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Invited Article

Development of Industrial-Scale Fission ^{99}Mo Production Process Using Low Enriched Uranium Target

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ABSTRACT

Molybdenum-99 (^{99}Mo) is the most important isotope because its daughter isotope, technetium-99m (^{99m}Tc), has been the most widely used medical radioisotope for more than 50 years, accounting for > 80% of total nuclear diagnostics worldwide. In this review, radiochemical routes for the production of ^{99}Mo, and the aspects for selecting a suitable process strategy are discussed from the historical viewpoint of ^{99}Mo technology developments. Most of the industrial-scale ^{99}Mo processes have been based on the fission of ^{235}U. Recently, important issues have been raised for the conversion of fission ^{99}Mo targets from highly enriched uranium to low enriched uranium (LEU). The development of new LEU targets with higher density was requested to compensate for the loss of ^{99}Mo yield, caused by a significant reduction of ^{235}U enrichment, from the conversion. As the dramatic increment of intermediate level liquid waste is also expected from the conversion, an effective strategy to reduce the waste generation from the fission ^{99}Mo production is required. The mitigation of radioxenon emission from medical radioisotope production facilities is discussed in relation with the monitoring of nuclear explosions and comprehensive nuclear test ban. Lastly, the ^{99}Mo production process paired with the Korea Atomic Energy Research Institute's own LEU target is proposed as one of the most suitable processes for the LEU target.

1. Introduction

With the invention of the scintillation camera by H.O. Anger in 1957, people started to analyze the table of isotopes searching for radionuclides that would be most suitable for nuclear medical *in vivo* application [1,2]. Among the existing 3,000 nuclides, technetium-99m (^{99m}Tc) turned out to be the most suitable nuclide. However, until the 1950s, very little was

known about the chemistry of technetium, because this is an artificial element that is practically not found in nature. Therefore, it was difficult to consider using ^{99m}Tc for a diagnostic isotope at that time.

There are three arguments that strongly support the use of [99m]Tc. First, the nuclear decay properties are ideal, because the energy (141 keV photon) is sufficiently high for penetrating the biological tissue delivering relative radiation dose to the patients. On the other side, the photon energy is sufficiently low for being adsorbed with high efficiency in a relatively thin sodium iodide (Na-I) detector used in the scintillation cameras at that time (SPECT later on). There is no other radionuclide that can compete with [99m]Tc. Second, ^{99m}Tc is available continuously based on the decay from its longer-lived mother isotope ^{99m}Tc, using the generator principle. The third aspect is a chemical aspect. In order to bring the ^{99m}Tc into a chemical form that allows it to bind to organic compounds, for instance, by complexation with corresponding ligands, one needs to reduce the primary +7 oxidation state down to +5, +3, or even to +1. Intensive research had been going on during the 1960s to solve this problem. There was a breakthrough at the end of the 1960s with the introduction of Sn^{2+} as reducing agent [3].

W.C. Eckelmann wrote: "On a practical level, the use of stannous ion was a key development and current radiopharmaceutical kits use the stannous reduction technique. With the advent of the [99]Mo/^{99m}Tc generator in the 1960s followed by the development of instant kits, the use of ^{99m}Tc-labeled compounds expanded rapidly" [4].

Consequently, the demand of the isotope molybdenum-99 ([99]Mo) exploded. However, any production technologies practiced until that time could not fulfill the growing demand. Today's [99]Mo production technologies have been basically developed in the 1970s. Since then, [99]Mo has been one of the most important isotopes. With a development of the [99]Mo production techniques, its daughter isotope ^{99m}Tc has been the most commonly used medical radioisotopes used in the field, accounting for > 80% of overall nuclear diagnostics [5].

More than 95% of [99]Mo is produced through fission of uranium-235 ([235]U) because [99]Mo generated from fission (fission [99]Mo) exhibits very high specific activity (~10^4 Ci/g) than the one produced by any other method. Historically, the most fission [99]Mo produced have been used in highly enriched uranium (HEU) targets. However, to reduce the use of HEU in the private sector for nonproliferation, [99]Mo producers are forced to convert their HEU-based process to use low enriched uranium (LEU) targets. The economic impact of a target conversion from HEU to LEU is significant. The overall cost for the production of fission [99]Mo increases significantly with the conversion of fission [99]Mo targets from HEU to LEU. It is not only because the yield of LEU is only 50% of HEU, but also

because radioactive waste production increases 200% [6,7]. Consequently, worldwide efforts on the development of [99]Mo production process that is optimized for LEU targets have become an important issue.

Isotopes of xenon (Xe) are produced from the nuclear fission of [235]U. The isotopic ratio of Xe varies according to the type of fission used: nuclear explosion, nuclear power generation, or radiopharmaceutical production. From this basis, the fingerprint of Xe emission to the atmosphere has been one of the important tools for nuclear test bans by monitoring nuclear explosion. Although the consumption of [235]U is significantly higher for power generation than for medical radioisotope production, emission of Xe from medical radioisotope production facilities has a dominant impact over Xe emission from nuclear power plants. It is not only because of the total Xe emission, but also because the isotopic ratio of Xe from medical radioisotope production is analogous to that from a nuclear explosion. Therefore, ensuring that radioactive Xe from radiopharmaceutical production is kept below a certain level is very important in both environmental and security aspects [8].

2.   Routes to produce [99]Mo

2.1.   Radiochemical routes to produce [99]Mo

In principle, there were two main routes to access [99]Mo on a close to industrial-scale production [6] (Fig. 1): (1) the [98]Mo (n, γ) [99]Mo process (cross section 0.13, $b = 0.13 \times 10^{-24}$ cm^2, the branching of [98]Mo is 24.13%); and (2) [235]U (n, f) [99]Mo (the fission cross section is 586, $b = 5.86 \times 10^{-22}$ cm^2, the fission yield of [99]Mo is 6.15%).

