

MODELLING OF V/HTR FUEL ELEMENTS AND COATED PARTICLES: NEEDS OF PIE IN SUPPORT TO THE EUROPEAN „RAPHAEL“ AND GEN-IV PROJECTS

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ABSTRACT

The fuel elements (spherical or compacts) of Very High Temperature Reactors (V/HTRs) are based on ceramic multilayer coated fuel particles, that represent the smallest constituent of the energy source in this type of reactors. As for the LWRs, the performance of the fuel element and its basic constituents has to be evaluated by modelling its behaviour under normal and accident conditions. In this context, the performance of the particle coatings (failure) and the consequent fission product release is of paramount importance. In the paper the main PIE-and characterisation methods needed to supply data for the current codes are described. The existing techniques and the main challenges for the future PIE needs in support of the European “Raphael” project and GEN-IV are presented.

1. INTRODUCTION

The fuel element in a modular High Temperature gas-cooled Reactor (HTR) is crucial for its safety and reliability. To this goal, ceramic multilayered coatings for nuclear fuel particles were developed for High Temperature Reactors. They are based on the synergy of the thermo-mechanical properties of silicon carbide (SiC) and pyrocarbon (PyC) to perform the coating of the fuel kernels, which should be able to retain most of the fission products release by the fuel during irradiation under normal and accident conditions.

Different types of nuclear fuel elements have been managed for the different HTRs developed all over the world in current reactor concepts and in the past. For example, pebbles (spherical fuel elements, 60 mm in diameter) are used in the Chinese reactor HTR-10. This was the concept developed in Germany in the nineteen sixties. On the other hand, the fuel is arranged in compacts (cylindrical fuel elements, approx. 26 mm in diameter, 39 mm in length) in the Japanese concept, which was also the concept for the reactor Fort St Vrain in USA.

In all reactor concepts, the coated particles constitute the basic energy producing unit, having the following coatings on the fuel kernel (see Fig.1) to retain the fission products:

- Buffer: porous pyrocarbon layer
- IPyC: internal, dense pyrocarbon layer
- SiC: Silicon carbide layer
- OpyC: external, dense pyrocarbon layer

Fuel kernels have been made of UO_2 , UCO , UC_2 , UO_2/ThO_2 . Fuel kernels constitute the first barrier for the release of the fission products. The **buffer layer** provides space to accommodate fission gas and can be compared to the plenum in the fuel rods for LWRs. It absorbs the swelling of fuel kernels during irradiation and protects the inner dense PyC-coating from damage due to recoil from fission fragments. The **IPyC-layer** prevents the reaction between the kernel and chlorine compounds released during SiC-deposition. It constitutes the second barrier against fission product release. The **SiC-layer** is the main load bearing component of the coating and the main fission product barrier. Finally, the **OpyC-layer** is meant to protect the SiC-layer from mechanical damage during the fuel manufacturing and provides an additional barrier against fission product release.

The present paper is a first attempt to review some of the most important Post-Irradiation Examinations (PIE)-methods applied in the past to coated particles. A simple model for the thermo-mechanical behaviour of the coated particles will be briefly discussed to introduce some of the main PIE to be performed in order to provide the necessary data to the modellers.

