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Dose Rate Calculations and Van-de-Graaff Irradiations for Testing Radiation Stability of Materials and Equipment

V. Makarashvili, S. Chemerisov, P. Tkac, G. F. Vandegrift, S. Zaijing, K. J. Quigley
Chemical Sciences and Engineering Division
Argonne National Laboratory, 9700 S. Cass. Ave. Argonne IL 60439

ABSTRACT

Dose rates and integrated total doses to various components (cameras, bottles, syringe and valve controllers, etc.) of the Mo-99 production experimental and commercial systems have been calculated in order to assess the radiation stability and reliability of those systems. The calculations have been performed using Monte Carlo particle transport code – MCNPX. The modeling results have been used as guidance to set up experiments at the Van-de-Graaff accelerator facility at Argonne to deliver desired doses (or dose rates) suggested by the calculations for a given source of Mo99/Tc99m. The low energy (3 MeV) Van-de-Graaff accelerator provides the capability of delivering high levels of electron/photon dose rates to critical components without presenting activation and handling hazards of the irradiated targets. The functionality of the irradiated critical components is monitored during and after the irradiations. Modeling and experimental results of our work are presented in this paper.

1. Introduction

At the Chemical Sciences and Engineering (CSE) Division of Argonne National Laboratory (ANL), experimental work is being conducted in order to support two private entities - NorthStar Medical Radioisotopes and SHINE Medical Technologies to establish accelerator-based Mo-99 production techniques. Mo-99 is a parent isotope of Tc-99m, which is widely used in various diagnostic medical imaging procedures. The work is supported by National Nuclear Security Administration's (NNSA) Global Threat Reduction Initiative (GTRI) to facilitate the establishment of a reliable domestic supply of Mo-99 for nuclear medicine while also minimizing the civilian use of high enriched uranium (HEU). NorthStar is pursuing an accelerated-based photo-nuclear approach exploiting Mo-100(γ, n)Mo-99 reaction on a metallic target, while SHINE plans to use accelerator driven D-T neutron source to produce Mo-99 as a fission product in a sub-critical uranyl-sulfate solution with low enriched uranium (LEU, < 20% enriched in U-235).

Both projects involve investigating and testing critical experimental equipment and materials for radiation hardness and stability. The low energy (3 MeV) Van-de-Graaff accelerator at the CSE Division serves this purpose. It is capable of delivering high levels of electron/photon dose rates to critical components without presenting activation and handling challenges. The desired dose levels are predicted using Monte Carlo particle transport code – MCNPX. Calculation results and experimental work for various Van-de-Graaff irradiations are presented in this paper.

2. MCNPX Modeling and Van-de-Graaff Irradiations

2.1. Alpha-Benzoin Oxime (ABO) irradiation

Precipitation of Mo-99 with alpha-benzoin oxime (ABO) is an important step in the LEU-Modified Cintichem purification process [1-2]. Primary concern is that ABO will radiolytically break down due to Mo-99 decay and the Mo recovery yield will decrease. In order to test this, the Van-de-Graaff accelerator was used to irradiate Mo-ABO precipitates at doses equivalent to more than 100 kCi of Mo-99.

