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**STATUS OF THE CHILEAN IMPLEMENTATION OF THE  
MODIFIED CINTICHEM PROCESS FOR FISSION <sup>99</sup>MO  
PRODUCTION USING LEU**

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**ABSTRACT**

In the frame of the CRP on “Developing Techniques for Small Scale Indigenous <sup>99</sup>Mo Production Using LEU Fission or Neutron Activation”, CCHEN is developing the capability to produce fission <sup>99</sup>Mo using low enriched Uranium (LEU) targets. To progress in the several activities Korean non irradiated natural Uranium foils have been used.

New calculations have been done to improve the estimation of power generated by the LEU target during its irradiation. Taking an irradiation period of 48 hours and the thermal flux of  $8.0 \times 10^{13}$  n/cm<sup>2</sup>·s, the total inventory of fission products at different decay times - using ORIGEN-S code - was determined. Xenon is the predominant gas produced during the Uranium foil irradiation; thus, Xenon will be used to establish a maximum conservatively bounding internal pressure of an annular type LEU-foil target.

Progresses have been reached in the conditioning of the hot cell to accept the modified Cintichem process. The hot cell was prepared with a stainless steel liner, two back doors moved pneumatically for feeding of the chemical solutions, a new design of the hot cell ventilation system and two new master slave manipulators will be installed. A special room will be constructed to install the filter batteries and the exhaust fans. Liquid and solid radioactive wastes will be temporary storage in a shielded vault. Shielding calculations of the vault was recently finished.

Regarding the development of the modified Cintichem process, a total of 19 experiences working with non irradiated natural Uranium and using the stainless steel dissolver designed following ANL indications were done. The Molybdenum recovery has reached over 80%.

## 1. Introduction

The Chilean Nuclear Energy Commission (CCHEN) has been participating from 2005 in the Coordinated Research Contract (CRP) of the International Atomic Energy Agency (IAEA) on the development of techniques for the native production on small scale of  $^{99}\text{Mo}$  from the fission of low enriched Uranium (LEU). The  $^{99}\text{Mo}$  of high specific activity produced using the Cintichem process will be used in the production of generators which will be distributed throughout the country to different Nuclear Medicine Centers.

The Cintichem process was developed by Argonne National Laboratory (ANL) and it was transferred to the participant countries of the CRP. The targets will be fabricated using LEU foils which are being produced by KAERI, South Korea. The target is made of two concentric aluminum tubes; between both tubes is the Uranium foil covered by both sides by Nickel foil which acts as a containment barrier of the fission products generated during the irradiation. The target which is an airtight assembly will be irradiated in the RECH-1 research reactor. After the irradiation the target is disassembled in a hot cell to remove the Uranium foil which is acidic dissolved to separate the  $^{99}\text{Mo}$  by means of a precipitation process. The solution of  $^{99}\text{Mo}$  is purified in two ion-exchange columns; after the quality controls the  $^{99}\text{Mo}$  is ready to be used in the production of generators.

## 2. Calculations

The targets will be irradiated using the RECH-1 research reactor which is a pool type reactor with a nominal thermal power of 5 MW. This reactor is operated by the Chilean Nuclear Energy Commission (CCHEN) at La Reina Nuclear Center. The RECH-1 is a light water-moderated, water-cooled and beryllium-reflected reactor and it employs MTR-type fuel assemblies. The reactor is being operated using a core configuration of 32 LEU fuel assemblies, which were fabricated by the CCHEN fuel fabrication plant using  $\text{U}_3\text{Si}_2\text{-Al}$  with a Uranium density of  $3.4 \text{ g/cm}^3$ .

The neutronic calculations were performed using WIMS-D and CITATION codes [1] for the 13 grams LEU foil target supposing it would be introduced in the positions D2 or D5 of the reactor grid. The results are given for the target irradiation system formed by the element to irradiate targets, the target basket and the target itself, Figure 1.