In the 1960s, in particular, the [98]Mo (n, γ) [99]Mo process was the main source used to meet the relatively low [99]Mo demand. The situation changed dramatically with the introduction of cold kits in the early 1970s. An enormous effort has been incorporated into the development of industrial-scale fission-based [99]Mo production. To date, fission-produced [99]Mo with very high specific activity in combination with the alumina (Al_2O_3) column-based ^{99m}Tc generators remains as the gold standard.

Radiochemically, it is not difficult to separate [99]Mo from a solution that contains the target element (uranium) and the complex mixture of the highly radioactive fission products. The challenge is keeping the high radioactive fission products—especially the volatile radioelements (noble gases and iodine)—safely under control. All classical chemical separation methods have been applied for [99]Mo separation from a target solution containing the fission products from [235]U.
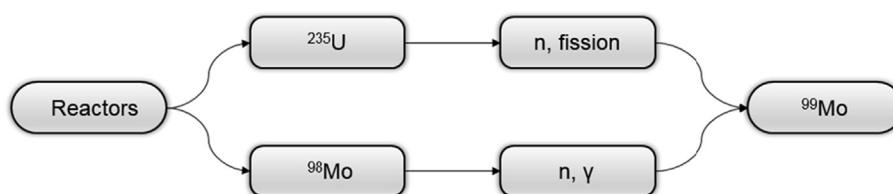

Fig. 1 – Two main routes to produce [99]Mo on an industrial scale. (A) Fission of [235]U. (B) Neutron capture of [98]Mo.

(1) Precipitation of the ^{99}Mo with alpha-benzoxim is used in the CINTICHEM process. CINTICHEM (a subsidiary of Medi-Physics Inc./Hofmann La-Roche) used the process until 1989 in the United States (US) at their reactor facilities in Tuxedo, NY, USA [9]. The CINTICHEM process is still in operation at the Badan Tenaga Nuklir Nasional (BATAN) Institute, Jakarta, Indonesia.

(2) Extraction of ^{99}Mo from a nitric acid process solution with di-(2-ethylhexyl)phosphoric acid (HDEHP) is applied at the Karpov Institute, Obninsk, Russia [10].

(3) Separation of ^{99}Mo using anion exchange from an alkaline process solution has been introduced by Sameh and Ache [11]. This process is applied in Petten (The Netherlands), and its modified version has been applied in several production sites worldwide: INVAP (Argentina), NTP (South Africa), and ANSTO (Australia).

(4) Adsorption of ^{99}Mo to Al_2O_3 column from weak acid process solutions has been demonstrated by Stang [12]. This approach has been used in most acid digestion-driven Mo processes.

(5) Volatilization can be used for ^{99}Mo separation from uranium and the fission products because MoO_2Cl_2 is a volatile compound. Recently, General Atomics published a patent that describes this approach. Related studies to implement this approach into a practical ^{99}Mo production process are underway [13].

2.2.   Aspects for selecting a suitable process strategy

When choosing the most suitable ^{99}Mo production strategy, irradiation conditions and available target configuration should be considered. When using fission of ^{235}U as the production route for ^{99}Mo, generation of fission heat must be considered. For the generation of 100 6-day Ci (6-day Ci; activities 6 days after the end of production) ^{99}Mo, heat comparable with that of the fuel elements is generated. The heating power of the targets during irradiation corresponds to about 25 kW. Consequently, the target configuration and target dimensions are very much dictated from the available cooling system of the irradiation position in the reactor. It is consequently logical if one uses the proven principles of the fuel elements for designing the corresponding ^{99}Mo targets. The first published radiochemical process for separating ^{99}Mo makes use of segments of original fuel elements made with HEU/aluminum alloy (meat: 93% ^{235}U alloyed with aluminum; cladding: aluminum) [12]. Another remarkable example is the AMOR (Anlage zur Mo Production Rossendorf) process [14]. A complete fuel element of the Rossendorf research reactor was used as a target for the AMOR process. Today, all industrial-scale producers of ^{99}Mo use dedicated targets with a configuration that is very close to the reactor fuels. Because early generation fuels were generally uranium−aluminum alloy cladded with aluminum shell, configuration of the corresponding targets became plates (Mallinckrodt, Petten, the Netherlands; INVAP, San Carlos de Bariloche, Argentina; ANSTO, Australian Nuclear Science and Technolgy Organisation, Lucas Heights, Australia; NTP Radioisotopes, Pelindaba, South Africa; PINSTECH: Pakistan Institute of Nuclear Science and Technology, Nilore, Pakistan) or pin type (Nordion Inc.: Chalk River Laboratories, Canada; NIIAR (RIAR) Research Institute of Atomic Reactors, Dimitrovgrad, Russia) [15]. Fig. 2 presents the flow diagram to determine a suitable fission ^{99}Mo process strategy.

