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Infiltration of highly radioactive materials: a novel approach to the fabrication of targets for the transmutation and incineration of actinides

K. Richter *, A. Fernandez, J. Somers

European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe, Germany

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Abstract

A procedure based on infiltration of aqueous metal solutions into pellets has been demonstrated for the production of targets containing highly radioactive materials. These targets will be used in the study of actinide transmutation and incineration (EFTTRA-T4). Impregnation of $MgAl_2O_4$ (spinel) pellets, with a green density of 50%, by an americium nitrate solution yielded pellets containing 8% americium. Following sintering the pellet densities were in the 96–98% range. The pellets are composed of two phases corresponding to spinel and an americium oxide. The Am phase is present as small particles with dimensions less than 2–3 μm, which are evenly distributed throughout the material. © 1997 Elsevier Science B.V.

1. Introduction

Although nuclear energy has been available for a considerable number of years, for both economic and environmental reasons, further research and development is required for the establishment of the most suitable means for the reduction and disposal of wastes. Several possibilities exist. The once through cycle requires that after the spent fuel has cooled sufficiently, it is transported to a waste disposal repository, where it is stored indefinitely. Although this procedure has the advantage that no reprocessing of the spent fuel is required, the possible interaction of ground water with various isotopic constituents (particularly those with long half-lives) requires detailed examination and the consequences thereof need to be determined for each disposal site.

In another scenario, the spent fuel can be reprocessed and the most active and long lived isotopes isolated. Once partitioned, these materials can be incorporated into fresh fuel and/or targets, and transmuted or incinerated by irradiation in a nuclear facility. This partitioning and transmutation (P and T) approach is an innovative option in the management of high level waste (HLW) generated by nuclear power production.

The investigations reported here form part of a multilateral collaboration on the experimental feasibility of targets for transmutation (EFTTRA). The aim of this collaboration is the investigation of the transmutation and incineration of both actinides and fission products supported in different matrix materials. Although UO_2 could be used as a matrix material, new actinides (Pu, Np, Am, etc.) are again produced from U-238 during the irradiation. This undesired effect can be eliminated by replacing UO_2 with a support material, which is inert with respect to neutron activation. These so called 'inert matrices' are selected on the basis of their

- compatibility with the coolant and cladding,
- thermal conductivity ($\lambda \geq \lambda_{UO_2}$),
- melting point (> 2000°C),
- resistance to damage by neutrons, fission products and α-decay (during storage).As it satisfies the above criteria, $MgAl_2O_4$ (spinel) has been chosen as the inert matrix material for the irradiation program EFTTRA-T4 and Am-241 the nuclide to be transmuted and incinerated.

For the fabrication of targets containing highly radioactive nuclides, traditional as well as new fabrication proce-

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* Corresponding author. Fax: +49-7247 951 599.

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dures have been investigated and assessed. Three possible fabrication routes for the production of transmutation and incineration targets are summarised in Fig. 1. In all three cases it is assumed that the active material will be incorporated into a matrix material. Traditional fabrication methods require several steps, including precipitation of the feed solutions, powder calcination, blending and milling of the powders, pellet pressing and sintering. The main handicap of these procedures lies in the handling of fine powders, which is difficult to automate and results in a build-up of radioactive dusts on the surfaces of the fabrication equipment and walls of the glove box housing. This can ultimately lead to an undesired increase in exposure of the operating personnel to harmful radiation. As the fabrication of fuels and targets for transmutation and incineration of actinides and fission products requires more stringent radiation protection measures (i.e., heavy shielding combined with remote handling), conventional procedures cannot be used easily.

An alternative procedure based on sol–gel coprocessing, developed originally for the production of MOX fuels [1], has also been used, within the SUPERFACT irradiation program, to fabricate a U–Pu–Am oxide fuel for the transmutation and incineration of americium [2]. Although this process avoids some of the disadvantages associated with conventional powder blending methods, and although it can be automated effectively, all fabrication steps have to be made within the glove boxes. Furthermore, the chemistry involved in the droplet to particle conversion step is not always readily adaptable to all types of matrix materials which are currently being considered for the fabrication of targets.

