

1

Title page

2 Names of the authors: Kamil Vavřinec Mareš, Jan John

3 Title: Recycling of Isotopically Modified Molybdenum from Irradiated CerMet Nuclear

4 Fuel – Part 1: *Concept Design and Assessment*

5 Affiliation(s) and address(es) of the author(s): Department of Nuclear Chemistry, Czech

6 Technical University in Prague, Břehová 7, 115 19 Prague 1, Czech Republic

7 E-mail address of the corresponding author: mareskam@jfifi.cvut.cz

8

<https://link.springer.com/article/10.1007/s10967-019-06456-2>

9 **Recycling of Isotopically Modified Molybdenum from**
10 **Irradiated CerMet Nuclear Fuel – Part 1: *Concept***
11 ***Design and Assessment***

12 Kamil Vavřinec Mareš¹, Jan John¹

13 ¹*Department of Nuclear Chemistry, Czech Technical University in Prague, Břehová 7,*
14 *115 19 Prague 1, Czech Republic*

15 **Abstract**

16 This paper deals with concept design and assessment of a process for the recovery of
17 isotopically modified molybdenum from irradiated nuclear CerMet fuels containing the
18 transuranium element (TRU) oxides in a metallic molybdenum matrix. The recovery of
19 isotopically modified Mo should enable re-use of this valuable resource especially in the
20 case of uranium-free fuels/targets for Accelerator-Driven Transmuters (ADT). The
21 process concept proposed is a modification of the standard hydrometallurgical way of
22 molybdenum processing. Further, the most significant expected radionuclidic impurities
23 in the molybdate raffinate were predicted. Separation of these impurities from the
24 concentrated molybdate solution will be described in the following parts of this mini-
25 series.

26 **Keywords**

27 Inert matrix fuel, CerMet, molybdenum, reprocessing

28 **Introduction**

29 Molybdenum has many applications as the inert matrix in nuclear fuel. As an additive,
30 ranging from 3 to 10 wt. %, molybdenum has been used in metallic fuels since the 1950s
31 [1,2]. For CerMet type fuel, comprising of fissile material ceramics (UO_2 , $\text{UO}_2 \cdot 2\text{UO}_3$,
32 PuO_2 , ThO_2) in an inert metallic matrix, 50 – 85 % molybdenum has been used to
33 optimise their physical and metallurgical properties [3]. Another example of the use of
34 CerMet nuclear materials are the thermoelectric generators based on CerMet materials
35 developed early in the 1970s, in which the radioisotope ^{244}Cm in its oxide form was used.
36 These contained 50 - 70 % molybdenum in the matrix [4]. The historical use of powder
37 metallurgy in nuclear technology for handling the minor actinides led to the idea of an
38 alternative use of U-free Mo-based CerMet fuel for the transmutation of plutonium and
39 the minor actinides [5]. In the following overview, these fuels are discussed according to
40 their composition. In addition to their description, focus is paid to the reprocessing of
41 each type of the fuel.

42 Uranium-Molybdenum Fuel (UMo)

43 One of the earliest references to the application of 3 – 10 wt. % molybdenum as a fuel
44 additive in the form of a uranium-molybdenum alloy for several power reactors was
45 described by Schulz and Duke [1], for uranium enriched to approximately 5 % ^{235}U . The
46 study of reprocessing options revealed that, due to the low solubility of uranyl molybdate,
47 a uranium-molybdenum alloy containing 3 wt. % molybdenum can only be dissolved up
48 to a maximum uranium concentration of $0.4 \text{ mol} \cdot \text{L}^{-1}$ (in an equilibrium concentration of
49 nitric acid of $1 \text{ mol} \cdot \text{L}^{-1}$). In less acidic solutions, the situation is even worse and the
50 maximum uranium concentrations that can be attained are even lower. Significant
51 increase in solubility is mentioned in the presence of ferric ions. In the presence of 1
52 $\text{mol} \cdot \text{L}^{-1} \text{ Fe}(\text{NO}_3)_3$ the solubility of uranium may increase to $1 \text{ mol} \cdot \text{L}^{-1}$ in $0.1 \text{ mol} \cdot \text{L}^{-1}$
53 HNO_3 . Another advantage of the addition of ferric nitrate is the long-term stability of the
54 resulting solutions (no precipitation occurs). The effect of different concentrations of
55 $\text{Fe}(\text{NO}_3)_3$ additive have been described by Schulz and Duke [1]; a better summary of
56 these results can also be found in some later publications, e.g. Schulz et al. [6].

