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Transmutation in Reactor and Aqueous Corrosion Resistance of Technetium Metal

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In the context of the French nuclear waste management act of 1991, two options have been considered following enhanced reprocessing of spent fuel. The reference option is the transmutation by neutronic bombardment, the second option is to immobilize the separated radiotoxic elements in dedicated matrices ensuring long term stability. This paper summarizes the research and development activities carried out by CEA in France, concerning technetium. Nearly 90% of the technetium-99 present in spent fuel is separated in the UP2-800 reprocessing plant at La Hague, producing about 900 kg of Tc each year. The first part of the paper deals with the irradiation experiment ANTICORP 1 which aims at transmuting ^{99}Tc under the form of metallic rods, in the core of the Phénix reactor. The goal of ANTICORP 1 is to achieve a transmutation rate of ^{99}Tc in ^{100}Ru greater than 20%. The main options chosen for the design and the safety study of the experiment are described. In addition, the planning of the irradiation and the post-irradiation exams foreseen, are detailed. The second part of the paper describes the studies carried out to investigate technetium metal as a potential containment matrix. The corrosion rate of this metal under water was measured over one year of alteration at 25 ˚C.

1. Introduction

In the context of the French nuclear waste management act of 1991, two options have been considered following enhanced chemical separation during spent fuel reprocessing. The reference option, transmutation by neutron bombardment in nuclear facilities, would reduce the initial radiotoxic inventory. The second option is to immobilize the separated long-lived radionuclides in dedicated matrices ensuring long term stability in geological disposal.

Long-lived fission products tend to exhibit greater solubility in the environment than the actinides, and could contribute more significantly to the residual radiotoxicity of a disposal repository. Three fission products have been studied in greater detail: ^{99}Tc, ^{135}Cs and ^{129}I. Although the beta radio toxicity of ^{99}Tc is far below the alpha radio toxicity of minor actinides, its high mobility and very long life (half-life of 2.11 10^5 y) increases significantly the very long-term risk during storage. Technetium is produced in the reactor mainly as ^{99}Tc by neutron capture in molybdenum arising from ^{235}U and ^{239}Pu fission reactions. The quantity of technetium-99 to be conditioned from the reference spent fuel (UO_2 with a burnup of 45 GWd·t_{iHM}^{-1}) is 872 kg/year based on a total of 800 metric tons spent fuel reprocessed per year, the production capacity of the UP2-800 plant at La Hague.[1]

It is technically feasible to separate significant quantities (> 90%) of the Tc in solution by the UP3/UP2-800 process, although about 10% of the Tc inventory is found in the form of insoluble dissolution fines.[1]

A large research and development program is undergoing in France[2] since 1992, to demonstrate the feasibility of transmutation of minor actinides (americium, curium and neptunium), which represent the majority of the long term radio toxicity elements in the waste, and also the main long-lived fission products (technetium, iodine and caesium). The first part of this paper deals with the main results obtained with Technetium. The second part of the paper describes the studies carried out to investigate technetium metal as a potential containment matrix.

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2. Transmutation of Tc in Reactor

2.1. Irradiation Experiment ANTICORP 1 In Phénix. The strategy of transmutation studies includes solutions based on homogeneous recycling[1] (with specific fuels) as well as heterogeneous recycling (with targets), in appropriate reactors relying on current technology: Pressurized Water Reactor (PWR) and Sodium cooled Fast Reactor (SFR).

ANTICORP 1 takes part of the irradiation program launched in Phénix,[3] and concerns the transmutation of ^{99}Tc in a SFR. From a neutronic point of view, a more efficient transmutation can be obtained in moderated subassemblies in fast reactor, than in standard PWR or SFR assemblies. Actually, such a design combined a high neutron flux irradiation and an enhancement of neutron epithermal captures for ^{99}Tc (^{99}Tc + n $\rightarrow$ ^{100}Ru + β^-). Taking this design as a reference, ANTICORP 1 is positioned inside a special rig locally moderated by mean of a CaHx moderator, and placed in the radial blanket of the Phénix core. CaHx was selected because this material presents a high thermal stability and good moderation properties.

