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# Fast / Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel FIRST-Nuclides

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[FIRST-Nuclides]



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## Executive Summary

The FP7 Collaborative Project FIRST-Nuclides (Fast / Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel) started January 1, 2012 and ended on December 31, 2014. The project was implemented by a Consortium with ten beneficiaries (Karlsruhe Institute for Technology (KIT) Germany, Amphos 21 Consulting S.L. (AMPHOS21) Spain, Joint Research Centre – Institute for Transuranium Elements (JRC-ITU) European Commission, Forschungszentrum Juelich GmbH (JÜLICH) Germany, Paul Scherrer Institut (PSI) Switzerland, Belgian Nuclear Research Centre- Centre d'Etude de l'Energie Nucleaire (SCK•CEN) Belgium, Centre National de la Recherche Scientifique (CNRS) France, Fundació Centre Tecnològic (CTM) Spain, Magyar Tudományos Akadémia Energiatudományi Kutatóközpont (MTA EK) Hungary, Studsvik Nuclear AB (STUDSVIK) Sweden). The CP aimed to provide new and comprehensive knowledge of the fast release of safety relevant radionuclides from light water reactors (LWRs) spent nuclear fuel (SNF) after failure of the canister in an underground repository. The research performed within the project was based on experimental investigations of high burn-up  $\text{UO}_2$  SNF, mainly from pressurised water reactors (PWRs) and boiling water reactors (BWRs), combined with modelling studies. The CP was organized in six workpackages.

After completion of the CP FIRST-Nuclides, a significantly broadened knowledge has been achieved by investigations covering 12 different types of high burn-up LWR SNF, IRF measurements at 45 different time steps for up to 20 isotopes using 3 different sample preparations. The experiments were performed in a standard leachant composition guaranteeing comparable results between the different groups. The obtained data include the dissolution based radionuclide release for different samples, sample sizes and preparations from PWR and BWR SNF under aerobic, anaerobic and reducing conditions in the standard leachant. The data include cumulative gap and grain boundary releases for caesium and iodine up to one year experimental duration as well as the determination of release rates. Release rates for some elements incorporated in the  $\text{UO}_2$  matrix (Se, Rb, Sr, ...), redox sensitive elements, and IRF of selenium were also determined. For  $^{14}\text{C}$  only few data could be obtained at the end of project as the analyses required specific analytical techniques and the results are still outstanding.

Results on the chemical state of Se were obtained by micro X-ray absorption near-edge structure (XANES) spectroscopy. A model is available for predicting the wetting of SNF and the time behaviour of radionuclide release. For evaluation and interpretation of the results, operational parameters have been made available. All data of the CP FIRST-Nuclides as well as the previously published data are compiled in a database available on the project webpage ([www.firstnuclides.eu](http://www.firstnuclides.eu)) for application in safety analyses. Some relations could be derived, relating the IRF of Cs and I with the fission gas release and the power rating of the high burn-up  $\text{UO}_2$  fuel.

One important improvement of FIRST-Nuclides in comparison to previous studies was the clearance of the fuel owners to publish the power plant specific data, such as burn-up, power rating and calculated fission gas releases. Releases from non-standard SNFs were also investigated, such as from extremely high burn-up TRISO fuel and from leaking VVER fuel assemblies.

The project aimed also to training and education of young scientists. This aim was achieved by a Lab exchange meeting, a training course and by mobility measures for PhD students. An important objective of CP FIRST-Nuclides was dissemination of the achieved knowledge. Detailed documentation of the scientific results can be found in three Annual Project Workshop Proceedings

(2012, 2013, 2014) [1-3]. These openly available proceedings contain all details and data. Up to now, 166 reports, publications and presentations at conferences document the achievements and results of FIRST-Nuclides.

The main outcomes of the FIRST-Nuclides project can be summarized as:

- IRF of fission gases, Cs, I,  $^{14}\text{C}$  compounds, selenium ( $^{79}\text{Se}$ ),  $^{99}\text{Tc}$ ,  $^{126}\text{Sn}$ , etc. from gap and  $\text{UO}_2$  grain boundaries:
  - This investigation covered, cumulative IRF measurements at 45 different time steps for 12 different types of high burn-up LWR fuel, for up to 3 sample preparations, and up to 20 isotopes. For Cs and I, the available database before the project has been improved significantly. Differences and similarities from gap and grain boundary release processes have been observed.
- Dependency of the IRF on power plant operational parameters:
  - In comparison to previous studies, the clearance of the fuel owners was obtained to publish the power plant specific data. This fact allowed relating the observed cumulative IRF and IRF rates to data such as burn-up, power rating and calculated fission gas releases. The relations are available to be applied in safety analyses. Releases from non-standard SNFs were also investigated, such as from extremely high burn-up TRISO fuel and from leaking VVER fuel assemblies.
- Dependency of the IRF and the leaching conditions:
  - The relation between the observed IRF of redox sensitive elements and elements incorporated in the  $\text{UO}_2$  matrix demonstrated clearly the effect of the leaching conditions. It is concluded that for the elements Tc, Sr, U and perhaps Se experiments should be performed under realistic environmental conditions.
- Transition between IRF and the significantly slower release processes due to  $\text{UO}_2$  matrix corrosion:
  - A way to define this transition was the application of different samples, sample sizes and sample preparations comprising pellets, segments, slices, fragments, powders, and cladding with attached fuel. The partners agreed upon a standard leachant which allowed better comparisons of results generated by the different labs. It could be shown that after about 0.5 to one year the release rates of Cs and I are in the same order of magnitude as observed for matrix dissolution.
- Modelling:
  - Mobilisation of radionuclides along the grain boundaries was modelled. This includes the penetration of water into the fuel sample and the subsequent migration of radionuclides along the wetted fractures and grain boundaries. Modelling also provided significant input for the definition of state of the fuel samples under investigation.

- Societal impacts
  - Following societal unities are affected by the outcome of CP FIRST-Nuclides: the implementers and regulators of a SNF disposal which will use the obtained data and knowledge for direct application in safety analyses and the improvement of the knowledge basis described in the Safety Case. This fact has also impact on general public as the trust into the argumentation by implementers and regulators is improved due to the broader knowledge of the processes in the SNF, release processes and chemical speciation of the relevant elements.
  - A close trustworthy scientific cooperation has been developed between the different labs and organizations which work under specific national regulations. This cooperation includes not only the Beneficiaries, but also the Associated Groups in Europe and USA. It includes the research organizations, and consultants but also the waste management organizations, utilities, and the producer of the fuel.
  - The process of the EURATOM funded cooperation as demonstrated by CP FIRST-Nuclides gained high attention outside of Europe, where, for example in USA, a close and trustworthy cooperation between different laboratories could not be established as competitive considerations would dominate (statement by a representative of an Associated Group from USA).

Key input data from the project to the safety analysis are “instant release fraction (IRF)” values of iodine, chlorine, carbon and selenium. Until the moment, the IRF of spent fuel was often related to its burn-up. With more data becoming available for high burn-up fuel, there is growing evidence that the fission gas release (FGR) and IRF depends much more on the linear power rate of the fuel than on the burn-up. The data gathered in FIRST-Nuclides give further evidence for this topic. Hence, the linear power appears to be a more relevant operational parameter to predict the FGR than the burn-up is. This can be explained by the fact that the FGR depends on the temperature of the fuel pellet in the reactor during operation which is related to the linear power, rather than on the burn-up.

The End-User Group in the CP FIRST-Nuclides representing European Waste Management Organizations stated that the subject of the CP “Fast / Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel (FIRST-Nuclides) is highly relevant for all waste management organisations involved in repository development for which direct disposal of spent nuclear fuel is foreseen. The IRF contributes substantially to the peak release after container breaching and its potential radiological consequences. Specifically, the results include (1) data from experimental determination of rapid release fractions for moderate and high burn-up UO<sub>2</sub> fuels, including doped fuels, expected to be used much more by reactor operators in the future, and (2) a data base for release of Cs and I from high burn-up fuel and comprehensive comparisons of IRF with fission gas release (FGR), which are necessary in order to be able to estimate IRF data for populations of fuel rods in various reactor operation conditions.

The partners of the project identified a series of open questions to be resolved in future investigations. The 3 years CP FIRST-Nuclides required huge investments to setup the experiments, to implement the required analytical tools and instruments and to get the clearance by the utilities to publish the spent fuel data. Some of the experiments have run only for short time, which does not

justify the level of investment. For this reason, a long-term project should be implemented allowing for the continuation of the experiments will maximize the outcome of the efforts invested. This will include investigation on MOX and rare activation isotopes such as  $^{36}\text{Cl}$ .

### References

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## 1 Introduction

The EURATOM FP7 Collaborative Project “Fast / Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel (CP FIRST-Nuclides)” contributes to the progress towards implementing of geological disposal in line with the Vision Report and the Strategic Research Agenda (SRA) of the “Implementing Geological Disposal – Technology Platform (IGD-TP)”. Waste forms and their behaviour represent a key topic in the SRA of IGD-TP. This key topic deals with understanding the behaviour of various wastes in geological repositories in particular with high burn-up spent uranium oxide (UO<sub>2</sub>) fuels. This waste type represents the source for the release of radionuclides after loss of the disposed canister integrity. For safety analysis, the time-dependent release of radionuclides from this spent high burn-up UO<sub>2</sub> fuel is required.

The emphasis in the IGD-TP SRA is given to high burn-up spent uranium oxide (UO<sub>2</sub>) fuels which is related to the progressive increase in burn-up. Significant improvements in the understanding of the performance of spent fuel under repository conditions have taken place. However, most of the published data on fast/instant release fractions (and also on the matrix dissolution) relate to fuel with burn-up values below 45 GWd/t<sub>HM</sub>. Over the next years the average burn-up will increase, reaching average values of about 60 GWd/t<sub>HM</sub>. Because of this, license applications related to disposal of such spent fuel elements may be inadequately supported unless further work is performed and the database extended.

There is presently a substantial amount of spent MOX being produced that needs to be disposed of. Due to extended cooling time for MOX fuel, investigations on this type of fuel have a lower urgency.

The project tackles the challenge of realistically describing the release of the first batch of radionuclides from disposed spent nuclear fuel upon canister failure (fast/instant release fraction). This first release consists of radionuclides (1) in gaseous form, and (2) with a high solubility in groundwater. Some important nuclides show only marginal retention on their way to the biosphere. In present safety analyses, these radionuclides have a significant contribution to dose to man. The basis for the calculated significant dose contribution is a simplified description of the release function. It is expected that a realistic release function results in lower peak dose rates, and thus contributes to acceptance of nuclear waste disposal.

The added value of the CP FIRST-Nuclides consists in a direct answer to the inadequately supported knowledge on fast/instant radionuclide release for license applications related to disposal of high burn-up UO<sub>2</sub> fuel. The outcome of the project is relevant for all types of host rocks in Europe. The knowledge and data obtained within the project will reduce the uncertainties and will provide for realistic data on the relevant radionuclide release for the Safety Case. The project also contributes to lowering of the vulnerability in access to infrastructure and competence by engaging those of the few adequate facilities in this activity.

