Journal of Nuclear Materials 395 (2009) 99–111

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Evaluation of silver transport through SiC during the German HTR fuel program

J.J. van der Merwe *

PBMR, Lake Buena Vista Building, 1267 Gordon Hood Avenue, Centurion 0046, South Africa

ARTICLE INFO

Article history:
Received 10 February 2009
Accepted 29 September 2009

ABSTRACT

For direct cycle gas cooled high-temperature reactor designs operating conditions may be limited as a result of excessive maintenance dose rates caused by the ^{110m}Ag source term on the turbine. The accurate prediction of silver fission and activation products' release during normal operation is required to ensure regulatory compliance and economic viability of planned power plants. Fuel qualification programs should provide satisfactory results to ensure correct analyses, but will not be available for many years. In the meantime data from the German fuel development program are utilized to develop and validate analyses methods. Previously, from primarily material and fuel component test results, transport models and parameters through all the fuel materials and components were derived. Good verification of silver transport in fuel materials and components were achieved with the exception of SiC. An earlier study of all German fuel irradiation tests identified a set of applicable tests to be used to evaluate silver transport through high-quality SiC. Simplified first estimate analyses were performed on different transport models. This was followed by an in depth study with a more complete diffusion model on all applicable irradiation test results to derive new transport parameters for silver in SiC. These new parameters were applied in an evaluation of some heat-up tests of irradiated fuel spheres to assess the range for which they are valid.

1. Introduction

For direct cycle high-temperature reactors utilizing low-enriched uranium fuel, the production, release, transport and subsequent deposition of silver fission and activation products in the main power system may pose maintenance problems due to excessive radiation levels to operating personnel [1]. For higher operating temperature designs, ^{110m}Ag release from fuel and deposition on high-maintenance components may lead to more expensive maintenance concepts or limit planned power and outlet temperature. Accurate analyses of silver release from fuel under all expected normal operating conditions is therefore of paramount importance. Erroneous prediction of the silver source term or unnecessary uncertainties used in analyses could have serious implications for the economic case of a planned power plant. It is therefore critical that the best possible calculation model is derived from the available information.

In deriving a new, or evaluating an existing calculation model, it is important to understand the exact fuel design, fission product production, and transport through fuel materials. This could be done by considering the fuel design, current transport models suggested, and evaluations against all available transport data.

Historically, fission product transport through fuel materials has been considered to obey Fick's laws of diffusion [2]. For silver, the limiting transport process is through the SiC layer as the other fuel materials offer much less retention at expected reactor operating temperatures. Although it was found that SiC does not retain silver completely, it does slow down silver transport substantially [3]. It was never shown that silver migrates through SiC by diffusion, but it was rather assumed that the transport mechanism responsible could be approximated by a diffusion model. Various experimental studies resulted in different diffusion coefficients for silver in SiC (e.g. [1,3,4]). Several diffusion based calculation models and software were developed [5,6].

Due to a perceived independence on temperature, the diffusion model for silver transport through SiC has been questioned [7]. Further work led to a suggestion that silver is not transported through SiC by diffusion but by a vapour transport mechanism [8]. A calculation model and software were then developed to perform silver release analyses from spherical fuel based on vapour transport [9].

Fuel qualification and characterization programmes are underway all over the world in and effort to resolve the issue. In the meantime, accurate and defendable analyses of a typical HTR's core's ^{110m}Ag source term are required. This study does not attempt to find the exact mechanism of silver transport, but to derive and defend a calculation model to predict the ^{110m}Ag source term under operating conditions, irrespective of the actual transport mechanisms.

Transport phenomena involved in the transport of silver through spherical fuel can be divided into two groups: A secondary

---

* Tel.: +27 12 641 1542; fax: +27 12 641 2704.
E-mail address: hanno.vdmerwe@pbmr.co.za

0022-3115/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2009.09.024

effects group that only has a limited consequence on the silver release source term. These include recoil, diffusion transport through UO_2, PyC and matrix material, and sorption on the fuel surface. These phenomena have either negligible effects (recoil and sorption) or are very well understood (diffusion through UO_2, PyC and matrix material) and do not have a controlling function on silver release.

Primary effects group control silver release under most reactor conditions considered. In this case, it is only silver transport through SiC which is also the least understood. In order to derive the best calculation model to predict the ^{110m}Ag source term, secondary transport phenomena must be quantified first through analyses of separate effects tests (material and component tests), before integral effects tests (complete fuel irradiation tests) can be analysed to study the transport of silver through the SiC layer.

Previously, all the fuel material, component and complete fuel irradiation tests have been investigated and considered for silver transport evaluations [10]. From fuel material and component test results, secondary effects phenomena have been verified and all models and parameters were derived which are briefly discussed in this paper. Using these models and parameters, simplified first estimate analyses of complete fuel irradiation tests were performed with both diffusion and vapour transport calculation models in order to establish the viability of these models to predict silver transport and release [11]. Based on these analyses results, a more complete diffusion model was developed and used to evaluate all the applicable German fuel irradiation tests in detail. Results of the first estimate analyses and its simplifying assumptions are briefly described in this paper. The detailed analyses are described here in some detail.

1.1. Fuel design

The primary containment barrier is the Triple Coated Isotropic Particle (TRISO) coated particle, which proved to be effective during various irradiation tests and experiments. Fission products formed in the fuel kernel either form stable oxides with oxygen released during the fission process, or have very long diffusion times through coating layers of the particle. The TRISO coated particles therefore retain fission products very effectively inside the fuel during normal operation. Exceptions are silver and strontium fission and activation products, which do not form stable oxides at operating temperatures and have relatively fast diffusion times through coated particle layers. Fortunately, strontium has a very high sorption isotherm from graphite and is also delayed by the binder used in matrix material manufacture that significantly delays strontium release. Silver, on the other hand, has no such delaying mechanisms and is readily released from spherical fuel spheres at elevated temperatures.

The fuel design is shown in Fig. 1. The design is based on the German fuel sphere design produced for the High-Temperature Reactor 500 (HTR-500) and HTR-Modul Proof Tests. This fuel type is generally regarded as state-of-the-art for German pebble fuel production and has been described in detail in many publications (e.g. [12] or [13]).

1.2. Silver fission and activation products

The main silver fission products are stable ^{109}Ag that activates to ^{110m}Ag (250 days half life), and ^{111}Ag (7.45 days half life). Both are low-yield fission products, with cumulative fission yields from uranium of only 0.028% and 0.017% for ^{109}Ag and ^{111}Ag, respectively. For plutonium this picture changes drastically and fission yields of 1.4% and 0.30% are achieved for the two nuclides respectively. Silver release is therefore a bigger concern for high burn-up fuel where plutonium fission forms a significant fraction of the power produced in the plant. Short-lived ^{111}Ag is only of some importance during accident events whereas ^{110m}Ag is a strong γ-emitting activation product that presents a considerable radiation danger in large quantities if not shielded. The main concern is the production in and release of ^{110m}Ag from spherical fuel elements, in particular during normal operation.

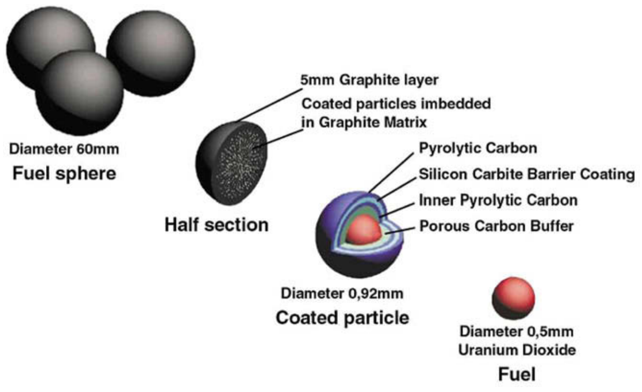

Fig. 1. Spherical fuel element design.

1.3. Silver fission and activation product sources

There are four distinct sources of radioactive silver in fuel spheres:

Firstly, the natural uranium and thorium contamination of the fuel materials that breed fissionable plutonium and ^{233}U that in turn produce fission products. This contamination is primarily in the matrix material of the fuel sphere and release of fission products created by fissions of this contamination only have to diffuse through the matrix material before being released. Only 0.2% of the expected ^{110m}Ag release during normal operation originates from this source.

Secondly, even under the best manufacturing conditions a small fraction of coated fuel particles will be defective. A particle is considered failed or defective if its coating layers are absent or are damaged sufficiently to allow the release of fission gases. Furthermore, under abnormally high-temperatures and power surges, coated fuel particles may start to fail. Under normal operating conditions, the failure fraction is so small that it contributes to only 1.5% of the expected ^{110m}Ag source term.

Thirdly, whether diffusion or alternative transport models are considered, the biggest contributor to silver release from high-quality fuel is intact coated particles. Intact coated particles are defined as particles that have all their coating layers intact, are impervious to fission gas release, and release only a very small fraction of their ^{137}Cs inventory.

A fourth source also exists that is important only for the activation product ^{110m}Ag: The natural contamination of the activation product precursor (^{109}Ag) in the fuel materials. This source is a surprisingly important source of ^{110m}Ag measured during irradiation tests where natural silver contamination of irradiation rig material may be significant. It is however a small source at expected reactor temperatures.

The contribution from intact coated particles under normal operation conditions are more than 98% for ^{110m}Ag. It is therefore clear that only the diffusion coefficients and actual transport mechanisms of silver through the coating layers of an intact TRISO particle, its subsequent transport through the matrix material and desorption into the gas coolant need to be investigated and qualified in detail. The primary metallic fission product barrier layer in a TRISO particle is the SiC layer and should be the focus in modelling silver transport in and release from a fuel element. The secondary transport processes, diffusion through UO_2, PyC and matrix material and sorption on the fuel surface cannot be ignored though, and must be quantified to ensure that evaluations of SiC transport models are free from any unaccounted effects.