The ANTICORP 1 experiment will consist mainly in:

- Demonstrating the technical feasibility of the transmutation of ^{99}Tc with at least a transmutation rate of 20% and at a different temperature than previous irradiation experiments.
- Studying the conditions of ^{99}Tc removal by transmutation in stable ^{100}Ru.
- Experimentally checking the validity of neutronic calculations.

2.2. Previous experiments.[4–6] Two transmutation experiments on ^{99}Tc were carried out in the High Flux Reactor (HFR) at Petten[7, 8] in the frame of the EFTTRA collaboration including CEA and European partners (ITU, FzK, EdF, NRG and IE). The Tc was under the form of metallic rods (4.8 mm diameter) and put inside a pin with a Phénix cladding and irradiated under a thermal neutron flux in the HFR core. The irradiation conditions of the two EFFTRA experiments are summarized in Table 1:

No significant changes in the characteristics of the targets (dimension and microstructure) were observed after irradiation

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TABLE 1: Irradiation Conditions of EFFTRA T1 and T2 Experiments[7, 8]

	EFTTRA T1	EFTTRA T2
Transmutation rate (at %)	6	15 to 18
Total fluence (m^{-2})	2.0 10^{26}	5.4 10^{26}
Fast fluence (m^{-2})	8.8 10^{25}	2.5 10^{26}
Temperature (K)	1100	1100

in the two cases. However, the Ru radial profile determined on a section of the rod after irradiation shows a strong effect of resonance shielding of the epithermal neutrons, which leads to a sharp decrease of the concentration of Ru created in the outer 150 µm of the rod, that leveled off in the inner region.

These two experiments have demonstrated that no technical limitations are foreseen to the use of technetium in metallic form as a target for the transmutation.

More recently, metallic technetium targets-discs (ϕ = 6 mm, th = 0.3 mm) have been irradiated in the high flux[9] reactor SM-3 of the Research Institute of Atomic Reactors (Russia). The goal was to prepare artificial stable ruthenium pure enough for non-nuclear industrial application. The transmutation rate has achieved 34, 51 and 71% thanks to a high level of epithermal neutron flux during irradiation (1.1 10^{14} $cm^{-2}s^{-1}$) and low thickness targets. This experiment performed on smaller sample than EFTTRA T1 and T2 has demonstrated too, the relevance of the transmutation of ^{99}Tc metallic targets.

2.3. Irradiation device and Target. The irradiation device consists in 3 pins, 100 mm long, each containing 2 ingots of ^{99}Tc in metallic form (6 g/ingot), encapsulated inside a stainless steel pin (Figure 1). The technetium rods of ANTICORP 1 were fabricated at the Institute for Transuranium elements (ITU) at Karlsruhe, starting with powder obtained by reducing ammonium pertechnetate (NH_4TcO_4) in a furnace at 873 K.

The fabrication method of the ingots is described in detail in Reference 10. The main characteristics of the technetium rods are: Diameter: 5.2 mm, length: 25 mm and density: 11.5 $g.cm^{-3}$. The cladding used for the pins is a standard Phénix cladding, made of 15x15Ti stainless steel, with an inner diameter of 5.65 mm.

A pin holder basket (Figure 2) is used to set up the 3 pins in radial position (pins separated by a 120° angle) and in axial position (Tc rods centered on the maximum flux plan of the Phénix core).

