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OVERVIEW OF ARGONNE PROGRESS RELATED TO IMPLEMENTATION OF MO-99 PRODUCTION BY USE OF A HOMOGENEOUS REACTOR

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ABSTRACT

The primary method for producing Mo-99 with a high-specific activity is irradiation of uranium targets. Uranium-235 in the targets undergoes fission, yielding ⁹⁹Mo among other fission products. The use of Aqueous Homogeneous Reactors (AHRs), or solution reactors, presents an attractive alternative to the conventional target irradiation method of producing ⁹⁹Mo in that solutions eliminate the need for targets and can operate at much lower power than required for a reactor irradiating targets to produce the same amount of ⁹⁹Mo. Babcock and Wilcox Technical Services Group is considering pursuing the Medical Isotope Production System (MIPS) as a means to produce Mo-99 commercially; Argonne researchers are assisting their analyses by (1) studying the aqueous chemistry of the MIPS under irradiation and Mo-recovery operations and (2) by developing a process for recovering Mo-99 from the irradiated fuel solution. Results thus far point to a high potential for the successful implementation of this technology.

1. Introduction

Technetium-99m (^{99m}Tc) is the most commonly used radioisotope in nuclear medicine. It is produced from the decay of its parent ⁹⁹Mo, which is sent to the hospital or clinic in the form of a generator. The primary method for producing ⁹⁹Mo is irradiation of uranium targets in a research or test reactor. Uranium-235 in the targets undergoes fission to yield ⁹⁹Mo among other fission products. The use of Aqueous Homogeneous Reactors (AHRs) or solution reactors presents an attractive alternative to the conventional target irradiation method of

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producing ^{99}Mo in that solutions eliminate the need for targets and can operate at much lower power than required for a reactor irradiating targets to produce the same amount of ^{99}Mo . As the name implies, solution reactors consist of an enriched uranium salt dissolved in water and acid and contained in shielded tank or vessel. Approximately 30 solution reactors have been built world-wide and operated over many years since the beginning of modern nuclear programs in the 1940s and 1950s. Most of these reactors are no longer in service; however, in the 1990s a renewed interest in solution reactors for the production of medical isotopes has prompted several countries, including the U.S., Russia, and China to initiate programs to assess the feasibility of utilizing AHR technology for medical isotope production applications on commercial basis.[1]

Because of (1) the low cost, small critical mass, inherent passive safety, and simplified fuel handling for the reactor and (2) the potential ease of recovering, processing, and purification of isotopes from the fuel, use of an AHR for the production of medical isotopes appears to be advantageous. These advantages stem partly from the fluid nature of the fuel and partly from the homogeneous mixture of the fuel and moderator in that an aqueous homogeneous reactor combines the attributes of liquid-fuel homogeneous reactors with those of water-moderated heterogeneous reactors.[1]

Babcock and Wilcox Technical Services Group is considering pursuing the Medical Isotope Production System (MIPS) as a means to produce Mo-99 commercially; Argonne researchers are assisting their analyses by (1) studying the aqueous chemistry of the MIPS under irradiation and Mo-recovery operations and (2) by developing a process for recovering Mo-99 from the irradiated fuel solution. Results thus far point to a high potential for the successful implementation of this technology. This paper presents an overview of the Argonne development activities and results during 2008. Individual papers also presented during this meeting will provide details of our results on predicting the stability of AHR fuel as pH and Eh vary due to radiolysis of nitrate and vessel corrosion,[2] radiolysis effects on the oxidation state of Mo and its recovery,[3] recovery of Mo from AHR fuel solutions using Termoxid sorbents,[4] and radiolysis effects on the composition and rate of gas generation in an aqueous homogeneous reactor.[5] Also presented are results on BET-surface-area and XRD analyses of two sorbents that have been the focus of our studies, Termoxid 5M and 52, which were developed for Mo recovery by the Termoxid Scientific and Production Company (Zarechnyi, Russia).

2. Results and Discussion

Stability of AHR Solutions as pH and Eh Vary Due to Radiolysis and Corrosion[2]

The composition of fuel solution for the MIPS design is a uranium concentration between 150 and 235 (as uranyl nitrate) at a pH of ~ 1 (0.1M HNO_3). Its operating temperature will be at about 85°C . The vessel could be either an iron or a zirconium alloy. Radiolysis of the nitrate solution will generate O_2 , H_2 , N_2 , and NO_x . Radiolysis of nitrate will have two effects on the fuel solution: (1) increase its pH and (2) change its redox potential (Eh). Radiolysis of water and, perhaps, nitrate will generate peroxide ion in solution, which will effect the Eh of the solution and, if in sufficient steady-state concentration and at high enough pH, lead to precipitation of uranyl peroxide. Corrosion of metals will also lead to an increase of pH in the fuel solution.