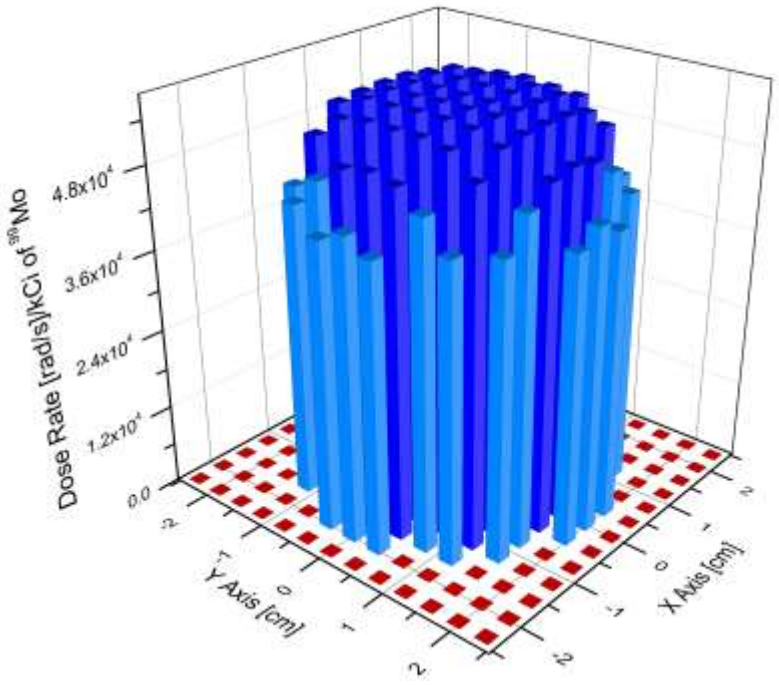

Figure 1. MCNPX dose rate results for the glass bead geometry

Two scenarios of ABO and Mo-99 complex were simulated with MCNPX [3] in order to determine the absorbed dose in ABO during the approximately 20 min processing time of this step with 1 kCi Mo-99 being processed. This simulation provided a link between Mo-99 activity and dose in ABO, which allowed us to correlate Mo-99 recovery with activity. Both

simulated geometries assumed total of 400 mg of ABO, which corresponds to a realistic mass during the separation process. The first scenario was modeled as two layers of glass beads (4-mm-diameter each) with a thin (around 46 μm) layer of Mo-ABO precipitate around each bead. The second geometry was much simpler--a single layer (about 204-μm-thick) Mo-ABO precipitate on top of a frit. The simulations gave 76.2 MRad and 148.3 MRad doses for the glass bead and the mono layer geometries, respectively. These two models represent two extremes of a realistic situation, when some of the precipitate would be deposited on the glass beads and some on the frit as a single layer. Therefore, a realistic 20 min dose in ABO from a 1 kCi Mo-99 source should be inside the range of doses provided by this simulation study. Simulation results for the glass bead geometry are presented in **Figure 1**.

