Mo-99 2014 TOPICAL MEETING ON
MOLYBDENUM-99 TECHNOLOGICAL DEVELOPMENT

June 24-27, 2014
Hamilton Crowne Plaza
Washington D. C.

Optimization of Processes for Waste Treatment and Disposal from Facilities Utilizing Aqueous Uranyl Salt Media for Medical Isotope Production

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ABSTRACT

Argonne is assisting SHINE Medical Technologies in the development of the production of Mo-99 using accelerator driven fission in an aqueous uranyl-sulfate target solution. Development of processes for waste treatment and disposal scheme for production of ^{99}Mo aqueous fissioning media presents a unique set of challenges for management of actinides, long-lived fission products, and environmentally labile radioisotopes. These processes drive the cost of waste disposal. Argonne has worked to develop separations schemes that can meet the necessary material throughputs and product specifications for aqueous uranyl-salt-based medical isotope production. Work is currently underway to assess the waste streams associated with all of the key facility functions to ensure that streams that are especially difficult to dispose, namely mixed and GTCC wastes, are not generated. As part of this effort, Argonne evaluated the expected partitioning of components within the process flowsheets based on the known chemistries and estimated separations efficiencies. Volumes and classifications of all waste streams based on a mass balance over the entire facility have been identified. Expected waste stream compositions were determined from the predicted target solution evolution, distribution factors for all separations processes, and waste consolidation. The likelihood that those waste streams can be treated to meet Class C requirements was evaluated to identify radionuclides limiting compliance, beneficial waste stream combinations, and possible process modifications. Unit operations where further optimization could lead to significant reductions in waste volumes or where uncertainties related to processing have been identified for further analysis. This effort included an assessment of production schedules and identification of potential improvements to the methods for treating liquid radioactive wastes for disposal.

1. Introduction

Metastable technetium-99 (^{99m}Tc) is used in more than 80% of medical diagnostic tests, which includes approximately 70,000 medical imaging procedures throughout the world daily [1]. Currently, Canada's Chalk River nuclear reactor and the Netherlands' High Flux reactor produce approximately 85% of Europe and North America's ^{99m}Tc supply [2]. The Chalk River reactor will shut down ^{99}Mo production in 2016, creating a worldwide shortage of ^{99m}Tc, unless reliable,

alternative production methods are developed. One possible production method based on accelerator-driven fission of ^{235}U is SHINE. SHINE utilizes a deuterium (^{2}H) beam line, a tritium (^{3}H) gas target, and a vessel containing a low-enriched uranium (LEU) salt solution surrounded by a light-water reflector. The ^{2}H ion beam is accelerated towards the chamber containing ^{3}H gas, generating high energy (14 MeV) neutrons when the ^{2}H and ^{3}H interact via a fusion reaction. The generated fusion neutron population is moderated and multiplied via a solid material then impinged on the LEU solution inducing fission of the ^{235}U. The fission reaction produces ^{99}Mo, which is the parent isotope of ^{99m}Tc. The vessel containing the LEU solution is kept subcritical to obviate concerns of a criticality accident [3]. The ^{99}Mo is isolated from the uranium and other fission and activation products using an adsorption column. The ^{99}Mo is further purified by subsequent washing and elution, and ultimately recovered by an LEU-Modified Cintichem (LMC) process.

In the baseline SHINE process, the uranium solution is recycled after the ^{99}Mo is removed. As the majority of fission products and actinides remain in solution, they build-up in the solution with each successive irradiation cycle. Consequently, the uranium in solution is periodically treated to remove the fission products and other actinides using the UREX process [4]. This requires conversion of the uranyl sulfate in solution to uranyl nitrate, the necessary UREX feed. After the UREX strip solution is run through an anion exchange (IX) column to remove any pertechnetate or iodide, the purified UREX product solution contains only uranium nitrate, which is denitrated and converted back to a sulfate solution for further irradiations.

The ^{99}Mo recovery process generates both liquid and solid wastes consisting of eluents, washes, glassware, and the column components. The raffinate of the UREX process contains the preponderance of the fission products and transuranic (TRU) elements and is therefore the major radioactive waste stream. The sulfate-to-nitrate and denitration processes also generate smaller amounts of radioactive waste in both solid and liquid form. The ^{99}Mo recovery column wash solutions are also contributors to the total waste volume. The liquid wastes are to be combined and grouted for disposal, though other processing options are also under evaluation. Gaseous wastes are to be treated to capture radioactive or acidic species as required to meet regulatory requirements. This paper describes a methodology that was used to assess the quantity and activity of wastes generated by SHINE processing, and identifies any additional treatment that may be required to assure that all wastes can be treated to economically meet the requirements for Class A or Class C low-level waste disposal.

