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SELECTION CRITERIA FOR CHOSING CARBONACEOUS MATRIX FOR HTR BLOCK TYPE DESIGN

Virginie Basini

Commissariat à l'Energie Atomique
CEA/Cadarache
DEC/SPUA/LMPC - 13108 St Paul lez Durance –
France
virginie.basini@cea.fr

François Cellier

AREVA NP, an AREVA and SIEMENS Company,
Plants Sector
10 rue Juliette Récamier - 69456 Lyon Cedex 06 –
France
françois.cellier@areva.com

Florence Bruguier

Commissariat à l'Energie Atomique
CEA/Cadarache
DEC/SPUA/LMPC - 13108 St Paul lez Durance –
France
florence.bruguier@cea.fr

Marie Pierre Vitali

CERCA
A Subsidiary of AREVA NP, an AREVA and
SIEMENS Company
BP 1114 – 26104 Romans sur Isère Cedex –
France
mariepierre.vitali@areva.com

ABSTRACT

In the framework of the ANTARES (AREVA New Technology for Advanced Reactor Energy Supply) programme, the Commissariat à l'Energie Atomique (CEA) and AREVA conduct R&D projects covering the mastering of fuel compact fabrication technology with the CAPRI (CEA AREVA PRoduction Integrated) line.

Fuel compacts consist of coated particles bonded in a close-packed array by a carbonaceous matrix. This matrix is made by treating a fully graphitized powder (natural graphite and/or needle or pitch coke origin) with a binding agent which is a phenol-formaldehyde resin. The resin bonded matrix has to fulfill a number of essential tasks in the fuel element. These tasks are directly influenced by the graphite matrix structure and by the graphite sourcing. A bibliographic review of past irradiation tests performed in the 70's has been done to assess the relationship between graphite matrix materials used and the in pile compact behavior. The goal was to specify compact properties required for the definition of coming SIROCCO irradiation tests in the OSIRIS reactor.

This paper presents the results of this bibliographic review. Compact properties leading to acceptable in pile behavior (i.e. dimensional changes, thermal conductivity and coefficient of thermal expansion) are highlighted and the influence of the matrix graphite structure is presented.

INTRODUCTION

An extensive R&D program aiming at mastering HTR fuels fabrication technology is in progress at AREVA NP and Commissariat à l'Energie Atomique (CEA) through the

ANTARES (Areva New Technology for Advanced Reactor Energy Supply) program [1]. Objectives are to recover past knowledge regarding TRISO particles and fuel compacts manufacturing, and to fabricate and characterize fuel elements required for irradiation and qualification purposes (for instance the coming SIROCCO irradiation tests planned in the OSIRIS reactor [2]).

In this context, a bibliographic review of past irradiation tests performed in France and U.K. in the 70's has been done in order to highlight and discuss compact properties leading to acceptable in pile behavior (i.e. dimensional changes, thermal conductivity and coefficient of thermal expansion) as well as the influence of the matrix graphite structure.

FUEL ELEMENT FABRICATION PROCESSES

A number of fuel element fabrication processes have been developed over the years.

Within the framework of the Dragon Project (DP), fuel compact matrix was made of a mixture of graphitized graphite powders and phenol formaldehyde resin (from 12 to 20 %) [3]. Different graphitized graphite powders were studied, from natural and artificial graphite to a mixture of both. The compacts were prepared individually by mixing the coated particles with the graphite matrix material and pressing the mixture in heated dies. According to DP reports, this method had many drawbacks including tedious mixing of each individual compact, unreliable particle distribution and difficulty to fill die. An overcoating process was thus

developed to overcome most of these drawbacks [4]. In the overcoating process, a layer of matrix material is applied onto each coated particle so that all of the required matrix material is arranged round the coated particles. The overcoated particles are introduced into a cylindrical die and warm molded (pressed) at 180 °C at a pressure of ~ 7 MPa to form the fuel compacts. The “green” compacts are subsequently carbonized by heating in flowing N₂ at a rate of 5°C/min to 900 °C, followed by heating to 1800 °C under high vacuum (to degas the compacts). Fuel particle volume fractions as high as 45 vol.% have been reported in the literature.