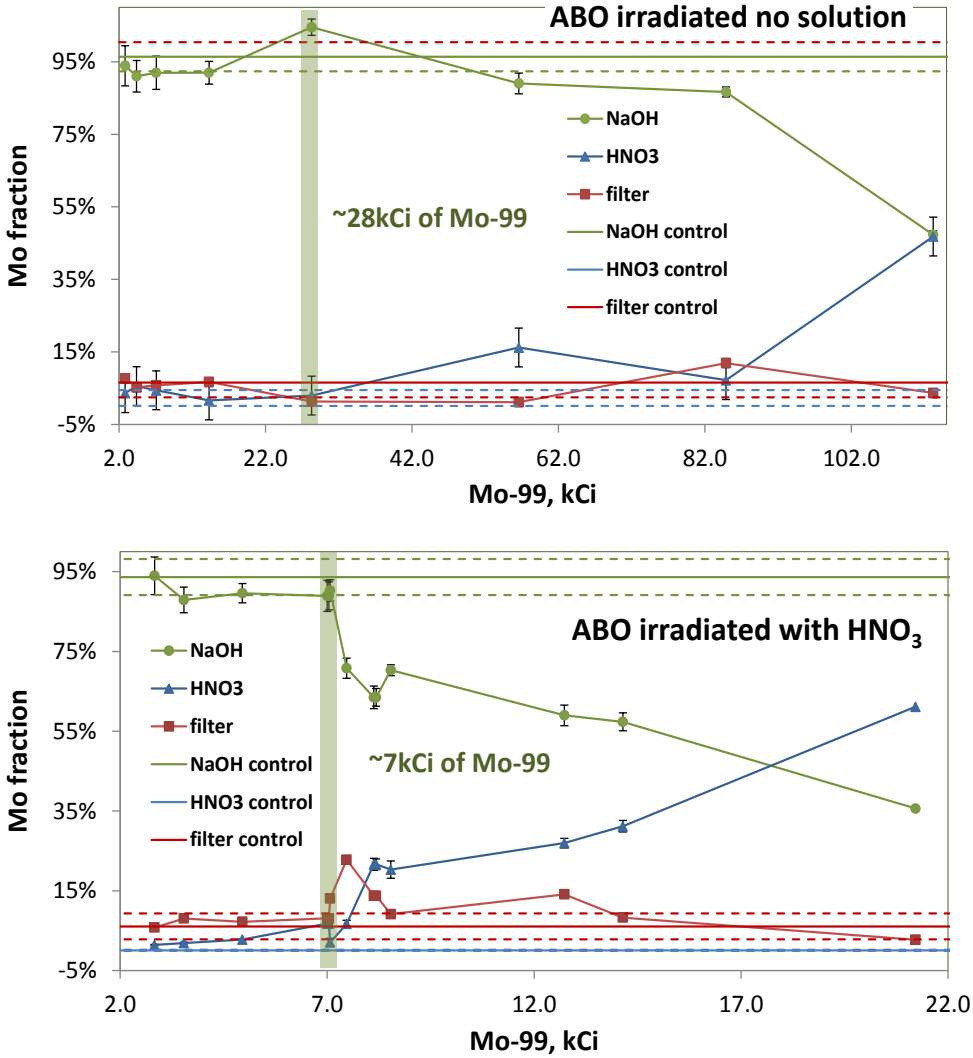

Figure 2. Mo recovery results for Mo-ABO irradiations with and without the presence of 0.1 M nitric acid.

Results of the radiation stability studies of Mo-ABO precipitate with and without the presence of nitric acid are shown in **Figure 2**. These studies were performed to investigate if intensive washing of ABO precipitate in the LEU Modified Cintichem process with 0.1 M HNO3 could somehow affect the recovery of

Mo-99 if several kCi of Mo-99 are processed. It was observed that when 0.1 M HNO3 (200uL) was present during the irradiation, it significantly affected the radiation stability of Mo-ABO complex. Mo recovery stayed unaffected up to 4.2 GRad (equivalent to 28 kCi for the conservative mono-layer case) without the nitric acid, while a significant drop in recovery was observed above 1 GRad (about 7 kCi) for the case when nitric acid was present during the irradiation. After washing the precipitate with 0.1 M HNO3, solution turned yellow indicating presence of some decomposed ABO precipitate. However, it should be noted that during normal processing, several portions of fresh 0.1 M nitric acid are used to wash ABO precipitate, and therefore, nitric acid and its radiolytic products are in contact with the precipitate for only a short period of time.

2.2 Radiolytic stability of the ABEC column

A key reagent of the TechneGen generator (NorthStar) is ABEC column that consist of polyethylene glycol (PEG) bonded to a polystyrene-divinylbenzene co-polymer bead. The ABEC column is highly selective for the pertechnetate ion under highly alkaline conditions, while molybdenum passes through the column. This study was focused on determining if radiolysis of the ABEC column used multiple times in 20-Ci (Mo-99) generator could affect the recovery of technetium due to a radiolytic degradation of PEG.

Monte Carlo calculations have been performed using MCNPX to estimate doses delivered to a 1.6 mL ABEC column during seven loadings (one every day) of a TechneGen generator with 20 Ci (at the first day) of Mo-99 in a 20 mL solution of 5 M KOH (1Ci of Mo-99/mL). The dead volume of the ABEC column was determined to be around 250 μL (15-16%). Based on the dead volume, 250 mCi (first loading) of Mo-99 was uniformly distributed as a source in the entire column. On the other hand, all 20 Ci of Tc-99m source was placed at the top third portion of the column. A schematic description of the simulation model is presented in **Figure 3.**

Integrated doses for a total of seven loadings were calculated and the results are presented as a pie chart in **Figure 4**. The chart shows 2.737 kGy, 0.036 kGy, and 0.73 kGy from Mo-99 beta and gamma and Tc-99m gamma cumulative doses, respectively. This amounts to the total dose of 3.5 kGy.

