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Long-term behaviour of a thorium-based fuel

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Abstract

The radiological impact of a Th-based fuel disposed off in a deep granite repository has been assessed from the simulation code MELODIE developed by IPSN. A normal evolution scenario has been considered with a possible release of the radionuclides after 1000 years (container failure) and their transport from the disposal to some outlets of the geosphere over periods of time as long as 10^6 years. The solubility of crystallized ThO_2, synthesized by calcination of thorium oxalate up to 1600°C, has been measured under various conditions of temperature and water composition; an upper limit value of 10^{-8} mol l^{-1} has been chosen for the calculations. As for a direct disposal of U-based fuels, the radiological impact of a Th-based fuel is essentially due to the labil fraction ($2 \pm 1\%$ of the total inventory) of the fission products, ^{129}I and ^{135}Cs. The contribution of the transuranium elements, ^{231}Pa, ^{229}Th and ^{226}Ra, mainly bounded to the ThO_2 matrix, increases over time, but remains lower up to 6×10^5 years. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

One of the main advantages of the thorium-based fuel cycle, compared with the uranium–plutonium cycle, is that it does not produce minor actinides (Am, Cm, Np) and specially plutonium in significant amount. Nevertheless, in the case of a thorium cycle, other radionuclides, such as ^{231}Pa, ^{229}Th and ^{230}Th, which may have a long-term radiological impact, are present in significant quantities.

Moreover, when the thorium and uranium spent fuels are supposed to be disposed off directly in a deep geological repository, their long-term behaviour is expected to be different, because the dissolution processes of the UO_2 and ThO_2 matrices are expected to be different. Therefore, we have focused our study on this behaviour, in the case of a granitic environment.

When assessing the long-term radiological impact of a radioactive waste disposal, one has to consider the possible transport of radionuclides, through groundwater, from the repository to some outlets of the geosphere. In a normal evolution scenario, the time to be considered covers the periods where the activities of the radionuclides confined in the packages are significant compared to the natural radioactivity, say several hundreds of thousands of years or more for the nuclear waste coming from the actual uranium spent fuel.

The aim of the present work was to estimate the residual risks of a thorium-based cycle and to make comparisons with an uranium-based cycle. In order to estimate the long-term behaviour of the radionuclides which could be released from a thorium-based fuel, we have used the MELODIE code, which has been recently tested in the case of an uranium-based fuel.

Since most of the radionuclides generated in the Th-fuel are assumed to be bound to the matrix and to be released congruently with the matrix dissolution, our first objective was to determine experimentally the solubility of ThO_2, under conditions as close as possible to the conditions prevailing in an underground repository in a granite formation.

The use of the MELODIE code requires also the knowledge of other experimental data such as the solubility of the radionuclide compounds formed in the near field as well as the retardation factors of the radionuclide species in the far field. The impact of all these data on the final results will be discussed.

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2. Input data and hypotheses

2.1. Repository concept and reference fuels

The repository concept (see Table 1), the amount of fuel to be disposed off, and their conditioning (TES container) are assumed to be the same than in the *Spent Fuel Performance Assessment* EC-project (SPA). For the present study, Th/U-MOX fuels replace UOX fuels, and Th/Pu-MOX fuels replace U/Pu-MOX fuels.

The characteristics of the reference fuels are given in Table 2.

2.2. Input data

The radionuclides inventories of the transuranic elements for the Th-fuel cycle are those given in [1]. The fission and activation products inventories are assumed to be the same for both U-based fuels and Th-based fuels, since no data are available in [1]. They are taken in [2] for Th/U-MOX fuels, and in [3] for Th/Pu-MOX fuels.

The container failure is assumed to occur after 1000 years. The radioactive decay over this period is taken into account in the inventory calculations.

Concerning the radionuclides release from the source term, it has been assumed that the specific Th fuels source term is similar to that of the U fuels, since no experimental data were available. This source term has been used in the framework of a French working group on direct disposal [4]. For that source term, the actinides and most of the fission products are expected to be bound to the matrix and are considered to be homogenously distributed in this matrix. Their release is controlled by the solubility of both the matrix and the radionuclide species (values selected from the EVEREST project [5]). The radionuclides formed by activation of the cladding (^{93}Zr) and its impurities (538 g of Ni and 50 g of Nb per kg of steel for the metallic parts; 100 ppm of ^{13}C, 10 ppm of ^{14}N and two atoms of ^{17}O for one atom of U in the fuel pellets) are assumed to be immediately released in the geosphere after the container failure. 1–3% of the total inventory of the volatile fission products (^{135}Cs and ^{129}I) are considered to be accumulated in the gap between the fuel matrix and the cladding and consequently released immediately after the container failure.