Among other HTR fuel development programs, German technology seems to be a reference. In this case, the fuel element is a graphitic sphere (pebble) of 60 mm diameter [5]. The process comprises four main steps:

- i) preparation of the raw material which is a mixture of natural and artificial graphite powders and phenolic resin (named A3-matrix),
- ii) overcoating process (similar to the Dragon process),
- iii) moulding of the fuel element by cold isostatic pressing at 300 MPa,
- iv) heat treatment of the spheres: carbonization at 800 °C and residual degasification at 1800 °C or 1950 °C.

A standard A3-matrix (A3-3) has operated satisfactorily since 1969 and a modified A3-27 since 1976. Composition and fabrication of these matrix materials are described in table 1 [5]. The fuel particle volume fractions was about 12 vol.%.

| Material and Fabrication | Standard matrix A3-3 | Matrix with synthesized resin A3-27 |
|---|--|---|
| Composition of raw materials: Natural graphite Petroleum coke graphite Resin binder | 64 wt % 16 wt % 20 wt % | 62.4 wt % 15.6 wt % 22.0 wt % |
| Binder | Phenolic resin prefabricated from phenol and formaldehyde | Synthesized resin 2 synthesized from phenol and hexamethylenetetramine during matrix formation |
| Moulding method | Quasi-isostatic cold moulding | |
| High-temperature treatment: Fuel elements Fuel-free matrix spheres | 1800 or 1950°C 1800°C | 1950°C 1950°C |

table 1 : Composition and fabrication of German pebble fuel matrix materials

The General Atomics (GA) HTR prismatic core design required much greater fuel particle volume fractions (about 60 vol.%) than ever achieved with any of the previous methods. A 3-step injection process was thus developed [6, 7]:

- i) mixing of coated particles and of a given percentage of graphite granulates (shim),
- ii) injection at 150-200°C of a mixture of pitch, natural graphite and binder,
- iii) final heating at 700-1000 °C (carbonization) and then at 1800 °C (degassing).

In France, the compacting process originally used by CERCA was the same as in the DP. Later on, CERCA proposed a process optimization. This optimization consisted in the suppression of the overcoating step of the DP compacting process. The main advantage, apart from simplicity, is the very good accuracy in coated particle weighing, and therefore in the quantity of uranium in the fuel compacts [8]. This new "CERCA process", recovered and used at present time in the CAPRI line [9, 10], differs from the overcoating one in that the graphite powder is first pre-agglomerated to form granules that are directly mixed with coated fuel particles. In the past, different natural and artificial graphite sources were studied for the matrix. This process was used with great success for the manufacturing of about 85,000 fuel compacts for the Marius critical experiment at CEA Cadarache. Fuel particle volume fractions as high as 50 vol.% were reached.

AS-FABRICATED FUEL ELEMENT PROPERTIES

The fuel element, and consequently the graphite matrix material, has to fulfill a number of essential tasks depending on the fuel element service conditions. Requirements for the graphite matrix are thus strongly influenced by the type of reactor design [11].

The graphite matrix development is thus an integral part of any fuel element development. In the case of a pebble-bed reactor [5], the matrix graphite acts as moderator for fission neutrons, offer protection against external forces and protect the coated particles from external corrosion attacks. The key properties of the pebble matrix to be kept within specified ranges are thus graphite density, strength and corrosion resistance.

In a prismatic core reactor, the fuel compacts are inserted in graphite fuel blocks. In this case, the graphite matrix design requirements can be summarized as follows [12]:

- the thermal and irradiation induced dimensional changes should be such that interaction with the graphite blocks is avoided,
- a relatively good conductivity to minimize compact thermal gradients,
- a good mechanical strength to protect the coated particles from external forces,
- to act as sacrificial layer in the event of chemical attack to minimize detachment risks and corrosion attacks on particles.

