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Monte Carlo simulation of Mo-99 isotope production with increased specific activity in WWR-K reactor

D. Sairanbayev, Sh. Gizatulin, A. Gurin, M. Aitkulov, K. Kisselyov, A. Nessipbay, A. Ashibayev, A. Kulakov, A. Shaimerdenov*

Institute of Nuclear Physics, 1 Ibragimov st., Almaty 050032, Kazakhstan

Abstract. The activation method used for the production of molybdenum-99 in the WWR-K reactor currently allows the maximum production of the specific activity of molybdenum-99 equal to (85 ± 11) GBq/g Mo as a result of seven-day neutron irradiation of natural molybdenum (VI) oxide. It is known that the reaction $^{98}Mo(n,\gamma)^{99}Mo$ is induced in the thermal region, and there are also large resonances in the energy region of about 12 eV and in the range of 0.4–10 keV, and these resonances do not compete with the radiative absorption reactions of other molybdenum isotopes in this area. Thus, an increase in the proportion of epithermal and thermal neutrons will lead to an increase in the production of molybdenum-99. The purpose of this work is to develop the design of an irradiation capsule that creates specified irradiation conditions. For this purpose, various designs of irradiation capsules with different materials that moderate neutrons were considered by calculation. Based on the results of Monte Carlo simulation, the optimal design of the irradiation capsule was selected, which makes it possible to increase the production of specific activity of molybdenum-99. Irradiating trioxide molybdenum with natural composition allows to increase the specific activity by 26%, while using trioxide molybdenum with a 98.7% enrichment molybdenum-98 – by 25%. The paper provides a description of the capsule designs considered and the results of computational modeling with MCNP code for molybdenum of different enrichments.

1 Introduction

Technetium-99m (Tc-99m) is a decay product of molybdenum-99 (Mo-99) and is the most used medical isotope for imaging. Currently, there is an increase in global demand for Tc-99m. About 95 percent of the world's supply of Mo-99 for medical use is produced in research and test reactors from targets containing uranium-235. To increase the specific activity of Mo-99, the targets contain weapons-grade highly enriched uranium (HEU). However, concerns about the spread of HEU have led to global efforts to end the civilian use of HEU in research and test reactors. Therefore, there is a need to research and develop alternative methods for producing Mo-99. One alternative method relies on neutron irradiation of targets containing Mo-98 in research and test reactors to produce Mo-99 through the neutron capture reaction $^{98}Mo(n, \gamma)^{99}Mo$ [1].

Reactor design parameters, operating power level, neutron flux available to irradiate targets, volume available in the reactor to accommodate targets, and reactor operating schedules are some of the key considerations when seeking a way to produce ^{99}Mo via the (n,γ) route. The thermal neutron activation cross section for the radiative capture reaction is only 0.13 barn, while the resonant integral of the reaction is 6.9 barn. A neutron flux of 5×10^{13} n/cm^2-sec or higher and irradiation periods of 4-6 days are necessary conditions for the production of ^{99}Mo of practical value. Using an enhanced flux of epithermal neutrons, it is possible to obtain ^{99}Mo with a specific activity of up to 3.4 Ci/g with samples of natural ^{98}Mo and up to 15 Ci/g with target samples enriched in ^{98}Mo, when irradiated in channels with beryllium moderators of appropriate thickness at a neutron flux of 1.7×10^{14} n/cm^2-sec. Targets for (n, γ) production can be made from natural molybdenum (24.13% natural ^{98}Mo) in the form of molybdenum trioxide (MoO_3) powder or granules encapsulated in aluminum or titanium cans or quartz ampoules. Targets in this form make it easier to extract ^{99}Mo after irradiation, since it can be dissolved in sodium hydroxide. However, targets must be of very high purity and sometimes even specially treated to remove any traces of rhenium and tungsten impurities to avoid $^{186/188}$Re and ^{188}W contamination. The use of targets made from enriched ^{98}Mo increases the specific activity by a factor of 4–8 depending on the epithermal flux and requires reuse of the enriched target for reasons of cost savings due to extraction and purification before reirradiation [2].

The WWR-K reactor is a unique multi-purpose light water research reactor with a thermal power of 6 MW in Kazakhstan. The coolant and moderator in the core are desalted water, the reflector is beryllium. After completing the process of converting the reactor to low-enriched fuel, the reactor uses uranium dioxide enriched to 19.7% in the uranium-235 isotope [3].

Currently, the WWR-K reactor is used for a wide range of both scientific and commercial work. To produce radioisotopes, as a rule, central irradiation channels with a maximum neutron flux density are used. During 7 days of irradiation, under standard conditions, in one of the central irradiation channels of the WWR-K reactor core, molybdenum-99 is produced with a specific activity equal to (85 ± 11) GBq/g molybdenum in ~10 g of MoO_3 powder target with natural content [4,5] when irradiated with thermal neutrons with a flux density of ~ 1.7 x 10^{14} n/cm^2-sec. It should also be noted that the production of Mo-99 was tested under irradiation with a thermal neutron flux of ~ 9.0 x 10^{13} n/cm^2-sec MoO_3 with molybdenum enriched up to 98.7% [6] of molybdenum-98 and a specific activity of 1 GBq/g was obtained [7]. To increase the specific activity of molybdenum-99, it is proposed to change the energy spectrum of neutrons in the irradiation zone of a molybdenum target. This is achieved by optimizing the neutron conditions in the standard capsule.

