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Journal of Nuclear Materials 274 (1999) 91–97

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

In-pile studies of inert matrices with emphasis on magnesia and magnesium aluminate spinel

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Abstract

Various inert matrices – oxide, nitride and metallic – were irradiated in the French Phénix reactor in order to study their behaviour under a fast neutron fluence ($E > 0.1$ MeV). This paper summarises the material selection criteria and the irradiation conditions of the MATrices for INcineration of Actinides (MATINA) 1 experiment. Emphasis is given on non-destructive examinations of the pins and on more complete examinations performed on ($MgO + UO_2$) and ($MgAl_2O_4 + UO_2$) pellets which were irradiated up to a fast neutron fluence of 2×10^{26} m^{-2}. For these pellets, dimensional examinations, scanning electronic microscopy pictures and electron-probe microanalyses, were performed before and after irradiation. Fission gas release was also studied. These preliminary results show a good behaviour of both magnesia and spinel under irradiation.

1. Introduction

Several research organisations are committed by the French law (30 December 1991) to perform sufficient progress in their studies before 2006 in order to give to the legislators a clear view regarding different options to treat long term radio-toxic wastes. In this frame, the nuclear reactor directorate of the CEA is directly involved to study transmutation ways of minor actinides from such waste stream.

To achieve a high transmutation rate, it is thought that one of the best solutions consists of conceiving two phase material targets in which the radioactive products are enclosed in an inert matrix. A guaranty about minor actinide target stability under radiation is therefore required.

The aim of the inert matrix is to keep its structure all along the irradiation and to have a good thermo-mechanical behaviour during the actinide transformation. To fulfil this last condition, the material thermal and mechanical properties should show only small variations under irradiation which may cause sources of damage, namely fast neutrons, fission products recoil and α-decays of some daughter isotopes of the initial actinide.

Indeed, in any case, materials are damaged by atom displacements generating vacancies and interstitials.

Then, even if recombination is possible, each material gives a different answer to these damages.

The general objective of the MATrices for INcineration of Actinides (MATINA) irradiations is to investigate the behaviour of the most promising materials to be used as inert matrices under the fast neutron flux of the Phénix reactor. In MATINA 1 irradiation, several compounds have been loaded in the reactor. In some cases, fissile uranium dispersed in the inert matrix has been added in order to evaluate the effect of actinide fission through fission product emission.

Ideally, to be a promising inert matrix candidate, the material to be irradiated must fulfil certain criteria regarding its physical, chemical and neutronic properties. Today the following points are considered:

- High melting or phase transformation temperature.
- Good thermal conductivity.
- Suitable mechanical properties.
- Low neutron cross-section and low generation rate of activation products.
- Good behaviour under radiation effects.
- Compatibility with the coolant and the cladding.

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0022-3115/99/$ – see front matter
PII: S0022-3115(99)00080-X

Furthermore, if a multi-recycling strategy is considered, the ability of the material to be reprocessed must also be considered.

These selection criteria have been studied for oxide and nitride ceramics as well as for metals. Some complementary data, not found in the literature, were obtained by CEA [1,2].

The MATINA 1 irradiation started in 1994 and it was decided to irradiate the following materials:

- Oxides: MgO, $MgAl_2O_4$, Al_2O_3, $Y_3Al_5O_{12}$.
- Nitride: TiN.
- Metal: W, V, Nb, Cr.
- Composite with oxides + UO_2 (19.5% ^{235}U enriched):

$MgO + 40\ wt\%\ UO_2$, $MgAl_2O_4 + 40\ wt\%\ UO_2$, $Al_2O_3 + 40\ wt\%\ UO_2$.

The present study deals with post irradiation results of these materials with emphasis on magnesia and spinel.

2. Irradiation conditions

Pellets of the above selected materials were fabricated by usual sintering, using powder technology process [1]. Consequently, they were loaded in 16 pins (with duplication of the pins containing magnesia and spinel). Adding three standard Phénix pins, a total of 19 pins was introduced in a capsule located in the internal Phénix core.

