

REPORT ON THE PARTICIPATION OF POLAND IN THE CRP ON "SMALL-SCALE INDIGENOUS PRODUCTION OF MO-99 USING LEU TARGETS OR NEUTRON ACTIVATION"

1. INTRODUCTION

Technetium-99m (^{99m}Tc), the daughter of molybdenum-99 (^{99}Mo) is the most commonly used radioisotope in nuclear medicine. Nearly all of the ^{99}Mo used is produced by the fission of ^{235}U in high enriched uranium targets (HEU), generally 93% ^{235}U . The replacement of low enriched uranium (LEU) targets for HEU targets requires many modifications in target fabrication and its chemical processing to efficiently separate ^{99}Mo .

The aim of presented work were studies on the fabrication process of LEU foil target for irradiation in reactor, its disassembly, chemical dissolution and final ^{99}Mo separation.

2. FABRICATION OF URANIUM TARGET FOR IRRADIATION

The uranium metal target for fission ^{99}Mo production consists of a thin LEU metal foil (150 μm) wrapped in a nickel foil (15 μm) encapsulated between two thin-walled, coaxial tubes made of Al 3003 alloy. The nickel foil serves as a recoil barrier and prevents the uranium foil from bonding with aluminum tubes.

As an alternative method for fission fragment absorbing barrier in LEU foil target, the plating of nickel on uranium surface was applied. An assumption was made, that if the Ni plating quality would assure good tightness, sufficient thickness and adherence to the uranium foil, it could considerably simplify the procedure of target assembly and as a consequence eliminate the trouble of sandwiching the foils.

In order to optimize the parameters and conditions of the process of uranium target assembly and disassembly, initial experiments were performed using dummy targets containing copper foil instead of the uranium foil. Finally, a uranium target containing NU foil was fabricated.

2.1. ASSEMBLY OF URANIUM TARGET

Assembly of the uranium target is a multistage process and requires application of several different devices. All devices necessary for the fabrication LEU target were designed, constructed and tested.

The following steps were applied for fabricating dummy target:

2.1.1. Preparation of components for target manufacturing

The Al tubes were cut to the length of 162 ± 0.1 mm. For the further marking of the gap, where the LEU foil would be placed, on the external surface of the outer tube, a longitudinal line was drawn. The surface of the inner Al tube was machined in order to obtain the required diameter and afterwards superfinished to achieve roughness around 0.04 μm . In order to prevent the uranium foil slipping during target assembly, in the inner tube a groove was made. The performed investigation showed that the groove depth should be the following:

$$LEU \text{ foil thickness} + 2 \times Ni \text{ foil thickness} - 0.013 \pm 0.007 \text{ mm}$$

while the width of this groove should be the following:

$$LEU \text{ foil wide} + 6 \text{ mm}$$

After machining, the Al tubes were cleaned and degreased according to following procedure:

- cleaning with surface-active agent,
- multiple rinsing in warm water,
- drying at room temperature,
- degreasing in 10 % NaOH solution (30 s)
- multiple rinsing in cold water,
- multiple rinsing in warm water,
- rinsing in distilled water,
- drying in the electrical dryer,
- holding at the temperature of 80°C under lowered pressure.

2.1.2. Dummy target assembling

For assembling Ni+Cu+Ni foil liner, the cooper foil was wrapped in nickel foil as shown in Fig.1. No rubber glue was used for sticking Ni-Cu foils.

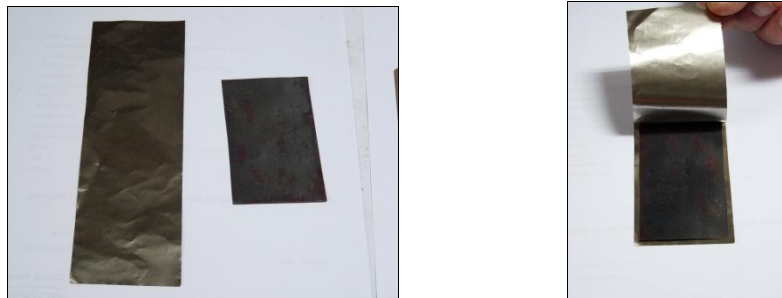


FIG. 1. Assembly of the Ni+Cu+Ni foil liner.

In order to facilitate insertion of the foil liner between Al tubes, above foil liner was first profiled by the use of special rolled section mounted in the turning lathe (Fig. 2). As a result of this process, the sandwiched liner gained the shape of an opened sleeve (Fig. 3).



FIG. 2. Preliminary profiling of liner after profiling foils.



FIG. 3. Ni+Cu+Ni foil liner.

The sandwiched liner prepared in such a way was loaded between two concentric aluminum tubes. As a slipping agent ethanol was applied. The gap between outer and inner Al tube was 150 μm . The assembled dummy target is shown in Fig. 4. This element was stored at the temperature of 80°C under lowered pressure.



FIG. 4. Assembly of the dummy target.

The next step in dummy target manufacturing was drawing of the assembled Al tubes in order to obtain junction of both Al tubes by increasing the diameter of inner tube using the stamp method. Performing this process assured obtaining a rigid position of the copper foil between the concentric tubes. The die drawing of the annular target was conducted using specially constructed equipment, consisting of two hardened steel tubes and a pilot on which dies with a varied outer diameter were placed (Fig. 5). Movement of the dies was affected by a pneumatic servomotor. It was found that single drawing by the use of die with outer diameter \varnothing 26.490 mm was satisfactory.