2 Materials and Calculations

2.1 Materials

The object of study is molybdenum trioxide powder – MoO_3. Under normal conditions, MoO_3 powder weighing 5 g is poured into a sealed quartz ampoule having an outer diameter of 17.5 mm (wall thickness 2 mm), a height of 35 mm and filled with air. Two quartz ampoules are placed in an aluminum capsule with an outer diameter of 52 mm, a height of 80 mm and filled with water. The aluminum capsule is installed in a standard irradiation channel, washed with water from the primary circuit. Water constantly circulates in the channel and capsule. The three-dimensional design of the irradiation capsule and the appearance of the molybdenum trioxide powder ampoule are shown in Figures 1 and 2, respectively. For the proposed design of the irradiation device, one ampoule is used, having

an outer diameter of 18.5 mm (wall thickness 2 mm), a height of 67 mm and also filled with air, filled with 10 g of MoO_3.

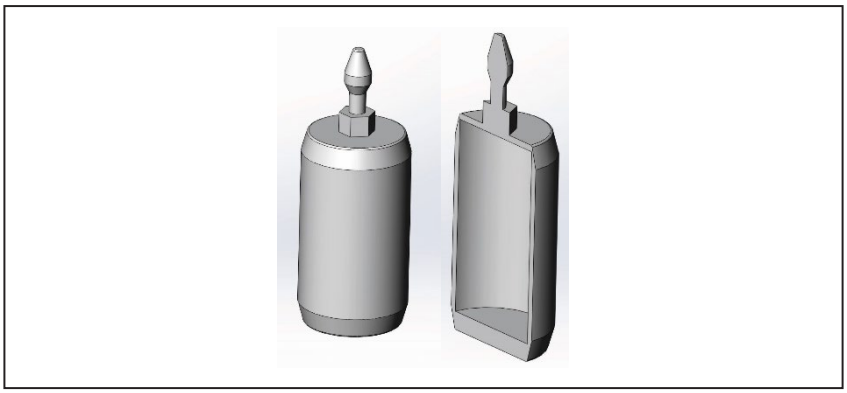

Fig. 1. Irradiation capsule.

The MoO_3 filling density for natural and enriched 98% Mo-98 is 1.58 g/cm^3. Natural molybdenum contains seven stable isotopes: Mo-92 (14.84%), Mo-94 (9.25%), Mo-95 (15.92%), Mo-96 (16.68%), Mo-97 (9.55%), Mo-98 (24.13%) and Mo-100 (9.63%) [8]. Molybdenum, enriched in molybdenum-98, contains the following isotopes: Mo-92 (0.01%), Mo-94 (0.09%), Mo-95 (0.01%), Mo-96 (0.01%), Mo- 97 (0.67%), Mo-98 (98.67%) and Mo-100 (0.54%).

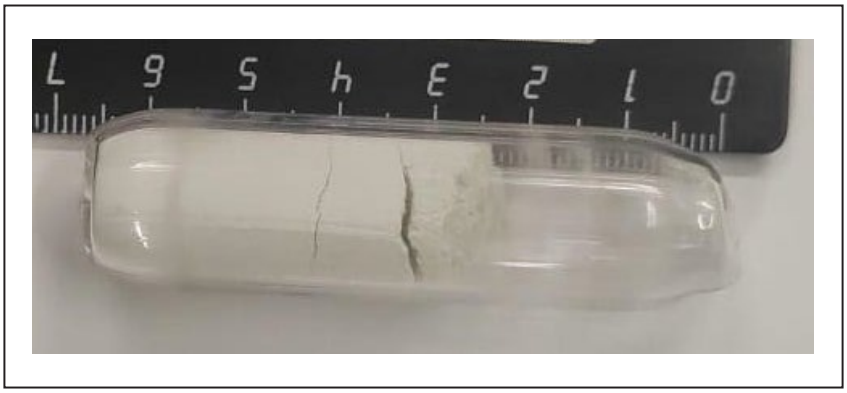

Fig. 2. Quartz ampoule with molybdenum trioxide powder.

2.2 Basic equation

The activity of the produced molybdenum-99 was determined as follows. For a small amount of molybdenum-98 (N_{98}), where the effects of self-shielding and target burnout are insignificant, the activity (Bq) of the produced molybdenum-99 after irradiation time t can be approximately equal to [9]:

$$\lambda N_{99}(t) = (1 - e^{-\lambda t}) N_{98} \sum_j \overline{\sigma_j} \overline{\phi_j} \quad (1)$$

where λ – is the decay constant of molybdenum-99, $\overline{\sigma_j}$ – is the averaged over energy group j j, $\overline{\phi_j}$ - is the averaged over energy group neutron flux on the target, calculated using the Monte Carlo N-Particle code (Version 6.2) [10]. ENDF/B-VII.1 was used as a library of neutron cross sections [11]. The 100 energy groups [12] used in the sum of equation (1) give a fairly accurate (within flux uncertainty) estimate of the flux-integrated cross section, since flux and cross section did not change rapidly together within the same energy interval.
The specific activity of molybdenum-99 in trioxide molybdenum is given by formula:

$$SA_{99}(t) = \frac{\lambda N_{99}(t)}{m_{Mo}}, \quad (2)$$

where m_{Mo} – sum of masses of all molybdenum isotopes in molybdenum trioxide.