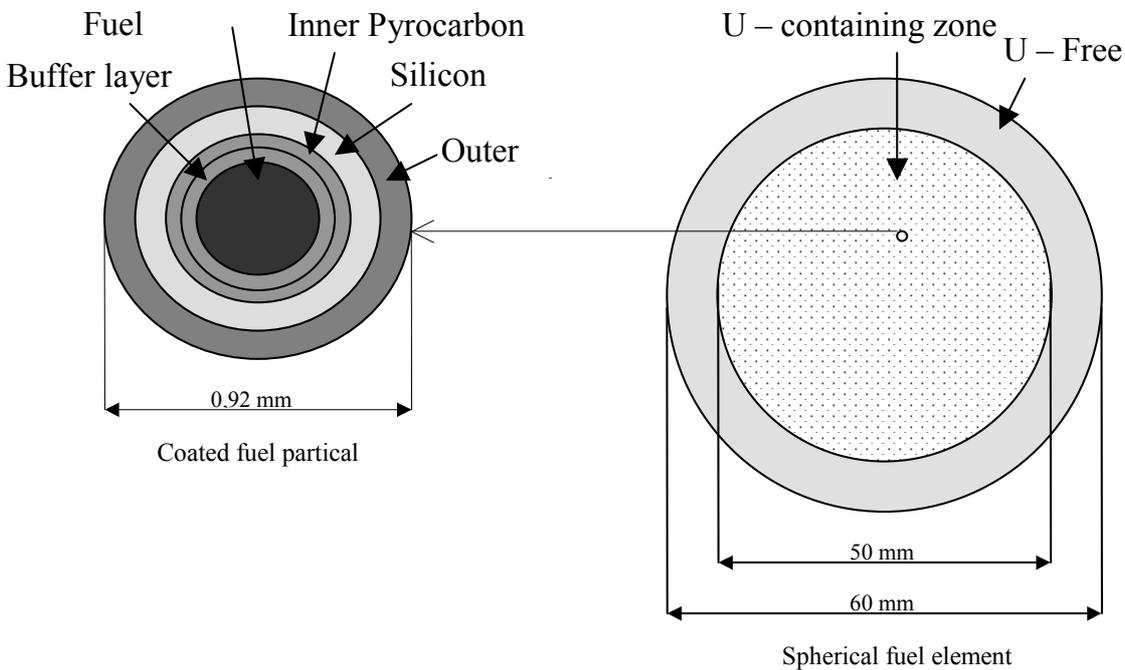


Figure 1. Spherical fuel element for a high temperature reactor containing coated particles

2. MODELLING

The principal mode of failure considered in the codes is the pressure vessel failure caused by the build-up of fission gas pressure in the kernel of the coated particle during irradiation (see, e.g., Ref. 1). In this model it is assumed that fission gas pressure builds up in the kernel and is partially released to the buffer layer regions. The IPyC, SiC and OPyC-layers act as structural layers to retain this pressure. The IPyC and OPyC-layers both shrink and creep during irradiation of the particle while the SiC exhibits only elastic response. Part of the gas pressure is transmitted through the IPyC to the SiC-layer.

Input parameters for the model include kernel diameter, buffer thickness, pyrocarbon and silicon carbide layer thicknesses, kernel and buffer densities and strength of the SiC-layer. A number of material properties have to be considered in the modelling of the particle behaviour under normal and abnormal irradiation conditions. In what follows, the main characterisation and PIE-methods will be described and the properties relevant for modelling purposes discussed.

3. LOSS-OF-COOLANT-ACCIDENT (LOCA) SIMULATION

The crucial aspect of the safety philosophy for a High Temperature Reactor (HTR) is the retention of fission products - particularly those of the iodine nuclides - in the fuel elements during operation and accidents. For this reason, the determination of the number of damaged particles constitutes the central objective of measuring the fission gas release in the reactor and also in the extensive post-irradiation examinations under accident conditions. In modern production methodologies, the heavy metal contamination of fuel elements is kept very low. Consequently, solely the number of defective particles establishes fission gas or iodine release.

During a loss-of-coolant accident, the temperature in the core of a HTR will increase. The amount of this increase depends on the geometrical design of the reactor and the nature of the accident. For the extreme case of pressure loss in the core with the failure of all heat sinks, temperatures as high as 2000°C can be reached in a medium size HTR. On the other hand, for the case of small HTRs and the MODUL-concept in

Germany, relatively low accident temperatures between 1400 and less than 1800 °C, typically 1620 °C, have been anticipated.

With the increase of the core temperature above normal reactor working temperature, fission products may be released from the fuel elements into the primary circuit and, eventually, into the environment. For a realistic assessment of the fission product release, the conditions in the reactor core during this accident scenario have to be simulated.