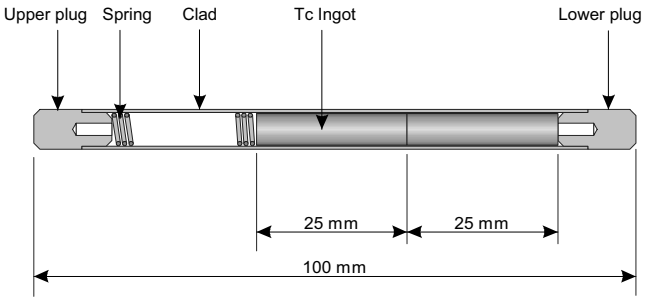

Figure 1. ANTICORP 1 pin drawings.

Figure 2. Pin holder basket.

The capsule is a standard KMC used for experimental irradiation and internally cooled by a low sodium flow. The pin holder basket is introduced and centered inside the body of the capsule, as it can be see in the Figure 3.

The capsule is then placed inside the central hole of a DMC-2 special irradiation rig that authorizes a local moderation of the fast neutron flux. The neutron spectrum is shifted toward the epithermal neutron zones by using a moderator material, CaHx, placed inside the special rig at the level of the Tc targets. This design allows rising the epithermal resonance neutron capture of ^{99}Tc during the irradiation.

2.4. Neutronic studies. In order to quantify the performances of the irradiation, different calculational methods were used. Calculations were performed with the ERANOS system associated with adjusted library ERALIB1 (based on JEF 2 evaluation). This system allows carrying out the whole neutronic characterisations. The adopted method is a heterogeneous calculation for the cell calculation in a fine energy mesh discretization and a spatial calculation in transport method, which takes into account photon propagation.

The self-shielded cross sections and scattering matrices are processed for every core material using both the subgroup method within each fine group and the slowing down treatment in many groups (1968 groups).

The DMC-2 with ANTICORP 1 pins irradiation are described in 2D cylindrical geometry for calculating the collision probabilities. The flux and current are calculated in a P1 approximation. The whole core calculations are processed in 33 energy groups in transport method (Figure 4).

The x-axis decrease of the neutron flux inside the position of the irradiation rig in the radial blanket is taken into account in the 2D (X Y) calculations. This neutron flux decrease leads to slightly different results for the three pins, depending on their position inside the capsule.

The maximal transmutation rate obtained in the Tc rods during irradiation in the front pin (the nearest to the center of the core of Phénix) is represented in the Figure 5.

As the maximal length of the irradiation will be 720 EFPD until the final shutdown of Phénix, the maximum transmutation rate of Tc in ANTICORP 1 will reach 24.85% in the front pin. The main values computed are reported in the Table 2.

The uncertainties to take into account on the fast neutron fluence and the integrated dose are ± 19%.

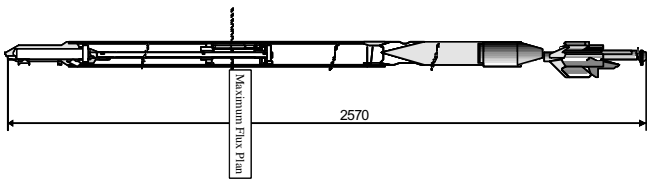

Figure 3. Irradiation capsule.

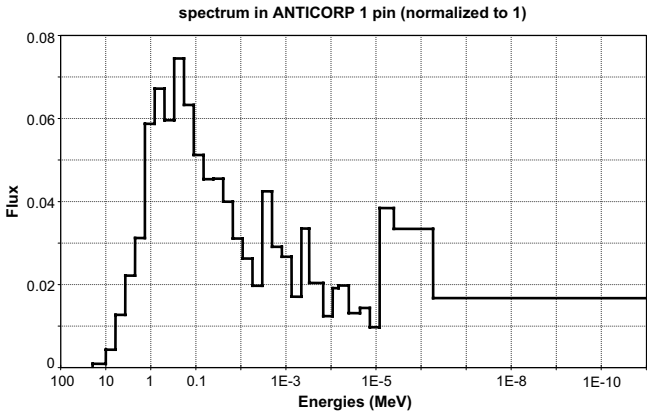

Figure 4. Spectrum (33 groups) in ANTICORP 1 irradiation.