3.   Historical overview of ^{99}Mo production processes

The first chemical process for the separation ^{99}Mo from fission products was demonstrated by a group in the Brookhaven National Laboratory (BNL), Upton, NY, USA [12]. They used small segments of an original fuel element: uranium−aluminum alloy (HEU) cladded with aluminum. The element did not pass the quality check for the fuel element. These segments were sealed in aluminum cans under a helium atmosphere. After irradiation in the reactor, the segments were digested with acid dissolving solution (nitric acid with mercury). The target solution was passed through an alumina column to separate ^{99}Mo from the acid solution containing fission products. The same separation technique was then used in several other processes. The original aim for designing this process was not to separate ^{99}Mo but ^{132}Te for the production of ^{132}Te/^{132}I generator, which played a dominant role in the pioneering time of nuclear medicine [12]. The same motivation for producing ^{132}Te from fission was the starting point for developing a separation process for fission products in the Central Institute for Nuclear Research (CINR), Germany [16]. ^{132}Te was separated in a simple distillation step during the dissolving process of natural uranium pellets in hydrochloric acid solution. After the tellurium and iodine separation, the uranium fission product solution was introduced to the alumina columns to separate ^{99}Mo by adsorption. This process is called LITEMOL [16]. The ^{99}Mo
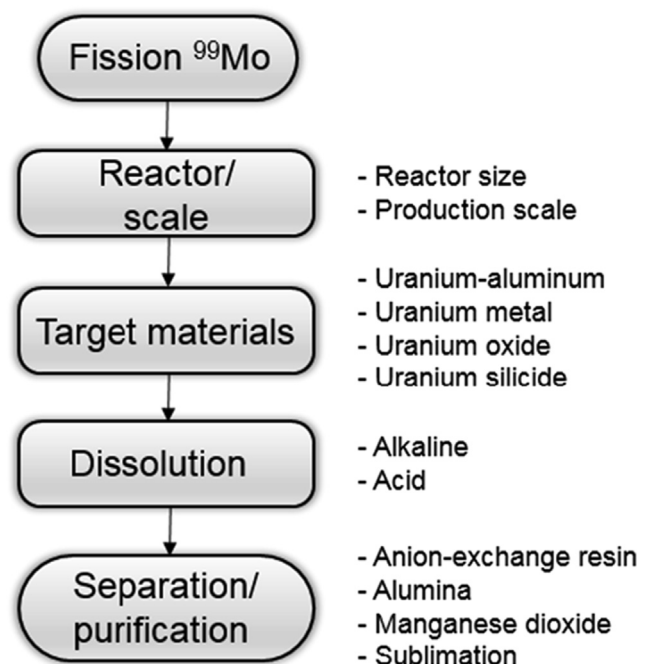

Fig. 2 − Fission ^{99}Mo production schemes for selecting production strategy.

obtained from the LITEMOL was the basis for the first commercially available fission-based ^{99}Mo/^{99m}Tc generator in Europe in 1964. This small-scale ^{99}Mo production process was in operation until 1980. In contrast to the development in BNL, pure natural uranium pellets were used as target for the LITEMOL process. The targets were irradiated in sealed aluminum cans with aluminum spacers. Up to 200 g uranium pellets (total inventory of ^{235}U is 1.4 g) were dissolved in hydrochloric acid solution. After oxidation with nitric acid solution, the process solution was passed through an alumina column for the separation of ^{99}Mo. ^{132}Te was the more important product in the early days, and for this purpose, the LITEMOL process was much easier compared to the BNL approach. In this process, ^{132}Te was obtained from the hydrochloric acid digestion as hydrogen telluride (H$_2$Te) by trapping with sodium sulfate (Na$_2$SO$_3$) solution [16]. In the 1960s, the neutron activation of ^{98}Mo was the main route used to produce the ^{99}Mo and corresponding ^{99}Mo/^{99m}Tc generators. With the growing demand for ^{99}Mo produced from the CINR, the LITEMOL process took on an accelerated pace toward the first industrial-scale fission-based ^{99}Mo production process in Europe, which became a basis for the first fission-based ^{99}Mo/^{99m}Tc generator introduced to the market in 1964. The ^{99}Mo/^{99m}Tc generators have been continuously produced in CINR until the reactor shut down in 1990 with the reunification of Germany.

Another interesting aluminum-free ^{99}Mo production process was developed in ANSTO. Here, uranium (IV) oxide (UO$_2$) pellets with an enrichment of 1.8% in ^{235}U (later increased to 2.2%) tempered at around 600°C are used. Thirteen pellets were irradiated in a rocket can at the HIFAR reactor. The irradiated pellets were then dissolved in nitric acid solution. The digestion solution was passed through an alumina column to separate the ^{99}Mo. This process was in operation starting early in the 1980s until late 2006 [6,17].

The CINTICHEM process, as it is still in operation at the BATAN Institute in Indonesia, makes use of tubular targets whose inner surfaces were electroplated with UO$_2$ (HEU). After dissolving in nitric acid solution, ^{99}Mo is separated by precipitation with alpha-benzoxime. The modified CINTICHEM process using uranium metal foil target in a tubular aluminum capsule was suggested for increased ^{99}Mo yield. After mechanically removing the aluminum capsule, uranium metal foil is dissolved in concentrated nitric acid solution contained in a closed processing vessel under pressure and increased temperature. The ^{99}Mo separation process was practically identical with the original CINTICHEM process (precipitation with alpha-benzoxime) [18,19].

The International Atomic Energy Agency (IAEA) has initiated an international Coordinated Research Process (CRP) in 2005, "Developing Techniques for Small Scale Indigenous ^{99}Mo Production Using LEU Fission or Neutron Activation." The CRP has been completed by 2011 with a technical report [6].

At the Karpov Institute (Obninsk, Russia), triuranium oxide (U$_3$O$_8$, HEU) powder was used as a target in specially designed cylindrical cans with a double wall for irradiation [10]. Extraction with HDEHP is used to separate ^{99}Mo. At that time, the operators diluted the U$_3$O$_8$ with zinc oxide (ZnO) in order to improve the release of fission heat.

A similar target system using pelletized uranium (IV) oxide (UO$_2$) powder was developed at the Nordion for the production of ^{99}Mo from the MAPLE reactor. However, this target system has never become operational.

Currently, there are two project ideas for fission-based ^{99}Mo production that works with aluminum-free fission targets: General Atomics patented the approach using a porous triuranium oxide (U$_3$O$_8$) target to extract the ^{99}Mo with chlorine containing gas stream at increased temperature [13,20]. Beyer et al. [21] suggested the use of fuel-like uranium (IV) oxide (UO$_2$) pellets as fission targets that are annealed at 1,600°C. These pellets represent a mechanically stable ceramic material that is attacked neither by nitric acid nor by any strong alkaline medium. However, the UO$_2$ can be oxidized via a *voloxidation* process, as it is applied in the reprocessing of uranium (IV) oxide (UO$_2$) fuel in the nuclear fuel cycle. During this strong exothermic reaction, the ceramic-like UO$_2$ pellets become completely collapsed, forming very fine powder of triuranium oxide (U$_3$O$_8$). Then the resulting powder can be easily dissolved in the nitric acid solution. The obtained target solution can then be treated with any of the previously discussed ^{99}Mo separation and purification techniques [20,21].