Infiltration of a liquid, solution or a melt into a solid porous material is another process by which composite materials can be fabricated and has been widely investigated in the production of non-nuclear ceramics (see for example Refs. [3–6]). As shown in Fig. 1, this process has the advantage that matrices with a low radioactivity or with, as in the case presented here, zero activity can be fabricated and formed into the required shape in an unshielded facility. The matrix material is then introduced into the shielded glove box and immersed in a solution (or melt) of the infiltrant in a controlled way. Thereafter the resulting material is treated, thermally or otherwise, to convert the infiltrant into the desired chemical form, and sintered to produce the product pellets. As the number of fabrication steps involving handling of highly radioactive material is considerably less than in either the powder mixing or sol–gel processes, unnecessary high exposure levels to the operating personnel can be avoided. Furthermore, as no precipitation or washing steps are required within the shielded area, the radioactive wastes produced in the process are negligible.

The infiltration process relies on the action of capillary forces to draw the solution into the pores of the host material. The application of this process to the fabrication of transmutation and incineration targets requires that the pellet is insoluble in the solution containing the infiltrant and that the infiltrant should be easily convertible into its desired chemical form. This could be a simple compound,

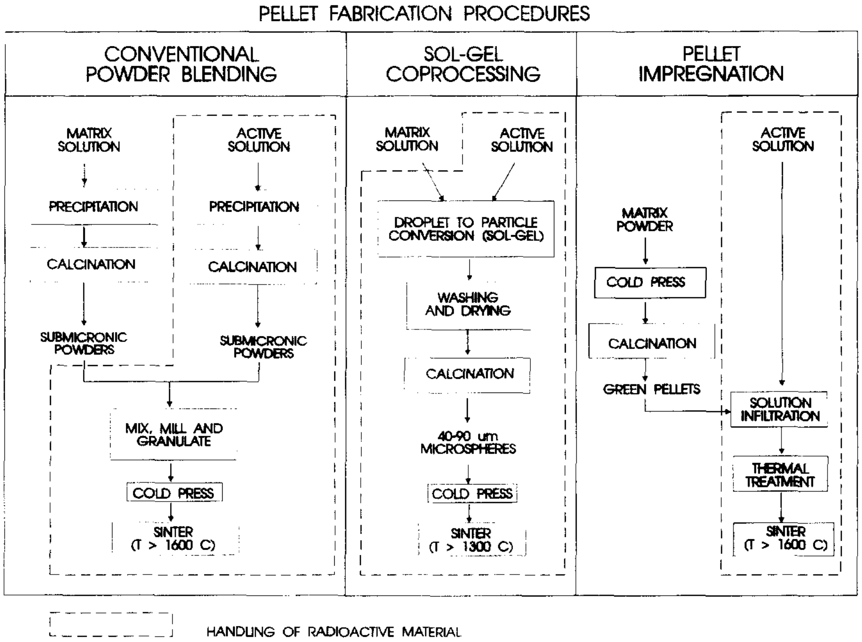

Fig. 1. Comparison of the steps involved in three fabrication routes for the production of highly radioactive targets for transmutation and incineration of actinides and fission products.

such as an oxide or nitride of the infiltrant metal, or a more complex compound formed by reaction of the infiltrant with the host matrix itself [7]. The concentration of the second phase introduced into the pellet should be controllable and uniformly distributed throughout the pellet. This can be achieved by careful adaptation of the concentration of the infiltrant solution to the porosity of the pellet. The control of the distribution of the second phase within the pellet during the infiltration step itself is most important when the two phases do not form a solid solution on sintering. Indeed in an earlier investigation [8], it has been shown that, due to the formation of a solid solution, the properties of $(Th_{0.98}U_{0.02})_2$ samples prepared by mechanical mixing of powders and solution infiltration were similar.

This paper presents the results obtained when the infiltration process was implemented for the fabrication of targets containing Am in a spinel matrix. These investigations are being continued and the infiltration of a number of metal (radioactive and non-radioactive) solutions into porous pellets is being investigated under various physical conditions to establish process data for this fabrication procedure.

2. Experimental

2.1. Target preparation

A commercially available spinel powder (Baikalox S33CR, Baikowski Chemie) was granulated, crushed and pressed into pellets in a bi-directional press operated at a pressure of 390 MPa. The resulting pellets had a diameter of 6.5 mm and height of 8–9 mm. Following calcination at 650°C for 4 h, gravimetric and geometric analysis of the samples indicated their porosity was 49%. This compares well with measurements made using a mercury porosimeter which gave an open porosity of 46%.