It is important to notice that, contrary to pebble-bed reactors, the requirements for mechanical integrity and corrosion rate are low for the prismatic core reactors, these functions being

already fulfilled by the graphite fuel blocks of the core structure.

For these reasons development work of graphite matrix materials followed different directions : improved corrosion and enhanced mechanical properties for the pebbles whereas the focus was made on thermal and neutron dimensional changes and thermal properties for the compacts [11].

It is well known that the irradiation behavior of graphites are markedly affected by the cristalinity degree of materials. The cristalinity degree can be evaluated by measuring X-ray crystallite size, L_c and L_a (figure 1). In natural graphite L_a is generally several times higher than L_c whereas the artificial graphites have $L_a \approx L_c$.

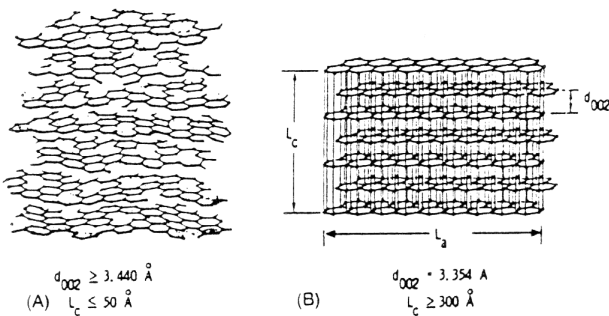


figure 1 : Cristalline graphite structure

Assuming that the initial shrinkage of graphite during irradiation is caused by the diffusion of basal plane vacancies to the crystal edges, a large L_a should both delay and reduce the overall dimensional changes [13]. Unfortunately, the advantage inherent in good cristalinity is usually offset by disadvantageous lower mechanical strength and anisotropic behavior [11]. The cristalinity of natural graphite being higher than artificial graphite, lower in pile dimensional changes are expected from natural graphite but lower strength and higher anisotropic behavior are also to be faced.

IN PILE COMPACT PROPERTIES

Since graphite matrix behavior was directly influenced by the graphite powder used, lot of development studies and irradiation experiments of matrix compacts were performed in the past. Different natural and artificial graphite powders were used to manufacture the compacts then some of compact key properties were measured after in-pile irradiation.

Dimensional changes

Experimental irradiations of several natural and artificial graphite matrixes were performed in French reactors (Osiris, Rapsodie and Siloe) as well as in DP and HFR reactors [11, 14, 15].

The axial variations with the fluence of compacts manufactured by using natural and needle coke graphites, and irradiated at 1200 °C, are reported in figure 2. In the axial direction, shrinkage of natural and needle coke graphite appear similar. After turn-round at about $5 \cdot 10^{21} \text{ n.cm}^{-2}$, an increased rate of expansion is observed for the needle coke graphite.

The radial variations with the fluence of matrixes irradiated at 1200 °C are reported in figure 3. Fuel compacts

based on needle coke graphite show greater shrinkage in that direction. A turn-round is observed at about $5 \cdot 10^{21} \text{ n.cm}^{-2}$ whereas natural graphite still shrinks.

Needle coke graphite compacts shrinks more rapidly in the radial direction than in the axial direction. Natural graphite compacts exhibit a more isotropic behavior.

