EUROPEAN COMMISSION

Community Research

# RAPHAEL

**Contract Number: 516508 (FI6O)**

# DELIVERABLE (D-BF2.4)

## Selection of potential matrixes and their fabrication routes for incorporation of spent HTR fuel


Author(s): **J. Fachinger……**
**M. Titov ……**
**A. Bukaemski**


Reporting period: 15/04/2005– 31/10/2005

Date of issue of this report : 05/10/2005

Start date of project : **15/04/2005** Duration : **48 Months**

| **Project co-funded by the European Commission under the Euratom Research and Training Programme on Nuclear Energy within the Sixth Framework Programme (2002-2006)** | | |
|---|---|---|
| **Dissemination Level** | | |
| **PU** | Public | |
| **RE** | Restricted to the partners of the RAPHAEL project | |
| **CO** | Confidential, only for specific distribution list defined on this document | **X** |

# Distribution list

| Person and organisation name and/or group | Comments |
|---|---|
| Werner von Lensa, FZJ (G) | Freigabe ISR: Datum 24.01.2006 |
| Marcel den Exter, NRG (Nl) | |
| Bernd Grambow, ARMINES (F) | |
| Reinhardt Odoj, FZJ (G) | Freigabe ISR: Datum 23.01.2006 |
| Heiner Brücher, FZJ (G) | Freigabe ISR: Datum 24.01.2006 |
| B. Carluec, FANP (F) | |
| V. Chauvet, STEP (F) | |
| E. Bogusch, FANP (D) | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |

| ReActor for Process heat, Hydrogen And ELectricity generation (RAPHAEL) | | |
|---|---|---|
| **Sub-project:** SP-BF<br>**Work package:** 2 | **RAPHAEL document no:**<br>RAPHAEL-0510-D-BF-2.4 | **Document type: D**<br>D=Deliverable / M=Minute /<br>P=Progress report / S=Support |
| **Issued by:** FZJ<br>**Internal no.:** VIP0509Deliverable-Selection of potential matrixes.doc | | **Document status:**<br>Final |

Document title

# Selection of potential matrixes and their fabrication routes for incorporation of spent HTR fuel

Executive summary

An important part of the R&D carried out nowadays in nuclear science is the waste management of spent fuel. A promising advanced reactor system is the HTR reactor, which uses coated fuel particles dispersed in graphite spheres or blocks as fuel elements. One concept for the final disposal of HTR fuel is to remove the graphite matrix and then to encapsulate the coated particles in a stable matrix, increasing the stability of spent fuel and reducing the necessary storage volume.
This report is a literature review of different matrices (SiC, $Al_2O_3$-, $ZrO_2$ and $TiO_2$ based ceramics, $Si_3N_4$ and ZrN) and compares them with respect to their suitability as encapsulation matrix.

Revisions

| Rev. | Date | Short description | Author | WP Leader | SP Leader | Coordinator |
|---|---|---|---|---|---|---|
| 00 | dd/mm/yyyy | First issue | Name, Organisation | Name, Organisation *Signature* | Name, Organisation *Signature* | Name, Organisation *Signature* |
| 01 | 05/10/2005 | First issue, draft | J. Fachinger FZJ | | | |
| 02 | 17/01/2006 | 2. Draft | J. Fachinger FZJ | | | |
| 03 | 25/01/2006 | Final version | J. Fachinger FZJ | B. Grambow EMN | W. von Lensa FZJ | E. Bogusch FANP |
| | | | | | | |

# Contents

# 1 Introduction

The incorporation of spent HTR fuel into a stable matrix can be employed to decrease the risk of radionuclide release from the final repository. The most promising material classes for this task are oxide, carbide or nitride ceramics, because of their significant advantages in comparison with glasses, concrete, bitumen and plastics.
The main criteria to judge the suitability of the selected matrix material are low porosity, high chemical and radiation stability, mechanical and thermal properties. Low porosity, high chemical and radiation stability are important factors, providing reliable isolation of spent fuel from the biosphere on the geological time scale. High mechanical stability should prevent the product damaging during transport to the repository site or by host rock pressure during disposal. High thermal conductivity is important to transfer heat generated by highly active spent fuel in order to prevent matrix/fuel composites from overheating.
However, not only the properties of the pure matrix material do matter. The ability of the matrix for proper incorporation of spent fuel is also valuable. The incorporation of spent HTR fuel in a matrix can be performed in different forms, depending on the spent fuel element disintegration degree, i.e. intact fuel pebbles, coated particles or fuel kernels. The type of the fuel containing unit to be incorporated, or the material of its outer surface, respectively, influences the selection of the preferential matrix material. The important role here is the compatibility of the matrix fabrication procedure with the particle outer layer. Good adhesion between incorporated particles and matrix is also desirable. The possible types of fuel containing units are presented below together with the material of their outer surface:

| Fuel containing unit: | Outer surface material: |
|---|---|
| Intact fuel pebble | Carbon |
| Coated particle | Carbon |
| TRISO coated particle without outer pyrocarbon layer | Silicon carbide (SiC) |
| Fuel kernel | Uranium/Thorium oxide |

Usually the fabrication of ceramic products can be divided into two main stages: fabrication of a green body (powder consolidation) and high temperature treatment. Analysis of existing methods of ceramic fabrication leads to the selection of the following potential methods for spent HTR fuel incorporation into a ceramic matrix. The green body can be formed by slip casting and injection moulding, and uniaxial pressing. The final product can be fabricated from green body by reaction-sintering, pressureless sintering or hot pressing. The fabrication procedure is material specific and should be optimised for every selected matrix material.
Additionally, for the task of spent HTR fuel incorporation into a ceramic matrix the following restrictions should be taken into account. An important factor is the product shrinkage during fabrication. The absence of shrinkage is the best option, since it prevents a product with incorporated spent units from cracking and voids formation. If the shrinkage is the inherent property of the fabrication procedure, special care should be taken to minimise the effects described above. If the incorporation of spent fuel units takes place in the form of fuel pebbles or coated particles, favour should be given to the fabrication procedures performing without significant external pressure. Fuel pebbles and coated particles can be damaged under external pressure, leading to the release of gaseous fission products. Also, the reaction of matrix material with inner pyrocarbon layer and buffer of coated particles can bring additional technological complications. Furthermore, the temperature during fabrication should not

exceed the maximal temperature allowed for HTR fuel (1600 °C). Higher fabrication temperatures can lead to an undesirable damaging of the fuel containing units.

# 2 Selection of potential matrix materials

Based on the criteria presented, and especially on the chemical stability of ceramic materials in contact with aggressive media, $Al_2O_3$, $ZrO_2$, $Si_3N_4$ and SiC can be proposed for the incorporation of spent HTR fuel. Another class of potentially suitable materials are $TiO_2$-based ceramics (Synroc).

Also an attention could be given to carbides and nitrides of Zr and Ti. However, in this case the use of hot isostatic pressing, providing high pressure and temperature, is required to fabricate dense products. This makes these materials hardly applicable for the task described.

The fabrication aspects of the materials mentioned are summarised in Table 1.

**Table 1. Fabrication aspects of different matrix materials**

| Type: | Material: | Potential fabrication procedure: | Compatibility: | Advantages / Disadvantages |
|---|---|---|---|---|
| Carbides | SiC | Slip casting or injection moulding, reaction-sintering at 1400–1600 °C | + Fuel pebbles, and coated particles<br>± Oxide kernels | + No shrinkage<br>+ Low porosity |
| Oxides | $Al_2O_3$ | 1. Cold pressing or injection moulding, sintering up to 1600 °C<br>2. Hot pressing at moderated temperatures | + Oxide kernels<br>± TRISO coated particles without outer pyrocarbon layer (pressure sensitive)<br>– Fuel pebbles and coated particles with pyrocarbon outer layer | + Low porosity<br>– Inherent shrinkage |
| | $ZrO_2$-based | | | |
| | Synroc | Hot pressing at 1200–1300 °C, 20 MPa | | |
| Nitrides | $Si_3N_4$ | Slip casting or injection moulding, nitridation at 1400–1450 °C; probably additional sintering with oxide additives at ~ 2000 °C | ± Oxide kernels and TRISO coated particles without outer pyrocarbon layer<br>– Fuel pebbles and coated particles with outer pyrocarbon layer | – High porosity (without additional sintering)<br>– High temperature (with additional sintering)<br>+ Moderate shrinkage |
| | ZrN | Cold pressing, hot pressing at ~1600 °C, ~ 1GPa | | – High pressure<br>– Complicated fabrication procedure |

All materials presented possess high chemical stability in aggressive aqueous media and advanced mechanical properties. The thermal conductivity varies in a wide range from about 2 W/Km for cubic $ZrO_2$ up to about 150 W/Km for SiC at 100 °C. A more detailed description of properties and fabrication aspects for the most promising materials is presented below.