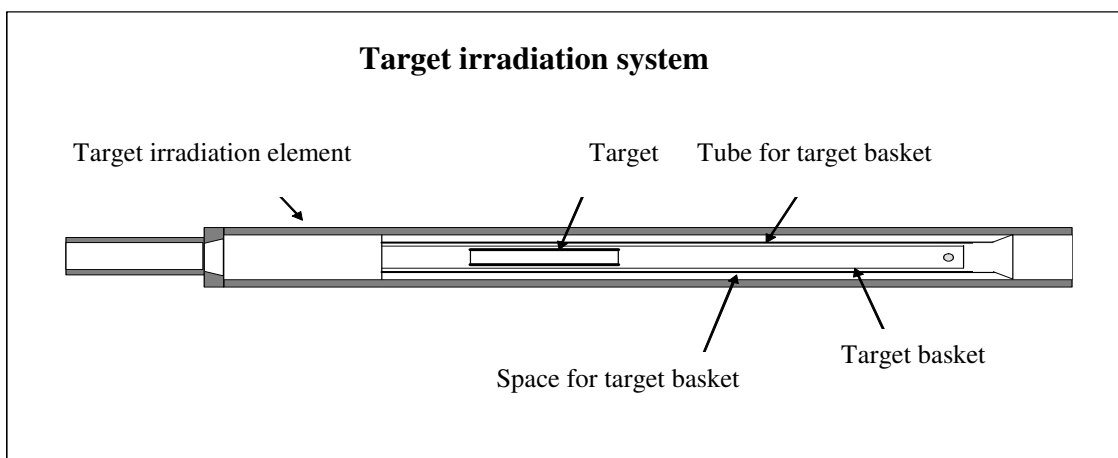


Figure 1: Irradiation system

The results show that when the foil is irradiated in the D5 position of the reactor grid, with a thermal neutron flux of  $8.0 \times 10^{13}$  n/cm<sup>2</sup>·s, it generates about 7.44 kW representing a heat flow of 72 W/cm<sup>2</sup>. In these conditions a maximum wall temperature of 81.3 °C is reached in the target, and the wall temperature to have onset of nucleate boiling is 123 °C. This maximum wall temperature is located approximately 10 cm from the top end of the target; that is, 6.9 cm from the top edge of the Uranium foil, and it has been obtained considering a uniform distribution of the heat generated in the plate.

The core reactivity, when the target is located in positions D2 or D5, is acceptable from the safety reactor point of view, Table 1. Therefore, positioning the target in D5, where the thermal neutron flux is higher, would be the best option. Nevertheless, a review of the thermal-hydraulic analysis and the target irradiation system design will be done. Two dimensional neutronic calculations were carried out for the same target system and the results are shown in reference [2].

$k_{\text{eff}}$	$\rho$ , pcm	$\phi_{\text{th}}$ , n cm <sup>-2</sup> s <sup>-1</sup>	P, kW	Position
1.031625	3,066	5.4 E+13	4.96	D2
1.037912	3,653	8.0 E+13	7.44	D5

Table 1. Effective multiplication factor, reactivity, average thermal neutron flux and average power generated by the foil in positions D2 or D5 of the reactor grid

To calculate activities the ORIGEN-S code [3] was used. For the calculations an irradiation time of 48 hours for a target containing 13 g of 19.75% enriched Uranium was considered. Due to the target could be located in D2 and D5 position, a constant thermal neutron flux of  $5.37 \times 10^{13}$  n/cm<sup>2</sup>·s<sup>-1</sup> (position D2) and of  $8.0 \times 10^{13}$  n/cm<sup>2</sup>·s<sup>-1</sup> (position D5) was taken.