To get a handle on the effects of pH and Eh variation on the oxidation states of major species and what compounds may be unstable to precipitation, thermodynamic models were implemented using the codes OLI ESP Stream Analyzer (OLI-SA) and “The Geochemist’s Workbench®” Release 3.0 (GWB). Thermodynamic modeling has identified four processes that could adversely affect Mo-99 production from a uranyl-nitrate AHR if they are not controlled or counteracted during reactor operation and molybdenum separations:

- Fission product anions such as TcO_4^- , IO_3^- , I^- , Br^- , HSeO_4^- and SeO_4^{2-} , that accumulate during burn-up may compete with HMoO_4^- or MoO_4^{2-} on anion exchanges, thus lowering molybdenum separation efficiency and influence subsequent product-purification processes.
- The loss of nitrate from the solution due to radiolysis and the corrosion of iron-bearing vessel components could cause the pH of the reactor solution to increase to a value at which uranyl oxide hydrate precipitates.
- The reactor solution could also become saturated with respect to uranyl molybdate at pH values as low as 1 depending on the solubility of this mineral, which is currently unknown.
- If the steady-state concentration of hydrogen peroxide in the reactor reaches values near 1×10^{-3} M, the uranyl-peroxide mineral studtite ($\text{UO}_2\text{O}_2 \cdot 4\text{H}_2\text{O}$) could precipitate at pH values less than 1. However, if the steady-state concentration of hydrogen peroxide is 1×10^{-6} M or lower, then the solution is predicted to become saturated with respect of uranyl peroxide at a pH value of around 2.

It should be noted that the results presented are based on theoretical modeling and, therefore, require further experimental study (especially studies accounting for kinetics and thermal effects) before they should be considered significant issues. They should only be looked at as guides to prioritizing experimental work.

Radiolysis Effects on the Oxidation State of Mo and its Recovery[3]

During reactor operation and after, the beta/gamma radiation from fission products will provide a significant dose rate to the fuel solution of an AHR that could reduce Mo(VI) to lower oxidation states. This study was initiated to quantify the effects and eventually to develop means to control the Mo(VI) oxidation state without poisoning the recycled fuel solution. Both batch and mini-column experiments were performed to show the effects of radiation on molybdenum sorption on anion exchangers. A 3 MeV electron Van de Graaff was used to irradiate solutions and columns. Several conclusions were reached in our as-yet limited studies: (1) radiation does act to reduce Mo to lower oxidation states and, therefore effect Mo yield; (2) nitrate media are more effective at maintaining Mo in the (VI) oxidation state than are sulfate media; and (3) Termoxid sorbents (and likely all anionic exchangers) are more effective for recovery of Mo(VI) from nitrate media than sulfate media. Further studies are planned to quantitate this effect in terms of actual MIPS operation.

Recovery of Mo from AHR Fuel Solutions Using Termoxid Sorbents[4]

For production of Mo-99, an AHR will operate for 3-7 days; the subcritical fuel will be allowed to decay in a cool-down period of 4-12 hours, then Mo-99 will be separated from the fuel solution using anion exchange. Alumina is typically used for the recovery of Mo(VI) from acid-dissolved targets, but the high concentrations of uranium in the LEU fuel make its use

impractical. Termoxid developed two sorbents T-52 (25 mole % SnO₂ and 75 mole % TiO₂) and T-5M (5 mole % ZrO₂ and 95 mole % TiO₂) that both show superior adsorption of ⁹⁹Mo from concentrated UO₂(NO₃)₂ solutions.

The ability of T-52 and T-5M to adsorb ⁹⁹Mo from solutions containing increasing concentrations of uranium under static and dynamic conditions was investigated. Additionally, the sorbents' resistance to irradiation and contact with several different solutions has been examined. Four different batches of each sorbent were obtained to determine the disparities among the batches. The data we are collecting on the sorption behaviors of T-52 and T-5M will be used to design a column for the efficient recovery of ⁹⁹Mo from an aqueous homogeneous reactor solution containing LEU. The MIPS fuel solution will likely have a concentration of uranyl nitrate in the range of 150-235 g-U/L and pH 1. Batch studies using T-52 and T-5M have been performed as a function of temperature, time, and uranium concentration. Static capacity for molybdenum has been determined by varying the molybdenum concentration. The ability of the sorbents to withstand chemical conditions expected in the Mo-recovery operation without decomposition or significant changes in Mo(VI) adsorption behavior has been investigated. Results have provided insight for the design of a column with optimal features for the recovery and purification of ⁹⁹Mo.