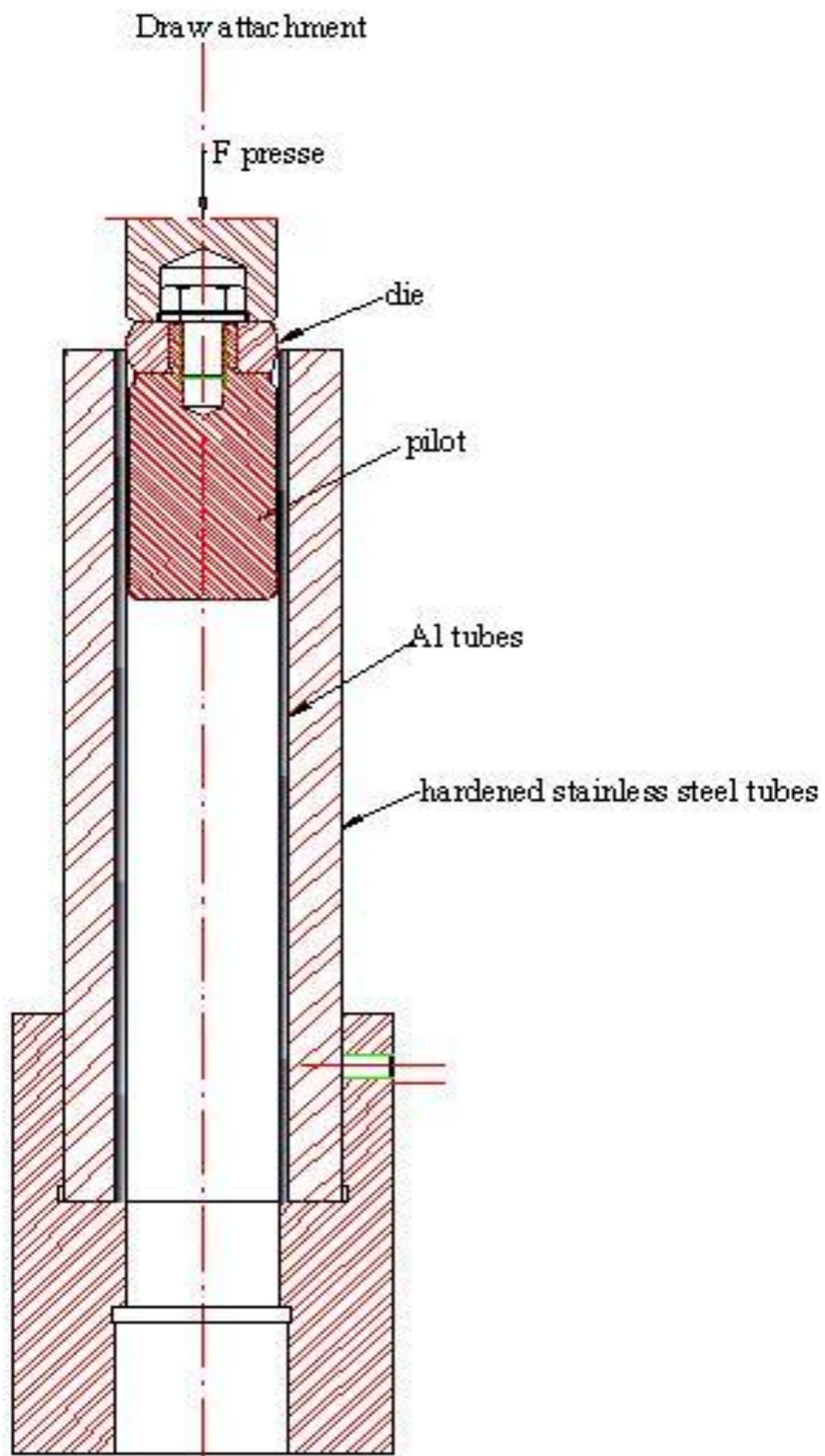


FIG. 5. Device for die drawing.

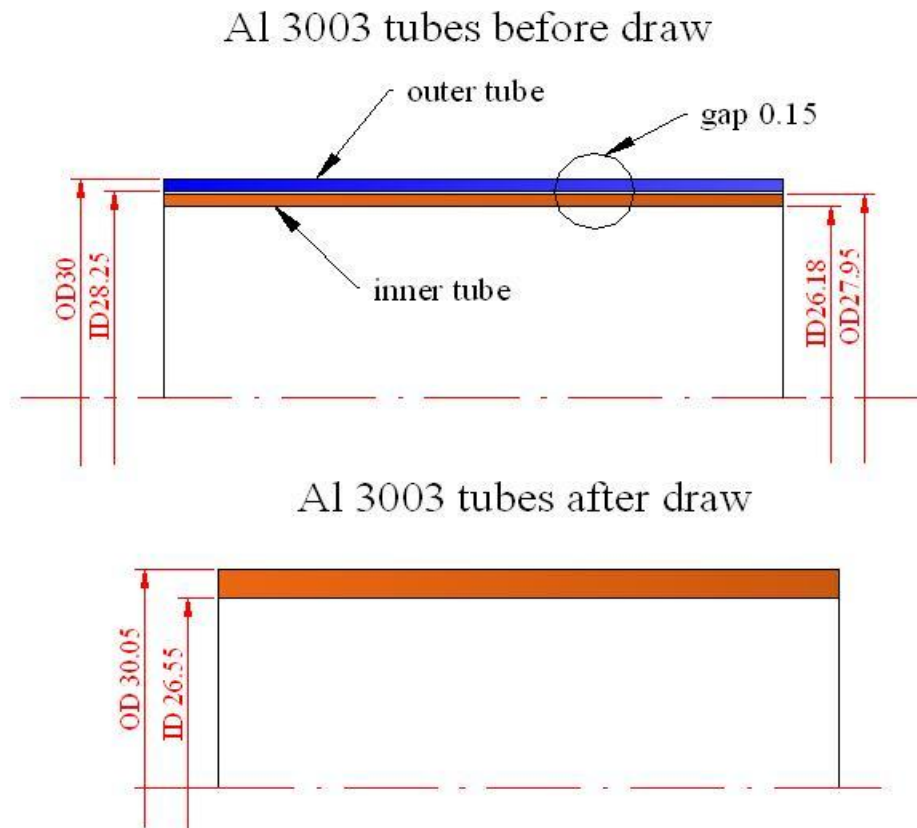


FIG. 6. Changes in diameters of Al tubes before and after drawing.