Due to a long shut down of Phénix, the decision was taken to withdraw this capsule by end 1996, to perform non-destructive examinations of the pins and more complete examinations, including destructive tests, of the MgO + UO_2 and $MgAl_2O_4$ + UO_2 pellets.

The irradiation conditions were the following:

- Irradiation time: 61 equivalent full power days.
- Fast neutron fluence ($E > 0.1$ MeV): $1.95 \times 10^{26}\ m^{-2}$.
- UO_2 burn up: 1.27%.
- Maximal linear power: 4300 W m^{-1}.
- Pellet central temperature: ~1073 K.

It must be noted that the two pins that have been opened for pellet examinations were replaced by two pins containing steel pellets. They have been placed together with the 17 remaining pins in a new capsule and are undergoing further irradiation to achieve more significant fission rates (fast neutron fluence: $5.6 \times 10^{26}\ m^{-2}$, 3.6% UO_2 fission rate).

3. Results of post irradiation examinations

3.1. Non-destructive examinations of the pins

Neutron radiographic examinations were performed on the 19 pins. The lengths of the inert matrix columns have been measured. The corresponding results are presented in Table 1.

Taking into account a precision of ±1 mm (or ±0.4%) on the column length, a difference smaller than 2 mm between the two measurements is not representative. Thus, we can say that there is no significant elongation of the inert matrix pellets, excepted for pin No. 8 (i.e. Al_2O_3), where a value of 1.3% was noted.

Table 1
Non-destructive examinations of the 19 pins

Pin No.	Pellet material	L_0 (mm) Column length before irradiation	L (mm) Column length after irradiation	$(L - L_0)/L_0$ Elongation (%)
1	MgO	252.3	252.1	−0.1
2	Standard	–	–	–
3	MgO	251.6	252.7	0.4
4	MgO + UO_2	253.7	253.7	0.0
5	V	249.7	250.7	0.4
6	$Y_3Al_5O_{12}$	250.0	249.6	−0.2
7	MgO + UO_2	253.5	252.8	−0.3
8	Al_2O_3	248.0	251.3	1.3
9	Al_2O_3 + UO_2	251.6	251.7	0.0
10	Nb	249.1	248.7	−0.2
11	Standard	–	–	–
12	Cr	247.0	247.2	0.1
13	$MgAl_2O_4$ + UO_2	253.5	254.1	0.2
14	$MgAl_2O_4$ + UO_2	254.5	252.3 [a]	−0.9 [a]
15	W	249.2	248.7	−0.2
16	TiN	251.8	252.7	0.4
17	Standard	–	–	–
18	$MgAl_2O_4$	251.5	251.9	0.2
19	$MgAl_2O_4$	252.1	250.7	–0.6

[a] Uncertain measurement, Standard, U, PuO_2.

This elongation of alumina is consistent with the swelling already reported by other authors [3,4]. For the pin No. 9, the presence of fissile material in Al_2O_3 induces a higher temperature and thus a better recombination of defects created. This explains a lower elongation than for the pin No. 8. This result is consistent even considering the relative measurement precision.

The pellet-cladding gap is observed on the pins all along the matrix column but it cannot be precisely evaluated because of the film brightness.

Diameter, ovality and length measurements performed on pins No. 7 and 14 ($MgO + UO_2$ and $MgAl_2O_4 + UO_2$) showed no significant radial deformation after irradiation. In addition, the axial gamma spectroscopy examinations, particularly for axial ^{137}Cs, ^{106}Ru and ^{54}Mn, show expected profiles as regard to the irradiation conditions.

3.2. Destructive examination of the $MgO + UO_2$ and $MgAl_2O_4 + UO_2$ pellets

3.2.1. Dimensional control – weighing – density

No pellet-cladding mechanical interaction was noticed for the two considered composite materials. No cracking can be observed on any of the pellets. Nevertheless, 2 ($MgO + UO_2$) pellets, out of 28, were found broken in two parts.

