary; therefore, this figure may not have the detail that the reader would like.) Samples were taken and analyzed at various stages of the process. These samples are indicated in Figure 1 and described below:

QC-I: Sample that reflects the starting composition of the depleted- or natural-uranium solution after the addition of the HEU spike.

QC-II: The filtrate from the molybdenum recovery/purification step by precipitation with α-benzoin oxime. Ideally, this would contain everything but the ^{99}Mo.

QC-III: The filtered redissolved precipitate. Other materials will not dissolve, and molybdenum is further purified.

QC-IV: Solution from a second purification.

QC-V: The final ^{99}Mo product, obtained following a third purification step.

The samples were analyzed by gamma-ray spectrometry for fission product nuclides by using a high-purity germanium detector, and by a gas-flow proportional counter (Eberline, Model SAC-4) for alpha-emitting nuclides. These data are comparable to results obtained at the University of Illinois [6].

Decontamination from Fission Products

Fission-product decontamination in different stages of processing the uranium solutions spiked with radionuclides from the June and July mock demonstrations are shown in Tables 1 and 2, respectively. Decontamination factors for QC-I to QC-V are reported as ratios of the µCi of the impurity to mCi of ^{99}Mo. Note that more isotopes were identified in the July analysis. Values not reported were below detection limits. In the future, analytical methods will be improved to decrease detection limits and measure more isotopes.

As seen in Tables 1 and 2, the precipitation step provides a high degree of decontamination to the ^{99}Mo and recovers ≥90% molybdenum from the dissolver solution. Most isotopes were below detection limits following the precipitation and redissolution of the precipitate.

Table 1. Gamma-Ray Analysis Results of June Mock Demonstration Using Natural Uranium with HEU Spike: Radionuclide Decontamination in Different Stages of ^{99}Mo Recovery and Purification by the Cintichem Process.

Nuclide	Half-life	Impurity Levels in Each Processing Step (µCi per mCi Mo-99)				
		QC-I	QC-II	QC-III	QC-IV	QC-V
^{147}Nd	11 d	216	7,750	-	-	-
^{141}Ce	32.5 d	281	10,400	-	-	-
^{132}Te	3.19 d	935	33,600	-	-	-
^{143}Ce	1.36 d	980	34,800	-	-	-
^{131}I	8.02 d	51	700	2.06	-	-
^{103}Ru	39.2 d	91	3,350	0.14	-	-
^{140}Ba	12.8 d	188	700	-	-	-
^{95}Zr	64.0 d	119	4,600	-	-	-
^{95}Nb	34.9 d	22	450	2.18	-	-
^{140}La	1.68 d	1702	60,000	-	-	-
		Mo-99 Activity in Each Processing Step Relative to that of QC-1				
^{99}Mo	66.0 h	100%	0.6%[a]	90%	87%	54%

[a]This activity was not measured but was assumed to be ~0.6% ^{99}Mo, the same as that observed in experiments run at the University of Illinois.

Table 2. Gamma Ray Analysis Results of July Mock Demonstration Using Depleted Uranium with HEU Spike: Radionuclide Decontamination in Different Stages of ^{99}Mo Recovery and Purification by the Cintichem Process.

Nuclide	Half-Life	Impurity Levels in each Processing Step (µCi per mCi Mo-99)				
		QC-I	QC-II	QC-III	QC-IV	QC-V
^{147}Nd	11 d	325	7,300	28.0	31.8	-
^{153}Sm	1.95 d	55.2	1,450	-	-	-
^{144}Ce	284.7 d	24.3	-	-	-	-
^{141}Ce	32.5 d	424	402	0.51	-	-
^{132}Te	3.19 d	927	18,350	-	-	-
^{143}Ce	1.36 d	1004	20,800	-	-	-
^{105}Rh	1.48 d	347	7,100	-	-	-
^{131}I	8.02 d	302	2,500	-	-	-
^{103}Ru	39.2 d	146	2,750	-	-	-
^{140}Ba	12.8 d	115	1,550	-	-	-
^{82}Br	1.47 d	44.2	-	-	-	-
^{105}Ru	4.44 h	126	2,800	-	-	-
^{127}Sb	3.9 d	24.3	-	-	-	-
^{97}Zr	16.9 h	99.3	-	-	-	-
^{95}Zr	64.0 d	156.7	3,300	0.75	0.51	-
^{95}Nb	34.9 d	24.3	350	-	-	-
^{140}La	1.68 d	1267.1	15,550	-	-	-
^{117m}Sn	13.6 d	-	-	0.33	0.24	0.46
		Mo-99 Activity in Each Processing Step Relative to That of QC-1				
^{99}Mo	66.02 h	100%	0.6%[a]	95%	90%	90%

[a]This activity was not measured but was assumed to be ~0.6% ^{99}Mo, the same as that observed in experiments run at the University of Illinois.

Decontamination from Uranium

Results of alpha counting for the QC samples are presented in Tables 3 and 4. As seen by these tables, the bulk of the uranium and ^{239}Pu is removed during the molybdenum precipitation step. Methods to decrease the detection limits for alpha-emitting contaminants will be developed and used for future demonstrations.

Table 3. Alpha Counting of Samples from the June Mock Demonstration

Sample[a]	CPM/25 µL[b]
Background	4±1
QC-I	134±4
QC-II	98±3
QC-III	6±1
QC-IV	4±1
QC-V	4±1

[a]Sample volumes varied from step to step.

[b]Background counts are not subtracted from sample count rates; CPM = counts per minute.

Table 4. Alpha Counting of Samples from the July Mock Demonstration

Sample[a]	CPM/25 µL[b]
Background	4±1
QC-I	294±5
QC-II	178±4
QC-III	6±1
QC-IV	5±1
QC-V	4±1

[a]Sample volumes varied from step to step.

[b]Background counts are not subtracted from sample count rates; CPM = counts per minute.

CONCLUSIONS AND FUTURE WORK

The cooperative RERTR project between ANL and BATAN is well underway, and significant progress has been made for developing an LEU target and modifying the current Cintichem process. Future work in molybdenum chemical processing will range from further tracer experiments to the irradiation and processing of a full-scale LEU target in 1996.

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