57 Ferris [2] further extended these studies. Fuels with 3 wt. % molybdenum content (e.g.
58 Detroit Edison Blanket) were dissolved in $6 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 and fuel with 10 wt. %
59 molybdenum (e.g., fuel CPPD-1) in $11 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 . The precipitate formation
60 observed, especially in the case of fuel with higher molybdenum content, was mitigated
61 by using ferric ions that form soluble complexes with molybdenum. Also, the positive
62 effect of phosphoric acid addition on the solubility of MoO_3 in nitric acid solutions as
63 well as the rate of dissolution of uranium-molybdenum alloys in boiling nitric acid
64 solution is described.

65 Reprocessing of fuel with 10 wt. % Mo and 20 % ^{235}U enrichment originating from the
66 Super Kukla reactor (operated from 1964 to 1978) has been described by Visser et al. [7]
67 as a follow-up of an early successful study by Perkins [8]. It was planned to reprocess
68 this fuel in the Savannah River Plant, where the reprocessing uses 7.5 vol. % TBP in n-
69 paraffin, and requires clear uranium solutions (no precipitates) with uranium
70 concentrations of $15 - 20 \text{ g}\cdot\text{L}^{-1}$. They highlighted the problem of low solubility of
71 molybdenum in the acidic medium. During the dissolution, formation of a red-brown
72 precipitate was observed. Scanning electron microscopy revealed that it contained non-
73 crystalline molybdenum with a low content of iron and small quantities of uranium [7]. It
74 has been reasoned that the precipitate is probably $(\text{UO}_2)_3\text{Mo}_6\text{O}_{21}$ containing 42 wt. % U
75 and 33 wt. % Mo, as was described before [6]. Extraction of uranium from the dissolved
76 fuel was tested for the uranium concentration of $16 \text{ g}\cdot\text{L}^{-1}$, and it was confirmed that
77 molybdenum remains unextracted upon contact with 7.5 vol. % TBP in n-paraffin [7].

78 Based on this data, it can be concluded that uranium-molybdenum based fuel can be
79 relatively easily dissolved in nitric acid, if the final molybdenum concentration is
80 relatively low (approx. $1 \text{ g}\cdot\text{L}^{-1}$, depending on the conditions). Thus one of the options for
81 uranium-molybdenum fuel (< 3 wt. % of Mo) is its direct dissolution in nitric acid or
82 dissolution with $\text{Fe}(\text{NO}_3)_3$ addition (for fuel with up to 10 wt. % of Mo). However, these
83 options for uranium-molybdenum fuel dissolution do not take into account the possible
84 recycling of the molybdenum.

85 **Uranium-Molybdenum Fuel with Aluminium (UMo+Al)**

86 Uranium-molybdenum based fuels with high aluminium content have been produced and
87 used primarily for research and test reactors since the 1980s. The main reason for their
88 use are their beneficial properties even when using a relatively low enriched uranium
89 (< 20 wt.% of ^{235}U) [9].

90 Herlet et al. [9] described a research program on the dissolution of uranium-molybdenum
91 fuels (10 wt. % molybdenum). The project included experiments with powder and fresh
92 pellets with addition of aluminium and three pellets irradiated inside the French OSIRIS
93 reactor. After the dissolution of such fuel, it was mixed (1:13) with a dissolved uranium
94 oxide (UOX) fuel and subsequently uranium and plutonium separated by the adapted
95 PUREX process [10,11]. The biggest issue was expected to be the solubility of
96 molybdenum ($\sim 1 \text{ g}\cdot\text{L}^{-1}$) in the presence of uranium, aluminium and nitric acid. The
97 dissolution experiments were performed so that the final aluminium concentration was 15
98 $\text{g}\cdot\text{L}^{-1}$, which corresponds approximately to a molybdenum concentration of up to 1.5 $\text{g}\cdot\text{L}^{-1}$.
99 ¹. In the summary of the results Herlet et al. [12] also described the dissolution kinetics.
100 For the reprocessing of Mo-based fuels, it is also important that the insoluble species and
101 behaviour of the solution over time are characterised. Immediately after dissolution the
102 solution was relatively clear, but the following day it was slightly cloudy. The insoluble
103 particles extracted by a 0.3 μm filter contained less than 0.6 wt. % of the fuel. They
104 consisted of more than 90 wt. % of molybdenum and aluminium. After this initial
105 filtration, the filtrate remained clear for more than a month. However, Helaine et al. [13]
106 noted that they were still looking for the most appropriate way to reprocess UMo+Al fuel
107 manufactured by mixing of UMo particles into the mass of aluminium alloy.

