Irradiation Capsules with Suspended LEU UO₂
Particles for $^{99}$Mo Production.

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ABSTRACT

Capsules, with suspended spherical particles of uranium (LEU) dioxide in water, are being developed to be used as high thermal neutron flux irradiation targets in research reactors to produce $^{99}$Mo from $^{235}$U fission.

Particles are maintained in suspension by external agitation and water radiolysis equilibrium recombination pressure is reduced with hydrogen incorporation. Micron size fused spherical UO₂ particles will be produced in an induction coupled radiofrequency plasma equipment.

Out of pile experiments were performed to collect molybdate anion in solution, separate it from adsorbed surfaces and wash the particles for a next cycle of irradiation. Experiments in thermal neutron beams and in the proximities of the nuclear core of research reactors are being designed.

One of the interests in this system is that the size of the particles is smaller than the penetration depth in UO₂ of the fission products. They are collected from the liquid medium and particles can be used several irradiation cycles without need of reprocessing them. Nuclear residues are drastically reduced.

1. Introduction

The SPIM (System of Production of Medical Isotopes) is an initiative of technological innovation in CNEA for the development of the production of $^{235}$U fission products from particles of uranium dioxide (UO₂) with low-enriched uranium in aqueous suspension for their use in nuclear medicine. The main idea of this method is that the fission products can be removed from the water because the size of UO₂ particles is less than the distance traveled by fission products before losing their energy.
This innovative technology development requires planning and conducting various tests to determine the hydrodynamic behavior of UO$_2$ particles in aqueous suspension, irradiation with thermal neutrons to evaluate yields of extraction and purification of radioisotopes of interest, procedures for waste management, security reports, etc. This project is aimed at the production of $^{99}$Mo due to its growing demand in the international market [1,2]. These developments, in turn, are linked to international programs through which is intended to replace the use of highly enriched uranium (HEU) by low-enriched uranium (LEU), in particular in $^{99}$Mo production, as it can be seen that are the current trends in radiochemical research worldwide [3].

One of the central objectives of the SPIM project is the design of irradiation capsules contemplating dimensional aspects, materials, construction, pressure and temperature, heat transfer, water radiolysis, particle agitation and instrumentation. Irradiation vials are analyzed for thermal neutron beam irradiations and also capsules to be irradiated in areas of high neutron flux, close to the nucleus of experimental reactors, such as the RA-3 or RA-6 in irradiation boxes or in the RA -10 or OPAL in irradiation tubes in the reflector zone.

The purpose of this initiative is not only to obtain irradiation targets where fissile material can be reused without reprocessing, but also to obtain parameters for designing nuclear reactors with suspended particles for use in the production of $^{99}$Mo and extraction of other fission products of interest, especially for nuclear medicine [4, 5].

The aspects described in this work are the preparation of UO$_2$ particles, adsorption of molybdate anion on their surface, irradiation of samples in low thermal neutron flux beams, the design of an irradiation capsule and some concepts that can be considered for the design of a prototype aqueous suspended particles reactor to obtain $^{99}$Mo [6].

2. Basic ideas

High energy fission products are transported through the surrounding medium until they are stopped travelling a finite penetration range. Table 1 shows penetration ranges of $^{137}$Cs and $^{99}$Mo in uranium dioxide and water with the initial energies they posses as fission products of $^{235}$U.

Table 1. Penetration ranges of $^{137}$Cs and $^{99}$Mo in UO$_2$ and water expressed in microns.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Energy</th>
<th>UO$_2$</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MeV</td>
<td>µ</td>
<td>µ</td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>60</td>
<td>5.73</td>
<td>18.0</td>
</tr>
<tr>
<td>$^{99}$Mo</td>
<td>90</td>
<td>7.15</td>
<td>21.2</td>
</tr>
</tbody>
</table>

In Figure 1 the path of 1000 $^{99}$Mo fission products with an initial energy of 90 MeV spanning five microns in uranium dioxide and ending in water are shown. It is observed that virtually all products finish their journey in the water. Also, some uranium atoms can be moved outside of the particle by knock-on near the solid surface and entering the water zone.
Figura 1. Calculated trajectories of $^{99}$Mo in 5 $\mu$ of UO$_2$ and final stopping in water (TRIM).