With the goal of simulate these accident conditions, the KÜFA (German acronym for “Cold-Finger Device”) was developed (see Fig. 2). The basic function of this device is to heat the fuel elements up to the expected temperature in a dynamic He-atmosphere, and then to measure the fission product release. In the cold finger, protruding into the furnace, the solid fission products are plate-out whereas a continuous He-circulation through a cold trap allows the measuring of the gaseous fission products (85Kr). The device described has been already installed in a hot cell at the Institute for Transuranium Elements and has been thoroughly described in Ref. 2 and 3.

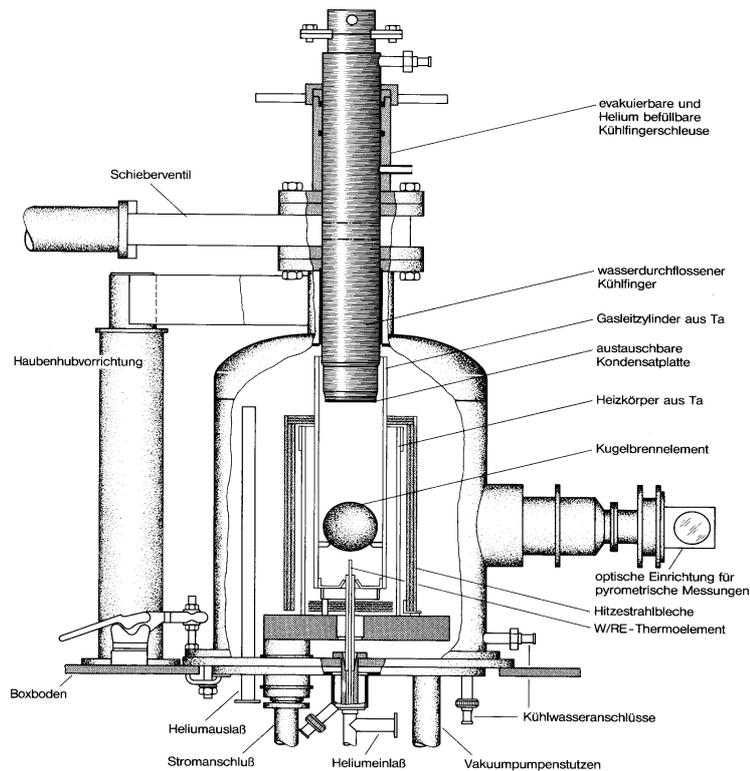


Figure 2. Cold-finger installation for the simulation of the LOCA-accident

4. DECONSOLIDATION

After irradiation or heat treatment in the KÜFA-installation, an electrolytic process with the goal of obtaining individual coated particles has been developed to disintegrate fuel elements. The ultimate aim of the procedure is to be able to identify broken or damaged particles. The process is carried in two stages: In the first stage, the sphere (the method can be also applied to compacts) is partially deconsolidated to yield a cylinder through the centre of the fuelled region (Ref. 4). The second stage is to deconsolidate the previously obtained cylinder, stepwise, as schematically shown in Fig. 1. Each step gives rise to a sample of electrolyte solution, graphite matrix and the associated coated particles (CP). Each individual CP comprises, at this stage, the SiC and IPyC-layers and the kernel.

The method was developed by A.E.R.E.-Harwell and, with some modification, installed in the hot cell laboratory of the Kz-Juelich, Germany. The apparatus (see figure 3) consists of a motor to rotate the sample, which is attached to two holders connected to a direct current source, constituting the anode of the electrolytical system. The spherical fuel element is submerged in a beaker containing the cathode (a Pt-Ir

net, having an approx. 10 mm mesh), immersed in the electrolyte (2n HNO₃). The fuel element rotates at about 1 rpm.

During the procedure, the current is maintained at about 6 A. Through the anodic oxidation, the graphitic matrix is disintegrated during the process and the CPs fall to the lower part of the beaker. This process leaves a cylinder of about 20 mm in diameter in about 10 h. After that, this cylinder is placed vertical (see Fig.4), constituting again the anode, and disintegrated stepwise (2 to 5 mm disintegration steps), leaving typically 1.5 to 3 g of coated particles per step.