In 1976, Sameh and Ache [11] developed a pure alkaline digestion process to treat fuel-like target plates consisting of uranium–aluminum alloy (UAl$_x$, HEU) cladded with aluminum. This was a revolutionary development in ^{99}Mo production technology, which allowed producers to meet the global demands for ^{99}Mo. Because the policy of governments at that time was to immediately shut down the fuel cycle, this alkaline digestion process could not be achieved until 1982. However, only 100 batches of ^{99}Mo have been produced in Karlsruhe, Germany, before the production facility was closed in 1983, for political reasons. Later, however, the process advanced to become the most efficient industrial-scale ^{99}Mo production process worldwide. Sameh transferred the technology to Mallinckrodt at Petten in 1996. This became the most reliable and safest production site for ^{99}Mo with a market share of 30–40%. Furthermore, this process has been adopted by INVAP and NTP. Moreover, INVAP transferred the Argentine process to the ANSTO and NRC (Inshas, Egypt). The main radiochemical step in this process is the digestion of the uranium–aluminum alloy target in the sodium hydroxide (or potassium hydroxide) solution with strong hydrogen formation. During the process, uranium and transuranium elements are precipitated as a mixture of uranium oxides (UO$_2$) and sodium diuranate (Na$_2$U$_2$O$_7$). The precipitates are separated from the solution by filtration. ^{99}Mo remains in the alkaline digestion with aluminates. Finally, ^{99}Mo is separated by a series of anion exchangers. A really deep purification of ^{99}Mo is achieved via adsorption of ^{99}Mo to manganese dioxide (MnO$_2$), and two subsequent anion-chromatographic steps followed by sublimation. The processes operating at INVAP, NTP, and ANSTO differ only slightly in the purification steps, according to their target specification.

The previously developed aluminum-free process at the CINR (Rossendorf, Germany) based on natural uranium pellets could by far not meet the fast-growing demand for ^{99}Mo. At the same time, when A. Sameh [11] developed the alkaline

digestion process in Karlsruhe (West Germany), another fission-based ^{99}Mo production process was developed, which was called the AMOR process, in East Germany [14]. Because the only available and validated target was an original fuel element as it is used for the research reactor, a complete fuel element has been used for ^{99}Mo with the AMOR process. One target fuel element consisted of 180 g uranium with 36% enrichment as uranium−aluminum alloy (UAl$_x$), and nearly 1 kg aluminum. Basic digestion technology was ruled out because of the very large quantity of aluminum that would increase the liquid waste stream to unacceptable levels. An acid digestion process with nitric acid solution (with mercury, Hg) was applied as described by Stang [12]. Adsorption to alumina column was used to separate ^{99}Mo from the acid digestion of uranium and fission products. More than 400 batches of ^{99}Mo have been successfully produced during the operation period of this process, starting from 1981 until the reactor shut down in 1991. The acidic waste solution containing uranium and aluminum was stored for decay. After the 4-year cooling period, attempts to produce recycled targets were made via reprocessing.

4. Conversion of fission ^{99}Mo target from HEU to LEU

4.1. Backgrounds for conversion

Every year, about 50 kg of HEU is used for ^{99}Mo production. The KSA (Karlsruhe-Sameh aluminide) process, as applied at Petten, is currently the standard procedure in terms of target composition, time requirement, yield, and safety aspects. The target plates manufactured by CERCA (Areva Group, Paris, France) consist of 5.3 g HEU (enrichment 93%) as uranium−aluminum ally (UAl$_x$) and 26.3 g aluminum from the cladding and matrix (after cutting of cladding edges to minimize the aluminum content in the process and waste stream). The aluminum/uranium ratio is 5.8 by weight, and 45 by molar. All process parameters have been optimized based on the target specification to give the best ^{99}Mo yield in comparison with other HEU target processes [6,7].

Recently, an international consensus has been established to reduce the use of HEU in the private sector: fuels for research reactors and targets for the production of medical radioisotopes. The US has promoted the conversion of HEU to LEU for civilian nuclear facilities, such as research reactors and medical radioisotope production. Through the Reduced Enrichment for Research and Test Reactors program, launched in 1978 by the U.S. Department of Energy, fuels from > 40 research reactors have been successfully converted from HEU to LEU. The US has also made the political decision to exclude HEU-based ^{99}Mo from the US market starting in 2017. Because the US ^{99}Mo market accounts for 50% of the world market, the announcement of the decision brought immediate response from major producers of medical radioisotopes.

The IAEA has been supportive of the technical aspects generated from the conversion. The IAEA organized an international working group and launched technical meetings to support the LEU conversion [6,7]. From the conversion, the overall cost of the production of fission ^{99}Mo increases significantly not only because the decreased fission yield with reduced ^{235}U contents, but also because the radioactive waste production increases by 200%. Comparison of uranium−aluminum alloy targets according to the producers and enrichments is presented in Table 1.

The economic aspect of the conversion was analyzed by the Organisation for Economic Co-operation and Development Nuclear Energy Agency High-Level Group (OECD-NEA HLG) [22].