108 CerMet Mo-based Fuel for light water reactors (DepMo)

109 The possibility of transmutation of plutonium and minor actinides in light-water reactors
110 (LWRs) using CerMet fuel with a molybdenum matrix is discussed by Bakker et al. [5].
111 The advantage of LWRs comes from experience with the transmutation of plutonium in
112 MOX fuel (Mixed oxides). However, for LWRs the intended molybdenum content
113 requires the use of molybdenum depleted in ^{95}Mo (DepMo), since ^{95}Mo has a relatively

114 large cross section for thermal neutrons – see Table 1. The possibility of producing
 115 isotopically modified molybdenum at a reasonable price has been re-confirmed recently
 116 [14]. Such CerMet fuel is expected to have considerably better behaviour during
 117 operation, amongst other reasons, due to its excellent thermal conductivity ($\lambda = 116 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at 600 °C [5,15]), which reduces the maximum temperature in the central part of the
 118 pellet, and therefore the release of gaseous fission products will be lower [16]. The
 119 thermal conductivity of molybdenum is very close to that of molten sodium, a commonly
 120 used coolant in fast reactors (thermal conductivity at melting/freezing point of sodium is
 121 $85.8 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ [17]).
 122

123 **Table 1** The neutron absorption cross section of the molybdenum isotopes in the thermal,
 124 epithermal, and fast energy groups [5]

Molybdenum Isotope	Neutron Absorption Cross Section (b)		
	Thermal Range ($10^{-5} \text{ eV} < E < 0.625 \text{ eV}$)	Epithermal Range ($0.625 \text{ eV} < E < 0.1 \text{ MeV}$)	Fast Range ($E > 0.1 \text{ MeV}$)
92	0.01	0.02	0.03
94	0.01	0.03	0.05
95	7.51	0.40	0.10
96	0.25	0.08	0.04
97	1.08	0.23	0.10
98	0.06	0.06	0.04
100	0.10	0.05	0.03

125 According to preliminary design, active zone, using DepMo as an inert matrix for the
 126 transmutation of transuranic elements (TRU), should contain approximately 20 % fuel
 127 rods, which would contain up to 70 vol.% of DepMo and 30 vol.% of
 128 $(\text{TRU}_{0.36}\text{Er}_{0.03}\text{Y}_{0.07}\text{Zr}_{0.54})\text{O}_2$ [5], where TRU could be plutonium, americium or other
 129 transuranium elements such as Np, Am, Cm [18]).

130 **CerMet Mo-based fuel for ADT (^{92}Mo)**

131 From Table 1 it is evident that for a fast reactor fuel the isotopic composition of
 132 molybdenum is not as important as it is for the conventional reactors using uranium

133 fission by thermal neutrons. However, in the case of ADT it is necessary to achieve the
134 optimum neutron balance, because otherwise a transmutation ability decrease would
135 occur as well as a possible increase in operational costs due to increase in accelerator
136 performance [19]. Again, the most preferred isotope is ^{92}Mo , due to the low absorption
137 cross section for all types of neutron. Its usage also reduces the production of long-lived
138 ^{99}Tc [19].

139 Currently, it is proposed to transmute oxides of Pu, Am and Cm by ADT, but elements
140 such as americium affect the transmutation fuel design. During americium transmutation,
141 the relatively large amount of helium produced (5 times more than with conventional
142 UOX fuel), may cause swelling of fuel pellets [20]. This problem can be also solved
143 using the CerMet type fuel [16,21], because the molybdenum matrix is a suitable barrier
144 in preventing the release of gases up to 1100°C [16].

145 Recently, uranium-free CerMet Mo-based fuels for ADT were prepared and irradiated in
146 two experiments as part of the EUROTRANS project under the names FUTURIX-FTA
147 (Fuels for Transmutation of Transuranium Elements in Phénix - Fortes Teneurs en
148 Actinides) [22-25] and HELIOS (Helium in Oxide Structure, irradiation in high flux
149 reactor in Petten, The Netherlands) [26,27].

150 The analysis presented above shows the need to use isotopically modified molybdenum
151 in the CerMet fuels with a molybdenum matrix in order for such fuels to be used in both
152 LWRs and ADTs. The aim of this study has been to design concept of a process for the
153 recycling of molybdenum – separation of bulk metal from the irradiated fuel –
154 compatible with the radiochemistry operations in hot cells in order to reduce the costs of
155 using isotopically modified molybdenum. For the re-fabrication of new fuel,
156 concentration of any radionuclides in the recovered metal should be minimised.
157 Therefore, another aim was to analyse the proposed recycling scheme for the potential
158 break-through of the fission products, or fissile elements, into the raffinate. To study the
159 options for decontamination of the raffinate liquors (separation of the broken-through
160 radionuclide contaminants) has been the aim of the successive parts of this complex

161 project that has been carried out as a part of ASGARD (Advanced fuels for Generation
162 IV reactors: Reprocessing and Dissolution) programme [28].