Table 2 shows the total activity of <sup>99</sup>Mo in Ci and the specific activity in Ci of <sup>99</sup>Mo/mg of Mo at different irradiation times, when the target is irradiated at the thermal neutron flux of  $8.0 \times 10^{13}$  n/cm<sup>2</sup>·s during 48 hours. At the end-of-irradiation the activity of produced <sup>99</sup>Mo was 155 Ci, that is, 11.92 Ci of <sup>99</sup>Mo per gram of LEU irradiated. The specific activity of 116.24 Ci of <sup>99</sup>Mo/mg of Mo (<sup>97</sup>Mo, <sup>98</sup>Mo, <sup>99</sup>Mo and <sup>100</sup>Mo) was obtained. The total activity of the actinides (<sup>237</sup>U, <sup>239</sup>U, <sup>239</sup>Np and <sup>240</sup>Np) was 21.69 Ci/g U, and the total activity of the fission products was 30,800 Ci.

Irradiation Time, h	6.0	12.0	18.0	24.0	30.0	36.0	42.0	48.0
<sup>99</sup> Mo, Ci	23.91	46.42	67.69	87.37	106.09	123.37	139.70	155.00
A <sub>sp</sub> , Ci/mg Mo	154.66	147.04	140.82	134.79	129.49	124.62	120.22	116.24

Table 2. Activity of <sup>99</sup>Mo at different irradiation times with a thermal neutron flux of  $8.0 \times 10^{13}$  n/cm<sup>2</sup>·s

It has been defined that the beginning of the production of generators will be 24 hours after the end of irradiation; in this case, the initial activity of <sup>99</sup>Mo and the total activity of fission products will be 121 Ci and 1,720 Ci, respectively.

### 3. Target Assembly

**Rolling of natural U foils:** The metrological characterization of the 33 KAERI NU foils allowed to state a thickness average of 137.2 µm, with a minimum value of 95 µm and a maximum value of 207 µm. Due to the high variation of thicknesses, it was decided to make cold rolling of the foils. They

were placed in a stainless steel SAE 304 envelope of 0.025 mm of thickness, and this envelope was placed in another stainless steel SAE 304 envelope of 0.8 mm of thickness.

The direction of the cold rolling was done in the width of the foil to maintain the length of 100 mm. In each rolling passage the reduction was 3%, obtaining a total reduction of the foil thickness between 10% and 27%. The thin foils were metrologically characterized, and the average thickness was reduced from 137.2  $\mu\text{m}$  to 117  $\mu\text{m}$ . The quality of the surface of the rolled foil is much better than that of the non rolled foil.

**Own manufacture of thin natural U foils:** The technology to produce Uranium metallic foil is being developed. In general, metallic Uranium is placed in a low carbon steel frame to protect the U from oxidation during the hot rolling. In order to avoid the adhesion between the Uranium and the steel, the steel surfaces have to be covered with an emulsion of yttrium oxide (yttria) and ethanol. Once the surfaces are impregnated with the protective coating and dried, the set is assembled and welded using TIG weld. The hot rolling process is done at 630°C and the total reduction reached was 97%. The obtained foils are shown in Figure 2. The dimensions of the foils are given in Table 3.

Table 3. Characterization of Natural Uranium Foils

Foil	FUN-01	FUN-02
Thickness, mm	0.201	0.330
Length, mm	501	676
Width, mm	46	33



Figure 2: Natural Uranium Foils

**Target assembling for  $^{99}\text{Mo}$  production:** Three tubular targets were prepared for assembling with natural Uranium foil from KAERI. For this, an assembling form was prepared; it allows establishing the dimensions the tubes have to be mechanized and the selection of the write expensor to use according to the exact dimensions of the Uranium foil to be used; this procedure was named “Virtual Assembly of the Target”.

Previous to the target assembly, the mechanized Al-3003 tubes were degreased, cleaned in ultrasound and superficially cleaned with NaOH at 70°C. The next step was the assembly of the foil set Ni-U-Ni, and complete target assembly, Figure 3.

