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Production of Molybdenum-99 Using Neutron Capture Methods

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January 2011

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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

Pacific Northwest National Laboratory (PNNL), operated by Battelle, has identified a reference process for producing molybdenum-99 (^{99}Mo) for use in a chromatographic generator to separate the daughter product, technetium-99m (^{99m}Tc). The reference process uses the neutron capture reaction of natural or enriched molybdenum oxide via the reaction ^{98}Mo(n,γ)^{99}Mo. The irradiated molybdenum is dissolved in an alkaline solution, whereby the molybdenum, dissolved as the molybdate anion, is loaded on a proprietary ion exchange material in the chromatographic generator.

The approach of this investigation is to provide a systematic collection of technologies to make the neutron capture method for ^{99}Mo production economically viable. This approach would result in the development of a ^{99m}Tc generator and a new type of target. The target is composed of molybdenum, either natural or enriched, and is tailored to the design of currently operating U.S. research reactors.

The systematic collection of technologies requires evaluating new metallurgical methods to produce the target, evaluating target geometries tailored to research reactors, and developing chemical methods to dissolve the irradiated target materials for use in a chromatographic generator. A technical specification for testing the target and neutron capture method in a research reactor is also required.

This report includes identifying research and demonstration activities needed to enable the deployment of a neutron capture production method, including irradiations of prototypic targets, chemical processing of irradiated targets, and loading and extraction tests of ^{99}Mo and ^{99m}Tc on the sorbent material in a prototypic generator design. The prototypical generator design is based on the proprietary method and systems for generating isotope products. The proprietary methods and systems described in this report are clearly delineated with footnotes.

Ultimately, the ^{99m}Tc generator solution provided by the system has exactly the same chemical and radiochemical characteristics as the ^{99m}Tc currently produced by standard generator systems.

Analysis results indicate that:

- The production of ^{99}Mo is a function of the neutron flux in the thermal and epithermal region, the target volume, and the target geometry. Calculations show that neutron self-absorption is not very important such that large (2-cm OD or more) cylinders of molybdenum can be irradiated without significant losses.
- Efficient use of the target volume design is a function of simultaneously optimizing the amount of molybdenum that can be inserted into each irradiation capsule and the amount of interconnected porosity within the specimen body to enhance the rate of post-irradiation dissolution.
- Neutron capture of natural molybdenum may effectively achieve up to 1 Ci/g ^{99}Mo in a 144-hour irradiation period when using the fuel annulus plus a beryllium reflector configuration.

Acronyms

AA	atomic absorption
AES/SAM	scanning auger electron spectroscopy
AFM	atomic force microscope
AMS	automated microfluidic system
Bq	Becquerel
Ci	Curie
CIP	cold isostatic pressing
Cu-EDA-SAMMS	copper ethylene diamine self assembled monolayers on mesoporous supports
EDA	ethylenediamine
EDS	electron dispersive X-ray
EMSL	Environmental Molecular Sciences Laboratory
EOI	end of irradiation
ESEM	environmental scanning electron microscopy
GIXA	glancing incidence X-ray analysis
HEU	highly enriched uranium
IC	ion chromatography
ICP-MS	inductively coupled plasma-mass spectrometry
LEU	low enriched uranium
m	micron (i.e., 1e-6)
m^2	square meter
MCNP	Monte Carlo N-Particle (code)
MCNPX	Monte Carlo N-Particle eXtended
^{98}Mo	molybdenum-98
M&TE	measuring and test equipment
NAS	National Academy of Sciences
n/cm^{2-s}	neutron per square centimeter per second
nm^2	nano-meter squared or square nanometer
NMR	nuclear magnetic resonance
NRA	nuclear reaction analysis
NRU	National Research Universal (reactor)
(n,γ)	(neutron, gamma) nuclear reaction
OES	optical emission spectroscopy

PIXE	particle-introduced X-ray emission
PNNL	Pacific Northwest National Laboratory
RBS	Rutherford backscattering spectroscopy
R&D	research and development
RPL	Radiochemical Processing Laboratory
SAED	selected area electron diffraction
SAMMS	Self Assembled Monolayers on Mesoporous Supports
S&E	science and engineering
SEM	scanning electron microscopy
SDPD	structure determination from powder data
SIMS	secondary ion mass spectroscopy
SVE	small volume elution
TRIGA	Training, Research, Isotopes, General Atomics
^{99m}Tc	technetium-99 (meta stable), half life 6 hours
^{99}Tc	technetium-99 (long lived) half life 213,000 years
WSU	Washington State University
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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1.0 Introduction

In late 2007, North America experienced a critical shortage of the isotope Molybdenum-99 (^{99}Mo) over a period of several weeks because of an extended shutdown of the National Research Universal (NRU) reactor in Chalk River, Canada. Molybdenum-99 is a critical isotope used in the production of its daughter radioisotope Technetium-99m (^{99m}Tc). Technetium-99m is used in the majority of diagnostic imaging procedures in the United States. Subsequently, in the interest of nuclear security and nonproliferation, the National Academy of Sciences (NAS) commissioned a study on the production of medical isotopes.[(a)] The NAS study recommended the irradiation of low enriched uranium (LEU) in a fission reactor instead of the customary highly enriched uranium (HEU) for domestic production of ^{99}Mo. However, radiochemical separation of a plurality of uranium fission products is required to produce the ^{99}Mo. The radiochemical separation of the uranium fission products from the desired ^{99}Mo generates significant volumes of radioactive wastes that require management and disposal.

An advanced method for producing ^{99}Mo involves the neutron capture reaction, ^{98}Mo(n,γ)^{99}Mo, which is illustrated schematically in Figure 1.1 where neutron bombardment of the ^{98}Mo produces ^{99}Mo and gamma emission:

Figure 1.1. Neutron Capture Reaction that Produces ^{99}Mo

Neutron capture-produced ^{99}Mo has the main advantage of greatly simplifying the subsequent processing scheme while producing greatly reduced waste streams compared with the uranium fission approach.

Self-Assembled Monolayers on Mesoporous Supports (SAMMS) is a proprietary new technology for molybdenum ion exchange and subsequent separation of the decay product ^{99m}Tc. Pacific Northwest National Laboratory (PNNL) conducted screening tests with SAMMS to determine its effectiveness for molybdenum ion exchange and ^{99m}Tc separation. Different anionic forms of SAMMS were tested and have been shown to effectively separate ^{99}Mo from its daughter product ^{99m}Tc using very-low-activity ^{99}Mo target material produced via the neutron capture reaction.[(b)]

(a) Committee on Medical Isotope Production Without Highly Enriched Uranium; National Research Council.

(b) JJ Toth, LR Greenwood, CZ Soderquist, W Chouyyok, GE Fryxell, LA Darnell, and SV Mattigod. 2010. *A Novel Ion Exchange Technique for the Production of Clinical Grade Technutium-99m Using (n,γ)Molybdenum-99.* PNNL RPT-59220, Rev 0, Pacific Northwest National Laboratory, Richland, Washington.

The tests were designed to examine the effectiveness of SAMMS as a generator material to produce ^{99m}Tc when integrated into the customary radiopharmaceutical processing scheme. The initial screening tests performed by PNNL employed very-low-level activity ^{99}Mo, 0.3 mCi/g molybdenum.

The proposed approach for producing clinical grade ^{99m}Tc is shown on the system description in Figure 1.2. Purified molybdenum is placed is an approved target for placement in a research reactor. The molybdenum in the target is irradiated with a neutron flux of at least 1E+12 neutron/cm^2-second, in order to produce ^{99}Mo with a specific activity of at least 1 Ci/g ^{99}Mo. The irradiated molybdenum in the target is shipped to a radiological processing facility where the ^{99}Mo in the target is dissolved and is loaded onto the proprietary SAMMS sorbent in a column. The SAMMS in the column acts as a ^{99m}Tc generator, when the column is eluted at the end-user's facility. The end-user may recycle the generator back the radiological processing facility after its use. Waste generated during the generator production is handled as low level waste (LLW) and can be disposed of a licensed Treatment Storage and Disposal Facilities. LLW might also be generated at the user facility, but the volumes are minimal.

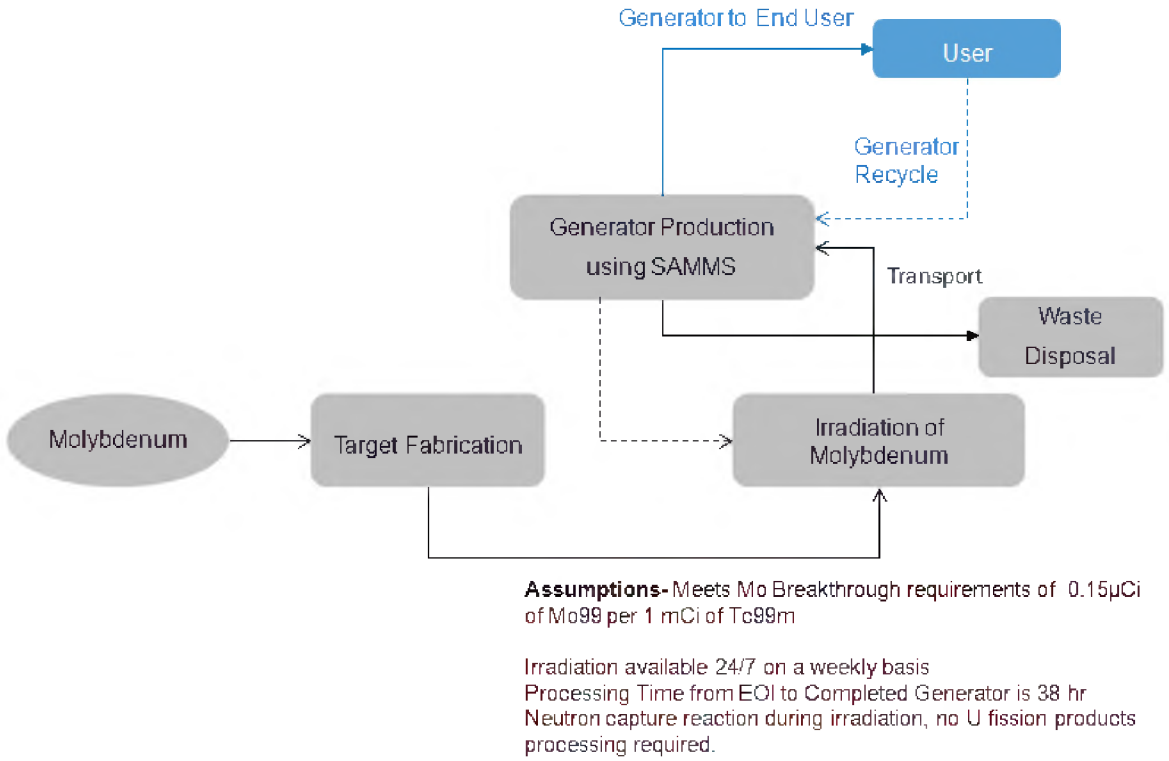

Figure 1.2. System Description of Neutron Capture Process

Based on the preliminary results obtained by PNNL indicating the production of ^{99}Mo in a research reactor and the preliminary results obtained by PNNL indicating the generation and selective separation of ^{99m}Tc from molybdenum, Perma-Fix requested PNNL to further investigate the utility of neutron capture ^{99}Mo to enable suitable production in research reactor environments.

This report presents the results of activities to develop a research and development plan, including the following elements:

- calculating ^{99}Mo-projected specific activities in a various research reactor environments with the intention of achieving suitable specific activities of ^{99}Mo.
- developing a preliminary target concept to enable suitable specific activities in research reactor environments
- developing target fabrication approaches for achieving 80% theoretical density molybdenum.
- identifying dissolution and separation methods to extract irradiated Mo from the target for loading onto the sorbent material
- identifying research and demonstration activities needed to enable the deployment of neutron capture production methods, including irradiations of prototypic targets, chemical processing of irradiated targets, and loading and extraction tests of molybdenum and technetium on the sorbent material in a prototypic generator design
- developing cost and schedule for carrying out identified research and development activities in subsequent projects.

2.0 Molybdenum-99 Production Calculations

In order to estimate ^{99}Mo production in a full scale research reactor, it is necessary to compare calculations to actual measurements. In this section, calculations for the specific activity of ^{99}Mo after 24 minute irradiations are compared to actual measurements performed by Gamma Emission Spectroscopy.

Estimates of ^{99}Mo yield from neutron capture on ^{98}Mo may be produced by integrating the total capture cross section at the gamma energy ranging from 10^{-9} to 10^{1} MeV. Ninety-five bins of average cross section corresponding to the neutron capture reaction for ^{98}Mo(n,g)^{99}Mo are used to integrate the total capture cross section.

Preliminary field tests of neutron capture reactions to produce ^{99}Mo from molybdenum oxide included tests performed by PNNL. High-purity molybdenum powder (99.999%) was loaded into a capsule for reactor irradiation and then irradiated for 24 minutes. The product ^{99}Mo has a half life of only 2.7 days and approaches equilibrium after about 5 days. Little is gained by longer irradiation. A large target (many grams of molybdenum) can be irradiated because the cross section is fairly small, and self-shielding is small. If the neutron flux is high enough, many curies of ^{99}Mo can be made in a single irradiation.

^{98}Mo (n, γ) ^{99}Mo	(cross section is 0.13 barns, 7.2 barn resonance)
^{99}Mo $\rightarrow$ ^{99m}Tc + β^-	($t_{1/2}$ = 2.7 days)
^{99m}Tc $\rightarrow$ ^{99}Tc + γ	($t_{1/2}$ = 6 hours)
^{99}Tc $\rightarrow$ ^{99}Ru + β^-	($t_{1/2}$ = 212,000 years)

The research reactor used for this test is located on the campus of Washington State University (WSU) in Pullman, Washington. The research reactor at WSU is a 1-MW reactor with Training, Research, Isotopes, General Atomics (TRIGA) fuel and a thermalfluence of about 2e10^{12} n/cm^2–s (thermal) outside the core. The profile of the neutron flux in position D8 of the reactor is shown in Figure 2.1. Position D8 is out of core.

For small quantities of ^{98}Mo (N_{98}), where self-shielding and target burn-out effects are negligible, the ^{99}Mo production rate can be approximated by

$$\frac{dN_{99}}{dt} = -\lambda N_{99} + \sum_j \overline{\sigma}_j \overline{\phi}_j N_{98} \qquad (2.1)$$

at irradiation time t, where λ is the ^{99}Mo decay constant ($\lambda = \ln 2/t_{1/2}$), $\overline{\sigma}_j$ is the energy group j-averaged (n,γ) cross section[1], and $\overline{\phi}_j$ is the energy group-averaged neutron flux at the target position calculated with Monte Carlo N-Particle eXtended (MCNPX)[(a)] (version 2.6.0)[2-3]. Additionally, the transmutation of the ^{99}Mo product has been neglected—its inclusion would simply introduce a modification to λ in Equation (2.1) that is of the order of the uncertainty of itself. The 95 energy groups used in the

(a) MCNPX is a general-purpose radiation transport code.

Equation (2.1) sum gave a reasonably accurate (within flux uncertainty) estimate of the flux-integrated cross section because flux and cross section did not vary rapidly together within the same energy bin.