### 1.1 Objectives

The fast/instant release of radionuclides released immediately after failure of the canisters is expected to contribute significantly to the dose to man. The released inventory, and in some cases

the chemical form of the radionuclides, are subject to uncertainties. In response to this, the overall objectives of FIRST-Nuclides are to:

1. provide improved data for the fast/instant release fraction for high burn-up spent UO<sub>2</sub> fuel,
2. establish correlations between the experimental FGR and the fast/instant release of non-gaseous fission products, in particular for <sup>129</sup>I, <sup>79</sup>Se and <sup>135</sup>Cs,
3. reduce uncertainties with respect to the fast/instant release of <sup>129</sup>I, and <sup>14</sup>C,
4. determine the chemical form of the relevant elements in order to evaluate the retention processes.

The experimental programme place emphasis on:

- Quantification of instantly/fast released of safety relevant elements, including their isotopic composition and, if possible their chemical form.
- Determination of gap and grain boundary inventories.
- Determination of the fast/instant release fraction in dependence on characteristic fuel data.
- Accessibility of, and transport properties on grain boundaries.
- Quantification and characterization of exchange processes along the grain boundaries.
- Determination of the transition between instant/fast release and the significantly slower release processes due to radiolytically driven matrix corrosion.

Modelling aims on decreasing the uncertainty with respect to the fast / rapid radionuclide release from high burn-up UO<sub>2</sub> fuel and to provide for procedures for estimating the fast / instant release for all types and characteristics of SNF to be disposed of in a single repository including SNF from different types of reactors, enrichments, burn-up, power rating and other properties. For this purpose, correlations were derived relating the fast / instant release for Cs or I to the burn-up, power rating and calculated fission gas release (in-pile data) of the fuel. The outcome of the project is an important part of the Safety Assessment independent on the host rocks or disposal concepts.

## 1.2 Partners in CP FIRST-Nuclides

The CP started January 1, 2012 and ended on December 31, 2014. Materials, methods and techniques for investigations on spent nuclear fuels (SNF) need to be applied in heavily shielded hot cells.

The project was implemented by a Consortium with ten beneficiaries (Karlsruhe Institute for Technology (KIT) Germany, Amphos 21 Consulting S.L. (AMPHOS21) Spain, Joint Research Centre – Institute for Transuranium Elements (JRC-ITU) European Commission, Forschungszentrum Juelich GmbH (JÜLICH) Germany, Paul Scherrer Institut (PSI) Switzerland, Belgian Nuclear Research Centre-Centre d'Etude de l'Énergie Nucleaire (SCK-CEN) Belgium, Centre National de la Recherche Scientifique (CNRS) France, Fundació Centre Tecnològic (CTM) Spain, Magyar Tudományos Akadémia Energiatudományi Kutatóközpont (MTA EK) Hungary, Studsvik Nuclear AB (STUDSVIK) Sweden).

Thirteen organisations have contributed to the project without any funding as *Associated Groups (AG)*, i.e. organisations from France (Commissariat à l'énergie atomique et aux énergies alternatives, CEA), United States of America (Los Alamos National Laboratory, SANDIA National Laboratories),

United Kingdom (Nuclear Decommissioning Authority (NDA), National Nuclear Laboratory (NNL), University Cambridge, Centre for Nuclear Engineering of the Imperial College London, University Lancaster), Finland (Posiva Oy, Teollisuuden Voima (TVO)), Czech Republic (ÚJV Řež, a. s.), Spain (Ciemat) and Germany (Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH). These groups had particular interest in exchange of information. During the duration of the CP FIRST-Nuclides, a close cooperation was developed between the partners and the Associated Groups.

A group of six implementation and regulatory oriented organizations (SKB (Sweden), NAGRA (Switzerland), ONDRAF/NIRAS (Belgium), ANDRA (France), BfS (Germany), and ENRESA (Spain)) have participated as “*End-User Group (EUG)*”. This group ensured that end-user interests (waste management organisations and one also regulator) were reflected in the project work, and they reviewed the project work and the scientific-technical outcome.

### 1.3 Organization of the project

With respect to the determination and quantification of the fast/instant release fraction of radionuclides from high burn-up spent nuclear fuel and the application of this information to the Safety Assessment and Safety Case for geological disposal, the work plan has the following elements and aims:

- Selection, characterization and preparation of materials and set-up of tools for handling and transportation of the highly radioactive material,
- Experimental determination of fission gas release,
- Experimental investigation of rim and grain boundary diffusion,
- Dissolution based radionuclide release and to the extent possible the chemical speciation of the relevant isotopes,
- Modelling of migration/retention processes and of chemical speciation of fission products in the spent fuel structure, on the grain boundaries, and in pellet interfaces.
- Assessing and discussing the potential impact on the Safety Case.
- Documentation of the State-of-the-Art with regular up-dating, stepwise build-up of scientific-technical reporting, its Dissemination and Communication, as well as Training, and
- Project coordination and management.

To achieve the aims, the CP FIRST-Nuclides was structured in the following workpackages:

WP 1: **Samples and tools:** Selection, characterization and preparation of materials and set-up of tools.

WP 2: **Gas release + rim and grain boundary diffusion:** Experimental determination of fission gases release. Rim and grain boundary diffusion experiments.

WP 3: **Dissolution based release:** Dissolution based fast/instant radionuclide release.

WP 4: **Modelling:** Modelling of migration/retention processes of fission products in the spent fuel structure.

WP 5: **Knowledge, reporting and training:** Knowledge Management, State-of-the-Art report, general reporting, documentation up-date, dissemination and training.

**WP 6: Project management.**

A sufficiently good characterization of SNF materials with respect to its use in power plants, irradiation history, burn-up and power rates have been achieved [1]. The most important result of WP1 was the permission for publication of key parameters of the SNF samples by the fuel owners.

## 2 Previous Investigation

The state-of-the-art of the instant / fast radionuclide release from SNF have been documented during the initial phase of FIRST-Nuclides [2, 3], and updated according to the achieved results[4]. The following section gives an overview on the instant / fast radionuclide release based on dissolution experiments various SNF materials, samples and experimental techniques.

Oversby and Shawn [5]; Wilson, [6-8]; Wilson and Shawn, [9]; Wilson and Gray, [10]: Two bare fuel specimens were prepared from, T.B. Robinson (HBR) (burn-up of 30 GWd/t<sub>HM</sub>) and Turkey Point (TP) (burn-up of 27 GWd/t<sub>HM</sub>) PWR and leached in Yucca Mountain relevant J-13 water. The experiments were carried at 25 and 85°C.

Forsyth and Werme, [11]; Forsyth, [12]: Experiments performed with 20mm long fuel/clad segments of SNF from Oskarsham-1 BWR SNF (burn-up of 42 GWd/t<sub>HM</sub>), Rignhals-1 BWR SNF (burn-up between 27.0 and 48.8 GWd/t<sub>HM</sub>), and Rignhals-1 PWR SNF (burn-up of 43 GWd/t<sub>HM</sub>). The experiments were carried out at room temperature and leaching time of 7 days.

Gray and Wilson, [13]; Gray, [14] measured the gap and grain boundaries inventories from different PWR SNF's: ATM-103 (burn-up of 30 GWd/t<sub>HM</sub>), ATM-104 (burn-up of 44 GWd/t<sub>HM</sub>) and ATM-106 (burn-up of 43 and 46 GWd/t<sub>HM</sub>), and from BWR SNF's: ATM-105 (burn-up of 31 and 34 GWd/t<sub>HM</sub>). The SNF was removed from the cladding and placed in a glass vessel along with the empty cladding segment. The experiments were performed in deionised water (DIW) over 1 week at hot cell temperature under ambient atmosphere. Grain boundary inventory measurements on the SNF specimens were performed after completion of the gap inventory measurements. Following one week exposure to water, the SNF fragments were dried, crushed, and screened using screens with 20 to 30 µm openings, depending on the grain size of the SNF being prepared. The grain boundary inventory measurements consisted of placing 0.5 g of the screened SNF grains in a 50 mL beaker along with 20 mL of 0.1 M HCl. Periodically over 3 h, the acid was removed, filtered, and replaced with fresh acid.

Serrano et al., [15] investigated irradiated fuel samples prepared from two SNF pins: UO<sub>2</sub> (burn-up of 54 GWd/t<sub>HM</sub>) and MOX (burn-up of 30 GWd/t<sub>HM</sub>). Sequential batch leaching experiments in DIW at room temperature under ambient atmosphere were performed. On completion of the chosen contact period, the samples were transferred to clean vessels containing fresh leachant. The leaching times encompassed an interval between 24 hours and 54 days. The used vessels were rinsed with 1N HNO<sub>3</sub> for 1 h at room temperature. During the tests, the vessels were kept close-tight; after the longest leaching time, no significant loss of leachate from the bottles was observed. The leaching tests with irradiated fuel were performed in a hot cell, at ambient hot cell temperature of 25 ± 2°C. The data correspond to a leaching time of 31 days. The matrix contribution was subtracted.



Glatz et al., [16] investigated three MOX SNFs (burn-up of 12, 20 and 25 GWd/t<sub>HM</sub>) and three UO<sub>2</sub> SNFs (burn-up: one with 30 GWd/t<sub>HM</sub> and two with 50 GWd/t<sub>HM</sub>) rodlets, each one of about 6 cm long. Both ends of each sample were closed by means of tight stainless steel end-caps. One UO<sub>2</sub> fuel rod with a burn-up of 50 GWd/t<sub>HM</sub> was provided with two series of defects (in each case, 3 holes of 1 mm diameter each), one series at the top and in contact with vapor, and the other series at the bottom of the rodlet and in contact with the leaching solution. In all the other samples, the defects were placed in the centre of the rodlet and the autoclave was filled completely with the leaching solution. MOX fuels were fabricated following the MIMAS blend process. The leaching experiments were carried out in autoclaves equipped with Ti-liners using DIW at 100°C under anoxic or reducing conditions. The data correspond to a leaching time of 365 days without the matrix contribution.

Loida et al., [17] reported the initial release of <sup>137</sup>Cs from various SNF measured in MgCl<sub>2</sub>-rich and concentrated NaCl solutions at 25, 90, 100, 150 and 200°C. These experiments cover mainly SNF with a burn-up between 36 and 50 GWd/t<sub>HM</sub>. Most of the <sup>137</sup>Cs IRF are below or in the range of the pessimistic values compiled by Poinssot and Gras (2009) [18]. An IRF of 3.7% of the total <sup>137</sup>Cs was measured in a leaching experiment with a spent nuclear fuel sample from the NPP Biblis (KWB, discharged June 1979; burn-up of 36.6 GWd/t<sub>HM</sub>) in concentrated NaCl solution at 200°C. This value is slightly higher than the pessimistic <sup>137</sup>Cs IRF estimate for fuel with a burn-up of 41 GWd/t<sub>HM</sub>.