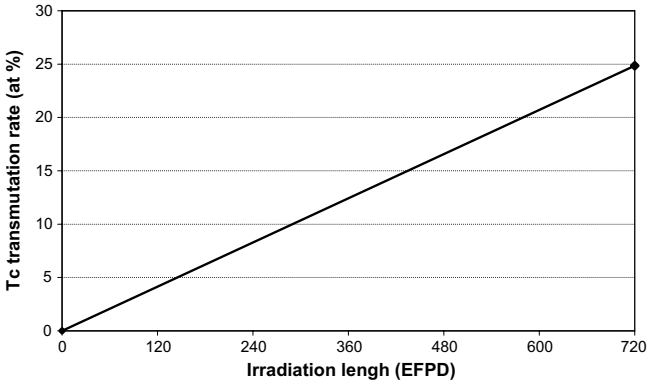

Figure 5. Evolution of the ^{99}Tc transmutation rate during irradiation in the front pin.

TABLE 2: Irradiation Conditions Calculated for ANTICORP 1 Pins

	Front pin	Rear pin
Transmutation rate (at %)	24.85	24.53
Total fluence (m^{-2})	1.3 10^{27}	1.2 10^{27}
Fast fluence (m^{-2})	4.3 10^{26}	3.8 10^{26}
Integrated dose (dpa $_{Fe}$)	18.2	15.7

The pseudo half-life of the ^{99}Tc under irradiation (time corresponding to the transmutation of 50% of the ^{99}Tc in ^{100}Ru) is closed to 1790 EFPD.

The power delivered in the Tc rod under irradiation results mainly from the interaction of:
- Gamma from the Phénix core,
- gamma from radiative captures (E_γ = 6.7 MeV),
- beta decay of ^{100}Tc on ^{100}Ru (E_β = 1.315 MeV).

The different contributions to the total power delivered in the Tc rods, calculated for the front pin (nearest of the core center), are gathered in the Table 3. This table shows that the major contribution to the power comes from the beta decay. The uncertainties on the calculated linear power are ± 25%.

TABLE 3: Contributions to the Total Linear Power

	Linear Power ($W.cm^{-1}$)
Gamma from the core	3.3
Gamma (radiative capture)	5.3
Beta decay	8.8
Total linear power	17.4

2.5. Thermal studies. Modeling with the finite elements code CAST3M was performed for the thermal design of the pins. This modeling allows calculating the operating temperatures of the Tc rods and the cladding during irradiation. For safety reason, the irradiation designer has to check that sufficient margin will be kept all along the irradiation, to prevent from Tc rod melting or eutectic formation with cladding. For the ANTICORP 1 design, the lower temperature to be considered for the safety study corresponds to the eutectic between Nickel (element of the cladding) and Technetium, which occurs at 1768 K.

The temperatures calculated in normal operating conditions reach respectively 759 and 675 K in the Tc rods and the cladding. By taking into account all the uncertainties related to the characteristics of the pins (geometry of rods and cladding, thermal conductivity of the Tc and the filling gas, …) and the irradiation conditions (linear power, coolant temperature, …), the calculation shows that the temperature will never exceed respectively 991 and 726 K. This result underlines that no risk of melting is expected for ANTICORP 1 pins, in these irradiation conditions.

As the evolution of the thermal conductivity, caused by the Ru formation under irradiation (up to 25% Ru for 720 EPFD) will be very slight,[11] the temperature of the rods will be quite stable until the end of the irradiation.

Compared to the EFTTRA experiments, the temperature of the ANTICORP 1 Tc rods will be obviously lower (759 K against 1100 K). These new irradiation conditions will allow checking the influence of temperature of the technetium rods on the behavior of the target under neutron flux (swelling in particular).