In the HEU era, UAl$_x$ target with alkaline digestion proved to be the most efficient ^{99}Mo production process. However, the global threat reduction initiative in these days and conversion of HEU targets used in the medical radioisotope production to LEU created a dramatic change in the situation [23]. Today, worldwide efforts on the development of new LEU targets, and the ^{99}Mo production process that is optimized for the new target have become important issues. Conversion of the target from HEU to LEU causes significant changes in the fission ^{99}Mo production. Target composition, density, and its irradiation characteristics have been changed. Consequently, the chemistry of the fission ^{99}Mo production process is required to be reoptimized. Process modification is encouraged to reduce the impact of the significant increment of the radioactive wastes caused by the conversion of HEU target to LEU [6].

4.2. Needs for the high-density LEU targets

To compensate for the loss of yield caused by the reduction of ^{235}U from the conversion of HEU to LEU for the fission ^{99}Mo

Table 1 − Target composition of uranium (HEU and LEU)−aluminum alloy target widely used by current major producers, in comparison with KAERI LEU−aluminum alloy target.			
	HEU (93%) CERCA	LEU (19.75%) CERCA	LEU (19.75%) KAERI
Density (g U/cm^3)	1.25	2.6	2.6
^{235}U/plate (g)	4.9	3.7	3.3
Uranium total/plate (g)	5.3	19	16.62
Aluminum total/plate (g)	26.3 (after cutting of frame)	30	37.95
Aluminum/uranium ratio (Al/U, by weight)	5	1.6	2.28
Aluminum/uranium ratio (Al/U, by molar)	45	13	20
Aluminum needed for unit ^{235}U mass (1 g ^{235}U)	5.12	9.12	11.54

HEU, highly enriched uranium; KAERI, Korea Atomic Energy Research Institute; LEU, low enriched uranium.
Note. From "Non-HEU production technologies for molybdenum-99 and technetium-99m," by International Atomic Energy Agency (IAEA), 2013, IAEA Nuclear Energy Series, No. NF-T-5.4.

target, the density of the LEU target had to be increased. In general, conventional HEU—aluminum alloy target has 1.3 g uranium per cubic centimeter (U/cm^3). By contrast, the LEU-—aluminum alloy target that is widely used has 2.6 g U/cm^3. To completely compensate for the reduction of ^{235}U enrichment from 93% to 19.75%, the density should be increased 4.7-fold. Several types of targets have been suggested through the international society. Uranium metal foil was proposed by an international group of researchers including Argonne National Laboratory and Korea Atomic Energy Research Institute (KAERI). [19]. Although uranium metal has the highest density of 19.1 g/cm^3, it was difficult to apply to the commercial process because of the difficulties in fabrication and handling during the production process. Sameh [24] proposed the use of uranium silicide target. Uranium silicide is one of the typical fuel types for research reactors, and it has a potential to have up to 5.8 g U/cm^3 of meat density [24,25]. Process-wise, however, both U-metal and U-silicide target technologies are totally different in the processes. U-metal and U-silicide targets require nitric acid and hydrofluoric acid as their digestion solution, respectively. The development of high-density UAl$_x$ targets has been suggested by the researchers of KAERI. Conventional UAl$_x$ targets are produced by using pulverized UAl$_x$ powders. Next, the UAl$_x$ powders are produced through five steps of melting, casting, heat treatment, component analysis, and crushing, giving the maximum density of 2.6 g U/cm^3. With the unique centrifugal atomization technique of KAERI, UAl$_x$ powders are produced in one step, and uranium density up to 4.6 g U/cm^3 is achievable by using the centrifugal atomization technology. The uranium density of 9.0 g U/cm^3 is achievable by using U-metal powders produced by the centrifugal atomization technology. For KAERI's fission ^{99}Mo process, plate-type LEU target with UAl$_x$ meat and Al-6061 cladding is used. Plate-type targets are produced from the powders via compression, assembly, welding, and hot rolling procedures [15]. Conformation of the KAERI target is presented in Fig. 3.

As the KAERI atomized UAl$_x$ target is similar to conventional targets material-wise, the production process does not really differ from currently used processes: the alkaline digestion. Compared with conventional pulverized UAl$_x$ powders, KAERI's powders prepared by the unique centrifugal atomization technology have spherical shape, smoother surfaces, and smaller surface area. Therefore, those differences may lead to minor different dissolution behaviors during the chemical process.

5. Conditions for future LEU-based fission ^{99}Mo production process

5.1. Reduction of intermediated level liquid wastes

From the conversion of target material from HEU to LEU, radioactive wastes increase by decreased production yield. This is because of the increase in the number of targets used to have the same productivity. Consequently, aluminum and digestion solution in the waste stream increase, too. In particular, reduction of the intermediate level liquid wastes (ILWs), directly resulting from the dissolution of target, is
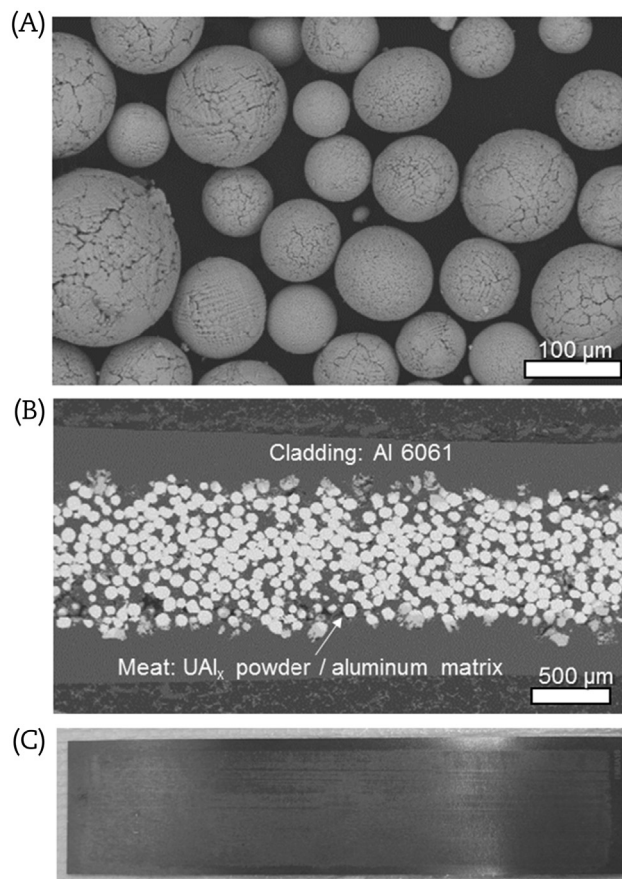