Overall, T-52 shows superior uptake of Mo(VI) from an AHR solution containing high concentrations of uranium-185-285 g-U/L. At higher temperatures (55 and 85°C), T-52 adsorbs Mo(VI) 30% (55°C) and 50% (85°C) better than T-5M. In addition, both sorbents have a higher capacity for Mo in the temperature range of 55-85°C (0.55 meq/g) than at 25°C (0.25 meq/g). Both sorbents would be usable to recover ⁹⁹Mo from an AHR fuel solution. Future work will optimize the recovery operation and design the full-scale recovery column.

Radiolysis Effects on the Composition and Rate of Gas Generation in an AHR[5]

The first solution reactors earned the name "water-boilers" because of the observed bubbling or frothing that result from the radiolytic decomposition of water by fission fragments and subsequent evolution of radiolytic gases (H₂ and O₂). Because nitrate ion also undergoes radiolytic decomposition, uranyl-nitrate-based AHRs will also generate N₂ and NO_x in the off gas. The radiolytic decomposition of nitrate ion will also have the effect of increasing the pH of the fuel solution. The rate and composition of the radiolytic gas generation is of practical importance for the design and operation of AHR for two reasons. First, the design of the reactor off-gas system depends on the generation rate and the composition of the gas stream. Second, an increase of the fuel-solution pH can lead to the formation of the precipitates.

The aim of this project is to obtain reliable data for radiolytic gas formation in model nitrate solution. We are using 3 MeV-electron Van de Graaff to irradiate the solutions. To evaluate radiation-induced gas formation in acidic solution of nitrates, we designed an experimental setup that can accommodate the high dose rates required to simulate AHR operation. The gaseous products of radiolysis will be analyzed using a SRI 8610 gas chromatograph with a high-sensitivity TCD (thermal-conductivity detector). For O₂, N₂, and NO_x, helium is used as a carrier gas, while Ar is used for the detection of the H₂. Total gas evolution will be measured via a monometer directly attached to the glass tube during the radiation. We will initially evaluate radiolytic gas formation in a NaNO₃ solution containing HNO₃, measuring the dependence of the

composition and rate of gas formation on the concentration of the nitrate and pH of the solution. Once we are confident in our methods and apparatus, we plan to repeat similar experiments for uranyl nitrate solutions. The end result of this research will be recommendations for pH control measures and design of the off-gas system for a nitrate-based AHR. However, before final design is initiated, the results of this study will need to be validated by irradiation of actual LEU nitrate solution in a neutron flux, where fission particles will have a strong influence on the radiolysis of water and nitrate.

BET and XRD Analyses of the Termoxid Sorbents

Several batches of Termoxid 5M and 52 were examined using surface-area determination and x-ray diffraction (XRD). The objective was to determine if differences in sorption behavior between batches purchased in 2002 and in 2008 could be explained by physical differences. Termoxid-52 specimens from 2002 were labeled as Radsorb lot 2002-002, Radsorb lot 6, Radsorb lot 4, and Termoxid-52M. Isosorb lot 5, Isosorb lot 2002-001, Termoxid-5M are all are Termoxid 5M. Batches purchased in 2008 are labeled T5M-1, T5M-2, T5M-3, T5M-4, T52-1, T52-2, T52-3, and T52-4. The particle size distribution of Radsorb lot 5 and Isosorb lot 6 were 0.2-0.4 mm; all the other sorbent lots were 0.4-1 mm.

Surface area measurements were obtained by adsorption isotherm measurements using the method of Brunauer, Emmett, and Teller (BET).[6] The BET analysis used nitrogen (N₂) as the adsorbed gas, with 5-point isotherms fitted to the form:

$$\frac{P}{P_0} = a + b \left[V_A \left(\frac{P_0}{P} - 1 \right) \right]^{-1},$$

where P/P_0 is the relative pressure, and V_A is the volume of N₂ adsorbed (at STP), and the parameters a and b are related to adsorption energy and monolayer surface area. All fits had a linear correlation coefficient of better than 99.9%. The measured values appear in Table 1. Also appearing in Table 1 are determinations of geometric surface area obtained by electron microscopy.[7] Note that the BET surface area exceeds the geometric surface area (the apparent surface area of the roughly spherical particles) by $\sim 5\frac{1}{2}$ orders of magnitude. Such large BET surface areas are characteristic of nanostructured materials, such as those used in catalysis or for chemical separations.