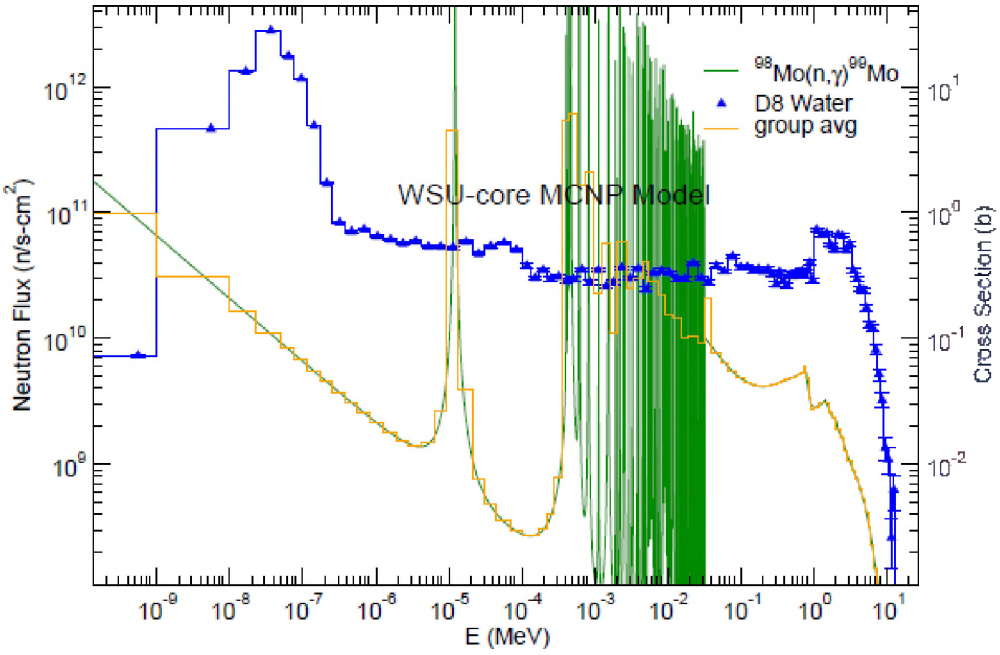

Figure 2.1. Log-Log Plot Superimposing the Neutron Flux of Position D8 in Water with the Cross Section for the Reaction ^{98}Mo(n,γ)^{99}Mo. The group average shows the integrated flux over the discrete 95 energy bins. Further reading of the ^{98}Mo cross section is given in note (a)[a].

The solution of Equation (2.1) gives the ^{99}Mo activity (Bq) produced after irradiation period t according to:

$$\lambda N_{99}(t) = \left(1 - e^{-\lambda t}\right) N_{98} \sum_j \overline{\sigma}_j \, \overline{\phi}_j \tag{2.2}$$

where the number of ^{98}Mo atoms is of course calculated from the mass of natural molybdenum oxide MoO_3 in the target as

$$N_{98} = M_{MoO_3} \frac{95.94 \text{ g/mole-Mo}}{143.9382 \text{ g/mole-MoO}_3} \frac{0.2413 \text{ g-}^{98}\text{Mo}}{1 \text{ g-Mo}} \frac{N_A}{97.9054 \text{ g/mole-}^{98}\text{Mo}} \tag{2.3}$$

where N_A is the Avogadro constant. The Equation (2.2) activity increases linearly with t for irradiation periods much less than the ^{99}Mo decay half-life ($t_{1/2}$) of 65.94 h. The short-time production rate within the approximations given is calculated to be 323±0.6% Bq/mg-min. A comparison of the measured and calculated ^{99}Mo production for a 24-minute irradiation is shown in Table 2.1.

(a) 42-Mo-98 JNDC EVAL-AUG89 JNDC FP Nuclear Data W.G

Table 2.1. Gamma Emission Spectroscopy Results for the Natural Molybdenum Oxide Samples Irradiated for 24 Minutes on April 28, 2010, Under Project 59220

Gamma Counting Results								
Procedure RPG-CMC-450, Gamma Energy Analysis; Measuring and Test Equipment (M&TE): Detector G, T								
Reference Date: April 28, 2010, 11:31 a.m. End of Irradiation (EOI)								
	A MoO_3 10-0563		B MoO_3 10-0564		C MoO_3 10-0565		D MoO_3 10-0566	
Isotope	Bq/mg ±1 s		Bq/mg ±1 s		Bq/mg ±1 s		Bq/mg ±1 s	
^{99}Mo Measured	8.04E+3	± 4%	7.92E+3	± 4%	7.88E+3	± 4%	7.72E+3	± 2%
Estimate of ^{99}Mo produced	7.75E+3	±0.6%	7.75E+3	±0.6%	7.75E+3	±0.6%	7.75E+3	±0.6%

The results indicate the calculations to estimate the ^{99}Mo produced after 24 minutes of irradiation in D8 are 7.75E3 Bq/mg, and compare to the measured values of between 7.72 and 8.04E+3 Bq/mg. Thus the calculated activity of ^{99}Mo produced in D8 is bound by the measured activity.

A second irradiation test for 24 minutes was performed in position D8 on August 4, 2010. The source of the molybdenum oxide was the same as used in the April 28th tests. Two samples of 100 mg of MoO_3 each were packaged in polymeric vials, being careful to prevent any cross contamination. The vials in this test were also irradiated in position D8. Table 2.2 indicates the values for ^{99}Mo and other isotopes measured by Gamma Spectroscopy.

Table 2.2. Gamma Emission Spectroscopy Results for the Samples Irradiated Aug 4, 2010, Under Project 59220

Gamma Counting Results				
Procedure RPG-CMC-450, Gamma Energy Analysis; M&TE: Detector G, T				
Reference Date: August 4, 2010 11:26 AM				
	MoO_3 (A) 10-0938		MoO_3 (B) 10-0938	
Isotope	Bq/mg ±1 s		Bq/mg ±1 s	
^{24}Na	3.94E+1	± 4%	3.22E+1	± 4%
^{41}Ar	1.64E+3	± 3%	7.13E+2	± 4%
^{51}Cr	<8 E+0		<8 E +0	
^{56}Mn	1.71E+1	± 9%	2.92E+1	± 5%
^{99}Mo	7.44E+3	± 2%	6.92E+3	± 4%
^{185}W	<1.E+4		<1.E+4	
^{187}W	1.56E+2	± 4%	1.34E+2	± 3%
^{198}Au	5.86E-1	± 58%	1.46E+0	± 28%
^{199}Au	3.25E+0	± 23%	3.59E+0	± 22%

In addition to out of core position D8, it is also necessary to examine the in–core gamma energy spectrum, as described in Section 3.0 of this report. Estimates of the in-core spectrum for the center of the core, position D5, were produced by using the MCNP code configured for the research reactor at WSU.

The results of the MCNP calculations are illustrated on figure 2.2. Moving from out-of-core to the center, the thermal region from about 1E-7 to 1E-8 MeV displays a flux increase from about 3E+12 to 6 E+12 n/s-cm^2, or a factor of 2. However, the epithermal or resonance region from about 1E-1 to 1E-6 MeV displays a flux increase from 4E+10 to 4E+11 n/s-cm^2, or a factor of 10.

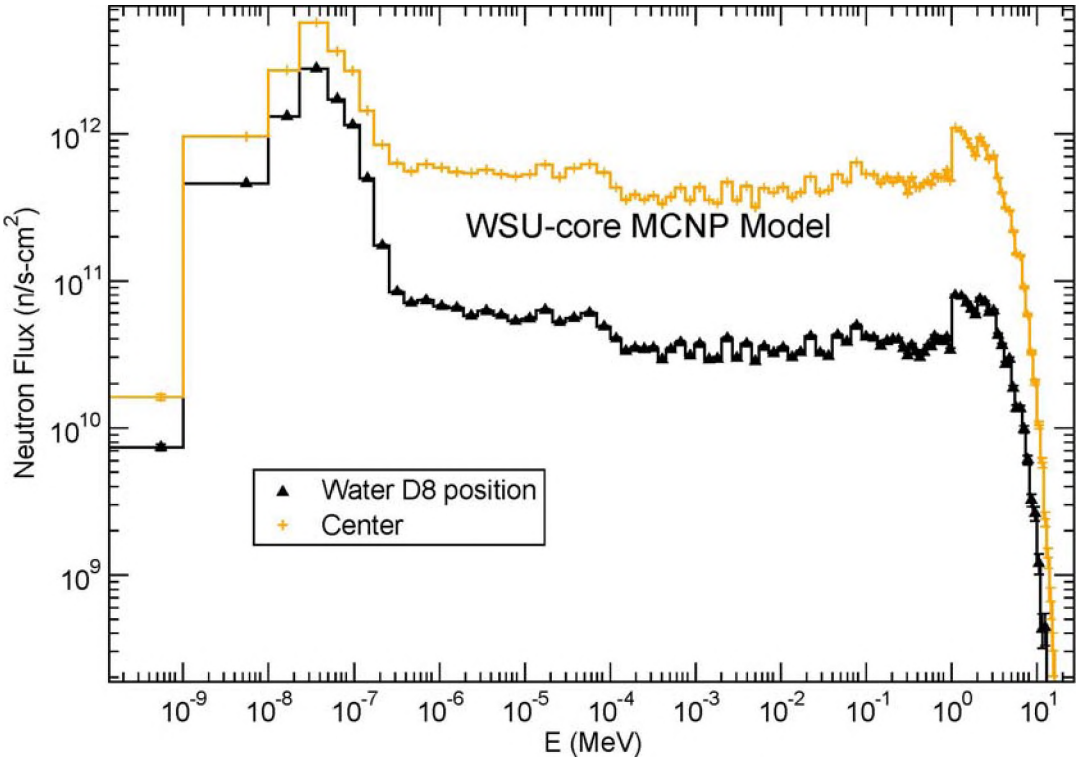

Figure 2.2. Log-Log Plot Superimposing the Neutron Flux of Position D8 in Water (out-of-core) with Center of the Core (position D5)in the Research Reactor at WSU

The huge increase in epithermal or resonance region flux over the thermal flux and its concomitant increase in its contributions to Mo99 production is illustrated in figure 2.3. In the out-of core position, thermal neutron flux less than or equal to 5.5e-7 MeV contributed 50% of the total Mo99 production. Moving from out-of-core to the center, the thermal neutron flux contributes only 16% of total Mo99 production. Figures 2.2 and 2.3 illustrates why it is necessary to consider spectral differences to calculate ^{99}Mo activity, and not use thermal flux contribution alone.

When considering cylinders of molybdenum or molybdenum oxide it also important to account for self shielding effects. Self shielding effects and fuel geometry are addressed in section 3.

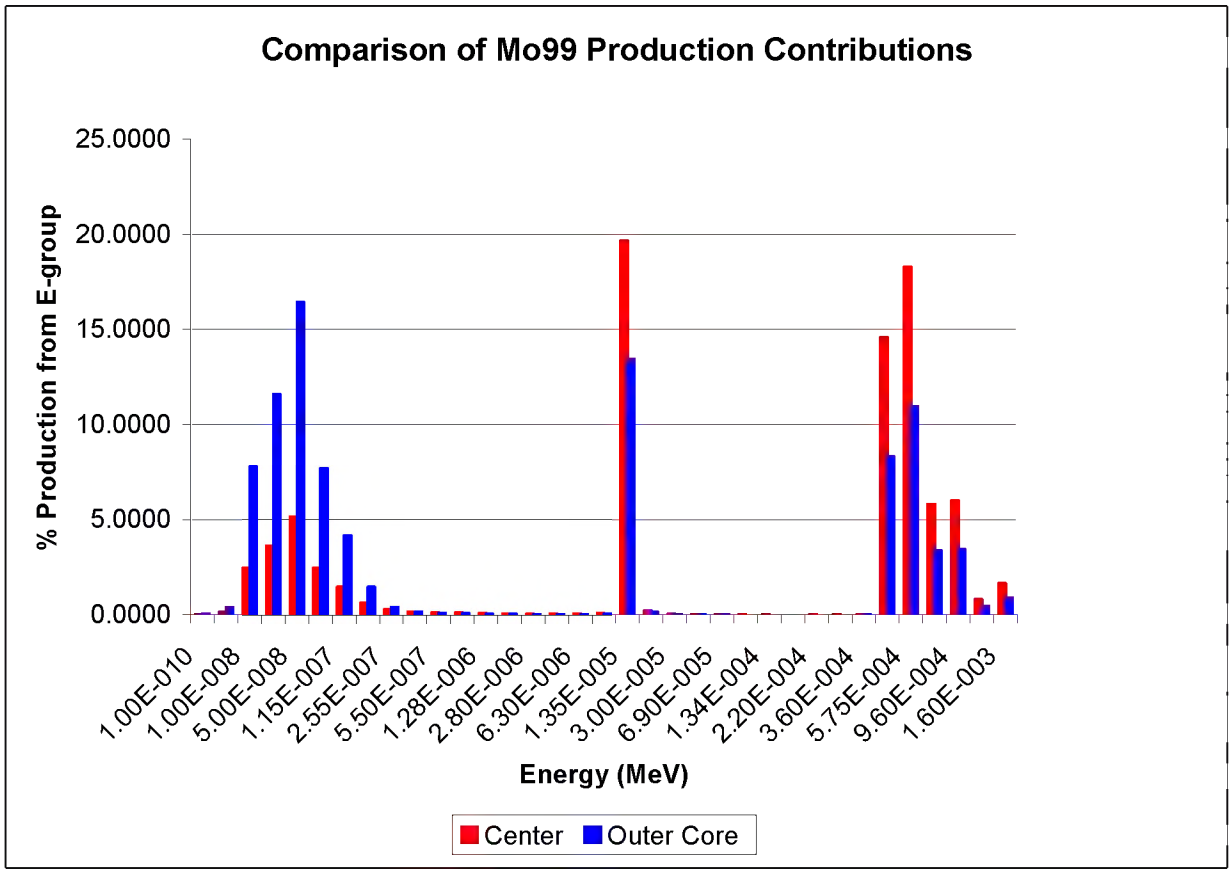

Figure 2.3. Semi-Log Plot Illustrating the Percent Contribution of ^{99}Mo Production as a Function of Target Position in the WSU Research Reactor

3.0 Molybdenum-99 Modeling Calculations of Full Scale System in a Research Reactor

The purpose of the modeling was to conduct the series of similar analyses performed with the Monte Carlo N-Particle (MCNP) code to assess the capability of the different target configurations to produce ^{99}Mo of sufficient specific activity (Ci ^{99}Mo/g) at the WSU research reactor. The modeling established which features of the target configuration provide the highest specific activity of ^{99}Mo.

The technical approach was to select and to model ^{99}Mo production of three different target configurations in the core of research test reactors composed of uranium zirconium hydride (UZrH) fuel.[(a)] The three different target configurations were selected based on previous testing performed by PNNL at the WSU research reactor in Pullman, Washington. The targets consisted of pressed molybdenum with a bulk density of 8 g/cc. The target configurations consisted of 1) molybdenum cylinders, 2) molybdenum cylinders and annuli surrounded by beryllium, and 3) molybdenum cylinders surrounded by UZrH fuel with and without beryllium or lead reflectors/absorbers. The configurations are further described below.

- Water Hole D8—calculations for very small target only for reference information. Core position D8 refers to the perimeter of the core surrounded by the core pool.
  - Water Hole D5—11 slugs 3 cm tall, 2 cm diameter stacked from core center. Core position D5 refers to a location at the core center.
- Beryllium Shield—Same configuration as water hole above except shielded with Be.
  - Be Shield—11 slugs 3 cm tall, 2 cm diameter stacked from core center with a 0.25-cm Be reflector surrounding the molybdenum.
  - Be Cylinder—11 annuli 3 cm tall, 0.25 cm thick, inner diameter 2 cm with a Be cylinder 2 cm in diameter at the center
- Fuel Annulus—1 molybdenum slug 38 cm tall, 2 cm diameter inside of a fuel annulus 0.7 cm thick, inner radius 1.05 cm
  - Fuel Annulus+Be—same as above but surrounded by a beryllium reflector 0.16 cm thick and an inner radius of 1.74 cm. In practice the outer radius of the fuel annulus would be 1.75 cm, so the inner radius of the Be reflector would be slightly larger.
  - Fuel Annulus+Pb—same as above, but replace Be with Pb
  - Fuel Annulus+Be-Hydrogen—same as "Fuel Annulus+Be" except the hydrogen inside the zirconium hydride fuel has been removed from the material description
  - Fuel Annulus+Pb-Hydrogen—same as "Fuel Annulus+Pb" but hydrogen has been omitted from the fuel material description.

(a) Zirconium hydride fuel is typically used in TRIGA test reactors. More information about the composition of the fuel may be found at http://www.ga-esi.com/triga/products/fuel.php.