The fundamental idea of SPIM project is that the particle size is less than the penetration range of fission products. Thus, the fission products would be physically separated from the particle where they were generated. Fission products will be extracted with different methods according to whether they are soluble, insoluble, gaseous, or some other property that differentiates them. Accordingly, the preferred particles size for producing $^{99}$Mo it is chosen to be 6 $\pm$ 1 $\mu$. If it is found that is relevant that uranium atoms do not contaminate the surrounding water, particles can be covered with an innocuous layer, of for example chromium [7].

The concentration of the particles will be related to the size of the reactor and the values required for criticality. Illustratively in Figure 2 effective k values for cylindrical reactors of different diameter and height sizes are shown depending on the volume concentration of the particles of uranium dioxide. From these calculations (SCALE 6.1) it can be inferred that the volume concentration of particles of UO$_2$ with low enriched uranium must be between 1 and 3 % v/v. This concentration is also needed to guarantee that fission products generated in one UO$_2$ particle does not implant itself inside another passing by particle.

Figure 2. $K_{\text{eff}}$ vs LEU UO$_2$ particle concentration for different cylindrical reactor sizes totally surrounded with 30 cm water reflector.
3. UO₂ particles preparation

The selected method for the manufacture of uranium dioxide particles of 6 ± 1 μ size consists of two stages. The first is the homogeneous precipitation of a solution of uranyl nitrate in the presence of urea [8,9,10] to guarantee a uniform size distribution and the second step is the melting of treated precipitates in an inductively coupled plasma (ICP) equipment of 15 kW power and 2.5 MHz frequency [11,12]. This system produces fused spherical particles without porosity. In Figure 3 it is sketched a diagram indicating powder and gases incorporation into the plasma zone, the cooling chamber of molten spherical particles, cyclonic separator, filter and product collecting zones. In Figure 4 it is shown the processing zone of the equipment and at the right of the figure spherical tungsten particles that were melted at temperatures above 3422 °C with sizes between 5 and 25 μ diameter. This type of plasma can easily melt uranium dioxide whose melting point is 2850 ± 30 °C [13].

Figure 3. Spheroidization ICP process scheme.

Figure 4. Plasma chamber and spherical tungsten powder produced.
Initial tests were performed with 10 µ size particles of natural UO₂ (Figure 5) obtained from the rectification of sintered pellets after separating the fine and coarse extremes of the initial size distribution curve that had particles ranging between 0.1 and 100 µ [4]. The coarse particles were separated by wet sieving and the fines using differential decantation times in water.

*Figure 5. Final particle size obtained distribution of natural UO₂.*

These UO₂ particles are shown in Figure 6 photographed at 800X in an optical microscope (a and b) and with 1000 X and 7000 X in a scanning electron microscope (c and d). In each figure the size scale is indicated. The samples a and b differ in the concentration of particles present and were prepared in between two plane glasses with separations of approximately 100 and 200 µ respectively. The surface area of these particles is 0.318 ± 0.003 m²/g and its shape is generally platelet like, where two dimensions are larger than the thickness.

*Figure 6. UO₂ powder of 10 µ mean size coming from pellet rectification after fine and coarse refinement.*
The orange-red color is characteristic of UO$_2$ in thickness less than 150 µ as can be followed in Figure 7 from UV-visible thin films spectra [14,15].

![Figure 7. Optical density vs wavelength for different film thicknesses (left) and oxygen/uranium ratios (right).](image)

These particles of uranium dioxide can be spheroidized in the high temperature plasma to perform hydrodynamic and chemical testing. They will be also used dissolved in nitric acid for setting up the homogeneous precipitation process after which LEU particles can be prepared.