2.1.3. Encapsulation of dummy target

After assembly was completed, the dummy target was encapsulated by TIG welding (Castolin TIG 1702 AC/DC) of both ends of concentric Al tubes. For this purpose a stand for TIG welding with AC/DC welding machine, protective gas, specially constructed rotation and positioning system was built. The concentric tubes together with a Cu heat receiver were placed in the holder of the rotation system.

Three welding methods with helium or argon as protective gases (TIG AC, TIG DC–with pulse and TIG DC–with “touch striking”) were tested. The quality of the welds was examined using microscopic cross-section. The best results were obtained for welding TIG DC–with pulse with helium as a gas protective (Fig. 7).

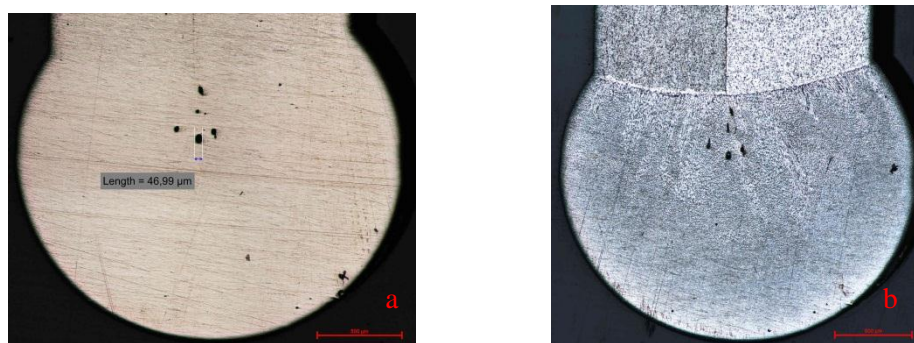


FIG. 7. Microscopic cross section of the welds: a) the weld non-etched, b) the weld etched by Keller's reagent.

2.1.4. Target leak tightness control

The leak tightness of the dummy uranium target was tested using a helium mass spectrometer leak detector according to the standard procedure PN-ISO-9978 (bombing test) [1]. The main parameters of this test were the following: bombing pressure of helium 0,5±0,6 MPa, bombing time 1h. The level of leakage conductance of helium from the uranium target was between 10^{-3} and 10^{-4} $\mu\text{Pa m}^3 \text{s}^{-1}$.

2.2. DISASSEMBLY OF URANIUM TARGET

For disassembly, both ends of the target were cut off without chips. The outer tube was cut along its length. The inside tube was pushed out, and the uranium foil recovered for processing. For this purpose the prototype cutting machine and the device for irradiated target expansion and recovery of Ni+U+Ni liner were constructed (Fig. 8).

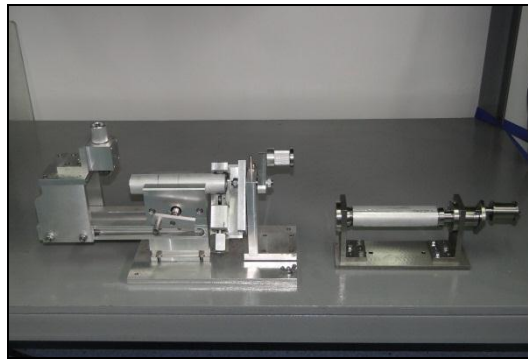


FIG.8. Prototype of equipment for disassembling the LEU target.

2.3. PREPARATION OF THE NATURAL URANIUM (NU) TARGET

Based on the results obtained during investigation performed using the dummy LEU target, the process of assembling the target containing NU foil was carried out.

Specifications of the used elements were as follows:

1. Ni+NU+Ni liner:
 - NU foil dimension: 50 x 83 x 0.131 mm
 - Ni foil dimension: 56 x 172 x 0.015 mm
 - Sandwich Ni-U-Ni thickness: 0.161 mm

2. Outer tube dimension:
 - Outer diameter: 29.995 mm
 - Inner diameter: 28.255 mm
 - Length: 162 mm

3. Dimension of inner tube after rolling and superfinishing
 - Outer diameter: 28.030 mm
 - Inner diameter: 26.202 mm
 - Dimension of groove: \varnothing 27.709 x 56 mm
 - Length: 162 mm

Assembly of the NU target was conducted in the same manner as it was described for dummy target.

Welding of the ends of the Al tubes after its assembly was performed by the means of the following parameters:

1. Settings of TIG welder:

Level 1. $J_1=51\text{A}$, $t_1=0,2\text{s}$, $J_s=25\text{A}$ (52%), $J_E=20\text{A}$ (40%), $t_2=2\text{s}$,
GPr =1, G-L=5, G-H=15, F-P=100Hz, dcy=33%, I-G=60%,
Level 2. HFt=0,01, Ito=5, Acc=0,5

2. Tungsten electrode (1,5% La, color of gold) $\varnothing = 1,6\text{ mm}$,
3. Speed of welded element rotation: 3rpm,
4. Protecting gas – helium, flow: $Q = 10\text{ l/min}$.

Leak tightness control of the prepared target was performed using the “bombing test” and showed that leakage conductance of helium from the target was $6 \times 10^{-3} \mu\text{Pa m}^3 \text{s}^{-1}$, whereas according to the PN-ISO 9978 [1] sealed radiation source is called as tight, when actual leakage conductance of helium does not exceed value of $10^{-2} \mu\text{Pa m}^3 \text{s}^{-1}$.

The placement of NU foil inside the manufactured target was inspected by the means of X-ray radiography (Fig. 9). A fabricated NU target is shown in Fig. 10.