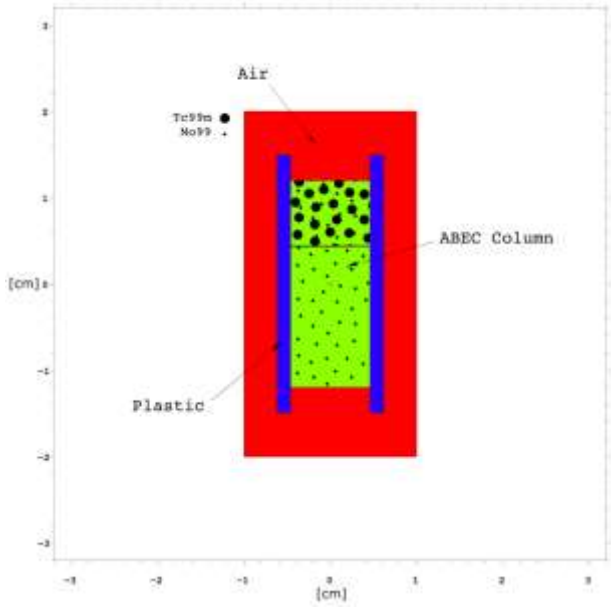

Figure 3. A schematic illustration of the ABEC column MCNPX geometry

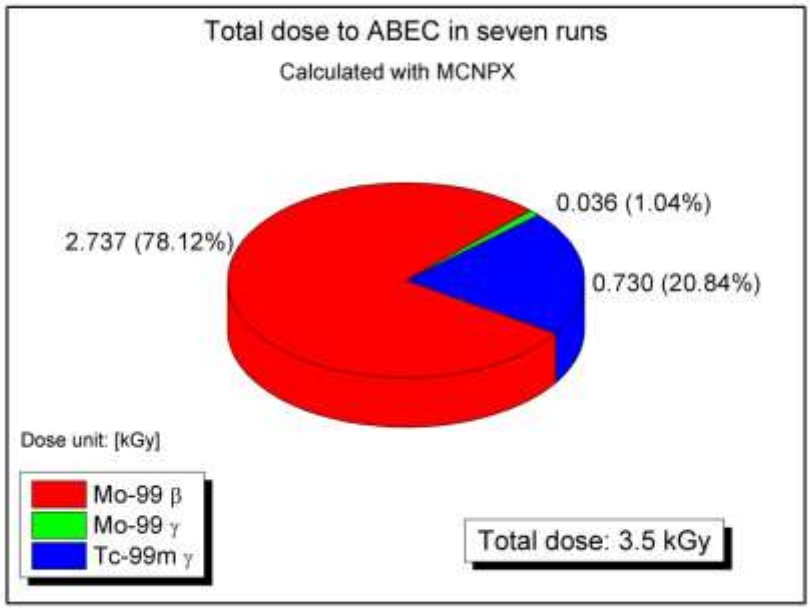

Figure 4. Cumulative doses of Mo-99 (beta & gamma) and Tc-99m (gamma) deposited as a result of seven consecutive loadings (one every day) of the ABEC column.

In order to check radiolytic stability of the resin, seven ABEC columns were irradiated at 5, 10, 20, 50, 100, 200 and 500 kGy using the Van de Graaff generator with continuous flowing of 5M KOH during the irradiation. The experimental setup is shown in **Figure 5**. It was observed that polyethylene glycol (PEG), which is an active component of the ABEC column, or its degradation products were partially eluting by KOH solution during the irradiation. However, the tests performed on irradiated resins by NorthStar have shown that even significantly higher doses than 3.5kGy did not affect the recovery of Tc-99m, and the content of Mo-99 in the product vial meet USP specifications.

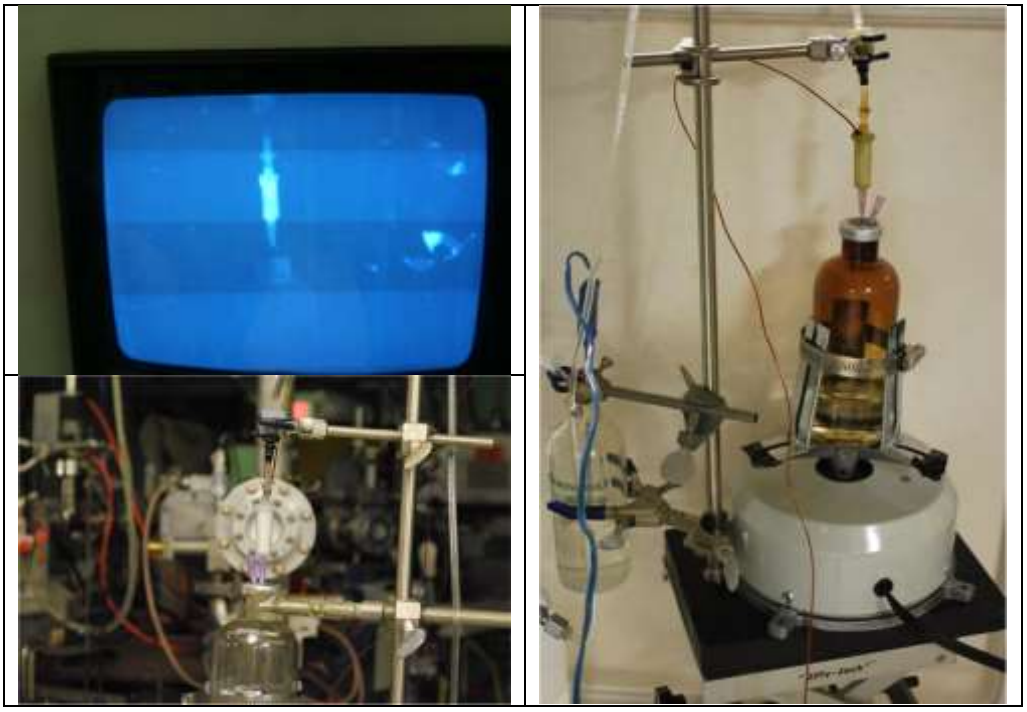

Figure 5. Setup for the ABEC column irradiations. During the irradiation, a solution of 5M KOH was flowed through the ABEC columns, and the columns were rotated to achieve an even dose rate throughout the column.