1.4. Transport phenomena

Models, equations and parameters of silver transport through fuel materials have been described in literature, [5], or [2], and are only briefly described here. Due to relatively large diffusion coefficients of silver in UO_2, the majority of ^{109}Ag formed during fission in the fuel kernel is released even at modest reactor temperatures. The contributions of recoil and knock-on effects, which are geometrical in nature, are only significant at low temperatures (<700 °C) where silver release is unimportant.

After fission products have recoiled into neighbouring fuel materials, they are transported through the fuel materials to the surface of the fuel sphere. The diffusion calculation model assumes that fission products are primarily transported through fuel materials according to Fick's law of diffusion [14].

$$J_x = -D\frac{dN}{dx}$$

By taking into account fission product production (S) and decay terms (λc) in spherical geometry the diffusion equation becomes:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) - \lambda c + S$$

The diffusion coefficient D is dependent on the temperature according to the Arrhenius equation:

$$D = D_0 e^{\frac{-E_A}{RT}}$$

The alternative vapour transport model suggests that silver leaks through nano-sized cracks in the SiC layer [11]. All models accept diffusion transport through the matrix material. The most important boundary condition used in solving the diffusion equation is transport from the fuel surface to the coolant gas through a mass transfer coefficient that is controlled by a sorption isotherm.

2. Material and component tests evaluations

Material tests are usually separate effect tests that focus on only one or maybe two phenomena at a time. A particular parameter can then be appraised and possibly quantified in order to simplify the assessment of integral effects tests later on. Specific material tests are evaluated first to ensure that all parameters are quantified as well as possible before integral effect evaluations of full sphere irradiation tests are performed.

2.1. Sorption isotherms

Standard procedures such as isopiestic methods did not yield good results and few attempts have been made to determine silver sorption isotherms during the German fuel program. The caesium sorption isotherm, however, has been studied very well and is described in detail in literature [15]. The only published silver sorption investigation did not provide sorption isotherms, but showed desorption spectra of caesium and silver using an identical experimental setup and test conditions [16]. Using these spectra and the sorption subroutine of the fission product software product GETTER [6], sorption isotherms for silver were derived [10]. Silver sorption only plays a role at temperatures below 700 °C. Most modern high-temperature gas cooled reactor designs are planned to operate with reactor outlet temperatures between 750 °C and 950 °C, so that the silver sorption isotherm will not influence the total ^{110m}Ag source term significantly.

2.2. Matrix material transport

Transport of silver through original, oxidized and fast neutron irradiated graphitic matrix material has been investigated in detail by measuring the ^{110m}Ag release kinetics and concentration profiles from cylindrical samples [17]. The release kinetics and concentration profiles both satisfied Fick's law of diffusion and diffusion coefficients for temperatures between 800 °C and 1300 °C were derived. Silver retention in A3-3 matrix material increases with irradiation up to ~7 displacements per atoms (equivalent to a fast neutron flux of approximately 5×10^{25} m^{-2}). Diffusion coefficients show typical Arrhenius behaviour where R is the universal gas constant (8.3145×10^{-3} kJ. mol^{-1} K^{-1}) and T is the absolute temperature.

Original A3-3: $D = 6.80 \times 10^{1} e^{-262/RT}$ m^2 s^{-1}
Irradiated A3-3: $D = 1.60 \times 10^{0} e^{-258/RT}$ m^2 s^{-1}

Pebble fuelled HTRs employ dynamic core loading schemes so that an equilibrium core contains from fresh fuel to highly irradiated spent fuel. For best estimate analyses, the irradiated diffusion constant and activation energy has been used. This can be justified as the ^{110m}Ag inventory is small in the beginning of a sphere's irradiation life and releases are modest due to the fact that the ^{235}U fission yield for ^{109}Ag is very small. Later in a sphere's life when the matrix material is highly irradiated, the ^{110m}Ag inventory grows very quickly as high silver yield ^{239}Pu and ^{241}Pu fission contribution becomes significant. For best estimate analyses this may be fair, but for safety analyses design calculations, a more conservative approach is required.

It may be overly conservative to simply assume the fastest diffusion coefficient for safety analyses. A more fitting approach would be to assume that irradiation effects have a linear effect on the silver retention ability of A3-3 matrix material. It will still be conservative in the sense that the high inventory and highly irradiated end-of-life fuel will have faster silver transport than experimentally measured. However, the fresh fuel release (although several factors less than end-of-life fuel release) will not be underestimated. The recommended best estimate and design silver diffusion coefficients is thus:

Best estimate: $D = 1.60 \times 10^{0}\, e^{-258/RT}$ m^2 s^{-1}
Design limit: $D = 1.10 \times 10^{1}\, e^{-260/RT}$ m^2 s^{-1}

2.3. Coated particle transport

The transport of silver through coating layers of a coated particle has been studied in depth by many researchers [2]. Compared to transport through the SiC layer, transport through the UO_2 kernel and PyC layers are relatively quick. The diffusion coefficients of silver in the UO_2 kernel and PyC layers are 200 and 500 times larger than SiC diffusion coefficient at 1000 °C. Both German and United States fuel development programs suggested the same diffusion coefficients for UO_2 kernel and PyC layers.

Best estimate UO_2: $D = 6.70 \times 10^{-9}\, e^{-165/RT}$ m^2 s^{-1}
Best estimate PyC: $D = 5.30 \times 10^{-9}\, e^{-154/RT}$ m^2 s^{-1}

For safety analyses to determine design limits, an uncertainty for the above diffusion constants of a factor of two was suggested before [18]. This uncertainty, or even more conservative factors, has only a small effect on the overall silver release rate. The most efficient barrier to the release of silver in an HTR fuel element remains the SiC layer and it has been studied in detail (e.g. [1], [2], [3] and [8]). Numerous diffusion constants were derived with scatter up to one order of magnitude of the diffusion coefficient at any temperature. Silver is released from particles that retain caesium, which means from coated particles with intact SiC layers, but ion implantation experiments suggest that silver does not undergo bulk SiC diffusion [1]. This anomaly was resolved by suggesting implanted silver is stopped primarily in the SiC grains, while fission product silver in a fuel element is transported along crystal grain boundaries caused by disorganized material caused by traces of free silicon [3]. Other studies did not agree, as the scatter in the reported data exceeds the expected variations in SiC structure and the silver path length travelled through the SiC coatings [8]. From ion implantation studies and diffusion coupled investigations [19] an alternative transport model that entails transport of silver though cracks in the SiC layer were developed and used to perform a first estimate analyses of some German irradiation data [9].

Before this current study, the most comprehensive study was performed by Amian and Stöver on loose particles that had been previously irradiated in compacts or test spheres. Irradiation temperatures varied from 400 °C to 1050 °C and burn-ups between 2.3% and 12.1% Fissions per Initial Metal Atom (FIMA) with fast fluences between $0.5 \times 10^{25}\ \mathrm{m}^{-2}$ and $8.2 \times 10^{25}\ \mathrm{m}^{-2}$ were achieved. Annealing temperatures between 1000 °C and 1500 °C were used for up to 2340 h. Different particle types had different fuel kernel materials with slight variations in coating dimensions. Diffusion coefficients for silver in silicon carbide was derived for all types of kernels (UO_2, UC_2, ThO_2, mixtures, etc.) and for reference quality fuel (UO_2, $(U, Th)O_2$) and published in [3]:

All fuel types: $D = 4.5 \times 10^{-9}\, e^{-218/RT}\ \mathrm{m}^2\,\mathrm{s}^{-1}$
Reference fuel only: $D = 3.6 \times 10^{-9}\, e^{-215/RT}\ \mathrm{m}^2\,\mathrm{s}^{-1}$

Measurements made on loose particles remain problematic. The silver inventory in a single particle is very small and measurement errors on such small activities continue to be challenging. Furthermore, it must be asked if packing into a sphere and high-temperature heat treatment during final annealing of fuel spheres do not affect coated particle characteristics. Measurements in material samples only also remain problematic. Geometric effects, irradiation fluxes and temperatures cannot be repeated and these effects on silver transport cannot be comprehended.

The exact SiC transport mechanism cannot be derived from the available material test data. Innovative and new material tests must be invented and performed to understand the exact mechanism. Considering tests and experiments already performed, which yielded varying results and contradicting mechanisms, it seems unlikely that clear proof will be available any time soon. The only recourse in the meantime is to evaluate all the available real data, in other words, the actual measured release from complete fuel spheres under conditions that are similar to expected reactor conditions.

3. Applicable irradiation tests

A study of all available irradiation tests has been performed and applicable tests that might be used to derive silver transport models and parameters have been described [10]. Table 1 shows all applicable irradiation tests to be considered. All values in Table 1 are as reported in the literature before any evaluation has been performed. Temperatures and fluencies are often pre-irradiation targets and burn-ups are first-calculated estimates. All tests are listed from most applicable to least applicable. Applicability in this case is defined according to fuel type, irradiation conditions and availability of irradiation data and silver fractional release results.

Ideally, considered irradiation tests must have tested fuel containing low-enriched UO_2 TRISO coated particles, where coating layers are as close as possible to that of the reference fuel design. To ensure that silver release evaluations are governed by SiC retention, coated particle failure and defect fractions must be very low.

Irradiation history refers to the availability of data (such as time-dependent temperatures, release rates of fission gases, neutron fluxes, etc.) describing irradiation conditions which coated particle fuel in the test were exposed to. Ideally the irradiation history must be comparable with expected reactor conditions considered and detailed data sets must be available. Unfortunately much of the German detailed data have been lost or are very difficult to find. In some cases only ‘single values’ could be found, for example, a single maximum fuel temperature rather than all the temperatures measured during irradiation. The most important irradiation history parameter required is the fuel temperature, as evaluations matching fractional releases do not require accurate estimates of the inventory.

Fractional silver release data is required to perform evaluations. In some cases, silver released from a sphere is given as an absolute amount, and it is necessary to calculate the total silver inventory from burn-up. The availability of fractional release rates for other radionuclides is very valuable in evaluating silver fractional release data. Release over birth ratio (R/B) for krypton fission gases are valuable indicators of coated particle performance and caesium fractional release rates indicate the quality of SiC layers.