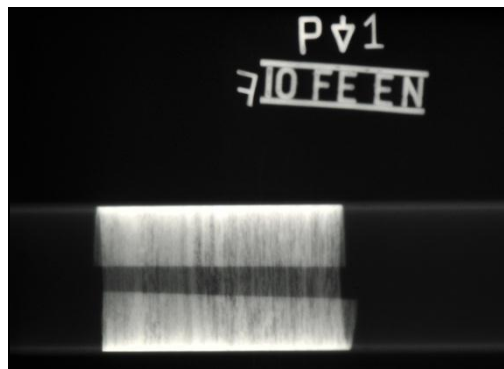


FIG. 9. Radiography of NU target



FIG. 10. The view of fabricated NU target.

2.4. ELECTROPLATING NICKEL ONTO URANIUM AS FISSION-RECOIL BARRIER [2]

The principal difficulty in plating uranium is that it oxidizes readily in air and water and the resulting oxide layer makes it impossible to obtain uniform and adherent deposits.

Therefore preparation of the uranium metal surface prior to plating was found to play a key role in the quality of the resultant coating. For obtaining a good mechanical bond, the procedures applied are comprised of degreasing, cleaning the surface of the most of uranium oxide, and etching the uranium to obtain a rough surface.

2.4.1. Pretreatment of uranium prior to plating

Six methods of pretreatment of the uranium surface comprised of etching natural uranium (NU) in 5M FeCl₃, in the mixture of NiCl₂ + HNO₃, in chlorides and anodic etching were used and compared. It was found that the best method of pretreatment of the uranium surface prior to Ni plating is double anodic etching of NU foil in 3 M HNO₃ solution. This method appears to almost completely remove the oxides layer from NU surface. In this method three-electrode cell was used. The cell contained: NU foil as a working-electrode, Pt foil as a counter electrode and Ag/AgCl reference electrode. The electrochemical process was carried out for 4 minutes with a current density 59 mA/cm². After anodic etching, the NU foil was immersed for 2 min. in 8 M HNO₃ heated to 40°C to remove the anodic oxidation products. This procedure was repeated twice.

2.4.2. Deposition of nickel on uranium surface

For fixing nickel on the uranium surface, two methods were used. According to the first, nickel deposits were obtained in an electroless plating from solution containing except nickel also some amount of phosphorus. The phosphorus as hypophosphite reducing agent was used in the electroless nickel plating solutions. However this method was used only for plating readily available uranium rods. Long storage before use caused their surface to be highly oxidized and corroded and the plating failed.

The second method used for fixing nickel on the uranium surface was galvanic plating. For this purpose the Watts bath was used, containing NiSO₄ · 7H₂O (34g/100ml), NiCl₂ · 6H₂O (4.7g/100ml), H₃BO₃ (3.8g/100ml). Volume of electrolyte solution was 40 ml. The cell consisted of uranium cathode (3.6 cm²) and nickel anode (8 cm²). An electrochemical process was carried out for 1 h, at current density of 30 mA/cm² at 50°C.

For the plating experiments, the NU foil strips of 10 × 50 mm and 150 μm thickness were used.

The results of galvanic plating of uranium foils pretreated by single anodic etching are illustrated in Fig. 11 as a cross section along the perpendicular axis of the foil.

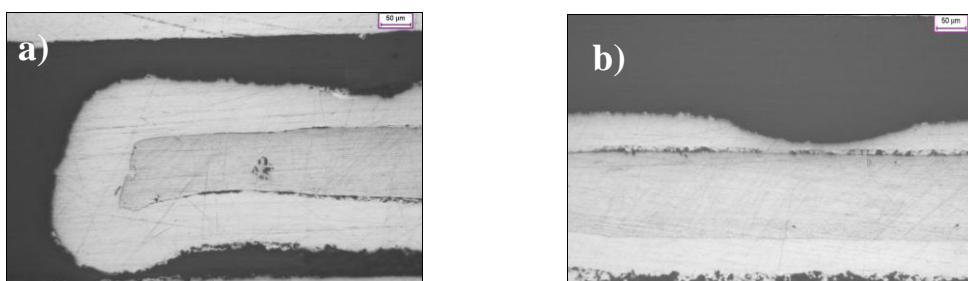


FIG. 11. The cross sectional view of NU foil covered by nickel layer. Galvanic plating of uranium foils pretreated by single anodic etching.

Complete coverage and quite good adherence could be observed; however, the thickness of nickel deposit was higher on the corners and edges in comparison with the middle parts of NU foil. Fig. 11b illustrates pitting in nickel deposition. Pitting is better visible on Fig. 12 showing microscopic photograph of Ni deposits with enlargement. This defect forming resulted from hydrogen reduction proceeding on NU cathode during the electrochemical process. In spite of this defect, nickel layer fixed on NU surface pretreated electrochemically is uniform and compact.

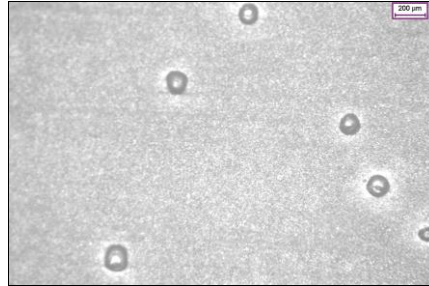


FIG. 12. The pitting in nickel deposits.

The results of galvanic plating of uranium foils pretreated by double anodic etching are illustrated in Fig. 13.

