

MAKING OF FISSION ^{99}Mo FROM LEU SILICIDE(S):

A RADIOCHEMISTS' VIEW

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ABSTRACT

The present-day industrial scale production of ^{99}Mo is fission based and involves thermal-neutron irradiation in research reactors of highly enriched uranium (HEU, > 20 % ^{235}U) containing targets, followed by radiochemical processing of the irradiated targets resulting in the final product: a ^{99}Mo containing chemical compound of molybdenum. In 1978 a program (RERTR) was started to develop a substitute for HEU reactor fuel i.e. a low enriched uranium (LEU, < 20 % ^{235}U) one. In the wake of that program studies were undertaken to convert HEU into LEU based ^{99}Mo production. Both new targets and radiochemical treatments leading to ^{99}Mo compounds were proposed. One of these targets is based on LEU silicide, U_3Si_2 . Present paper aims at comparing LEU U_3Si_2 and LEU U_3Si with another LEU target i.e. target material and arriving at some preferences pertaining to ^{99}Mo production.

1. Introduction

The advent of the diagnostic use of $^{99\text{m}}\text{Tc}$ (half-life = 6.02 hours) in the nuclear medicine led to an increasing demand for this radionuclide. The most convenient way for obtaining $^{99\text{m}}\text{Tc}$ is from ^{99}Mo (half-life = 66.02 hours); $^{99\text{m}}\text{Tc}$ is namely a decay product of ^{99}Mo which can be obtained by different nuclear reactions. However, the present practical sources of ^{99}Mo are research reactors *via* the thermal-neutron induced reaction: $^{98}\text{Mo}(n,\gamma)^{99}\text{Mo}$ or by fission of ^{235}U . The fission path yields a product with a specific activity several orders of magnitude higher than the product of the (n,γ) reaction. [1]. ^{235}U is one of the three naturally occurring nuclides of uranium, which contains (by weight) 0.0055 % ^{234}U , 0.720 % ^{235}U , and 99.2745 % ^{238}U [2]. Natural uranium can be enriched in ^{235}U to almost 100%.

The relatively short half-life of ^{99}Mo forces the hospitals using $^{99\text{m}}\text{Tc}$ for diagnostic purposes to purchase weakly at least one $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator. This combined with a vast number of $^{99\text{m}}\text{Tc}$ -based nuclear medical procedures carried out on patients all over the world generates a still increasing demand for $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generators. An unimpaired production of sufficient quantities of ^{99}Mo - the precursor for $^{99\text{m}}\text{Tc}$ - is indeed a condition *sine qua non* for any large scale production and marketing of such generators.

The present-day industrial scale production of ^{99}Mo is mostly based on the thermal neutron irradiation of targets comprising particles of "highly enriched uranium", HEU, > 20%, generally 93% ^{235}U containing chemical compounds, sometimes mixed with aluminum particles and pressed together to form a plate. Some examples of such compounds are: uranium oxide, uranium-aluminum alloy or uranium aluminide etc. The actual targets are obtained by wrapping target material(s) i.e. "meat" in aluminum foil and tightly sealing the whole (cladding).

The neutron irradiations of the prepared targets are carried out in nuclear research reactors with a thermal neutron flux of preferably $\geq 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$. An irradiation takes a few days and is followed by a few days lasting “cooling” i.e. decaying of the short lived radionuclides in the irradiated target. The thermal-neutron fission of ^{235}U produces energy (about 200 MeV per fission) and a great number of radionuclides - including gaseous ones - with mass numbers ranging from 73 to 159. One of these radionuclides is ^{99}Mo . Some radionuclides of uranium, neptunium and plutonium are also produced due to the $^{238}\text{U}(n,\gamma)$ reactions followed by β^- decay.

Numerous methods for radiochemical processing of irradiated HEU targets leading to final product, a ^{99}Mo -containing molybdenum compound are presently available and are partially documented in the open literature. A short overview of such processing methods has recently been published [1] but the summary and two articles in an earlier document [3] also provide ample information on ^{235}U fission based production technologies for ^{99}Mo (and $^{99\text{m}}\text{Tc}$) as well. Moreover, the 25 previous proceedings of the RERTR Meetings held from 1978 to 2003 represent an almost inexhaustible source of knowledge and experience relevant to the processing of HEU targets. Typically, an irradiated target is treated with aqueous NaOH solution resulting in dissolution of “meat” and aluminum cladding. The solution obtained is filtered and the solid residue is treated with a solution of NaOH and H_2O_2 and then filtered. Both alkaline filtrates contain ^{99}Mo (as molybdate) which is then isolated by means of a number of different ion exchange columns and eventually converted into final product e.g. solid ammonium molybdate [4].