Metrological and weighing results, performed before and after irradiation, are given in Tables 2 and 3.

Dimensional variations are small for all the examined pellets. However, increase of diameter and height were observed for $MgO + UO_2$ while a slight re-densification under fast neutronic flux was measured for $MgAl_2O_4 + UO_2$. This last observation about $MgAl_2O_4 + UO_2$ is in agreement with observations done on pure $MgAl_2O_4$ pellets irradiated both in the High Flux Reactor in Petten, The Netherlands, [5] and in the EBR II reactor, Argonne National Laboratory, Idaho, USA [6].

The slight swelling observed for magnesia could be related either to a porosity increase or to a structural change, e.g. amorphization or chemical reaction with other compounds such as lanthanides, inducing a theoretical density decrease. These two possibilities have to be confirmed by ceramographic examinations.

3.2.2. Fission gas release

MATINA pins were initially filled with a natural xenon–krypton gas mixture in order to detect a potential pin failure. After irradiation, isotopic analyses were performed on these gases after puncture test. Results correspond to natural isotopic ratios of these two gases. No ^{85}Kr was detected.

Indeed, knowing the very low fission rate, the quantity of fission gases produced is low and calculated closed to 2.5 cm^3 ($T = 273$ K and $P = 0.1$ MPa), which part of ^{85}Kr is 0.3 cm^3 ($T = 273$ K and $P = 0.1$ Mpa). So, it can be concluded that after irradiation, the volume of fission gas released was lower than detection limit i.e.

Table 2
Dimensional control – weighing – density. Pin 7: MgO + 40% UO_2

Pellet No.	Height (mm)			Diameter (mm)			Mass (g)			Density (g cm^{-3})		
	before	after	Δ (%)	before	after	Δ (%)	before	after	Δ (%)	before	after	Δ (%)
31	8.795	8.896	+1.1	5.020	5.035	+0.3	0.8297	0.8356	+0.7	Geo [a] 4.766	4.716	−1.06
36	8.705	8.988	+3.0	5.021	5.045	+0.4	0.8217	0.8442	+2.7	Geo [a] 4.767	4.699	−1.44
57	8.671	8.695	+0.2	5.024	5.041	+0.3	0.8198	0.8183	−0.2	Geo [a] 4.770	4.69	−1.68
										Hyd [b] 4.81	4.73	−1.66

[a] Geometrical density deduced from diameter and height measurements and from weighing.
[b] Hydrostatic density deduced from the pellet volume measurement liquid immersion and from weighing.

Table 3
Dimensional control – weighing – density. Pin 14: $MgAl_2O_4$ + 40% UO_2

Pellet No.	Height (mm)			Diameter (mm)			Mass (g)			Density (g cm^{-3})		
	before	after	Δ (%)	before	after	Δ (%)	before	after	Δ (%)	before	after	Δ (%)
30	9.071	9.065	−0.07	4.949	4.942	−0.1	0.8355	0.8352	−0.03	Geo [a] 4.788	4.803	+0.31
35	9.044	9.040	−0.04	4.948	4.943	−0.1	0.8316	0.8311	−0.06	Geo [a] 4.783	4.785	+0.04
										Hyd [b] 4.82	4.83	+0.21
55	8.761	8.758	−0.03	4.954	4.948	−0.1	0.8096	0.8068	−0.30	Geo [a] 4.794	4.791	−0.07

[a] Geometrical density deduced from diameter and height measurements and from weighing.
[b] Hydrostatic density deduced from the pellet volume measurement by liquid immersion and from weighing.