Each of the test conditions described above is based on 144 hours of irradiation. However, it is worth noting the decay of ^{99}Mo in the target after 72 hours of irradiation and the diminishing returns of irradiating longer. Figure 3.1 shows the production of ^{99}Mo in a specimen target located out-of-core from 12 to 144 hours. After 72 hours, the production of ^{99}Mo is 3.8 curie. After 144 hours, the production of ^{99}Mo is only 5.6 Ci, or only 1.8 Ci more than produced during the first 72 hours. The two target positions for the purpose of modeling calculations are graphically shown in Figure 3.2. Position D8 is outside of the core, and position D5 is inside the core where the higher flux is produced.

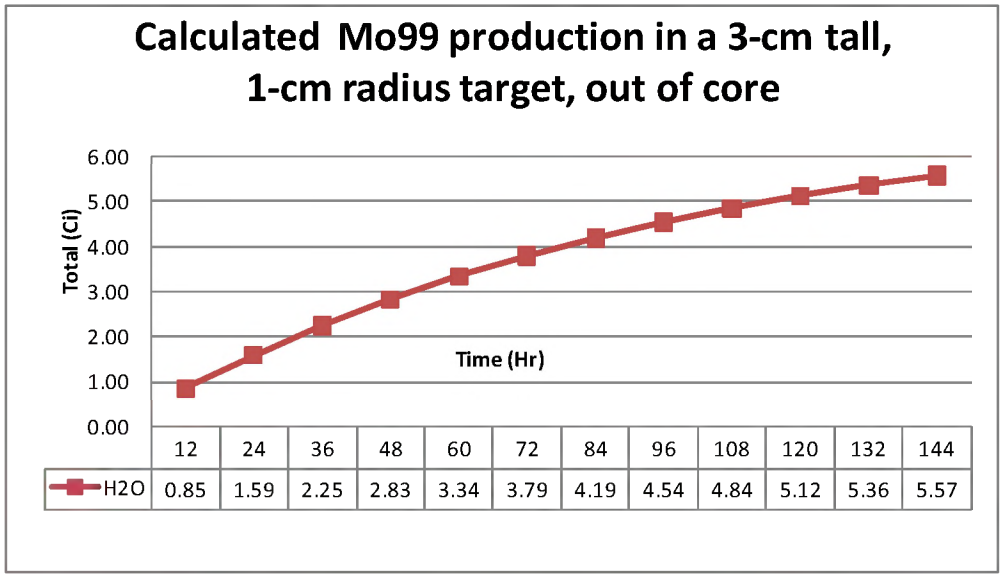

Figure 3.1. Asymptotic Profile for ^{99}Mo Production with Time

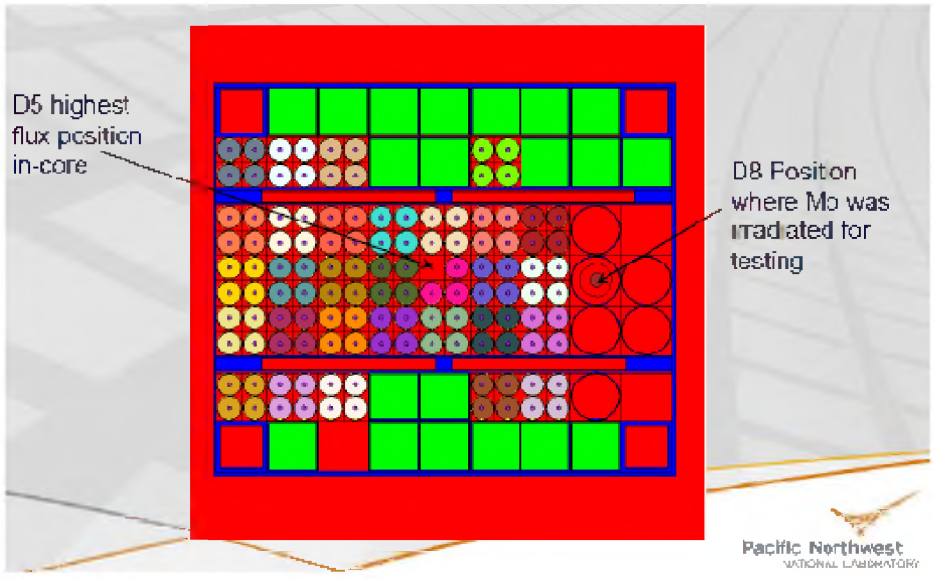

Figure 3.2. Schematic for the WSU Reactor. The figure shows the two locations used for modeling ^{99}Mo production, position D5 and position D8.

Each core position (D5) has four fuel elements. A molybdenum target can replace one of the fuel elements in the assembly. The modeling results are shown on Table 3.1. There is a trade-off between total curies of ^{99}Mo and the specific activity produced. The table shows that it is possible to produce about 1000 Ci @ 1.0 Ci/g in a single fuel annulus and a beryllium reflector (1 target position at peak flux in D5). Alternatively, about 1000 Ci @ 0.4 Ci/g may be produced with a larger molybdenum target cylinder in just water. This option is lower cost and has no delay due to fabrication and approval of the fuel annulus.

In each of the examples, a four-fold increase in the total curie values can be achieved with four targets replacing four fuel locations. The four-fold increase is possible assuming that the molybdenum targets are located far enough apart so that flux reduction due to the reduced fuel in the reactor is not a problem. The maximum number of the targets which can replace fuel locations will depend on the flux reduction. Determination of the flux reduction requires additional modeling.

It should be noted that if a license amendment for increasing the power to the reactor is pursued, and the power to the reactor is increased by a factor of 2× to 4×, a concomitant improvement in production is achieved.

A four-fold improvement in production and in specific activity is achieved by replacing the natural molybdenum target (24% ^{98}Mo) with an enriched ^{98}Mo target (96% ^{98}Mo), assuming it is possible to obtain sufficient ^{98}Mo at an affordable cost.

Table 3.1. Summary—144-Hr Irradiation of In-Core Mo Metal Powder; 8 g/cc, 2-cm Diameter

Geometry	^{99}Mo Activity (Ci)	Activity (Ci/gm)	Cell Mass (g)	
Water Hole D8 Out of core	5.57	0.074	75.39	(a)
Water Hole	31.78	0.4216	75.39	(a)
Beryllium Reflector	31.65	0.4199	75.39	(a)
Beryllium Center	33.70	0.4471	75.39	(a) (b)
Fuel Annulus	852.0	0.8921	955.04	
Fuel Annulus + Beryllium Reflector	960.7	1.0059	955.04	
Fuel Annulus + Lead Reflector	941.1	0.9854	955.04	
Fuel Annulus – Hydrogen	728.1	0.7624	955.04	
Fuel Annulus - Hydrogen + Beryllium Reflector	962.7	1.0080	955.04	
Fuel Annulus - Hydrogen + Lead Reflector	830.2	0.8693	955.04	

(a) These values are the ideal condition at the center of the core for a 3-cm-tall target; all other cases correctly average over the entire core height of 38 cm.

(b) The molybdenum annulus was 0.25 cm thick.

The hypothetical case of removal of hydrogen from ZrH fuel was only a modeling exercise to determine shielding effects of the fuel. Removal of hydrogen from zirconium hydride fuel would have undesirable safety implications and is not being proposed here.

PNNL investigated the use of the Advanced Test Reactor for irradiation of molybdenum to generate ^{99}Mo. The concept assumed that a second rabbit tube, similar to the one recently designed and

implemented at the ATR, would be built, inserted in a small B hole, and dedicated to the ^{99}Mo production effort. A prototypic rabbit capsule was modeled at the core centerline and about 8 inches from the top of the fuel to illustrate the production variation that might be seen.

To generate the preliminary results, phenomena such as self shielding, parasitic absorption, and depletion of the product were not included. These factors may change the results by 10 to 50%; however, a more detailed design effort should be able mitigate these factors. The total flux used in the calculations was 2.4e14 neutron/cm^2-sec at the centerline (Table 3.2).

Table 3.2. Summary of ATR Calculations to Estimate ^{99}Mo activity for 3, 6, and 7 Day Exposures

Target at Fuel Centerline in ATR B4 Irradiation Tube				Target at 8 inches from Top of Fuel in ATR B4 Irradiation Tube			
Irradiation Time [d]	Mass ^{99}Mo [g]	Activity ^{99}Mo [Ci]	Specific Activity (Ci/g Mo)	Irradiation Time [d]	Mass ^{99}Mo [g]	Activity ^{99}Mo [Ci]	Specific Activity (Ci/g Mo)
MoO_2				MoO_2			
3	1.79E-05	8.6	1.27	3	1.16E-05	5.6	0.73
6	2.63E-05	12.6	1.87	6	1.71E-05	8.2	1.08
7	2.79E-05	13.4	1.99	7	1.81E-05	8.7	1.15
Sintered Molybdenum Powder				Sintered Molybdenum Powder			
3	9.54E-05	45.8	1.27	3	6.20E-05	29.8	0.73
6	1.40E-04	67.3	1.87	6	9.11E-05	43.7	1.08
7	1.49E-04	71.5	1.99	7	9.68E-05	46.5	1.15
Molybdenum Metal				Molybdenum Metal			
3	1.22E-04	58.5	1.27	3	7.92E-05	38.0	0.73
6	1.79E-04	86.0	1.87	6	1.16E-04	55.8	1.08
7	1.90E-04	91.4	1.99	7	1.24E-04	59.4	1.15

4.0 Process Chemistry

4.1 Chemistry of $^{99}TcO_4^-$ Production by Neutron Irradiation of Naturally Occurring Molybdenum

This section describes the chemistry of laboratory tests for dissolving and producing ^{99m}Tc in a generator. The ^{99m}Tc is chemically separated from the irradiated molybdenum by a simple process that is described below. The irradiation does not measurably change the chemistry of the molybdenum. Practically all of the mass of the irradiated molybdenum is stable; only a tiny fraction is ^{99}Mo. The mass of technetium and ruthenium is extremely small, too small to affect the chemistry.

Few other radionuclides form except ^{99}Mo, as shown in Table 2.2. Most of the naturally occurring isotopes of molybdenum capture a neutron to form another stable isotope. One of the naturally occurring isotopes, ^{100}Mo, captures a neutron to form ^{101}Mo, a beta emitter with a 14-minute half life. The ^{101}Mo will decay within 3 to 4 hours, leaving only ^{99}Mo and ingrown ^{99m}Tc. Producing the ^{101}Mo requires the target to be decayed after irradiation, before it may be shipped to the Radiochemistry Processing Laboratory (RPL). However, the decay of ^{101}Mo occurs while the irradiated specimen is being removed from the reactor and packaged for shipment.

In prototype testing the irradiated target will have up to 1 curie of ^{99}Mo, which has moderately high dose and must be handled in a hot cell or shielded glove box. The ^{99}Mo in the irradiated target has several gammas (particularly 740 keV) and an energetic beta (1.2-MeV endpoint energy). The ^{99m}Tc has a single gamma (142 keV) that contributes to the dose.

4.2 Purity of Molybdenum Target

The purity of the molybdenum target is critical. The final product, ^{99m}Tc, must be free of other radionuclides. One of the common trace impurities in high-purity molybdenum is tungsten, which activates readily to produce ^{187}W, a 23.9-hour beta emitter that we have observed in our testing. Most other impurities will also activate. The target molybdenum must be purchased in extremely high purity or must be chemically purified before irradiation. Purification is simpler before irradiation because the unirradiated material is non-radioactive. The purity can be easily measured by irradiating a sample of the molybdenum and then gamma counting the product.

The target molybdenum is best purchased in high purity, not manufactured at our laboratory. However, if necessary, RPL can purify the molybdenum by a combination of methods such as anion exchange in dilute sulfuric acid, extraction into amyl acetate with toluene dithiol, and distillation as a halide in a tube furnace. The chemistry will need to be designed to eliminate the particular contaminants found in a given batch of molybdenum. The contaminants will probably vary from batch to batch of molybdenum and from one vendor to another. The molybdenum can be purified and converted back to molybdenum metal powder as follows:

1. Run the ion exchange or solvent extraction chemistry, which produces molybdate salt free of contaminants such as tungsten.
2. Convert purified product to MoO_3 by evaporation with concentrated HNO_3.

3. Wash solid MoO_3 with dilute HNO_3 to remove other cations and then evaporate off residual HNO_3.
4. Dissolve solid MoO_3 in NH_4OH to produce solution of $(NH_4)_2MoO_4$.
5. Pass the $(NH_4)_2MoO_4$ solution through ammonium-form cation exchanger to remove other cations.
6. Evaporate the solution dry and calcine to high-purity MoO_3 in a tube furnace.
7. Reduce the MoO_3 to Mo metal powder with hydrogen in a tube furnace.

Producing high-purity molybdenum will require a clean area to work, high quality reagents, and quartz or Teflon labware.

5.0 Target Fabrication and Dissolution

Efficient use of target volume design is a function of simultaneously optimizing the amount of molybdenum that can be inserted into each irradiation capsule and the amount of interconnected porosity within the specimen body to enhance the rate of post-irradiation dissolution. The fabrication approach is described in an invention disclosure produced during the course of this project.[(a)]

Specimen fabrication must be developed for a moderately high density form of molybdenum (80 to 85% dense) that contains interconnected porosity and therefore is susceptible to high rates of dissolution in subsequent post-irradiation, solution-based, isotope extraction.

Specimen fabrication of pressed targets is not included in the R&D planning (in appendix A) because the powder form is sufficient for the scope of work of the present technology issues. However the technical approach for pressing specimens is included for future reference.

5.1 Keys

- The pellet density must simultaneously optimize both the amount of Mo that can be inserted into irradiation capsules and the amount of interconnected porosity within the Mo body to enhance the rate of post-irradiation dissolution.
- Pellet-to-pellet densities and dimensions should be sufficiently reproducible to meet irradiation capsule design tolerances (to be defined).
- Pellets should be sufficiently strong to handle and properly load into capsules.

The technical approach to achieve the goals for target fabrication is as follows: obtain high-purity and fine-size (preferably sub-micron) W-free Mo powder and characterize particle size (d_{50} and size distribution) and morphology (via scanning electron microscopy [SEM]).

5.2 Technical Approach

- Develop a sintering curve for cold isostatically pressed (CIPed) pellets measuring ~0.6-in. ϕ × 1-in. long (full size specimens will be fabricated after sintering conditions are determined).
- A minimum of 10 pellets will be CIPed and sintered in hydrogen at five temperatures between 1000 and 1800°C for 0.5 hour and 4 hours.
- Densities will be determined via the Archimedes method and double checked by geometric measurements and calculation.
- Pellets exhibiting densities between 80 and 90% of theoretical will be further characterized by helium pycnometry (to determine how much of the porosity is open to the surface of the pellet) and SEM (to visually determine pore size and the degree of pore interconnection)

(a) Battelle IPID number 16819-E, Cold Isostatic Pressing of Molybdenum for Medical Isotope Production, Aug. 5, 2010. Richland, Washington.

- In addition, the dissolution rates and crush strengths of the pellets will be evaluated as a function of sintering temperature (for each given sintering time).
- It is envisioned that a second round of sintering will be required to validate and/or optimize sintering conditions that yield porous pellets that maximize the amount of Mo for each reactor insertion (i.e., pellet density) as well as the rate of pellet dissolution.
- Further work may include an evaluation of centerless grinding and/or drilling or press-forming of a central hole in the pellet, depending on the final pellet design.

Based on the above results, the need for a pore former will be considered. A viable pore former that has been used successfully to make relatively strong, sub-dense Zr pellets is naphthalene. It can be fully removed after CIPing before sintering, thereby minimizing contamination of the resulting metal body.

Once optimal sintering conditions are determined, scale-up to final pellet dimensions (nominally 0.630 in. $\phi \times 2.25$ in. long) will be demonstrated, and a series of six similar pellets will be fabricated to determine run-to-run dimensional and density variability.

It is anticipated that the potential future need for 28 to 56 pellets per week can be readily accommodated with relatively minor modifications in process equipment, including purchasing additional CIP bags and fabricating a fixture that allows multiple pellets to be sintered simultaneously in a given heat treatment operation.