2. Methodology

The unit operations-level SHINE Medical Technologies process flow diagrams for the Mo-99 production process were adapted into an Excel® workbook to enable a more comprehensive quantification of the SHINE facility mass balance. The correct facility mass balance is critical to aid the independent quantification of the process wastes generated during chemical processes in the SHINE facility; process wastes from off-gas management are currently outside the scope of this study. Figure 1 shows a simple schematic of the target-solution treatment process. The process vessels and streams were based on those included in a set of process flow diagrams (PFD) provided to Argonne by SHINE Medical Technologies. The values for bulk stream properties (densities, mass and mole percentages of molecular species) in a given stream are derived from the values included in the diagrams or developed from detailed process knowledge.

The radionuclide compositions in the irradiated solutions are based on the values supplied by SHINE that were calculated using the ORIGEN code. The separation factors (as stream split values) are based on laboratory data when available, or best estimates from process knowledge when not. It is expected that the split factors will be refined as more laboratory data become available or engineering-scale testing commences. Where necessary, changes were made to individual operations to better align the output compositions with available data.

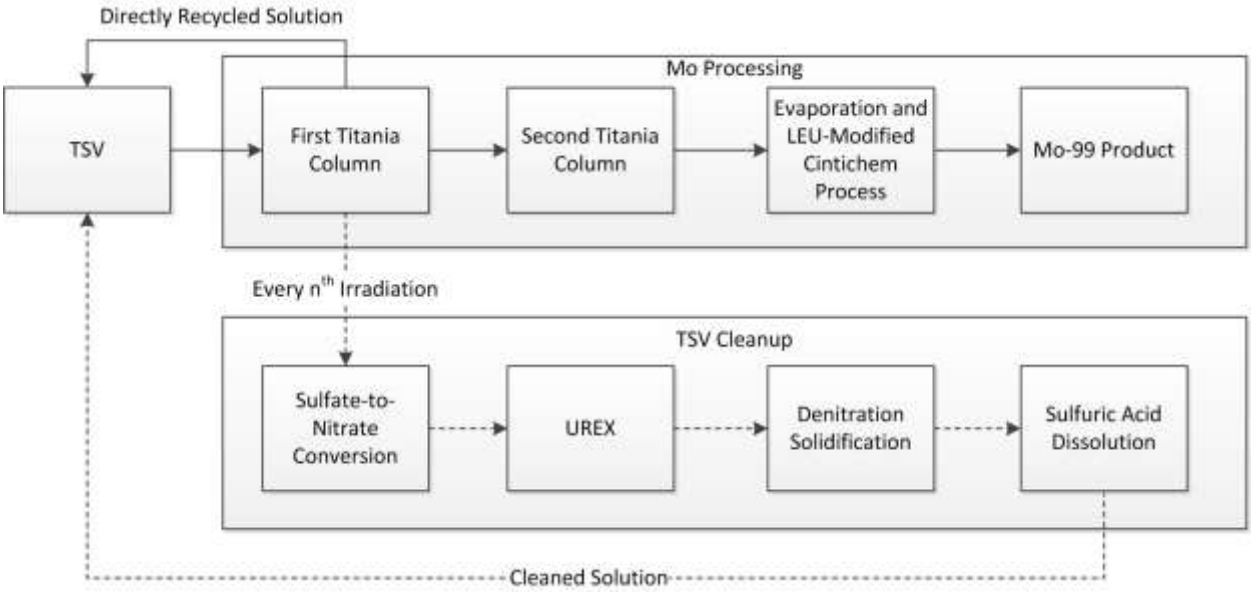

Figure 1. Block diagram of the SHINE facility uranyl-sulfate solution processing operations.

The workbook consists of 46 separate worksheets covering all of the major inputs, streams and processes. Each major facility operation is represented to provide stream compositions in terms of total moles, grams, or curies of a given species in a stream. All of the major waste streams are identified and compiled. All of the worksheets except for the last have the same overall structure. The first 13 rows of a worksheet include the name and identifier of the process and diagrams illustrating each of the processes to show inlet and outlet streams. Rows 13 through 18 give stream names, densities, flow rates, and volumes. Rows 20 through 43 are a listing of the cold chemicals, which are carried through all of the worksheets as molecular species and are tracked separately from the fission product and actinide elements in rows 45 through 143.