2.3 MCNP calculation

Figures 3 and 4 show a horizontal section of the WWR-K reactor core and a vertical section of the irradiation capsule, modeled by the MCNP6 code, where the entire WWR-K core and its main components are modeled in three-dimensional geometry (X, Y, Z). For most fissile isotopes, MCNP6 uses continuous cross-section data from ENDF/B-VII.1 (80c). In addition, MCNP uses continuous energy nuclear and atomic data libraries ranging from 10^{-11} to 20 MeV for all isotopes and up to 150 MeV for some isotopes. Modeling radiative transfer in matter involves tracking particles according to established probabilistic laws, commonly known as cross sections. An important feature of MCNP is the ability to calculate eigenvalues keff for fissile systems.
The MCNP model was built in accordance with the actual dimensions of the WWR-K reactor. Tallies were created to calculate the 100 group neutron energy spectrum and the reaction rate of ^{98}Mo(n, γ)^{99}Mo in a quartz ampoule. The MCNP6 input file included 500 cycles, consisting of 50 inactive and 450 active cycles with 3,000,000 stories per cycle. To normalize a criticality calculation by the steady-state power level of a reactor, the following conversion is used [13]:

$$\left(\frac{1\ joule/sec}{watt}\right)\left(\frac{1\ MeV}{1.602\times10^{-13}\ joules}\right)\left(\frac{fission}{180\ MeV}\right) = 3.467\times10^{10}\ \frac{fission}{watt} - sec \quad (2)$$

As the WWR-K research reactor operates at a power level of 6 MW, the tally scaling factor would be: *P(W=6* x *10^6)* x *3.467* x *10^{10}* x *υ(2,459)=5.12* x *10^{17}neutrons/sec*.
To test the MCNP model, the fluxes of fast and thermal neutrons in the central and peripheral irradiation channels, the average specific activity of molybdenum-99 for 7 days of irradiation with natural MoO_3 in the central channel were measured and calculated and compared with the measured values. Tables 1 and 2 provide a comparison of measured and calculated data. Thermal and fast neutron fluxes were measured using fluence monitors. Fluence monitors were wires made of iron and cobalt, which were contained in a sealed aluminum housing. The following nuclear reaction ^{54}Fe(n,p)^{54}Mn occurred on iron, through which fast neutrons with energies above 1 MeV were detected. The following nuclear reaction ^{59}Co(n,γ)^{60}Co occurred on cobalt, through which thermal neutrons with energies below 0.683 eV were detected. Irradiation was carried out at a reactor power of 6 MW.