5.3 Target Dissolution

After irradiation, the capsule is opened, and the molybdenum is retrieved. The irradiated molybdenum is then loaded into a tube furnace boat, placed in a tube furnace, and oxidized to MoO_3 in oxygen gas at approximately above 300°C. The oxidized target is removed from the furnace and cooled and then dissolved in warm ammonium hydroxide. The MoO_3 will dissolve in a few minutes, forming a solution of ammonium molybdate in ammonium hydroxide according to the reactions below.

$$2Mo + 3O_2 \rightarrow 2MoO_3 \text{ (tube furnace reaction)}$$
$$MoO_3 + 2NH_4OH \rightarrow (NH_4)_2MoO_4 + H_2O$$

Ammonium molybdate is freely soluble in water and in ammonium hydroxide

$$(NH_4)_2MoO_4 \rightarrow 2NH_4^{+}{}_{(aq)} + MoO_4^{2-}{}_{(aq)}$$

The chemical form of the daughter is $^{99}TcO_4^-$. The recoil energy from beta decay of ^{99}Mo is too small to eject the ^{99}Tc atom. The charge changes from -2 to -1.

$$^{99}MoO_4^{2-}(aq) \rightarrow {}^{99}TcO_4^-(aq) + \beta^-$$

The TcO_4^- ion is also freely soluble in water. The ammonium molybdate solution is gently evaporated dry to expel the ammonium hydroxide, leaving colorless, crystalline ammonium molybdate. The dry

ammonium molybdate is dissolved in a small volume of high-purity water to make a solution of only ammonium molybdate with ingrown $^{99m}TcO_4^-$. No other anions are present.

Because this chemistry is done at neutral or high pH, the chemical form of the molybdenum is always simple MoO_4^{2-}. When molybdenum is handled under acidic conditions, it condenses to polynuclear species such as $Mo_7O_{24}^{6-}$. If other oxyanion anions such as tungstate, silicate, and phosphate are present, they are readily incorporated into these polynuclear species. A very large number of these polynuclear compounds of molybdenum are known. The chemistry is kept simple by avoiding acidic conditions and other oxyanions.

6.0 Prototypical Design with SAMMS ^{99m}Tc Generator

Basis: Target Irradiation 1 Ci/g.
Generator Size: 1.6 Ci

In 2006. the U.S. demand for ^{99}Mo ranged from between 5,000 and 7,000 6-day curies per week.[a] A 6-day Ci is the quantity of ^{99}Mo that is priced based on its unit radioactivity calibrated six days after the generator leaves the production facility. The half life of ^{99}Mo is 66 hours. To have 1 Ci remaining in a generator after 6 days of decay, the producer must ship a generator containing 4.54 curies.[b]

To determine the amount of ^{99}Mo produced at the end of irradiation, the production facility must take into account the decay during target removal, shipment to the production facility, and production time. The decay during target removal, shipment and production yields a loss of 40% (48 hours). Further, recovery of ^{99}Mo from the irradiated targets to the generator is about 90%. To have 1 Ci for shipment requires irradiation of 1.85 curie.

Combining the decay loss and yield during the production with the 6-day decay loss at the user, results in reach 6-day Ci produced at the generator facility, approximately 8.4 Ci must be produced at the end of irradiation.

In the use of the neutron capture reaction ^{98}Mo(n,γ) ^{99}Mo, the specific activity of the molybdenum at the end of irradiation is 1 Ci/g Mo. Because of the relatively low specific activity of the produced ^{99}Mo, the volume of generator eluant requires concentration for effective labeling. It is necessary to overcome the large eluant generator volumes with a small volume elution, as used in similar generator systems using similar reactor-produced isotopes.[c]

A schematic of the proposed generator and small volume elution system based on 1 Ci/g of irradiated target material is shown in Figure 6.1. The use of ion exchange materials such as SAMMS for the production of ^{99m}Tc is the basis for the generator design. The description of the SAMMS generator shown in Figure 6.1 represents PNNL patent-applied-for technology for the method and system of isotope product generation.

(a) National Research Council, Medical Isotope Production Without Highly Enriched Uranium©2009.
(b) See ADR ET-08, Pitcher.
(c) *App Rad Isotopes*, 66(2008) 1876-1880.

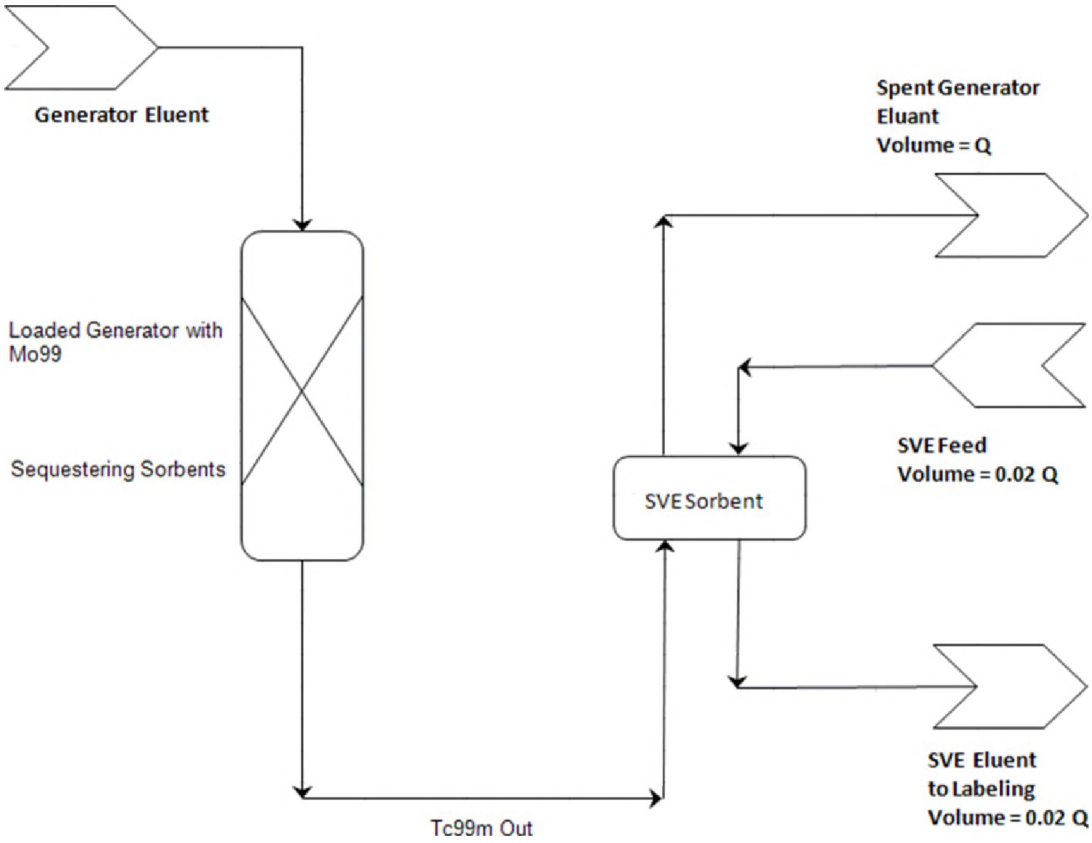

Figure 6.1. Schematic of Generator/Small Volume Elution System Based on 50:1 Concentration Ratio of the ^{99m}Tc in the Spent Generator Eluant. (Solution volumes are estimates only must be confirmed in laboratory tests.)

The ^{99}Mo produced in the target is dissolved and loaded on the generator sorbent. The ^{99}Mo decays to ^{99m}Tc and detaches from the sorbent and to the generator eluant. In addition, the ^{99m}Tc solution is passed through additional sorbents in the same column (or in a separate column) which sequesters or traps any ^{99}Mo breakthrough and associated anions and cations. The resulting ^{99m}Tc stream is free of ^{99}Mo, ^{98}Mo, copper and chloride and is used as feed to the small volume elution (SVE) column.

In the SVE column, the ^{99m}Tc is free to load on the SVE sorbent without interference from competing anions and cations such as ^{99}Mo, ^{98}Mo, copper and chloride. The volume of the SVE column is at least 50 times less than the volume of the generator column.

For a 1.6 Ci ^{99}Mo generator, the volume of the generator sorbent is driven by the mass of molybdenum loaded on the sorbent. The mass of the molybdenum required for a 1.6 Ci generator is shown on Table 6.1 as 15.3 g. The loading the copper ethylene diamine self assembled monolayers on mesoporous supports (Cu-EDA-SAMMS) is 76 mg/g, requiring 201 grams of sorbet, assuming 100% recovery. solution eluted is 100-200 mL. The effluent form the generator is fed to the SVE column loaded and loaded with the ^{99m}Tc. The volume of the sorbent in the SVE column is estimated to be 3-4 mL. The SVE column is then washed with solution to elute the loaded ^{99m}Tc from the SVE column. A summary of the inventory for a 1.6 Ci generator is provided below.

Producing a 1.6-Ci generator based on 1 Ci/gram at the end of irradiation requires 15.3 g of natural molybdenum, or a pressed target of 1.9 cc. (The pressed target size is just an example. One target can be used to produce more than one generator.) After irradiation, the activity of the target is 15.3 curies. After 48 hours of processing, the target decays to 9.17 curies. Assuming 90% recovery of the ^{99}Mo in the processing, the amount of ^{99}Mo shipped to the user is 8.3 curies. After 6 days of decay, the generator contains 1.6 curies of ^{99}Mo. The mass balance assumes no enrichment of ^{98}Mo.

Table 6.1. Mass Balance for the Production of 1.6 Curies ^{99}Mo Generator via ^{98}Mo(n,γ)^{99}Mo in a University Research Reactor—Full Scale

^{98}Mo(n,γ)^{99}Mo		1.6 Curie Generator
Target:		
	Mass of Molybdenum Metal (g)	15.3
	Bulk Density of Molybdenum Metal, g/cc	8
	Volume of Molybdenum Metal (cc)	1.9
	Enrichment	0%
	Specific Activity at EOI Ci ^{99}Mo/g	1
	Activity of Target at EOI (curie)	15.3
Processing Summary		
	Activity of Target, after 48-hr Processing, curie	9.174
	^{99}Mo Yield of Processing	90%
	Activity of generator to shipment, curie	8.26
Generator Summary		
	^{99}Mo Activity of Generator when shipped to user	8.26
	^{99}Mo Activity after 6-days	1.82
	^{99m}Tc Activity based on 87.5% of ^{99}Mo decay chain	1.59

Note: The summary shows the ^{99}Mo activity of the 15.3 g target after 6 days is 1.82 curies, (1.82/15.3) or 0.12 Ci/g.(120 milli-Ci/g). The generator must be tested with the same activity to verify its performance under challenging conditions.

A Research and Development Plan on Appendix A assimilates the results of the basis of design for conducting a demonstration of a prototypic quantity of ^{99}Mo in the generator material in conformance with the established functional requirement. The established functional requirements are elucidated on AppendixA-1. Appendix A-1 also forms the basis for the prototypical demonstration phase of the project.

7.0 Conclusions and Recommendations

This study provided further evidence that neutron capture on natural pressed molybdenum targets using research reactors will provide a usable activity of ^{99}Mo. The study provides additional support for the basis of designing a ^{99m}Tc generator with a SAMMS sorbent, or blend of sorbents, to achieve clinical grade ^{99m}Tc from (n,γ) ^{99}Mo.

The study revealed that the UZr fuel may be used to produce quantities of up to 1000 Ci of ^{99}Mo in a single fuel pin assembly. However, modifications of the fuel geometry are necessary to achieve improved production and activity. The fuel geometry must be shaped in the form of an annulus so that pressed molybdenum powder may be embedded inside the fuel annulus. Beryllium surrounding the fuel annulus provides additional neutron reflection to increase the specific activity of the molybdenum, according to modeling results. The results suggest that using a pressed molybdenum target will achieve high utilization of the reactor volume. The potential for rapid dissolution of the pressed molybdenum target shows promise when the targets are fabricated with pore-formers, but this result needs to be confirmed with testing.

8.0 References

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Appendix A

Research and Development Planning

Appendix A: Research and Development Planning

Pacific Northwest National Laboratory (PNNL) understands that molybdenum-99 (^{99}Mo) production by using the (n,γ) nuclear reaction with natural molybdenum (molybdenum-98 [^{98}Mo], 24%) results in inexpensive but low specific-activity ^{99}Mo. The technology requirements for processing ^{99}Mo from the (n,γ) activation method is within reach, but requires addressing several technology issues to be a viable method in the United States.

The technology issues included in this scope of work are 1) production of sufficient quantities of ^{99}Mo in a research reactor for its use in radiochemical testing, 2) generation of ^{99m}Tc in column tests and its subsequent separation from molybdenum and ^{99}Mo sufficient for clinical requirements, and 3) concentration of the generated technetium-99m (^{99m}Tc) sufficient for labeling. SAMMS has been demonstrated to effectively load ^{99}Mo from a variety of aqueous solutions and generate ^{99m}Tc.

Molybdenum-99 adsorption by Cu-EDA-SAMMS from aqueous media has previously been tested at PNNL.[(a)] These batch tests consisted of irradiating molybdenum oxide in a research reactor for 24 minutes to achieve 0.3 milli-Ci/g molybdenum, dissolving the target in ammonia, and contacting aliquots of the solution with Cu-EDA-SAMMS. Following a 1-hour equilibrium, the loading of molybdenum measured from 76 mg/g. Following rinsing and 3-day generation, the ^{99m}Tc concentrations in solutions measured 66 to 132 times the concentration of the ^{99}Mo activity in the same solution, depending upon the pH of the generation solution used. This test demonstrated that Cu-EDA-SAMMS could effectively generate and separate ^{99m}Tc from low-activity ^{99}Mo produced using the (n,γ) nuclear reaction.

This proposal outlines the production of ^{99}Mo in a research reactor with up to 60 hours of irradiation time. In order to perform the 60-hour irradiation, the first task is to complete an irradiation test plan. The test plan will define the project and experiment responsibilities, target design parameters, capsule assemblies, irradiation test assembly and the shielded cask. It is anticipated the irradiation experiment may use an enriched ^{98}Mo target if it can avoid the requirement for an in-core test. Purification of the enriched ^{98}Mo is anticipated to remove unwanted tungsten.

Simultaneously, the bench scale and flow through experiments may proceed using tracer quantities of ^{99}Mo produced at the WSU facility by irradiation for 4 hours or less.

The bench-scale, flow-through, column testing will be conducted to evaluate SAMMS materials and candidate ^{99m}Tc concentrating materials in both a generator and a sequestering (guard) column using ^{99}Mo produced in a research reactor.

At the conclusion of the bench-scale flow-through column tests the two 60-hr irradiation experiments will proceed and deliver prototypic quantities of ^{99}Mo to the hot cells for testing of the ^{99m}Tc generator.

This information will 1) fully assess the performance of SAMMS to generate ^{99m}Tc and the potential clinical use, 2) evaluate the engineered design and performance of the molybdenum metal target, target

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(a) A Novel Ion Exchange Technique for the Production of Clinical Grade Technetium-99m Using (n,γ) Molybdenum-99. JJ Toth, LR Greenwood, and CZ Soderquist, RPT-59220-01 Rev 0. Pacific Northwest National Laboratory, September 2010.

retrieval, and target packaging systems when irradiating enriched molybdenum (^{98}Mo) in a 1-MW research reactor for 60 hours, and 3) provide the necessary information to produce a full-scale generator column design, including performance specifications of the SAMMS sorbents, which can be included in a purchasing specification.

A.1 Technical Approach

The ^{99}Mo project will be performed in five tasks. The purpose of the project is develop a sound technical baseline for in-field scale-up of a system for ^{99}Tc generation using low activity ^{99}Mo feed. During the first task sufficient design detail will be develop to prepare the technical approach for the two 60-hour irradiation experiments. The experimental test plan will consider involving several separate entities including PNNL Radiological Processing Laboratory, Washington State University Nuclear Radiation Center, and Idaho National Laboratory (INL). The WSU Nuclear radiation Center is the baseline scheme for the irradiation. The INL laboratory provides experience in target design and fabrication, similar to the target designed and fabricated for the ^{153}Gd project in progress.