163 **Results and discussion**

164 Design of the Scheme for the Separation of Molybdenum from ADT Fuel

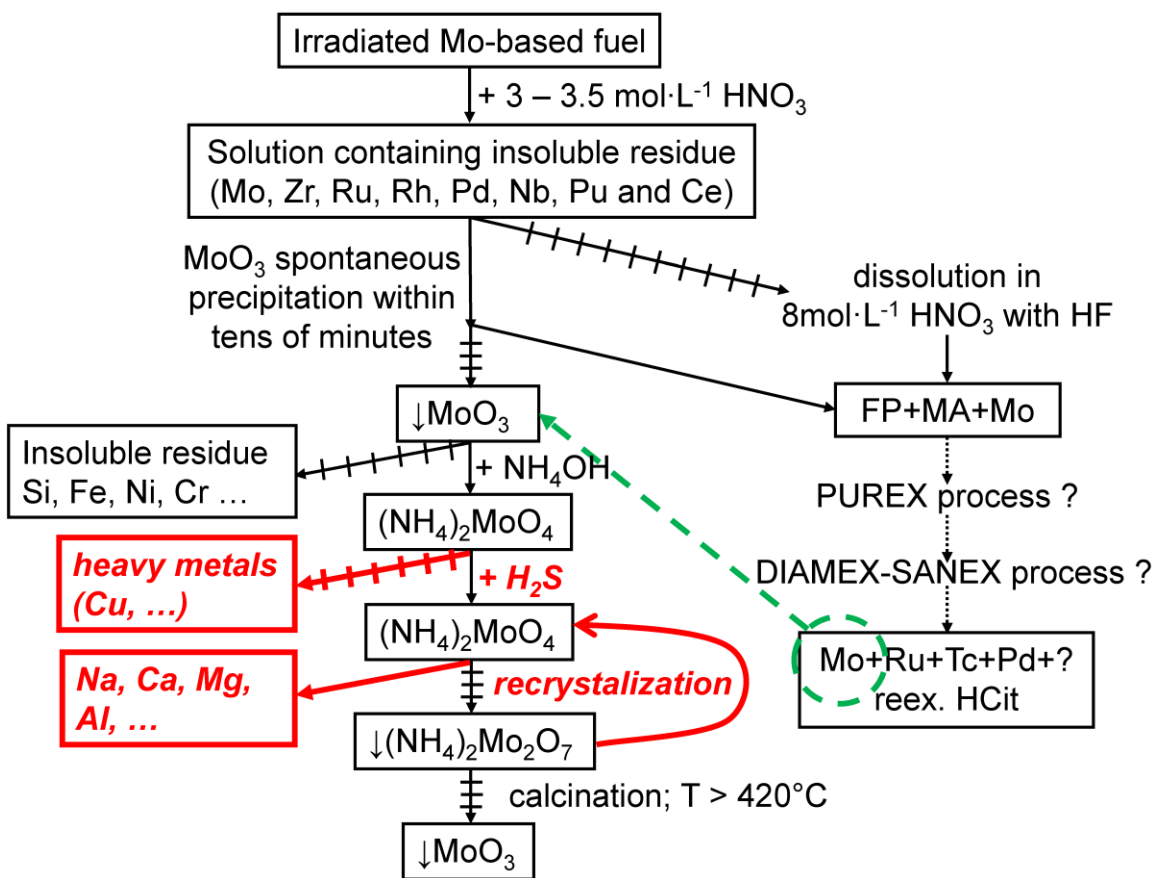
165 From the review above, it follows that, as far as we are aware except for the current
166 project, nobody else has previously considered recovering used molybdenum from the
167 existing fuels. However, due to the high price of ^{92}Mo -enriched molybdenum, which
168 should be used as inert matrix for transmutation of minor actinides in ADT fuels, a way
169 to not only recover but even to recycle the molybdenum from the matrix should be
170 developed. If ^{92}Mo -enriched molybdenum recycling can be effected, it could also find use
171 in recycling the DepMo (without ^{95}Mo) used in CerMet fuel for light water reactors (see
172 above).

173 Flowsheet Proposal

174 When considering ^{92}Mo -enriched molybdenum reprocessing, one of the first
175 considerations must be the fact that these Mo-based fuels do not contain uranium. This is
176 important because in such cases the requirement for reprocessing in a PUREX-like
177 process is not a must. However, it should be considered that most separation processes
178 for spent nuclear fuel reprocessing, comprising the separation of corrosion and activation
179 products, fission products and TRU are designed for $1 - 3 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ media.
180 Unfortunately, molybdenum is poorly soluble in acids (only up to *ca.* $1 \text{ g}\cdot\text{L}^{-1}$) and,
181 depending on pH, it forms a number of complex chemical forms ranging from polymeric
182 (containing up to more than 24 atoms of molybdenum per molecule, even at a low
183 concentration) to molybdenyl [29].