In Table 1 considered irradiation tests are divided into three groups: Highly applicable irradiation tests have sufficient information available and a good degree of certainty is ensured by many literature sources. Transport parameters derived from these evaluations must be considered the most valuable and weigh the most in terms of importance. Medium applicable irradiation tests may require some more data or assumptions have to be made. Derived transport parameters must be considered less important than the high applicable results. Low applicable irradiation tests require significant assumptions that would reduce the value of derived transport parameters and therefore should have the lowest weight when final transport parameters are considered. Many other irradiation tests have been considered as well but rejected as significant data is missing, could not be sourced, and in some cases, $^{110\mathrm{m}}$Ag was not even measured.

4. Fuel irradiation tests: first estimate evaluations

The first estimate evaluations were performed only to decide which models could reproduce the experimental results and to decide which model to develop further. Both first estimate evaluations performed used readably available data as is listed in Table 1. Several assumptions were made to simplify the analyses.

It was assumed that all irradiations conditions were constant through out all irradiation cycles and that the easily available data were correct. The majority of released silver is released as fission product ^{109}Ag before being activated to $^{110\mathrm{m}}$Ag. Released ^{109}Ag is deposited on cups and capsules that house the test spheres. Contrary to what happens in a reactor, released ^{109}Ag is not removed from the neutron flux field and deposited in the cooler areas of the main power system, but remain in the neutron flux field. ^{109}Ag continues to be activated in the cups and capsules at a similar rate to what ^{109}Ag is activated in the fuel elements.

Fractional release is experimentally determined by comparing the $^{110\mathrm{m}}$Ag activity on the cups and capsules that house the test

Table 1
Considered irradiation tests.

Experiment	Irradiation time (EFPD)	Maximum fuel temperature (°C)	Burn-up% FIMA	Fractional silver release	Fuel type
High applicability					
HFR-K3/1	359	1200	7.5	2.2×10^{-3}	UO_2 fuel reload 19
HFR-K3/2	359	920	10	4.5×10^{-4}	UO_2 fuel reload 19
HFR-K3/3	359	920	10.6	3.8×10^{-4}	UO_2 fuel reload 19
HFR-K3/4	359	1220	9	1.8×10^{-2}	UO_2 fuel reload 19
FRJ2-K13/1	396	1125	7.5	1.9×10^{-2}	UO_2 fuel reload 19
FRJ2-K13/2	396	1150	8	2.0×10^{-2}	UO_2 fuel reload 19
FRJ2-K13/3	396	1150	7.9	1.7×10^{-2}	UO_2 fuel reload 19
FRJ2-K13/4	396	1120	7.6	3.9×10^{-2}	UO_2 fuel reload 19
FRJ2-K15/1	533	970	14.1	7.5×10^{-4}	UO_2 fuel reload 21
FRJ2-K15/2	533	1150	15.3	3.2×10^{-3}	UO_2 fuel reload 21
Medium applicability					
R2-K13/1	517	1170	10.2	3.9×10^{-2}	UO_2/Th fuel
R2-K13/4	517	980	9.8	2.7×10^{-3}	UO_2/Th fuel
R2-K12/1	308	1100	11.1	3.3×10^{-2}	UO_2/Th fuel
R2-K12/2	308	1280	12.4	1.4×10^{-2}	UO_2/Th fuel
FRJ2-K11/3	260	1150	11.5	4.0×10^{-2}	UO_2/Th fuel
FRJ2-K11/4	260	1152	8.5	5.4×10^{-2}	UO_2/Th fuel
Low applicability					
R2-K12/3	308	1200	10.3	2.4×10^{-2}	UC_2/Th fuel
R2-K12/4	308	1050	11.8	6.3×10^{-3}	UC_2/Th fuel
FRJ2-K10/3	291	1250	73	5.6×10^{-2}	UC_2 fuel
FRJ2-K10/4	291	1240	70	2.5×10^{-2}	UC_2 fuel
FRJ2-P27/1	232	1080	7.6	1.8×10^{-2}	Compact U fuel
FRJ2-P27/2	232	1320	8	8.2×10^{-3}	Compact U fuel
FRJ2-P27/3	232	1130	7.6	2.0×10^{-2}	Compact U fuel
FRJ2-P23/1	177	1250	12.5	1.4×10^{-1}	Compact Th fuel
FRJ2-P23/2	177	1210	12.5	1.4×10^{-1}	Compact Th fuel
FRJ2-P23/3	177	1472	11.9	4.0×10^{-1}	Compact Th fuel
FRJ2-P23/4	177	1310	12.1	4.6×10^{-2}	Compact Th fuel
BR2-P21/1	380	1350	9	1.1×10^{-1}	Compact U fuel
BR2-P21/2a	380	1550	10	2.2×10^{-1}	Compact Th fuel
BR2-P21/2b	380	1550	9	6.0×10^{-2}	Compact Th fuel
BR2-P22/2	257	1350	6	5.0×10^{-3}	Compact Th fuel

spheres and the total ^{110m}Ag produced during irradiation. The ratios of ^{109}Ag released to ^{109}Ag produced (the ^{109}Ag fractional release) and ^{110m}Ag released to ^{110m}Ag produced (the ^{110m}Ag fractional release) is therefore the same as long as the released silver nuclides remain in the same irradiation field as the fuel. The differences between ^{109}Ag and ^{110m}Ag absorption cross sections and neutron flux spectra in the fuel and cups cause differences between production of ^{110m}Ag from ^{109}Ag of less than 10%. This is less than the expected measurement uncertainty of ^{110m}Ag on cups and capsules or the calculated ^{110m}Ag inventory in the test spheres ($\sim$10%), cross section uncertainties ($\sim$20%) and flux uncertainties (10%). Therefore this assumption is adequate as a first estimate. It was conservatively assumed that fuel spheres were irradiated at a constant centre temperature and fission power and coolant temperatures were adjusted accordingly.

4.1. Molecular vapour transport release model

For the MVR calculation model two statistical quantities, nano-tube failure fraction (NTF) and total nano-tube cross-sectional surface, must be derived [9]. For example, an NTF of 10% would mean that 10% of 14,400 particles in a sphere would release silver through nano-tubes and the other 90% would fully contain all silver inside the particle. NTF is a statistical quantity since it could vary from sphere to sphere depending on the reasons for the existence of nano-tubes. NTF can be determined from observed Ag release fractions from available test data if the nano-tube cross-sectional surface is known or fixed. Since NTF has never been observed in coated fuel particles, the cross-sectional surface area is unknown. For each particle, a fixed, accumulated total nano-tube diameter of 2.5×10^{-7} m was used. All values listed here are arbitrary; they were selected based on the fact that these values could reproduce the limited available data reasonably well in a first evaluation. In total 12 irradiation tests have been analysed. From this an average NTF value of 7.51% was derived and compared with a simplified diffusion model for experimental data considered as shown in Fig. 2 [11].

4.2. Diffusion model

The first estimate diffusion evaluation 31 selected irradiation tests (from Table 1) are plotted against maximum centre temperatures achieved during irradiation in Fig. 3 [11]. All data points be-

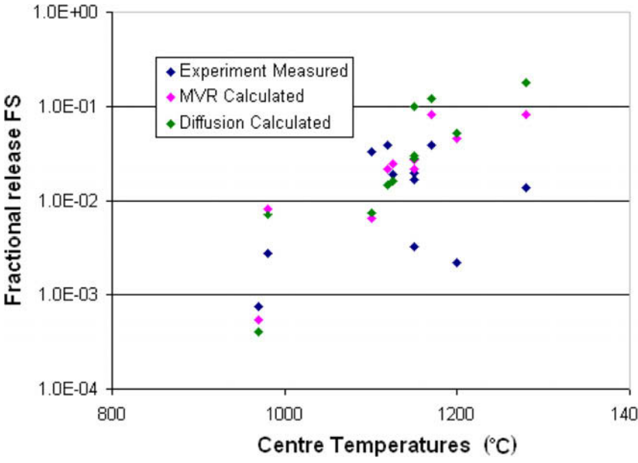

Fig. 2. Fractional ^{110m}Ag release: experiment vs. MVR vs. diffusion.

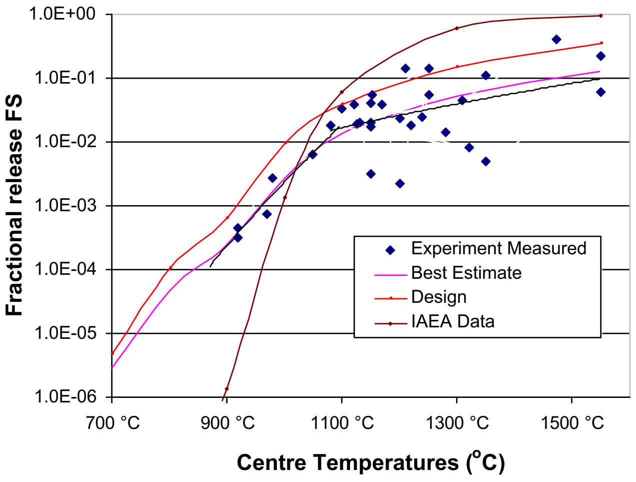

Fig. 3. Fitted IAEA and first estimate best and design limit curves.

low 1100 °C were fitted by one line and all data points 1100 °C and higher by a second fitting line. These fitting lines represent the average of the data for the two temperature regimes and provide guidelines as to where a diffusion curve should go through the plotted experimental data. All data points are plotted and are considered equally important for this first estimate. A diffusion curve is drawn by using the existing accepted SiC diffusion constant [2] and the current diffusion calculation model used at PBMR. The SiC diffusion coefficient was adjusted so that a diffusion curve based on the new diffusion calculation model would follow the two fitted lines as closely as possible. A new design limit diffusion curve was drawn by setting the SiC diffusion coefficient so that 95% of the experimental data lies below the diffusion curve.