In the late 1970’s politicians and others came to the realization that the fuel used in many nuclear research reactors contains weapon-grade HEU. Subsequently a “Reduced Enrichment for Research and Test Reactors” (RERTR) program was established (in U.S.A) in “1978 to develop the substitute fuel of higher-density, low enriched uranium, which is not suitable for weapons” [5]. In the wake of that program studies were undertaken on converting the HEU based ^{99}Mo production to LEU one.

2. Present status and proposals

2.1. LEU target materials and targets

In order to yield the same ^{99}Mo quantity as an HEU target an LEU target has to contain five to six times more uranium than an HEU one. Moreover, in some cases adequately more uranium accompanying material such as aluminum in uranium aluminum alloy and interstitial aluminum powder (all being components of “meat”) as well as aluminum cladding have also to be accommodated. Such enlarged targets would then probably require some rather costly modifications of the existing reactor irradiation facilities. A possibility to circumvent such costs consist of keeping the targets and irradiation facilities unchanged or slightly modified but to find and use an uranium rich target material of high density. Consequently, the development of LEU targets to be used for replacing of HEU targets in existing reactor irradiation facilities should meet the following requirements [6]: (i) existing target geometry should not be modified; (ii) materials and fuels should be acceptable for reactor operators; (iii) target production should be straightforward, i.e. “low-tech” one. An intensive search for LEU targets complying with these requirements begun already in the eighty’s of the last century but it is still going on.

Although different, more or less potential LEU target materials and targets have been considered and some even tested most of the research has been focused on the development of LEU uranium metal foil and LEU uranium silicide, U_3Si_2 , based targets. However, in the last decade the emphasis has mainly been put on LEU foils which are primarily being developed at Argonne National Laboratory (Argon, Illinois, USA).

LEU metal containing about 20 % ^{235}U has a density of about 19.0 g cm^{-3} [2] and contains approximately 9.5×10^{21} atoms of ^{235}U per cm^3 LEU. One of the reported prototypes of uranium-foil targets contains a 130μ thick uranium metal foil enclosed between two coaxial zirconium tubes [6, 7]. The ends of the pairs of tubes are welded on, and the whole is filled with He and sealed. Note that not a pure LEU is used for production of foils but one doped with 100 ppm Al and 450 ppm Fe. This is in order to facilitate formation of necessary fine-grain structure during a complex heat treatment of foils. “A random, fine grained-structure limits effects caused by anisotropic growth of the uranium” [7]. Before being put between two metal tubes the uranium foil must be (electrochemically) provided with a 10 - 15 μm -thick metal (Zn or Al) layer to serve as fission fragment-recoil barrier preventing sticking of foil to the inner of the tubes [7].

The post-irradiation handling of targets starts with disassembling of the targets (accompanied by the removal and collection of fission gases) and ends with removing the LEU foil from the target.

LEU silicide, U_3Si_2 , with uranium containing about 20 % ^{235}U has a density of about 12.2 g cm^{-3} [8] and it contains approximately 5.7×10^{21} atoms of ^{235}U per cm^3 (40 % less than in LEU foil). This uranium silicide is easy to prepare by melting uranium metal and silicon, followed by grinding of the solid product till very fine particle are obtained. These are then mixed with aluminum powder and the mixture is used as a “meat” within an aluminum cladding. Note that such targets are commercially available and are presently applied as fuel elements in many research reactors.

The high density i.e. number of ^{235}U atoms per cm^3 of the above-mentioned silicide and consequently its potential utility to serve as a target material for production of fission ^{99}Mo led to a number of studies of its properties relevant to such production [6, 9]. It is now obvious that the ongoing production methods for LEU U_3Si_2 and targets based on it do not require much research and development. Consequently, their production can thus be described as being straightforward and indeed “low-tech” [6].

U_3Si_2 is not the only known uranium silicide [8]. There is another one, namely U_3Si , which is much denser than the other silicides (including U_3Si_2). The U_3Si has a density of 15.6 g cm^{-3} [8] i.e. 27.8 % higher than that of U_3Si_2 ! A LEU U_3Si with uranium containing about 20 % ^{235}U will contain approximately 7.5×10^{21} atoms ^{235}U per cm^3 (only 21.1 % less than in LEU foil). This silicide is formed by heating uranium and U_3Si_2 according to the reaction:



at about $800 \text{ }^\circ\text{C}$ [8].