Fig. 3 — LEU—aluminum alloy target made with centrifugal atomization process. (A) Election micrograph of spherical LEU—aluminum alloy powder produced by centrifugal atomization. (B) Election micrograph of target cross section showing clear boundary of cladding and meat. (C) Plate-type LEU—aluminum alloy target designed for the KAERI process. Target dimension is about 200 × 48 × 1.6 mm. KAERI, Korea Atomic Energy Research Institute; LEU, low enriched uranium.

very important not only because of their high activity but also owing to the difficulties in the solidification treatment for final disposal. Despite the high salt content in uranium digestion, the alkaline dissolution process was the most efficient option for HEU-based targets. However, the growing need for the development of an advanced fission ^{99}Mo process became apparent because of the dramatic increase of ILWs caused by the conversion to LEU. To be solidified for final disposal, the ILWs with high salt concentration should be significantly diluted and conditioned with water or other conditioning solutions. Finally, the total volume of wastes increases by 25-fold when solidified with the conventional cementation method. Every year, about 15,000 L of ILWs is expected for the production 10,000 6-day Ci/wk fission ^{99}Mo from LEU targets, to cover global needs. After cementation, the total volume will become 375,000 L, corresponding to 1,875 drums (200 L). In the next few years, for the production of fission ^{99}Mo from LEU-based targets, an advanced fission

Table 2 − Activities of noble gas radionuclides generated from the fission Mo-99 production on the weekly production of 2,000 6-day Ci.

Inert gas radionuclides	Activity (Ci) at 24 hr EOB
Kr-85	2.65×10^{-1}
Kr-85m	2.27×10^{1}
Kr-87	3.93×10^{-3}
Xe-131m	2.36×10^{0}
Xe-133	2.63×10^{3}
Xe-133m	1.11×10^{2}
Kr-85	2.65×10^{-1}
Xe-135	1.04×10^{3}
Xe-135m	5.94×10^{1}
Inert gas total	3.86×10^{3}

EOB, end of bombardment.

^{99}Mo production process with less waste generation will be required [6,26].

5.2.   *Mitigation of radioactive noble gas*

Emission of radioxenon (Xe) from the medical radioisotope production is controlled via the gaseous waste treatment system with multiple steps of mitigation and confinement. First, process equipment and production hot cells are made as closed system with leak-tight parts to minimize effluence of Xe from the system. In spite of the leak-tight systems, it is impossible to completely confine Xe in the system. Therefore, a proper combination of equipment to reduce the xenon emission is installed in the medical radioisotope production facility. However, the conventional system for Xe treatment is huge and costly. This makes it difficult to introduce a xenon reduction system in medical radioisotope production facilities. Therefore, development of a compact Xe adsorption module is requested [8].

Radioisotopes of xenon and krypton are generated from the fission of uranium. Major products from the production of fission-based radioisotopes are Xe-131m, Xe-133, Xe-133m, Xe-135, Xe-135m, Kr-85, Kr-85m, and Kr-87 (Table 2).

Currently, most commercial producers of ^{99}Mo use alkaline digestion of uranium. The Korean process is also based on the dissolution in the basic media. Most of the xenon in the irradiated fission ^{99}Mo targets is released during dissolution of the targets. Therefore, the fission ^{99}Mo production system should be made as a closed system operated under a weak vacuum condition to minimize the potential release of radioactive gases.

For the treatment of off-gas from the process, all the off-gas and carrier gas from the dissolver unit and the other process equipment should be collected in a gas storage tank using vacuum transport. After collection, off-gas in the tanks can be transported to the off-gas treatment system to remove humidity, gaseous iodine, and other by-products (Fig. 4).

In the fission Mo-99 production process with caustic digestion, most iodine remains in the liquid phase as negatively charged iodide form. In the acidic dissolution process, most of the iodine floats and it is difficult to control the emission, mostly because of its very high radioactivity. Table 3 shows the radioactivity of iodine generated from the fission Mo-99 production.

Xenon is an inert gas with low adsorption characteristics. Therefore, a typical xenon treatment system has a bulky size with low efficiency. This requires substantial space and budget for the establishment of a proper xenon treatment system with desired performance specifications. This represents a main obstacle for radiopharmaceutical producers to equip the xenon treatment system. KAERI developed a compact xenon adsorption module with chilled carbon column. At the operation temperature of −20°C, the system exhibited a 149.6-hour delay with 689 g carbon. Compared with the operation at room temperature (20°C), only 1/3,700 carbon quantity (in weight) is required (1/980 in volume). It stands for 32 tons of carbon required to achieve 5 GBq/d of Comprehensive Nuclear-Test-Ban Treaty Organization (CTBTO)-recommended xenon emission guideline, which can be reduced to only 8.5 kg. Fig. 5 shows the compact xenon adsorption test module used in the experiments.
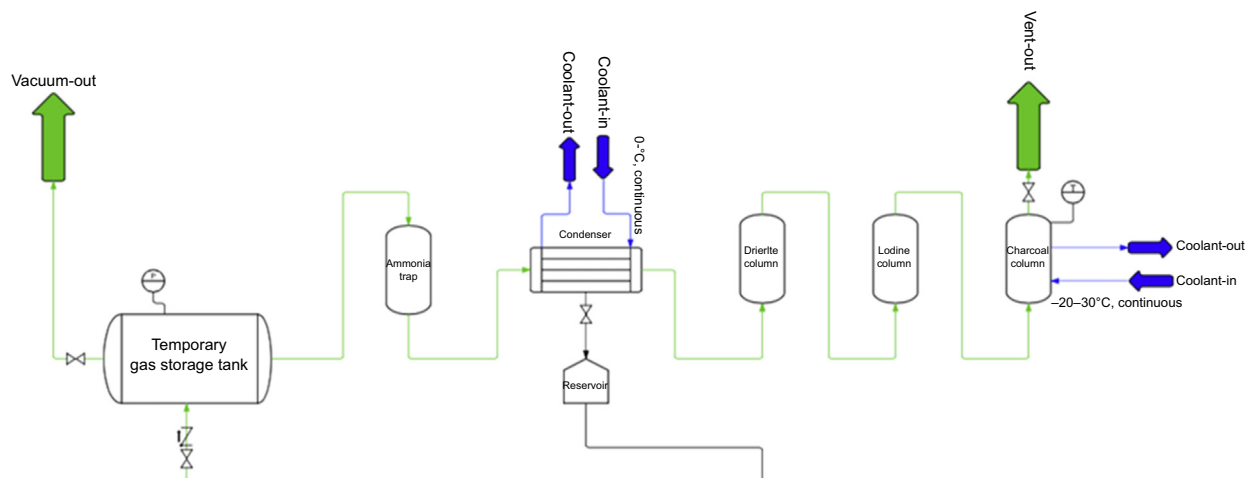