Americium oxide was dissolved in nitric acid and made up to a metal concentration of ~ 400 g/l. The pellets were immersed individually in this solution for a period of 5 min. The targets for the EFTTRA-T4 irradiation were produced in a similar way, the details of which will be published elsewhere [9].

Following their removal from solution, the pellets were treated at 700°C for 4 h under an Ar/H_2 atmosphere. In this step, the americium nitrate was converted by pyrolysis into an oxide. After sintering under an Ar/H_2 atmosphere at 1600°C for 6 h, the pellet diameters were 5.4 mm, their height 7 mm and their density 96–97% of the theoretical value.

2.2. Americium content

The americium content, defined, except where otherwise stated, as the weight of americium to the total weight of the sample, of the fabricated pellets was determined by gravimetric analysis before impregnation and after both calcination and sintering of the impregnated pellets. In addition, the Am content was determined by means of gamma spectroscopy. For these measurements, pellets were placed individually in a cylindrical stainless steel container (∅ = 5.5 mm) which was open at one end. Gamma counting was achieved using a HpGe detector located below a measurement well under a glove box. Five gamma energies (59.5, 103.0, 125.3 and 208 keV) were used in the Am determination, and a correction for the self absorption of the gamma rays, based on the height of the sample was also incorporated.

An absolute determination of the americium content was achieved by a calibration measurement, made under the same experimental conditions, using a pellet containing 8.0% Am in spinel, which was fabricated by conventional powder mixing and blending, pressing and sintering procedures. Although the americium content of this pellet is known, and a uniform distribution of the americium obtained, the size of the Am particles within the inert spinel matrix is not the same for both fabrication routes. No correction for a possible influence of this effect on the determination of the Am content using gamma spectroscopy has been included.

2.3. Radiation dose rate measurements

Measurements of the radiation dose rate of the samples were made using a thermoluminescence dosimeter (TLD) in the form of a film which is normally used by the personal as a finger dosimeter. For 'contact' measurements of the radiation dose rate, the pellets were positioned individually in an open ended steel holder so that one end of the pellet was flushed with the holder opening and was in contact with the 8 mm thick plexiglass wall of the glove box. Thereafter, the TLD was placed on the opposite side of the plexiglass wall for a given time. The dose received by the TLD was then evaluated using a Universal Toledo monitor. Measurements of the activity of the pellets were also made using a Geiger type Panoramic 470A detector. Although this type of detector can be placed directly against the plexiglass wall, the ionisation chamber is about 60 mm away from the front of the detector.

3. Results and discussion

3.1. Americium content

Gravimetric analysis, before infiltration and after thermal treatment and sintering of the impregnated pellets, showed that the pellets produced had an americium content of 7.7%. Measurement of the Am content by gamma spectroscopy, as described above indicated that the pellet contained 7.8% americium. This satisfactory agreement

Table 1
Radiation dose rate measurements of spinel pellets containing americium

Sample [a]	Pellet weight (mg)	Am weight (mg)	Activity (contact) (μSv/h)	Activity (Panoramic detector) [b] (μSv/h)
7.7% Am in Am–Spinel (infiltration)	610	47	158000	1800
8.0% Am in Am–Spinel (mechanical mixture)	310	25	116000	1600
$(Am_{0.06}U_{0.94})O_2$	700	42	27000	260

[a] All samples were in the form of pellets with diameter of 5.3 mm and heights varying between 3.3 and 7.4 mm.

[b] Due to its housing, a contact measurement made with the Panoramic detector gives a measurement in effect at 60 mm distance from the contact point of the housing.

between both of these measurement methods was also found for the targets produced for the EFTTRA-T4 irradiation program itself [9].