The retardation coefficient, R, which translates the interaction between the radionuclide and the geosphere is a simple function of the distribution coefficient, K_d, and of the total and cinematic porosity, ω_{tot} and ω_c: $R = 1 + \rho(1 - \omega_{tot})/\omega_c K_d$; ρ being rock density. R is assumed to be constant in the geosphere (K_d varies according to the degree of consolidation of the rock mass and therefore with the porosity). The values of radionuclides retardation coefficients have been selected from the EVEREST project [5].

The description of the granitic massif and the hydraulic parameters used in the present study are detailed in [5]. The biosphere is based on a self-sustained agricultural system structure. The individual dose calculations are applied to an average individual of a critical group living in a small village. This village is located in a place suitable for a great variety of agricultural practices under mean temperate French climate conditions. This agricultural region is centred on a river stream, the outflow rate of which is at least equal to 5×10^7 m^3 y^{-1}. The doses are due to an external irradiation, by living on a contaminated ground, an external

Table 1
Repository concept characteristics

Repository	500 m depth, in horizontal galleries
Area of a gallery	15 m^2, 25 m between each gallery
Total extension	2600 m × 1300 m
Container	• Multiple-use container 'T.E.S.' (French acronym for transport, storage and disposal) • 2 Th/U-MOX assemblies and 1 Th/Pu-MOX assembly in each container
Amount disposed off	15 000 t of Th/U-MOX (32 490 assemblies) 5000 t of Th/Pu-MOX (10 830 assemblies)

Table 2
Characteristics of the reference fuels

Fuel	Burn-up	Characteristics
UOX	33 MWd/kgHM	Initial enrichment: 3.5% of U-235
Th/U-MOX	33 MWd/kgHM	From a 900 Mwe PWR in equilibrium Isotope ratio: 91.61% of U-233
U/Pu-MOX	43,5 MWd/kgHM	Standard assembly type REP AFA
Th/Pu-MOX	33 MWd/kgHM	First generation plutonium (80.2% of total Pu)

irradiation, by inhalation of contaminated air, and an internal irradiation, by consumption of contaminated water and food. The dose factors are taken from the complete studies carried out in the frame of the Everest project [5].

2.3. The MELODIE code

The MELODIE code (acronym of 'Modèle d'Evaluation à LOng terme des Déchets Irradiants Enterrés' is a simulation code which has been developed at the Nuclear Protection and Safety Institute (IPSN) in order to model the transport of radionuclides in the geosphere from a repository system to the outlets. The geosphere model MELO is based on the METIS computer code which models the transient transport of radionuclides into the geosphere by the finite element method in two dimensions. A simplified 'source term' has been added to the original code to model the degradation of the waste packages and the release of radionuclides into the geosphere. The code has been extended to the third dimension by using a multi-layer representation. This version is referred to as a'quasi-3D version' [5].

2.4. Scenario

For the present study, only the normal evolution scenario has been considered. For this scenario, the release of radionuclides is associated with the movement of groundwater in the host rock which is assumed to remain mainly unaltered and have properties as good as reasonably expected (no non-detected heterogeneity or conductive feature). The outlets considered for dose calculations are river outlets.

For a normal evolution scenario, the maximum radionuclide release into the biosphere occurs in the range 10^4–10^6 years. The time scale considered in the present work is thus 'time after container failure – 10^6 years'.

3. Experimental

3.1. Synthesis and characterization of ThO_2

Pope and Radford [6] have shown that thoria synthesized by calcinating a precipitate of thorium oxalate up to 1450°C is very well crystallized. Moreover, sintered pellets prepared from this powder have a high density value (>9.5 kg l^{-1}) close to the theoretical one (10 kg l^{-1}). For these reasons, we have chosen to measure the solubility of ThO_2 powder synthesized through the oxalate route described in [6]. Thorium oxide calcinated at 1600°C was produced by heating at first 900°C for 10 h and 1600°C for 10 h.

The powder was characterized using several techniques: X-ray powder diffraction, granulometry and BET method for the grain size and the specific surface area. The average grain size was between 10 and 50 μm. The specific surface area was measured to be about 0.2 m^2 g^{-1}.

3.2. Leaching experiments

Two compositions of synthetic granite waters were used for the solubility experiments. They present different chloride and carbonate concentrations and also different pH values. These compositions, calculated to be at equilibrium, are given in Table 3. They depend slightly on temperature.

The leaching experiments were performed using the usual batch procedure with a contact time of 31 days and an m/V (mass of powder to volume of solution) ratio of 20 kg m^{-3}. After the separation of the two phases by centrifugation at 3500 rpm and ultracentrifugation at 50,000 rpm, the thorium concentration in solution was measured by ICP-MS, using a Fisons Plasma Quad apparatus and the procedure detailed in [7].