2.3 Irradiations of HDPE bottles

The NorthStar short-term plan for production of Mo-99 is to use the University of Missouri Research Reactor (MURR)in ColumbiaMissouri. Mo-99 will be produced using activation reaction Mo-98(n, γ)Mo-99 using enriched Mo-98 targets. There was a concern about the radiation stability of plastic HDPE bottles to be used to move the Mo product from the MURR recovery hot cell to the dispensing cell. Therefore, Argonne performed an experimental study to measure the radiation stability of HDPE bottles, which can be used to transfer ~450 Ci of Mo-99. The first part of the study was to calculate the dose the bottle will receive over period of two weeks with starting activity of 450 Ci of Mo-99. Then, the irradiation experiments were performed using the Van de Graaff electron accelerator.

MCNPX was used to model the dose absorbed in a high-density polyethylene (HDPE) container from a 450 Ci (1500 mL with 300 mCi/mL) Mo-99 source (in equilibrium with Tc-99m) in a 5 M KOH solution. Power (and dose) deposition was treated in separate simulations for beta and gamma radiation sources. Source particles were sampled uniformly inside the solution volume with appropriate energy distributions (continuous for beta and discrete energy lines for gamma). The weights for the source particles were set such that they matched the strength (particles/sec) of a 450 Ci Mo-99 source. Total heating (tally type 6 [MeV/g] per source particle) was converted to absorbed dose rate [rad/hr] and absorbed power [W] and were tallied for the solution, container body, and container cap. The absorbed dose rate results for the initial source activity (450 Ci) are summarized in **Table 1**.

Table 1. Dose rate results obtained from MCNPX

	Bottle	*Cap*	*Solution*
	Dose Rate [krad/hr]		
Mo-99 beta	21.0	3.9	164.5
Mo-99 gamma	9.9	2.4	37.5
Tc-99m gamma	3.5	0.8	24.5
Total	**34.4**	**7.0**	**226.6**

Decay corrected integrated absorbed dose in the HDPE bottle in two weeks of exposure time was also calculated for each source of radiation. This was done by multiplying **Table 1** values by $(1-\exp(-\lambda t))/\lambda$ where λ is the decay constant of Mo-99 and t is the decay period of two weeks. These results are presented in **Table 2**. Based on the dose rate results, the total dose to the bottle (from all sources) amounts to 3.17 Mrad.

Table 2. Total absorbed dose in the bottle

	Total dose in two weeks
	[Mrad]
Mo99 beta	1.94
Mo99 gamma	0.91
Tc99m gamma	0.32
Total	**3.17**

The setup for irradiation of HDPE bottles is shown in **Figure 6**. The dose rate delivered by 20 μA beam at 25" from the window was determined using oxalic acid dosimeter [4]. Three sets of bottles were irradiated at VDG and general information is listed in **Table 3**.