Quiñones et al., [19]: Three UO<sub>2</sub> PWR SNFs were studied: U-568 (burn-up of 29.5 GWd/t<sub>HM</sub>), B4 (burn-up of 53.1 GWd/t<sub>HM</sub>) and AF-02 (burn-up of 62.8 GWd/t<sub>HM</sub>). A whole disc of approximately 2 mm thick, cut from the rods, together with the cladding were prepared. The weight of the SNF contained in these discs was about 2 g. Static batch leaching experiments were performed in 70 mL volume borosilicate glass vessels. All tests were performed at room temperature, in a hot cell with air atmosphere. The leachant consisted of 50 mL of carbonated granitic water (CGW), whose composition in mol/kg<sub>H2O</sub> was: Na<sup>+</sup> 4.09·10<sup>-4</sup>; K<sup>+</sup> 1.46·10<sup>-4</sup>; Mg<sup>2+</sup> 2.51·10<sup>-4</sup>; Ca<sup>2+</sup> 2.47·10<sup>-4</sup>; Cl<sup>-</sup> 2.37·10<sup>-4</sup>; Si 4.99·10<sup>-4</sup>; SO<sub>4</sub><sup>2-</sup> 7.19·10<sup>-5</sup>; HCO<sub>3</sub><sup>-</sup> 1.07·10<sup>-3</sup>; F<sup>-</sup> 1.05·10<sup>-5</sup>; PO<sub>4</sub><sup>3-</sup> 1.04·10<sup>-7</sup>; Al<sup>3+</sup> 1.85·10<sup>-7</sup>; U<sub>total</sub> 2.32·10<sup>-9</sup>; pH around 7.0. The leachant was deaerated by purging with inert gas for several hours prior to the start of the leaching. During each contact period, the vessels remained sealed. The leaching experiments were performed by taking aliquots of leachate (1 mL) without replacement from the reaction vessel. Data represent average values of repeated measurements, the values referred to are quite high in comparison with values reported for others authors. The leaching time was 500 days for U-568 SNF, and 600 days for B4 and AF-02 SNFs.

Roudil et al., [20, 21] analysed five PWR SNFs, four UOX with a burn-up of 22, 37, 47 and 60 GWd/t<sub>HM</sub>; one MOX with burn-up of 40 GWd/t<sub>HM</sub>. Two kinds of samples were used: 20 mm segments with cladding and powder samples with a particle size of 20 – 50 µm, the powder sample were only prepared for the SNF with a burn-up of 60 GWd/t<sub>HM</sub>. The experiments were carried out under oxic conditions at room temperature (25°C). The gap inventories were determined by static leaching experiments in carbonate containing water (HCO<sub>3</sub><sup>-</sup> = 10<sup>-3</sup> M) with 20 mm clad segments. The tests under air atmosphere lasted for 62 days. Solution was sampled after 3, 10, 24 and 62 days.

Experiments to determine the inventory at the grain boundaries were carried out only on UOX PWR fuel with a burn-up of 60 GWd/t<sub>HM</sub>. Leaching experiments were carried out on SNF powder according to a protocol similar to the one developed and validated by Gray [13]. SNF fragments were sampled from the centre of a clad 35 mm segment previously leached for one week in carbonated water to eliminate the gap inventory. Sampling the fragments at the centre of the segment also eliminated

the contribution of the rim. Powder samples with a particle size fraction of 20–50  $\mu\text{m}$  were prepared by grinding and sieving in a hot cell. The number of grains in each particle was estimated at about forty. Pseudo-dynamic leach tests, under air atmosphere in hot cell, were carried out on 567 mg of powder in 25 mL of carbonated water ( $\text{NaHCO}_3 = 10^{-2} \text{ M}$ ) to prevent any precipitation of uranium used as a matrix alteration tracer. After each cycle the solutions were filtered and analyzed. Fresh water was added to the leaching reactors. Thirty cycles were carried out, initially of short duration (1–2 h) to avoid any precipitation resulting from leaching of the oxidized  $\text{UO}_{2+x}$  layer, then longer (24–48 h). When the ratio of the released fractions was equal to 1 it was assumed that the complete inventory at the grain boundaries was leached during the preceding cycles.

Roudil et al., [21]: studied the IRF from fragments and grains from the pellet peripheral zone near or in contact with the cladding using a PWR SNFs with a burn-up of 60  $\text{GWd/t}_{\text{HM}}$ . Each fuel segment was first slotted to obtain two cylindrical portions separated from the core and consisting of cladding and peripheral fuel. The cladding was separated from the fuel. The resulting fragments were separated in 20 and 50  $\mu\text{m}$  fractions. The leach tests were carried out with 282 mg of powder in 25 mL of bicarbonate water to prevent any precipitation of uranium used as a matrix alteration tracer. After each cycle, 17 mL solution was removed, filtered, analyzed and contacted again with the fuel powder for the next cycle. Twenty cycles were performed in all. The initial cycles lasted a few hours; the subsequent cycles were then maintained for 24 hours each.

Kim et al., [22] measured gap and grain boundaries in three different PWR fuel rods: SFR1 (burn-up of 39.6  $\text{GWd/t}_{\text{HM}}$ ), SFR2 (burn-up of 39.6  $\text{GWd/t}_{\text{HM}}$ ), SFR3-a (burn-up of 45.8  $\text{GWd/t}_{\text{HM}}$ ) and SFR3-b (burn-up of 65.9  $\text{GWd/t}_{\text{HM}}$ ). The fuel specimens were prepared by cutting the fuels rods to slices of 2 mm thickness. The gap inventory was measured with a SNF pellet without cladding. The SNF together with the cladding were put into a bottle filled with 100 mL of distilled water and put under the hot cell operation conditions. After a soaking of the SNF and cladding, 5 mL of the solutions were sampled in > 7 days intervals. Sawdust produced during the cutting of fuel rod SFR1 and crushed powder produced by crushing the specimens after the gap inventory experiment were used for measurement of the nuclide inventories in the grain boundaries. The powder was leached in 50 mL of 0.1M HCl for about 20 minutes and the solution was sampled by filtering it with a 0.2 filter. The solution was replaced with a fresh acid and subsequently sampled.

Fors, [23, 24] used a commercial  $\text{UO}_2$  SNF with a burn-up of 59.1  $\text{GWd/t}_{\text{HM}}$  and an average power line of 250KW/m. A 10 mm long segment was cut. A core drilled in the segment to separate the fuel centre from its peripheral rim (725  $\mu\text{m}$  thickness). The fuel containing the high burn-up structure (HBS) material was detached from the Zircaloy cladding by use of external stress in a screw clamp. The de-cladded fuel fragments contained about 15 wt.% HBS. The millimetre-sized fragments were leached in 10 mM NaCl and 2mM  $\text{NaHCO}_3$  solution at initial pH of 8.1 at a hydrogen pressure of 4.1 MPa. The experiment was carried out at ambient hot cell temperature,  $23 \pm 4^\circ\text{C}$ . The leachate was not stirred. The published results refer to a leaching time of 7 days.

Johnson et al., [25] published results performed at Studsvik and Paul Scherrer Institute (PSI). At Studsvik laboratories, 4 commercial  $\text{UO}_2$  SNFs were used: Ringhals 3 (PWR, burn-up of 58.2  $\text{GWd/t}_{\text{HM}}$ ), Ringhals 4 (PWR, burn-up of 61.4  $\text{GWd/t}_{\text{HM}}$ ), Ringhals 3 (PWR, burn-up of 66.5  $\text{GWd/t}_{\text{HM}}$ ) and North Anna (PWR, burn-up of 75.4  $\text{GWd/t}_{\text{HM}}$ ).

Two samples were cut from near the middle of each of the four fuel rods: a fuel corrosion sample, consisting of a 20 mm segment, cut at mid-pellet height, containing one complete and two half

pellets. These samples are referred to as closed rod samples. In another set of tests, referred to as open rod samples, adjacent fuel rod segments of 20 mm length were cut from each of the four rods and were weighed. The cladding was carefully sawn on both sides of the segment periphery and force was applied to the halves until the fuel broke away from the cladding. The two cladding halves, together with detached fuel fragments were collected in a glass vessel with glass filter bottom (100–160  $\mu\text{m}$  pores) and weighed again. Then they were leached according to the same procedure as for the closed rod samples. An initial solution sampling 2 h after test start was also carried out for all samples of this test series. The samples, kept in position by a platinum wire spiral, were exposed to 200 mL of synthetic Allard groundwater in a Pyrex flask. pH was stable around 8.3 and carbonate remained constant during all the tests. The contact periods were 2 h, 7, 21 and 63 days. The composition of the Allard water can be found in [26].

At PSI, 3 commercial SNFs from Leibstadt BWR ( $\text{UO}_2$  burn-up of 65.3  $\text{GWd}/t_{\text{HM}}$ ), Gösigen PWR ( $\text{UO}_2$  burn-up of 64  $\text{GWd}/t_{\text{HM}}$ , and MOX burn-up of 63  $\text{GWd}/t_{\text{HM}}$ ) were investigated. The length of the fuel rod segments were 20 mm each (two pellets). For the rim samples the inner part of the fuel was removed mechanically by drilling, leaving an asymmetric ring of fuel bonded to the cladding. One rim sample was left open, whereas a tight-fitting PVC plug was placed through the entire length of the other rim sample. In order to investigate if the fuel surface available for the leachant's attack has a significant impact on the leach rate, a number of samples were broken into two halves by cutting the cladding on opposite sides.

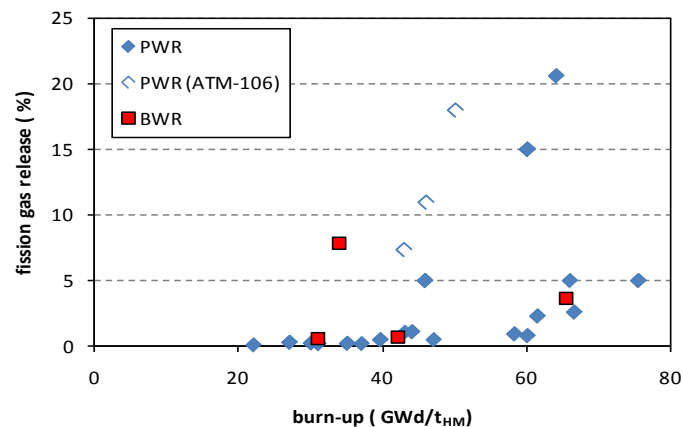
Glass columns (total volume approx. 250 mL) with a sealed outlet cock for sampling and an implemented glass filter in order to retain solid particles were used. Approximately 200 mL of buffer solution (28 mM borate buffer, pH 8.5, containing 20  $\mu\text{g}/\text{g}$  NaI as iodine carrier) were used per sample for the leaching experiments. As the objective of the measurements was to obtain the rapid release fraction of certain radionuclides, the experiments were performed in air-saturated buffer solutions. After filling the columns with the sample and buffer solution the supernatant air volume was removed through a hole in the piston cylinder which was closed afterwards to avoid additional air intake. Subsamples of 20 mL each were taken after 7, 14, 21, 28 and 56 days, whereas the last sampling of 30 mL per leach solution was performed after 98 days.