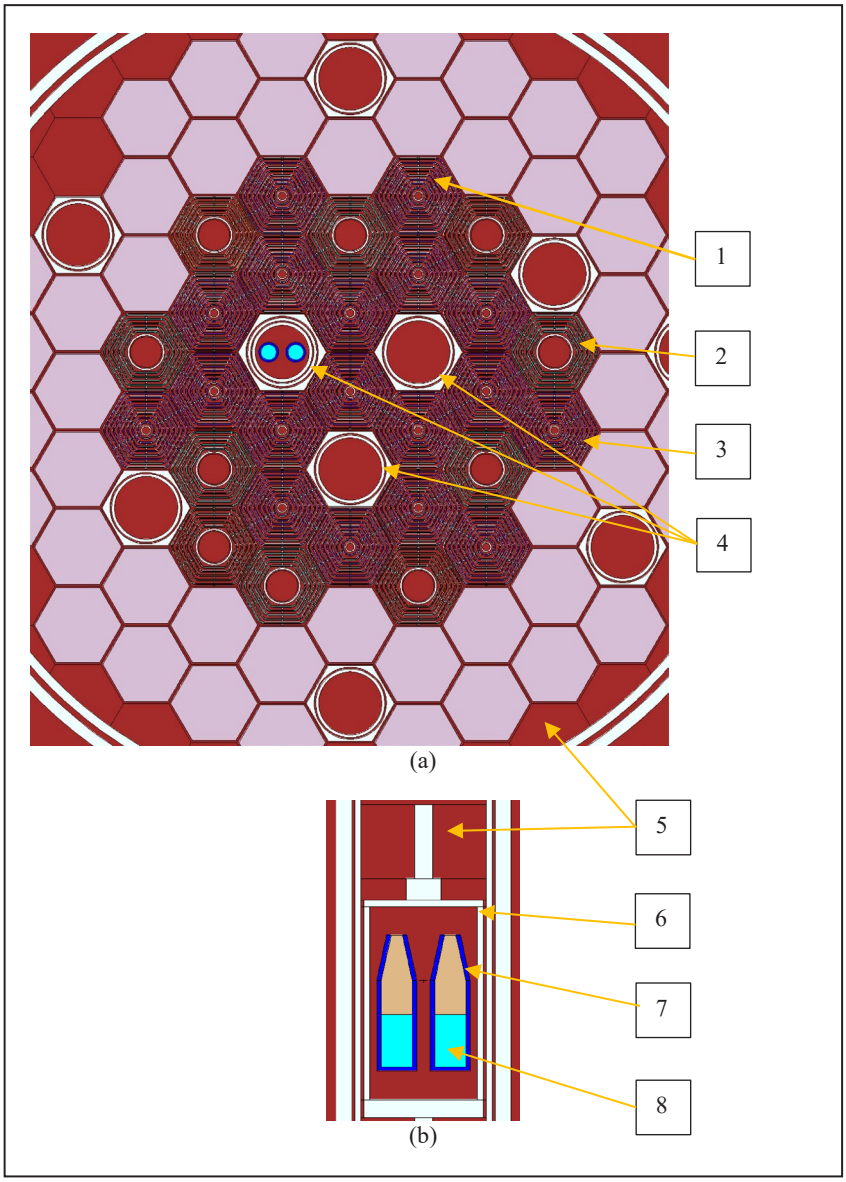

Fig. 3. MCNP model of current core (a) of WWR-K reactor and irradiation capsule with ampoules (b): (1) fuel assembly (FA) 1-type, (2) FA 2-type, (3) beryllium block, (4) central irradiation channels, (5) water, (6) irradiation capsule, (7) quartz ampoule, (8) MoO_3.

Table 1. Neutron flux density in irradiation channels [n/cm^2-sec].

Channel	**Experiment (E)**	**Calculation (C)**	**C/E**
	$E_n < 0.683$ eV		
central	(1.71±0.18) x 10^{14}	(1.67±0.03) x 10^{14}	1.02
peripheral	(8.53±0.41) x 10^{13}	(8.69±0.17) x 10^{13}	1.02
Channel	$E_n > 1.0$ MeV		C/E
central	(4.11±0.17) x 10^{13}	(4.11±0.08) x 10^{13}	1.00
peripheral	(5.68±0.33) x 10^{12}	(5.13±0.10) x 10^{12}	1.11

Table 2. Specific activity of molybdenum-99 [GBq/g Mo].

Irradiation duration	Experiment (E)	Calculation (C)	C/E
7 days	85±11	82±1	0.96

The uncertainty for the experimental result of molybdenum-99 specific activity was based on the difference of the experimental data, obtained by irradiating trioxide molybdenum in the central irradiation channel of the reactor core from September, 2023 to February, 2024. It is clear, acceptable agreement was obtained between the measured and calculated data, allowing the model to be used for other calculations.

Numerous calculations have shown that for the standard irradiation channel of the WWR-K reactor it is not possible to optimize the irradiation conditions for molybdenum with increased specific activity. Based on this, it was proposed to change the design of the WWR-K reactor core and install an irradiation device in the center of the core, around which there are six beryllium blocks. The irradiation device is a hexagon with a hole for the capsule. The irradiation capsule is located in the center of the horizontal plane of the WWR-K reactor core. This device allows to increase the thickness of the neutron moderator material. The computational model of the proposed WWR-K reactor core is shown in Figure 4.

In the first option of the irradiation device design, the space between the hexagonal aluminum surface and the hole is filled with beryllium pebbles and water. The capsule with a quartz ampoule containing MoO_3 powder is also filled with beryllium pebbles and water. The filling density of beryllium pebbles is 1.11 g/cm^3. The figure 4(b) illustrates proposed capsule design (PCD) with homogenous material which consists of beryllium pebbles and water.

In the second option of the irradiation device design, the space between the hexagonal aluminum surface and the hole is filled with ceramic aluminum oxide (Al_2O_3) pebbles and water. A capsule with a quartz ampoule containing 10 g of MoO_3 powder is also filled with Al_2O_3 pebbles and water. The Al_2O_3 filling density is 2.382 g/cm^3.