4. Molybdate anion (MoO$_4^{2-}$) adsorption

UO$_2$ particles will be suspended in water during irradiation; the $^{235}$U fission produces new elements, many of them radioactive, among which is $^{99}$Mo. All fission products leave the interior of the particles where they were generated due to the high initial energy and the selected small size of the particles. In contact with water, at a pH close to 7, molybdenum will probably be in solution as the molybdate anion, MoO$_4^{2-}$. Uranium dioxide has an isoelectric point between 4.5 and 6 [16,17,18] which will make that molybdate anions can remain adsorbed in the double layer of solvated ions surrounding the particle.

After several trials at different pH’s it was determined that values greater than 9 releases much of the molybdate anions adsorbed on the surface of UO$_2$ particles. Filtering and centrifugation were tested for separating the particles from the liquid. Normally a sodium molybdate solution was used and molybdenum concentrations in the separated and washing solutions were measured using an ICP optical emission detection equipment.

The resulting procedure consisted in the determination of the proportion of anions adsorbed on the surface of the particles; how to remove the remnants and a final rinse of the particles with pure water so as to reuse them again. Two sets of measurements were performed with 50 ml solutions of sodium molybdate (Na$_2$MoO$_4$) at concentrations of 5 and 0.5 ppm of Mo in contact with 11 g of UO$_2$ particles. The solutions were filtered, washed with a 50 ml NaOH solution of
pH 11 and finally rinsed with 50 ml of pure water. A third procedure, centrifuging instead of filtering to separate the particles from the different solutions, was tested with a 1 ppm Mo sodium molybdate solution with 0.25% agarose concentration; this solution maintains the particles suspended without agitation. The washing and rinsing liquids were similar to the previous separations, and the UO₂ quantities and volumes involved were the same. The results of these three procedures are shown in Table 2. The presence of U is ought to nanoparticles coming from the breaking of the platelet like particles.

**Tabla 2.** Mo and U concentration of solutions in contact with UO₂ particles at different processing steps. Mo and U concentrations are measured with an error of 10%.

<table>
<thead>
<tr>
<th>Procedure:</th>
<th>Filtering</th>
<th>Centrifugating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample:</td>
<td>[Mo] 5 ppm</td>
<td>[Mo] 0.5 ppm</td>
</tr>
<tr>
<td>Step</td>
<td>Solution</td>
<td>Mo (ppm)</td>
</tr>
<tr>
<td>1</td>
<td>Initial (Na₂MoO₄)</td>
<td>5.8</td>
</tr>
<tr>
<td>2</td>
<td>First separation</td>
<td>5.1 (88 %)</td>
</tr>
<tr>
<td>3</td>
<td>Washing (NaOH)</td>
<td>0.58 (10 %)</td>
</tr>
<tr>
<td>4</td>
<td>Rinsing (H₂O)</td>
<td>0.19 (3 %)</td>
</tr>
</tbody>
</table>

The values in Table 2 in parentheses indicate the amount of Mo extracted in each step. The percentages initially adsorbed on the surface of the particles were 12% and 16% for concentrations of 5 and 0.5 ppm respectively and in the case, were the initial liquid with agarose and 1 ppm of Mo was separated by centrifugation, was 75%. Considering that the error of the Mo concentration value had an error of 10% in each measurement, the overall extraction of molybdenum in the three cases was 101, 116 and 100 %, indicating final good extraction results.

5. **Irradiation at low thermal neutron flows**

We have designed a test to irradiate a sample of suspended particles of natural UO₂ in the thermal neutrons beam of the RA-1 reactor in the Constituyentes Atomic Center with a flow of 4.5x10⁷ n.cm⁻².s⁻¹ (Table 3). The purpose of this test is a proof of concept of the separation of ⁹⁹Mo obtained from the fission of ²³⁵U present in natural UO₂ particles. The material to be irradiated during 8 hours are 11 grams of natural UO₂ particles suspended in a 50 ml 0.25% agarose solution that present tixotropic properties.