184 If we accept the necessity of the addition of $1 \text{ mol}\cdot\text{L}^{-1}$ ferric nitrate to increase the
185 solubility (used in the separation of uranium from UMo fuels [1,6]), the solution will

186 have an even higher ionic strength, and it will be difficult to predict its behaviour. In
 187 addition, we are constantly confronted with the possibility of precipitation in further steps
 188 [30]. For this reason, it is probably most appropriate to separate the molybdenum
 189 precipitate at the beginning of the reprocessing process. Then, the molybdenum fraction
 190 and the rest of irradiated fuel solution would be reprocessed separately, as is proposed in
 191 work of Ménard [31]. Based on this concept, the following flowsheet has been proposed
 192 for the reprocessing of Mo-based ADT fuels (Fig. 1).



193

194 Fig. 1 Hypothetical flowsheet for the reprocessing of ADT fuel with molybdenum inert
 195 matrix based on a standard molybdenum hydrometallurgical process. **bold italic** steps are
 196 unsuitable for radiochemical operations - the aim is to replace them. (The **dashed green**
 197 arrow refers to the molybdenum, which is partially dissolved in acidic media – it should be
 198 returned to the main molybdenum fraction. Solid arrows denote liquid phase. Crossed-out
 199 arrows denote solid phase, and dotted arrow denotes unspecified processes)

200 *Step 1 – Fuel dissolution*

201 Fuel dissolution in 3 – 3.5 mol·L⁻¹ HNO₃ is assumed as proposed by Ménard [31]. This
202 should result in the dissolution of virtually all of the molybdenum, and a significant
203 portion of the fission products, and in the formation of a kinetically unstable solution in
204 nitric acid. Before the precipitation of molybdenum oxide from this solution begins, it
205 can be quickly filtered as there is a time window of about 6 hours during the process
206 when the dissolved molybdenum solution does not contain any solid phase. At this point,
207 it might be useful to consider avoiding the coprecipitation of fission products, plutonium
208 and minor actinides by addition of suitable complexants. Due to this relatively unusual
209 kinetic phenomenon it is obviously possible to separate molybdenum from the majority
210 of the other elements relatively easily.

211 Similarly to fast reactor fuel reprocessing [32], the filtered insolubles may be leached
212 using 8 mol·L⁻¹ HNO₃ with the addition of 0.05 mol·L⁻¹ HF (or 1 mol·L⁻¹ HF according
213 to [31]) or with the addition of Cr(NO₃)₄ to dissolve the plutonium, transplutonium
214 elements, and fission product residues. On the other hand, such processes would increase
215 the requirements for corrosion resistance of the construction materials and convert
216 plutonium to fluoride complexes of Pu(IV) and Ru to volatile RuO₄. The resulting
217 solution may be mixed with the molybdenum trioxide precipitate washing solution. The
218 solution obtained will be suitable for conventional separation of plutonium,
219 transplutonium elements, and fission products by solvent-extraction processes.

220 *Possible problems in Step 1:*

- 221 • Occurrence of insoluble fission residues can be expected during the dissolution of
222 high-burnup ADT targets/fuel. This phenomenon is well known from dissolving
223 both conventional UOX fuel [32] with burn-up exceeding ca. 30 MWd·t⁻¹
224 and the MOX fuels [32]. The insoluble residues containing Zr, Ru, Rh, Pd, Nb, Ce
225 and residual fissile material [32] will need to be removed.
- 226 • Trace amounts of fission products, plutonium and minor actinides will be
227 transferred into the molybdenum fractions – further radiochemical separation
228 steps may be needed; the concentration of fission products present in the resulting

229 precipitate of molybdenum oxide should be minimised, therefore a washing step
230 may be required.

231 • A fraction of the molybdenum will follow the fission products, plutonium and
232 minor actinides streams due to the partial solubility of molybdenum in nitric acid
233 or due to the formation of an insoluble residue. This may pose a problem with
234 precipitation during the molybdenum liquid-liquid extraction processes and/or the
235 loss of isotopically modified molybdenum; its return into the molybdenum stream
236 should be ensured (dashed arrow on Fig. 1).

237 • Isotopic dilution of ^{92}Mo by fission molybdenum will occur.

238 *Step 2 – Molybdenum recovery and purification*

239 The proposal is based on standard molybdenum hydrometallurgical processes.
240 Dissolution of MoO_3 may be performed in ammonia, for example, via the patented
241 process [33]. Together with molybdenum, only a small fraction of the fission products
242 such as Y, Zr, Nb and the lanthanides should dissolve in such step.

243 *Possible problems in the Step 2:*

244 • Most of the impurities co-precipitated with the MoO_3 will be partially dissolved,
245 as well (depending on their solubility product constants).