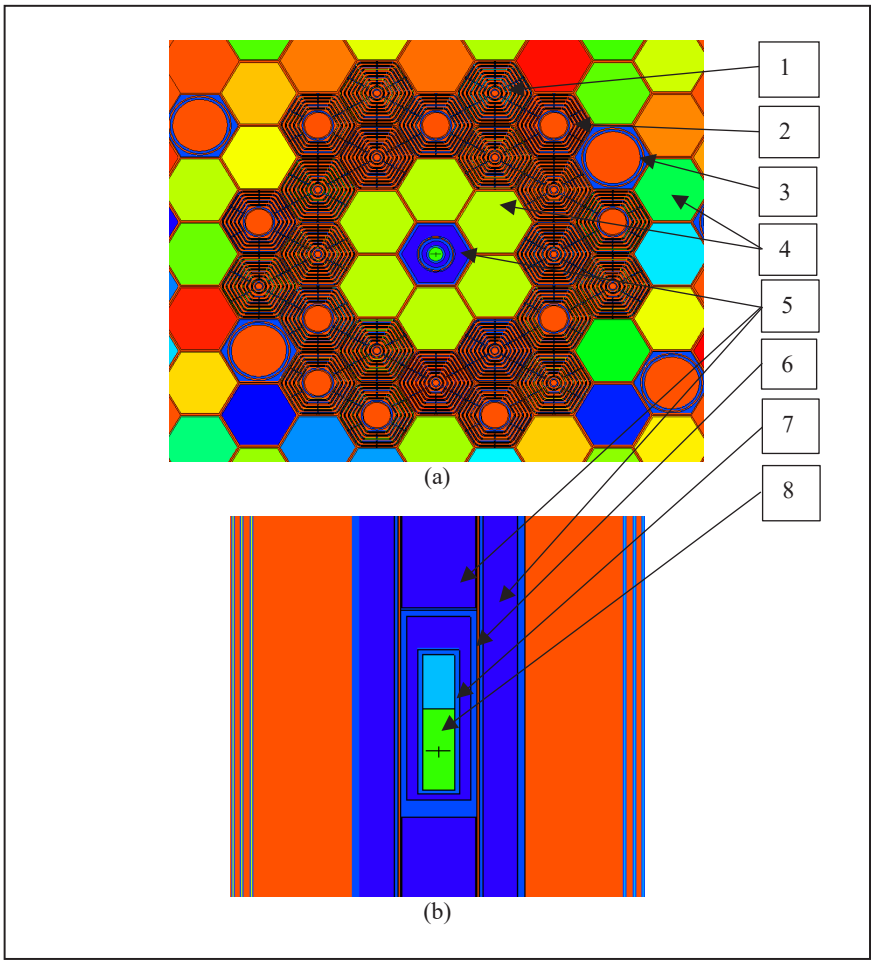

Fig. 4. MCNP model of the modernized WWR-K core with 6 beryllium blocks: (1) fuel assembly type 1, (2) fuel assembly type 2, (3) irradiation channel, (4) beryllium block, (5) neutron moderator filling, (6) irradiation capsule, (7) quartz ampoule, (8) MoO_3.

3 Results and Discussion

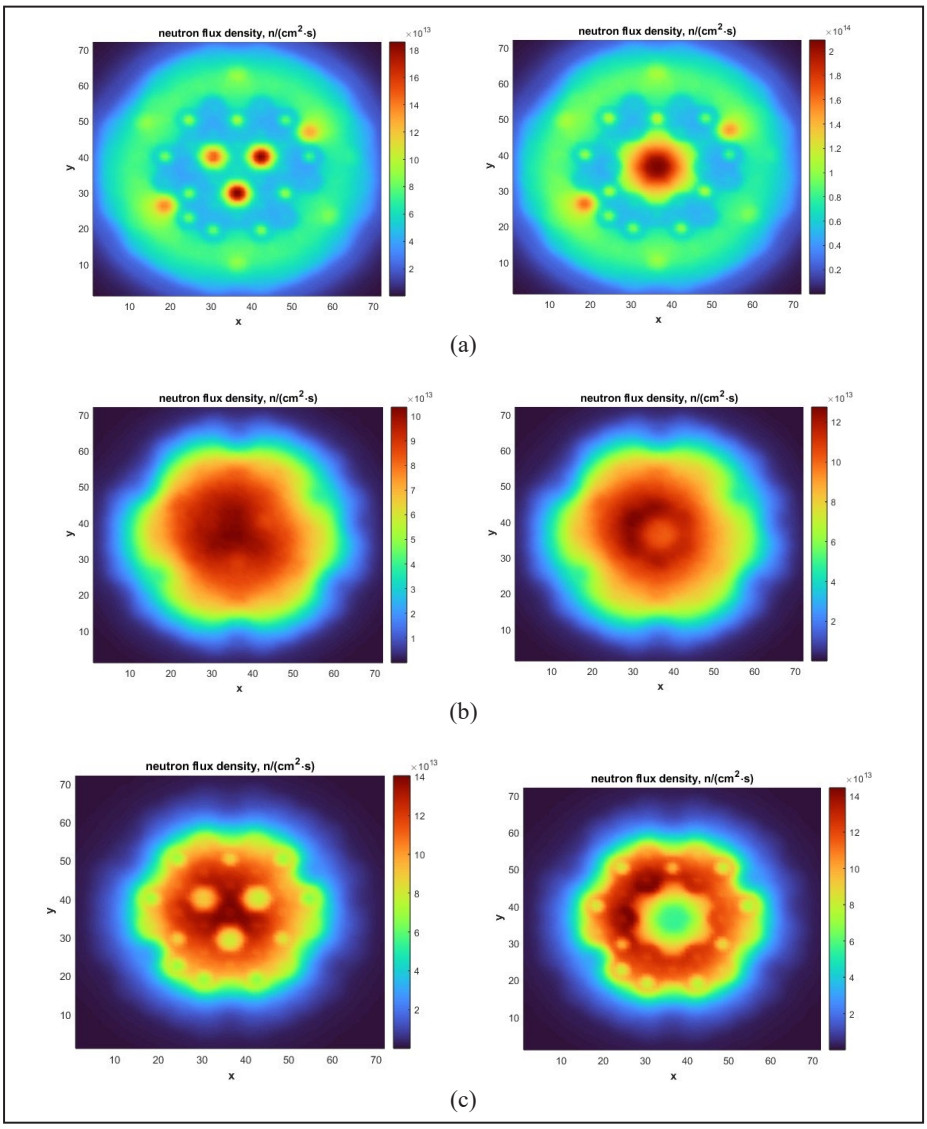

Fig. 5. Distribution of neutron flux density over the reactor core, on the left - for the current core, on the right - for the modernized core: (a) - thermal neutrons E < 6.25 eV, (b) - epithermal neutrons and fast neutrons E> 0.1 MeV.