## 2.1 Silicon carbide, SiC

Silicon carbide is a chemically very stable material, insoluble in water and acids even at elevated temperatures [1,2]. The theoretical density of SiC is 3.17 g/cm$^3$, its Vikers hardness ~22–24 GPa, and its thermal conductivity ~150 W/K m at 100 °C [1,3]. Despite the fact that silicon carbide is a theoretically thermodynamically unstable material it is not likely to cause serious problems in the case of spent HTR fuel incorporation.

SiC is readily compatible with the graphite surface of fuel pebbles and coated particles, with the silicon carbide surface of TRISO coated particles without outer pyrocarbon layer, providing a good adhesion of the matrix and fuel containing units in the final product. It is not directly compatible with oxide fuel kernels, because of the formation of gaseous products at high temperature during fabrication. However, this problem could be partially solved by maintaining a pressurised CO atmosphere during temperature treatment.
The most suitable option for spent HTR fuel incorporation is the reaction-sintered silicon carbide [4]. The procedure starts with the mixture of α-SiC powder, carbon, and optionally binder and additives. The spent fuel units should also be added in this step. The mixture is formed into the desired shape by slip casting or injection moulding, which are almost pressureless procedures. The binder, if present, is burned out at temperatures at the range of 300–600 °C. The green body is then exposed to molten silicon at high temperature (1450–1600 °C [5,6]). The silicon reacts with the carbon (and with the carbon coating of the fuel containing unit, if present) to form in situ β-SiC, which binds the original α-SiC particles and fuel containing units together. The final product is a usually fully-filled solid block. The careful adjustment of the SiC / C / binder ratio in the original mixture allows to obtain a high-quality ceramic without inclusions of free carbon or metallic silicon.
The advantages of reaction-sintered silicon carbide are simple pressureless fabrication procedure (slip casting or injection moulding), the possibility to obtain fully dense material, and a direct compatibility with fuel pebbles and coated particles to be incorporated.

## 2.2 Silicon nitride, $Si_3N_4$

Silicon nitride is a very chemically stable material, which does not react with water, acidic or basic solutions [1,2]. The theoretical density of $Si_3N_4$ is 3.19 g/cm$^3$, its Vikers hardness ~16–18 GPa, and its thermal conductivity ~28 W/Km at 100 °C [1,3].
The use of an appropriate atmosphere during fabrication makes silicone nitride compatible with oxide fuel kernels and the silicon carbide surface of TRISO coated particles without outer pyrocarbon layer. However, the fabrication of composites from $Si_3N_4$ and carbon coated fuel pebbles and coated particles seems to be problematic and requires additional investigations. In any case a good adhesion of $Si_3N_4$ and the fuel containing units cannot be expected.
The fabrication of reaction-sintered silicone nitride starts from a mixture of silicon powder, optionally with silicon nitride seeds, and sintering aids (such as $Al_2O_3$ and $Y_2O_3$) [4,7]. The spent fuel units should also be added in this step. The mixture is formed into the desired shape by slip casting or injection moulding. The green body is then placed in a furnace under a nitrogen containing atmosphere and nitrided at temperatures between 1400 and 1450 °C. At this step the nitrogen penetrates the porous compact and begins to react with Si to form β-$Si_3N_4$.
The primary disadvantage of reaction-sintered $Si_3N_4$ is its low density (typically below 90 % from theoretical) [4]. Further sintering with oxide sintering aids can increase the final product density. For instance, gas ($N_2$) pressure sintering at 2000 °C leads to products with densities above 98 % from theoretical [7]. However, the high sintering temperature of 2000 °C could lead to damaging of fuel containing units, making the application of this procedure to spent HTR fuel incorporation into $Si_3N_4$ matrix problematic.