The high density of U_3Si prompted many researchers to assess its application as fuel for any type of reactors [10]. The envisaged fuel elements were based on the mixture of very small particles of U_3Si and aluminum. In recent years much attention has been directed towards the

investigation of the neutron-irradiation induced swelling of U_3Si [10, 11]. However, an experimental study cited about 20 years ago [12] showed that a significant swelling (ca. 20 volume %) developed at 770 K (≈ 500 °C) and an integrated irradiation dose level of 8.1×10^{25} fissions per cm^3 . Note that a 150 h irradiation of 6 g cm^{-3} LEU as U_3Si particles (6.2 g) in a thermal-neutron flux of $10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ gives rise to 9.5×10^{19} fissions per cm^3 ; a value significantly lower than the above quoted one. Besides swelling some other aspects of the fuel preparation and utilization of LEU U_3Si and its based fuel targets were studied as well e.g. [13, 14].

Although, the research pertaining to utility of U_3Si to serve as a fuel material is not completed yet, there is a real chance that it will appear to be suitable for reactor use. Moreover, the suitability for reactor use points out a possibility of application of U_3Si as a target material for production of fission ^{99}Mo . It seems that the use of U_3Si as a target material has not been explicitly considered as yet.

2.1.1. Conclusions on target materials and targets:

The research and development of *LEU foil* based (tentative) targets for production of fission ^{99}Mo resulted in usable targets but sophisticated and probably not easy to produce and to handle after irradiation. Their production is obviously not a “low-tech” one. However, there is only one bulk chemical element to be processed radiochemically, namely uranium.

LEU U_3Si_2 target material is easy to produce and to obtain from commercial sources. The targets can be made by mixing LEU silicide powder with aluminum particles and subsequent cladding of the mixture with aluminum. The target remains intact till the start of the dissolution i.e. no elaborate handling of the targets after the irradiation is needed. There are three bulk chemical elements to be processed radiochemically, namely aluminum, silicon and uranium.

For the second mentioned silicide, namely the *LEU U_3Si* target material and target etc see (above) the analogues: *LEU U_3Si_2* . Moreover, it seems that the earlier expected swelling of LEU U_3Si due to the thermal-neutron irradiation will be minimal and thus poses no obstacle for its use in targets for production of fission ^{99}Mo .

2.2. Radiochemical processing of irradiated LEU targets

Thermal neutron irradiation of LEU based targets results not only in the formation of fission products of ^{235}U but also in the formation of relatively large amounts of ^{239}Pu (half-life = 2.4×10^4 year) due to the $^{238}U(n,\gamma)^{239}U$ reaction followed by the β^- decay of ^{239}U (half-life = 23.5 minutes) into ^{239}Np (half-life = 2.3 days) and β^- decay of the latter radionuclide to ^{239}Pu .

The development of methods for radiochemical processing of both LEU foils and LEU U_3Si_2 based targets after their thermal-neutron irradiation and subsequent cool down time can be followed by studying many publications in the proceedings of the RERTR meetings as well as in the proceedings of other conferences and articles in scientific journals. The free accessible information is quite abundant, however, not always complete, perhaps because of the possible economic implications of such information.

A compilation by G.F. Vandegrift and co-authors of current processes for production of ^{99}Mo [6] provides also an excellent insight in the development and testing of different routes for

radiochemical processing of irradiated LEU targets with emphasis on uranium foil and U_3Si_2 based ones. One should mention that the authors of this compilation have been actively involved in the research pertaining to both mentioned target materials. However, in 1996 “A decision has been made to suspend R&D activities on this (= U_3Si_2) fuel“(probably meant targets) [6].

The results of the continued work [15] on chemical processing of irradiated LEU foil resulted in a procedure starting with dissolution - (in a closed vessels) at elevated pressure and temperature (4.8 MPa = 48 bar; 260 °C) - of Al recoil barrier and conversion of U into solid oxides using a NaOH solution. In a second step the alkaline solution was pressurized with oxygen (0.7 MPa = 7 bar), and then again heated at elevated pressure and temperature (48 bar; 260 °C). Such treatment results in formation of solid $Na_2UO_2O_7$ (diuranate), and in a solution containing ^{99}Mo and some other fission products. Although these processing steps “proceeded smoothly” [15] some problems may probably be expected due to the relatively high pressures and temperatures and the use of oxygen.