Clarens et al., 2009 [27], González-Robles, 2011 [28], Serrano-Purroy et al., 2012 [29] investigated 4 commercial  $\text{UO}_2$  SNFs, three from PWR (burn-up of 48, 52, 60,  $\text{GWd}/t_{\text{HM}}$ ) and one from a BWR (burn-up of 53  $\text{GWd}/t_{\text{HM}}$ ). The temperature was  $(24 \pm 6)^\circ\text{C}$ . From the SNFs with a burn-up of 48 and 60  $\text{GWd}/t_{\text{HM}}$ , three different SNF samples corresponding to the central axial position (labelled CORE), the periphery of the SNF pellet (labelled OUT) and to an emptied cladding segment with small amounts of SNF attached to the inner wall called CLAD. In order to remove fines attached to the grain surface, the CORE and OUT powder SNF fractions were washed several times with acetone. Static experiments for powder samples, CORE, OUT and CLAD, were carried out in  $(50 \pm 0.1)$  mL borosilicate glass test tubes of  $(150 \times 25)$  mm with thread and a plastic screw cap. The tubes were placed on a rotating stirrer. Static leaching experiments were carried out with two synthetic leaching solutions: bicarbonate (BIC), which composition in mM was: 19  $\text{Cl}^-$ ; 20  $\text{Na}^+$ ; 1  $\text{HCO}_3^-$ , pH 7.4; and Bentonitic Granitic Groundwater (BGW), which composition in mM was: 93.9  $\text{Cl}^-$ ; 45.2  $\text{SO}_4^{2-}$ ; 0.9  $\text{HCO}_3^-$ ; 117.9  $\text{Na}^+$ ; 1.1  $\text{K}^+$ ; 15.4  $\text{Ca}^{2+}$ ; 17.3  $\text{Mg}^{2+}$ ; pH of 7.6. The experiments were carried out under oxidizing conditions and with about 0.25 g of SNF [27-29].

Static experiments for pellet samples of the 4 SNF's were performed in a  $(50 \pm 0.1)$  mL flask and daily shaken during 5 to 10 minutes to avoid the risk of breaking the flask by mechanical shaking [28]. The head space of the gas phase was  $(3 \pm 1)$  mL, in powder samples, and  $(10 \pm 1)$  mL in pellet samples. To avoid initial U saturation and secondary phase formation, the solution was completely replenished two times at the beginning of each experiment.

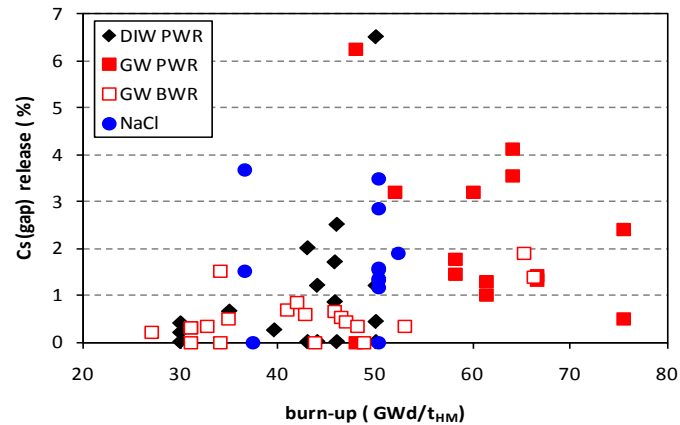
### 3 State of the Art on the fast/instant release before FIRST-Nuclides

The literature data were evaluated with respect to different relations of the fast release of fission products. In **Fig. 1** the calculated fission gas release (%) as function of the average burn-up for PWR and BWR fuels is plotted. In the figure, it is possible to differentiate two branches in the FGR. The steep branch corresponds to ATM-106 PWR fuels (burn-up between 43-50 GWd/ $t_{HM}$  [13, 14], SFR PWR fuel (burn-up of 45.8 and 65.9 GWd/ $t_{HM}$ )[22], Gösgen PWR fuel (burn-up of 64 GWd/ $t_{HM}$ ) [25], a PWR fuel (burn-up of 60 GWd/ $t_{HM}$ )[27-29] and ATM105 BWR fuel (burn-up of (34 GWd/ $t_{HM}$ ) [13, 14]. This behavior is correlated to high linear power rates of the fuel element. In the case of ATM-106 PWR fuel, these fuels do not have an unusual high power rating, thus this is not the reason for the high FGR [25]. The fuel assembly was fabricated in the 1970s and had a reported density of 10.05–10.3 g/cm<sup>3</sup> [30], significantly lower than the typical densities of about 10.5 g/cm<sup>3</sup> of present-day fuels [31]. Such a low density can result in significantly higher FGR because of a higher fraction of open porosity [32]. For this reason, it can be assumed that the high FGR and associated rapid release values of the ATM-106 fuel are anomalous and not representative of fuel assemblies in present day use [25].



**Fig. 1** Previous investigations: Fission gas release (FGR) as function of the average burn-up.

Besides the FGR, the IRF of Cs corresponding to gap contribution, which includes the release from the gap interface between the cladding and the pellet, and the fractures, was determined under several leaching conditions. **Fig. 2** shows the Cs gap release as function of the average burn-up in distilled water (DIW) [13, 16, 22], simulated groundwater (with different HCO<sub>3</sub><sup>-</sup> concentrations) [5, 7, 9-12, 27-29] and in saturated NaCl solutions [17].

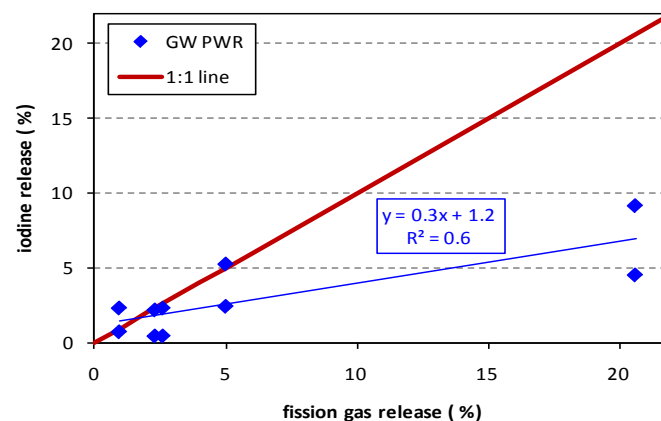


**Fig. 2** Previous investigations: Cs gap release as function of the average burn-up in different solutions.

Regarding the performance assessment, the  $^{129}\text{I}$  provides an important contribution to the computed dose to man. For this reason, correlations between FGR and iodine release are of high interests. **Fig. 3** shows the iodine release as a function of the total FGR in experiments performed with PWR fuel in groundwater solution [25].  $^{129}\text{I}$  releases are still in almost all cases below the FGR. From the plotted data, a correlation can be fitted and expressed as:

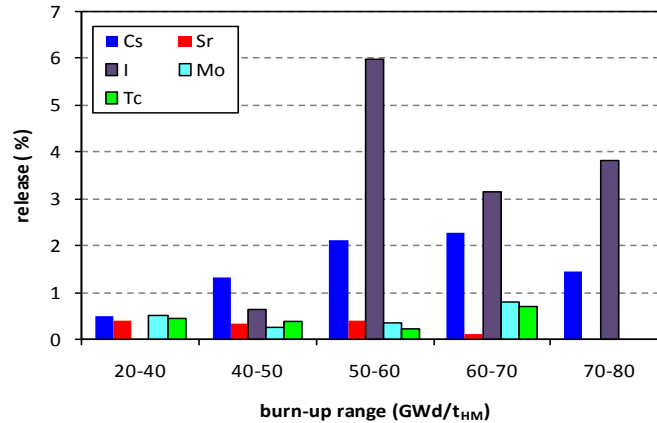
$$\text{Iodine release} = 0.3 \times \text{FGR} + 1.2 \quad \text{eq. 1}$$

However, the coefficient of determination is extremely low ( $R^2=0.6$ ), even, if one data point of a high linear power rate fuel was neglected.

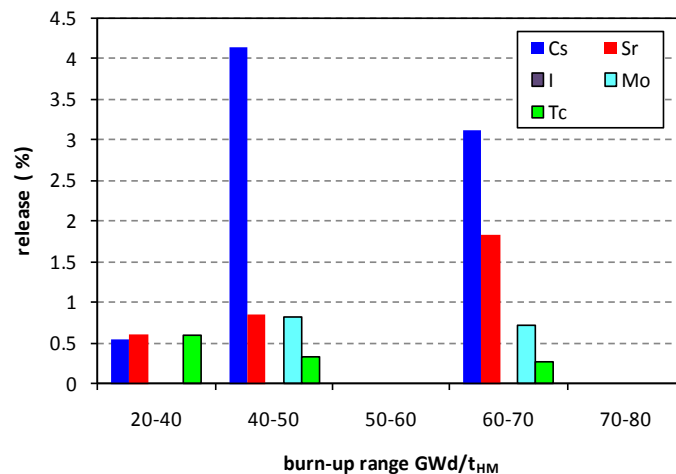


**Fig. 3** Previous investigations: Correlation between leached iodine release and FGR in groundwater for PWR fuels, original data from [25].

The release of fission products from the gap (that includes the release from the gap interface between the cladding and the pellet as well as the fractures), is shown in **Fig. 4**, and from the grain boundaries in **Fig. 5**, as function of the burn-up. The "gap" experiments were performed with pellets or fragments, while the experiments investigating the release from the grain boundaries were done using powder of the SNF.



**Fig. 4** Previous investigations: Fission product release from the gap as function of the burn-up (experiments using pellets or fragments).



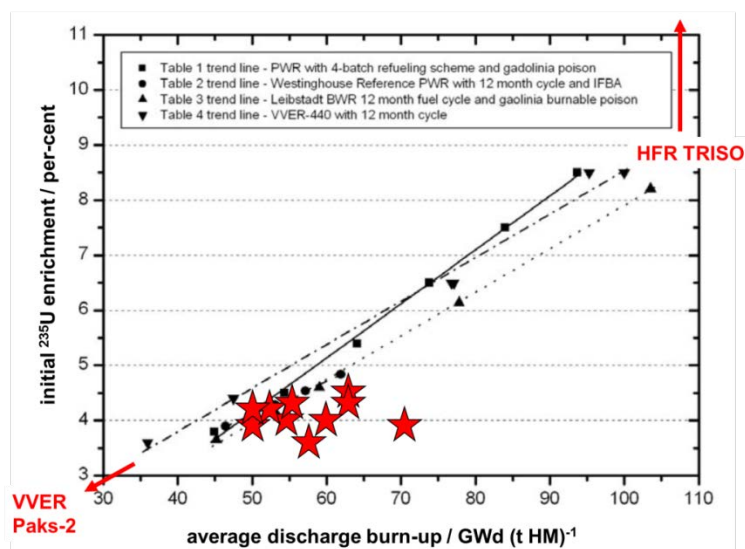
**Fig. 5** Previous investigations: Fission product release from the grain boundaries as function of the burn-up (powder experiments).