## 2.3 $ZrO_2$-based ceramics

$ZrO_2$-based ceramics are highly chemically durable [1,2] and are well known as irradiation-stable materials [8]. The Vikers hardness of $ZrO_2$-based materials is 12–18 GPa in dependence

from its material composition and phase. Specially designed $ZrO_2$-based ceramics achieve a unique high fracture toughness, up to 15 Mpa $m^{1/2}$ [9], comparable with stainless steel. However, the thermal conductivity of zirconia is rather low, in the rage of 2 W/Km at 100 °C [1,3].
Zirconia is a well-known polymorph that occurs in three forms: monoclinic, cubic and tetragonal. Pure zirconia is monoclinic at room temperature and is thermodynamically stable [9]. The addition of stabilising oxides, like CaO, MgO, $CeO_2$ or $Y_2O_3$ allows to generate zirconia-based solid solutions in tetragonal and cubic phases, which are of practical interest in the frame of the present task.
Cubic stabilised zirconia is readily compatible with thoria and urania oxide fuel kernels, because of their unlimited mutual solubility. Therefore a good adhesion or even the formation of a solid solutions is expected on the matrix-fuel kernel interface. Compatibility can also be achieved with the silicon carbide surface of TRISO coated particles without outer pyrocarbon layer by selection of an appropriate sintering atmosphere. However, the carbon surface of fuel pebbles and coated particles can bring significant problems to the fabrication procedure.
In the case of oxide fuel kernel incorporation, the most suitable method of green body forming is uniaxial pressing as an efficient, simple and technological method. Special methods, such as vibropacking and usage of a bimodal powder mixture, can additionally increase the green density and, therefore, decrease the shrinkage during sintering. In the case of coated particle incorporation, the green body can be produced by injection moulding (almost pressureless) to reduce the risk of their damage. Thereafter, the green body is exposed to high temperatures up to 1600 °C to produce a dense compact. The sintering temperature can be reduced by the application of special powder treatment methods, such as activation milling. Hot pressing also allows lower temperatures than pressureless sintering and usually leads to better final products, but this procedure is more complicated and, in the case of coated particles incorporation, can lead to their damage.
The advantages of $ZrO_2$-based ceramics are their good compatibility with oxide kernels and the possibility to obtain high-density ceramics with good microstructure. From the other hand, the incorporation of carbon coated fuel pebbles and coated particles seems to be problematic.

## 2.4 Alumina

Alumina is a highly chemically stable material. The theoretical density of pure $Al_2O_3$ is 3.97 g/$cm^3$, its Vikers hardness ~22 GPa, its fracture toughness ~4 Mpa $m^{1/2}$, and its thermal conductivity ~20 W/Km at 100 °C [1,3]. $\alpha$-$Al_2O_3$ is thermodynamically stable and represents the only phase of practical interest.
Cubic-stabilised alumina is compatible with thorium and uranium oxide fuel kernels. The compatibility can also be achieved with the silicon carbide surface of TRISO coated particles without outer pyrocarbon layer by the selection of an appropriate sintering atmosphere. However, the carbon surface of fuel pebbles and coated particles can bring significant problems to the fabrication procedure.
The green body forming and sintering procedures (including hot pressing) are essentially the same as for $ZrO_2$-based ceramics. The sintering temperature of 1600 °C can be reduced in case of $Al_2O_3$ by usage of activation milling or the addition of small amounts of different sintering aids, such as $TiO_2$, MgO and $Y_2O_3$.
The advantages of $Al_2O_3$ are its compatibility with oxide kernels and its possibility to obtain high-density ceramics with good microstructure. From the other hand, the incorporation of carbon coated fuel pebbles and coated particles seems to be problematic.

### 2.5 Synroc

Synroc is a mineral-analogue multimineral $TiO_2$-based ceramic, consisting mainly of perovskite, zirconolite and hollandite. Synroc minerals occur naturally and have survived in a wide range of geological and geochemical environments for hundred thousands of years [10–12]. The theoretical density of Synroc is in the range of 4–5 g/cm$^3$, and Vikers hardness is ~10 GPa [11,12].

Because Synroc is an oxide ceramic, it possesses the same compatibility with fuel containing units as $Al_2O_3$. This means that it is suitable for the incorporation of oxide fuel kernels and probably TRISO coated particles without outer pyrocarbon layer, and is not suitable for carbon coated fuel pebbles and coated particles.

The fabrication of Synroc starts with careful mixing of the main constituent powders, with following calcination at a temperature of about 750 °C in a hydrogen containing atmosphere. The calcine is then milled and eventually mixed with titanium powder [10,11]. The spent fuel units should also be added after this step. High-density final products from Synroc are produced mainly by hot pressing, as it is known from the literature [10–12]. Typical fabrication parameters are a pressure of 20–50 MPa and a temperature between 1200 and 1350 °C.