2.6. Post irradiation exams. After irradiation the ANTICORP 1 capsule will be transferred and dismantled in the Phénix hot cells. Non-destructive exams, as diameter profilometry, neutron radiography and gamma spectrometry, will be carried out on the 3 pins. Then the 3 pins will be transferred to the LECA facility in the Cadarache CEA center, to perform destructive exams. Only one pin will be cut to remove the 2 Tc rods, and carry out at least the following exams: dimensional control, metallography exam, X-ray diffraction examination, micro hardness, radial distribution of Ru control (EPMA) and chemical analysis.

2.7. Schedule. The irradiation of the ANTICORP 1 capsule in Phénix started on June 2003 and will last until mid-2008 in order to achieve the goal of 720 EFPD of irradiation. Up to now (May 2005) more than 7.5% of the ^{99}Tc (calculated data) have been already transmuted in ^{100}Ru. The post irradiation exams are planned from the second half of 2008. As done for the EFTTRA T1 experiment and if the targets reveal a good behavior, CEA plans to extend the irradiation of the remaining pins, in the frame of a further experiment in another reactor.

3. Aqueous Corrosion Resistance of Technetium Metal

3.1. Context of the studies. Various Tc immobilization routes have been examined, including metal matrices such as Nb alloys.[1] In addition to these studies, and in view of the properties of technetium itself, the aqueous corrosion resistance of pure Tc metal has been assessed.

Its solubility in aqueous media is highly dependent on its oxidation state. Technetium exists at several oxidation states between 0 and +VII. Under reducing conditions it is found at oxidation state +IV and exhibits relatively low solubility (10^{-9} $mol{\cdot}L^{-1}$ at equilibrium with TcO_2,[12] whereas under oxidizing conditions the stability of the TcO_4^- ion enhances its solubility and mobility.

3.2. Technetium Metal Alteration Process. Although reductive redox conditions prevail in a deep geological repository site of the type under consideration in France,[13] the possibility of oxidizing dissolution of technetium must be taken into account because of the beta radiation field and water radiolysis at the interface. Water radiolysis generates both oxidizing species (OH°, H_2O_2, etc.) and reducing species (H°, H_2, etc.), and can locally modify the redox conditions leading to the dissolution of the TcO_4^- ion. The redox buffering capacity of the surrounding environment will be crucial for the existence of oxidizing conditions at the Tc/H_2O interface. The mechanism considered is similar to the one discussed for dissolving uranium in spent fuel.[14]

The technetium dissolution reaction depends on the interface potential and on the possible presence of precipitates or complexants in the system. A leaching experiment was first conducted to monitor the Tc release versus time in pure water.

3.3. Experimental. *Materials*: This preliminary experiment was carried out on a piece of Tc metal taken from one of the technetium rods prepared for the ANTICORP 1 experiment for transmuting ^{99}Tc subjected to a moderated flux in the Phenix reactor as part of the EFTTRA (Experimental Feasibility of Targets for TRAnsmutation) project. The rods were fabri-

cated in an arc furnace at the ITU in Karlsruhe and cast into a cooled ingot mold. Their density exceeds 99% of the theoretical density (dth = 11.48 g·cm^{-3}).[15] The leached specimen was a rod segment (m = 2.28 g, L = 9.56 mm, diameter = 5.2 mm, S = 1.98 cm^2) untreated except for decontamination with ethanol.

Leaching and analysis procedure: The specimen was leached for one year at 25 ˚C in pure aerated water (V ≈ 100 mL) in a PTFE Savillex container. Solution samples were taken at various intervals (1, 7, 10, 30, 90, 180 and 360 days) and analyzed by beta counting to determine the Tc quantities released (Eurisys IN 20 alpha-beta counter) and by chemiluminescence (Turner Design TD20-20 luminometer) to detect any hydrogen peroxide in solution.

3.4. Results and Discussion. The beta activity in solution (Bq·mL^{-1}) and the corresponding aqueous technetium concentration versus time are given in Table 4. After one year leaching, no adsorption of Tc was detected after acidification of the solution in the vessel. Under the test conditions the technetium showed very little corrosion; assuming the rod surface was uniformly altered, the mass loss after 1 year of aqueous leaching represented a metal thickness of 0.015 µm.