Data shown in **Fig. 4** and **Fig. 5** are taken from the above quoted references. The interpretation of the two figures is far from being obvious. For example, in **Fig. 4**, the iodine gap releases seem to be largest for fuel with a burn-up of 50-60 GWd/t<sub>HM</sub>, whereas Mo and Tc releases seem to be independent of the burn-up. In **Fig. 5**, a high strontium release from grain boundaries is shown for the burn-up range between 60 and 70 GWd/t<sub>HM</sub>. This effect can be explained either by an easily soluble Sr phase present on the grain boundaries, or if the investigated fuels underwent completely different burn-up and temperature histories, ramping, etc. Furthermore, these data include experiments of different durations. These two figures show clearly the need for investigations of the fast / instant release with respect to the experimental periods, and the definition of gap and grain boundary release in the Collaborative Project “Fast / Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel (CP FIRST-Nuclides)”. Additionally, it could be shown that the release of fission gas from UO<sub>2</sub> fuel is strongly correlated with the linear heat rating, which is dependent on fuel temperature [33-35].

## 4 Investigations performed in CP FIRST-Nuclides

In the last years, the discharge burn-up of nuclear fuel has increased in all types of nuclear power plants. This increase is a consequence of the cost reduction associated with nuclear power by the utilities.

To achieve burn-ups above 50 GWd/t<sub>HM</sub>, higher initial enrichments are required reaching up to almost 5 wt.% <sup>235</sup>U (see Fig. 6). As an example, the increase of the initial enrichment of the UO<sub>2</sub> fuel and the related peak burn-ups<sup>1</sup> are shown in Fig. 7 for the German nuclear power plants. The highly enriched fuels need a compensation of the excess reactivity by the burnable neutron poison gadolinium. Minimization of the potential fission gas release is anticipated by reduction of the power rates. Accordingly, the high burn-up SNF investigated in FIRST-Nuclides addressed these modern fuels, which differed significantly from materials used in previous investigations. Compared to previous investigations, more data of in-pile operation parameters have been collected, which may be correlated to the IRF data (see Tab. I).

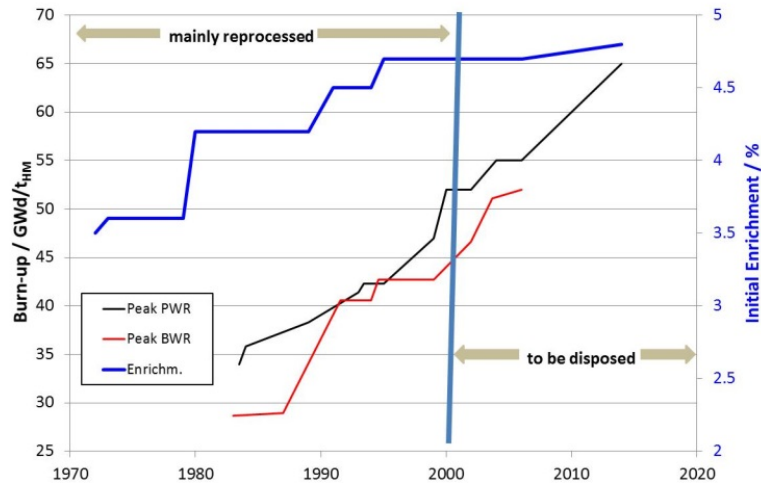


**Fig. 6** Initial enrichment as function of the average discharge burn-up [36].

Stars indicate the SNF materials investigated in FIRST-Nuclides

Detailed documentations of the work performed and the scientific results can be found in three Annual Project Workshop Proceedings (2012, 2013, 2014) [37-39]. These openly available proceedings contain scientific/technical contributions by the partners covering all details and data. For this reason details and single data are not repeated in this document.

<sup>1</sup> PWR fuel assemblies have similar axial-burn-up shapes relatively flat in the axial mid-section (peak burn-up from 1.1 to 1.2 times the assembly average burn-up) and under-burned fuel at the ends of the rods (burn-up of 50 to 60% of the assembly average).



**Fig. 7** Evolution of initial enrichment between 1970 and 2020 and the peak burn-up of German power plants. Data taken from [40, 41].

#### 4.1 Materials and Methods in CP FIRST-Nuclide

The workpackage WP1 “**Samples and tools**” covered the selection of the samples, a sufficiently good characterization of SNF materials and the required tools such as reaction vessels or analytical techniques for the experimental investigations. The permission for publication the key parameters of the SNF samples by the fuel owners was obtained for all the samples. This WP1 was led by Volker Metz, KIT-INE.

Many of the published results on the fast/instant release fraction (IRF) have been determined with spent fuel irradiated either with relatively low or extremely high neutron fluxes which are not typical of present spent fuel waiting for disposal. Procedures for selection, characterization and preparation of relevant spent nuclear fuel (SNF) samples were established in this WP. All experimental-working project partners (KIT, JRC-ITU, JÜLICH, PSI, SCK-CEN, CNRS, CTM, EK and STUDEVIK) contribute to this workpackage. Most of the partners studied high burn-up spent nuclear fuels irradiated in commercial nuclear power plants, while the JÜLICH group studies the so-called TRISO fuel irradiated in a research reactor at the Petten EC Joint Research Centre. CNRS investigates unirradiated TRISO particles, which will be used in successive corrosion experiments under alpha irradiation. EK studies damaged and leaking VVER fuel rods with a burn-up below 27 Gwd/t<sub>HM</sub>, which were stored in water for several years after an incident at the Paks-2 reactor.

One of the first activities in WP1 covered the compilation of fuel characteristics from the samples. The IRF depends on critical characteristics of the SNF such as manufacturing process, burn-up history and fuel temperature history, ramping processes and storage time. Therefore, characteristics of various high burn-up spent nuclear fuel rods were collected: type of nuclear reactor, its electrical power, types of fuel assemblies, fuel manufacturing information and the discharge date of the fuel to be investigated. With respect to the cladding, the characterization covered the composition, diameter, thickness and the initial radial gap width between pellet and gap. The information regarding the pellet comprises the initial enrichment, geometry, grain size, density and specifics of



the production process. The irradiation history covers the burn-up, the irradiation time and the number of cycles as well as the maximum and average linear power rate.

Data on fuel samples, which are available for the FIRST-Nuclides partners, were collected by means of a questionnaire (**Tab. I**). The questionnaire was designed with strong support by the EUG. The requested information was classified according to three information levels: (i) essential information representing the minimum data that should be available for the fuel chosen for the study, (ii) parameters and data, which are not directly measured, but derived from calculations, and (iii) supplemental information referring to characteristics that may be needed depending on the studies to be performed. Critical parameters of the selected fuel samples are compared to those of high burn-up fuels which need to be disposed of in Europe, to assure the relevance of the samples for the Safety Case.

**Tab. I** Questionnaire for retrieving the fuel sample information from the partners

Data category	Information level	Parameter
reactor type	essential	BWR, PWR, VVER etc.
coolant	essential	light water
fuel material data prior to irradiation	essential essential	UO <sub>2</sub> , MOX etc. enrichment additives etc., fuel stoichiometry, nitrogen, chlorine contents, fuel density (as fabricated)
fuel material data after irradiation	essential supplemental essential essential	calculated RN inventories measured RN inventories pellet dimensions grain size
fuel assembly design	essential	lattice geometry, e.g. 10X10 fuel rod diameter
fuel rod data	essential	rod type: standard or test rod internal rod pre-pressure burn-up profile ( $\beta$ -scan) fission gas release
cladding composition	essential supplemental	alloy type and composition derived calculated RN inventories measured RN inventories nitrogen, chlorine contents
irradiation data	essential derived	power history, cycle start and end dates fuel centre peak irradiation temperature
pellet sample data	essential	calculated burn-up, measured burn-up,

Data category	Information level	Parameter
	supplemental	calculated RN inventories, measured RN inventories, position of sample in rod ceramography, microscopy
cladding sample data	supplemental	oxide thickness

Spent fuel rods are owned mainly by the reactor operating utilities. KIT, JRC-ITU, JÜLICH, PSI, SCK-CEN, CTM, EK and STUDESVIK confirmed the access to the spent fuel material to be used in the project; they have the full rights to perform investigations and to publish the key parameters of the SNF samples.

The **Tab. II** summarizes the data of the fuel samples investigated during the CP FIRST-Nuclides. Details are reported in the respective deliverable D1.1 [1].

**Tab. II** Overview of the fuels to be investigated within CP FIRST-Nuclides.

		PWR	BWR	THTR/ VVER
<b>Discharge</b>		1989 -2008	2005 – 2008	
<b>Producer</b>		Areva	Areva/ Westing-house	
<b>Cladding</b>	Material	Zry-4 – M5	Zyr 2	Graphite / Zr1%Nb
	∅ / mm	9.50 - 10.75	9.84 - 10.2	
	Thickness / mm	0.62 - 0.73		
<b>Pellet</b>	Enrichment / %	3.80 – 4.94	3.30 -4.25	2.4 -16.8%
	Grain size / μm	5-40	6 - 25	20 -80
	Density / g cm <sup>-3</sup>	10.41	10.52	10.8
	Specifics	standard; NIKUSI production	standard; Al/Cr addition	
<b>Irradiation</b>	Burn-up / GWd/t <sub>HM</sub>	50.4 – 70.2	48.3 – 57.5	10 - 107
	Cycles	2 - 14	5 – 7	
<b>lin. Power</b>	average W/cm	186 -330	160	130–228
<b>Fission Gas Rel.</b>	%	4.9 – 23	1.2–3.1	

**Tab. III** and **Tab. IV** provide details of SNF used by the partners of FIRST-Nuclides.

**Tab. III** SNF form PWRs used for dissolution based IRF investigations

Partner	PWR / Enrichment	Rod ID / Fuel type	Burn-up GWd/t <sub>HM</sub>	Av. / max. lin. power / W cm <sup>-1</sup>	FGR / %
KIT	KKG 3.8% <sup>235</sup> U	test rod	50.4	260 / 340	8.4 measured
PSI	KKG 4.3% <sup>235</sup> U	standard	56.6	285 /	13.2
PSI	KKG 5.5% Pu <sub>fiss</sub>	MOX	63	306 /	26.7
SCK·CEN	Tihange 1 4.3% <sup>235</sup> U	standard	54.3	300 / 400	14.1
Studsvik	Vandellòs 2.8% <sup>235</sup> U	VG81 + 8% Gd	54.4	136 /	4.2
Studsvik	North Anna (USA) 4.0% <sup>235</sup> U	AM2K12 standard	70.2	186	5.0