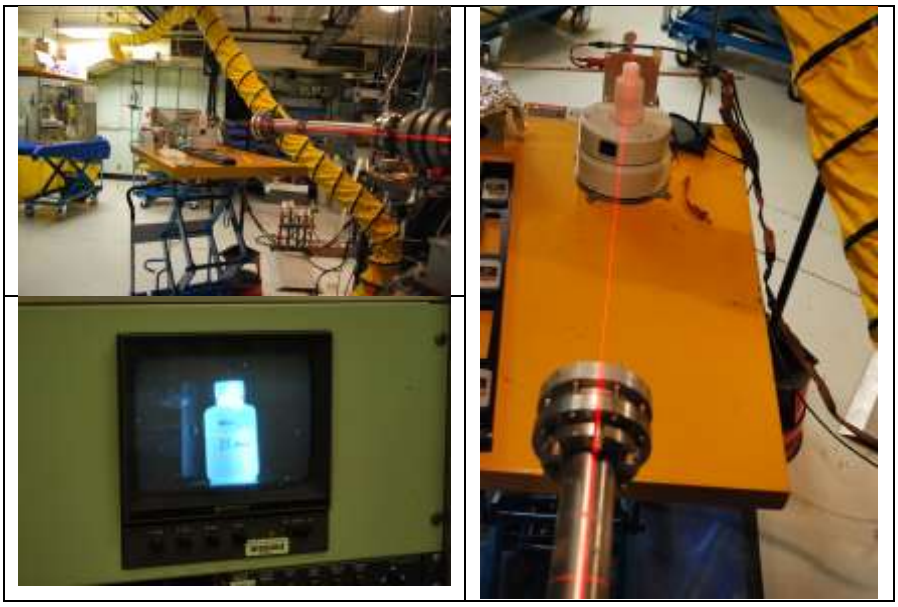

Figure 6. Setup for the irradiation of HDPE bottles. During the irradiation, bottles were filled with K_2MoO_4 in 5 M KOH (0.2 g-Mo/mL), and the bottles were rotated to achieve an even dose rate throughout.

Table 3. General information for HDPE bottle irradiation using VDG

#	Bottle	Brand (part number)	Mouth	K_2MoO_4 in 5M KOH	KNO_3
1	HDPE + PP cap	VWR (16059-068)	narrow	0.2g-Mo/mL	-
2	HDPE + PP cap	Nalgene (2002-0004)	narrow	0.2g-Mo/mL	-
3	HDPE + PP cap	Nalgene (312104-0002)	wide	0.2g-Mo/mL	0.12M

It should be noted that VWR bottles in experiment 1 (**Table 3**) were made of softer HDPE material than Nalgene bottles.

The bottles in Experiment 1 received doses of 0.124; 1.42; 3.31 and 15.35 MRad. Bottles in second irradiation received doses of 0.74; 1.46; 2.98 and 5.99 MRad. **Figure 7** shows the photograph of irradiated bottles from second irradiation.

As the irradiation time increases the coloration of bottles is obvious and was expected; however, the solution of K_2MoO_4 in 5 M KOH turned brown as well. Over time, brown precipitate has formed. The sample of brown precipitate was filtered through fine filter and extensively washed with deionized water. After washing, the precipitate was re-dissolved using 1:1 mixture of HCl/HNO_3 and submitted for ICP-MS analysis. The sample was tested for molybdenum and common impurities that could be present in starting material used to prepare Mo solution. ICP-MS analysis of the brown precipitate shows that major component was Mo (86.2%) indicating reduction of Mo(VI) to MoO_2.

Figure 7. Picture of irradiated HDPE bottles containing K_2MoO_4 in 5M KOH (0.2g-Mo/mL). Bottle on very left is non-irradiated bottle containing K_2MoO_4 in 5M KOH

Third set of irradiations was performed with wide mouth HDPE bottles containing 100 mL of K_2MoO_4 in 5 M KOH with 0.12 M KNO_3. The bottles received doses of 0.12; 0.74; 1.42; 2.2; 3.2; 6.5 and 14.6 MRad. Photograph of irradiated bottles is shown in **Figure 8**. Irradiated solutions remained colorless and no precipitate was observed even after prolonged time. Experiments showed that presence of oxidizer, such as KNO_3, is necessary to avoid reduction of Mo and formation of precipitate due to radiolysis.

Figure 8. Photograph of irradiated HDPE bottles containing K_2MoO_4 in 5 M KOH (0.2 g-Mo/mL) with 0.12 M KNO_3.

3. Conclusions

A number of Van-der-Graaff irradiation experiments have been performed to study radiation stability and performance for various parts and materials for the Mo-99 production systems. Results for the Mo-ABO precipitate, ABEC column and HDPE bottles were presented in this paper as a few good examples. Other irradiation studies include IR and OTR (Optical Transition Radiation) cameras for the NorthStar accelerator based photo-nuclear experiment as well as syringe and valve controllers for the TechneGen generator. It should be noted that MCNPX modeling of these experiments provides very useful link between the source activities and the corresponding dose rates (or total dose) that are chosen for each irradiation. Van-de-Graaff experiments coupled with MCNPX calculations prove to be a successful and valuable method to investigate radiation hardness and stability of different critical components. Low energy (3 MeV) and high dose rate of the Van-de-Graaff accelerator allows short irradiation times and safe, activation-free handling of the irradiated targets.

4. Acknowledgments

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5. References

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