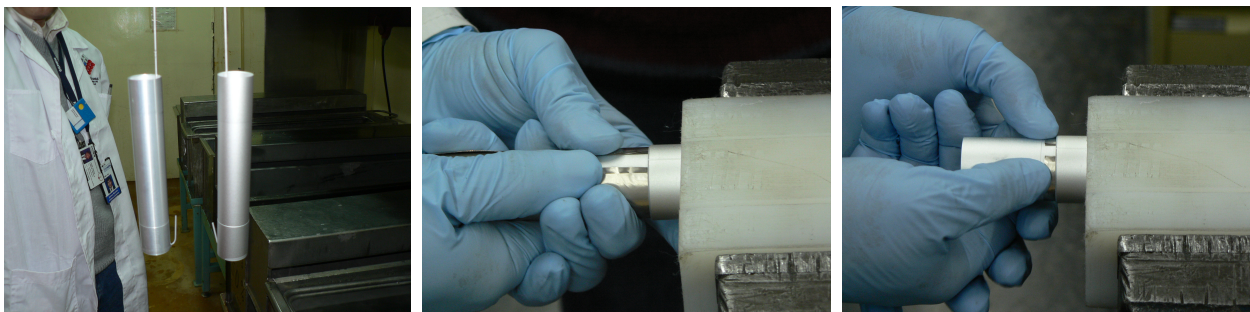


Figure 3: Target Assembly

Once the target was ready, it has to be expanded to obtain the best union between the inner and outer Aluminum tubes to diminish the possible gap of air produced between the foil set and the aluminum tubes. The first control that the Uranium foil is put in the right position is utilizing X-Ray radiography. Figure 4 shows the X-Ray radiography taken to one target assembled utilizing natural Uranium foil. The characteristics of natural Uranium foils to assemble three targets are shown in Table 4.

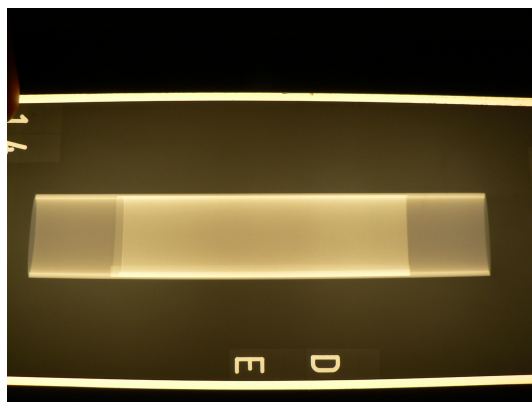


Figure 4: Inspection by X-Ray Radiography

Target	Natural U Foils - KAERI				Ni Foils	Uranium, g
	Nr.	Length, mm	Width, mm	Thickness, mm	Thickness, mm	
TUN-24	17	103.03	60.36	0.116	0.014	12.78
TUN-25	18	102.82	59.81	0.141	0.014	12.81
TUN-26	24	101.94	60.70	0.133	0.014	13.20

Table 4. Natural Uranium target

#### 4. Chemical Process

For recovering the  $^{99}\text{Mo}$  produced in the irradiated target the modified Cintichem process is used [4]. The equipment used is a stainless steel dissolver connected to a cold finger to trap the fission gases and nitrogen oxides produced during the dissolution process in nitric acid of the Uranium and Nickel foils. The rest of the equipment are bottles of one and two mouths and columns made in Pyrex glass which are rejected as radioactive solid wastes after each process.

The dissolver was designed and constructed at CCHEN, using as guide information sent by ANL. It was made using a tube of stainless steel SAE 316L type Mannesmann without seam and suitable for working at high pressures and temperatures, and aggressive atmospheres. Its wall thickness is 1/8", its external diameter is 2", and its length is 261 mm. The lid and the bottom were made of stainless steel SAE 316 and the welding was TIG type with inert gas Argon. The dissolver is closed pressing the lid against the cylinder with four bolts that guarantee the mechanical resistance and the air

tightness of the dissolver. Between the lid and the body of the dissolver a Viton O-ring special for using at high temperatures is placed.

Up to now, 19 chemical tests have been done with non irradiated material following the modified Cintichem process with the addition of the respective carrier elements, one of them was 5 mg of Mo. The 11 first tests were done using as raw material uranyl nitrate, and after, 6 tests were run with Uranium shavings; finally, the last 2 tests were done using as raw material non irradiated natural Uranium foils of 10.6 gr and 10.7 gr, respectively. In the dissolution process the temperature was 180 °C and the pressure reached 720 psi.