246 • The presence of radionuclides may complicate (need for additional radiation
247 protection) the standard industrially used purification steps – steps 3 and 4 –
248 (marked in bold italics) on Fig. 1.

249 Based on the above considerations, it can be concluded that alternative procedures to
250 sulphide precipitation and/or recrystallization have to be developed for the separation of
251 the remaining impurities, particularly the radionuclides, from the concentrated molybdate
252 solution resulting from MoO_3 dissolution. As a first step in new separation procedure

253 development, identification of the expected radionuclide impurities is required. This can
254 be accomplished by a holistic analysis of the chemical properties of the system
255 components.

256 Prediction of the Expected Impurities in Solution of $(\text{NH}_4)_2\text{MoO}_4$

257 In standard hydrometallurgical production of molybdenum, precipitation by H_2S and
258 recrystallization (steps marked bold italics in Fig. 1) are used for purification because
259 these processes successfully remove heavy metals such as Cu [34], possibly also all the
260 2.A analytical class cations, and in excess of ammonia also the third analytical class.
261 These processes perform well; however, the presence of radionuclides may complicate
262 their use (see above). Therefore, how to replace these procedures has been investigated in
263 this project. Exact estimation of the remaining contaminants and their concentrations is
264 practically impossible without performing experiments with real solutions, however,
265 some conclusions may be drawn when considering the general chemical properties of the
266 potential contaminants. It is clear that the most important will be the removal of
267 radionuclides (especially in terms of radiation protection during the manufacturing of fuel
268 from the recycled molybdenum) and of the isotopes having a high cross section for fast
269 neutrons (neutron poisons).

270 It should be also considered that molybdenum isotopes are also formed during fission and
271 these cannot be chemically separated, and will thus accumulate in the recycled ^{92}Mo .
272 Hence, the quality of the original ^{92}Mo -enriched molybdenum will deteriorate and isotope
273 separation may be needed after a few cycles. Especially in such a case, it will be
274 necessary to get rid of all the radioactive impurities that would render unusable most of
275 the technologies for molybdenum isotope separation, e.g. in gas centrifuges [35].

276 The impurities expected from the flowsheet (see Fig. 1) belong among fission and
277 corrosion products, and cladding materials. The most important radionuclide impurities
278 are fission products with high fission yields, especially those with similar chemical
279 properties (forming anions) as molybdenum e.g. Nb and Tc. The presence of impurities
280 will strongly depend on the chemistry of the previous step – bulk molybdenum

281 separation. If the most probable method for separation of Mo – the ADM (ammonium
282 dimolybdate) method – is used, alkali metals like Cs or Rb, as well as alkaline earth metal
283 like Sr may also be expected as impurities in Mo solutions [34].

284 Also taking in account their nuclear properties, it can be assumed that the main fission,
285 corrosion and activation products that will not be precipitated by ammonium hydroxide
286 will include: ^{14}C ($T_{1/2} = 5730$ years), ^{90}Sr (29 years), ^{99}Tc (10^5 years), ^{107}Pd (10^6 years),
287 ^{125}Sb (2.8 years), ^{134}Cs (2.06 years), ^{135}Cs ($2.6 \cdot 10^6$ years) and ^{137}Cs (30.07 years). Due to
288 their relatively high initial concentrations in the irradiated fuel and moderate to long half-
289 lives, they could cause an increase in activity of the molybdenum solution. The volatile
290 radionuclides, such as Ru in the form of volatile RuO_4 (if present), can be stripped by
291 bubbling with gas.

292 Finally, it should be noted that the procedures for selected radionuclide separation from
293 the concentrated molybdate solutions may find use in molybdenum recycling even if the
294 dissolution of ADT fuel would be by the acidic method only and all molybdenum would
295 be dissolved with the actinides and fission products by e.g. addition of $\text{Fe}(\text{NO}_3)_3$. The
296 reason for this conclusion is the fact that the conversion of the various molybdenum
297 species to metal is always carried out from MoO_3 , $(\text{NH}_4)_2\text{Mo}_6\text{O}_{19}$ or $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ [34].
298 Hence the separation of any potential remaining impurities may easily proceed from the
299 concentrated solution of ammonium molybdate prior to its conversion to molybdenum
300 trioxide.

