RERTR 2008 — 30th INTERNATIONAL MEETING ON REDUCED ENRICHMENT FOR RESEARCH AND TEST REACTORS

October 5-9, 2008
Hamilton Crowne Plaza Hotel
Washington, D.C. USA

RADIOLYSIS EFFECTS ON MOLYBDENUM OXIDATION STATE AND RECOVERY FROM AQUEOUS-HOMOGENEOUS-REACTOR FUEL

Artem Gelis, Sergey Chemerisov, Allen Bakel, and George Vandegrift
Chemical Sciences and Engineering Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439 USA

ABSTRACT

As part of our R&D in the area of Aqueous Homogeneous Reactor design for the ^{99}Mo production, we are investigating the effects of radiation on the recovery of ^{99}Mo from the irradiated solution. An effect of high energy, 3 MeV, electron irradiation on the Mo sorption behavior has been studied. The nitric acid solutions containing 235 g-U/L at pH=1.05 were spiked with ^{99}Mo. The solutions were irradiated at two doses of 109 kGy and 218 kGy and then passed through the alumina containing columns. According to the obtained data, the irradiation causes a significant increase in the ^{99}Mo concentration in the column effluents through the alumina sorbent. One of the possible explanation of the observed effect is the reduction of Mo(VI) to Mo(V) species that have lower distribution coefficients on this sorbent.

1. Introduction

The primary method for a production of ^{99}Mo/^{99m}Tc generator is irradiation of uranium targets. Uranium-235 in the targets in nuclear reactors undergoes fission reactions yielding ^{99}Mo among other fission products. The use of Aqueous Homogeneous Reactors (AHRs), or solution reactors, presents an attractive alternative to the conventional target irradiation method of producing ^{99}Mo in that solutions eliminate the need for targets and can operate at much lower power than required for a reactor irradiating target reactor to produce the same amount of ^{99}Mo.Radiation is known to affect the chemical behaviour of solutions. The work described here is particularly concerned with the redox behaviour of Mo in the. The product Mo is separated from U and other fission products as the MoO_4^{2-} ion. Reduction of Mo(VI) to Mo (V) is of concern in this context because the reduced Mo ion is not efficiently captured by the ion exchange method used.

The radioactivity of the aqueous fuel is quite high. After 5-7 days of the fission, it is dominated by the short-lived beta-gamma emitting fission products with a wide range of the particle energy.

2. Results and Discussions

Because both nitric and sulfuric acids were considered as a solution medium of the homogeneous reactor, our experiments included both. The solutions were irradiated using a Van De Graaff linear accelerator with the electron energy of 3 MeV. The experimental work was started with the static sorption tests using Termoxid-52 ion exchanger. The dose was calculated to be 53 kGy (5.3 MRad) using a procedure described in [1]. The sorption tests were conducted in 2-3 hours following the irradiation. The tests were done in the presence of uranium and without it. The experimental scheme is shown in Figure 1.