The technical approach includes a set of preliminary radiochemical tests (Task 2) and a follow-on task of column tests with low-activity ^{99}Mo (Task 3). These two tasks refine and demonstrate the performance of the generator sorbents to perform in column settings to generate ^{99m}Tc while sequestering molybdenum, and subsequently concentrating the ^{99m}Tc sufficient for labeling. During the second task (Task 2), PNNL will examine the loading of molybdenum, pertechnetate, copper, and chloride on the powdered form of SAMMS using low-activity ^{99}Mo tracers produced in a research reactor with specific activity less than or equal to 3 milli-Ci/g. This effort will determine which ligand chemistry (of the candidates selected) to use in the guard column in subsequent column tests with low-activity and prototypical-activity ^{99}Mo and to assist in selecting the SVE column sorbents.

The third task (Task 3) will consist of column tests supported in three main sub-tasks. Part 3A will characterize the column performance of Cu-EDA-SAMMS generators, demonstrate the development of the powdered form of Cu-EDA-SAMMS, and finally demonstrate the development of thiol-SAMMS materials as a sorbent in stand-alone guard columns with low-activity ^{99}Mo feed. All tests in Task 3 use either low-activity ^{99}Mo or cold (un-irradiated molybdenum). Cold molybdenum will be used to determine the performance of full-sized (sized to 1600 millicurie Mo99), packed columns for molybdenum loading and breakthrough, while measuring the hydraulic performance and turbidity of the column effluent. The breakthrough behavior of molybdenum through the full-size column configurations in this task should closely match the breakthrough behavior of the ^{99}Mo of the low-activity ^{99}Mo column tests at $^{1}/_{10}$ scale. Cold tests will also be performed at 1/10th scale.

The second part of Task 3 (Task 3B) will characterize the breakthrough profiles of effluents from columns containing the Cu-EDA-SAMMS generator sorbent, the thiol-SAMMS guard-column sorbents, and SVE column candidate sorbents, all using real-time continuous counting in a laboratory system of $^{1}/_{10}$ full-scale. The third part Task 3 (3C) will optimize the columns operating together.

Task 4 will support the development and radiochemical testing of a generator, a guard, and an SVE column using prototypic-activity ^{99}Mo (270 millicurie/g) in hot cells. Task 4 will evaluate the performance of the design basis in a remote handling environment, $^{1}/_{10}$ scale of a 1600 millicurie ^{99}Mo generator. This task will confirm the breakthrough performance, characterize ^{99m}Tc elution profiles, and

support the development of a design guide before field deployment. The prototypic activity of ^{99}Mo needed for Task 4 requires a longer irradiation of molybdenum (approximately 60 hours) in the research reactor and thus employs the target design, fabrication, nuclear quality assurance, and experimental test planning performed in Task 1.

Task 5 will execute the 60-hour experimental test plan designed in task 1. A key part of the technical feasibility is to use the data produced in tasks 2 and 3 to produce the SAMMS materials and prove its performance in task 4, in column tests in the hot cells with prototypic ^{99}Mo activity.

A.2 Description of the Performance Tests

Task (1). Irradiation Test Planning

Commercial quantities of neutron-capture ^{99}Mo have produced in the past at the University of Missouri Research Reactor. Because of the widespread use of fission produced ^{99}Mo, the University of Missouri ceased production of ^{99}Mo via neutron capture. Because of the need for testing a new generator approach to producing high specific activity ^{99m}Tc from neutron capture ^{99}Mo, targets need to be designed and fabricated for subsequent irradiation. The irradiation is expected to require 60 hours using enriched ^{98}Mo (99%). PNNL could coordinate with staff at the selected reactor site to establish target and retrieval requirements. PNNL could also translate the requirements into a specific engineering design. In addition, the selected laboratory (either PNNL or INL) could design and provide the capsule and targets to be used in the irradiation experiment. A shielded package would be used in the shipment of the irradiated target to PNNL. The shielded package would be contained within a certified "Type A" radiological container. The Nuclear Radiation Center could review and approve the design packages. Upon submittal of a final design package to the Nuclear Radiation Center, the Safety Review Board would review for its approval before starting target and shielded cask fabrication in Task 5. A sketch of a proposed target capsule is provided on Figure A.1. A sketch of a proposed shielded package is provided on A.2. The final designs would be provided as a deliverable to task 1, Irradiation Experiment Planning (Preliminary Design). During the test planning, experimental responsibilities for the following will be defined

- Design, fabrication and QA documentation of the targets to be inserted, position D8 (baseline design).
- Performing thermal hydraulic, structural and neutronic calculations of the experimental assembly
- Receiving ^{98}Mo powder and directing purification
- Preparing the Safety Review Package to be submitted to the Safety Review Committee
- Conducting the irradiation test
- Transporting the irradiated targets to RPL and loading into the Hot Cell
- Recovery of the enriched ^{98}Mo at the conclusion of the testing

The quality standard to be applied to the design, test, and build effort for the molybdenum powder targets would be ANSI/ANS-15.8-1995, *Quality Assurance Program Requirements for Research Reactors,* per NRC Reg Guide 2.5, referred to in NUREG-1537, *Part 1, Guidelines for Preparing and Reviewing Applications for the Licensing of Non-Power Reactors*.

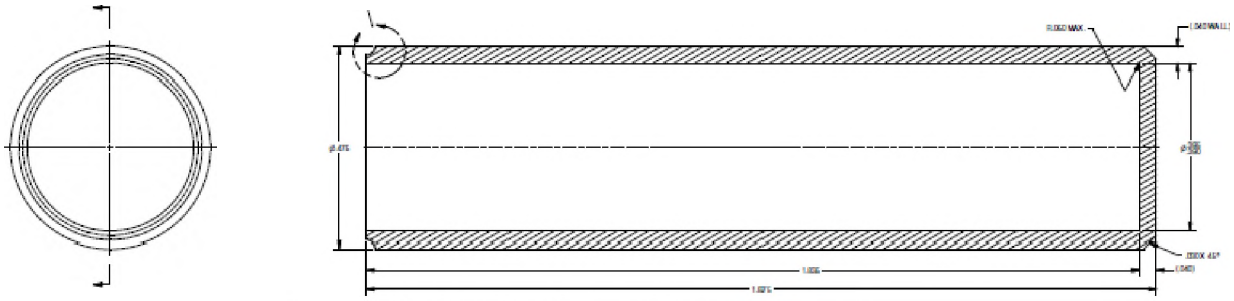

Figure A.1. Sketch of a Target Capsule Concept

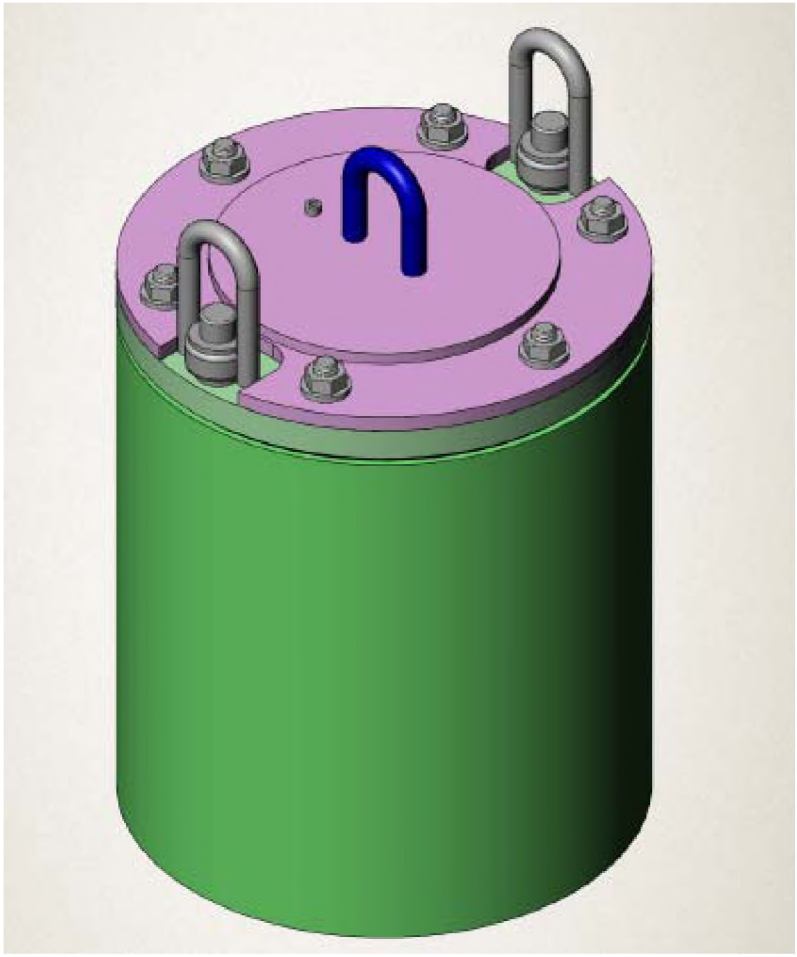

Figure A.2. Sketch of a Proposed Shielded Cask Concept

The proposed scope of the target retrieval system to produce specimens of 270 milli-Ci/g ^{99}Mo includes the use of enriched molybdenum provided by Cambridge Isotope Laboratories.

Task (2) Sorbent Optimization Tests

PNNL would conduct batch contact testing of low-activity ^{99}Mo samples with Cu-EDA, thiol, and other candidate SAMMS sorbents to determine the extent of sorption for molybdate, pertechnetate, copper, and chloride.

The synthesis routes and pretreatments of the SAMMS material before contact is to be carried out by instructions as developed before testing. The batch contact tests would be carried out for 1 hour at ambient temperature. The results of the batch contact tests would be used to determine the distribution of molybdate, pertechnetate, copper, and chloride between the solid (SAMMS) and liquid (loading, rinsing, and SVE solution) phases.

The distribution of molybdate and pertechnetate may be carried out using low-activity solutions. The distribution of copper and chloride would be carried out using cold tests. These test data provide input to select which candidate samples of SAMMS material to use in subsequent testing, either as the guard column or as an SVE (Small Volume Elution) column. The tests would be conducted with low-activity ^{99}Mo (3 milli-Ci/g) produced by irradiating natural molybdenum for 4 hours. Irradiating samples for 4 hours may employ double-encapsulated polymeric vial targets to seal the molybdenum powder (at the research reactor such as WSU).

Task (3) Technetium-99m Recovery Improvements with SAMMS in Column Tests

The ^{99m}Tc generator system used three main ion exchange columns. The three columns operate in series. The first column contains the ^{99m}Tc generator, which is previously loaded with ^{99}Mo. The second column is a guard or sequestration column to capture molybdate, copper, and chloride from the generating solution. The third column (Small Volume Elution column or SVE) loads the pertechnetate on a small volume of sorbent. Upon completion of the pertechnetate loading, the pertechnetate is eluted and prepared for subsequent labeling. A material balance for the ^{99m}Tc and ^{99}Mo would be maintained throughout the process steps. This task would also use ^{99}Mo irradiated from natural molybdenum to a specific activity of about 3 milli-Ci/g.

Task (3A). Characterize SAMMS Loading, Generation, and Elution in Laboratory Column Tests

Task 3A would consist of PNNL testing to demonstrate SAMMS generation of ^{99m}Tc that feeds into the sequestration (guard column). The data generated in these tests would be necessary to design the automated laboratory system, Task 3B below.

Task (3B). Characterize Performance for Loading, Generation, and Elution with Real-Time Measurements

Column feed, generation, and elution studies would be performed to examine the loading and elution profiles for the generator using supplied SAMMS materials. Examinations of the elution profiles as a function of column geometry (column diameter and height) would be compared with and without trace quantities of chloride present in the feed to the columns. Dependant variables measured also include batch contact loading performance, final particle size, final pore distribution, and final specific surface area.

Candidate technetium generation reagents identified in Task 2 will be evaluated under dynamic flow conditions. The SAMMS material would be packed into a generator test column of fixed geometry. The

test column will be inserted into an Automated Microfluidic System (AMS), as shown in Figure A.3. The AMS and the associated software control would enable controlled elution profiles to be obtained from a fixed generator column under highly reproducible flow conditions. The elution behavior of Tc could be documented via two measurement methods. The first method is through the use of radiochromatography (indicated as "flow-through detector"), which enables on-line, real-time detection of a transient signal of Tc as it elutes from the column. Additionally, a fraction collector can be used if there is a need to evaluate low levels of radioactivity, which would require longer detection intervals or higher spectral resolution on more specialized detection systems (i.e., HPGe detector).

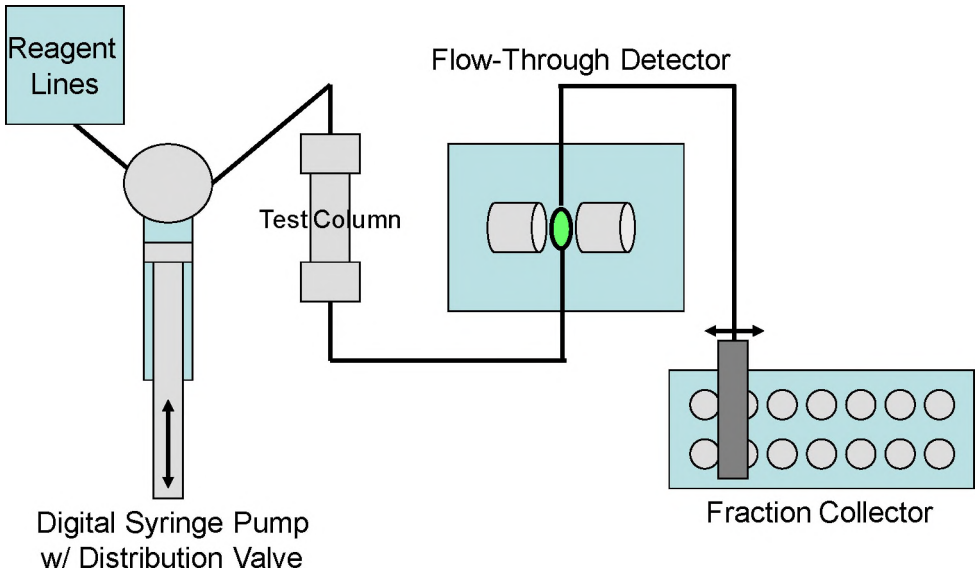

Figure A.3. Illustration of the AMS to Characterize the Elution Behavior of ^{99m}Tc from Test Sorbent Media Using Various Effluent Solutions, Flow Rates, Column Dimensions, etc. On-line radiochromatography and fraction collection capabilities enable elution profiles to be observed with high resolution and sensitivity, respectively.

The AMS would make possible the recording of Tc elution profiles in high resolution under various generating conditions. Conditions that would be evaluated may be 1) reagent, 2) reagent strength, and 3) column flow velocity (flow rate). Figure A.4 shows actual radiochromatography data for the elution profiles of a medical isotope from a column through an AMS. Each trace A, B, and C represents three different reagent concentrations. Reagent A is clearly optimal, as it requires the least volume of reagent to completely milk the medial isotope from the generator column. Similar tests would be performed to illustrate the kinetic behavior of the isotope/sorbent system (e.g., optimization of flow rate). This technique enables a "fine-tuning" of elution conditions to be established.