Fig. 4 − Off-gas treatment module for the fission ^{99}Mo process based on the alkaline digestion. For effective handling of the process off-gas stream, the gas is first collected in a vacuum tank. Then, humidity and radioelements are removed along the stream, step by step.

Table 3 − Activities of noble gas radionuclides generated from the fission Mo-99 production for the weekly production of 2,000 6-day Ci.

Nuclides	Activity (Ci, from 2,000 6-day Ci Mo-99 Production) at 24 hr EOB	Half-life	Daughter nuclides
I-125	4.76×10^{-12}	60.14 d	Te-125
I-128	2.92×10^{-19}	24.99 mo	Te-128, Xe-128
I-129	2.99×10^{-7}	15,700,000 yr	Xe-129
I-130	1.61×10^{-1}	12.36 hr	Xe-130
I-131	8.70×10^2	8.04 d	Xe-131m, Xe-131
I-132	2.02×10^3	2.30 hr	Xe-132
I-133	2.23×10^3	20.9 hr	Xe-133
I-135	3.64×10^2	6.61 hr	Xe-135m, Xe-135

EOB, end of bombardment.

5.3. Fission ^{99}Mo process based on alkaline digestion for LEU−aluminum alloy targets

A fission ^{99}Mo process for the plate-type dispersion targets made with atomized UAl$_x$ powders was developed by KAERI. The overall process scheme of the KAERI process is similar to the conventional alkaline digestion process, which has been used for the HEU−aluminum alloy targets. The scheme for the KAERI process with process equipment is presented in Fig. 6.

In the KAERI process, LEU targets with UAl$_x$ meat and alloy cladding (aluminum 6061) are dissolved in sodium hydroxide solution in the dissolver. During dissolution, unreacted uranium and majority of other fission products form precipitates, and are removed from the solution via filtration. Sintered metal powder membrane with 10-μm average pore size was used as the filter medium. The precipitates formed dark brown or greenish brown filter cake at the bottom of the filter unit (Figs. 7A and 7B).

A component analysis of the uranium precipitates was performed with energy-dispersive spectrum and X-ray diffraction (Fig. 7C) [27]. It presented the precipitates as a mixture of mostly uranium oxide and sodium diuranate (Na$_2$U$_2$O$_7$).

The filtrate solution contains ^{99}Mo and iodine elements as their major radionuclides. Iodine in the filtrate solution can be removed by ion exchange or silver-based adsorbents. In the KAERI process, silver-coated alumina was used for the iodine removal column (Fig. 7D).

Chemically, the molar amount of the total radionuclide in the filtrate solution is very small (~0.1% total fission products). Majority in chemical quantity are the salts and dissolved aluminum (~270 g/L). Through the secondary precipitation step to reduce salt/aluminum concentration in the filtration solution, the treatment of ILWs and solidification can become easier. By adding a buffer solution to the filtrate solution, parts of the salts and majority of the aluminum form sludge, and they can be removed via secondary filtration. After precipitation, the aluminum concentration in the solution was reduced to ~50 ppm. Then the majority of the salts and the aluminum in the process can be managed as solid wastes (Fig. 7E).

Furthermore, the handling of ILWs becomes easier because of their reduced salt concentration: formation of scale, slurry, and clogging of the waste transport pipes can be prevented. Another advantage of the salt/aluminum precipitation step is the coprecipitation of radioactive impurities, without affecting the solubility of ^{99}Mo in the filtrate solution. Additional steps for the separation and purification of ^{99}Mo can be simplified. Further separation and purification steps may be required to acquire medical-grade ^{99}Mo solution. Combination of columns with anion exchange resins (DOWEX, Chelex), alumina, or manganese (IV) dioxides (MnO$_2$) can be used, as they have been used in conventional alkaline digestion processes.

Fig. 5 − Compact xenon adsorption test module with chilled carbon column.

