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A Technical Demonstration of the Initial Stage of Mo-99 Recovery from a Low Enriched Uranium Sulfate Solution

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ABSTRACT

In support of the commercialization of the SHINE Medical Technologies production process we report results confirming the technical viability of the initial stage of Mo-99 recovery from a Low Enriched Uranium (LEU) sulfate solution, a direct downscale demonstration of the proposed industrial separation process. From a flow sheet designed by Argonne National Laboratory we have undertaken the experimental validation at Los Alamos National Laboratory. This involved developing methodologies for the preparation/analysis of uranium sulfate fuel, safely containing the fuel during irradiation at a LANSCE facility dedicated to this process, and chemical flow sheet testing using a titania column. We observed near quantitative recovery of separated Mo-99 and uranium fuel products, the uranium recovery allowing for the possibility of fuel recycle. The feasibility of recycle has also been confirmed by re-irradiating the LEU fuel that has passed through the column separation process, and then once again separating out the fission generated Mo-99.

1. Introduction

Current chemical processing techniques for the recovery of Mo-99 from irradiated solid HEU or LEU targets start with a target dissolution process.[1] Both the aqueous homogenous reactor concept and accelerator-driven technology for Mo-99 production would utilize aqueous LEU fuels; the later system being developed by SHINE Medical Technologies Inc. There is the potential to recycle solution fuels if the Mo-99 can be recovered from the vast excess of irradiated uranium solution,[2] with titania based sorbents being proposed for efficient Mo-99 recovery from both uranyl sulfate and uranyl nitrate fuels.[2a,b] Previously we have shown that Mo-99 can be effectively recovered from both irradiated uranium nitrate and irradiated uranium sulfate solution,[3] with the higher radiolytic stability of sulfate *vs*. nitrate making it an attractive media for aqueous solution based LEU production of Mo-99.[2] The next step in process development is to confirm that high % Mo-99 recovery can be achieved

using a column separation process that more accurately reflects process conditions, a direct downscale of plant operation both in terms of volume of target fuel and (ultimately) Mo-99 activity levels. We report our recent work in our attempt to achieve this goal. This has included designing sample containment for up to 150 mL of solution, accessing a new capability for multiple irradiations at LANSCE (Los Alamos Neutron Science Center), the development of new chemical procedures and processes and the development of a semi-automated column separation apparatus that can ultimately be used in a hot cell. This work supported, and continues to support, the Department of Energy's National Nuclear Security Administration's Global Threat Reduction Initiative in their effort to realize large-scale non-HEU Mo-99 production in the US, and specifically the path to commercialization being pursued by SHINE.

2. Experimental Chemistry

A pH 1 stock solution of uranium (uranyl(VI)) sulfate fuel was prepared from an LEU uranium nitrate stock solution in nitric acid, the enrichment being 19.5 wt. % ^{235}U. For the preparation of the uranyl sulfate solution, aqueous uranium nitrate was heated to dryness multiple times, with the additional of H_2O and H_2SO_4. Raman spectroscopy was used to ensure that < 0.5 mole % nitrate (*vs.* uranium) remained in the sulfate solution by a technique that we described previously.[3] Depleted uranium standard solutions were used to determine the molar absorptivity (L mol^{-1} cm^{-1}) of the visible spectrum λ_{max} peak of uranium in 1 mol/L H_2SO_4.[4] This was used as the basis of the development of a simple assay technique for the analysis of the uranium sulfate fuel, and all column fractions that contained uranium. By this method we determined the uranium concentration of the initial fuel to be 0.63 mol/L, with the same concentration value determined by Davies-Gray titration.[5] For the first irradiation 150 mL of the prepared uranium sulfate stock was used. For the second and third irradiations the majority of the fuel came from the uranium solutions that had been previously irradiated and recovered from column separation of Mo-99. The experimental details for all three irradiations are given in Table 1. The main technique used to analyze the irradiated solution, and the separation chemistry solutions, was gamma spectroscopy. I-131 speciation measurements were made through solvent extraction into chloroform (iodine extraction) and chloroform containing excess natural iodine (iodide exchange and extraction), with the un-extractable fraction presumed to contain mainly iodate.