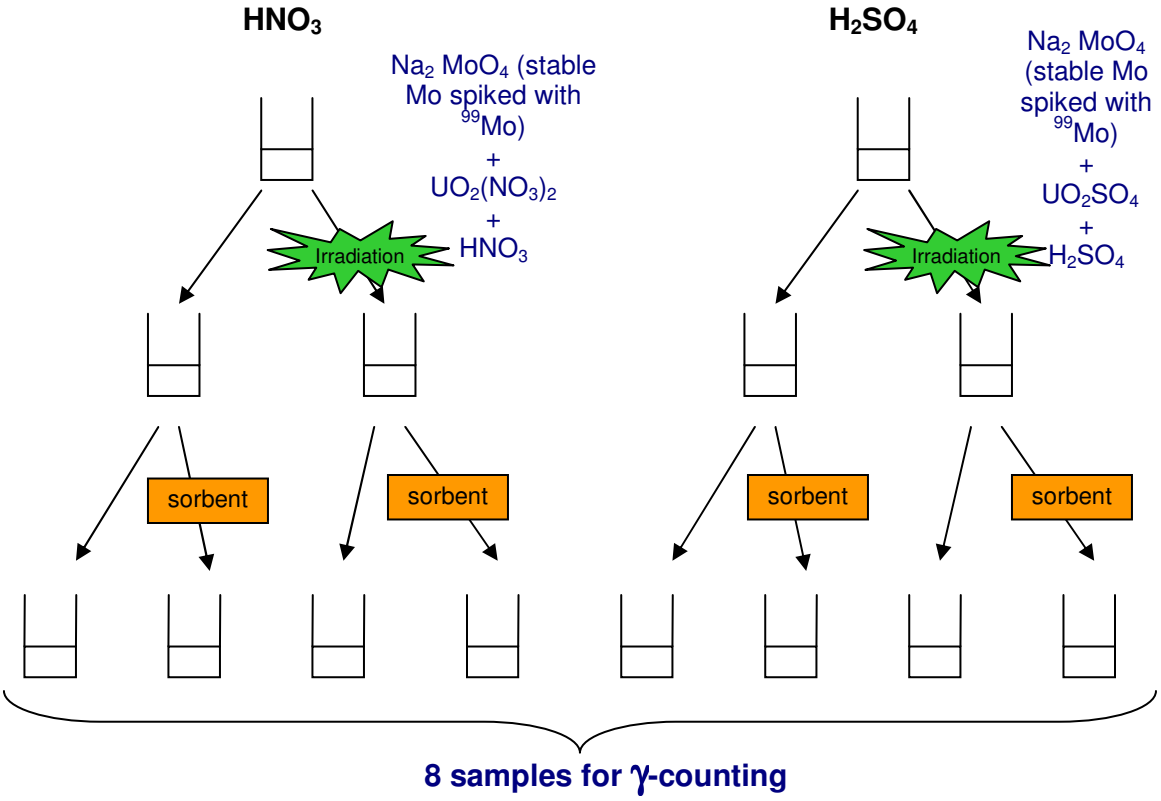


Figure 1. The experimental scheme of the irradiation tests with ^{99}Mo

The distribution ratio, K_d was calculated according to the formula:

$$K_d = \frac{A_0 - A_S}{w} / \frac{A_S}{V}$$

Where:

A_0: ^{99}Mo activity before sorption

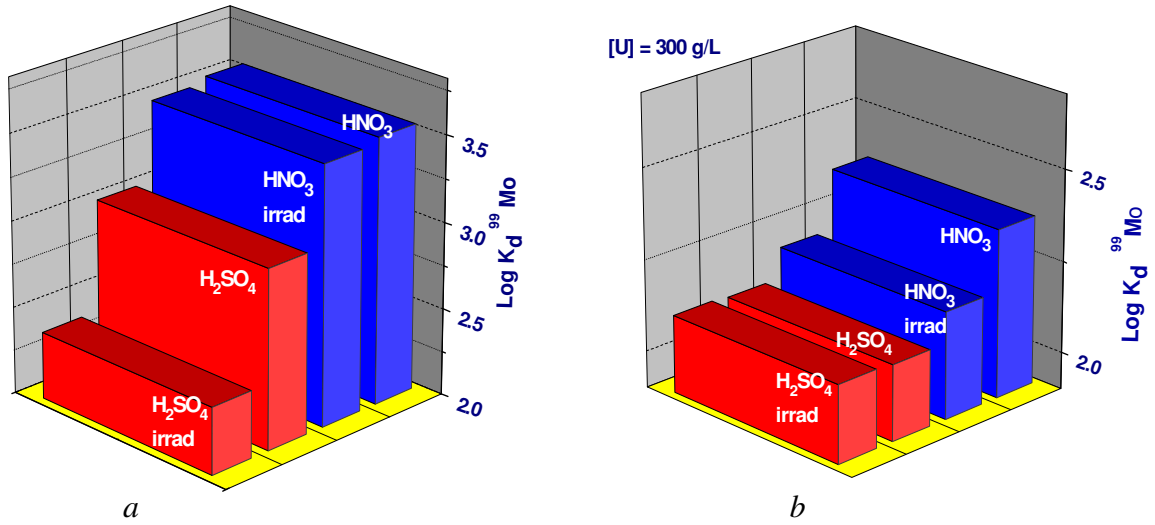
A_S: ^{99}Mo activity after sorption

w: weight of sorbent, g

V: volume of solution in contact with the sorbent, mL.

After the sorption, the solutions were filtered through Whatman paper disk filters. Duplicate aliquots of the solution were taken for gamma counting on a Ge well-type detector. The deviation between the duplicate samples was well-below 1% in all cases.

The total concentration of Mo(VI) was 10 mg/L; when uranium was added to the solutions its concentration was 300 g/L, pH was about 1.0. No change in the pH of the solutions was observed in the course of the irradiation. The results are presented in Figure 2*a* and 2*b*.



a *b*

Figure 2. The measured Kd values for irradiated and nonirradiated solutions: effect of the 3 MeV electron irradiation on the Mo sorption on Termoxid-52: *(a)* without uranium and *(b)* with 300 g/L of uranium

The Mo sorption in nitric acid without $UO_2(NO_3)_2$ is not affected by irradiation. However, in the presence of 1.26 M $UO_2(NO_3)_2$ (300 g-U/L), the distribution ratios decrease for both irradiated and non-irradiated solutions, and K_d is somewhat lower for the irradiated solution- 155 vs. 230.

In sulfuric acid the irradiation causes a decrease of K_d from ~1100 to 240. The presence of 1.26 M UO_2SO_4 eliminates the difference between two solutions, dropping the distribution ratios down to near 130 in both cases.

The decrease of K_d in the uranium-free sulfuric acid solutions can be explained by partial reduction of hexavalent Mo to a lower oxidation state, resulting in a formation of Mo(V) species, which has lower partitioning coefficients on an anion exchanger. The same reduction probably occurs in the nitric acid solutions, but Mo(V) could be quickly oxidized by NO_3^- groups. This

re-oxidation is likely time dependent and might have occurred during the time between the irradiation and the beginning of the sorption tests.