The design limit also includes the upper limit uranium and thorium fuel contamination, and design diffusion coefficients for PyC and matrix material transport. Both the best estimate and design limit curve show an inflection at approximately 900 °C. This is the point where the natural uranium, thorium and silver contamination contributions to the silver source term becomes significant.

Fig. 3 shows that a carefully selected set of diffusion constants can in principle simulate the irradiation tests results very well. Diffusion theory remains a viable option to model silver transport and further detailed analyses of all applicable irradiation tests are required. Since nano-tube failures were never observed experimentally and verification and validation of the molecular vapour transport release model is very limited, it was decided to perform the in depth analyses with an updated diffusion calculation model.

5. Fuel irradiation tests: detailed evaluation

An abbreviated account of the detailed analyses of all high and medium applicable tests (Table 1) is described here due to space limitations of journal publications. Detailed information of each irradiation test evaluation can be found in the reference [10]. The detailed evaluation starts with fuel spheres from the top of the table, performing analyses of the most important tests first. Evaluations of the irradiation tests were very similar and only the first evaluation will be described in some detail.

5.1. HFR-K3

Irradiation test HFR-K3 was a two times accelerated irradiation test of four low-enriched uranium fuel spheres irradiated in a BEST-rig in the high flux reactor (HFR) at Petten, the Netherlands. Important test element data of HFR-K3 is listed in Table 2 with expected PBMR fuel specification and irradiation data. A first evaluation of HFR-K3 fission product release was performed shortly after completion of the first post-irradiation examination [20]. After this evaluation more information about the irradiation test was released and further examinations of the fuel and rig materials changed original fluxes, estimated burn-ups, and temperatures achieved. Further evaluations were performed on this test, most notably [21].

5.1.1. Input data

Analyses of thermocouple data and results reported by the RUBICON data handling computer code used at HFR provided all fuel surface temperatures used in this evaluation. Neutron fluxes were taken from the metrology report [22] and the first HFR-K3 evaluation [20]. The cross sections used in the burn-up calculation were based on cross sections used in previous HFR evaluations [23] and updated to yield correct fission power and burn-up values. Gamma heating was deduced from data from the HFR-K6 irradiation test from two different locations in the HFR core.

5.1.2. Results

Fission powers produced during irradiation and total burn-up achieved were calculated first to ensure that calculated temperatures are as close as possible to actual values. The fission powers were calculated using the best available thermal neutron fluxes and cross sections that have been corrected to yield the correct burn-up. These newly calculated fission powers where then used with estimated gamma heating to determine fuel temperatures. He/Ne coolant gas temperatures were adjusted to ensure that calculated and measured surface temperatures agree. Centre fuel temperatures were then calculated from surface temperatures and total power produced (fission and gamma) in each test sphere.

Fractional releases are simply the total measured released ^{110m}Ag activity divided by the total ^{110m}Ag inventory in the fuel sphere. For test sphere 3, no measured value is reported for the graphite cup. It is not possible that there is no silver in the graphite cup. Some silver must be measurable just from contamination sources alone. The absence of a value means that the measurement failed and not that no silver was measurable. Comparing fractional

Table 2
HFR-K3 Test element specification and irradiation data.

Parameter	Unit	1	2	3	4	PBMR
Specification						
Uranium content	g	10.22	10.22	10.22	10.22	9.00
^{235}U enrichment	%	9.82	9.82	9.82	9.82	9.6
CP content		16,350	16,350	16,350	16,350	~14,500
Failed CP content	per FE	0	0	0	0	–
Irradiation data						
Burn-up (FIMA)	%	7.53	10.02	10.57	8.97	9.8
Neutron fluence (>0.1 MeV)	10^{25} m^{-2}	4.1	6.1	6.3	4.3	2.7
Average centre temperature	°C	1247	1121	1115	1278	1040
Max power output	kW/FE	2.72	3.41	3.61	3.42	2.1

releases from sphere 2 and other test spheres, it can be conservatively estimated that the fractional release on the graphite cup should be between 1.6 and 2.2 × 10^{-4}. For the sake of conservatism the higher value is included in the total fractional release.

Measured values were obtained by dissolving the graphite cups that housed the fuel spheres during irradiation and by leaching the surfaces of the stainless steel containers and measuring the ^{110m}Ag concentration in the liquids. Thus there are some additional sources of ^{110m}Ag in fuel spheres and graphite cups that should be considered; firstly the natural uranium and thorium contamination of the graphite cups. The total mass of the graphite cups that house each sphere (∼190 g) is approximately the same as the mass of graphite in a test sphere (∼200 g). It can be conservatively assumed that uranium and thorium contamination in the graphite cups is at least as much as contamination in the fuel sphere. This graphite contamination was reduced to an effective uranium contamination only and added to the fuel-free zone contamination.

In addition to natural uranium and thorium contamination in the cups, the graphite of which the cups and fuel spheres are manufactured also contains silver as an impurity. The original evaluation gives a value of 0.8 ± 0.5 ng/g silver graphite [20]. Thus a fuel sphere of mass 209 g of which 200 g is graphite, will contain 1.6 × 10^{-7} grams of silver. The number of silver atoms in the fuel sphere will be 8.8 × 10^{14} atoms. Only 48% of these will be ^{109}Ag so that the number of ^{109}Ag atoms is 4.2 × 10^{14} atoms. For a 60 mm diameter sphere, the volume concentration of ^{109}Ag will be between 3.7 and 6.0 × 10^{12} ^{109}Ag atoms per cm^3. In other references the natural silver contamination in A3-27 is estimated at 2.7 ng/g, which translates to about 1.3 × 10^{13} ^{109}Ag atoms per cm^3 [24].

The graphite cups and steel capsules also contain silver as a contaminant. At Studsvik during the R2-K12 irradiation tests, the reserve graphite cups used in that irradiation rig were measured prior to irradiation. Silver contamination was found to be as high as 180 ng/g, and for low temperature irradiation tests, these contaminations dominate the measured silver outside the test sphere. Therefore, total silver contaminations between 8 × 10^{12} and 2.6 × 10^{13} ^{109}Ag atoms per cm^3 for each test capsule must be considered.

Using two input data sets based on two of the previous evaluations recommendations, diffusion coefficients were derived for all four test spheres in Table 3. The temperatures and diffusion coefficients listed are the average centre fuel temperatures for each test sphere and diffusion coefficients at those specific temperatures. For the hotter test spheres there is very little difference between diffusion coefficients derived from the two data sets. For the two cooler test spheres, contamination of irradiation rig materials dominate measured release fractions and derived diffusion coefficients are much more dependent on the data set used. A range of contamination values was considered in order to derive realistic diffusion coefficients. For the purpose of final evaluation of all derived diffusion coefficients, the Venter data coefficients may be seen as the lower limit and the Christ data coefficients as the upper limit of the range of coefficients for this test.

5.2. FRJ2-K13

Four AVR reload 19 fuel spheres with LEU-TRISO fuel in a two-capsule irradiation rig were inserted into the reflector outside the core of the FRJ2-DIDO reactor in Jülich, Germany. The evaluation was done very similar to the HFR-K3 evaluation and similar assumptions were made and similar effects were taken into account. Measured irradiation temperatures were derived from published graphs and good estimates of the neutron fluxes were made from reported values [25]. Cross sections were selected to achieve correct burn-ups and plutonium contributions supplied in the literature [24].

The fraction of silver on the steel capsules for test spheres 1–3 has a constant value of 1.3 × 10^{-2} although fractions on the graphite cups vary between 3.7 × 10^{-3} and 7.5 × 10^{-3}, which suggests

Table 3
Summary of derived diffusion coefficients.

Fuel sphere	Best estimate		Upper limit	
	Temperature	Coefficient (m^2 s^{-1})	Temperature	Coefficient (m^2 s^{-1})
HFR-K3 – Christ data				
1	1247 °C	7.63 × 10^{-18}	1247 °C	1.53 × 10^{-17}
2	–	–	1099 °C	1.37 × 10^{-17}
3	–	–	1099 °C	1.50 × 10^{-17}
4	1278 °C	2.55 × 10^{-17}	1285 °C	5.10 × 10^{-17}
HFR-K3 – Venter data				
1	1231 °C	7.75 × 10^{-18}	1231 °C	1.55 × 10^{-17}
2	1121 °C	6.58 × 10^{-18}	–	–
3	1115 °C	5.96 × 10^{-18}	–	–
4	1285 °C	2.63 × 10^{-17}	1285 °C	5.26 × 10^{-17}
FRJ2-K13				
1	1131 °C	1.67 × 10^{-17}	1131 °C	2.56 × 10^{-17}
2	1149 °C	1.71 × 10^{-17}	1149 °C	2.57 × 10^{-17}
3	1148 °C	1.43 × 10^{-17}	1148 °C	2.37 × 10^{-17}
4	1127 °C	1.79 × 10^{-17}	1127 °C	2.64 × 10^{-17}
FRJ2-K15				
1	920 °C	1.50 × 10^{-18}	920 °C	3.21 × 10^{-18}
2	1095 °C	7.82 × 10^{-18}	1095 °C	1.15 × 10^{-17}
R2-K12				
1	1123 °C	7.39 × 10^{-18}	1123 °C	1.48 × 10^{-17}
2	1289 °C	1.68 × 10^{-17}	1289 °C	3.36 × 10^{-17}
R2-K13				
1	1211 °C	1.64 × 10^{-17}	1211 °C	4.30 × 10^{-17}
4	1020 °C	3.33 × 10^{-18}	1020 °C	6.66 × 10^{-18}
FRJ2-K11				
1	1168 °C	4.93 × 10^{-17}	1168 °C	9.82 × 10^{-17}
2	1164 °C	4.99 × 10^{-17}	1164 °C	9.98 × 10^{-17}

that the silver fraction from the steel capsules is dominated by some other source than the fuel sphere. This is out of line with measurements made after the HFR-K3, R2-K12 and R2-K13 irradiation tests where capsule steel fractions were always less than graphite cup fractions.