X-ray diffraction (XRD) was measured using the K α line of copper (wavelength of 0.1381 nm) in a diffractometer. In order to obtain proper instrument resolution of the diffraction lines, the samples had to be crushed to a fine powder so that they could be evenly dispersed on the diffractometer sample plate. Measurements were made on the as-received (crushed) material, and in some cases on material that had been degassed under vacuum at 150°C during the BET measurements. The observed diffraction patterns did not match known structures in the JCPDS-ICDD (Joint Committee on Powder Diffraction Standards, International Center for Diffraction Data) database. No further attempt was made to solve the crystal structure, since the object of the present study is to identify possible variations in the material among batches. As Figure 1 illustrates, the data indicate remarkable reproducibility among the sorbent types.

The XRD data for both the T5M- and T52-type specimens showed significant diffraction peak broadening (characteristic of small scattering domain sizes) and pronounced small-angle scattering (characteristic of large density fluctuations). The XRD peak widths of both sorbent types indicate crystal domain sizes of between 9 and 11 nm. The pronounced small-angle scattering ($2\theta < \sim 2^\circ$) is characteristic of material having large density fluctuations at the nanometer scale; i.e., the 9-11 nm crystal domains are likely also distinct nanoparticles consolidated into the larger spherical particles. Unfortunately, the diffractometer employed for the XRD measurements was not designed for quantitative analysis of small-angle scattering.

Table 1. BET surface area determination of sorbents.

Sample	Type	BET surface area (m ² /g)	Projected area per particle, (cm ²)*	Geometric surface area (m ² /g)*	BET/Geometric surface area
Radsorb lot 2002-002	T52	92			
Radsorb lot 6	T52	90			
Radsorb lot 4	T52	85			
Termoxid-52M	T52	96	0.0043	0.0021	45700
T52-1	T52	90			
T52-2	T52	100			
T52-3	T52	85			
T52-4	T52	88			
Isosorb lot 5	T5M	141			
Isosorb lot 2002-001	T5M	154			
Termoxid-5M	T5M	152	0.0036	0.0023	66500
T5M-1	T5M	142			
T5M-2	T5M	140			
T5M-3	T5M	147			
T5M-4	T5M	143			

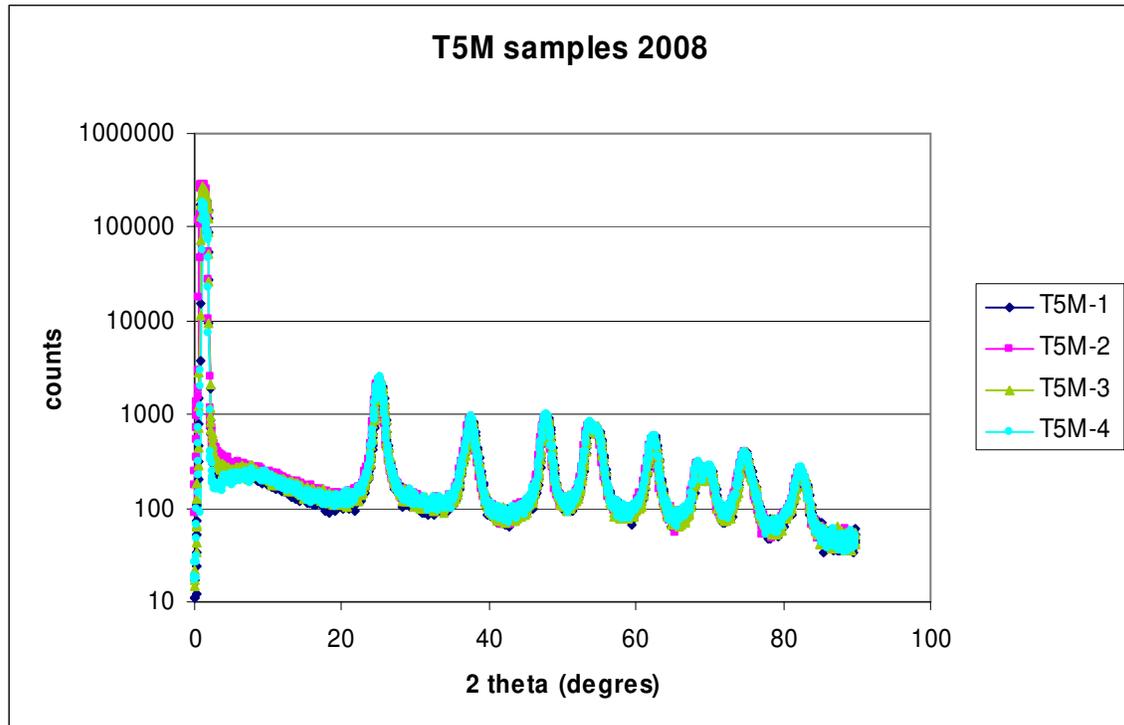
* Based upon data provided in reference [7].