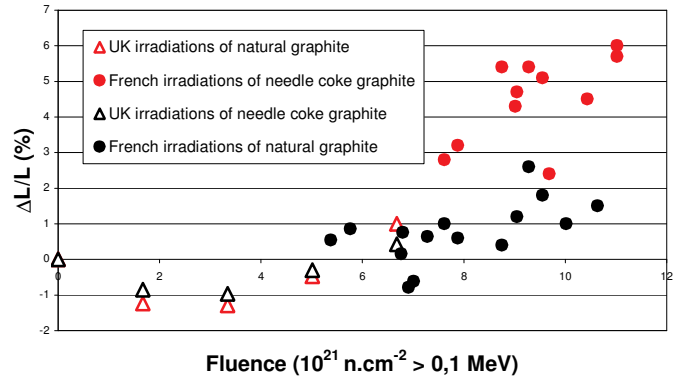


figure 2 : Axial dimensional changes of graphite matrixes irradiated at 1200 °C

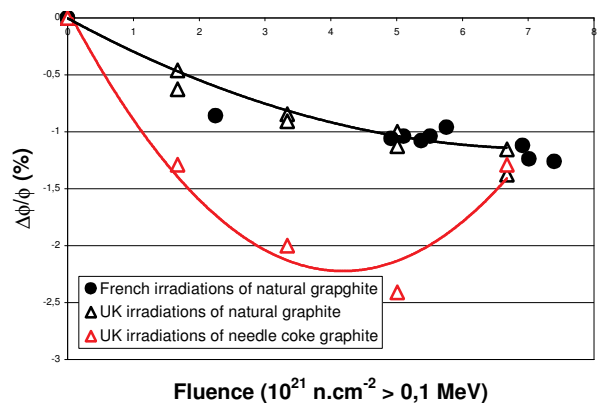


figure 3 : Radial dimensional changes of graphite matrixes irradiated at 1200 °C

A mixture of natural and artificial graphite powders was used in Germany for pebbles matrix [5] and was also studied in France [16]. A comparison of the results is presented in figure 4. For pebble matrix, artificial graphite powder made from needle coke was used. Results plotted in figure 4 correspond to calculated values of dimensional changes issued from former German models [5]. For the compacts matrix, artificial graphite powders made from pitch coke was used. Experimental values are plotted in figure 4.

The behavior of natural and pitch coke powder mixture is really closed to natural dimensional changes. Pebbles A3-matrix shrinkage appears higher than the compacts matrix one. This is in agreement with the fact that pitch coke has lower dimensional changes than needle coke [15], and also that for different mix-rate of natural and artificial graphite, dimensional changes can be predicted by a mixing law [16].

The addition of some content of artificial graphite seemed to be a good compromise between mechanical properties and irradiation behavior [17].

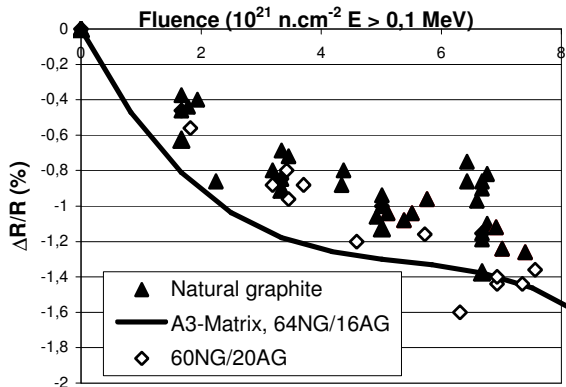


figure 4 : Dimensional changes of different mix-ratio graphite powders

Coefficient of thermal expansion

The Coefficient of Thermal Expansion (CTE) has been measured on natural graphite [14] and needle coke graphite compact matrix [18] as well as on pebble A3-matrix [5]. The results are reported in figure 5. Measurements were made in the axial direction between 20 °C and 400 °C.

Really closed CTE values are obtained and a low variation with irradiation is observed. This is in agreement with graphite blocks post irradiation results which show that a lower variation of CTE is observed for medium as-fabricated CTE values (around 3-4 $10^{-6} K^{-1}$).

Irradiations of fuels compacts loaded with 20 vol.% TRISO particles show that the dimensional change behavior (thermal and neutron dimensional changes) is similar to that of the graphite matrix alone [12].