The leftmost column lists the components in each stream. Each stream is represented as a column in the worksheet with components listed as grams, moles, or curies (depending on the worksheet) corresponding to the species of interest. Several highlighted columns correspond to a vessel in which an operation occurs rather than process streams. These vessels are shown in the drawings above the highlighted column for reference. The values in these vessel columns correspond to user-defined split factors that represent the transformation (reaction, dissolution, evaporation, etc.) that occurs within that vessel to produce the outlet stream compositions. In some cases multiple columns in tandem are used to represent processes with more than two outputs or with more complicated manipulations such as chemical transformations. Outlet streams are identified as gas-phase, liquid-phase, or solid corresponding to the type of waste.

As the waste evaluation process has evolved, the workbook contents have been adapted due to an improved understanding of the underlying processes, specific requirements of researchers at Argonne, and on-going effort to eliminate errors and improve usefulness.

3. Results

Based on the results of the mass balance developed for the combined SHINE product recovery and solution treatment processes, no wastes are expected to exceed the Class C specifications for low level waste. The initial results of the analysis indicated that the process will generate Class A and Class C low level wastes. The initial distribution is given in Table 1 and Table 2 for the liquid and solid process wastes that were identified, respectively. Scrubber wastes generated from vent-gas treatment are omitted. Table 1 shows the relative waste volumes generated for the target solution recycle—where the irradiated solution is processed to recover ^{99}Mo and recycled without additional treatment. Table 2 shows the distributions for wastes generated when the solution is treated after ^{99}Mo recovery to remove fission products and prior to recycle. As can be seen, in both cases the waste volumes are dominated by the solidified liquid wastes stemming from the various separations processes. The target solution is only periodically treated to remove fission products, so over an annual operation the wastes generated are a weighted average of these two cases. Substantially more waste is generated if cleanup is required over a short interval.

Table 1. Relative volumes of wastes generated per irradiation without cleanup.

Per Irradiation	Solidified Liquid Waste	Glassware
Density (g/cm^3)	6.6	2.3
Molar Flow Rate	98%	2%
Volume	96%	4%

Table 2. Relative volumes of wastes generated per irradiation with cleanup.

Per Irradiation	Solidified Liquid Waste	Glassware
Density (g/cm^3)	6.6	2.3
Molar Flow Rate	99.8%	0.2%
Volume	99.6%	0.4%

The wastes streams that comprise the liquid component of the solidified liquid wastes are listed in Table 3 and Table 4 for the irradiation cycles without and with solution cleanup, respectively. As above, the liquid wastes arising from the vent scrubber are omitted in this analysis. The solidified liquid waste collects the major liquids streams that arise from the product recovery columns and spent target solution cleanup. If the solution clean-up is omitted, as when the target solution is recycled directly, the UREX raffinate is not generated and the total waste volumes are much lower, but the radionuclide concentration is much higher.

Table 3. Relative amounts of liquid wastes generated per irradiation cycle.

Per Irradiation	Extraction Column Spent Washes	Concentration Column Spent Eluate	LMC Liquids
Density (g/cm^3)	1.01	1.01	1.02
Molar Flow Rate	32.5%	66%	0.5%
Volumes	32.2%	67%	0.5%
Activity	23%	65%	12%

Table 4. Relative amounts of liquid wastes generated per irradiation and cleanup cycle.

Per Irradiation	Extraction Column Spent Washes	Concentration Column Spent Eluate	LMC Liquids	UREX Raffinate
Density (g/cm^3)	1.01	1.01	1.02	1.02
Molar Flow Rate	3.2%	6.4%	0.05%	90.3%
Volumes	3.2%	6.5%	0.05%	90.1%
Activity	3.8%	10.5%	2.0%	83.7%

Calculations were performed to (1) estimate the maximum waste loadings in grouted waste forms made with individual or combined waste streams that will meet Class C requirements for radioactivity, (2) estimate the number of 55-gallon drums of each waste form that would be generated per year, and (3) estimate the amounts of water required to produce those waste forms. The waste streams considered include contaminated titania and IX-resin solids, $Ba/SrSO_4$ precipitates, glassware, and several liquid wastes in amounts generated by a relatively frequent cleanup cycle. The calculations provide the minimum amount of grout matrix material required to immobilize the waste streams generated during one year in waste forms meeting NRC regulations for Class C (or possibly Classes B or A). The curie values for regulated radionuclides used in these calculations were taken from the ORIGEN results provided by SHINE for decay times up to 1 year. The masses and chemical compositions of the individual waste streams are based on analyses of the chemical separation processes at ANL. Because the distribution during processing is on a chemical basis, the isotopic contents of individual waste streams were calculated in the same proportions as the distributions of elemental masses. This is a conservative assumption that all the radionuclides generated during the irradiations are present in the waste streams to be grouted.