	1st Irradiation	2nd Irradiation	3rd Irradiation
Irradiation date	11th Dec. '12	9th Jan. '13	28th Jan. '13
Uranium conc. (mol/L)	0.63	0.65	0.64
Solution density (g/mL)	1.19	1.20	1.21
% recycle irradiated uranium	0 %	78 %	77 %
pH before irradiation	1.0	1.2	1.1
pH after irradiation	1.1	1.2	1.2
Mo-99 production (μCi)	1000	900	1100

Table 1. Experimental details for the three LEU irradiations at LANSCE.

3. Irradiated Sample Containment and Sample Irradiation Capability

During irradiation the uranyl sulfate fuel was contained in a stainless steel inner container fitted with a Swagelok valve. The stainless steel inner container was then sealed in a stainless steel outer container filled with 500 mL of water to provide neutron moderation and some fission energy absorption. The stainless steel outer and inner bottles provided two layers of containment and were pressure rated to well above the gas pressures predicted to be generated from radiolysis of water. Only high radiation resistance plastic components used (outer bottle O-ring and inner bottle valve packing). The sample in the inner container was degassed (freeze-pump-thaw) before irradiation to minimize background air gas and then placed under an Argon atmosphere (*ca.* 600 Torr). After irradiation, the headspace gas was expanded into an evacuated cylinder (500 cm^3) and stored to allow the volatile fission products to decay. The analysis of the water radiolysis gases, H_2 and O_2, by mass spectroscopy is currently in progress. Samples were irradiated at Target 4, Los Alamos Neutron Science Center (LANSCE) using neutrons produced through the bombardment of a tungsten carbide spallation target, with a thermal neutron flux of 10^9 n/(cm^2/s). This involved the development of a new irradiation capability, including the construction of a sample delivery and retrieval system.

4. Column Separation Process

A schematic of the column separation process is shown in Figure 1. The input parameters for the column separation experiments were provided by Argonne National Lab. These input parameters were designed to be a direct down-scale of SHINE's planned plant scale column operation and were obtained after running a VERSE (Versatile Reaction Separation) computational simulation based on Mo-99 batch and column separation data. The column would first be pre-equilibrated with a 0.1 mol/L H_2SO_4 wash before being loaded with the irradiated uranium solution, washed with 1 mol/L H_2SO_4 and finally water – all in an upward flow direction. Then the column would be stripped with base in the downward direction. The column bed was packed with Sachtopore TiO_2 sorbent (NP 110 µm particle size 60 Å pore size) which binds Mo(VI) in acidic solution, and is then striped of this species into basic solution.

The experimental operation of the column was very close to the stripping and loading conditions described in the downscale design, and this included operating at the designed flow rates for passing the solution through the column. The only two deviations from the down-scale input parameters were in irradiated uranium solution load volume, which was still kept within 5 mL of the optimized operating parameter, and the amount of water wash solution that was added. While 1.0 mol/L NH_4OH was considered as the base solution, the downscale process called for heating the column and inlet tubing to 80 ºC. To avoid the possibility of volatilizing ammonia, 0.1 mol/L NaOH was used as the base strip. This led to an increased volume of water being added in an attempt to wash more of the H_2SO_4 from the column. In addition, more 0.1 mol/L NaOH solution was required to neutralize the sulfuric acid still on the column than would have been the case for 1.0 mol/L NH_4OH.