Prior to measuring BET surface area, it was necessary to de-gas the sorbent material under vacuum at elevated temperature (150°C). The vacuum heat treatment in each case caused a visual darkening of the material from amber (T52 type) or light yellow (T5M type) to a dark brown appearance. Exposure to air after the measurements returned the samples to their original color within a few hours.

3. Conclusions

Argonne has been performing research in several areas required to develop the MIPS for ⁹⁹Mo. Primary objectives are to (1) understand the solution chemistry of nitrate-based AHRs during irradiation and ⁹⁹Mo recovery, (2) collect data necessary to optimize molybdenum recovery and

design the plant-scale molybdenum-recovery system, and (3) collect data necessary to design the off-gas system. The work presented is preliminary and ongoing. Our results-to-date are helping to prioritize future development activities and show no show-stoppers and point to a high potential for the successful implementation of this technology.



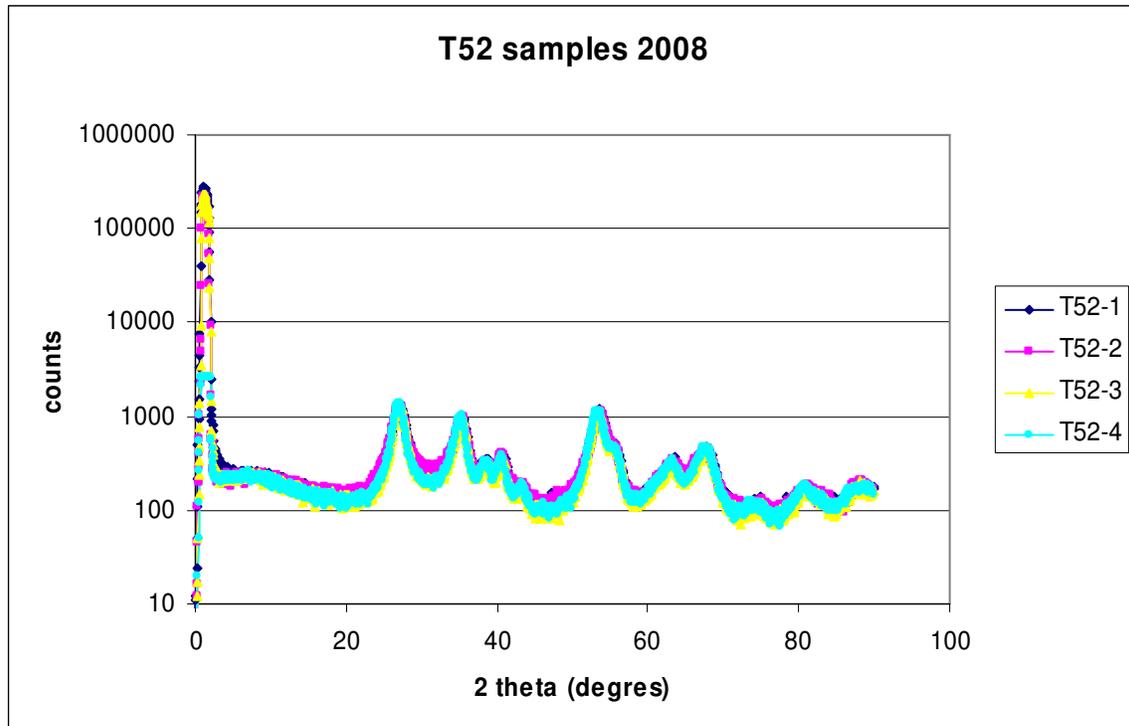


Figure 1. Measured XRD for T5M-type (above) and T52-type (below) sorbent materials from the batches received in 2008. Note the logarithmic intensity scale. Note the relatively broad diffraction peaks (FWHM of $\sim 0.9^\circ$ 2-theta) and the copious scattering at 2-theta $< 2^\circ$. These diffraction patterns do not differ in any significant way from those reported previously on older batches.

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