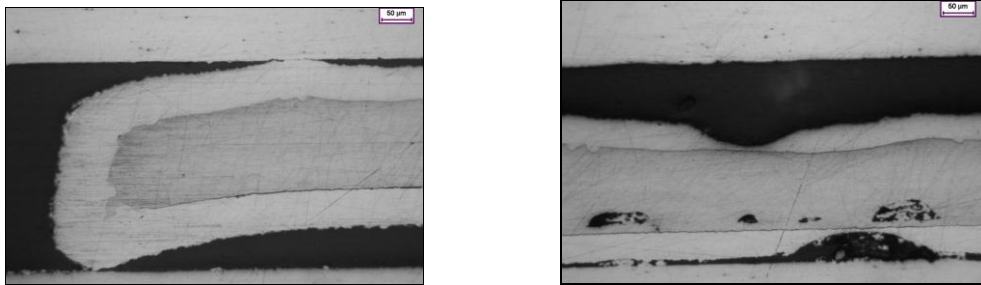


FIG. 13. The cross sectional view of NU foil covered by nickel layer. Galvanic plating of uranium foils pretreated by double anodic etching.

Double anodic etching of NU foil preceding deposition process contributes to very good coverage and adherence for nickel plating on NU substrate. In this case also pitting can be observed, but this defect does not deteriorate the coating density of Ni layer.

The thickness of this layer was evaluated microscopically and it was $\sim 53 \mu\text{m}$. An important observation is that no considerable overplating at the edges of the foil occurred, although it could change when full-sized foil would be plated. Such effects may exceed the tolerance needed to maintain the desired fit within the target. In such a case, the option may include rolling of the plated foil to a uniform thickness prior to assembling the target.

Remark: The results of this study confirmed that pretreatment of uranium substrate prior to plating plays a key role in the quality of the obtained plates. The success of chemical pretreatment was dependent to some extent on the purity of the uranium and on its metallurgical state (cast, rolled or wrought). The best quality of nickel deposits were obtained on anodic etched NU foil. This method seems to completely remove the oxides layer from NU surface. The thickness of the nickel plates obtained in this study is sufficient to act as a fission-recoil barrier.

3. MOLYBDENUM SEPARATION FROM URANIUM TARGET

3.1. TARGET DISSOLUTION

Dissolution studies were performed using the rods of natural metal uranium in an apparatus, constructed at ANL, USA [3,4]. The mock up dissolver solutions were prepared by dissolving a number of natural metal uranium samples in the mass range from 13 to 18 g in 40 mL of nitric acid at about 140°C. Initial nitric acid concentration was calculated to obtain 1M final concentration of HNO₃. The dissolution time was approximately 100 minutes. During dissolution the pressure was measured in time intervals about 5 min till it achieved a stable value. The final pressure in the dissolver depended upon the amount of uranium dissolved, what is shown in Fig. 14.

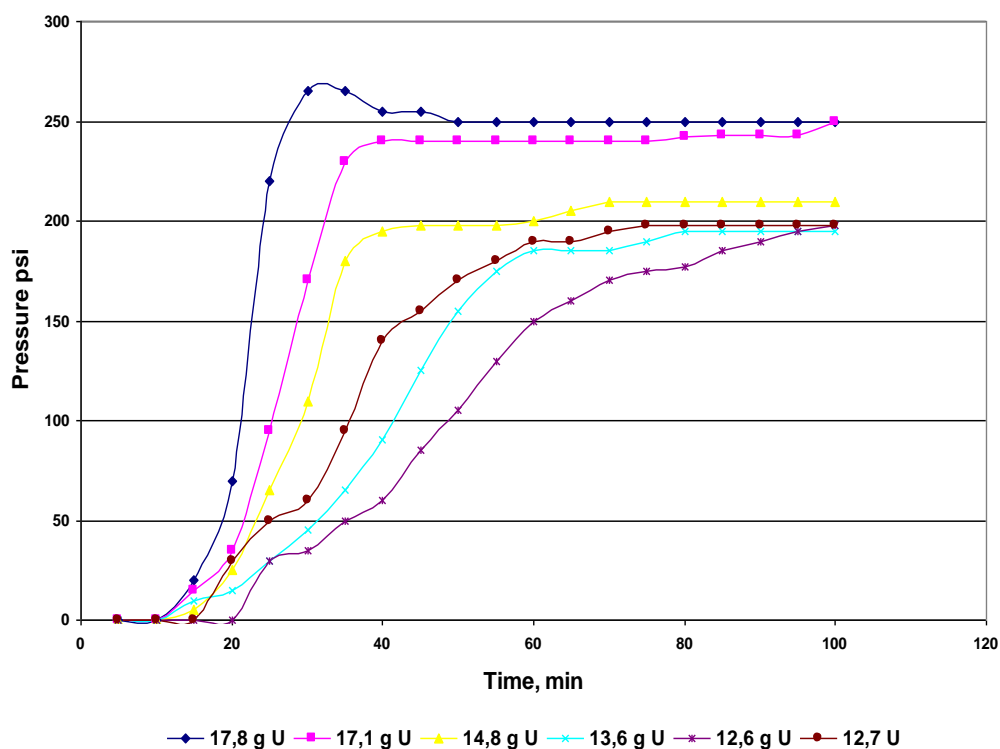


FIG. 14. Variation of pressure in dissolver with time during dissolution of uranium.

Fig. 15 presents the relationship for uranium dissolved together with Ni foil as a potential barrier for fission products. In this case the pressure increased by about 20 psi.