The separation equipment was composed of the following general components: source and collection vessels, tubing, column, pumps, valves, heating tapes and a heating block. The feed solutions and strip solution (see Figure 1) were held in plastic bottles, typically Nalgene or Falcon tubes. From these source vessels, 1/8" OD PTFE tubing led to the piston pumps

(Eldex A-60-S) and 1/16" OD stainless steel (316) tubing led from the piston pumps to the column via valve heads. Valco multiposition microelectric valves were used at the top and bottom of the column; valves were actuated only when the direction of solution flow was changed. The YMC America column was packed with titania and connected to the stainless steel tubing using Swagelok quick connects.

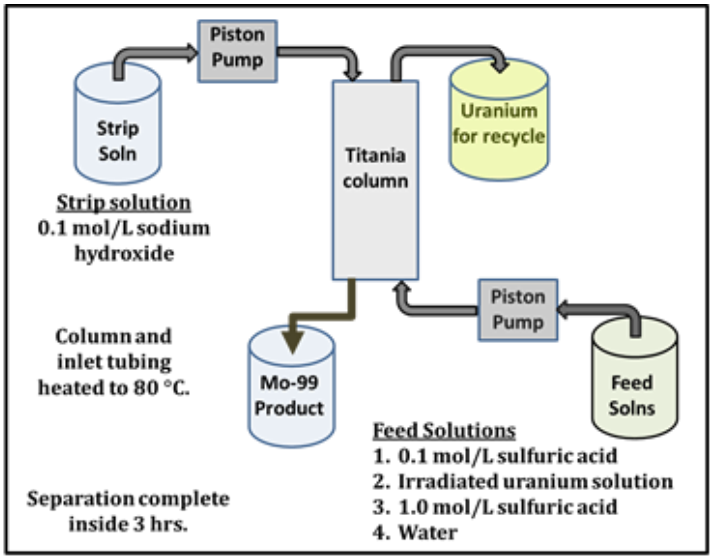

Figure 1. Schematic representation of the titania column process for Mo-99 recovery.

5. Column Separation Chemistry Results

In each sample irradiation *ca.* 1 mCi of Mo-99 was produced by end of beam and there were no major changes in solution pH after sample irradiation (Table 1). Once samples were taken for gamma spectroscopy, iodine speciation and uranium concentration measurements, the remaining irradiated uranium solution was used for the column separation experiments. The titania column separations were highly successful, with a high % recovery of Mo-99 in a low volume of basic (0.1 mol/L NaOH) solution for separation of the first and second irradiated solution (Table 2). While the 1st irradiated LEU solution contained only uranium that had previously been un-irradiated, the 2nd irradiated LEU solution contained all of the 1st irradiated solution that had previously been passed through a titania column. In turn, the 3rd irradiated solution contained all of the 2nd irradiated solution that had previously been passed through a titania column separation. At this extent of irradiation these results show that once the Mo-99 has been removed from the uranium sulfate fuel the fuel can be recycled to produce more Mo-99. The high volume of NaOH solution required to recover almost all the Mo-99 after the 3rd sample irradiation can be attributed to testing of the elution process for adaption of the separation procedure for hot cell operation.

Titania column separation	1st Irradiation	2nd Irradiation	3rd Irradiation
Volume of LEU sulfate feed (mL)	129	128	136
Volume of NaOH strip required for > 94 % Mo-99 recovery (mL)	9.3	9.7	22.3
Mo-99 activity balance (%)	97	102	95

Table 2. Summary of column separation results.