The fraction of silver on the steel cups for test sphere 4 is 3.1×10^{-2} which is much higher than for the other spheres although the factions on the graphite cups remain comparable. The sphere 4 measurement must be questioned and most probably is a transcription error where the 1 and the 3 have been swapped. If this is the case, the silver fraction for all capsules is exactly the same and may be from silver contamination of the steel. Considering a reasonable silver contamination of 10 ppm of the capsule steel could explain the measured silver fraction on the steel capsule.

Natural uranium and thorium contamination of the graphite cups that housed the test spheres were treated in the same way as for the HFR-K3 evaluation. Similarly, it was assumed that comparable silver contamination of the graphite cups existed. Much uncertainty remains about silver contamination of the steel capsules. For best estimate analyses it was assumed that the silver fraction measured from the steel capsules was predominantly from natural silver contamination of rig materials and a fraction of 1×10^{-2} was deducted from the measured fraction of this source. This leaves a fraction of 3×10^{-3} from test sphere release which is significantly more than what was measured in HFR-K3 and R2-K12, and very similar to what was measured during R2-K13. By ignoring any silver contamination in the steel capsules and assuming that all measured silver originated from the test spheres, an upper limit diffusion coefficient can be derived. The lower diffusion coefficient set will be used in deriving the final best estimate coefficients, and the upper limit results to derive final coefficients that may be used for safety and design analyses.

5.3. FRJ2-K15

Three AVR reload 21-1 fuel spheres with LEU-TRISO fuel in a two-capsule irradiation rig were inserted into the reflector outside the core of the FRJ2-DIDO reactor in Jülich, Germany. Silver fractional releases were only successfully measured for test spheres 1 and 2. Neutronic and thermohydraulic data were extracted from the original irradiation progress reports. Fractional releases of silver from the test spheres during irradiation were taken from literature [26]. AVR reload 21 fuel represents the best-quality German fuel manufactured and considerably lower heavy metal contaminations in the matrix materials were achieved than for previous batches. Natural uranium and thorium contamination of graphite cups that housed the test spheres were treated in the same way as for HFR-K3 and FRJ2-K13 evaluations. Similarly, it was assumed that comparable silver contamination of the graphite cups existed. No measurement data for fractional silver release on steel capsules are available in the literature but only fractional release activities of the graphite cups on spheres 1 and 2. Considering the activity ratios of FRJ2-K13, it was conservatively assumed to use a capsule activity equal to the cup activity for best estimate analyses, and two to three times the cup activity for design limit values. Correspondingly, the natural silver contaminations in the steel capsules were also adjusted. The lower diffusion coefficient set will be used in deriving the final best estimate coefficients, and the upper limit results to derive final coefficients that may be used for safety and design analyses.

5.4. R2-K12

In this experiment, four fuel elements were irradiated in a four-capsule rig in the R2 reactor core at Studsvik, Sweden. Two elements contained mixed oxide $(Th,U)O_2$ TRISO particles and the other two elements contained a two-particle system. The two-particle fuel was an investigation into the viability of combining fissile UC_2 and fertile ThO_2 TRISO particles. The two-particle system was abandoned and only the one-particle test spheres are considered here. The test spheres contained 10,960 TRISO particles imbedded in A3-27 matrix material. The total heavy metal load of 6.08 g per sphere consisted of 1.12 g uranium enriched to 89.6% and 4.96 g thorium. Effective uranium contaminations used in evaluations were 2.2×10^{-5} and 1.0×10^{-6} in fuel and fuel-free zones, respectively [27]. Measured surface temperatures and thermal neutron fluxes were extracted directly from the literature [28]. The evaluation was performed along the same lines as the HFR and FRJ2 evaluations.

At Studsvik during the R2-K12 irradiation tests, reserve graphite cups used in that irradiation rig were measured prior to irradiation. Silver contamination was found to be as high as 180 ng/g or around 8.3×10^{14} ^{109}Ag atoms per cm^3 [24]. It is not known if the reserve graphite cups are really representative of the irradiated graphite cups. For example, the irradiated graphite cups may have undergone high-temperature annealing prior to insertion in the irradiation rig that may have reduced the natural silver contamination. By reducing this contamination by a factor of 10 and taking into account the relative weight of the graphite cups, a maximum ^{109}Ag contamination in graphite materials of 7.8×10^{13} atoms/cm^3 was used. The case where natural silver contamination might have been reduced to levels estimated for other irradiation rig graphite cups (1.3×10^{13} ^{109}Ag atoms/cm^3) have been investigated as well. After considering recommendations from previous evaluations and all calculated results, diffusion coefficients were derived for both test spheres.

5.5. R2-K13

This experiment was a combined test with high-enriched $(Th,U)O_2$ spherical fuel and low-enriched UCO/ThO_2 block fuel segments from a block fuel assembly. The two fuel spheres were inserted into capsules 1 and 4 of a four-capsule fuel rig. The test spheres contained 19,780 EUO 1674 TRISO particles imbedded in A3-27 matrix material. The total heavy metal loading of 11.3 g per sphere consisted of 1.14 g uranium enriched to 89.0% and 10.1 g thorium. The evaluation was performed analogously to the R2-K12 evaluation. Measured surface temperatures and neutron fluence values were taken directly from the annual KFA project reports. Diffusion coefficients were derived for both test spheres using the same reasoning as for the R2-K12 evaluation.

5.6. FRJ2-K11

Two spheres from AVR reload 13 and two spheres from AVR reload 15 with HEU-TRISO fuel were inserted into the reflector outside the core in a two-capsule irradiation rig. Irradiation test conditions were extracted from annual KFA project reports and the irradiation report [29]. Post-irradiation examinations were performed on all test spheres but fractional fission product releases were successfully measured for spheres 3 and 4 only. In this test it was attempted to keep surface fuel temperatures constant in the region of 1000 °C. Therefore coolant gas temperatures were adjusted to ensure that calculated and experiment-estimated surface temperatures agreed. Natural uranium and thorium contamination in the matrix material of the test spheres were in the order of 1×10^{-4} [30]. Post-irradiation-examinations were performed at Harwell in the UK [31]. Fractional releases of silver from test spheres during irradiation were 4×10^{-2} for both spheres. This evaluation was performed analogously to the other FRJ2 evaluations. The lower diffusion coefficient set was calculated using best estimate input data and will be used in deriving final best estimate coefficients. Upper limit results are simply a factor of two higher and may be used for safety and design analyses.

5.7. Detailed evaluation discussion

All six applicable irradiation tests have been evaluated with the best available information and assumptions based on the best available engineering judgement. The level of information available for each irradiation test varies greatly from almost complete neutronic and thermohydraulic histories available for HFR-K3 to only brief summaries for FRJ2-K11. Furthermore it is unknown whether the quality of the SiC layers changed significantly from the early tests to the latest. Comparing derived diffusion coefficients in Table 3, there are significant differences between diffusion coefficients derived for the earliest (FRJ2-K11) test and the latest (FRJ2-K15) tests. Similarly, there appears to be an influence from the irradiation facility used. The FRJ2 tests appear to have higher diffusion coefficients compared to the HFR and R2 tests.

What is important for all irradiation tests, irrespective of facility or fuel tested is the effect of natural uranium, thorium and silver contamination occurring in the fuel and irradiation rig materials. Especially for lower irradiation temperatures (<1100 °C), naturally occurring silver in graphite cups dominate measured fractional release. Natural silver contamination was only measured on R2 graphite cups and estimated for A2-27 matrix material used in fuel sphere manufacture. Silver contamination in irradiation capsule steels is unknown; however, measurements made during FRJ2-K13 appear significant. Another complicating effect that contributes to uncertainty in results is the efficiency of wet chemistry techniques used to leach and remove released silver from irradiation rig materials and the accuracy of gamma spectrometry used to measure ^{110m}Ag activities in the leach solutions.

Considering the above, it must be asked whether all irradiation tests should be weighed equally in determining a final diffusion coefficient for silver in SiC. Confidence in diffusion coefficients derived from the HFR-K3 irradiation test is higher than in any of the other evaluations and is significantly higher than for FRJ2-K11. If weighing of results is to be considered, the first question to be answered is, what weight to apply to which evaluation? This is highly subjective and since the 'better' evaluations generally produced lower diffusion coefficients, it can be viewed as an attempt to lower diffusion coefficients in order to simplify reactor analyses. It was therefore decided to rather consider all irradiation tests evaluated as equal and err on the conservative side. The only exception is where both evaluations performed for HFR-K3 using Christ and Venter data respectively will be used. In effect HFR-K3 irradiation test evaluation for spheres 1 and 4 will therefore be weighted by a factor of two. For the two colder spheres, 1 and 2, the Venter and Christ data represent the lower and upper limits and are used to evaluate best estimate and design limits.

All derived diffusion coefficients were plotted against average centre fuel temperatures in Fig. 4. The following best estimate and design limit diffusion coefficients were derived by fitting all results to a straight line:

$$\text{Best estimate:}\quad D = 1.14 \times 10^{-13}\,\mathrm{e}^{-109/RT}\,\mathrm{m}^2\,\mathrm{s}^{-1}$$
$$\text{Design limit:}\quad D = 2.28 \times 10^{-13}\,\mathrm{e}^{-109/RT}\,\mathrm{m}^2\,\mathrm{s}^{-1}$$

The recommended IAEA diffusion coefficient is also plotted against temperature in Fig. 4. All derived diffusion coefficients for all test spheres evaluated are below the recommended IAEA diffusion coefficient line except for the lowest temperature sphere (FRJ2-K15/1). Almost all design limit diffusion coefficients are also below the IAEA line with FRJ2-K11 and FRJ2-K15/1 being the exceptions. It appears that the currently recommended diffusion coefficient is overly conservative. Considering that the current SiC coefficient was derived from particle heat-up tests after being irradiated in compacts, it might also be possible that the silver retention ability of a TRISO particle somehow improves during the sphere-making process.