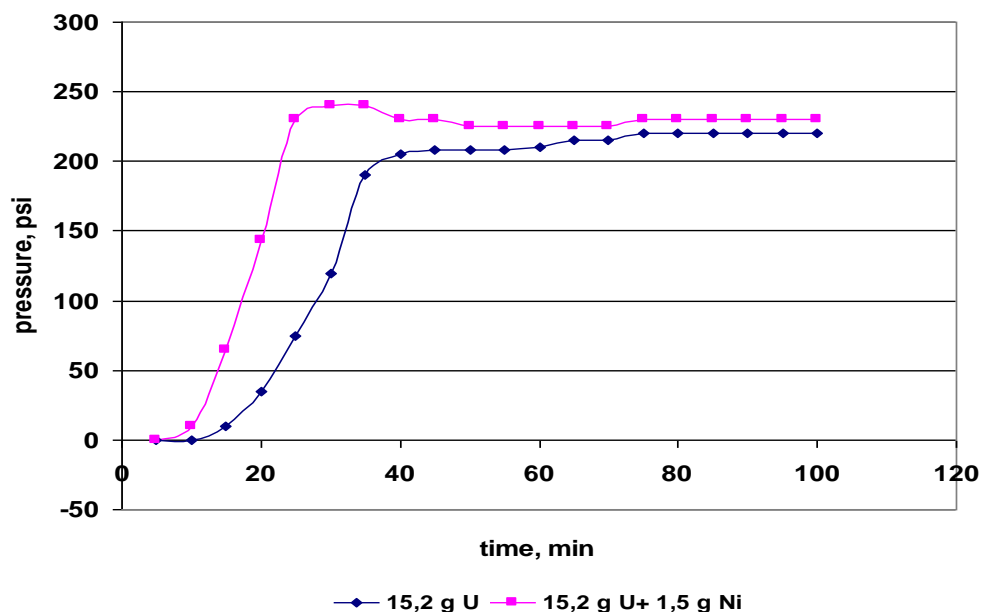


FIG. 15. Comparison of pressure in dissolver with time for pure uranium and uranium wrapped in Ni foil of 10% of uranium mass.

Remark: The temperature is measured on the outer surface of dissolver and this can differ from the temperature inside it. It is difficult to stabilize and reproduce it. This point requires improvement.

3.2. MOLYBDENUM SEPARATION PROCESSES

Three methods of Mo separation were studied:

- (1) precipitation of Mo by α -benzoin oxime
- (2) solvent extraction
- (3) adsorption on alumina

3.2.1. Precipitation of Mo by α -benzoin oxime (α -BP)

Molybdenum precipitation from the dissolver solution was performed using the procedure recommended in the Cintichem process. In all experiments, 20 mL of 2% α -benzoin oxime in 0.4M NaOH was added to the uranium solution containing Mo spiked with ^{99}Mo (10 mg/mL). The α -BP precipitate was collected on the fritted glass filter mounted in a glass container of 51 mm diameter (Fig. 16). To facilitate the filtration of precipitate a layer of 2 g of glass beads (100-150 μm diameter) was used.

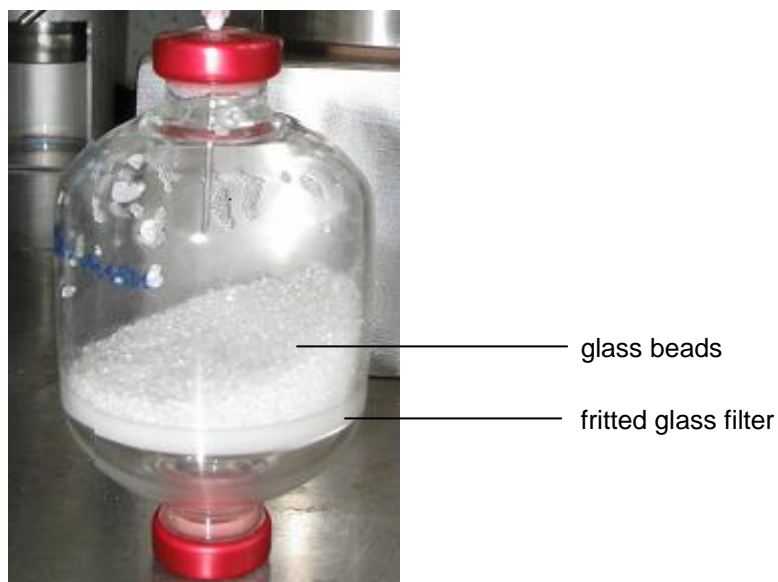


FIG. 16. Dissolution column.

The α -BP-Mo precipitate was washed with 20 mL of 0.1M HNO₃. The precipitate was dissolved in 10 mL of boiling 0.4M NaOH with 1% H₂O₂. The yield of Mo recovery was determined measuring the ⁹⁹Mo activity by gamma spectrometry. Results are shown in Table 1.

TABLE 1. RECOVERY OF MO FROM URANIUM SOLUTION

Batch No.	Uranium mass [g]	Recovery yield of Mo after α -BP-Mo precipitation [%]	Recovery yield of Mo from the first column AgC/AC [%]	Recovery field of Mo from the second column AgC/ZrO/AC [%]
1.	12.4	86,0 \pm 1.0	82,5 \pm 2.1	80,1 \pm 1.9
2.	17,8	88,8 \pm 0.9	86,3 \pm 2.0	83,1 \pm 2.1
3.	17,1	87,6 \pm 1.2	84,4 \pm 1.9	80,2 \pm 1.8

The molybdenum solution was further purified from I and Ru by column chromatography. ¹³¹I and ¹⁰³Ru were used as tracers. A first column contained the layers of activated charcoal (AC) and silver-coated activated charcoal (AgC) and a second column contained the layers of activated charcoal (AC), silver-coated activated charcoal (AgC) and hydrated zirconium hydroxide (ZrO) (see Fig. 17 and 18).