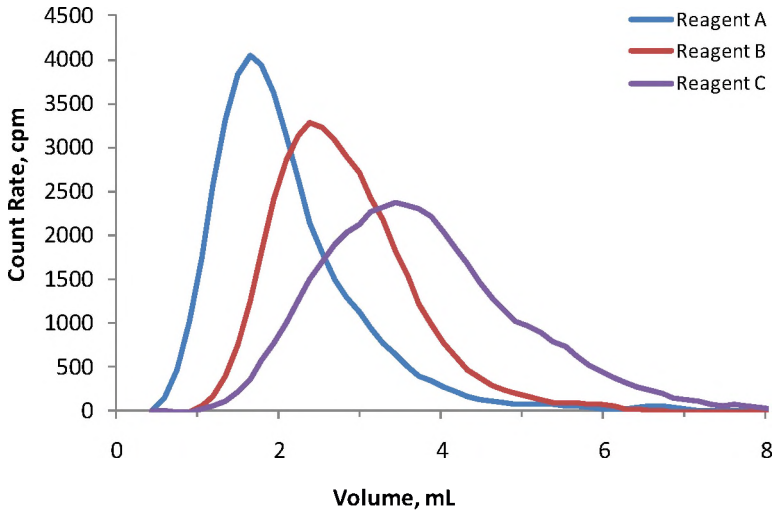

Figure A.4. Demonstration of a Set of Optimization Experiments Using AMS System Coupled to a Radiochromatography Detector. The effects of reagent strength (A, B, and C) on medical isotope elution volume are rapidly and efficiently characterized.

Task (3C): SVE Load/Elute Optimization Studies with Automated Laboratory Equipment

The SVE column is a secondary column that is fluidically connected in tandem to the generator column. The SVE column is necessary in this system to verify that the final ^{99m}Tc product could be collected in a small volume that is compatible with labeling and subsequent patient injection. The ideal SVE column would quantitatively capture Tc from the generator column during the milking process in a forward-flow direction. Next, a secondary Tc eluent solution will be delivered to the SVE column to strip the Tc product. The Tc strip solution must be capable of fast, low-volume elution of Tc to confirm that the product is of sufficient activity concentration for effective patient dosing. To further minimize the Tc product volume, the flow direction delivered to the SVE column during the elution sequence could be fluidically reversed (see Figure A.5). As seen here, the reverse-flow direction of the eluent solution through a column results in significantly reduced Tc product volume.

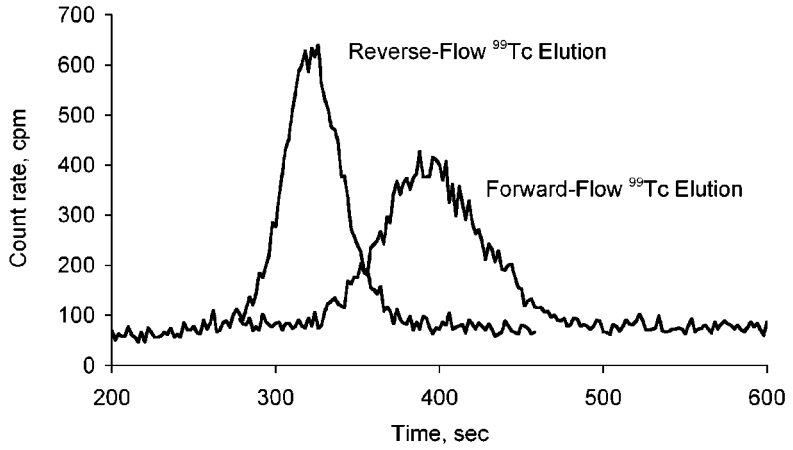

Figure A.5. Two Profiles for ^{99}Tc Being Eluted from a Small-Volume Column. Under identical conditions, the trace is eluted under opposite flow direction as the load direction exhibits a significantly sharper elution profile.

Task (4). Characterize Generator Performance with Prototypical Molybdenum-99

PNNL should test the generator and elution column using a fully staffed and equipped hot cell complex (Shielded Analytical Laboratory) or one of the new hot cells recently commissioned at RPL. The tasks required to perform the tests would include equipment development for the source recovery station, target sectioning system, target dissolution system, procurement of a calcining furnace, balances, preparation and issuing plans, permits and test instructions, sampling and assaying of the dissolved target, column loading and elution, and assaying of the eluted product. Staff should be qualified to the operating procedures. Procedure validation and remotability testing should be performed before commencing work. Task 4 would employ radiochemical separations of ^{99}Mo irradiated from enriched molybdenum to a specific activity of 270 milli-Ci/g at the end of irradiation.

A material balance flowchart of the ^{99}Mo is shown on the flowchart in Figure A.6. A description of key steps and issues of suggested hot testing are provided below:

Decladding by Breaching

The capsule containing the molybdenum powder is fabricated from a machined aluminum tube and welded or brazed to the specification required for use in the reactor core. The molybdenum powder is double-encapsulated, and the capsule is double walled. Breaching the capsule in the hot cell with a tube cutter is the preferred methodology, depending upon the clearances between the inner and outer capsules. Protruding ragged edges resulting from breaching the outer capsule will be problematic for breaching the inner capsule. Cutter and holding geometry will be tested in mock-up tests.

Oxidation of the Molybdenum Metal in a Furnace

As indicated in Section 5, the irradiated molybdenum is removed from the inner capsule and then loaded into a tube furnace boat, placed in an atmosphere-controlled muffle furnace, and oxidized to MoO_3 in oxygen gas at approximately above 300°C. Cold tests confirm the temperature and material loss prior to hot tests. The oxidized target is removed from the furnace and cooled, and then it is dissolved in warm

ammonium hydroxide. The MoO_3 will dissolve in a few minutes, forming a solution of ammonium molybdate in ammonium hydroxide.

Some testing on a small scale is necessary to determine the physical characteristics of the MoO_3 formed when calcining in the muffle furnace. Off-the-shelf equipment can be used including ceramic crucibles and a muffle furnace capable of temperatures in excess of 300°C. The furnace must be capable of a controlled ramp-up in temperature to allow for smooth conversion of the molybdenum to MoO_3. The off-gas from the furnace will be passed through a sintered metal filter or other suitable collection system to capture any radionuclides dispersed from the crucible during oxidation.

Dissolution with Ammonium Hydroxide

Although the dissolution step is straightforward, some technology development is required to optimize the amount of ammonium used to dissolve the MoO_3. Reagent-grade molybdenum oxide will be used to test and to optimize the dissolution process. Small aliquots of MoO_3 will be treated with ammonium solutions of varying concentrations at different solution-to-solids ratios. The mixtures will be heated to promote dissolution. The extent of dissolution will be assessed visually. Based on the results of these experiments, the optimal condition will be chosen for the oxidized target dissolution.

Feed Adjustment

The feed adjustment requirements will be dictated by the outcome of the target dissolution process development and feed volume requirements for the ion exchange column to load molybdenum on the column of sufficiently high loading. The ion exchange process can be successfully operated at pH ranging from 3 to 8, so there is a wide margin for this parameter in the Cu-EDA-SAMMS feed. As a first approximation, pH 5 is a reasonable target for the molybdate pH in the feed. However, the concentration should be optimized to recover the maximum amount of ^{99}Mo. It is anticipated that this volume will be in the range of 1 to 2 L. This factor will also influence the feed adjustment requirements.

Column Loading

Column performance requirements are dictated by the basis for the design in Section 6.0, indicating the loading of molybdenum to 76 mg/g of resin. The total volume of the column will depend upon the sorbent material properties (such as solid particle density and total ligand capacity per unit surface area of the sorbent). In addition, composite properties associated with the column (such as bed density and bed voidage) are inherently column specific and are a result of how the column was packed with sorbent. Effective bed loading depends on feed concentration and flowrates. The kinetics of the Cu-EDA-SAMMS was shown to reach equilibrium in 1 hour in previous work with ammonium molybdate solution.

Column Rinsing and Technetium-99m Generation

The specifics of the column rinsing and ^{99m}Tc generation will need to be determined in Task 3. Specific parameters that need to be optimized include chemical pretreatment of the column sorbents, the flowrates (bed volumes/minute), the composition of the feed displacement and rinse chemistries, and the composition of the ^{99m}Tc generation solution. The ^{99m}Tc generation (column elution) will be scheduled every 24 hours for at least 3 successive days.

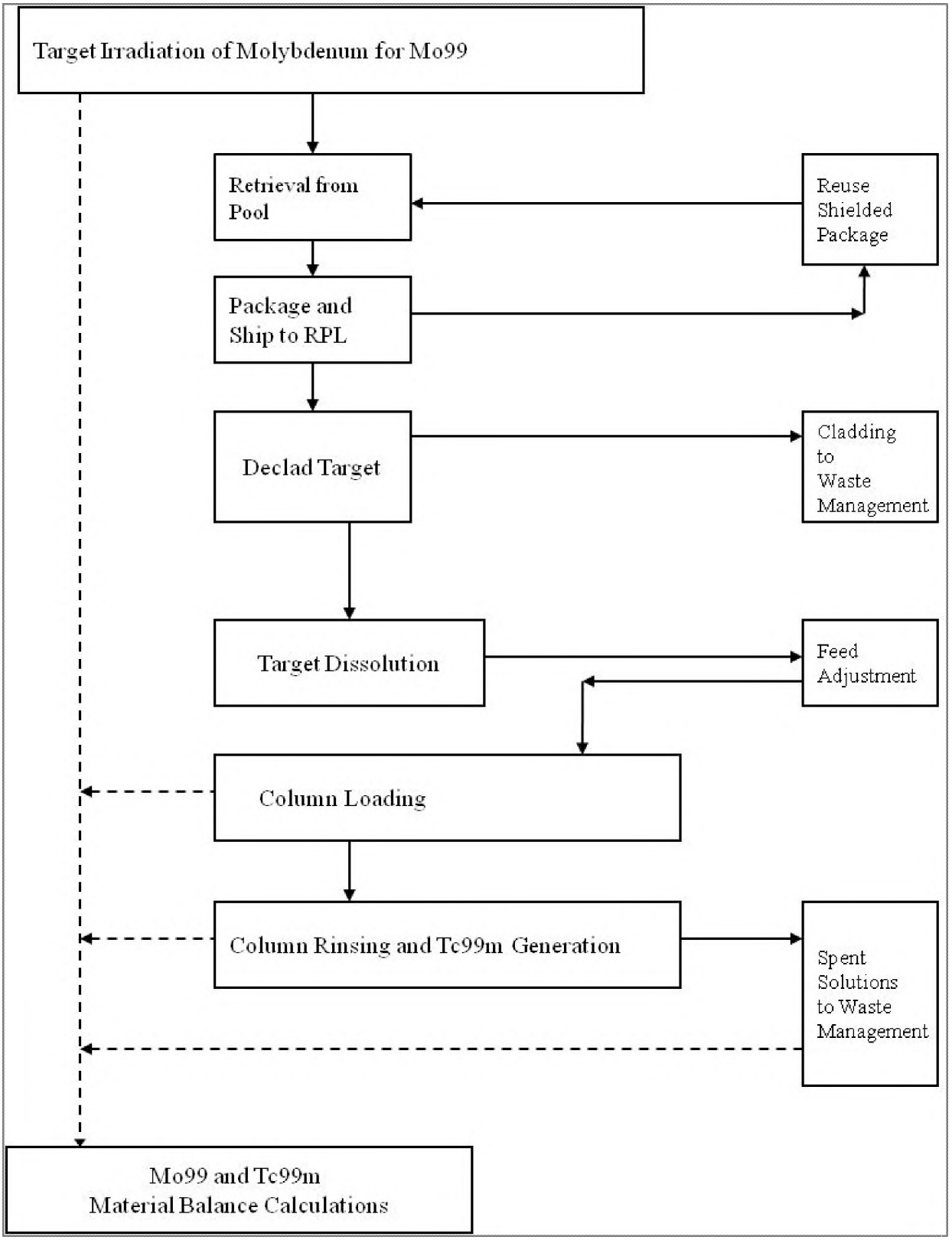

Figure A.6. Process Flow for Processing the Targets and Recovering the ^{99}Tc in a Hot Cell (Task 4).

Task (5). Irradiation Test

The scope of task 5 would be to irradiate the 2-g ^{98}Mo specimens and ship to RPL for Hot Cell processing. The activity of the samples at End of Irradiation (EOI) would be 270 milliCi/g. The irradiation time anticipate is 120 hr, but the actual time would be based neutronic calculations performed in Task 1. Enriched ^{98}Mo would be purified employing the process chemistry described in section 4.2.

A schematic of the proposed irradiation test scheme at the WSU reactor is shown on figure A.7. Irradiation of Mo at the Oregon State University reactor facility may be considered if a target shuttle or similar system may be employed.

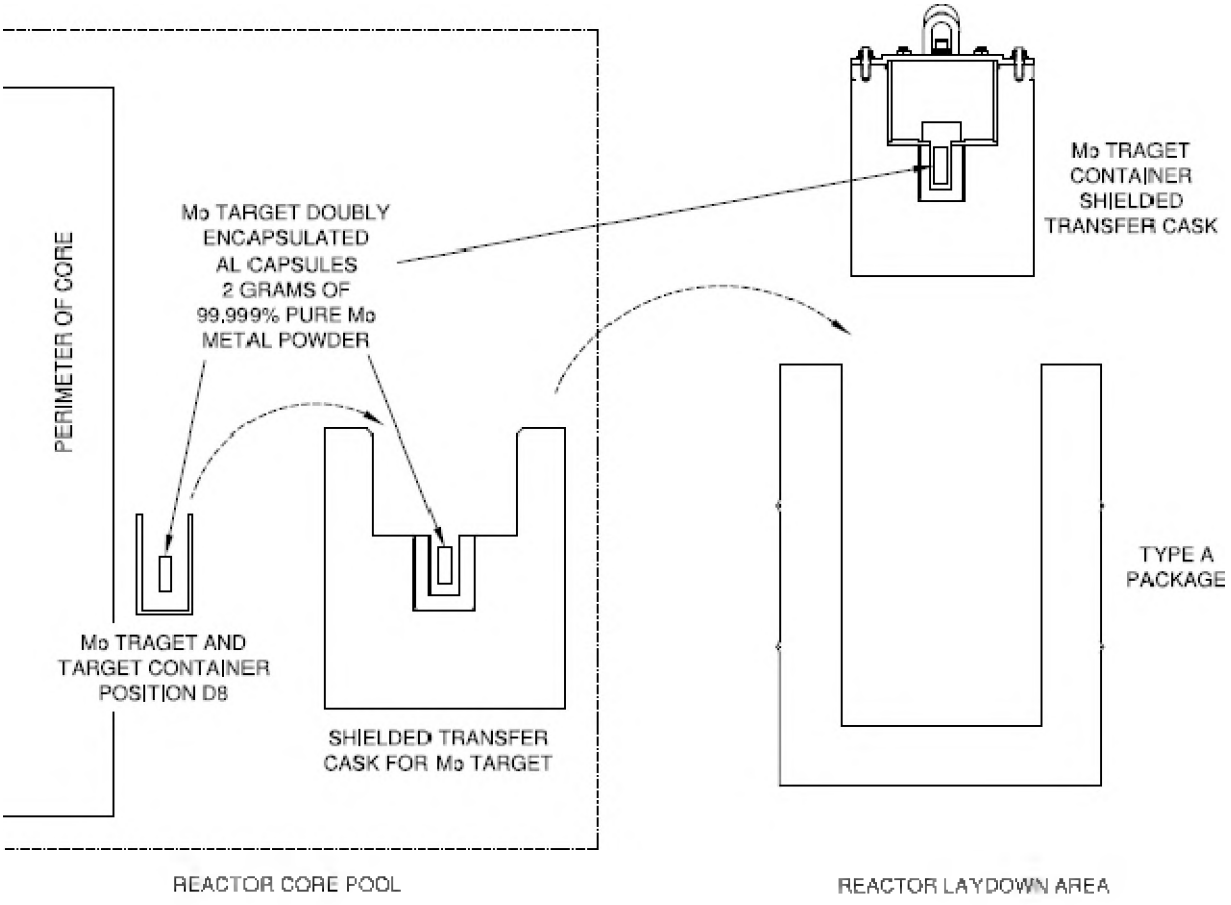

Figure A.7. Suggested Process Scheme for Irradiating 2-g of Enriched ^{98}Mo in Position D8 at WSU

A.3 Schedule

Task 1 would consist of experimental planning, and performing preliminary thermal, structural and neutronic calculations required for the safety review documentation in order to perform task 5. Task 1 might be started concurrently with Task 2, or in advance. Task 1 would be scheduled to be complete in 12 weeks.