As already mentioned, the ultimate goal of this process is to obtain individual CPs, which can be tested to determine the damaged ones. To this goal, in several laboratories a method based on the gamma-spectrometric measurement of individual CPs was developed. The method was called IMGA and allowed the identification of damaged particles.

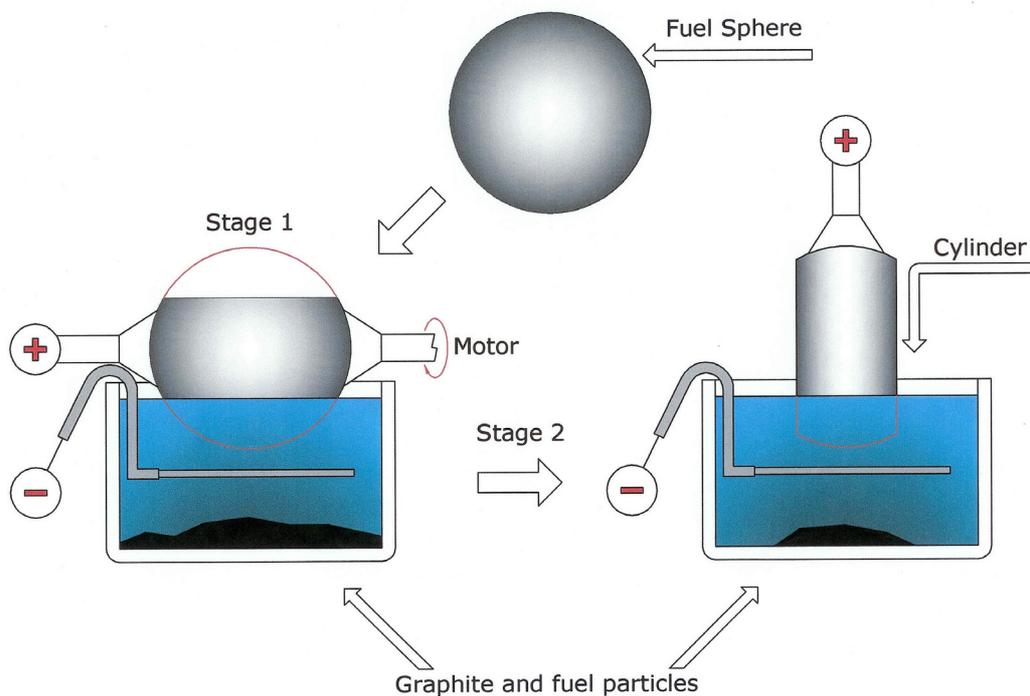


Figure 3. Stepwise deconsolidation of a spherical fuel element

5. ANISOTROPY OF PYC-LAYERS

Pyrocarbon is one of the key materials in the development of the coating of CPs. It has to be deposited (using Chemical Vapour Deposition (CVD)-technology) with two different densities onto two different substrates. The main challenge of this technology is the control of a perfect isotropic deposit, since this is crucial for an optimal sealing together with a perfect matching with the thermo-mechanical behaviour of the SiC-layer.

Carbon has hexagonal crystallography ($a = 2.461 \text{ \AA}$ and $c = 6.708 \text{ \AA}$) and is, hence, intrinsically anisotropic. Nevertheless, since graphitic carbon is not made of crystallites, but has a long range ordering that depends on the so-called graphene planes (graphene planes have the highest atomic density known in nature). The challenge is to develop at long range, a bulk isotropic material, starting from this highly anisotropic crystallographic unit cell. This can be accomplished by CVD in a fluidised bed, which significantly increases the surface/volume ratio, achieving high deposition rates.