The scientists of ANL have been and still are working on the design and elaborate experimental testing of different routes that should lead to the separation of ^{99}Mo from alkaline filtrate (see above) and eventually result in a product free of chemical and radioactive impurities i.e. a $^{99}Mo/^{99m}Tc$ generator fit to medical use. The details of their efforts reported in 2002 [15] illustrate the complexity of the mainly chemical problems to be solved prior to any attempt to realize an industrial scale chemical processing of irradiated LEU foil targets. However, this stage has not been reached as yet.

It seems that at present not much research and development pertaining to radiochemical processing of irradiated LEU silicide (U_3Si_2) based targets is going on. Such a target consists in principle of a mixture of LEU U_3Si_2 and aluminum powder kept together by an aluminum (alloy) cladding. It was possible to dissolve the (non-irradiated) cladding and “meat” aluminum in an aqueous NaOH- $NaNO_3$ solution but the attempts to properly dissolve irradiated cladding and silicide particles in a H_2O_2 -NaOH were less successful [16]. The authors of the latter paper announced a continuation of the development of uranium silicide process but in 1996 the work on LEU silicide targets has been discontinued. The results of work in the period 1993-1996 are summarized in [6] where on page 53 two footnotes inform that (i) Both U and U_3Si_2 catalyze auto-destruction of H_2O_2 and (ii) Later experiments used atomized, spherical U_3Si_2 powder instead of jagged comminuted powder.

An almost ready to use protocol for the production of fission ^{99}Mo from LEU uranium silicide, U_3Si_2 based targets was (co) developed by A.A. Sameh [9]. Starting with an irradiated mixture of LEU U_3Si_2 -Al and cladding the aluminum is removed by an alkaline digestion process resulting (after filtration) in some (20 %) fission products (including ^{99}Mo) containing filtrate and a residue of silicide particles with 85% of formed fission products (including ^{99}Mo). The central feature of the present protocol is the treatment of the residue with a mixture of HF, H_2O_2 and KIO_4 at room temperature, leading to formation of UF_4 and its iodine catalyzed oxidation to UF_6 . After addition of KOH and H_2O_2 , followed by boiling of the solution (in order to eliminate the excess of peroxide) an alkaline, ^{99}Mo and some fission products containing solution is obtained. The recuperation of ^{99}Mo from this solution can be achieved by a number of steps similar to those in radiochemical processing of HEU targets.

A two step dissolution procedure for U_3Si_2 has been applied as a part of a destructive analysis of U_3Si_2 fuel for burnup determination [17]. First the Al clad and Al in the “meat” were

dissolved in aqueous HNO_3 solution containing some Hg^{2+} as a catalyst facilitating dissolution of Al. A fraction of fuel material goes into solution as well. The obtained suspension is filtered and - as second step - the residue is treated with 10 molar HNO_3 and 0.1 molar HF solutions and the whole is filtered again. The remaining silica residue appeared to be free of U, Pu and probably some fission products (^{99}Mo ?). Further research is needed in order to establish the dissolution behavior of ^{99}Mo .

Not much information could be found as to the chemical properties of U_3Si relevant to its possible use as a target material for production of fission ^{99}Mo . However, it is known that U_3Si reacts with concentrated HCl, HNO_3 , and H_2SO_4 but not with 1 molar solution of NaOH [12].

2.2.1. Conclusions on radiochemical processing of targets

The research on and development of methods eventually to be used for the industrial scale radiochemical processing of *LEU foil* and *LEU U_3Si_2* have as yet not reached their goals, namely the delineation of practical processing protocols. However, it seems that the present status of the LEU U_3Si_2 related activities fairly approaches that goal.

The open information on the research and development of radiochemical processing of targets suggests that a try-and-error approach rather than a knowledge based one forms the basis of the selection and adoption of different chemical agents and reactions (to be) involved in the processing. Moreover, many chemical statements lack their proof.

It is worth while to evaluate the suitability for radiochemical processing of irradiated *LEU U_3Si* based targets.

3. General conclusion

A decision to convert an existing HEU based production of fission ^{99}Mo to a LEU based one or to set up a new production should be followed by a thorough study of the degree of maturity of different (tentative) protocols for ^{99}Mo production. Present paper may perhaps facilitate the process of gauging the maturity of available protocols. However, it seems that simplicity of the production of LEU U_3Si_2 based targets as well as the state of development of the chemical processing of these targets are now somewhat more favorable than the LEU foil based ones. It speaks for itself that both production lines and indeed the proposed U_3Si based target and its chemical processing still need more research and development.

A post 2004 RERTR Meeting remark: According to an oral contribution to this meeting by G.F. Vandegrift (ANL) the development of LEU foil targets and their chemical processing has significantly progressed during the last few years.

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