4. Results and discussion

4.1. ThO_2 solubility

The solubility results of ThO_2 in synthetic granite waters are reported in Table 4 where they can be compared with data obtained under the same experimental conditions, but with deionized water. From these results, it seems that the presence of limited amounts of salts does not affect the solubility of ThO_2, even if an increasing solubility of Th(IV) hydrous oxide with an increasing NaCl concentration has been already observed

Table 3
Composition of the synthetic granite waters used in the present study (concentrations obtained at equilibrium and given in mmol l^{-1})

Sample	T (°C)	pCO_2	pH	Ca	Na	K	Cl	HCO_3^-	CO_3^{2-}	S
1	25	10^{-6}	9.7	0.47	2.31	0.0055	1.0	0.047	0.013	0.5
2	25	10^{-3}	8.8	92.5	25.9	0.066	200.0	0.007	0.0005	5.0
3	90	10^{-6}	8.5	0.074	4.24	0.031	1.0	0.67	0.018	0.5
4	90	10^{-3}	7.2	54.0	100.0	0.78	200.0	0.047	0.00016	5.0

Table 4
Solubility results obtained for different waters at 25 and 90°C and for a time of contact of 31 days

Water	Final pH	Temperature (°C)	$10^9 C_{Th}$ (mol l^{-1})
1	8.0	25	0.01 ± 0.005
2	6.6	25	<0.2
Deionized water	8.5	25	0.06 ± 0.02
3	9.2	90	2.5 ± 0.3
4	7.1	90	9.5 ± 0.3

and discussed from predictive models [8] over the NaCl concentration range 0.6–3.0 mol l^{-1}. Moreover, no influence of carbonate anions can be pointed out for the pCO_2 range under consideration.

On the other hand, an increase of two orders of magnitude on the solubility values is observed at 90°C compared to 25°C. This behaviour is probably to be connected to a very slow process of degradation of the solid/solution interface. The external layer of ThO_2 could be transformed in a more stable and more soluble amorphous hydroxide $Th(OH)_4$.

An important point to outline is that crystallized ThO_2 is more insoluble ($C_{Th} \leqslant 2 \times 10^{-10}$ mol l^{-1} at 25°C) than the amorphous hydrous thorium oxide (C_{Th} varying between 10^{-6} [9] and 10^{-9} mol l^{-1} ([8,10]) in neutral solutions). It is also much more insoluble than UO_2 (C_U up to 2×10^{-4} mol l^{-1} under oxic conditions or around 10^{-6}–10^{-8} mol l^{-1} under reducing conditions [11]). Nevertheless, an upper limit value of 10^{-8} mol l^{-1} is chosen for the calculations with the MELODIE code because a contact with the natural waters, a temperature of 90°C and a possible hydratation of the solid surface over very long periods of time, tend to increase somewhat the Th solubility limit observed experimentally under laboratory conditions. In the frame of a French working group on direct disposal [4], a solubility value of 10^{-5} mol l^{-1} was taken for UO_2 for the calculations with MELODIE.

4.2. Thermal output calculations

We have used the repository concept developed in the case of a disposal of U-based fuels [4] and in the *Spent Fuel Performance Assessment* EC-project (SPA). For these projects, two UOX and one U/Pu-MOX assemblies have been considered in each T.E.S. (French acronym for transport, storage and disposal) container. For the purpose of the present study, the same distribution has been considered for the Th-based fuels. In order to assess the transposition of the repository concept developed for U-based fuels to Th-based fuels, preliminary calculations have been performed based on thermal output calculations. Thermal considerations for the repository design impose a maximum residual heat of about 2000 W per container before disposal. Considering the reference Th-based fuels previously defined, thermal output calculations indicate that no major differences are observed and the transposition of the repository concept developed for U-based fuels to Th-based fuels is thus valid for the purpose of the present work.

Nevertheless, these are preliminary conclusions since the burn-up of the reference Th-based fuels is lower than for the U-based fuels, but it is not the scope of the present study to investigate the influence of increased burn-up of the fuels on the optimisation of the repository and container designs. Future studies will be specially developed in this direction.

4.3. Radiological impact of a Th fuel cycle

The radiological impact of a thorium fuel cycle is indicated in Fig. 1.

The contribution of the actinides to the total effective dose is lower than for the fission and activation products up to 10^6 years. It increases with time and represents 12% of the total dose rate at 10^6 years. The end of decay chains radionuclides has a major importance in relation to the total dose rate. The dose rate is thus mainly due to ^{231}Pa up to 2×10^5 years, then to ^{226}Ra. ^{229}Th is the third-most important radionuclide. ^{239}Pu is the fourth-most important radionuclide up to 5.5×10^4 years. After this time, and up to 10^6 years, ^{237}Np takes the fourth place. The total effective dose rate of the actinides in-

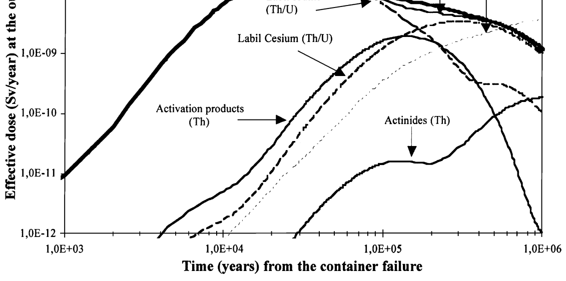

Fig. 1. Radiological impact of a deep geological disposal of spent Th-based fuel.

creases over time during the entire simulation period. The value at 10^6 years is 1.43×10^{-10} Sv/years.