3.2. Radiation dose rate of the infiltrated pellets

Measurements of the radiation dose rate of spinel pellets with 7.7% Am produced by the infiltration procedure and with 8% Am by mechanical mixing of spinel and americium oxide powders are presented in Table 1 and compared with the activity of a uranium pellet containing 6% Am ($(U_{0.94}Am_{0.06})O_2$). Although the quantity of americium present in each sample is similar, the activity of the spinel–Am pellets is far higher than the U–Am pellet. This effect is directly attributable to the lower absorption of the gamma rays (59.5 keV), emitted on decay of the americium, by the spinel compared to uranium. The dose rate of a pure AmO_2 pellet (0.64 g, $\varnothing = 6.1$ mm and length $l = 4.15$ mm) has also been measured with a TLD detector [10]. In this case, the contact measurement was made through a glove of 0.5 mm thickness, rather than the 8 mm plexiglass in this set of measurements. Nevertheless it is noteworthy that the pure AmO_2 pellet exhibited a dose rate of 221 mSv h^{-1}. Even although the mass of Am was an order of magnitude higher, the activity of the pure AmO_2 pellet is very similar to those fabricated in these investigations. This is due to the high self-absorption of the emitted gamma rays by americium itself, so that only the surface regions of the pure AmO_2 pellet contribute to the radiation dose rate.

3.3. Americium distribution within the pellets

3.3.1. Radiography

As spinel and americium oxides have a large difference in density and hence a notable difference in their absorption of high energy photons, X-ray radiography can provide qualitative information of the macroscopic distribution of americium within the pellet. Radiographs of pellets with 7.7% Am, prepared by the infiltration procedure, and with 8.0% Am prepared by pressing of mixed powders are shown in Fig. 2. The speckled nature of the radiograph of the pellet prepared by mechanical mixing of the powders (Fig. 2a) is due to the larger size of the individual Am containing particles within the pellet (see below). In the case of the pellets prepared by the infiltration procedure, no such speckled pattern is observed. The radiograph of the pellet prepared by the infiltration procedure (Fig. 2b) shows a gradual increase in intensity (i.e., decreased X-ray penetration) on passing from the outside edge towards its central axis. This merely reflects the increased path length

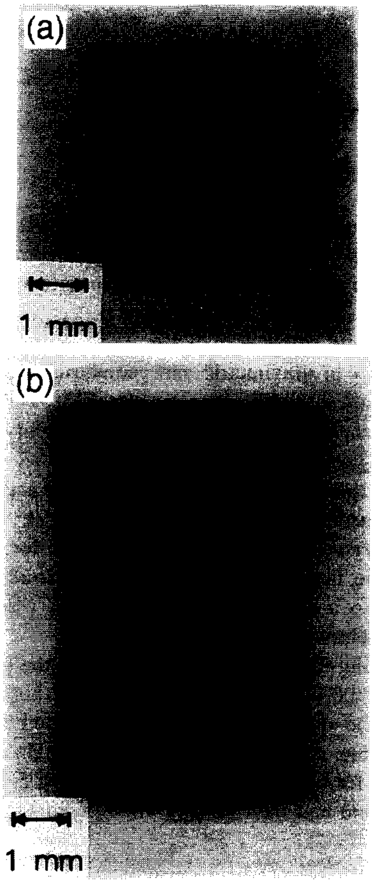

Fig. 2. X-ray radiographs of spinel samples containing Am: (a) pellet with 8.0% Am fabricated from mechanically blended AmO_2 and spinel powders, (b) pellet with 7.7% Am fabricated by the infiltration technique.

for the X-rays through the sample. The uniformity of this increase in intensity is a first indication that the Am is uniformly distributed throughout the sample.

3.3.2. Ceramography and α autoradiography

The pellets used in the above measurement were then sectioned and polished, and the α radiation resulting from the americium decay was used to take α autoradiographs (see Fig. 3) from the polished faces. The α autoradiograph of the americium sample prepared by mechanical mixing of spinel and AmO_2 powders (Fig. 3a) shows that a macroscopic homogeneous distribution of relatively large (up to 100 μm) Am containing particles was achieved. The α autoradiograph of the infiltrated pellets (Fig. 3b) does not distinguish individual particles containing Am which again indicates that they are substantially smaller than those formed in the mechanical mixture. The uniform nature of the α autoradiograph of the pellet prepared by solution infiltration, also indicates that the americium is relatively evenly distributed throughout the pellet.

Optical microscopy of the pellet prepared from a mechanical mixture of the starting material powders (see Fig. 4) reveals the presence of a number of large holes, up to 1 mm, and americium particles with a grain size of 10–50 μm. The larger holes are most likely formed by removal of large particles during the polishing procedure itself. The micrograph of the infiltrated sample (Fig. 5) exhibits smaller pores than in the case of the pellet formed from the mechanical mixture of the powders. In addition, the particles containing americium are less than 2–3 μm, i.e., they are significantly smaller than those found in the mechanical mixture.