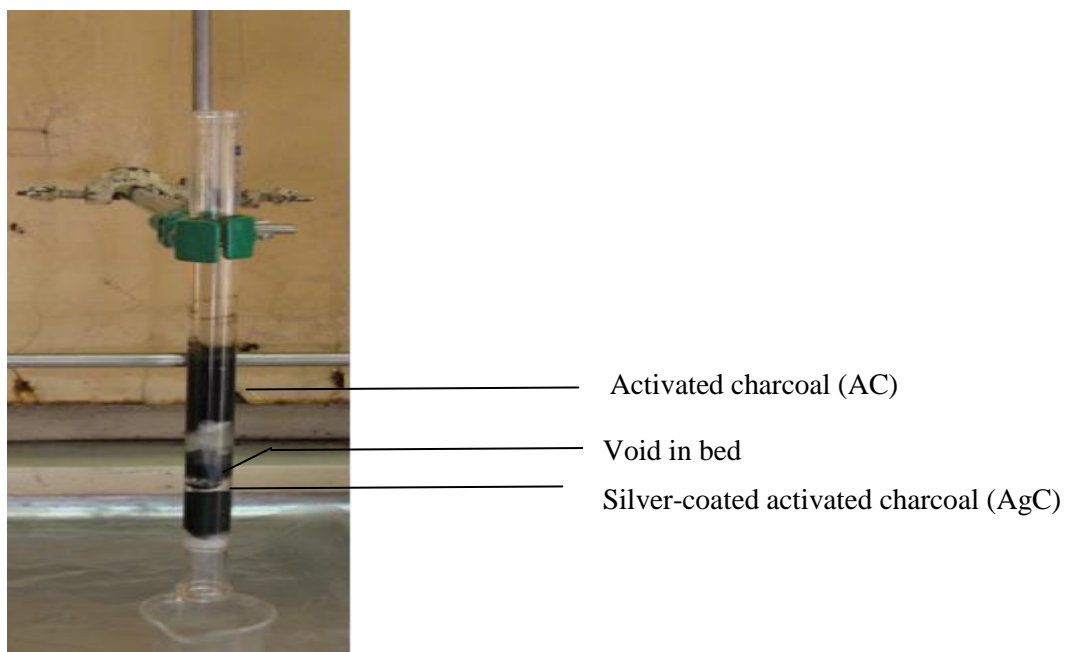


FIG. 17. First column AgC/AC.

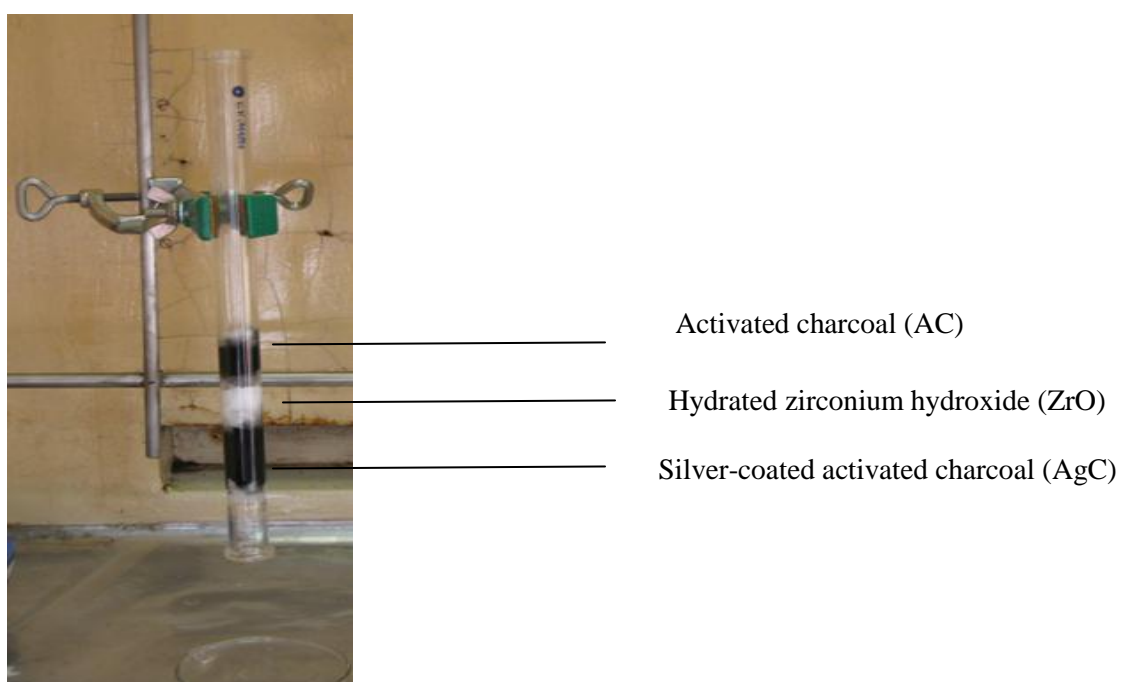


FIG. 18. Second column AgC/ZrO/AC.

Purification of Mo solution on these two columns resulted in decreased yield about 12%.

The decontamination factor for ruthenium was about 400 and for iodine about 200. Results are shown in Table 2.

TABLE 2. DECONTAMINATION FACTOR FOR ^{103}Ru AND ^{131}I

Batch	Mass		Decontamination factor	
	Mo, mg	U, g	^{103}Ru	^{131}I
1.	5	13,6	373	216
2.	5	17,8	397	222
3.	5	12,4	390	218

Remark: The purification columns worked with some problems - after introduction of Mo solution in the columns, the layers of the beds were broken creating the voids (see Fig. 17). This can cause the deterioration of decontamination factors particularly for iodine.

3.2.2. Solvent extraction

Solvent extraction with di-(2-ethylhexyl)-phosphoric acid (HDEHP) was the second method of Mo separation from uranium which was studied. The 15% of HDEHP in carbon tetrachloride was used for molybdenum and uranium extraction. Three extraction steps were required to achieve the highest yield of Mo separation. Over 94% of Mo was finally extracted from 5M HNO_3 at room temperature. Mo was back-extracted using 0.5M HNO_3 with addition of 1% H_2O_2 . The recovery yield amounted to about 81% (see Table 3).