(A)

(B)
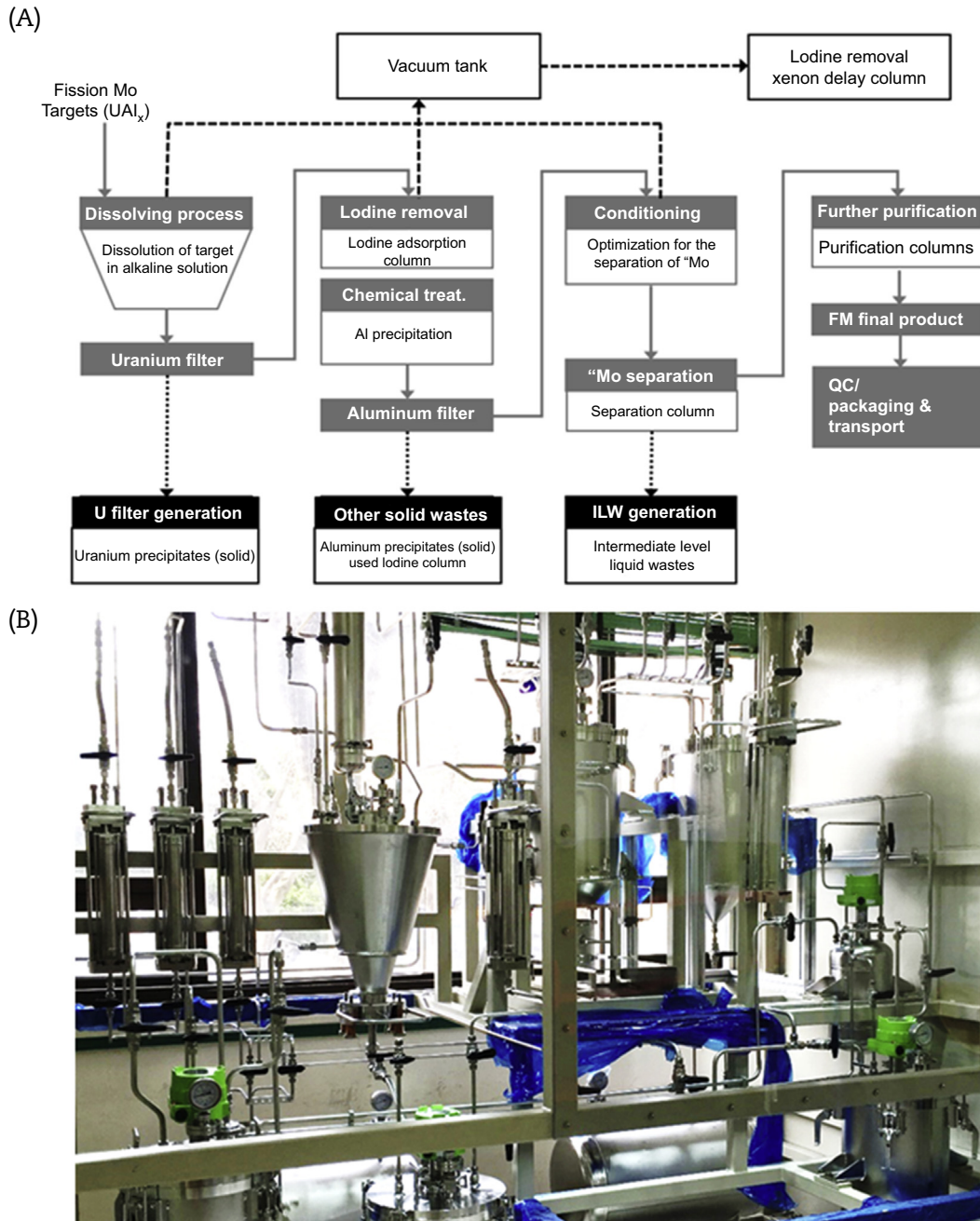
Fig. 6 — Scheme for the KAERI process with process equipment. (A) Process scheme of KAERI process designed for the alkaline digestion of LEU—aluminum alloy target made with centrifugal atomization technology. (B) Process equipment with dissolver, reaction vessels, off-gas modules and separation column. KAERI, Korea Atomic Energy Research Institute; LEU, low enriched uranium; QC, quality control.

Process off-gas is removed from the process after it is collected in a vacuum tank. From the off-gas, moistures and volatile iodine compounds should be eliminated by dehumidification and adsorption, respectively. Iodine can be removed by triethylene diamine-impregnated carbon, silver-, or copper-based adsorbents.

Radioactive noble gas can be eliminated by decay through prolonged emission through carbon beds, as shown in the previous chapter.

6.   Summary

Molybdenum-99 has been one of the most important isotopes for > 50 years, considering that its daughter isotope, ^{99m}Tc, is the most commonly used medical radioisotope, which covers 85% of overall nuclear diagnostics. More than 95% of ^{99}Mo is produced through fission of ^{235}U. In this review, we gave an overview of ^{99}Mo, from its discovery and propagation toward the future. First, radiochemical routes for the production of

Fig. 7 – Aluminum precipitates. (A) Filter cake collected from the uranium precipitates after dissolution. (B) Scanning electron micrograph of uranium precipitate. (C) Energy-dispersive X-ray spectroscopy (EDX) spectra taken from the precipitates with atomic ratio. (D) Silver coated alumina used for the removal of iodine from the digestion solution. Inset shows the EDX mapping showing distribution of silver nanoparticles on the alumina surface. Scale bar in inset: 100 μm. (E) Aluminum precipitates removed from the digestion solution.

[99]Mo have been presented. The aspects for selecting a suitable process strategy were also given. A historical overview of [99]Mo production process was provided to inspire the development of future processes. Important present-day issues were also mentioned. Issues originating from the international initiative for the conversion of fission [99]Mo targets from HEU to LEU were likewise discussed. Radioxenon issues related with the monitoring of nuclear explosions and comprehensive nuclear test–test ban were also discussed, in this review. A strategy to reduce ILWs from the fission [99]Mo process was also suggested. KAERI's novel target technology with centrifugal atomization was proposed for the development of new LEU target, which can be directly applied to the current [99]Mo production process without having major changes. Finally, KAERI's own [99]Mo production process for the new LEU–aluminum alloy targets was proposed to achieve reduction of ILW generation and xenon emission.

Conflicts of interest

All authors have no conflicts of interest to declare.

Acknowledgments

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