**Tab. IV** SNF form BWRs used for dissolution based IRF investigations

Institution	BWR / enrichment	Rod ID / Fuel type	burn-up GWd/t <sub>HM</sub>	Av. / local lin. power / W cm <sup>-1</sup>	FGR / %
JRC-ITU	not available 3.7% <sup>235</sup> U	standard	42.2 <sup>a</sup> / 45.0 <sup>b</sup>	215 <sup>c</sup> / 290 <sup>d</sup>	2.3
PSI	KKL 4.2% <sup>235</sup> U	standard	57.5	160 / 270	2.6
CTM	not available 4.2% (see D1.2)	standard	54.2 <sup>a</sup> / 57.0 <sup>b</sup>	160 <sup>c</sup> / 275 <sup>d</sup>	3.9
Studsvik	Olkiluotao 4.25% <sup>235</sup> U	D07 standard	50.2	143 / 145	1.5
Studsvik	Olkiluoto 4.25% <sup>235</sup> U	L04 standard	54.8	146 / 162	3.1
Studsvik	Oskarshamn 3 3.5% <sup>235</sup> U	5A2 standard	57.1	160 /	2.4
Studsvik	Oskarshamn 3 4.1% <sup>235</sup> U	O3C1 Cr <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> doped UO <sub>2</sub>	59.1	175 /	1.3

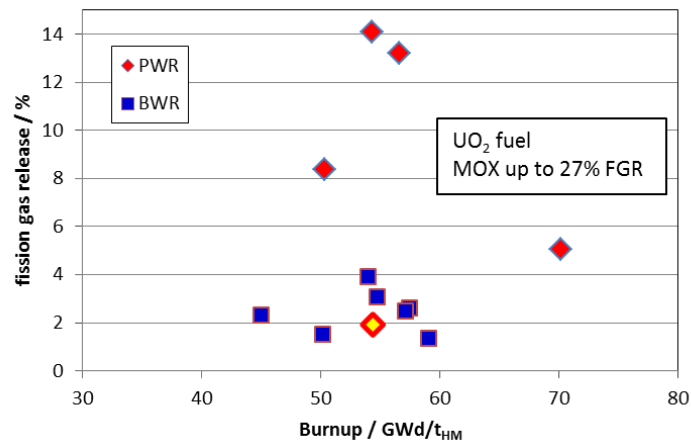
<sup>a</sup>) Average fuel rod burn-up

<sup>b</sup>) Calculated burn-up at sample position

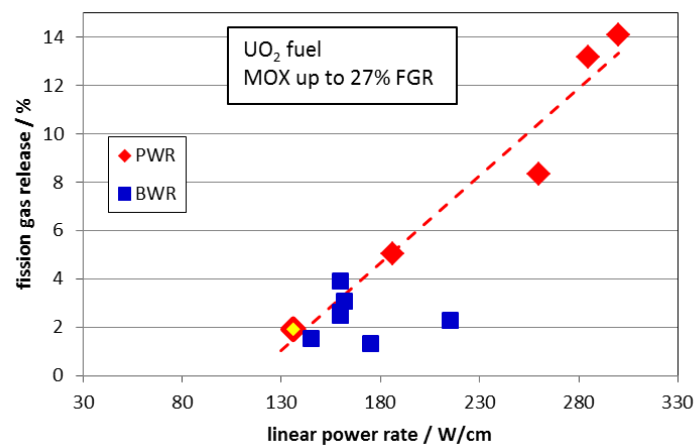
<sup>c</sup>) Average linear power during irradiation at sample position

<sup>d</sup>) Maximum linear power during irradiation at sample position

**Fig. 8** shows the correlations of FGR with the burn-up and the linear power rate (**Fig. 8a** and **Fig. 8b**, respectively). It can be observed that FGR does not correlate with the burn-up for the samples under investigation in FIRST-Nuclides but it correlates (**Fig. 8a**).



a) FGR as function of the burn-up

b) FGR as function of the linear power rate  
dashed line: fit according eq. 2**Fig. 8 Relation of FGR to burn-up and average linear power rate**

The PWR SNF sample with FGR of 1.92 % corresponds to sample VG81 (see **Tab. III**; 2.8 % <sup>235</sup>U enrichment and doped by 8 wt.% Gd). No correlation is observed between FGR and linear power rate of BWR samples. On the contrary, for the PWR fuels under investigations, a linear correlation can be derived:

$$\text{FGR} = (0.072 \pm 0.010) \times \text{lin. power rate} - (8.40 \pm 2.46), R^2 = 0.94 \quad (\text{eq. 2})$$

According to the requests by the EUG, leaching experiments with SNF have been performed using several kinds of samples: (1) Pellets: according to the fuel production process, (2) Segments: cuts through the middle planes of different pellets, (3) Slices: cut through a single pellet, (4) Fragments: pieces or portions of fuel, (5) Powders: fuel material obtained after declad, milling and sieving. (6) Cladding with attached fuel. Pellets, segments and slices can be prepared with and without cladding. Different samples were applied: KIT clad pellet and fragments under reducing conditions, SCK-CEN

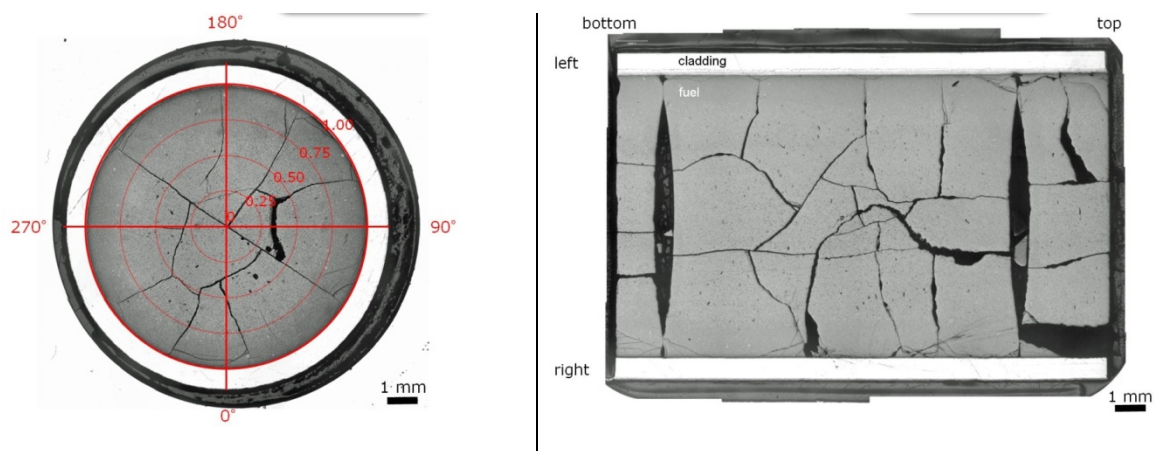
clad and declad (fragments + cladding) segment, PSI clad pellets and fragments, Studsvik fragments together with cladding, ITU and CTM: 2.5-2.8 mm segments of BWR pellets and powders. The analyses covered the isotopes/elements shown in **Tab. VI**. In order to improve the basis for comparison of the results from different laboratories, a standard leachant was defined and agreed upon, consisting of 19 mM NaCl + 1 mM NaHCO<sub>3</sub> at pH 7.4 to 8.2

## 4.2 Characterisation of SNF materials used in FIRST-Nuclides

A detailed characterization of the SNF used by KIT have been performed by JRC-ITU. In the 1980s, a series of fuel rod segments were irradiated in the Swiss Gösigen PWR (KKG) to analyze the performance of UO<sub>2</sub> fuels, which had been fabricated with different sintering and gelation manufacturing methods. For each irradiation test, five segments and additional dummy segments were mounted to make a full-length KKG fuel rod. The fuel of rod SBS1108 was fabricated by Kraftwerk Union AG. Most fuel pellets had been initially enriched with 3.8 wt.% <sup>235</sup>U in segment N0204 of the fuel rod. In each of the fuel rod segments with NIKUSI pellets, two pellets adjacent to the upper and lower isolation pellets were made of U<sub>nat</sub>. The fuel rod SBS1108 was irradiated in four cycles for 1226 days total irradiation, which started in 1985 and ended on May 27, 1989. Segment N0204 achieved an average burn-up of 50.4 GWd/t<sub>HM</sub>; an average linear heat generation rate of 260 W/cm is reported for SBS1108 N0204.

Following investigations were performed: ceramography, measurements of the outer oxide layer on the cladding, analysis of the pellet cladding interaction zone, measurement of the porosity, and quantification of metallic particles.

SNF samples were characterized in details: Optical micrographs of the microstructure of the spent fuel sample were performed by SCK-CEN. JÜLICH investigated irradiated TRISO fuel by SEM analyses. JRC-ITU and CTM performed also SEM analyses with the respective fuel. Studsvik applied laser ablation analysis on some samples for investigating the selenium distribution, but also the distribution of other elements/isotopes over cross sections of pellets.



**Fig. 9** Macrographs of a radial and axial cut samples (including coordinates (red) for ceramography reference) .

### 4.3 Experimental determination of fission gases release. Rim and grain boundary diffusion experiments.

The experimental determination of fission gases release and the rim and grain boundary diffusion experiments were organized in WP 2: “**Gas release + rim and grain boundary diffusion**”. This workpackage was led by Detlef Wegen, JRC-ITU.

Work package two is divided into the two components “Experimental determination of fission gas release” and “Rim and grain boundary diffusion”. In the first component the focus was on the quantification of fission gases and fission gas release in high burn-up (HBU)  $\text{UO}_2$  spent nuclear fuels (SNF). Fission gas sampled in the plenum of a fuel rod were analysed as well as the grain boundary inventory and the cross sectional distribution of fission gases and volatile fission products. KIT analysed fission and activation products in the fission gas sampled at JRC-ITU from the plenum of a fuel rod segment by puncturing [42, 43] (quadrupole gas mass spectrometer (GAM400, In Process Instruments). The development, testing and implementation of analytical methods for fission and activation products have started in the first project year. Leaching experiments in which gas and solution analyses were performed [44]. STUDEVIK investigated the radial fission gas and volatile fission product distribution (Xe, I, and Cs) by Laser-Ablation Mass Spectroscopy (LA-MS) on HBU boiling water reactor (BWR) SNF [44-46].

The second component “Rim and grain boundary diffusion” dealt with investigations on oxygen diffusion in spent  $\text{UO}_2$  fuel. The examination of diffusion mechanisms resulted in the quantification of water penetration into the fuel (grain and grain boundaries) structures and subsequently, couple the diffusion/corrosion phenomena. Furthermore, investigations on irradiated and unirradiated fuel kernels separated from high temperature gas cooled reactor (HTR) fuel have been performed which are complementary to those on light water reactor (LWR) fuel.

The experimental part of WP2 started in project month 4 and ended in project month 36 [44, 47-51]. In the first project year the focus was on setting up experimental facilities, characterisation and preparation of samples. In the second year of the experimental work programme in WP2 first results have been obtained by the partners but also new challenges arose. In the last project year most of the experiments have been finalised and evaluated. JRC-ITU started investigation on diffusion effects in the first project year with the characterisation and preparation of spent fuel samples to be used for corrosion experiments in  $\text{H}_2^{18}\text{O}$  water. It was planned to determine the  $^{18}\text{O}/^{16}\text{O}$  depth profiles using a shielded SIMS (secondary ion mass spectrometry) to quantify the oxygen diffusion into spent nuclear fuel (SNF) [51]. Jülich worked on spent high HTR fuel, investigating the microstructure and of the elemental distribution of the fuel kernel and of the coatings before and after leaching [51, 52]. Unirradiated TRISO fuel particles are investigated by the CNRS at the ARRONAX cyclotron. The particles are irradiated using a  $\text{He}^{2+}$ -beam in the dose rate range of 0.8 – 4.4 kGy/min. The corrosion of  $\text{UO}_2$  TRISO particles was investigated in view of grain boundary effects and secondary phase formation and the influence of hydrogen [51, 53-55].