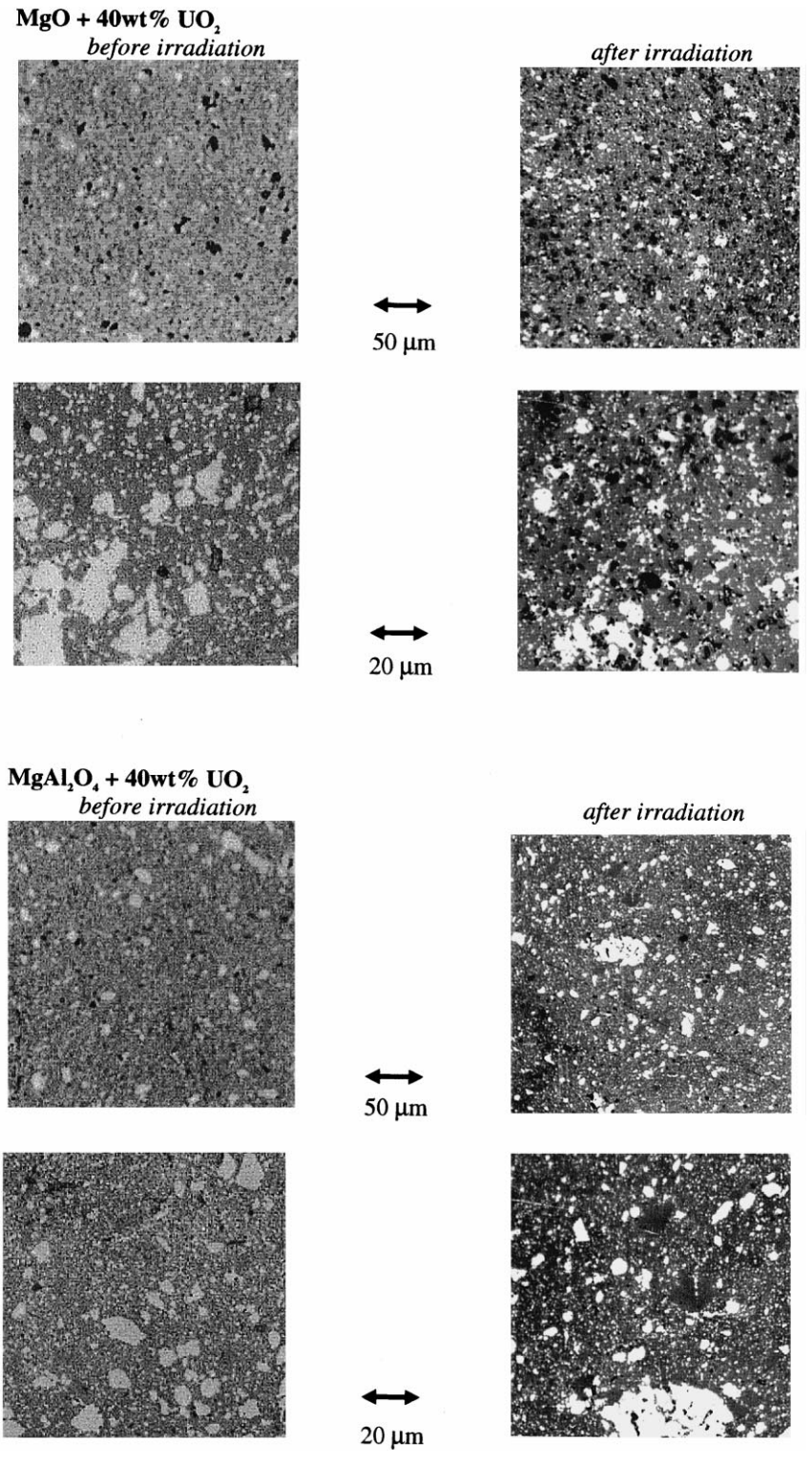

Fig. 1. Ceramographic examination results.