Direct measurements of the degree of preferred orientation of the crystallites of pyrocarbon coatings deposited on spherical fuel particles have proved difficult. A first attempt was made by Bokros et al.^[5-10], using a modified X-ray diffraction technique to determine the so-called Bacon Anisotropy Factor (BAF) of strips of pyrocarbon removed from discs coated together with particles in the same fluidising bed. This is an index through which measurement ascertains the degree of anisotropy of a carbon deposit. It is derived from the pole figure method usually apply in XRD-measurements. Values of BAF increase from unity (ideal isotropic material) to higher values as the preferred orientation of the graphene layers increases. Regrettably, this method has proven to be very difficult to apply to coated particles.

For this reason, several laboratories all over the world have developed optical methods using reflected polarised light. As some of other physical properties, light reflection intensity varies with the absorption in the crystal, which is more important for the light rays perpendicular to the basal planes. In fact, when measured at a wave-length of 545 nm, the reflection parallel and perpendicular to the graphene planes are 32 and 9% of the incident intensity. This property is used to evidence the anisotropy of the graphite deposit.

The English Dragon project and CEA-France, developed in the pas the Degree of Anisotropy by Reflectance^[11] (DAR-index) as:

$$\mathbf{DAR = R_{90^\circ} / R_{0^\circ}}$$

where:

$$\mathbf{DAR = (1 + \gamma + BAF) / (2 + \gamma * BAF)}$$

$$\text{and } \gamma = R_{\min} / R_{\max} = 9/32$$

The measurement is obtained by rotation of the analyser (without polarisation), parallel to the deposition plane. The optical window size can be varied but, typically, 25 µm is used.

In USA, GA developed the Optical Anisotropy Factor, or OAF-index^[12]. The photometry is the same except that the polarisation is rotated (without analyser) parallel or perpendicular to the deposit. In this case an oil objective has to be used. Again:

$$\mathbf{OAF = R_{90^\circ} / R_{0^\circ}}$$

With the following relationship between OAF and BAF index:

$$\mathbf{BAF \approx 1 + 0.77 (OAF - 1)}$$

At ORNL^[13] and Jülich (FzJ)^[14], the developed the OPTAF-index, also defined as:

$$\mathbf{OPTAF = R_{\min} / R_{\max}}$$

The optics for OPTAF is more complicated as for previously discussed indexes. A continuous cross-polar measurement is made during the rotation of the sample (under an oil objective), and the result is the maximum and minimum reflectance after disregarding the deposit plane.

Under fast neutron irradiation pyrolytic carbon undergoes densification and the coating shrinks. The shrinking of the pyrocarbon coating onto a stable substrate induces a tangential stress, which can be relaxed by irradiation creep and by re-orientation of the pyrocarbon crystallites. In order to calculate the steady state tangential stress in the pyrocarbon coating, reliable measurements of the overall dimensional changes and the preferred orientation of the crystallite are required. For this reason, comparative measurements before and after irradiation should be performed, using the same technique if possible.

6. ELECTRON-PROBE MICRO-ANALYSIS (EPMA)

One powerful tool to measure the distribution of the fission products in kernel and coating materials is the Electron Microprobe Analysis (EPMA). This technique provides also information on the chemical state of the fission products and their transport behaviour in the different coating layers.

Highly irradiated coated particles (50% FIMA) were analysed by Förthmann et al. (Ref. 15) using a CAMECA MS 46 electron microprobe analyser. As an example, in Fig. 4 some of the results that can be obtained using this technique are presented.