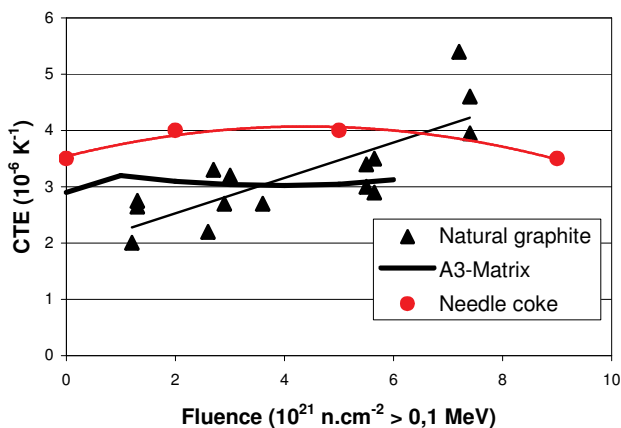


figure 5 : CTE of graphite matrixes

Thermal conductivity

The matrix thermal conductivity was mostly studied for the German pebbles A3-matrix [5]. A thermal conductivity model taking into account temperature, composition and fluence dependence (temperature: 20 °C–1000 °C, composition: A3-3 and A3-27, fluence : between 0 and 10 $10^{21} n/cm^2 E > 1 MeV$) was developed. Using these calculated values, thermal conductivity changes of fuel element matrix materials as a function of neutron fluence at 1000 °C are shown in figure 6. A thermal conductivity decrease occurs during irradiation. This phenomenon tends to saturate with neutron dose.

German model also takes into account the particle volume loading, which leads to lower thermal conductivity values. Particle volume loading of German pebbles was about 12 % vol, Unfortunately, past UK or French irradiations tests were performed on high particle volume loading (about 35 vol %) and thus, corresponding thermal conductivity values cannot be compared with those from German models. However, a thermal conductivity value of 25 W/m.K is given in reference [19] for petroleum coke matrix. This value is close to the A3-matrix conductivity and means that the graphite source has less influence than the particle volume loading.

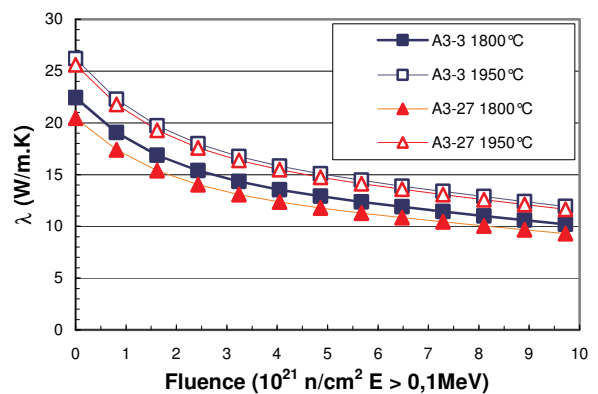


figure 6 : Changes of thermal conductivity of fuel element matrix materials as a function of fluence

CONCLUSION

AREVA and the Commissariat à l'Energie Atomique are conducting R&D projects on HTR fuels, whose aim is the mastering of fuel elements fabrication technology in the frame of the ANTARES (Areva New Technology for Advanced Reactor Energy Supply) program.

A review of past fabrication and irradiation tests performed in the 70's has been done. The major conclusions of this work are:

- Requirements for the graphite matrix depend upon the service conditions and so, are strongly influenced by the type of reactor design.
- In a prismatic core, the main requirements for the compacts matrix should be a low neutron and

thermal dimensional changes and a relatively good thermal conductivity.

- Matrix materials containing a well graphitized filler powder such as natural graphite powder, show the more promising results. Such fuel compacts should have satisfactory dimensional behaviour under irradiation conditions.
- Good in-pile feedbacks are available on German pebbles A3-matrix. The mixture of natural and artificial graphite seems to be a good compromise between mechanical properties and irradiation behaviour.

These results will be useful to specify fuel compacts for the coming SIROCCO irradiation tests to be performed in the OSIRIS reactor in parallel with the fuel fabrication development work. Main objectives of these irradiation tests are to verify the fuel quality in terms of integrity and fission products retention (SIROCCO 1) and to verify the aptitude of the reference particle to withstand V/HTR conditions (SIROCCO 2) [20].

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