301 Recent alternative studies

302 Three alternative routes for molybdenum reprocessing have been recently tested in the
303 ASGARD project [28]: one pyrochemical and two hydrometallurgical. Re-sublimation of
304 molybdenum from the mixture of 60 wt.% molybdenum and 40 wt.% cerium as
305 plutonium surrogate yielded the best results at 900°C after 6 hours of treatment, but in
306 one step only 86 % recovery of molybdenum has been achieved [36]. In the same study,
307 dissolution of molybdenum, molybdenum-cerium and molybdenum-plutonium oxide
308 pellets in the presence of iron was studied followed by extraction by tri-*n*-butyl phosphate

309 or two DIAMEX type extractants (N,N'-dimethyl,N,N'-dioctylhexylethoxymalonamide –
310 DMDOHEMA; N,N,N',N'- tetraoctyldiglycolamide – TODGA). Another work [37]
311 focused on the molybdenum extraction from acidic solutions by CYANEX[®] 600 (a
312 mixture, which contains mostly bis(2,4,4-trimethylpentyl)phosphinic acid [38]). Efficient
313 extraction was possible from HNO₃ in solution, co-extraction of iron and zirconium could
314 be suppressed by cyclohexanediaminetetraacetic acid. Molybdenum could be stripped
315 from the loaded organic phase containing CYANEX[®] 600 by using ammonium
316 hydroxide [39].

317 **Conclusions**

318 Based on a literature review, it has been concluded that if separation of impurities will be
319 required in the final stage of hydrometallurgical molybdenum reprocessing, it will
320 proceed from the (ammonium) molybdate solution prior to its conversion to molybdenum
321 metal (independent of the route selected for the reprocessing of the fuel with a
322 molybdenum matrix). Assuming the standard hydrometallurgical method of molybdenum
323 reprocessing is adapted, potential radionuclide impurities in the (ammonium) molybdate
324 at the final stages of the process were identified to be caesium, strontium and technetium.

325 Study of the options for decontamination of the raffinate liquors (separation of the listed
326 radionuclide contaminants) has been the aim of the successive parts of this complex
327 project. The results will be presented in the next papers in this mini-series.

328 **Acknowledgements**

329 This study was supported by the ASGARD Project supported by EU within the 7th
330 Framework Programme (EC-GA No. 295825), the Grant Agency of the Czech Technical
331 University in Prague (grants No. SGS12/199/OHK4/3T/14
332 and SGS15/216/OHK4/3T/14), and by the Centre for advanced applied science, Project
333 Number CZ.02.1.01/0.0/0.0/16_019/0000778, supported by the Ministry of Education,
334 Youth and Sports of the Czech Republic.

335 **References**

- 336 1. Schulz W W, Duke E M (1959) Reprocessing of Low Enrichment Uranium
337 Molybdenum Alloy Fuels. U.S. AEC, HW-62086
- 338 2. Ferris L M (1961) Aqueous Processes for Dissolution of Uranium-Molybdenum Alloy
339 Reactor Fuel Elements. U.S. AEC, ORNL-3068
- 340 3. Moore J W et al. (1961) Method of Making Nuclear Fuel Elements. US Patent
341 3,006,832
- 342 4. Rankin D T et al. (1971) Hot Pressing Techniques for Fabricating Cm_2O_3 for
343 Radioisotopic Fuel Forms. Savannah River Laboratory DP-1270
- 344 5. Bakker K et al. (2004) The Use of Molybdenum-Based Ceramic-Metal (CerMet) Fuel
345 for the Actinide Management in LWRs. Nucl Technol 146: 325-331
- 346 6. Schulz W W, Burns R E, Duke E M (1962) Nitric Acid Dissolution of Uranium-
347 Molybdenum Alloy Reactor Fuels. Ind Eng Chem Process Des Dev 1: 156-160
- 348 7. Visser A E, Pierce R A, Laurinat J E (2008) Purification of Uranium from a
349 Uranium/Molybdenum Alloy. Separ Sci Technol 43: 2775-2785
- 350 8. Perkins W. (1972) Processing Piqua Fuel in 221-H. DPST-72-540
- 351 9. Herlet N et al. (2003) Reprocessing U-Mo Spent Fuels: Research Program. In: RRFM
352 2003 Transactions: 245-246
- 353 10. Herlet N et al. (2005) Reprocessing UMo Spent Fuels: Dissolution Studies on
354 Unirradiated and Irradiated Materials. Presentation at the RRFM 2005 – 9th
355 International Topical Meeting on Research Reactor Fuel Management, Budapest,
356 Hungary, 10-13 April 2005
- 357 11. Jevenelle A et al. (2004) U-Mo Spent Fuels Reprocessing First Experimental Results
358 on Unirradiated Fuels. In: RRFM 2004 Transactions: 222-225
- 359 12. Herlet N et al. (2005) Reprocessing U-Mo Spent Fuels: Dissolution Experiments on
360 Non-Irradiated and Irradiated Materials. In: RRFM 2005 Transactions: 169-173
- 361 13. H elaine E et al. (2006) Research and Test Reactor Fuel Reprocessing at Areva NC La
362 Hague. In: RRFM 2006 Transactions: 172-177
- 363 14. Smirnov A Yu et al. (2015) Isotopically Modified Molybdenum: Production for
364 Application in Nuclear Energy. Phys Procedia 72: 126-131