Figure 5 demonstrates the distribution of neutron flux of various energies along the center of the horizontal plane for the current core and the modernized core with 6 beryllium blocks in the center. This figure shows an increase in thermal neutrons in the central irradiation position.

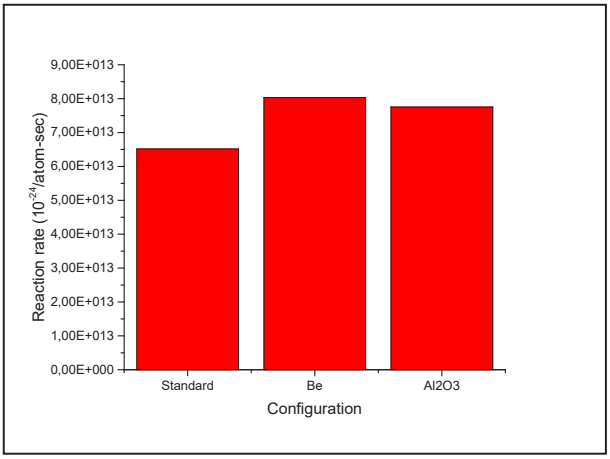

Fig. 6. Reaction rates in MoO_3 for different fillings.

Figure 6 shows the reaction rates for producing molybdenum-99 for the standard capsule design (SCD), and the first and second options of irradiation designs. From this figure we can see the maximum value of the reaction rate at for aluminum oxide was 7.75 x 10^{13} per molybdenum atom per second, for beryllium – 8.03 x 10^{13}. The relative deviation of the reaction rate calculations was 1.5%.

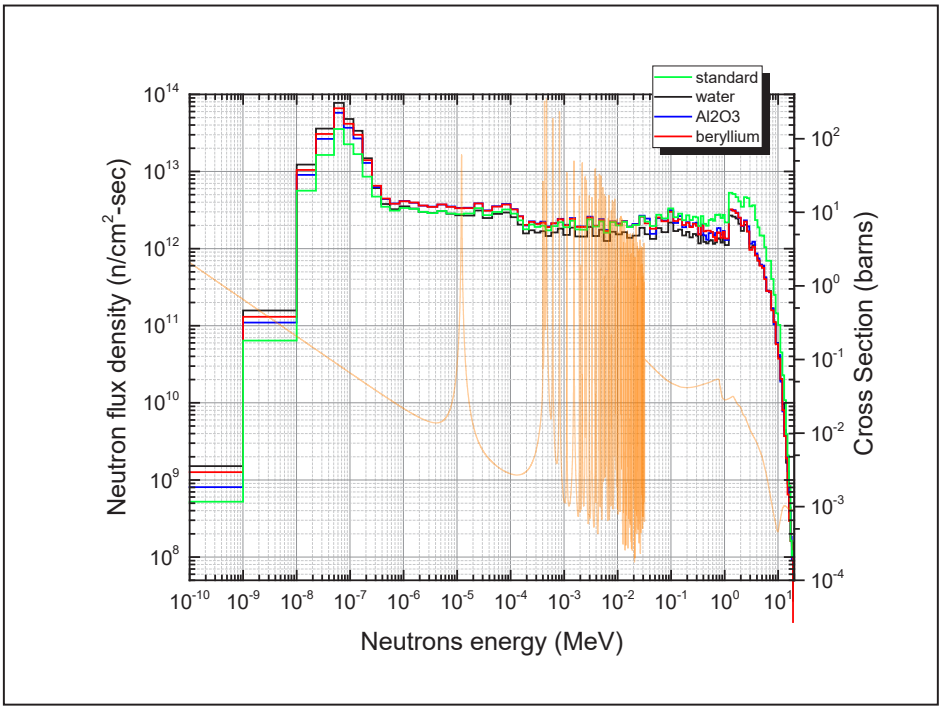

Fig. 7. Logarithmic diagram of superposition of neutron flux in modernized core with different fillings and SCD on cross section of $^{98}Mo(n,\gamma)^{99}Mo$ reaction.

Figure 7 illustrates the neutron flux for the 100 group neutron spectrum on a MoO_3 target for various designs with and without shields, as well as a standard capsule.
The increase in the reaction rate with beryllium is associated not only with the moderating ability of the material, but also due to an increase in neutrons due to the photoneutron reaction (γ,n) and the neutron multiplication reaction (n,2n), as shown in Figure 7.