The irradiations will be carried out at room temperature and the low activity samples will be extracted with special procedures in a chemical hood with the required minimal shielding. The centrifugal separation scheme performed out of pile will be repeated as post irradiation experiments. In all steps gamma emissions will be measured with HPGe detectors.
Table 3. Irradiation conditions in a thermal neutron beam of 4.5x10^7 n.cm^-2.s^-1.

<table>
<thead>
<tr>
<th>Irradiation time</th>
<th>Decay time</th>
<th>Activity</th>
<th>Contact dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>hours</td>
<td>Hours</td>
<td>µCi</td>
<td>µSv/hr</td>
</tr>
<tr>
<td>8</td>
<td>16</td>
<td>5</td>
<td>100</td>
</tr>
</tbody>
</table>

This experiment is similar in some aspects to one in which UO₂ particles were irradiated in an aluminum matrix and isotopes were measured at different separation steps, in the aluminum matrix and inside the uranium oxide particles [19].

6. High power irradiation capsules

Irradiation capsules are neutron targets. The expected advantages are that LEU UO₂ particles can be used several irradiation cycles without reprocessing, the generated residues are minimized, the \(^{99}\text{Mo}\) extraction will be quicker and a more automate process can be implemented. Unlike a loop irradiation [20] the capsule are closed systems; it is needed that the suspension of particles and the radiolysis of water be controlled in some way.

6.1. Capsule design criteria

The capsule design geometrical criteria is that it can have the possibility to be irradiated in boxes at grid positions of pool reactors of the RA-3 or RA-6 type reactors; the possibility that it can be positioned in the channels to obtain \(^{99}\text{Mo}\) in the Australian OPAL reactor and the RA-10 to be built in the CAE limits its size to cylinders of less than 50 mm. The other design criteria that was considered is that the relationship between the amount of \(^{235}\text{U}\) (using LEU) and lateral surface of the capsule is maintained in similar values per unit area of heat extraction in irradiation miniplate targets used normally to obtain \(^{99}\text{Mo}\) from uranium aluminides. These values are typically comprised between 0.02 and 0.03 grams of \(^{235}\text{U}\) per square centimeter of heat extraction surface. With these considerations it is possible that the speed of the cooling water and the surrounding section in capsules will be similar as in the case of miniplate targets: about 5 m/s and 10 cm\(^2\) section surrounding the capsule and flows lower than 5 liters per second. Moreover, irradiation of the capsule with a high thermal neutron flow was calculated for a position near the nucleus of the RA-3 reactor and trying to use existing transportation shielding and eventually hot cells.

Preliminary data from these conditions are as follows. The capsule is cylindrical and made of stainless steel 304L, external dimensions of 40 mm diameter and a length of 130 mm; the thickness of the side wall is 0.5 mm; lids must accommodate filling and emptying valves. The interior volume of the capsule is 120 cm\(^3\). The capsule will be subject to internal pressure not greater than 10 atmospheres. Instrumentation on prototypes is desired to measure, at least, temperature and pressure.

The total amount of \(^{235}\text{U}\) can be 5 grams corresponding to 28.5 g of UO₂. UO₂ particles are spherical, with no porosity, with a density of 10.93 g/cm\(^3\) [21] and a mean diameter of 6 ± 1 µ. The total volume of the particles is 2.6 cm\(^3\) with a concentration in between 2 and 3 v/v %. Uranium is enriched to 20% in the isotope \(^{235}\text{U}\) (LEU). Thermal neutron irradiation flow is 8 x 10\(^{13}\) n.cm\(^{-2}\).s\(^{-1}\). The rate of fissions produced is 3.3 x 10\(^{14}\) f/s. The total amount of heat generated
during irradiation is 10.6 kW (1 Watt = 3.1 x 10^{-10} f/s). The density of heat which must be extracted by the side walls is approximately 80 W/cm². Under these conditions the amount of $^{99}$Mo produced, considering a yield of 6.2% per fission, with a irradiation cycle of 7 days, is approximately 500 Ci, something equivalent to 3 normal miniplates.