The most stable oxidation state of Mo in solution is (VI), but its speciation is very complex. The literature data are insufficient and contradictory in places [**2**]. At pH less than 0 (> 1 M acid concentration), MoO_2^{2+} is the major species, while at pH above 2, poly-nuclear Mo-O anionic species prevail. So, there is a poorly defined mixture of the Mo complexes at pH 1.

The redox potential of the Mo(VI)/Mo(V) couple at pH=0 is 0.50 V [2], and so Mo(VI) could be reduced by a strong reducing agent as a hydrogen radical, formed during the radiolysis of water in the acidic region.[3] The speciation of Mo(V) is even less studied than the Mo(VI) speciation, but it is likely that Mo(V) exists in the cationic form of $Mo_2O_4^{2+}$, which does not adsorb on the anion exchanger.[2]

In the cases when uranium salts are present, the concentrations of SO_4^{2-} and NO_3^- are 1.26 M and 2.52 M, respectively. These anions compete with anionic Mo species for the active sites of the anion exchanger resulting in decreasing the Mo partitioning coefficients.

To prevent possible re-oxidation of the Mo species, the following sorption tests were done under irradiation. The nitric acid solutions containing 235 g-U/L at pH=1.05 were spiked with ^{99}Mo. The solutions were irradiated at two doses of 109 kGy (10.9 MRad) and 218 kGy (21.8 MRad). The columns were filled with acidic alumina Al_2O_3 (Bio Rad 100-200 mesh). The experimental setup is shown in Figure 3.

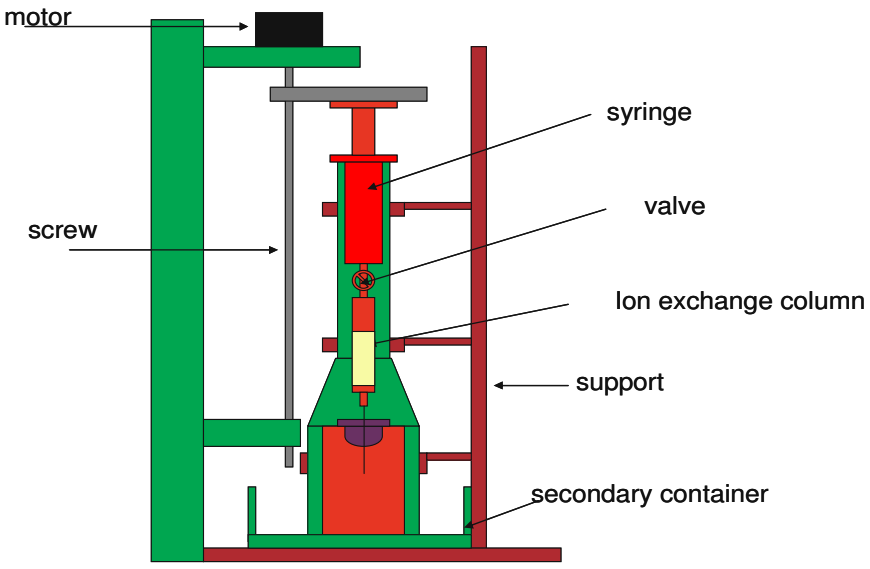


Figure 3. The column irradiation setup.

The solutions were irradiated while in the syringe for 45 min with the valve closed. After stopping the beam, the valve was opened, and the motor was turned on to move the irradiated solution out of the syringe and onto the column. The irradiation continued for 15 minutes needed

to pass the solutions through the column. The temperature was maintained at 60 ºC using a heat gun for all the tests. Some experimental details and the results are presented in Table 1.

Table 1. The ^{99}Mo activity in the effluent- irradiation effect

Test #	1	2	3	4
Weight of Alumina, g	2.641	2.647	1.509	1.495
Dose, kGy	no irradiation	109	no irradiation	218
Activity of ^{99}Mo in the effluent, %	2.4	4.9	15.6	27.7

According to the data, the irradiation causes a significant increase in the ^{99}Mo concentration in the effluent through the alumina sorbent in nitric acid – uranyl nitrate solutions. This is interpreted as evidence of partial reduction of Mo(VI) to Mo(V) during irradiation. As a next step, the column irradiation tests will be conducted with Termoxid-5M and 52 sorbents.

3. Acknowledgement

The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

Work supported by the U.S. Department of Energy, National Nuclear Security Administration's (NNSA's) Office of Defense Nuclear Nonproliferation, under Contract DE-AC02-06CH11357.

4. References:

[1] Draganić I. "Oxalic acid: the only aqueous dosimeter for in-pile use" Nucleonics 21, 2, (1963) p. 33

[2] Holleman-Wiberg "Inorganic Chemistry", Academic Press 1995, p. 1385

[3] Spinks and Woods "Introduction to Radiation Chemistry", J. Wiley and Sons, 1990, p. 262