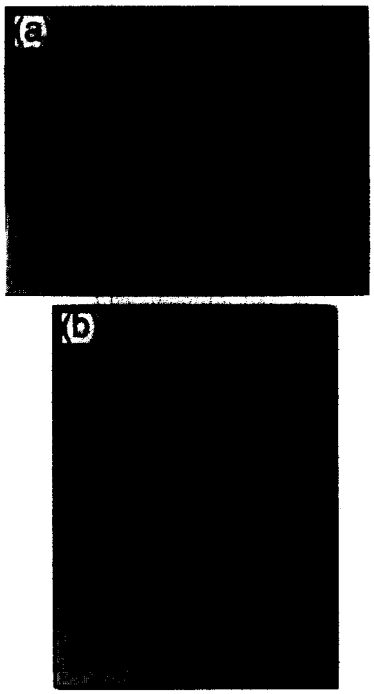

Fig. 3. α autoradiographs of spinel samples containing Am: (a) pellet with 8.0% Am fabricated from mechanically blended AmO_2 and spinel powders, (b) pellet with 7.7% Am fabricated by the infiltration technique.

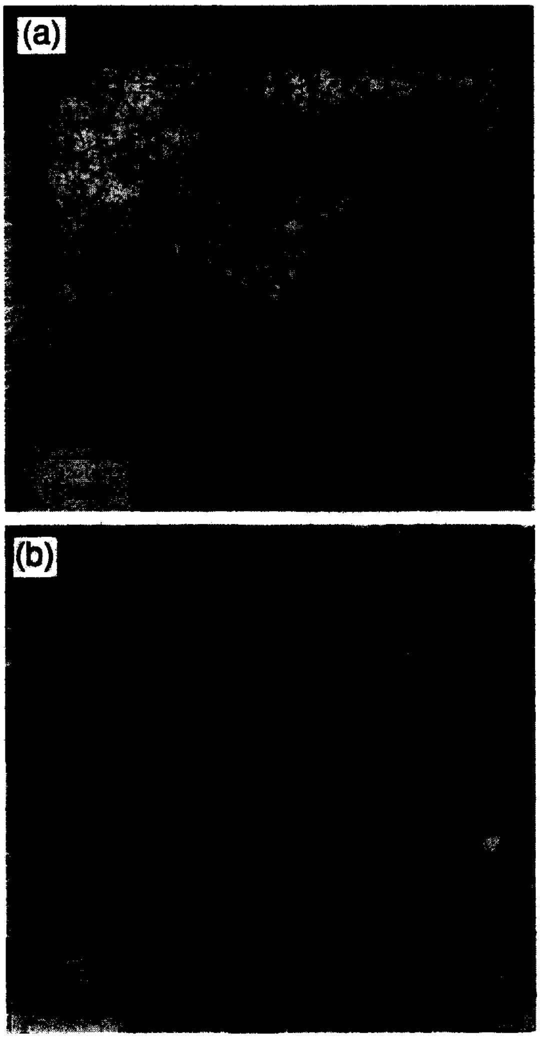

Fig. 4. Optical micrographs of a spinel pellet with 8.0% Am fabricated from mechanically blended AmO_2 and spinel powders. Particles containing Americium are observed as white features against a grey background due to spinel.

Initial investigations on the composition of the Am-containing particles indicate that a reaction between Am and the spinel occurs with the formation of a compound with a perovskite structure, whose chemical composition awaits confirmation. As the chemical composition of the Am-containing particles is independent of the fabrication routes implemented here, this reaction is specific to this case (Am-spinel) and has no bearing on the general application of the process.