Task 2 would consist of the necessary tasks, as described in our scope of work above, to be conducted over 12-24 weeks of the project. This would include time to synthesize candidate SAMMS materials and perform low-activity irradiations of molybdenum at the research reactor at WSU. Data produced concurrently in task 3, (column tests) conducted during the last 12 weeks of performance of task 2 would be used to further refine the SAMMS materials.

Task 3 (column tests) would employ the use of tracers to optimize column performance in radiological fume hoods. Task 3 is scheduled to be complete 36 weeks after start.

Tasks 4 and 5 would occur concurrently and support the irradiation and hot cell testing of prototypic ^{99}Mo, in the Shield Analytical Laboratory of RPL. Tasks 4 and 5 would be scheduled to be complete in 12 weeks.

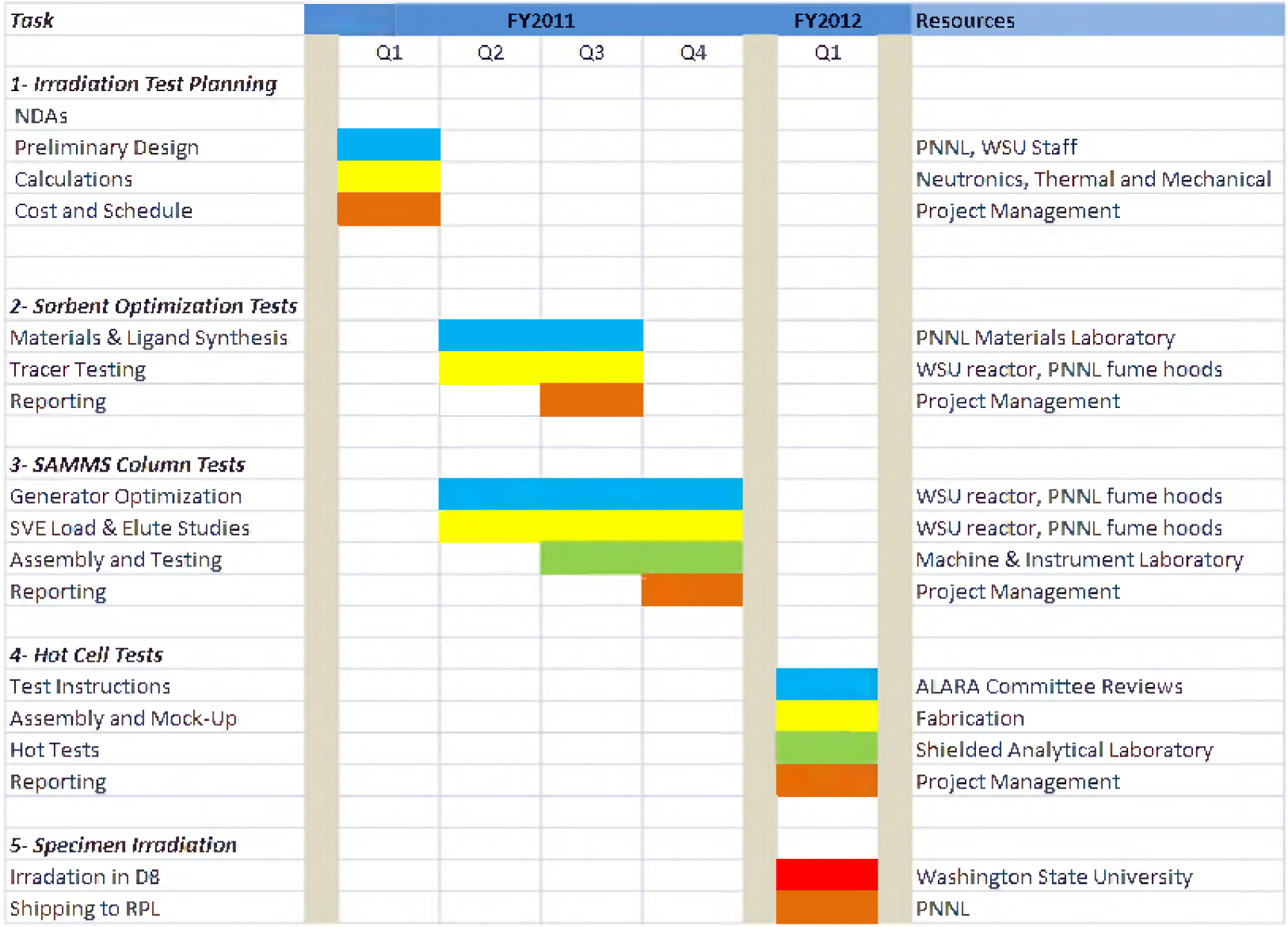

Figure A.8. Schedule of Activities to Support ^{99}Mo Generator Performance Optimization, using the WSU reactor as a basis

Project Management and Principal Investigators

James J. Toth, P.E., is a Senior Research Engineer in PNNL's Radiological Science and Engineering Group. His experience is focused on developing and starting up new or one-of –a kind chemical, separations, or manufacturing processes and carrying new process commissioning to completion. In his most recent assignment, Mr. Toth was responsible for providing evidence and a technical basis for the process design of a cesium removal, ion exchange, adsorption process using an organic elutable resin for the Bechtel National Waste Treatment Plant, one of the nation's largest engineering and construction projects. His responsibilities have included test planning, oversight, and actions necessary to close technical issues. He holds two U.S. patents.

Chad L Painter is a Program Manager in PNNL's Nuclear Systems Design, Engineering & Analysis group. His experience is focused on testing and building unique one-of-a-kind test capsules and targets for irradiation in both commercial and test reactors. His management experience includes oversight of an irradiation test program intended for the JOYO fast reactor in Japan, building tritium-producing burnable absorber rods for the Watt's Bar reactor, and designing, testing, and qualifying a plutonium sealed source. Early on in his career, he was a Nuclear Navy qualified submarine officer and was qualified to operate three different naval reactors.

Glen E. Fryxell is a Staff Scientist (Level V) at PNNL, with a PhD in organic chemistry, and he has served as a Technical Group Manager for the Materials Synthesis Group (2000–2003). For the last 20+ years, Dr. Fryxell's research has focused on organic synthesis, materials synthesis, silane chemistry, and the interfacial elaboration of materials using self-assembled monolayers. He is a co-inventor of SAMMS and has developed these materials for a wide variety of environmental applications, such as the sequestration of toxic heavy metals, radionuclides, and oxometallate anions. Dr. Fryxell is named as inventor in 16 U.S. Patents, and he has over 100 peer-reviewed publications and 85 invited presentations. In 2009, he was named Battelle Distinguished Inventor. Fryxell's work has been recognized in part with an R&D 100 Award (2007), a Micro/Nano 25 Award (2007), a Federal Laboratory Consortium Award for Technology Transfer (2006), an ACS Innovative Industrial Chemistry Award (2006), an Environmental Business Journal Technology Merit Award (2005), and an R&D 100 Award (1998).. The 1997 *Science* paper describing SAMMS was the first report of the chemical modification of mesoporous materials using self-assembled monolayers and has been cited over 900 times since publication.

Larry Greenwood is a Laboratory Fellow at PNNL with a PhD in Nuclear Physics and has served as a team lead for the Radiochemical Applications Team. He is recognized as an expert on the measurement of neutron exposure in fission reactors and accelerator-based neutron sources. He developed techniques for neutron spectral analysis and developed the SPECTER computer code, which is widely used to calculate fundamental radiation damage in irradiated materials. He helped to develop the International Reactor Dosimetry File 2002 as a consultant to the International Atomic Energy Agency and operates a laboratory for the International Monitoring System of the Comprehensive Test Ban Treaty Organization. Research interests and experience include the development of novel neutron detectors, advanced gamma spectroscopy techniques, and the production of medical isotopes. He has over 160 publications.

Chuck Soderquist has been a radiochemist with PNNL since 1996. His background is radioanalytical and inorganic chemistry. For many years, he has been the lead scientist for radioanalytical separations in the group he works in. Other recent projects include a new process for spent nuclear fuel separations,

production of gadolinium-153 from irradiated europium, and production of radium-223 for medical use. Before coming to PNNL, he managed the radiobioassay group at a commercial radiochemistry laboratory.

Budget

Budgets (or anticipated costs) were developed from the scope of work for each task, as described above. The estimated budget for each work element was based on PNNL prior experience in building unique one-of-a-kind test capsules and targets for irradiation in test reactors as well as ion exchange performance testing programs. Resources include Science and Engineering (S&E) labor, materials and laboratory equipment, chemical analytical support, technical exchange and oversight, and reporting. The costs for irradiation are based on published costs at Washington State University. However irradiation at alternative facilities would be evaluated in task 1.

Cost Estimate for
Irradiation Preliminary Design, Sorbent Optimization Studies,
Column Tests, Prototypic Irradiation and Hot Cell Tests.

Phases	Estimates of Cost
Task 1	$ 95,000 – 120,000
Task 2	$ 123,000 - 150,000
Task 3	$ 320,000 - 400,000
Task 4	$ 535,000 - 670,000
Task 5	$ 443,000 - 550,000
Sub-Total	$ 1,516,000 - 1,890,000
Project Management and Scientific Development (15%)	$ 227,000 - 280,000
Total for All Tasks	$ 1,745,000 - 2,170,000

Actual costs in a formal proposal would include cost sheets, after a contract mechanism is in place with the correct assumptions for fee. Assumptions include irradiation of enriched ^{98}Mo. Targets would be fabricated at INEL.

Facilities

State-of-the-art equipment is maintained at PNNL for characterization of the SAMMs materials for separation of molybdate and pertechnetate.

Inorganic analytical instrumentation includes a variety of lasers for solid sample ablation analysis, two electrothermal vaporization units, laser ablation for inductively coupled plasma/mass spectrometry (ICP/MS), thermal ionization mass spectrometry, ICP/optical emission spectroscopy (OES), flame and graphite furnace atomic absorption (AA), ion chromatography (IC), scanning electron microprobe (SEM) and environmental SEM (ESEM), and a transmission electron microscope, including electron dispersive X-ray (EDS) and selected area electron diffraction (SAED) capabilities.

Additionally, if needed, the principal investigators have access to a suite of leading-edge analytical equipment located in the Environmental Molecular Sciences Laboratory (EMSL), a National User Facility at PNNL (which Battelle operates for DOE). The EMSL has nine state-of-the-art nuclear magnetic resonance (NMR) spectrometers (six for solids and three for liquids) that can be used to obtain high-resolution ^{27}Al, ^{29}Si, ^{31}P, and ^{1}H spectra at field strengths ranging from 100 to 750 Mhz. With these spectrometers, new dipolar dephasing techniques can be used that provide information not only on the individual nuclei (X) but also on the connectivity to other nearby nuclei (Y). There are three X-ray diffraction (XRD) systems that include a general-purpose Philips X'Pert with a vertical θ-θ goniometer (190-mm radius), a Special Applications Philips X'Pert with a vertical θ-θ goniometer (220-mm radius), and a Four-Circle X-ray Diffraction System, which is a Philips X'Pert Materials Research Diffractometer with a horizontal, high-resolution θ-2θ goniometer (320-mm radius). The analysis software associated with this XRD instrumentation consists of Jade (Materials Data Inc., Livermore, California), which supports comprehensive analysis of XRD patterns, including search/match phase identification, peak profile fitting, indexing, unit cell refinement, etc.), and analysis programs such as Shadow and Riqas (MDI), Rietica (ANSTO, Australia), and X'Pert Plus (Philips). These profile fitting and Rietveld programs support applications such as quantitative analysis and crystal structure determination from powder data (SDPD). In addition, the Philips programs X'Pert Graphics & Identify, X'Pert Epitaxy, X'Pert Texture, and glancing incidence X-ray analysis (GIXA) support the analysis of the various data obtainable from the Four-Circle XRD system. Surface sensitive techniques, such as X-ray Photoelectron Spectroscopy (XPS), scanning auger electron spectroscopy (AES/SAM), secondary ion mass spectroscopy (SIMS), Rutherford backscattering spectroscopy (RBS), nuclear reaction analysis (NRA), and particle-introduced X-ray emission (PIXE) are available. Structural topography methods, including the atomic force microscope (AFM), are readily available to sort out changes in surface composition, structure, and chemistry.

Several Battelle staff are world-renowned for pioneering techniques in ICP/MS, including a recent R&D 100 Award for developing ICP/ion trap/MS. Analytical chemistry specialists at Battelle also have extensive experience in the characterization of complex solid and solution matrices through numerous long-standing programs at the Hanford Site to characterize such material.

Appendix B

Process Integration and Requirements

Appendix B: Process Integration and Requirements

Describes Full-Scale Application	
Application:	Production of ^{99m}Tc for Medical Purposes
Target Market:	Radiopharmiceuticals
Final End Users:	Hospitals and Medical Centers
Application Features:	Produce medical isotopes without using uranium
	^{99}Mo production using the neutron capture of an enriched target of ^{98}Mo (96%)
	Use of Column Generators capable of milking Tc99m
Constraints:	Mo obtained may be highly contaminated with stable isotopes
	Limitations of research reactors to produce Mo99>1 Ci/gram Mo
	NRC and USP Contraints for Tc99m Medical Isotope Production
Describes Prototype Demonstration	
Application:	Production of ^{99m}Tc for Research Purposes
Test Conditions	In accordance with RPL Test Plans, Permits and Test Procedures
End Users:	Internal Technical Reviewers , Client Reviews
Application Features:	1/10th scale radiochemical test
	capable of achieving (ϕ =Tc99m/Mo99) where ϕ>6,700
	capable of achieving 25 millicurie Tc99m/mL, equivalent, in eluant when using target irradiatedto 1 Ci/g Mo
	Full scale cold testing 360 mL sorbent volume
	Hydraulic testing for column performance. Permeability drop (according to darcy's law) is less than 10 % over the 6-day life of the column.
Constraints:	enriched Mo98 contaminated with stable isotopes

Test Scoping Statement 01

Title:	**Develop Operating Conditions for Cu-EDA-SAMMs Sorbents to meet Molybdenum Loading Requirements**
Deliverable:	A white paper providing the recommended Cu-EDA-SAMMs, supporting laboratory data, and recommended operating conditions for use in technetium (^{99m}Tc) generators.
How:	Chloride and sulfate forms of candidate copper-EDA SAMMS will be loaded with ammonium molybdate and radiolytic solutions containing ^{99}Mo ammonium molybdate in prototypic column tests to develop a loading curves (BV vs. C/C_o) at different flowrates and ionic strengths. Loading performance will be documented by measuring the molybdate and ^{99}Mo in column influent and effluent solutions.
Standard Preparation Methods:	SAMMS-Synthesis, column tests, liquid scintillation or gamma counting Test Instructions will be prepared in accordance with RPL practices.
Testing Scale:	column tests, & tracer tests in radiological fume hoods.
Success Criteria:	Determine the required loading conditions and recommend preferred candidate SAMMS materials necessary to achieve the required molybdate loading capacity on the generator column.

Test Scoping Statement 02

Title:	**Develop Physical Property Conditions for Cu-EDA-SAMMs Sorbents to meet Column Hydraulic Performance**
Deliverable:	A white paper providing the recommended Cu-EDA-SAMMs, supporting laboratory data, and recommended PSD, shape and operating procedures for use in full-sized generator columns. Darcy coefficient will maintain constant within 10%, throughout the 6-day column life.
How:	Candidate copper-EDA SAMMS will be functionalized on candidate amorphous silica supports and tested in columns. Candidate sorbents will be fractionated for fines prior to tests. Candidate sorbets will be functionalized in manners prevent breakage.
Standard Preparation Methods:	SAMMS-Synthesis, column tests, hydraulic tests. Test Instructions will be prepared in accordance with RPL practices.
Testing Scale:	hydraulic tests, column tests, size distribution, sorbent stability. Cold tests.
Success Criteria:	Determine the required functionalization, handling, fines separation and column loading conditions necessary to achieve the required hydraulic performance.