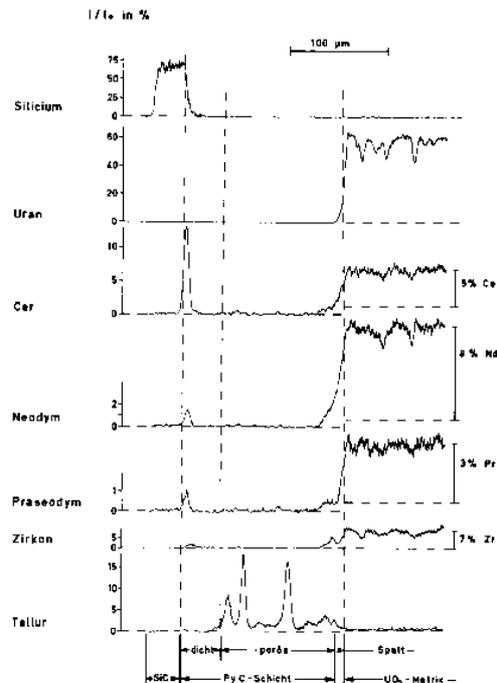


Figure 4. Line scans of some fission products, matrix and layer components of the coated particles with UO_2 -kernels (after Ref. 15)

The release of fission products from the coated particles depends on their chemical state in the kernel material and on the retention properties of the coating. A typical example is the different behaviour of the rare earths in oxide and carbide kernels. They are found in high concentrations in the oxide kernel matrix, forming solid solutions with very low vapour pressures. On the other hand, the rare earth carbides have relatively high dissociation pressures, resulting in a higher release of these fission products from carbide kernels.

The poor rare earth retention of the porous and dense pyrocarbon layers can be seen from the line scans in Fig. 4. Ce and Nd are collected at the boundary of the SiC-layer. On the other hand, Cs does not form stable compounds in either oxide or carbide kernels and, therefore, it shows the highest release from both oxide and carbide kernels but it is retained in the SiC-layer. Similar behaviour has been observed for Sr, Ba and I. Sr and Ba are not retained by the dense pyrocarbon layer but their release is lower than that of Cs because of the lower vapour pressures of SrO and BaO.

7. FISSION GAS RELEASE

As already stated, several mathematical models regard the particle coating as a miniature pressure vessel. For this reason, the knowledge of the actual pressure inside the particle coating is of paramount interest for the prediction of particle failure. In general, the value of the fission gas pressure is calculated from the amount of fission gas released by the kernel and the volume of the internal porosity in both kernel and buffer layer available to accommodate the gases.

The amount of gas can be measured by cracking the coating of an intact irradiated particle and measuring all the Xe, Kr, CO and CO_2 , with a mass spectrometer. On the other hand, the porosity, which has to be

calculated from the densities and dimensions of both kernel and coating are not very easy to measure and, since the dimensional and density changes during the irradiation are not very well known, the pressure inside a particle at a given burnup is substantially uncertain.

In Ref. 16, a direct method for the determination of the gas pressure inside fuel particles has been described. The method is based on the cracking of one particle by submitting it to hydrostatic pressure. Subsequently, the pressure is reduced until gas evolves from the cracks induced in the coating. The pressure at which this occurred can be read by observing when the bubbles begins to exude from the cracks.

The device was designed for pressures up to 10 Mpa (which is beyond the strength of the coatings and was enough to induce cracks on them) and was made of capillary borosilicate glass. The pressure was established by simply measuring the force apply to the liquid (heavy viscous liquid paraffin) in the capillary tube using a balance.

8. STRENGTH OF SiC

A method for measuring the strength of SiC-coatings using biaxial flexural tests of hemispherical samples obtained from coated particles was presented by Evans et al^[17]. The hemispherical samples used for this test were prepared by mounting the fuel particle in resin and, afterwards, polishing it down to its diameter. The UO₂-kernel was then removed and the remaining layers extracted from the resin. Afterwards, the PyC-layers could be removed by burning.

The loading of the hemispherical samples was performed using two different methods: the first loading the hemisphere with a loading sphere onto a support ring, the second, loading the hemispherical shell with a loading cylinder onto a plane base.

The flexural techniques have several advantages. The strengths of the outer and inner surface layers of the shells can be measured independently, tests can be performed at temperatures relevant to the reactor application, and good statistical strength data can be obtained (failure always occur from the inherent flaws and every specimen gives valid strength data.). On the other side, however, the tests do not give strengths that relate directly to the internal pressure conditions that apply during burnup, although the strengths under internal pressure can be evaluated with good accuracy from a statistical analysis.

