DEVELOPING TECHNIQUES FOR SMALL SCALE INDIGENOUS MOLYBDENUM-99 PRODUCTION USING LEU FISSION AT TAJOURA RESEARCH CENTER-LIBYA

Chief Investigator: Sami M. Alwaer
Tajoura Nuclear Research Center (TNRC)
P.O. Box: 30878, Tripoli – Libya
samiwaer@yahoo.com

1. INTRODUCTION

The object of this work was to assist the IAEA by providing the Libyan country report about the Coordination Research Project (CRP), on the subject of “Developing techniques for small scale indigenous Mo-99 production using LEU-foil” which took place over five years and four RCMs. A CRP on this subject was approved in early 2005. The objectives of this CRP are to: transfer know-how in the area of $^{99}$Mo production using LEU targets based on reference technologies from leading laboratories in the field to the participating laboratories in the CRP; develop national work plans based on various stages of technical development and objectives in this field; establish the procedures and protocols to be employed, including quality control and assurance procedures; establish the coordinated activities and programme for preparation, irradiation, and processing of LEU targets [a]; and to compare results obtained in the implementation of the technique in order to provide follow up advice and assistance.

Technetium-99m ($^{99m}$Tc), the daughter product of molybdenum-99 ($^{99}$Mo), is the most commonly utilized medical radioisotope in the world, used for approximately 20-25 million medical diagnostic procedures annually, comprising some 80% of all diagnostic nuclear medicine procedures [1,2]. National and international efforts are underway to shift the production of medical isotopes from highly enriched uranium (HEU) to low enriched uranium (LEU) targets [3]. A small but growing amount of the current global $^{99}$Mo production is derived from the irradiation of LEU targets. The IAEA became aware of the interest of a number of developing Member States that are seeking to become small scale, indigenous producers of $^{99}$Mo to meet local nuclear medicine requirements. The IAEA initiated Coordinated Research Project (CRP) T.1.20.18 “Developing techniques for small-scale indigenous production of Mo-99 using LEU or neutron activation” in order to assist countries in this field [4]. The more significant world crises are related to the availability of the $^{99}$Mo/$^{99m}$Tc generator, because of its extensive use and the short half life precluding significant anticipation [5].

1.1. BRIEF HISTORY

In July 2005, a consultancy was held to review and recommend for selection proposals for research contracts and agreements. These proposals were evaluated, submitted for approval to the Research Contracts Meeting in September 2005, and approved. Subsequently, the first Research Coordination Meeting (RCM) was held 6-9 December, 2005 in Vienna, Austria, the second RCM was held 16-20 April, 2007 in Bucharest, Romania, the third RCM was held 13-16 October, 2008 in University of Missouri Research Reactor (MURR) Columbia, Missouri, USA, and the final RCM was held 12-16 December, 2011 in Austria, Vienna.
Additionally, two workshops were held in 2006 related to the CRP:

a) LEU Foil Target Fabrication, Irradiation, and Chemical Processing Using the LEU-Modified Cintichem Technique, National Atomic Energy Agency of Indonesia (BATAN), Serpong, Indonesia, 6-11 March 2006.

b) Operational Aspects of \(^{99}\)Mo Production, IAEA Headquarters, Vienna, Austria, 28 November-1 December 2006.

Two papers have been published on this work; the first about the feasibility study of “Thermal Hydraulic Analysis of LEU Target for \(^{99}\)Mo Production in Tajoura Reactor” [6] and the second “Feasibility Study of the Theoretical Calculations of Fission \(^{99}\)Mo Production by the Irradiation of LEU Metallic Uranium Foil at Tajoura Research Reactor” [7].

Tajoura Nuclear Research Center (TNRC), Libya, has been implementing the technology for \(^{99}\)Mo isotope production using LEU-foil targets, (this target is made of an LEU metallic uranium foil inserted between two concentric aluminium cylinders), to obtain new revenue streams for the TNR-reactor and desiring to serve the Libyan hospitals by providing the medical radioisotopes. Korean target will be used in this work which will be irradiated for 72 hours in the reactor core at flux equal to 1.0 \times 10^{14} \text{N/Cm}^2.\text{S}. The target will stay 10 hrs. in the reactor pool for cooling before disassembling it inside a hot cell located in the reactor building. The LEU-foil will be transferred to chemical hot cell pneumatically. A special set up has been designed for the processing of the LEU-foil. The set up consists of the dissolver with controlled pressure, nitric acid will be used for dissolution, cold trap cooled in liquid nitrogen for removing the fission gases, precipitation of \(^{99}\)Mo by fresh 2\% alpha-benzoin oxime will be done and purification of the final product by using two chromatographic columns. The first one contains AgC (carbon coated with silver nitrate) and the second one is a combined column with C, HZO-1 (hydro zirconium oxide) and AgC. The final product of \(^{99}\)Mo solution will be filtered with 0.22 μm filter. The final radioactivity of \(^{99}\)Mo is expected to be >150 Ci and 95\% purity.