The contribution of products formed by irradiation of the cladding and its impurities (^{93}Zr, ^{59}Ni, ^{94}Nb) to the total effective dose is higher than for the actinides and lower than that of the fission products up to 5×10^5 years. After this time, the contribution of the actinides is more important. The dose is due to ^{59}Ni up to 10^6 years. ^{93}Zr, which has a low solubility, precipitates and has no significant effect on the effective dose in the first million of years. However, it should be outlined that these activation products are only controlled by the capacity of the geosphere to retain them, except for ^{93}Zr which precipitates. Their retardation coefficient, need to be adjusted to precise the radionuclide output order, and consequently the dose rate calculations.

The total effective dose is mainly due to the fission products as shown in Fig. 1. Among them, the dose mainly originates from the labil activity, and is directly proportional to the part of inventory involved. The eventual segregation of ^{99}Tc and ^{107}Pd at the grain boundary does not change this conclusion. (In an additional study, 100% of these radionuclides have been assumed to have migrated from the matrix to the grain boundary. In this case the leaching rates which have been considered are much higher.)

In order to evaluate the influence of the burn-up of the fuels on the doses values, calculations were performed taking into account inventories provided by the Research Center of Jülich [12]. Despite the high difference in the burn-up (60 MWd/kgHM instead of 33 MWd/kgHM), the radionuclides activities are only slightly higher in the new inventories. Three different cases can be analysed:

- If the release is 'solubility limit controlled' (case of ^{93}Zr), the dose is independent of an increase in its inventory.
- If the release is 'controlled by the matrix dissolution' (case of actinides and fission products), the effective dose is directly proportional to a variation of the inventory, as long as the radionuclide solubility is not reached. For instance, the activity of ^{79}Se is 1.27 times higher in the new inventory than in the previous one and it is shown that this factor of 1.27 is conserved in the radiological doses (see Fig. 2).
- If the radionuclide is instantaneously released after the container failure and if it is not 'solubility limit controlled' (case of the activation products and of the labil ^{129}I and ^{135}Cs), the dose is directly proportional to its inventory.

Finally, the radiological impact of an uranium fuel repository (calculated dose from [4]) can be compared with that of a thorium fuel repository (present study) in Fig. 1. Although the U-based fuel matrix is more degradated than the Th-based fuel matrix, because of its higher solubility (assumed to be 10^{-5} mol l^{-1}), there is no significant differences between the two systems for the activation and fission products. This is due to the fact that: the inventories are the same, the source terms are equivalent and the major contribution up to 10^6 years is due to the labil activity (same proportions of ^{135}Cs and ^{129}I). Consequently, the main differences result in the actinide contribution which is higher in the case of U-based fuels than for Th-based fuels, due to higher degradation of the fuel matrix.

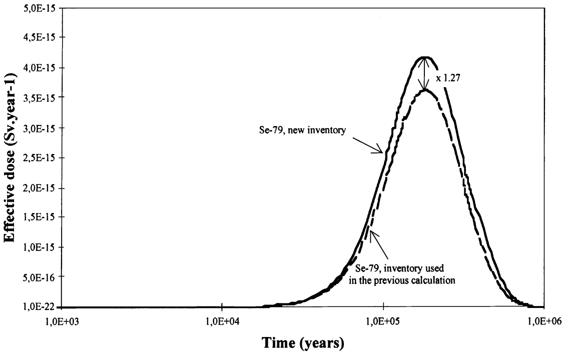

Fig. 2. Effective dose rate of Se-79 versus time; comparison of the calculations for two different inventories corresponding to two different burn-up (33 and 60 MWd/kgHM).

5. Conclusion

In conclusion, in the normal evolution scenario, the actinides contribution (most important ^{231}Pa) to the total dose is rather small. Fission products (mainly labil ^{129}I and ^{135}Cs) give the highest contribution, followed by activation products (^{59}Ni, ^{94}Nb). Consequently, there is no large difference with U-based fuels, even if the dissolution rate of the matrix is in favour of Th-based fuels. This is essentially due to the same source term hypotheses between Th-based and U-based fuels. The source term hypotheses are thus to be improved in order to determine what is Th-based fuel specific compared with U-based fuel.

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