6.2. Particles suspension

The suspension occupies between 75 and 90% of the capsule volume. To keep UO$_2$ particles in suspension it is necessary to generate a forced agitation. The method developed for these purposes is the generation of surface bubbles in a field of oscillating pressure. The oscillating field is generated by a vibration in the axial direction of the vertically oriented capsule. This system includes two stages. The first is the formation of bubbles on the surface of the suspension and the second is that the bubbles at some distance beneath of the liquid/gas interface surface sink to the bottom of the capsule [22,23]. Bubble formation on the surface is due to the vibrational modes at the liquid surface. Migration of bubbles in a stationary oscillating field is due to Bjerknes forces that cause that at frequencies below the bubbles resonance they are routed to the antinodes of the pressure waves [24]. The descent of the bubbles at frequencies below the resonance of the system will depend on how deep the bubbles are [25]. This effect is shown in Figure 8 where for shallow depths (0.1 in abscissa) bubbles that are above the curves are directed to the bottom of the container. In this figure, the empty circles indicate positions of bubbles that moves away from the curves (unstable) and the black circles indicate that bubbles approaches the curve (stable). In the first case the bubbles are directed to the surface or to the bottom, in the second bubbles remain stationary in the position of the curve in accordance to the acceleration of vibratory field and the depth at which it is located. There is also a tendency for bubbles to approach the side walls [26]. Several tests were carried out in a "shaker" of 11 kN (kilo Newtons) to obtain the most efficient parameters of frequency and amplitude of vibration to generate bubbles under pressure. Transparent capsules were used to visualize the phenomena (Figure 9); oscillations reaching values of 45 times gravity acceleration were tested.

![Figure 8. Bubble movement in a liquid column in an oscillating field of low frequency.](image)
It was determined that the frequency range under which the proposed system works is between 90 and 110 Hz. The optimal filling for the production of bubbles on the surface is over 75% of the total internal volume of the capsule. The amplitude of the vibration to present the phenomenon must be greater than 3 mm peak to peak; with bigger amplitudes the plenum can be less than 10% of the capsule total volume. As the internal pressure in the capsule is increased it is more difficult to generate the desired effect. Agitation is really intensive.

Figure 9. Transparent capsule mounted in a 11 kN shaker.

6.3. Water radiolysis

The capsule will be irradiated in a very close position to the reactor core. It will be subjected to gamma radiation and thermal, epithermal and rapid neutrons. Fission products will be produce fundamentally by the thermal neutrons capture. These high energetic particles will be mainly the responsible of the radiolysis of water inside the capsule.

Figure 10. Computational simulation of species present because of water radiolysis. At right the effect of pressurizing with hydrogen is shown [27,28].
Recombination pressures of water radiolysis products can be stabilized at lower values solubilizing hydrogen in the capsule [29, 30, 31, 32, 33] as shown in Figure 10. The presence of pressurized hydrogen drastically diminishes the partial pressure of the species present after few minutes.

The kinetic energy of the fission products is 80% of the released energy. Another 5% is gone with the neutrinos. For the purposes of radiolysis calculations inside the capsule it is only necessary to consider the fission products kinetic energy, whereas the neutrons, gamma and electron radiation or positrons generated is around 10%. Also, fissions produced by neutrons generated inside the capsule are not considered, as well as fissions coming from activation products, such as plutonium. Hitherto, the energy produced by fission within the capsule involved in radiolysis will be less than 170 MeV. Part of this energy is deposited in the particles as the fission products are stopped in their trajectory in the 6 µ UO₂ particle matrix. It can be considered that the average energy deposited in the water is about 140 MeV per fission (70%) of the generated with a mean LET of 3800 keV/µ. This will be the energy involved in water radiolysis. These values are applicable for calculating the hydrogen pressure required in the capsule to maintain it as low as possible in a steady state of the recombination reactions of the decomposition of water. The fission of ²³⁵U releases approximately an energy of 200 MeV distributed as shown in Table 3.