### 4.3.1 Experimental determination of fission gas release

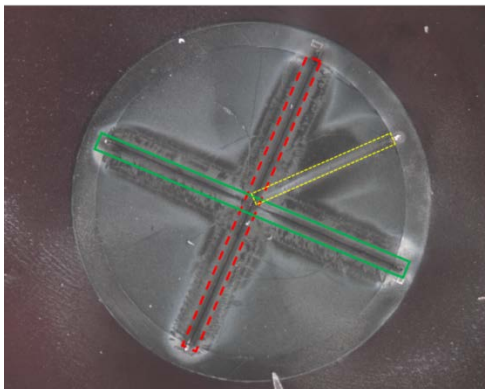
JRC-ITU has examined the release of the fission products  $^{88}\text{Sr}$ ,  $^{87}\text{Rb}$ ,  $^{137}\text{Cs}$ , and  $^{136}\text{Xe}$  from powder of irradiated BWR  $\text{UO}_2$  ( $54\text{GWd}/t_{\text{HM}}$ ) originating from the core region of the fuel pin. The sample was heated in a Knudsen cell coupled to a mass spectrometer under vacuum conditions at a rate of  $10\text{ K/min}$  until complete vaporization of the fuel at  $2460\text{ K}$ . The measured release profiles indicate two release mechanisms for  $^{137}\text{Cs}$ , one with rather low intensity starting just below  $1000\text{ K}$  and a second significant release after  $1500\text{ K}$ . The release of the fission products  $^{88}\text{Sr}$ ,  $^{87}\text{Rb}$ ,  $^{137}\text{Cs}$ , and  $^{136}\text{Xe}$  has been semi-quantified [56].

KIT performed leaching experiments on a well characterised samples of cladded PWR fuel and PWR fuel fragments under  $\text{Ar}/\text{H}_2$  ( $p_{\text{T}} = 40\text{ bar}$ ;  $p_{\text{H}_2} = 3\text{ bar}$ ) in bicarbonate water ( $19\text{ mM NaHCO}_3 + 1\text{ mM NaCl}$ ). After a cumulative contact time of 246 days, 15% of the fission gases ( $\text{Kr} + \text{Xe}$ ) were released into the gas phase for the cladded fuel pellet while for fuel fragments 11% of the fission gases ( $\text{Kr} + \text{Xe}$ ) inventory were released after 27 days [43, 57, 58].

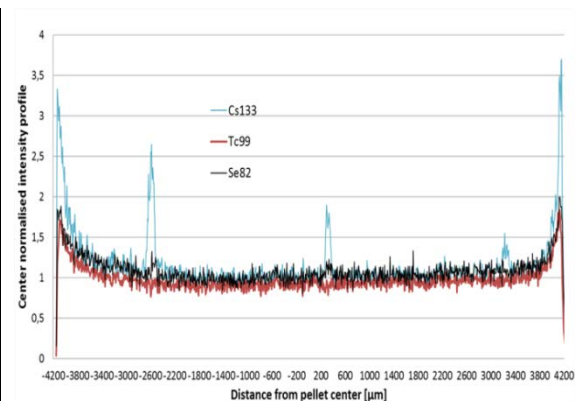
### 4.3.2 Determination of element profiles

STUDSVIK applied Laser Ablation Inductively Coupled Plasma Mass Spectroscopy analysis on fuel cross-sections from a standard  $\text{UO}_2$  fuel (sample 5A2) and from a Al/Cr additive fuel (sample C1). The caesium and iodine profiles measured on both fuels are very similar and follow the radial burn-up profile. Caesium, iodine and to some extent selenium also appear to collect in some fuel cracks. Selenium was tentatively identified by the good agreement of the isotopic ratios of mass 77, 79 and 82 with the calculated inventory. Chromium and especially aluminium are heterogeneously distributed in the Al/Cr-additive fuel [46].

Sample 5A2 (Standard  $\text{UO}_2$ )



**Fig. 10** Overview of sample 5A2 after laser ablation



**Fig. 11** Normalised intensity profiles on 5A2 ( $60\text{ }\mu\text{m}$  beam) of  $^{133}\text{Cs}$ ,  $^{99}\text{Tc}$  and  $^{82}\text{Se}$

The red dashed line in Fig. 10 corresponds to the radial laser ablation profiles

**Fig. 11** shows that  $^{133}\text{Cs}$  appears to be more strongly associated with fuel cracks (at ca  $-2,600$  and  $300\text{ }\mu\text{m}$ ) than  $^{99}\text{Tc}$  and  $^{82}\text{Se}$ .

### 4.3.3 Rim and grain boundary diffusion

JÜLICH investigated  $\text{UO}_2$ TRISO coated particles from spent HTR fuel (burn-up  $\sim 100 \text{ GWd/t}_{\text{HM}}$ ).  $\text{UO}_2$  fuel kernels were exposed to synthetic groundwater (19 mM NaCl and 1 mM  $\text{NaHCO}_3$ ) for 276 days under oxic (air) and anoxic/reducing ( $\text{Ar}/\text{H}_2$ ) conditions. The U release was below detection limit. During 276 days maximal 0.2 %  $^{90}\text{Sr}$  and 8 %  $^{134/137}\text{Cs}$  were released from grain boundaries. Depending on the environmental conditions, different release functions were observed. ESEM (environmental scanning electron microscope) investigations showed on samples leached in oxic environment, numerous intragranular open pores acting as new accessible leaching sites and white spherical spots containing Mo and Zr. Under anoxic/reducing conditions numerous metallic precipitates (Mo, Tc and Ru) filling the intragranular pores and white spherical spots containing Mo and Zr, were detected [52].

CNRS studies the oxidation of  $\text{UO}_2$  in unirradiated HTR fuel kernels by  $\alpha$ -radiolysis products of water. Radiolysis products are produced by 66.5 MeV  $\text{He}^{2+}$  beam irradiation of water in the ARRONAX cyclotron giving a dose rate of 4.37 kGy/min. The obtained results show that gaseous  $\text{H}_2$  produced by water radiolysis completely inhibits the  $\text{UO}_2$  corrosion by interaction between  $\text{H}_2$  and the  $\text{UO}_2$  surface. The  $\text{UO}_2$  radiolytic corrosion expressed as a function of the absorbed dose show a ten-fold higher dissolution rate for the lower dose rate (0.8 kGy/min) than that found for the higher one (4.4 kGy/min). If OH radicals are produced near the  $\text{UO}_2$  surface they interact directly with the  $\text{UO}_2$  surface and not with each other to form  $\text{H}_2\text{O}_2$ . In this case also the radiolytic corrosion is higher than in presence of molecular  $\text{H}_2\text{O}_2$ . It is also shown that the  $\text{UO}_2$  radiolytic corrosion under  $\text{He}^{2+}$  radiation occurs essentially on the grain boundaries and not on the crystallized  $\text{UO}_2$  grains [53, 59].

JRC-ITU analysed and modelled diffusion profiles measured on  $\text{UO}_2$  by parallel diffusion processes. No new experimental results on oxygen diffusion experiments have been obtained because during refurbishment of the autoclave in the hot cell, intended for oxygen diffusion experiments, a Ti-welded tube joint broke. For safety reasons a replacement of the complete autoclave setup was necessary. Despite all efforts undertaken it was not possible to get the set-up back in working conditions because of the delivery time of special valves needed. It was decided to prolong WP2 from 33 to 36 months and to publish the results in an open journal with reference to FIRST-Nuclides [60, 61].

Under oxic conditions multiple oxygen diffusion processes were observed which fits with the finding of oxidation processes along grain boundaries which are suppressed under influence of hydrogen where  $\text{UO}_2$  corrosion is inhibited. Such behaviour is also found in case of irradiated TRISO fuel. Under oxic conditions, (1) an initial release of  $^{90}\text{Sr}$  and Cs from freely available surface sites occurred and (2) a delayed release from sites which were closed at the beginning and became accessible during ongoing corrosion. This second release was not detected under the presence of hydrogen and in the case of TRISO metallic precipitates were found in pores. Under oxic conditions, all metallic precipitates were dissolved.



## 4.4 Dissolution based fast/instant radionuclide release

The determination of the dissolution based fast/instant radionuclide release was performed in WP3 “**Dissolution Based Release**”. This workpackage was led by Karel Lemmens, SCK-CEN.

### 4.4.1 Details of investigations in WP 3

The overall objectives of WP3 were the quantification of the fast release of gaseous and non-gaseous activation and fission products into the aqueous phase during spent nuclear fuel leach tests, and – to the extent possible - the determination of their chemical speciation. The experiments covered high burn-up spent nuclear fuels (HBU-SNF) having a burn-up mostly in the range of 50 to 60 GWd/t<sub>HM</sub>, different irradiation histories, reactor types and sample positions in the fuel rods. Special emphasis was given to the determination of IRF values of caesium, iodine, selenium and carbon-14 (from fuel and cladding) as well as to the redox speciation of selenium. Additionally, dissolution rates for relevant isotopes were determined for damaged VVER fuel elements (to be disposed of in Germany, Hungary and Finland). The results from experiments using fuel samples with/without cladding allow an evaluation of the effect of the presence of the cladding material.

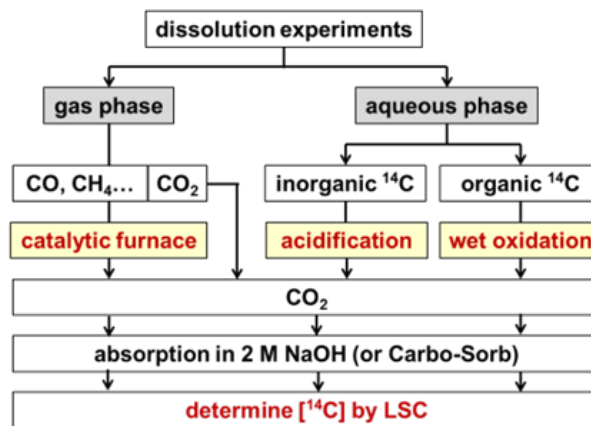
Seven institutes were involved in WP3, i.e. KIT, JRC-ITU, PSI, SCK-CEN, CTM, Studsvik and EK. All of these institutes, except for EK, have performed leach experiments on samples of high burn-up fuels in laboratory conditions. The CTM experiments were performed in the laboratories of JRC-ITU. EK did not perform laboratory experiments, but has contributed by collecting and interpreting the isotopic dissolution data of damaged and leaking VVER fuels that had been stored in storage pools in the period 2003-2007 (damaged fuel) and 2009-2010 (leaking fuel).