TABLE 4: Technetium Concentration Versus Time at 25 ˚C in Pure Aerated Water (363 ac = acidified solution)

Time days	A_i Bq.mL^{-1}	$u(A_i)$ Bq.mL^{-1}	$[Tc_{aq}]$ mol.L^{-1}
1	0,49	0,25	7,9E-09
7	1,45	0,44	2,3E-08
10	1,9	0,57	3,1E-08
36	9,36	0,94	1,5E-07
91	36,1	1,8	5,8E-07
197	96,8	4,8	1,6E-06
363	225,7	6,7	3,7E-06
363 ac	227,8	6,8	3,7E-06

Mass loss (ML): The technetium mass loss at each sampling time t_i is estimated according to eq 1 :

$$ML_i = \frac{A_i \times V_i}{A_S(Tc) \times a_{rod}} \quad (1)$$

A_i : Measured activity in the leaching solution at t_i in Bq.mL^{-1},

As(Tc): ^{99}Tc specific activity (6.246.10^5 Bq.mg^{-1}),

V_i : Leaching solution volume at t_i in mL

a_{rod} : Tc sample surface area in m^2 (geometric).

The values calculated for each sampling time and their combined standard uncertainties[16] are plotted against time on Figure 6. The dissolution of Tc seems to require an induction period during which the release is very low and after which a continuous and virtually linear technetium release into solution is observed under these experimental conditions.

Alteration rate: Estimating the rate by linear regression from the mass loss between 36 and 363 days yields a dissolution rate of 0.49 ± 0.06 mg m^{-2}·d^{-1} at 25 ˚C, with an uncertainty of twice the standard uncertainty on the slope.

In comparison with UO_2 spent fuel matrix, this rate of dissolution is one order of magnitude lower in simular experimental conditions.[11] Moreover, from a safety point of view, the reducing conditions expected in a repository will probably limit the migration of technetium into the near-field. In addition to the Tc release, a hydrogen peroxide concentration of 7.10^{-8} mol·L^{-1} was detected in solution, suggesting that water radiolysis occurred under β irradiation.

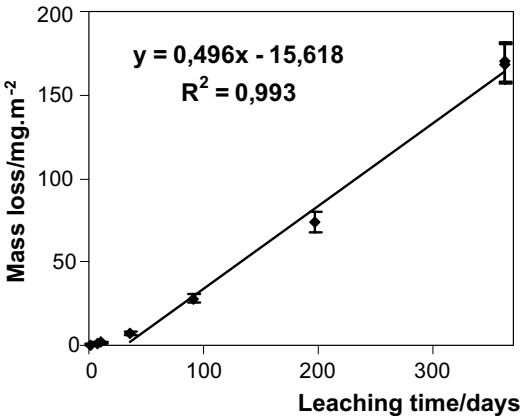

Figure 6. Mean alteration rate of Tc metal in pure water at 25 ˚C.

4. Conclusion

More than 7.5% of the ^{99}Tc have been already transmuted into ^{100}Ru in the ANTICORP 1 experiment in Phénix. At the end of the irradiation, planned in mid-2008, a rate of transmutation closed to 25% will be reached. ANTICORP 1 will make it possible to bring further information in comparison with EFFTRA T1 and T2 experiments.

The mean alteration rate (0.49 ± 0.06 mg·m^{-2}·d^{-1}) for technetium over one year of alteration at 25 ˚C is encouraging in terms of long-term behavior. A comprehensive investigation to identify the precise alteration mechanisms (oxidizing dissolution under radiolysis, effect of dissolved oxygen in aerated media, etc.) will determine whether this matrix is qualified for possible use in a geological repository. A fuller understanding of the alteration mechanisms will require the development of an electrochemical approach suitable for investigating metal corrosion.

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