2. TAJOURA NUCLEAR RESEARCH CENTER (TNRC)

Tajoura Reactor is a pool type reactor, moderated and cooled by light water located at the Tajoura Nuclear Research Center (TNRC). The reactor was designated to carry out experiments in the fields of nuclear physics and nuclear engineering, neutron activation analysis, solid state physics and isotope production. The reactor was put into operation at a power level of 10 MW in September 1983. [8] The reactor was completely converted to low enriched uranium (LEU, 19.7\% of \(^{235}\)U) fuel. Tajoura Reactor has 44 vertical irradiation channels (6 in the 8TFA fuel assemblies, 9 in removable Beryllium reflector units, 19 VCR in the stationary reflector blocks, and 10 VCV in reactor core Al vessel). Fig. 1 shows the Tajoura core horizontal cross section. Type IRT-4M at the end of 2006; the new fuel is an alloy (matrix) of aluminum and uranium-dioxide (\text{UO}_2–\text{Al}) with aluminum cladding.
3. EXPERIMENTAL

3.1. ANNULAR TARGET ASSEMBLY INSTRUCTIONS [9]

3.1.1. Prepare the Target Tubes

Machine the inner and outer tubes to the dimensions identified. Clean-off machining fluids from tubes using standard machine shop method.

3.1.2. Obtain dimensions of the inner and outer tubes prior to assembly

a. Measure and record the I.D. and O.D. of the inner tube.
b. Measure and record the I.D. of the outer tube.

3.1.3. Clean the tubes, use powder-free latex gloves to handle the tubes to prevent particulate contamination of the weld faying surfaces

3.1.4. Place in ultrasonic cleaner containing a solution of detergent for ~10 minutes at ~90°C, thoroughly rinse tubes in running water.

3.1.5. Bright Dip consists of 90 vol% concentrated H₃PO₄/5 vol% H₂SO₄/5vol% HNO₃, thoroughly rinse tubes in running water.

3.1.6. Hot-air dry tubes for at least ten minutes at ~125°C using a heat gun (Fig. 2).
4. Prepare the Uranium Foil for Annular Target Assembly

4.1. Two ready targets have been prepared with LEU-foils with different sizes. Table. 1. shows the measurements for LEU foils.

<table>
<thead>
<tr>
<th>No. of Foil</th>
<th>Width (mm)</th>
<th>Length (mm)</th>
<th>Thickness (micron)</th>
<th>Av. Thickness (micron)</th>
<th>Weight (g)</th>
<th>Weight (235U)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>44.1</td>
<td>76</td>
<td>154 142 159</td>
<td>152</td>
<td>8.20</td>
<td>1.63</td>
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<td>124 156 105</td>
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<td>176 162 176</td>
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<tr>
<td>2</td>
<td>44.2</td>
<td>76</td>
<td>169 180 126</td>
<td>158</td>
<td>8.41</td>
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<td></td>
<td></td>
<td></td>
<td>155 122 166</td>
<td>148</td>
</tr>
</tbody>
</table>

4.2. Envelope the uranium foil with the pre-cut nickel-foil fission recoil barrier (Fig. 3).

5. Annular Target Assembly
5.1. Coat the inside of the inner tube with “dry graphite”. This will act as a lubricant for the draw plug and prevent the inner tube from galling when drawing the inner/outer tubes together.

5.2. Clean the outer surface of inner tube ends to remove any excess graphite lubricant using a lint-free cloth moist with acetone.

5.3. Make a longitudinal permanent marker/SCRIBE mark on the outer tube to identify foil gap position. Wrap the uranium/nickel foil around the inner tube, slide the inner tube into the outer tube and ensure that the foil gap is lined up with the scribed mark on the outer tube (Fig. 4).

5.4. Electron Beam (EB) weld target ends and helium leak test the assembled target (Fig. 5).

5.5. Fig. 6 shows the LEU target horizontal, vertical cross sections, and dimensions [10].
6. Target Irradiation

Ready target will be irradiated in the reactor for 72 h. at a flux equal to 1.0 \times 10^{14} \text{n/cm}^2\cdot\text{s}, and a special rig has been made to handle the target during the irradiation. Fig. 7. shows a small rig suitable for the LEU target and suitable for the reactor system.

7. Disassembling the LEU target

7.1. After irradiation, the target will be cooled in the reactor pool for 10 h. then the target will be transferred to a hot cell in the reactor building. Finally the target will be transferred to another
hot cell which is just near to the first one where the target will be disassembled by using a special cutter (Fig. 8).

![FIG. 8. LEU target cutter.](image)

7.2. A special tool has been made to determine the edges of the LEU target during the disassembly; another particular piece was manufactured for the purpose of the expansion of the shear longitudinal tube, Fig. 9 & 10 respectively [11].