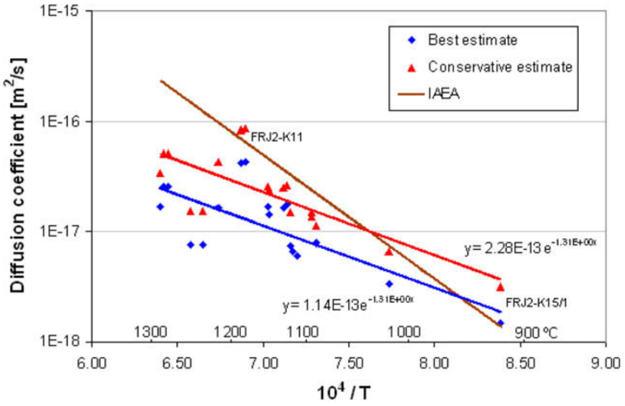

Fig. 4. Diffusion coefficients from the detailed evaluation.

6. Evaluation of post-irradiation heat-up tests

The highest average central fuel temperature evaluated during the detailed irradiation test evaluation was 1289 °C. During postulated accident events, fuel temperatures are expected to rise to 1600 °C for design base accidents and up to 1800 °C for beyond design base accidents. The ^{110m}Ag source term during accident events is only of secondary importance due to the relative small inventory in the core, but the release of ^{111}Ag may be significant. It is therefore important to understand the range of applicability of diffusion coefficients derived to ensure that release behaviour during temperature transients do not differ to such an extent as to warrant different diffusion coefficients. Behaviour of fuel spheres under high-temperature transients, as expected during loss of forced coolant events, is best studied through heat-up tests of irradiated fuel spheres in the famous KÜFA-instrument. First investigations into the behaviour of fuel spheres and coated particle compacts during post-irradiation heating have been performed [32].

Only heat-up tests of complete spheres of sufficient quality and applicable fuel design are considered for this evaluation. During the German fuel development program, a total of twenty-nine high-quality fuel spheres underwent post-irradiation heat-up investigations. They were two spheres from each of HFR-K3 (1 and 3) and FRJ2-K13 (2 and 4), respectively, and 25 spheres taken from the AVR. Not all heating tests have detailed data available, and only a selection of these tests is evaluated below. Previously, fuel performance and ^{137}Cs release behaviour of HFR-K3/1 and /3, FRJ2-K13/2 and /4, as well as AVR 76/18 were evaluated [33]. Fuel failure and caesium release were modelled according to the Martin–Goodin–Nabielek model. It was recommended at the time that the study be expanded to include ^{110m}Ag and ^{85} Kr but this was never done.

Further work on coated particles at temperatures up to 2500 °C showed that at temperatures above 1900 °C, thermal decomposition occurs very rapidly and all fission products including gases are released [34]. For lower temperatures up to 1700 °C, the SiC decomposition rates were negligible and coated particles preserve their ability to retain fission products. At temperatures above 1700 °C, SiC becomes highly permeable to caesium, strontium and silver although gaseous fission products are still retained by the outer PyC layer. Further IMGA studies performed on coated particles from deconsolidated fuel spheres showed that at temperatures of 1800 °C, very large fractions of caesium and other metallic fission products are released without necessarily observing fission gases release [35].

6.1. HFR-K3

Two of the test spheres, 1 and 3 were selected for post-irradiation heat-up testing. The first sphere in the HFR-K3 experiment underwent post-irradiation heat-up testing at 1600 °C for 500 h. The ^{110m}Ag fractional release during the experiment is shown in Fig. 5. The measured release curve appears very flat, as if a non-diffusion process has occurred. It was exactly this type of behaviour that gave rise to the MVR theory [9]. The IAEA current diffusion coefficient over-estimates the release significantly, while the newly-derived diffusion coefficient is much closer. The strange non-diffusion curve is not replicated by either calculated curve, but at least the new diffusion coefficient describes measured release behaviour much better than previous diffusion parameters.

The third test sphere of the HFR-K3 test underwent post-irradiation heat-up testing at 1800 °C for 100 h. After heat-up testing the test sphere was deconsolidated and caesium inventories of coated particles were measured with IMGA [35]. It was found that about 50% of coated particles analysed showed release of about 80% of ^{137}Cs inventory while the rest showed release of about 40% of ^{137}Cs inventory. Even though fission gas release suggests a modest fuel failure fraction, the majority of 'unfailed' particles released their metallic fission products. By using a 'silver retention failure rate' of 50% at the end of irradiation, the release curves of Fig. 6 can be drawn.

6.2. FRJ2-K13

Sphere FRJ2-K13/2 was heated for 138 h at 1600 °C. ^{85}Kr release measured during heat-up, suggests no coated particles failures. Measured and calculated ^{110m}Ag fractional releases are plotted in Fig. 7. Fractional release was calculated with both the existing IAEA diffusion coefficient and the newly-derived diffusion coefficient. Similar to the HFR-K3/1 1600 °C heat-up test, the IAEA diffusion coefficient produces a very high fractional release. The new diffusion coefficient also over-predicts fractional release, but at the end of heating produces a final fractional release very close to the measured value.

The fourth sphere of the FRJ2-K13 test was subjected to 1600 °C heating for 138 h and then a further 100 h at 1800 °C. The 1600 °C heating period produces results very similar to the 1600 °C heating tests performed on the HFR-K3/1 and FRJ2-K13/2 test spheres. The existing IAEA diffusion coefficient significantly over-predicts release for heating times less than about 140 h, while the newly-derived diffusion coefficient also over-predicts release, but to a lesser extent. During the 1800 °C heating period, the ^{85}Kr release increased a hundred-fold and caesium release by three orders of magnitude. Complete silver release was measured after 71 h of heating at 1800 °C. This curve could only be reproduced with the new diffusion curve if 100% failure (in terms of silver retention ability) is assumed. Fractional release curves are shown as before in Fig. 8.

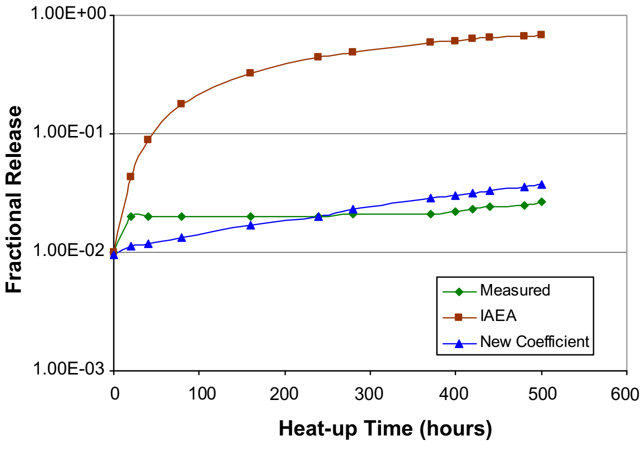

Fig. 5. Silver release during heat-up of HFR-K3/1.

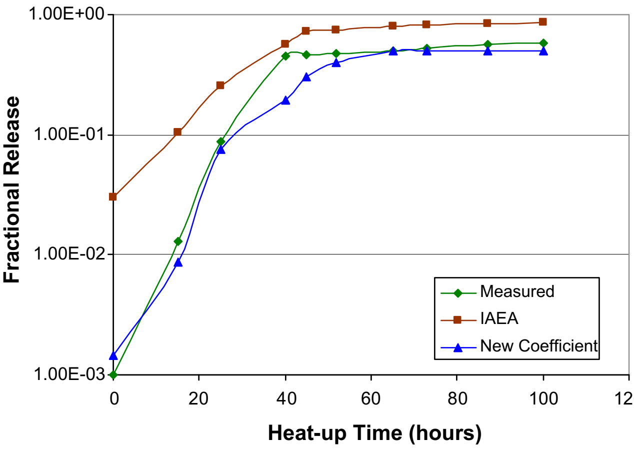

Fig. 6. Silver release during heat-up of HFR-K3/3.

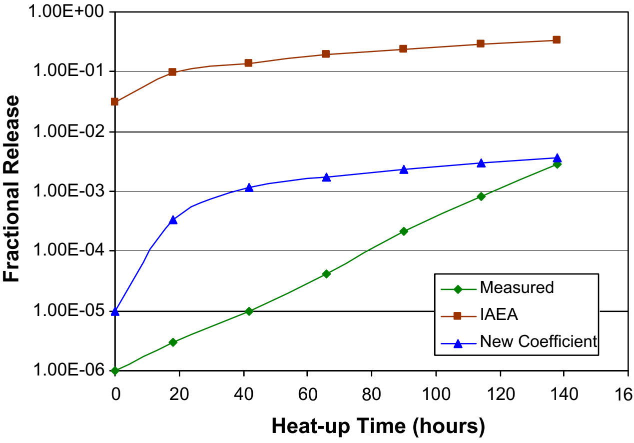

Fig. 7. Silver release during heat-up of FRJ2-K13/2.

6.3. AVR 74/11

Fuel sphere AVR 74/11 was irradiated in the AVR for approximately 850 full power days where it achieved a burn-up of 6.2% FIMA and a fast fluence of 1.6×10^{25} m^{-2} [24]. It contained 16,400 LEU-TRISO particles. After irradiation in the AVR, the fuel sphere was subjected to heat-up testing at 1700 °C for 180 h. ^{85}Kr fractional release measurements show no failure during irradiation or subsequent heating for the first 83 h. After 89 h of heating the ^{85}Kr fractional release measurement suggests a coated particle failure fraction of up to 9×10^{-4}.