- 365 15. Porta J, Aillaud J, Baldi S (1999) Composite Fuels: Neutronic Criteria for Selection
366 of Matrix, Core Control, Transients, and Severe Accidents. In: Proc. 7th ICONE-7110
367 16. Dehaut Ph et al. (1997) Composite Fuel Behaviour Under and After Irradiation. In:
368 Studies on Fuel with Low Fission Gas Release. IAEA: 23-33
369 17. Vohlídal J et al. (1982) Chemical tables for chemical and chemically oriented high
370 schools (in Czech). SNTL
371 18. Shwageraus E, Hejzlar P, Kazimi M S (2004) Use of Thorium for Transmutation of
372 Plutonium and Minor Actinides in PWRs. Nucl Tech: 279-292
373 19. Haas D et al. (2006) Properties of CerMet Fuels for Minor Actinides Transmutation
374 in ADS. Energ Convers Manage 47: 2724-2731
375 20. Konings R J M et al. (2000) The EFTRA-T4 Experiment on Americium
376 Transmutation. J Nucl Mater 282: 159-170
377 21. Porta J, Puill A (1998) U-Free Pu Fuels for LWRs – The CEA/DRN Strategy. In:
378 Proc. ARWIF: 169-186
379 22. Calabrese R et al. (2010) Heterogeneous Fuels for Minor Actinides Transmutation:
380 Fuel Performance Codes Predictions in the EFIT Case Study. Ann Nucl Energy 37:
381 867-874
382 23. Haas D et al. (2008) CerMet Fuel Behaviour and Properties in ADS Reactors. Energ
383 Convers Manage 49: 1928-1933
384 24. Fernández A, Konings R J M, Somers J (2003) Design and Fabrication of Specific
385 Ceramic-Metallic Fuel and Targets. J Nucl Mater 319: 44-50
386 25. Fernández A et al. (2002) Transmutation of Actinides. J Am Ceram Soc 85: 694-696
387 26. European Commission (2011) Accompanying document to the Report "Operation of
388 the High Flux Reactor in year 2009".
389 27. European Commission (2012) Commission Staff Working Paper Accompanying the
390 Document Report from the Commission to the Council and the European Parliament
391 "Operation of the High Flux Reactor in the Year 2010".
392 28. Advanced fuels for Generation IV reactors: Reprocessing and Dissolution –
393 ASGARD (2012–2015) EURATOM FP7-Fission-2011 project No. 295825,
394 <http://asgardproject.eu/>

- 395 29. Tkac P, Paulenova A (2008) Speciation of Molybdenum (VI) In Aqueous and
396 Organic Phases of Selected Extraction Systems. *Separ Sci Technol* 43: 2641-2657
- 397 30. Heinrich H (1964) Method of Reprocessing and/or Separating Nuclear Fuels. US
398 Patent 3,322,509
- 399 31. Ménard G et al. (2013): Dissolution of Irradiated Advanced Fuel: HELIOS Pin 5.
400 Presentation at the 3rd ASGARD project meeting, Warsaw, Poland
- 401 32. Štamberg K (2005) Nuclear fuels technology II (in Czech). CTU in Prague – FNSPE
- 402 33. Cheresnowsky M J (1988) Process for Producing Ammonium Molybdate from
403 Molybdenum Trioxide. US Patent 4,735,791
- 404 34. Sebenik R F et al. (2012) Molybdenum and Molybdenum Compounds. In: Ullmann,
405 F. et al. (eds.): *Ullmann's Encyclopaedia of Industrial Chemistry*. Wiley-VCH: 522-
406 565
- 407 35. Smirnov A Yu et al. (2015) Isotopically Modified Molybdenum: Production for
408 Application in Nuclear Energy. *Phys Procedia* 72: 126-131
- 409 36. Mühr-Ebert E L (2017) Dissolution Behaviour of Innovative Inert Matrix Fuels for
410 Recycling of Minor Actinides. *Forschungszentrum Jülich*, ISBN 978-3-95806-238-2
- 411 37. Bremer A, Stauch C, Geist A (2015) Extraction of molybdenum from CERMET
412 target dissolution solutions using CYANEX[®] 600. In: *Proc Global*: 1544-1546
- 413 38. Solvay Business Services Latvia SIA (2018) Safety data Sheet of CYANEX[®] 600
414 EXTRACTANT. Solvay Business Services Latvia SIA, PRCO90073221
- 415 39. Soderstrom M, Bednarski T, Yanez H, Soto A, Kamenetzky, Cocalia V (2010):
416 CYANEX[®] 600 for Molybdenum Recovery from Acidic Leach Solutions. In: *Cytec*
417 *Solutions for Hydrometallurgy and Mineral Processing* (15): 5-7