Test Scoping Statement 03

Title:	**Ability to meet design basis Tc99m recovery and operating requirements using prototypic activity Mo99 feed.**
Closure	Data that demonstrate the operability requirements for loading of prototypic activity Mo99, generation of Tc99m, achieving the Mo99 breakthrough requirement, copper breakthrough requirement, and maximizing Tc99m recovery in 1/10th scale column tests.
RPL Actions	**1.** Measure loading of low activity ^{99}Mo with CuEDA SAMMS in prototypic column tests. 2. Identify candidate sequestration sorbents for capturing copper, chloride, and molybdate. 3. Develop the loading performance of ^{99}Mo, copper, pertechnetate, sulfate and chloride with selected candidate sequestrating sorbents in prototypical column tests. Tests should include a range of pH chemistries typically encountered in column operation. 4. Measure Tc99m generation and recovery with CuEDA SAMMS and sequestration sorbents in prototypical column tests. Develop loading and elution generation curves using different flowrates, and feed displacements & elution chemistries.
Testing Scale:	Hot Cell, Shielded Analytical Laboratory, 1/10th full scale columns

Test Scoping Statement 04

Title:	**Demonstrate the disposability of the Tc99m generator ion exchange sorbents**
Deliverable:	A white paper providing the recommended disposal pathways for the candidate generator and SVE sorbents and supporting laboratory data.
How:	Candidate sorbents will be functionalized on candidate backbone materials and tested in columns. Sorbents will be aged the required amount of time and processed through disposal pathways required for disposal as LLW.
Standard Preparation Methods:	SAMMS-Synthesis, TSD procedures
Testing Scale:	laboratory testing, radiological fume hoods or TSD platforms
Success Criteria:	Specifying the required processing requirements and processing envelope for LLW disposal of spent sorbents.

Test Scoping Statement 05

Develop purchasing specification for CuEDA SAMMS

Closure

Characteristic data that demonstrate CuEDA SAMMS to meet Tc99m operability requirements in prototypical or full size column tests.

RPL Actions

Determine the physical properties of the sorbent required to meet hydraulic requirements.

1. Produce CuEDA SAMMS with recommended PSD, shape and BET performance measures.
2. Perform hydraulic testing on full-scale columns with CuEDA SAMMS sorbents.
3. Perform sorbent addition and replacement in full-scale columns.
4. Measure physical properties of the sorbent and identify appropriate physical properties for CuEDA SAMMS (PSD, shape, strength).

Determine the capacity of the sorbent required to meet chemical performance requirements.

5. Produce CuEDA SAMMS of various ligand chemistries as candidate sorbents.
6. Perform molybdate capacity tests on full-scale columns with CuEDA SAMMS. Produce loading profiles with variations of feed chemistries, (pH, saline, sulfate).
7. Perform molybdate capacity testing after chemical exposures, 7 day exposures.
8. Perform Tc99m yield/recovery tests on full scale columns.
9. Perform Tc99m yield recovery tests on full scale columns after chemical exposures, 7 days exposures.

Determine the stability of CuEDA SAMMS to limit extractable chemicals released during column tests.

10. Perform organic, ICP-MS (chemical), GEA and beta scintillation counting analysis on column feed and column effluents.

Test Scoping Statement 06

Title:	**Develop Operating Conditions for SVE Sorbents to meet Pertechnetate Loading Requirements**
Deliverable:	A white paper providing the recommended SVE Sorbent and supporting laboratory data, and recommended operating conditions for use in SVE columns.
How:	Chloride and sulfate forms of candidate SVE sorbents will be loaded with pertechnetate and radiolytic solutions to develop loading curves of Tc99, Tc95, or Tc99m (BV vs. C/C_o) at different flowrates and ionic strengths. Loading performance will be documented by measuring the Tc in column influent and effluent solutions.
Standard Preparation Methods:	SAMMS-Synthesis, column tests, liquid scintillation or gamma counting Test Instructions will be prepared in accordance with RPL practices.
Testing Scale:	column tests, & tracer tests in radiological fume hoods, $1/10^{th}$ full scale.
Success Criteria:	Determine the required loading conditions and recommend preferred candidate SAMMS materials necessary to achieve the required pertechnetate loading capacity on the generator column.

Test Scoping Statement 07

Title:	**Develop Physical Property Conditions for SVE Sorbents to meet Column Hydraulic Performance**
Deliverable:	A white paper providing the recommended SVE Sorbents supporting laboratory data, and recommended PSD, shape and operating procedures for use in SVE columns.
How:	Candidate copper-EDA SAMMS will be functionalized on candidate amorphous silica supports and tested in columns. Candidate sorbents will be fractionated for fines prior to tests. Candidate sorbets will be functionalized in manners prevent breakage.
Standard Preparation Methods:	SAMMS-Synthesis, column tests, hydraulic tests. Test Instructions will be prepared in accordance with RPL practices.
Testing Scale:	hydraulic tests, column tests, size distribution, sorbent stability. Cold test, full-scale column tests.
Success Criteria:	Determine the required functionalization, handling, fines separation and column loading conditions necessary to achieve the required hydraulic performance.

Test Scoping Statement 08

Title:	**Ability to meet design basis SVE Tc99m recovery and operating requirements using prototypic feed of Tc99m from the generator**
Closure	Data that demonstrate the operability requirements for loading of low activity Tc99m, and maximizing Tc99m recovery in 1/10th scale SVE column tests.
RPL Actions	**1.** Measure loading of low activity TC99m with SVE Sorbents in prototypic column tests. 2. Develop the loading performance of Tc99m. Tests should include a range of pH chemistries typically encountered in generator column operation. 3. Measure Tc99m SVE elution recovery with selected sorbents. Develop loading and elution generation curves using different flowrates, and feed displacements & elution chemistries.
Testing Scale:	Column tests, & tracer tests in radiological fume hoods, $1/10^{th}$ full scale.

Test Scoping Statement 09

Title:	**Demonstrate the disposability of the SVE ion exchange sorbent.**
Deliverable:	A white paper providing the recommended disposal pathways for the candidate generator and SVE sorbents and supporting laboratory data.
How:	Candidate sorbents will be functionalized on candidate backbone materials and tested in columns. Sorbents will be aged the required amount of time and processed through disposal pathways required for disposal as LLW.
Standard Preparation Methods:	SAMMS-Synthesis, TSD procedures
Testing Scale:	laboratory testing, radiological fume hoods or TSD platforms
Project Responsibility:	TBD
Success Criteria:	Specifying the required processing requirements and processing envelope for LLW disposal of spent sorbents.

Test Scoping Statement 10

Title:	**Develop purchasing specification for SVE Sorbents**
Generator Closure	Characteristic data that demonstrate the ability for SVE Sorbent to meet Tc99m concentrations requirements in full size column tests.
RPL Actions	Determine the physical properties of the sorbent required to meet hydraulic requirements. 1. Produce/Procure SVE sorbents with recommended PSD, shape and BET performance measures. 2. Perform hydraulic testing on full-scale SVE columns with candidate sorbents. 3. Perform sorbent addition and replacement in full-scale columns. 4. Measure physical properties of the candidate sorbent and identify appropriate physical properties for PSD, shape, sorbent strength to resist breakage. Determine the capacity of the sorbent required to meet chemical performance requirements. 5. Produce candidate sorbents of various ligand chemistries. 6. Perform pertechnetate capacity tests on full-scale columns with candidate sorbents. Produce loading profiles with variations of feed chemistries, (pH, saline, sulfate). 7. Perform pertechnetate capacity testing after chemical and radiological exposures, 7 day exposures. 8. Perform Tc99m yield/recovery tests on full scale columns. 9. Perform Tc99m yield recovery tests on full scale columns after chemical and radiological exposures, 7 days exposures. Determine the stability of candidate SVE sorbents to limit extractable chemicals released during column tests. 10. Perform organic, ICP-MS (chemical), GEA and beta scintillation counting analysis on column feed and column effluents.

Test Scoping Statement 11

Title:	**Ability to dispose of column effluents via a TSD.**
Issue Closure	Data that demonstrate the transportation and disposal requirements for radiolytic and RCRA metal column effluents.
RPL Actions	Determine the radiolytic and RCRA metal compositions and volumes of effluents produced from use with CuEDA SAMMS and SVE columns. 1. Measure radiolytic compositions of column effluents after designated decay periods. 2. Measure RCRA metal compositions of column effluents using CuEDA SAMMS and candidate SVE sorbents.
Testing Scale:	Column tests, & tracer tests in radiological fume hoods, $1/10^{th}$ full scale.

Test Scoping Statement 12

Title:	**Determine the surface dose and lead shielding required for generators and SVE sorbents.**
Deliverable:	A white paper providing the recommended shielding for the generator and SVE sorbent columns and supporting modeling data.
How:	Given the technical parameters for the generator and SVE columns, a) column heights b) column diameters c) mass of sorbents d) loading capacities e) elution chemistries, surface dose will be estimated using microshield computer code.
Standard Preparation Methods:	None
Testing Scale:	computer modeling
Success Criteria:	Specifying the required lead shielding for 800 milli-curie, 1.6 curie and 8 curie ^{99}Mo generators. Shielding will take into account self shielding and any Bremsstrahlung effects.

Requirements Elicitation Tool for Prototype Testing of Molybdenum-99 Medical Isotope Process

Process Step	Process Step	Functional Requirement	Allocated Requirement	Requirement Type	Issues
1.0	Reagent Supplier				
1.1	Produce Reagent	F.1.1.1 Mo98 enriched molybdenum (96% or greater Mo98)	P.1.1.1 2-gram of product shal be available in 90-days	Performance	Testing Schedule requires delivery performance
			P.1.1.1.2 Supplier shall have QA program and be qualified by PNNL	Performance	Must confirm Mo98 content by NAA test reconcilation
1.1	Produce Reagent	F.1.1.2 The enriched Mo powder shall contain < 2wt% < 500 micron	P.1.1.2.1 The supplier shall supply PSD measurements of Mo producr	Performance	Fines may generate dust in Hot Cells
			P.1.1.2.2 Fines < 50 micron shall be below 2wt%	Performance	Fines may generate dust in Hot Cells
1.1	Produce Reagent	F.1.1.3 Enriched molybdenum processed and free of metal contaminants < 1 PPM wt%	P.1.1.3.1 Mo98 product cert sheet must be compared to NAA test.	Design	Ability to remove W must be verified
2.0	Target Fabrication				
2.1	Fabricate targets	F.2.1.1 The target shall be contain molybdenum powder double-encapsulated in aluminum	P.2.1.1.1 The molybdenum powder specimen shall be free of cross contamination during transfer into the aluminum	Performance	-
			P.2.1.1.2 The aluminum encapsulants shall be separated by a gap for easy decladding	Design	-
2.1	Fabricate targets	F.2.1.2 The target shall be capable of irradiation outside core (position D8) for at least 4 hours and up to 60 hours.	P.2.1.2.1 The thermal, structural and thermal properties of the target during irradiation shall be calculated before testing	Design	-
2.1	Fabricate targets	F.2.1.3 The target shall pass a visual, He leak test and dipenetrant test subject to the requirements of the research reactor facility	P.2.1.4.1 No indicated He leakage greater then 1E-7 STD CC/sec is reference (reference ATR requirement).	Design	-
2.2	Decontaminate Type A Package	F.2.2.1 The received Type A package shall be decontaminated to NRC free release criteria	P.2.2.1.1 RPTs will decontaminate package to meet NRC Free Release Criteria. • NRC Free Release Criteria found in table E.3	Performance	o Table E.3. Multi-Agency Radiation Survey and Assessment of Materials and Equipment Manual (MARSAME) (January 2009) iNUREG-1575, Supp. 1.
2.3	Ship Type A package to Research Reactor	F.2.3.1 Certified Type A package labeled as empty radiological UN2910	-	Performance	-
2.4	Ship unirradiated Targets to WSU	F.2.4.1 The target shall meet the requirements for the reactor facility. An NDA with the reactor facility is required to establish the all functional requirements. The target shall meet the requirements for the Safety Review Board at the reactor site (WSU)	P.2.4.1.1 An experiment review package will prepared and submitted to the review board before the start of testing.	Performance	-
3.0	Irradiator Services				
3.1	Irradiate Target to produce Low Activity Mo99	F.3.1.1 The yield from the target shall between 0.3 and 3 millicurie Mo99/gm Mo	P.3.1.1.1 The target shall be exposed for between 24 minutes and 4 hours, using the WSU D8 position as a basis	Performance	-
3.2	Irradiate Target to produce Prototypic Mo99	F.3.2.1 The yield from the target shall between 100 and 300 millicurie Mo99/gm Mo	P.3.2.1.1 The target shall be exposed for between 40 hours and 120 hours, using the WSU D8 position as a basis	Performance	-
3.3	Ship Target to RPL	F.3.3.1 Verified Activity in Certified Type A package shall be below the transportation index	P.3.3.1.1 The package surface dose shall be below 50 mrem/hr. Package shall be smear-tested. Surface dose and smear-tests shall conform to Type A limitations.	Performance	-
3.4	Accept Irradiated target at RPL	F.3.4.1 Approved Procedure in Place for Transferring target to cell. Dose estimate, ALARA Review Committee Approval	P.3.4.1.1 The incurrred dose of transferring the target to the hot cell shall be calculated using microshield or other dose calculation routine.	Performance	-
4.0	Prototype Column Testing				
4.10	Place target into Hot Cell	F.4.1.1 The transfer shall minimize dose and radiological contamination to RA.	P4.1.1.1 The actual dose shall be compared to calculated dose to identify any unforseen dose issues.	Performance	-
4.20	Declad Target	F.4.2.1 The decladding shall occur in 2 hours without contaminating the Mo with aluminum	P.4.2.1.1 Cutting tools for decladding shall be sharp. Mock-Up tests shall be performed on unirradated samples.	Performance	-
4.30	Dispose of Cladding Waste	F.4.3.1 The cladding shall be disposed of as LLW	P.4.3.1.1 Specimens of the declad aluminum shall confirm absence of cross contamination from hot cell	Performance	-
4.40	Dissolve target	F.4.4.1 The Mo target shall be converted to MoO_3 and then dissolve in 2 hrs.	P.4.4.1.1 Volatile Mo in the furnace shall be mimimized to maximize recovery of Mo99	Design	-
4.50	Adjust feed	F.4.5.1 The dissolved Mo chemistry shall be compatible with the Mo loading on the sorbent.	P.4.5.1.1 Radiological Fume Hoods tests shall be performed to identify feed adjustments necessary	Performance	see Test Scoping Statement (TSS) 1
4.60	Load Column	F.4.6.1 The Mo shall be loaded on the column in less than 5.3 hrs based on 1.6 curie (6-day).	P.4.5.1.1 Radiological Fume Hoods tests shall be performed to identify column operating conditions	Performance	see Test Scoping Statement (TSS) 1, 2
4.70	Rinse Column	F.4.7.1 The column shall be rinsed in less than 3.5 hrs	P.4.5.1.1 Radiological Fume Hoods tests shall be performed to identify rinse operating conditions	Performance	see Test Scoping Statement (TSS) 3
4.80	Elute generator to milk Tc-99m	F.4.8.1 The column shall be eluted in less than 30 minutes	P.4.5.1.1 Radiological Fume Hoods tests shall be performed to identify elution operating conditions	Performance	see Test Scoping Statement (TSS) 3, 5
4.90	Elute SVE Column for 25 milliCi/mL	F.4.9.1 The SVE column shall elute Tc99m in less than 15 minutes	P.4.5.1.1 Radiological Fume Hoods tests shall be performed to identify SVE column operating conditions	Performance	see Test Scoping Statements 6,7,8,10
5.0	Disposal & Recycle				
5.1	Disposition Spent Solutions for Waste Disposal	F.5.1.1 Generated liquid waste shall be LLW	-	Performance	-
5.2	Disposition Spent Sorbents for Waste Disposal	F.5.2.1 Sorbent waste shall be LLW.	-	Performance	see Test Scoping Statements 4, 9
5.3	Recycle Enriched Molybdenum	F.5.3.1 The recovery of enriched Mo from the loaded column shall be 95% or greater.	P.5.3.1.1 Recovery of Mo98 shall be performed in radiological fume hoods after sufficient Mo99 decay	Performance	-

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