The heat-up test's evaluation is presented in Fig. 9. Even for the 1700 °C case the current IAEA diffusion coefficient over-predicts the silver fractional release by an order of magnitude. The best esti-

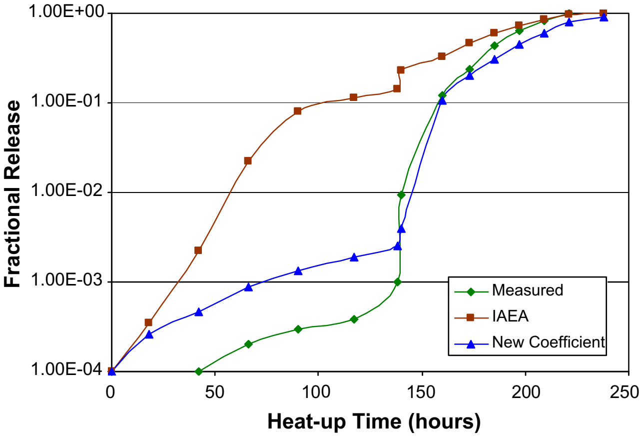

Fig. 8. Silver release during heat-up of FRJ2-K13/4.

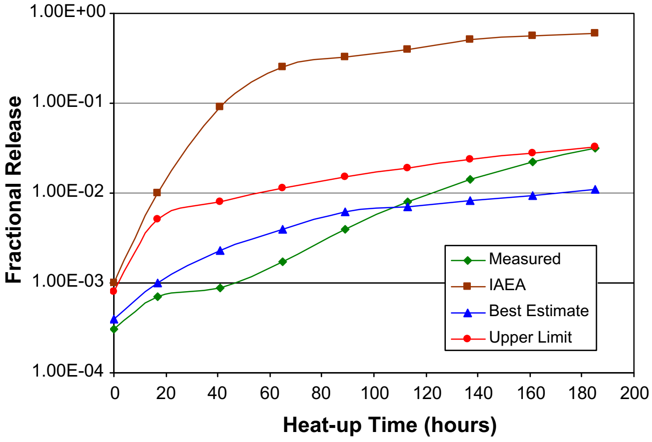

Fig. 9. Silver release during heat-up of AVR 74/11.

mate of the newly-derived diffusion coefficient is about a factor of three too low at the end of the heat-up. This is still within the previously accepted uncertainty limits for calculated ^{111}Ag release during loss of forced cooling accidents. To test this, the calculation was also performed with the upper limit of the newly-derived diffusion coefficient. The upper limit calculation matches the end of irradiation fractional release, which means that for this specific heat-up test, the newly-derived diffusion coefficient is still feasible.

6.4. AVR 71/22

Fuel sphere AVR 71/22 was irradiated in the AVR for approximately 480 full power days where it achieved a burn-up of 3.5% FIMA and a fast fluence of 0.9×10^{25} m^{-2}. It contained 16,400 LEU-TRISO particles. After irradiation in the AVR, the fuel sphere was subjected to heat-up testing at 1600 °C for 500 h. ^{85}Kr fractional release measurements show no failure during irradiation or subsequent heating.

The heat-up test's evaluation is presented in Fig. 10. This is a relatively low burn-up fuel sphere and both diffusion models over-predicted fractional release significantly. This could be due to the fact that the irradiation history of the fuel sphere is not modelled correctly or that silver transport through the coating layers of a coated particle is more dependent on irradiation time and total burn-up than currently accepted. An irradiation history as recommended in the latest literature was used [36], but it could be that this fuel sphere spent most of its time in cooler regions in the core, and this sphere is then more representative of the average AVR core.

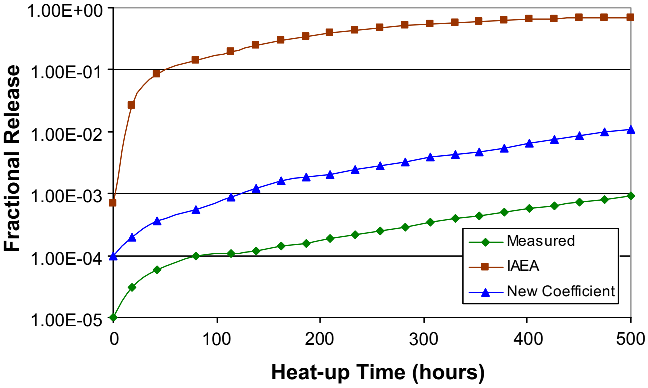

Fig. 10. Silver release during heat-up of AVR 71/22.

The newly-derived diffusion coefficient over-estimates measured fractional release consistently by an order of a magnitude and the IAEA diffusion coefficient by three orders of magnitude. In order to investigate whether this could be a burn-up induced phenomena, higher burn-up spheres heated up to similar temperature regimes have to be evaluated.

6.5. AVR 82/9

Fuel sphere AVR 82/9 was irradiated in the AVR for approximately 1300 full power days where it achieved a burn-up of 8.9% FIMA and a fast fluence of 2.3×10^{25} m^{-2}. It contained 16,400 LEU-TRISO particles. After irradiation in AVR, the fuel sphere was subjected to heat-up testing at 1600 °C for 500 h. ^{85}Kr fractional release measurements show no failure during post-irradiation heating.

The heat-up test's evaluation is presented in Fig. 11. This is a relatively high burn-up fuel sphere and the IAEA diffusion coefficient over-predicts the fractional release significantly. The newly-derived diffusion coefficient calculation matches the measured fractional release very well. When comparing this evaluation with AVR 71/22, it appears as if the diffusion coefficient is irradiation-dependent. Since the newly-derived diffusion coefficient is based on high burn-up irradiation test results, it may be that silver release during the early part of a fuel sphere's irradiation life is over-estimated.

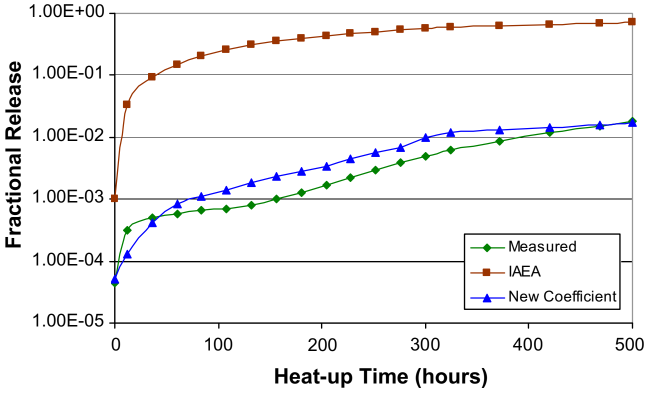

Fig. 11. Silver release during isothermal heating of AVR 82/9.

6.6. AVR 90/5

After evaluating two 1800 °C heat-up tests (HFR-K3/3, FRJ2-K13/4), which showed that for temperatures above 1700 °C, metallic fission product release is dominated by SiC layer degradation and not by transport mechanisms through materials, the only 1700 °C (AVR-74/11) and several 1600 °C heat-up tests at various burn-ups (HFR-K3/1, FRJ2-K13/2, AVR-71/22 and AVR-82/9), that showed that the new diffusion coefficient is applicable for temperatures up to 1600 °C and possibly 1700 °C, it is time to evaluate a complete loss of forced coolant (LOFC) accident test with the new diffusion coefficients.

Fuel sphere AVR 90/5 was irradiated in the AVR for approximately 1400 full power days where it achieved a burn-up of 9.2% FIMA and a fast fluence of $2.5 \times 10^{25}\,\mathrm{m}^{-2}$ [37]. It contained 16,400 LEU-TRISO particles. After irradiation in the AVR, the fuel sphere was subjected to heat-up testing to simulate a 1620 °C loss of forced coolant accident. The temperature was raised to 1620 °C for 30 h and then gradually cooled to 1145 °C over a period of 270 h. ^{85}Kr fractional release measurements show no failure during irradiation or subsequent heating. The heat-up test's evaluation is presented in Fig. 12. The newly-derived diffusion coefficient calculation matches measured fractional release very well. This demonstrates that the new diffusion model will be quite sufficient to model possible ^{111}Ag releases during a loss of forced coolant accident.

6.7. Discussion of heat-up tests

From the post-irradiation heat-up tests evaluated it is clear that the newly-derived diffusion coefficient may be used up to temperatures of 1600 °C with confidence. Results for 1600 °C heating tests tend to be slightly conservative which is acceptable for core analyses. Three high burn-up test spheres as well as spheres from AVR operation of burn-ups between 3.5% and 8.9% FIMA were evaluated. There appear to be some burn-up dependence on the transport of silver through SiC at 1600 °C. Silver release during the only 1700 °C heating test evaluated appears to obey the new diffusion coefficient, however, it is difficult to judge based on only one test. All tests performed above 1700 °C (1800 °C) show massive silver release and can only be modelled by assuming that the vast majority of coated particles fail in terms of metallic fission product retention.

This is supported by an evaluation performed on IMGA results from HFR-K3/3 [38]. In this study it was attempted to explain the observed caesium inventories in each coated particle after irradiation and heat-up testing. Very high diffusion coefficients were suggested, which in practice for silver transport means completely permeable coated particle layers. This failure fraction (in terms of metallic fission product retention) cannot be measured by ^{85}Kr release and therefore existing fuel failure curves are not applicable for temperatures above 1700 °C for metallic fission product release calculations. Unless future tests can prove the contrary, the retention of metallic fission products cannot be modelled by any other means than to accept complete release due to SiC degradation for temperatures above 1700 °C.

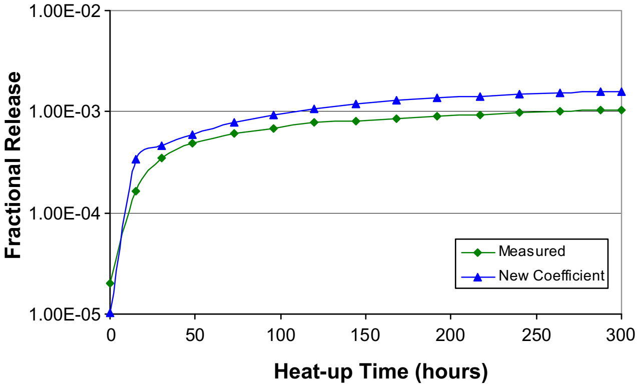

Fig. 12. Silver release LOFC simulation of AVR 90/5.