In order to know the total efficiency of the process of recovery and purification of Mo, samples of the final Mo solution were analyzed using neutron activation analysis (NAA). The results show that the yield of recovery of Mo was in average 80.7 %, and the presence of Uranium was under the detection limits of this technique for this kind of sample (< 1 ppm).

Element	Initial Mass
U	10.6 – 12.0g
Ni	1.9 g
Mo carrier	5.0 mg
Ru carrier	10.0 mg
Rh carrier	12.0 mg
I carrier	6.80 mg

Exp.Nr	Mo, mg	Mo %	I, mg	U, mg	Ru, mg	Rh, mg
13	3.97	79.5	-	-	-	-
14	4.44	88.8	1.68	<0.04	-	<0.36
15	3.54	78.8	-	-	<0.32	-
17	4.07	81.4	-	-	-	-
20	3.76	75.2	<0.05	<0.11	-	-

Table 4: Results of NAA of Mo solutions obtained by the modified Cintichem process

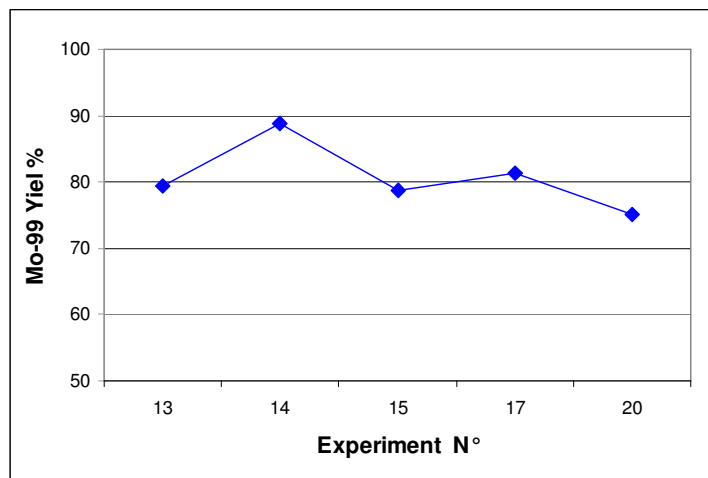


Figure 5: Yield of recovery of Mo applying modified Cintichem (with 5 mg Mo carrier)

The radiochemical process with irradiated material will be done in the high activity hot cell located in the underground of the Radioisotopes Production Laboratory at the La Reina Nuclear Center. The dimensions of the hot cell are 4 × 2.5 × 3.25 m; the walls were made of heavy concrete and 1.24 m of

thickness with a window of  $33 \times 68$  cm filled with white mineral oil R-95 Sonneborn. The original master slave manipulators will be replaced by two new Hans Wälischmiller manipulators which are being manufactured. Figure 6 shows a layout of the equipment inside of the hot cell.