Alternatively (Ref.18), ring samples were prepared by grinding the coated particles from two opposite sides nearly up to the equator, leaving a disc (typically some tens of microns thick) remains from which the kernel material can be removed mechanically. The method is called Brittle Ring Test and has several advantages according to the authors:

- Is based on a well established technique
- Gives values for the strength and Young's Modulus simultaneously
- Allows a simple analytical description of the deformation of the samples
- Is relatively easy to handle and, therefore, can be applied to a large number of samples
- Weibull statistics can be applied to the interpretation of the results, allowing the estimation of the influence of the geometry and strength distribution of the material

Using this technique also the mechanical properties of PyC-layers can be measured by producing "Biso" particles and then removing the buffer layer by chemical etching. In the case of the "Triso" particles the PyC-layers can be removed either by chemical etching (as reported in the paper) or by the burning as previously stated. Hence, entire or half-rings are tested by loading between two sapphire plates under a microscope. The load, the deflexion (strain) and the load at rupture are recorded.

9. THERMAL EXPANSION COEFFICIENT

One of the most challenging characterisation of coated particles is the measurement of the thermal expansion coefficient. The difficulty resides in the detail that CPs are, in fact, a composite material (PyC/SiC/PyC) in which is not easy to derive the corresponding properties from their constituents. An additional problem is represented by the small dimensions of the CPs with its consequent small coefficient of thermal expansion.

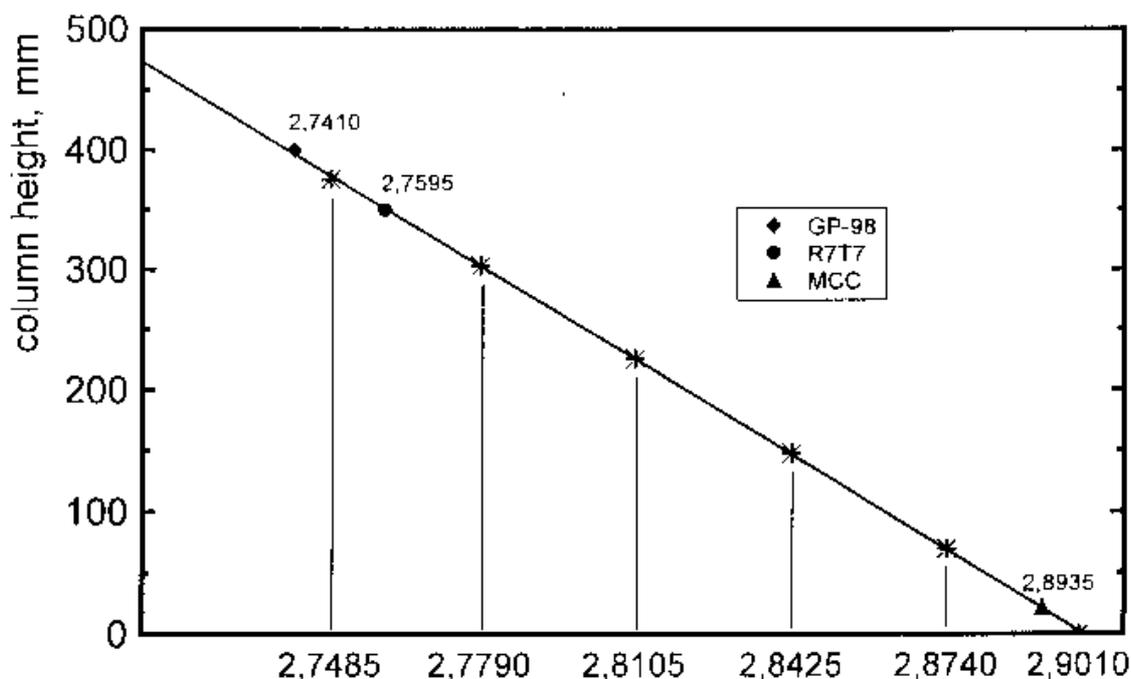


Figure 5. The density [g/cm³] as a function of the column height

Experimental methods and results are described in Ref. 19 to 21. The experimental set-up is based on an interferometer, the so-called experimental Fizeau system, which allows the measurement of small variation in the coefficients of thermal expansion. Using this technique, the thermal expansion coefficient of PyC, SiC and PyC/SiC-coatings were measured.