7. Conclusions and recommendations

Release of silver fission and activation products from fuel contamination and failed particles are only of importance at low temperatures when the radiological impact of ^{110m}Ag on maintenance is small (<700 °C). At higher temperatures, intact coated particles release dominates, with the SiC layer being the main retarding layer. Material test data for SiC transport show erratic results which lead to both high and extremely low diffusion coefficients or new contradicting mechanisms. An accurate model to analyze silver release from a high-temperature core that could be defended using all available test results was developed. Diffusion coefficients for silver in SiC were derived for both best estimate predictions and design limit analyses. It was found that the newly-derived diffusion coefficients for each test were below the current IAEA recommended diffusion coefficient line, which in turn is based on experimental work performed on fuel manufactured before 1978. Detailed evaluations performed during this study are primarily based on fuel manufactured after 1980. The differences between the existing IAEA diffusion coefficient and the newly-derived diffusion coefficients could be due to improvements in SiC manufacture that enhanced silver retention.

Heat-up tests of fuel elements irradiated during fuel tests and fuel elements from AVR operation were evaluated in order to justify the range of temperatures where the newly-derived diffusion coefficients are applicable. It was found that the new diffusion coefficients are valid for temperatures from 800 °C up to 1600 °C and may be used for accident analyses up to 1700 °C. Above 1700 °C it appears that major particle failure (with respect to silver retention) occurs and the new models should not be used at temperatures above 1700 °C.

Important lessons regarding the design, execution and evaluation of fuel irradiation tests were learned during this study:

(a) The irradiation conditions (temperature, neutron fluxes and burn-up) are important considerations to ensure that realistic core conditions are achieved, and also to produce a range of conditions to evaluate fuel performance through the whole envelope of expected core conditions. It is therefore recommended that fuel spheres are irradiated at temperatures not exceeding 1200 °C. However, it is also important to evaluate fuel performance at lower temperatures. Therefore irradiation temperatures in the range of 900–1100 °C should be considered for some later fuel irradiation tests.

(b) The irradiation rig design and placement of irradiation monitors and thermocouples are very important. In all irradiation tests, thermocouple failure is a major problem that influences the accuracy of measurements and even ended some tests prematurely. Only the highest quality thermocouples should be used and the test should be designed to ensure that thermocouple failure remains a minimum.

(c) At the end of the German fuel program, data were not recorded rigorously and a lot of important information from irradiation tests was lost. Similarly, older progress reports and data sets were not stored properly and a lot of information disappeared. For future irradiation programs it is vital that all data from irradiation tests are recorded at the end of each irradiation period and evaluated. In this way, discrepancies can be identified and resolved while the current personnel involved are still available.

(d) Especially for lower temperature irradiation tests (mean fuel temperature <1100 °C) the natural uranium, thorium and silver contamination in the irradiation rig materials dominate the measured ^{110m}Ag activity on rig materials. Determination of transport parameters and evaluation of fuel performance then becomes very complicated and uncertain. Only in one irradiation facility was the natural silver contamination measured for only one of the rig materials. It is therefore critical that all the rig materials are assayed for their uranium, thorium and silver content, as well as any other contamination that might influence the irradiation test results.

(e) The natural silver contamination of fuel matrix material is currently not specified. It appears that the natural silver contamination could be the dominant source term for HTR cores under lower power and temperature conditions. For pre-1980 fuel, German references suggest 2.7 ng/g as a maximum silver contamination level for A3-27 matrix material. For post-1980 fuel a lower value 0.8 ng/g is suggested. For future best estimate analyses it is recommended to use the higher value of 2.7 ng/g. As design limit the actual detection limit results measured on A3-3 matrix material should be used up until such time the actual silver contamination level on PBMR materials can be measured.

Acknowledgement

The authors wish to thank PBMR for allowing the publication of this work.

References

[1] H. Nabielek, P.E. Brown, P. Offerman, Journal of Nuclear Technology 35 (1977) 483–493.
[2] K. Verfondern et al., Fuel Performance and Fission Product Behaviour in Gas Cooled Reactors, IAEA-TECDOC-978, November 1997.
[3] W. Amian, D. Stöver, Journal of Nuclear Technology 61 (1983) 475.
[4] P.E. Brown, R.L. Faircloth, Journal of Nuclear Materials 59 (1976) 29–41.
[5] H. Krohn, R. Finken, FRESCO II, Jül-Spez-212, KFA, Jülich, 1983.
[6] K. Röllig, Rechenprogram GETTER, HRB Report GBRA 052 477, 2001.
[7] H.J. Maclean, R.G. Ballinger, Silver Ion Implantation and Annealing in CVD Silicon Carbide: The Effect of Temperature on Silver Migration, Second International Meeting on High Temperature Reactor Technology, Beijing, China, September 2004.
[8] H.J. Maclean, Silver Transport in CVD Silicon Carbide, Ph.D. Thesis, MIT, 2004.
[9] L.D. Olivier, PBMR 400 MW Core: Ag-110m MPS Source Term, ESKOM Technical Note 2006/001-ST, October 2006.
[10] J.J. van der Merwe, Modelling Silver Transport in Spherical HTR Fuel, Ph.D. Thesis, UP, 2009.
[11] J.J. van der Merwe, L.D. Olivier, Modelling Silver: Evaluation of German Experience, Fourth International Meeting on High Temperature Reactor Technology, Washington, DC, USA, October 2008.
[12] G.H. Lohnert et al., Nuclear Engineering and Design 109 (1988) 257–263.
[13] H. Nabielek et al., Ceramic Coated Particles for Safe Operation in HTR's and in Long-term storage, 33rd International Conference on Advanced Ceramic and Composites, Daytona Beach, Florida, USA, January 2009.
[14] J.B. Keshaw, J.J. van der Merwe, GETTER – A Model for Fission Product Release from Spherical HTR Fuel Elements, HTR 2006, Johannesburg, South Africa, October 2006.
[15] K. Hilpert et al., High Temperatures – High Pressures 20 (1988) 157–164.
[16] E. Hoinkis, D. Stritzke, Desorption of Cesium and Silver from a Graphitic Matrix Surface from Transport of Fission Products in Matrix and Graphite, Hahn-Meitner-Institut für Kernforschung B372, June 1983.
[17] E. Hoinkis, Journal of Nuclear Materials 209 (1994) 132–147.
[18] K. Röllig, PBMR Core Release Rates of Metallic Fission Products: Derivation of Design Values, HRB report, GBRA 058 345, 2002.
[19] D. Petti et al., Development of Improved Models and Designs for Coated-Particle Gas Reactor Fuels", INEEL/EXT-05-02615, December 2004.
[20] R. Christ, Spaltproduktfreisetzung bei HFR-K3, HRB Report GHRA 001343, August 1985.
[21] J.H. Venter, Fuel: HFR-K3 Recalculation Report, PBMR Report 100575, January 2007.
[22] R.W.A. Kraakman, W.P. Voorbraak, Neutron Metrology in the HFR – D138.03 Irradiation of Fuel Spheres, ECN-84-122, August 1984.
[23] J.J. van der Merwe, Verification and Validation of the PBMR Models and Codes used to Predict Gaseous Fission Product Releases from Spherical Fuel Elements, M.Sc. Thesis, RAU, February 2004.
[24] R Gontard, H Nabielek, Performance Evaluation of Modern HTR TRISO Fuels, HTA-IB-05/90, July 1990.
[25] G. Pott et al., Experiment FRJ2-K13: Bestrahlungsbericht, KFA Technical Note IRW-TN-92/85, October 1985.
[26] R. Schröder et al., FRJ2-K15: Gammaspektrometrie an Brennelementen und Kalotten. Nachrechnung des Spaltproduktinventars, FZJ Technical Note 15/94, 1994.
[27] R. Acharya, Analyses of R2-K12 Irradiation Experiment, GA report 906636, September 1983.
[28] B.F. Myers, H. Nabielek, Freizetzung fester Spaltprodukte aus HEU-partikeln, HBK-TN-1/83, 1983.
[29] B. Hürttlen, Bestrahlungsdaten FRJ2-K11, KFA Technical Note, IRW-Vorgang-0534, August 1980.
[30] H. Nabielek, Caesium freizetzung bei AVR-brennelementtemperaturen zwisch 1400 un 1600 °C, HBK-IN-4/86, 1986.
[31] P.E. Brown, A.J. Inns, Post-Irradiation Examination of Spherical Fuel Elements from Irradiation Experiments FRJ2-K10 and K11, AERE-G2240, December 1981.
[32] W. Schenk, A. Naoumidis, H. Nickel, Journal of Nuclear Materials 124 (1984) 25–32.
[33] J.L. Martin, H. Nabielek, Modelling of Fuel Element Heating Tests, HBK Technical Note TN-4/88, 1988.
[34] H. Nabielek et al., The performance of HTR fuel particles at extreme temperatures, HBK Technical Note TN-3/88, 1988.
[35] C.A. Baldwin, M.J. Kania, Fission Product Retention in TRISO Coated UO2 Particle Fuels Subjected to HTR Simulated Core Heating Tests, IAEA Specialist Meeting on Behaviour of Gas Cooled Reactor Fuel under Accident Conditions, Oak Ridge, Tennessee, 1990.
[36] H. Nabielek, K. Verfondern, M. Kania, Fuel and Fission Products in the Jülich AVR Pebble-Bed Reactor, Fourth International Meeting on High Temperature Reactor Technology, Washington, DC, USA, October 2008.
[37] H.J. Hantke, Performance of High Quality HTR-LEU Fuel Elements with TRISO Coated Particles – A Summary Report, HTA-IB-7/92, December 1992.
[38] K. Verfondern, Possible Explanation for HFR-K3/3 IMGA Results, ORNL/M-2248, 1992.