Most of the uranium passes straight through the column without binding, being collected in a large volume fraction (fraction 2, Figure 2). For Np-239, Ba-140, La-140, Ru-103 and Ce-143/141 similar behavior is observed, while a sizeable percentage of the Zr-95/97 and Te-132 remain irreversibly bound to the titania post-separation. These results are not surprising since the binding chemistry of many of these isotopes with titania was reported in our previous communication.[3] We also reported previously that I-131 had very complex chemical behavior, with the fission-produced iodine splitting between the acidic uranium and basic Mo-99 fractions, and with evidence of some I-131 irreversibly binding to titania (along with indirect binding through decay of bound Te-131m).[3] The column data reveals even more complex behavior, with a fraction of the iodine remaining with the uranium product, stripping with the 1 mol/L H_2SO_4, water and base fractions and sticking to the column. Of most significance is the I-131 that elutes with the Mo-99 product, where it will need to be removed through further Mo-99 product purification. Iodine speciation data analysis is still ongoing but preliminary analysis indicates that IO_3^-, I_2 and I^- are all present in the irradiated solution and that the ratios of each vary between each of the three irradiations. In addition, it would appear that I^- and I_2 are the dominant forms of iodine in the basic Mo-99 product. More detailed investigation of the Mo-99 product base fraction is ongoing to analyze for longer lived fission product contaminants such as trace Ru-103. In terms of radioisotope contaminants in the recycled uranium fuel, Ru-103, I-131, Ba-140, La-140 & Ce-143 had among the highest measured activities during the course of these experiments. During actual plant operation the dominant radioisotope activities will depend on a combination of the number of recycles and time elapsed between each recycle.

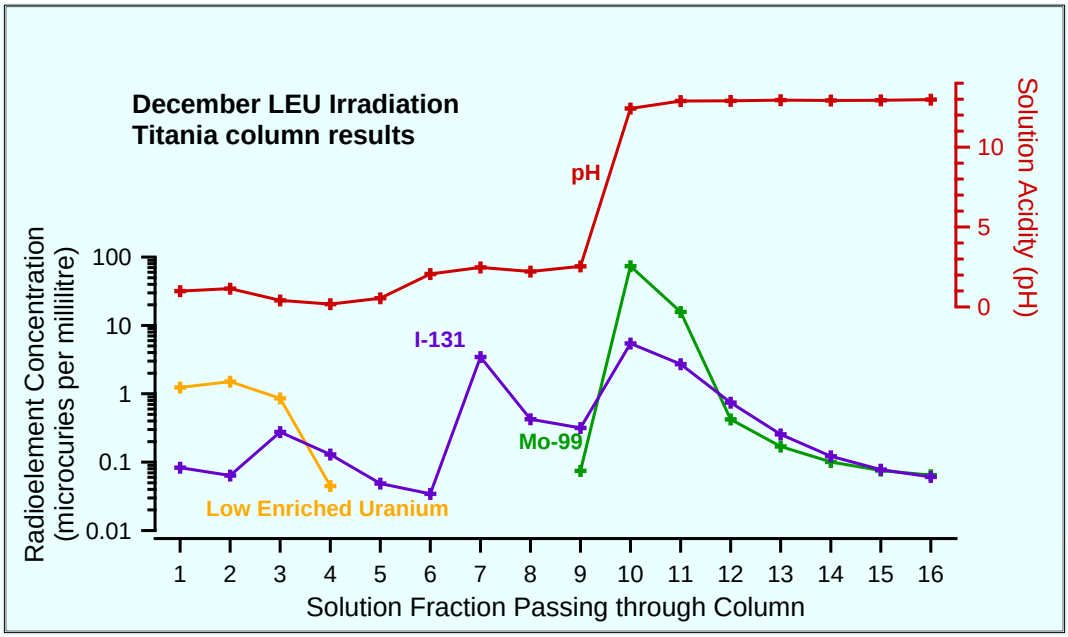

Figure 2. Column separation data for ^{99}Mo, ^{131}I & LEU. Radioelement concentrations werecalculated back to the time at the end of the column.

6. Conclusions

New sample containment methods, a new neutron irradiation capability at LANSCE and separation apparatus applicable to both fume hood and hot cell operation have been developed in support of domestic production of Mo-99. We have then applied these new capabilities to a technical demonstration of Mo-99 recovery from irradiated LEU sulfate solution using a titania column separation process. The separation chemistry results give strong evidence that plant scale recovery of Mo-99 can achieved in the chemical separation process favored by SHINE Medical Technologies. It also indicated that after titania recovery of Mo-99 the uranium fuel can be recycled to produce additional Mo-99.

7. References

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