The advantages of Synroc is its naturally proved geochemical stability and its compatibility with oxide kernels. The existence of an industrial-scale technology for the Synroc production is also valuable.

## 3 Conclusions

On the basis of the analysis performed the following matrix types and fabrication routes can be proposed for the incorporation of different fuel containing units:

- Graphite fuel pebbles and coated particles with or without outer pyrocarbon layer can be efficiently incorporated into a silicon carbide matrix, providing good adhesion between matrix and fuel containing units. The most suitable fabrication method is pressureless forming of a green body by slip casting of injection moulding, and reaction synthesis.
- Oxide fuel kernels and, probably, TRISO coated particles without outer pyrocarbon layer (SiC surface) can be incorporated into oxide ceramic matrixes, such as $ZrO_2$-based materials and $Al_2O_3$. The fabrication procedure includes cold pressing and pressureless sintering, which is simple and technological. Also hot pressing can be used to increase the quality of the final product and to reduce the fabrication temperatures. However, this method is more expensive and less technological.
- Oxide fuel kernels and, probably, TRISO coated particles without outer pyrocarbon layer (SiC surface) can also be incorporated into Synroc. The fabrication procedure in this case essentially employs hot pressing techniques.

The technological material most adapted for the task of incorporation of spent HTR fuel into a stable ceramic matrix seems to be silicon carbide. However, the thermodynamic stability of oxide matrixes can favour their choice in comparison to silicon carbide in some cases.

Other ceramic materials, such as nitrides or Zr and Ti carbides doesn't seem to offer any advantages in comparison to the matrixes selected above and are less technological to fabricate.

# 4 References

1. H. Kleykamp, Selection of Materials as Diluents for Burning of Plutonium Fuels in Nuclear Reactors, Journal of Nuclear Materials, Vol. 275, 1999, pp.1-11.
2. V.A. Robinovich, Z.Ya. Havin, Handbook of Chemistry, Chemistry, Leningrad, 1978.
3. W.E.C. Creyke, I.E.J. Scinsbury, R. Morrell, Design with Non-Ductile Materials, Applied Science Publishers, London and New York, 1982.
4. D.W. Richerson, Modern Ceramics Engineering: Properties, Processing, and Use in Design, Series: Manufacturing Engineering and Materials Processing, Marcel Dekker Inc., New York, 1982.
5. S.P. Lee, J.O. Jin, A. Kohyama, Fabrication and Properties of Reaction Sintered SiC Based Materials, Key Engineering Materials, Vol. 261-263, 2004, pp. 1475-1480.
6. U. Paik, H.C. Park, S.C. Choi, C.G Ha, J.W. Kim, Y.G. Jung, Effect of Particle Dispersion on Microstructure and Strength of Reaction-Bonded Silicon Carbide, Material Science and Engineering, A334, 2002, pp.267-274.
7. D.S. Park, B.D. Hahn, D.J. Baik, Microstructure and Properties of Sintered Reaction Bonded Silicon Nitride with Aligned Whisker Seeds, Key Engineering Materials, Vol. 287, 2005, pp.271-276.
8. W.L. Gong, W. Lutze, R.C. Ewing, Zirconia Ceramics for Excess Weapons Plutonium Waste, Journal of Nuclear Materials, Vol. 277, 2000, pp.239-249.
9. C. Piconi, G. Maccauro, Review: Zirconia as a Ceramic Biomaterial, Biomaterials, Vol. 20, 1999, pp.1-25.
10. B.D. Begg, E.R. Vance, S.D. Conradson, The Incorporation of Plunonium and Neptunium in Zirconolite and Perovskite, Journal of Alloys and Compounds, Vol, 271-273, 1998, pp.221-226.
11. S. Luo, L.Li, B. Tang, D. Wang, Synroc Immobilisation of High Level Waste (HLW) bearing a high content of sodium, Waste Management, Vol. 18, 1998, pp.55-59.
12. M. Muthuraman, K.C. Patil, Sintering, Microstructural and Dilatometric Studies of Combustion Synthesis Synroc Phases, Materials Research Bulletin, Vol. 31, N11, 1996, pp.1375-1381.