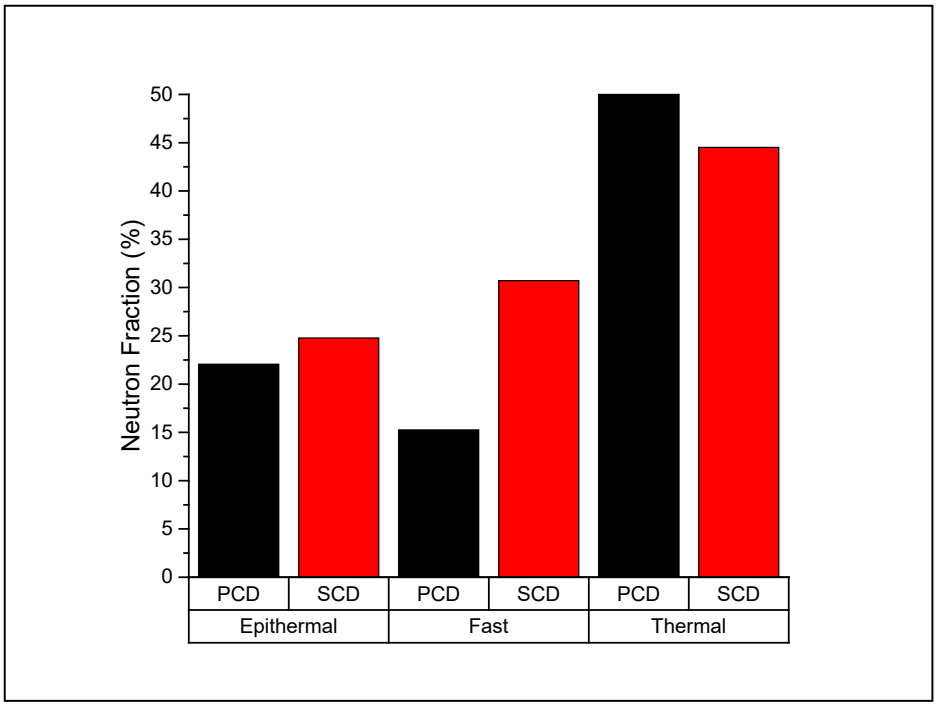

Fig. 8. Neutron fractions in PCD and SCD.

Figure 8 shows that the proposed optimization of irradiation conditions in a beryllium-filled design (PCD) leads to an increase in the fraction of thermal neutrons (E < 9 eV) by 18% and a slight decrease in the fraction of epithermal neutrons by 3% (9 eV < E < 0.11 MeV), and the share of fast ones (E > 0.11 MeV) decreases by 15%. Although Figure 7 shows that the flux of epithermal neutrons in the structure with beryllium filling is approximately 5% greater than in the standard one.

The activity levels of molybdenum-99 were calculated in a 10 g sample of molybdenum trioxide, both with and without beryllium and aluminum oxide fillings, after 7 d of irradiation in the WWR-K reactor core (Figure 4). Figure 9 illustrates the production dynamics of molybdenum-99.

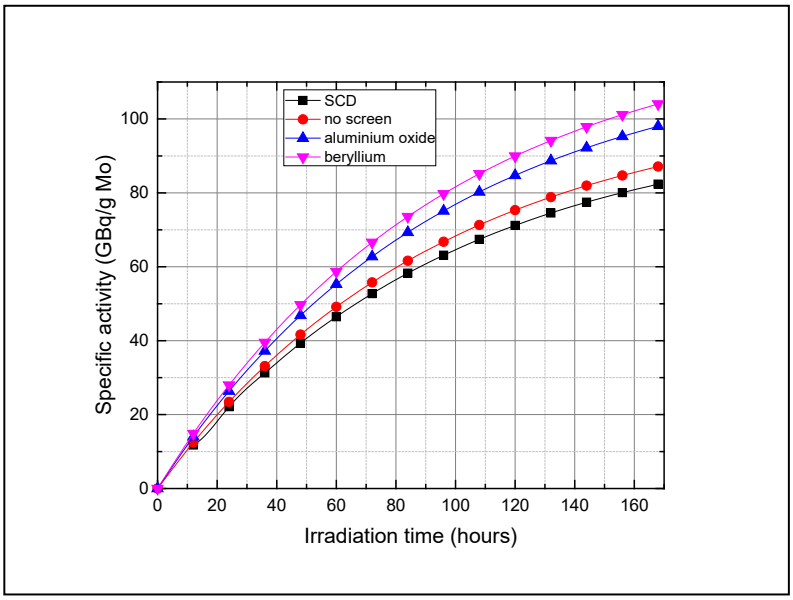

Fig. 9. Dynamics of molybdenum-99 production irradiating natural molybdenum over 7 d in modernized core and SCD.

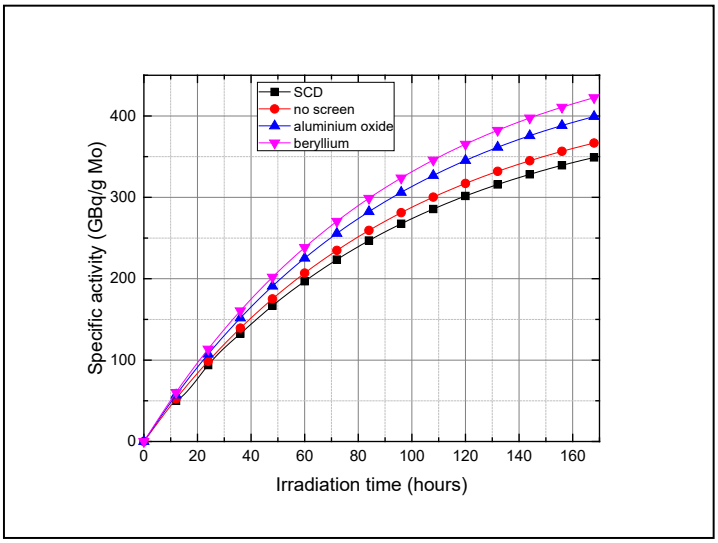

Fig. 10. Dynamics of molybdenum-99 production irradiating enriched molybdenum over 7 d in modernized core and SCD.