10. DENSITY MEASUREMENTS

Density measurements can be performed by a variety of methods but, under remote handling conditions, one of the most valuable (see e.g., Ref. 22) because of its rapidity and easy handling, is the sink-float method (Ref. 23). It is based on the principle that a linear density gradient can be established when two liquids, having different density, are properly mixed in a glass column. By introducing carefully calibrated standards, the correspondence between the height of the column (density of the liquid) and the density of the standards can be established. Afterwards, the density of the unknown samples can be easily determined by interpolation, reading the equilibrium position in the column, thus providing a reliable, easy to handle and very accurate method. The organic mixture consists, typically, of a-bromo-naphtalene, density about 1.49 g/cm³, and 1,1,2,2-tetrabromo-ethane, density about 2.97 g/cm³. Consequently, only densities lying between these two values can be measured. The apparatus is very stable and it meets the temperature and dimensional requirements of BS 3715 and ASTM D1505 – 60T.

In Fig. 5 the density as a function of the column height, as determined by using 6 different glass standards (crosses), is shown together with the density of three different types of active ²⁴⁴Cm-doped. It can be seen that a linear gradient could be established. This gradient could be maintained by holding the column at a constant temperature by immersion in a water bath. From such curves the density of the active glasses could easily be determined as a function of the cumulative dose, by just observing the position of active samples in relation to the standards.

11. THERMAL CONDUCTIVITY OF COATING LAYERS

The thermal conductivity of PyC and SiC is approx. 10 and 16 W.m⁻¹.K⁻¹[24]. Considering a coating thickness of about 50 μm, the temperature drop for the lower thermal conductivity will be about 2.2 °C. The conclusion can be drawn that, in principle there is no need for the measurement of the thermal conductivity variation in the PyC and SiC-layers due to irradiation effects. On the other hand, the temperature variation across the buffer layers (estimated thermal conductivity about 1 W.m⁻¹.K⁻¹) can be most important, as well as the changes expected due to the gas release from the kernel (thermal conductivity of Xe ≅ 0.02 W.m⁻¹.K⁻¹).

Table I. PIE-recommendations for Gen IV fuel development for V/HTR

PIE both after irradiation and after KÜFA-tests	Scanning Electron Microscopy
Fuel Element Deconsolidation	Transmission Electron Microscopy
Fission gas and CO/CO ₂ -release	Electron-Probe Micro-Analysis
Anisotropy (comparison before and after irradiation)	Mean strength and Weibull's modulus of SiC
Dimensional changes	Thermal conductivity of the buffer layer
Irradiation induced creep of PyC	Density measurements
Elastic properties	KCMI (Kernel/Coating Mechanical Interaction)
Poisson's ratio (in creep)	Gamma spectrometry
Ceramography	Burnup determination

12. GEN IV-RECOMMENDATIONS

A Gen-IV Fuel and fuel Cycle Project Management Board meeting was held to define PIE-techniques and the fuel properties that should be considered. In Table 1, the PIE-recommendations for Gen IV fuel development for the Very High Temperature Reactor (V/HTR) are gathered.

13. CONCLUSIONS

In the present paper, some of the most important PIE-techniques historically and presently installed in hot cells have been briefly described in connection to modelling needs. One of the most important issues is constituted by the need of having representative samples to measure some of the key properties of coated particles. The broad field of characterisation (PIE) of fuel elements has not been treated. Standard measurements like gamma spectrometry, ceramography, burnup determination, etc., have not been considered in the present paper. From the micro-analytical techniques, only EPMA has been discussed. One useful technique, Secondary Ion Mass Spectrometry (SIMS) has not been mentioned but it is considered to be able to deliver valuable results in the future.

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