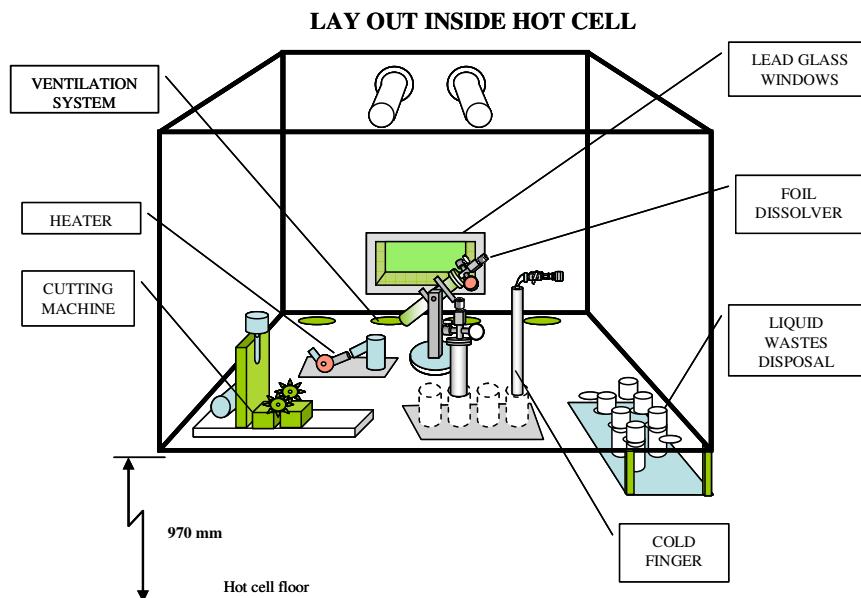


Figure 6: Layout of equipments inside the hot cell

## 5. Quality Controls

**Of the target:** The tightness of the target is controlled before its irradiation in the reactor with the purpose to assure that there is no risk of escape of radioactive material from the inside of the target during the irradiation, and the later treatment of the target. The first control is to submerge the target in liquid Nitrogen and then in boiling water, process in which greater flights are detected. The second control of the target is to put it under a test of detection of flights with a Helium detector, commonly used in the high vacuum technology, that allows detection of small flights. To proceed in the detection of flights, the target is put first in vacuum and after in a Helium atmosphere with a pressure of 10 psi. In the case of having some flight, Helium will filter towards the interior of the target. Later the target is put in a chamber with high vacuum, connected to the mass spectrometer detector tuned for the mass of the gas Helium ( $m=4$ ). In case of existing a flight in the target under test, the Helium that was introduced previously in its interior begins to emerge towards the interior of the vacuum chamber and will activate the Helium detector. So it is possible to establish in quantitative form the value of the volume of flight in the target, which is settled down that must be  $< 5 \times 10^{-7}$  std  $\text{cm}^3/\text{sec}$ .

**Of the final  $^{99}\text{Mo}$  solution:** Gamma spectrometry is used for one of the quality controls of the  $^{99}\text{Mo}$  final solution to determine the activity concentration of the sample, using an intrinsic Germanium detector. The efficiency of the detector was determined using a standard solution of  $^{152}\text{Eu}$  (liquid  $\text{EuCl}_3$ ) in a plastic bottle of 50 ml volume (50.98 g and 430 Bq/g at 21/02/2008) for a certain geometry. The detection system has a S100 multichannel analyzer.

In order to implement the alpha spectrometry technique for determining the level of contamination of the  $^{99}\text{Mo}$  solution with transuranic elements, the fundamental part is the development of the electroplating technique [5] where those radionuclides are isolated by a process of anionic exchange and then electroplated from the electrolytic solution on the surface of a steel disc. The development of the technique is in the phase of optimization of the electrochemical conditions and dynamics of the heavy ions diffusion. Special attention has been put in the reproducibility of the electroplated sample, and to avoid the problem of cross-contamination.

Once the electroplated sample was obtained the alpha spectrometry is done using a surface barrier detector. The calibration of the detector and the electronics has been done utilizing commercial standards of electroplated  $^{233}\text{U}$  and  $^{244}\text{Cm}$  on steel disc, provided by AREVA-CERCA-LEA.

## 6. Conclusions

The results obtained through neutronic, thermal-hydraulic and activity calculations guarantee the future production of fission  $^{99}\text{Mo}$  in the reactor RECH-1 irradiating target of LEU during 48 hours with a thermal neutron flux of  $8 \times 10^{13} \text{ n/cm}^2 \cdot \text{s}$ . The amount of produced  $^{99}\text{Mo}$  is enough to satisfy the present national market.

The methodology to assemble LEU targets and necessary quality controls has been developed. Additionally, the Uranium metallic foil production is being developed.

The modified Cintichem process has been applied dissolving non irradiated Uranium and Nickel foils and adding the different carriers; the mean value of Mo recovery was over 80%. A rotatory stainless steel dissolver was designed and constructed.

## 7. References

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