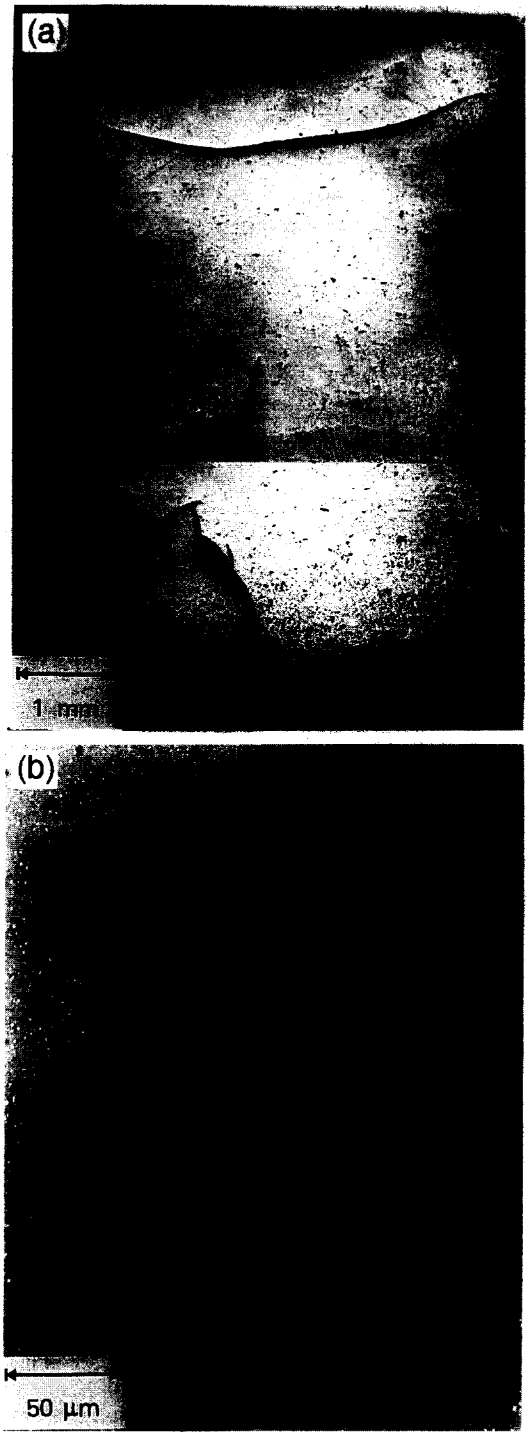

Fig. 5. Optical micrographs of a spinel pellet with 7.7% Am fabricated by the infiltration technique. Americium containing particles are observed as white features, with diameters less than 3 μm, against a grey background due to spinel.

4. Conclusions

The fabrication of highly radioactive targets for transmutation and incineration of long lived toxic isotopes generated by nuclear energy production, by infiltration of radioactive materials (INRAM), as reported here, offers many advantages. The number of fabrication steps involving highly radioactive materials are minimised and they can be automated or made remotely. The infiltrant is only present in liquid form which means that it could be transferred directly from the reprocessing plant for fabrication into targets without conversion into solid form. Thus the hazard of radioactive dusts can be minimised, if not avoided completely. In this way, a reduction in the exposure of personnel to harmful radiation and in the build up of contamination within the protective shielding of the glove-boxes can be achieved.

In these investigations, the feasibility of the INRAM fabrication process has been demonstrated for a case (americium in spinel) where the two components do not form a solid solution when sintered. The pellets produced have americium containing particles whose size is substantially smaller than that achievable by traditional methods involving mechanical mixing of powders of each component. A uniform americium distribution throughout the pellet was also attained. The maximum concentration of the second phase which can be obtained with a single infiltration step is determined by the porosity of the pellet and the concentration of the infiltrant solution. Higher americium concentrations could be achieved using multiple infiltration steps punctuated by thermal conversion of the nitrate to oxide.[1] However, no redissolution of the americium oxide in the infiltrant solution should occur.

Radiography proved to be a very convenient means by which the homogeneity and quality of the pellets produced by this method can be controlled. Further investigations to establish process data for the fabrication of materials, with tailored microstructures and infiltrant distributions, from a variety of matrices and infiltrants (Pu solutions, etc.) are underway. The process has already been used to fabricate americium–spinel targets for two fuel pins (EFTTRA-T4) which have been sent to HFR–Petten for irradiation.

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[1] Preliminary investigations have shown that the infiltrant (Ce or U) concentration within spinel pellets can be increased using multiple infiltration steps.

raphy and microscopy measurements. We also thank C. Leger, M. Burkhartz and Hj. Matzke for valuable discussions and for provision of information on their measurements of radiation damage in spinel which was supported by Electricité de France.

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