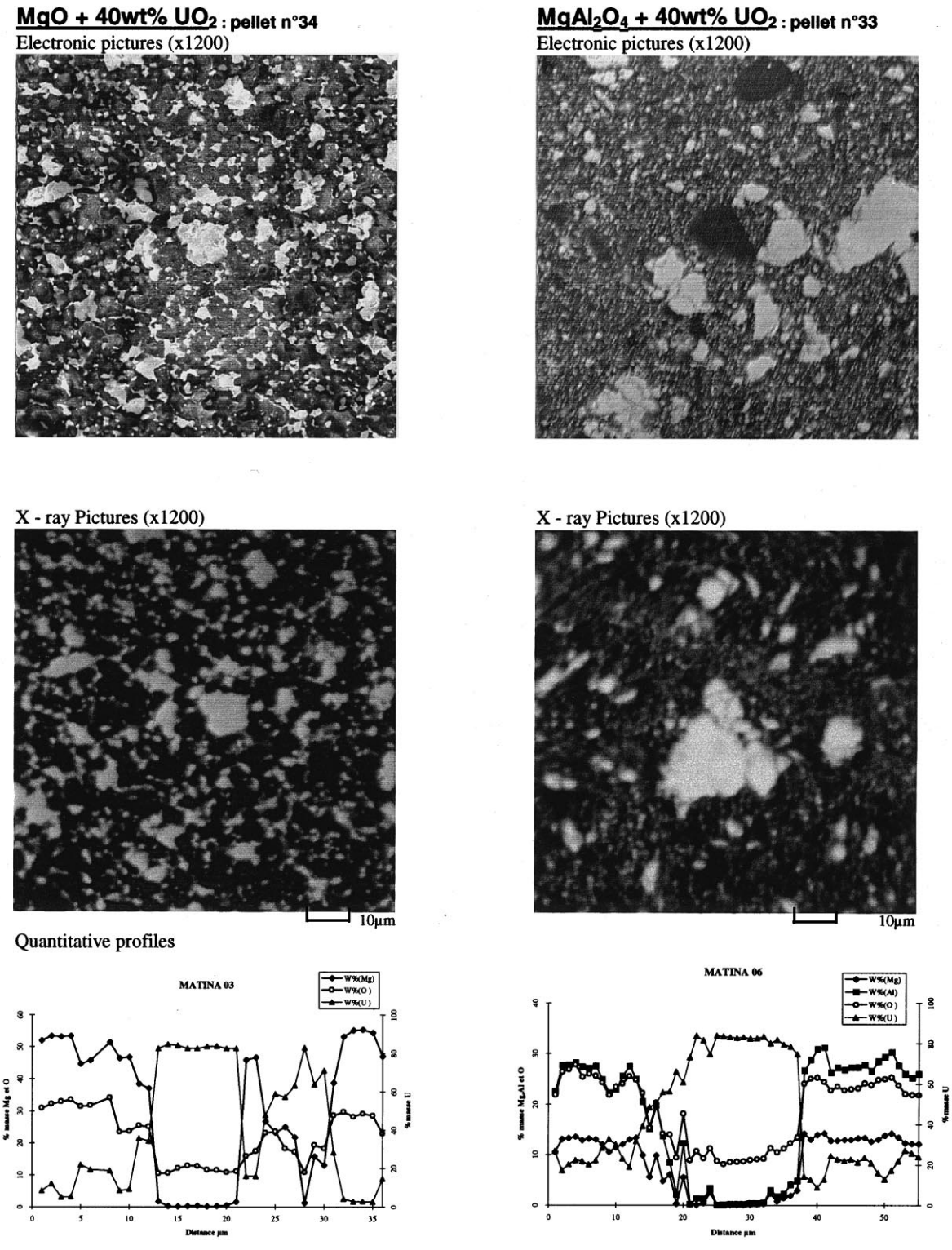

Fig. 2. Electron micro-probe analysis results.

about 0.05 cm^3 ($T = 273$ K and $P = 0.1$ MPa) thus the fission gas release rate is lower than 20%.