TABLE 3. RECOVERY YIELD OF MO FROM URANIUM SOLUTION DURING SOLVENT EXTRACTION

Batch No.	Recovery yield of ^{99}Mo in extraction, %	Recovery yield of ^{99}Mo in back-extraction, %
1.	95,80	82,00
2.	94,60	80,30
3.	94,00	81,40
4	93,20	80,70
<i>Average</i>	94.4± 1.09	81.1± 0.75

3.2.3. Adsorption on alumina

The adsorption of Mo on two different types of Al_2O_3 (acidic, neutral) in static (Al_2O_3 suspension) and dynamic (Al_2O_3 column) conditions was studied [5]. The capacity of acidic Al_2O_3 for MoO_4^{2-} was 67.5 mg Mo/g and 33.6 mg Mo/g in static and dynamic conditions,

respectively. The respective values for neutral Al_2O_3 were 51 mg Mo/g and 24 mg Mo/g. The highest amount of Mo adsorbed was obtained at HNO_3 (approximately 0.1M) solution, having pH value in the range from 1.0 to 2.0 (see Fig. 19).

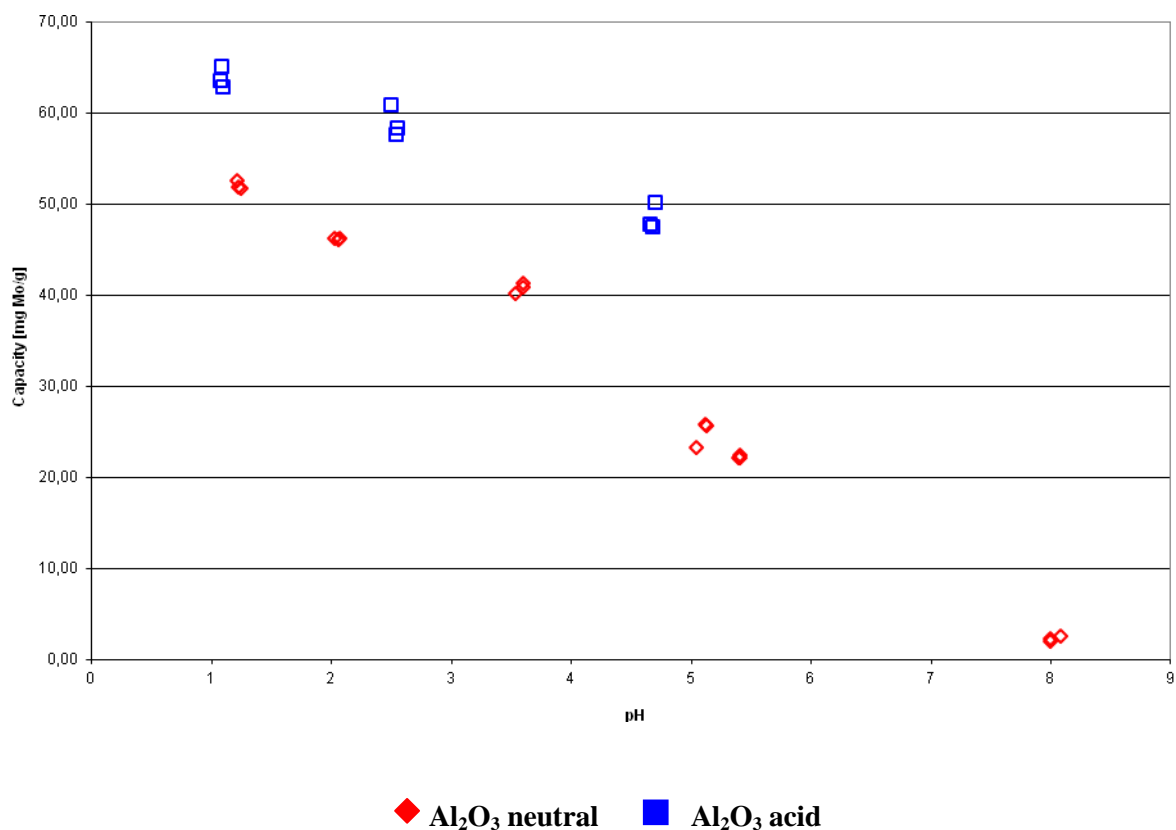


FIG. 19. Sorption capacity of MoO_4^{2-} on Al_2O_3 (acid and neutral) as a function of pH in HNO_3 solution.

TABLE 4. SORPTION CAPACITY OF MOO_4^{2-} ON ACIDIC AL_2O_3

Batch No.	Static capacity (mg Mo/g)		Dynamic capacity (mg Mo/g)	
	Al_2O_3 mass 0.3 g		Al_2O_3 mass 0.3 g	
1.	68.0	34.7		
2.	67.0	32.0		
3.	67.5	34.2		
<i>Average</i>	67.5 ± 0.5	$33,6 \pm 1.4$		

4. CONCLUSION

The achieved experimental results justify the conclusion that the target preparation and its disassembly, target dissolution and separation of molybdenum from the solution are a good starting point for testing the complete technology on irradiated uranium foils at the pilot plant scale of the process.

REFERENCES

- [1] PN-ISO 9978. Radiation Protection. Sealed Radiation Sources. Leak tightness tests (January 1999).
- [2] CIESZYKOWSKA, I., ŻÓŁTOWSKA, M., MIELCARSKI, M., Electroplating nickel onto uranium as fission-recoil barrier, *Nukleonika* **54** (2009) 29-32.
- [3] Medical Isotope Production Without Highly Enriched Uranium, The National Academies Press, Washington (2009).
- [4] VANDEGRIFT, G., BAKEL, A., CHEMERISOV, S., Overview of Argonne progress related to implementation of ^{99}Mo production by use of a homogeneous reactor, International RERTR Meeting, Washington (2008).
- [5] CHAKRAVARTY, R., SHUKLA, R., TYAGI, A., DASH, A., VENKATESH, M., Practicality of tetragonal nano-zirconia as a prospective sorbent in the preparation of $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator for biomedical application, *Chromatographia*, **72** (2010) 875-884.