Regulatory dose limits for Class C, B, and A wastes are summarized in two tables within NRC 10 CFR 61.55 that provide maximum curie contents for specific long- and short-lived radionuclides (Tables 1 and 2, respectively) on either mass or volume bases [5]. Nominal values for grout mixtures and densities were used to provide an initial assessment of production parameters and estimate the waste form volumes required to produce Class C-compliant waste forms with the individual and combined waste streams.

The grout used to produce the waste forms must be sufficiently fluid to fill the drums without significant voids, but sufficiently stiff to avoid separation of the aggregates (or encapsulated wastes) during curing. Most importantly, the water content of the waste form must be adjusted

to meet the acceptance criterion of no more than 1 volume% free liquid content within the waste drum. Although the appropriate formulations of grouted waste forms for SHINE waste streams will require testing to evaluate the effects of the chemicals in the wastes and determine the optimum relative amounts of water, cement, blast furnace slag, and other additives, the likelihood that Class C-compliant grouted waste forms can be made was evaluated based on typical grout formulations. The water/cement ratios of workable concretes are between about 0.38 and 0.65. A 2013 study by Westsik et al. confirmed the importance of the mix ratio on the production and performance of grouted waste forms: grouts made with a water/total dry mass ratio of 0.4 set too quickly and those made with a water/total dry mass ratio of 0.6 had unacceptably poor durability [6]. A water/dry mix ratio of 0.5 was used as a logical initial target in the present analysis, where the dry mix includes ordinary Portland cement and other additives. It is expected that additional process wastes such as crushed glassware can serve as aggregates in the grout or be encapsulated by the grout, but those are not included explicitly in the calculations. Instead, the mass and volume of the waste form matrix required to meet Class C limits are determined without regard to specific additives.

Both long- and short-lived radionuclides are regulated by the NRC, with some limits provided on a Ci per mass basis and others provided on a Ci per volume basis. Therefore, both the mass and volume of the grouted waste forms were estimated to determine compliant waste loading limits. The maximum waste loading was first determined from the mass-based limits for the long-lived alpha emitting transuranic nuclides with half-life greater than 5 years (predominantly Np-237, Pu-239, and Pu-241). The volume of a grouted waste form made with that maximum waste loading was then estimated to determine if the other regulated radionuclides met the volume-based limits.

The total mass of each waste stream to be grouted was calculated on a per-year basis using the masses of chemical components and fission products predicted to be in each waste stream based on the process flow diagrams provided by SHINE and processing efficiencies estimated by ANL. The mass distributions of elements between the waste streams to be grouted were used to calculate the fraction of the total Curies for each regulated isotope present in each waste stream. For example, if 40% of the mass of Cs is in Stream A, then 40% of the total inventory of Cs-137 generated per year was assigned to Stream A. The maximum waste loading meeting the limit for long-lived transuranic isotopes was calculated first using the regulatory Sum of Fractions rule [5]. The maximum waste loading gives a sum of fractions value equal to the Class C limit of 1.00 and establishes the minimum mass of the grout matrix required to meet the mass-based curie limit. The minimum mass of the grouted waste form was used to determine the required masses of water and dry mix (Portland cement and additives), which were added in a 1:2 mass ratio for all waste forms. The waste form volume was estimated from the required mass by using a specific volume of 7.34×10^{-4} m^3/kg to represent grouted waste forms made with light aggregates such as zeolite and crushed glass. The curie contents of isotopes regulated based on the volume of the waste form were then compared with volume-based regulatory limits to either verify that the mass-based loading was compliant or determine the lower volume-based limit. This approach provides the highest waste loading meeting the Class C limits for the amount of waste to be immobilized.

The results of formulations for compliant waste forms with individual and combined waste streams are summarized in Table 5. These annual results are based on one batch of target

solution with Mo-99 recovery once per week with cleanup every four weeks. Grouting of the waste solutions individually and as a combined waste stream was evaluated. The mass-based Class C limit for Pu-239 will drive the compliance for all waste streams except the LMC liquid waste, which would be limited by I-129 if immobilized in a separate waste form. The concentrations of radionuclides regulated based on Ci/volume (primarily Cs-137 and Sr-90) are well below their Class C limits in all other individual waste streams and when the liquid waste streams are combined. Because none of those concentration ratios exceed 0.1, classification of those waste form would be regulated by the long-lived radionuclides in NRC 10CFR61 Table 1 and the formulated grouted waste form would meet the Class C requirements.