3.2.3. Ceramographic examinations

A radial and an axial ceramographic examination were performed for each component. The eight pictures given in Fig. 1 show the changes due to irradiation for each type of pellet. In each case, pictures before and after irradiation are very similar, and no cracking can be seen.

Nevertheless, for magnesia composite, porosity increased under irradiation (slight increase of the fabrication closed nanoscopic porosity). This observation is in accordance with the density decrease which was observed by metrological examinations. The porosity increase should equally apply to open and closed porosity as metrological examinations show similar decrease for geometrical and hydrostatic densities.

For $MgAl_2O_4$ + UO_2, from pictures before and after irradiation, it was observed that the original sub-microscopic porosity disappeared. This observation is consistent with the measured density increase of these pellets.

In summary, except the above minor comments, the ceramographic analyses do not show significant material evolution for both materials. In particular, fuel inclusions after irradiation look, on a morphological point of view, identical to the initial product.

3.2.4. Electron-microprobe analyses

Electron-microprobe analyses were performed on each of the two pins. The large atomic number difference between UO_2 components from one side and magnesia or spinel from the other side leads to a very sharp contrast on the electronic images. UO_2 appears in white on a dark background. The results are given in Fig. 2.

For (MgO + 40 wt% UO_2), UO_2 appears as grains or clusters, homogeneously dispersed in the magnesia matrix. The size of these clusters varies between 1 and 10 μm on the various examinations performed.

For ($MgAl_2O_4$ + 40 wt% UO_2), we can see on one hand tiny UO_2 particles (<1 μm) mixed to spinel and on the other hand scattered UO_2 and spinel clusters the size of which reaches 30 μm in the studied areas.

Quantitative analyses were also performed across UO_2 clusters. (MgO + UO_2) analysis confirms the presence of pure UO_2 clusters in the practically pure magnesia matrix. ($MgAl_2O_4$ + UO_2) analysis confirms the presence of pure UO_2 clusters in the spinel matrix in which there are small UO_2 grains.

Due to the very low burn-up of these two pins, the fission product yield was too low to really distinguish a behaviour difference between the two matrices.

4. Discussion and future prospects

Non-destructive examinations of the MATINA 1 pins demonstrated good behaviour of the materials during the irradiation except for Al_2O_3. The small elongation of alumina is in total agreement with the previous result of swelling from the SANTENAY experiment [1], taking into account the respective fast neutron fluence and for the same sample temperature:

- SANTENAY, fast neutron fluence: 17×10^{26} m^{-2}, Al_2O_3 swelling: 28 vol.%.
- MATINA, fast neutron fluence: 1.95×10^{26} m^{-2}, Al_2O_3 swelling: ~4 vol.% (extrapolated from elongation Table 1).

Destructive examination of the composites (MgO + 40 wt% UO_2) and ($MgAl_2O_4$ + 40 wt% UO_2) pellets show a good behaviour of the material. Considering these first results, magnesia and spinel can be used as support for fissile compounds.

Furthermore, complementary examinations including R–X analyses are planned and will be available in the near future.

Taking into account irradiation conditions, these results can be compared to other experiments yet performed on the irradiation of the same materials. For a better understanding of the inert matrix behaviour under irradiation, more fundamental studies of the damage mechanisms, gas (fission gas and helium) diffusion and the effect of temperature on the materials should be performed. This fundamental approach should be linked to an analysis of fabrication processes and corresponding microstructural properties.

The next two MATINA irradiations (MATINA 1A, 2) consist of testing the same materials to higher neutron fluence, up to 5.6×10^{26} m^{-2} for MATINA 1A an 20 10^{26} m^{-2} for MATINA 2, the calculated necessary neutron fluence for achieving an efficient transmutation being about 40×10^{26} m^{-2}. Furthermore the dispersion of UO_2 in the matrix will be studied (micro-dispersion or macro-masses up to 200 μm).

In the same time, the effect of fission product recoil on the matrix has been studied at 18% and 32% of fission rate respectively in the HFR reactor [7].

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