**Table 3. Energy distribution in ²³⁵U fission [34].**

<table>
<thead>
<tr>
<th>Energetic particles involved</th>
<th>MeV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fission products kinetics</td>
<td>165</td>
</tr>
<tr>
<td>Prompt-γ</td>
<td>7</td>
</tr>
<tr>
<td>Fission neutrons kinetics</td>
<td>5</td>
</tr>
<tr>
<td>Fission products β emission</td>
<td>7</td>
</tr>
<tr>
<td>Fission products γ emission</td>
<td>6</td>
</tr>
<tr>
<td>Neutrinos</td>
<td>10</td>
</tr>
</tbody>
</table>

**6.4. Power density**

A capsule with 5 g of ²³⁵U (0.021 moles) near a reactor core receiving a thermal neutron flow of 8 x 10¹³ n.cm⁻².s⁻¹ will produce 3.3 x 10¹⁴ f/s, equivalent to 10 kW (1 W = 3.1 x 10¹⁰ f/s). If the capsule has a volume of approximately 100 cm³, the power density will be 100 kW/l.

In seven days irradiation the total number of fissions will be 2 x 10²⁰ corresponding to 3.3 x 10⁻⁴ moles; the quantity of consumed ²³⁵U, or burn up, will be 1.5 %. In this condition, considering a yield of 6.2 % per fission, the activity of ⁹⁹Mo produced will be of 500 Ci. The gaseous fission products produced are 28% per fission and the increase of pressure in the capsule plenum is less than 0.1 atmospheres.
7. Discussion.

In the designed irradiation capsule the amount of $^{235}$U present per unit length is equivalent to three normal miniplates used as targets for producing $^{99}$Mo. The heat removal surface of the capsule is lower than in the case of plate like targets but is offset by the fact that the internal temperature is uniform because of the forced bubble stirring to which is subjected. It can be considered that the capsule works at low temperature, compatible with the required heat extraction. A rough calculation estimates it in a inside uniform temperature of 70 °C.

It is desirable that the capsule have inside a filter for separating liquid from particles and further design should consider shielding and automate conditions of the extraction process. In automate conditions the volume of shielding material will drastically be reduced. Another important issue is the need of working at high power generation densities allowing that the following process of radioisotopes extraction be performed using the smaller volumes of solutions as possible.

8. Conclusions

It was shown that molybdenum in the presence of UO$_2$ particles can be extracted by different methods such as filtering or centrifugation in several steps such as washing in an alkaline solution and a final water rinsing, leaving particles ready for a new cycle of irradiation. This developments were necessary for being used after low flow irradiation tests with natural uranium that are being already arranged as an initial proof of concept in active material.

A high power irradiation pressurized capsule device is being designed with the elaboration of the conceptual engineering for controlling radiolysis with the solubilization of hydrogen under pressure and particles suspension with bubble agitation and heat extraction.

Capsule targets not only will produce smaller quantities of nuclear residues, but simplify fission products extraction, a more extensive use of $^{235}$U without reprocessing, an easier way for automate processes with smaller shielding involved, and also that they can be incorporated to small reactors for local production of, for example, $^{99}$Mo.

An important driving force for the development of capsule targets is that the information obtained can be used for the design of an aqueous suspended particles homogeneous reactor dedicated to radioactive fission products production. In homogeneous reactors the power needed to supply world wide $^{99}$Mo demand is just 2 MW, a near 200 fold increase in competitiveness.

9. References

   http://www.iaea.org/About/Policy/GC/GC54/GC54InfDocuments/English/gc54inf-3-att7_en.pdf