Comparing the maximum waste loadings with Class C limits provides confidence that compliant waste forms can be produced from the individual or combined waste streams with practical waste loadings. The Pu-239 limit for the combination of all the waste streams in a single grouted waste form occurs at 18% waste loading. This is a reasonable target, since waste loadings on the order of 20% are typical of grouted waste forms for similar waste streams [6]. Such a waste form would require about 660 kg of water (about 25% of the water in the waste streams) and 1320 kg dry mix to produce the grout, and would fill about ten 55-gallon drums to about 90% capacity. A slightly lower waste loading is recommended to accommodate possible processing upsets that result in higher fission product concentrations in the waste stream while remaining compliant.

Table 5. Results for Bounding Formulations of Grouted Waste Forms

Waste Stream	Titania/IX Column Wastes	$Ba/SrSO_4$ Solid Wastes	Combined Liquid Wastes[a]	Extraction Column Spent Washes	Concentration Column Spent Eluate	LMC Liquids	UREX Raffinate
			Waste Stream Composition				
Water (kg)	0	14.2	4416	624	1270	9.1	2516
Chemical Waste (kg)	0[b]	50.4	15.8	1.13	2.17	0.016	12.5
Fission Products (kg)	234	101	34.3	1.50	32.8	0.0033	0.006
Waste Solids (kg)	234	151	50.2	2.64	35.0	0.019	12.5
			Grouted Waste Form				
Maximum Waste Loading[c] (mass %)	23.40%	17.27%	9.89%	2.56%	10.75%	37.60%	15.84%
Limiting Nuclide	Pu-239	Pu-239	Pu-239	Pu-239	Pu-239	I-129	Pu-239
Waste Classification	C	C	C	C	C	C	C
Cs-137 Fraction of Activity Limit[d]	1.51×10^{-2}	6.40×10^{-4}	2.14×10^{-2}	4.26×10^{-2}	1.72×10^{-2}	2.24×10^{-2}	1.75×10^{-2}
Sr-90 Fraction of Activity Limit[d]	1.07×10^{-2}	4.62×10^{-4}	1.03×10^{-2}	2.06×10^{-2}	1.03×10^{-2}	1.08×10^{-2}	0
Tc-99 Fraction of Activity Limit[d]	2.00×10^{-3}	7.55×10^{-5}	2.16×10^{-3}	6.81×10^{-6}	1.59×10^{-6}	2.26×10^{-3}	5.66×10^{-7}
I-129 Fraction of Activity Limit[d]	3.47×10^{-4}	5.55×10^{-8}	1.91×10^{-7}	3.82×10^{-4}	1.63×10^{-6}	2.00×10^{-7}	6.06×10^{-6}
Minimum Mass GWF (kg)	999	873	507	103	324	0.05	79
Volume GWF, (m^3)	0.734	0.641	0.372	0.076	0.239	0.00004	0.058
Dry Mix (kg)	511	481	305	67	194	0.21	44
Water (kg)	255	241	152	34	96.8	0.011	22
Number of Drums[e]	3.92	3.43	1.99	0.40	1.28	0.0002	0.31

[a] Combined liquid waste combines spent washes, spent eluates, LMC liquids, and UREX raffinate waste streams.

[b] Mass of TiO_2 beads not included as waste.

[c] Maximum waste loading that meets NRC Class C limits.

[d] Calculated for inventory 180 days out-of-solution-vessel at limiting waste loading.

[e] Drums filled to 90% capacity.

4. Conclusions and Future Work

Laboratory tests are needed to formulate acceptable grouted waste forms made with these waste streams and other wastes added as aggregate, such as crushed glassware and titania and IX column materials. Optimization of the waste form should address performance requirements as well as waste minimization, such as resistance to leaching. A moderate laboratory testing project is recommended to (1) demonstrate the efficacy of grouting the combined SHINE waste streams, including organics, (2) determine appropriate grout formulations of OPC, slag, wastes, and water to meet fluidity requirements while minimizing residual free water, (3) evaluate interactions of the grout with crushed glass processing wastes to determine possible beneficial pozzolanic properties, (4) demonstrate adequate macro-encapsulation of large pieces of glassware other waste materials by the grout, and (5) demonstrate adequate physical and chemical durability (leach resistance) of grouted waste forms. The more realistic waste form formulations would allow for more accurate calculations of waste loading and total waste volumes and indicate the need for additional chemical treatment to retain soluble nuclides and RCRA-regulated constituents such as barium.

5. Acknowledgement

Work supported by the U.S. Department of Energy, National Nuclear Security Administration's (NNSA's) Office of Defense Nuclear Nonproliferation, under Contract DE-AC02-06CH11357. Argonne National Laboratory is operated for the U.S. Department of Energy by UChicago Argonne, LLC.

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