From Figures 9 and 10 it is clear that for natural molybdenum, the use of aluminum oxide filling with maximum neutron irradiation over 7 days made it possible to obtain molybdenum-99 with a specific activity of ~ 98 GBq/g, and with a beryllium screen – 104 GBq/g, without a screen – 92 GBq/g; for enriched molybdenum with aluminum oxide – 399 GBq/g, with beryllium – 422 GBq/g.

4 Conclusions

Therefore, optimizing the irradiation conditions for natural molybdenum in the WWR-K reactor has successfully increased the specific activity of produced molybdenum-99 from 82 GBq/g to 102 GBq/g, and for enriched molybdenum – from 335 GBq/g to 420 GBq/g. This enhancement leads to a decrease in production costs per unit of specific activity for molybdenum-99. Subsequently, this may lower the cost of the final product, a crucial outcome given that molybdenum-99 serves as the precursor for a socially significant radiopharmaceutical.

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References

[1] Verbeek P. Report on molybdenum-99 production for nuclear medicine 2010–2020. AIPES Report, November (2008). https://www.oecd-nea.org/med-radio/docs/200902_AIPESMolySupplyReport.pdf
[2] IAEA (2015). Feasibility of producing molybdenum-99 on a small scale using fission of low enriched uranium or neutron activation of natural molybdenum. Technical reports series, in Technical Report Series No. 478. Vienna, Austria: International Atomic Energy Agency. Available at: https://www.pub.iaea.org/MTCD/Publications/PDF/trs478web-32777845.pdf.
[3] Arinkin, F.M., Shaimerdenov, A.A., Gizatulin, S.K. et al. Core Conversion of VVR-K Research Reactors. At Energy 123, 17–24 (2017). https://doi.org/10.1007/s10512-017-0294-0
[4] Chakrova, E., Bannykh, V., Chakrov, P., Kutepov, V., & Fetssov, I. (2015). Technology for Production of Portable TC-99M Gel Generators Using Neutron Activated Natural Molybdenum Almaty, Republic of Kazakhstan [Country report: Kazakhstan]. International Atomic Energy Agency (IAEA): IAEA.
[5] G. E. Kodina, R. N. Krasikova, Methods of obtaining radiopharmaceuticals and radionuclide generators for nuclear medicine: a textbook for universities, Publishing House of MEI, Moscow (2014).
[6] 98.7% enriched in ^{98}Mo, spectroscopic grade, > 99.9% chemical pure, Center of Molecular Research, 2021.
[7] Gurin, A., Chakrova, Y., Matveyeva, I. et al. Analysis of molybdenum-99 production at the WWR-K research reactor. J Radioanal Nucl Chem (2024). https://doi.org/10.1007/s10967-024-09410-z
[8] Barling, J., Yang, J., Crystal Liang, YH. (2018). Molybdenum Isotopes. In: White, W.M. (eds) Encyclopedia of Geochemistry. Encyclopedia of Earth Sciences Series. Springer, Cham. https://doi.org/10.1007/978-3-319-39312-4_219.
[9] Toth, James J, Greenwood, Lawrence R, Soderquist, Chuck Z, Wittman, Richard S, Pierson, Bruce D, Burns, Kimberly A, Lavender, Curt A, Painter, Chad L, Love, Edward F,

and Wall, Donald E. Production of Molybdenum-99 using Neutron Capture Methods. United States: N. p., (2011). Web. doi:10.2172/1004126.
[10] Werner, Christopher John, Bull, Jeffrey S., Solomon, C. J., Brown, Forrest B., McKinney, Gregg Walter, Rising, Michael Evan, Dixon, David A., Martz, Roger Lee, Hughes, Henry G., Cox, Lawrence James, Zukaitis, Anthony J., Armstrong, J. C., Forster, Robert Arthur, and Casswell, Laura. MCNP Version 6.2 Release Notes. United States: N. p., (2018). Web. doi:10.2172/1419730.
[11] Brown DA, Chadwick MB, Capote R, Kahler AC, Trkov A, Herman MW end et. al., (2011). ENDF/B-VII.1 Nuclear Data for Science and Technology: Cross Sections, Covariances, Fission Product Yields and Decay Data. Nuclear Data Sheets. 112:2887-2996.
[12] Plaster, D. M., Santoro, R. T., and Ford, III, W. E. 1975. "Coupled 100-group neutron and 21-group gamma-ray cross sections for EPR calculations". United States. https://doi.org/10.2172/4208056. https://www.osti.gov/servlets/purl/4208056.
[13] J. E. Sweezy, T. E. Booth, F. B. Brown, J. S. Bull, R. A. Forster III, J. T. Goorley, H. G. Hughes III, R. L. Martz, R. E. Prael, A. Sood, A. J. Zukaitis, R. C. Little, H. R. Trellue, M. C. White, M. B. Lee, S. M. Girard. MCNP - A General Monte Carlo N-Particle Transport Code, Version 5 - Volume 2: User's Guide. Los Alamos National Laboratory Tech. Rep. LA-CP-03-0245 (Revised 2/1/2008).