![FIG. 9. Determine the Edges.](image)

![FIG. 10. Expansion.](image)

8. LEU-foil processing

8.1. Calculate the concentration of nitric acid needed for 40 ml of dissolver solution. This calculation is based on the grams of total uranium and grams of nickel fission barrier for the target to be processed [12].

\[
\begin{align*}
\text{Ni} + 8/3\text{HNO}_3 & \rightarrow \text{Ni(NO}_3)_2 + 4/3 \text{H}_2\text{O} + 2/3 \text{NO} \\
\text{U} + 4 \text{HNO}_3 & \rightarrow \text{UO}_2(\text{NO}_3)_2 + 2 \text{H}_2\text{O} + 2\text{NO}
\end{align*}
\]

8.2. Transfer the foil into the dissolver, and verify it is sitting directly on the bottom (use pushing tool if necessary).

8.3. Attach the dissolver to the vacuum pump (using the septum), open the valve between the septum and the dissolver, and evacuate the air from the dissolver (Fig. 11).
8.4. Use a syringe to inject 40 ml of dissolver solution (HNO₃), which will be added to the dissolver through the dissolver septum. Heat the dissolver by using the heat gun (Fig. 12).

8.5. When the dissolution will be completed, stop heating, allow dissolver to cool for 10 minutes and connect it to the cold finger. A special electric machine has been made and used for connecting the dissolver to the cold finger (Fig. 13).

8.6. By a special crane inside the hot cell the connected dissolver and cold finger have been handled up and transferred to a special stand. Insert the cold finger into the LN-Dewar, and liquid nitrogen flows to the Dewar (Fig. 14). Allow the pressure to stabilize, and then slowly open the cold-finger and dissolver valves. Keep the cold finger in the liquid nitrogen and
allow it to draw off the gas phase for 30 minutes. Close all valves and disconnect the dissolver from the cold finger by the same machine described in Fig. 14. The vacuum inside the dissolver should be measured with a pressure/vacuum gauge.

8.7. Set the dissolver upright and vent it through a hypodermic needle. Invert the dissolver and fix it in its place in the setup, and drain the solution into an evacuated double-ended bottle labeled “Raw Fission No. 1” through a 2-way “Luer-Lok” valve (Fig. 15). Inject 25 ml of 1M HNO$_3$ into the dissolver and agitate it with the manipulators, making sure the acid solution wets the entire inner surface of the dissolver. Drain the rinse solution from the dissolver into the “Raw Fission” bottle.

8.8. Add NaI carrier, 10% AgNO$_3$ in 0.1M HNO$_3$, shake, a white precipitate should form. Add 1.0 M HCl – additional precipitate should form and then add Mo carrier.

8.9. A sample of ~0.5 ml should be collected to measure the $^{99}$Mo content of the sample for calculating the process yield.

8.10. Pass the solution through 0.3µm and 0.2µm filter assembly into another bottle (Fig. 16).
8.11. Add 2.5% KMnO₄ solution slowly to the raw fission liquor until a deep pink color holds for ~30 seconds. Add 1.5 mL of Rh carrier to the raw fission liquor, and shake. Add Ru carrier and shake. Add fresh 2% alpha-benzoin oxime in 0.4M NaOH to the raw fission liquor, shake well. Wait about one minute. A white, flocculent precipitate should form.

8.12. Filter the precipitate through a 51-mm fritted-glass column. Make sure all liquid has been drained from the column. Wash the precipitate in the column five times with 10 ml of 0.1M HNO₃, shaking the column well after each wash has been injected. Drain these washes into the “Acid Wash” bottle (Fig. 17).

8.13. For dissolving the precipitate, inject 0.4M NaOH sol. with ~1% H₂O₂ into the column, vent through a charcoal filter. Heat the column that contains the solution with forced hot air until the solution begins to boil, drain the dissolved precipitate into a bottle.

8.14. Pass the dissolved precipitate through the AgC column. Gravity controlled flow through the column allows a flow rate of 1 - 3 ml/minute. Rinse the Ag/C column with 0.2M NaOH (Fig. 18). The solution should appear clear and colorless. Add NaI carrier to the bottle and add 10% AgNO₃ in 0.1M HNO₃ solution to the bottle. Shake well, and wait ~5 minutes.

8.15. The slurry in the bottle is fed to the AgC/ZrO/AC combination column. Gravity will allow a flow rate of 1 -3 ml/minute.
8.16. Using a one mL syringe, remove ~0.5-mL sample from the bottle and introduce it through the septum into the QC sample vial.

8.17. Pass product solution through the .02 µm filter into the final product bottle (Fig. 19).

8.18. All the steps that have been explained above in this work combined in one setup as shown in Fig. 20.

FIG. 18 Ag/C column or AgC/ZrO/AC combination column.

FIG. 19 Filtration of the final product solution through 0.02 µm filter.

FIG. 20 Combined setup for $^{99}$Mo production

CONCLUSIONS

This paper briefly presents the major activities on production of a fission $^{99}$Mo by LEU-foil target as new scientific achievements in TNRC. A special combined setup has been designed for all the chemical processes.
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REFERENCES

3. The 26th Annual Radiology Conference was arranged in Karachi on 29th – 31st October, 2010 at Sheraton Hotel Karachi.
7. The 6th International Conference on Isotopes, held in Sheraton Grande Walkerhill Hotel, Seoul, Korea from May 12 to 16, 2008.