The leach experiments by the various institutes were harmonized as much as possible to allow a better comparison of the leach data. For this reason, a standard leachant (19 mM NaCl and 1 mM NaHCO<sub>3</sub>) was used by most laboratories, and tests with similarly prepared samples (cladded fuel segments) were added by several laboratories. Nevertheless, there were also differences in experimental approaches, such as the redox conditions (reducing or oxidizing atmosphere), leaching mode (static or pseudo-dynamic), and alternative sample preparations (declad fuels, fuel fragments, fuel powders...). Both PWR and BWR fuels were tested. One test series with a MOX fuel was added as well. Test durations up to 1 year were planned, but for part of the experiments, this duration will be reached (or the results will be available) after the end of the project. The leachates were analyzed for a large number of radionuclides, depending on the techniques available in the participating laboratories. However, all laboratories have measured (or planned to measure) the most critical IRF radionuclides, i.e. Cs and I isotopes. Other isotopes that were measured by several, but not all laboratories are <sup>14</sup>C and <sup>79</sup>Se. For some isotopes, the analytical methods were improved in the framework of the project. Special efforts were made to characterize selenium in the spent fuel by solid state analyses. More details about the contribution of each institute are given hereunder.

**KIT** has performed leach experiments on a spent PWR UOX fuel with average burn-up of 50.4 GWd/t<sub>HM</sub>. They have tested in parallel the leaching of cladded fuel segments and fuel fragments. The tests were performed with the standard leachant in autoclaves under Argon/hydrogen gas atmosphere (i.e. under reducing conditions). Samples of the leachate were taken at regular time intervals, without renewal of the solution, i.e. in static mode. The IRF of relevant radionuclides such

as I, Cs, Tc, Sr and U isotopes was determined and reported for test durations up to 245 days. The autoclave set-up also allowed the measurement of the fission gas release during the leach tests. A test with cladding an adhering residues was prepared as well, but these results were not yet available at the end of the project.

A method for the extraction and determination of  $^{14}\text{C}$  has been developed. The method allows the separation and quantification of inorganic and organic  $^{14}\text{C}$  species in gaseous and aqueous samples. A scheme is shown in **Fig. 12**. The analytical separation procedure involves several steps (i.e. acid stripping and wet oxidation) during which the inorganic and organic carbon fractions are extracted and converted into  $\text{CO}_2$  which is then absorbed in washing bottles containing 2 M NaOH. A catalytic furnace between two sets of washing bottles ensures oxidation of reduced compounds like CO or  $\text{CH}_4$ . The content of  $^{14}\text{C}$  (weak  $\beta^-$  emitter) in the NaOH solutions is determined by liquid scintillation counting (LSC). Tests performed with inorganic and organic  $^{14}\text{C}$  reference materials indicated that the chemical yield of the separation method is > 88% for both the inorganic as well as the organic  $^{14}\text{C}$  fractions. The efficiency of the catalytic furnace was successfully tested using  $\text{CH}_4$  with a yield of ~99% for the conversion of methane to  $\text{CO}_2$ .



**Fig. 12** Scheme of the  $^{14}\text{C}$  extraction procedure

**JRC-ITU** has performed leach experiments on a spent BWR UOX fuel with an average burn-up of 42.22  $\text{Gwd/t}_{\text{HM}}$ . They have tested in parallel the leaching of cladded fuel segments and fuel powders that were taken separately from the core zone and the rim zone of the fuel. The tests were performed with the standard leachant in glass test tubes under air atmosphere (i.e. under oxidizing conditions). At each sampling, the leachate was completely renewed, so the tests were done in pseudo-dynamic mode. The IRF of I, Cs, Tc, Sr, Rb, Mo and U isotopes was determined and reported for test durations up to 190 days.

An analytical method has been developed for the determination of  $^{90}\text{Sr}$  at ultratrace levels using the seaFAST system and ICP-MS detection. A method for the determination of  $^{79}\text{Se}$  species at trace levels by high resolution ICP-MS coupled to an automated chromatographic system has been developed. The analytical figures of merit of the method for the determination of  $^{90}\text{Sr}$  at ultratrace levels are a detection limit of 36  $\text{fg/g}$  (0.2  $\text{Bq/g}$ ) representing an absolute amount of 9  $\text{fg}$  (50  $\text{mBq}$ ). The repeatability is below 2%. The method has been tested using nuclear spent leachates analogues prepared in a buffer of NaCl 19  $\text{mol/L}$  and  $\text{NaHCO}_3$  1  $\text{mmol/L}$  pH 8.06 with a uranium concentration

from  $1 \times 10^{-7}$  to  $10^{-5}$  mol/L. The method to determine  $^{79}\text{Se}$  species at trace levels was applied to diluted nuclear spent fuel leachates analogues consisting in a buffer solution (NaCl 19mM,  $\text{NaHCO}_3$  1 mM pH 7.4) with uranium concentration varying from  $10^{-7}$  to  $10^{-5}$  M with individual Se species in different concentrations. The detection limit is 12 pg/g, representing an absolute amount of 3 pg, with repeatability between 0.2 and 1 %. The method preserves Se species presents in the sample.

**PSI** has performed leach experiments on a spent BWR UOX fuel with an average burn-up of 57.5  $\text{GWd/t}_{\text{HM}}$ , spent PWR UOX fuel with an average burn-up of 56.5  $\text{GWd/t}_{\text{HM}}$ , and spent MOX fuel with an average burn-up of 63  $\text{GWd/t}_{\text{HM}}$ . They have tested in parallel the leaching of cladded fuel segments, the leaching of fuel fragments, and the leaching of separated claddings with some adhering fuel residues. The tests were performed with the standard leachant in glass columns under air atmosphere (i.e. under oxidizing conditions). After 7 days, the leachate was removed completely and then replaced by fresh leaching solution. Afterwards, samples of the leachate were taken at regular time intervals, without renewal of the solution, i.e. in static mode. The IRF of I and Cs isotopes was determined and reported for test durations up to 182 days. Tests with completely cleaned claddings (without fuel residues) were planned as well, but the results were not yet available at the end of the project. In collaboration with Studsvik, samples of the BWR fuel were analysed with micro-XRF and micro-XAS to determine the selenium distribution on the micro-scale, its oxidation state and its structural environment (next-neighbour distances and coordination numbers).

**SCK-CEN** has performed leach experiments on a spent PWR UOX fuel with an average burn-up of 50.5  $\text{GWd/t}_{\text{HM}}$ . They have tested in parallel the leaching of cladded fuel segments and opened fuel segments where the cladding and fuel fragments are separated from each other but leached together. The tests were performed with the standard leachant in glass columns under air atmosphere (i.e. under oxidizing conditions), identical to the columns used by PSI. After two complete leachate renewals in the first days, samples of the leachate were taken at regular time intervals, without further renewal of the solution, i.e. in static mode. The IRF of I and Cs isotopes was determined and reported for test durations up to 357 days. Apart from these, many other isotopes were analysed, among others  $^{14}\text{C}$ ,  $^{99}\text{Tc}$  and  $^{238}\text{U}$ .

**CTM** has performed leach experiments on a spent BWR UOX fuel with an average burn-up of 45  $\text{GWd/t}_{\text{HM}}$ . They have tested in parallel the leaching of cladded fuel segments and fuel powders that were taken separately from the core zone and the rim zone of the fuel. The tests were performed with the standard leachant in glass test tubes under air atmosphere (i.e. under oxidizing conditions). At each sampling, the leachate was completely renewed, so the tests were done in pseudo-dynamic mode. The IRF of I, Cs, Tc, Sr, Rb, Mo and U isotopes was determined and reported for test durations up to 190 days. The experiments of CTM were performed in the laboratories of JRC-ITU. CTM has collaborated with JRC-ITU also for the improvement of the analytical procedures for the measurement of  $^{90}\text{Sr}$  and  $^{79}\text{Se}$  (see higher under activities JRC-ITU).

**Studsvik** has performed leach experiments on samples of six types of a spent fuel, i.e.

- BWR UOX fuels with an average burn-up of 50.2  $\text{GWd/t}_{\text{HM}}$  (test on cladded segment), 54.8  $\text{GWd/t}_{\text{HM}}$  (test on cladded segment), and 57.1  $\text{GWd/t}_{\text{HM}}$  (test on fragments + separated cladding)
- An Al/Cr doped BWR UOX fuel with a burn-up of 59.1  $\text{GWd/t}_{\text{HM}}$  (test on fragments + separated cladding)

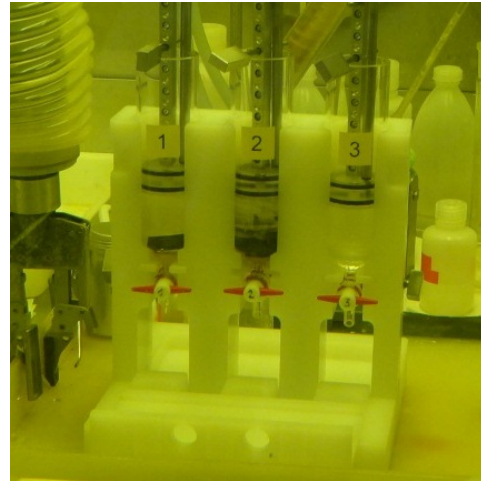
- A Gd doped PWR UOX fuel with an average burn-up of 54.4 GWd/t<sub>HM</sub> (test on fragments + separated cladding)
- A spent PWR UOX fuel with an average burn-up of 70.2 GWd/t<sub>HM</sub> (test on fuel powder)

The tests on clad fuel segments and fuel fragments + separated cladding were performed with a slightly modified standard leachant (10 mM NaCl and 2 mM NaHCO<sub>3</sub>) in glass test tubes under air atmosphere (i.e. under oxidizing conditions). At each sampling, the leachate was completely renewed, so the tests were done in pseudo-dynamic mode. The IRF of I, Cs, Tc, Sr, Rb, Mo, Se, U and many other isotopes was determined and reported for test durations up to 364 days. The tests on fuel powder were performed using a simultaneous grinding and leaching method. Laser Ablation Inductively Coupled Plasma Mass Spectroscopy analyses was applied on fuel cross-sections from the BWR fuel with burn-up 57.1 MWd/t<sub>HM</sub> and the Al/Cr doped BWR fuel, to reveal the radial profile of Cs, I and Se.

Examples for the different experimental devices for the dissolution based release investigations are shown in **Fig. 13**.



KIT



SCK-CEN



PSI



Studsvik

**Fig. 13** Set-up for dissolution based IRF measurements used by some beneficiaries

**MTA EK** has collected and interpreted the isotopic dissolution data of damaged and leaking VVER fuels that had been stored in storage pools in the period 2003-2007 (damaged fuel) and 2009-2010 (leaking fuel). The damaged fuels had a burn-up in the range 10.1-26.7 GWd/t<sub>HM</sub>. The leaking fuel had a burn-up of 14 GWd/t<sub>HM</sub>. The leachant was in this case the water of the storage pool. In the case of the damaged fuel, the pH of water was ≈7 in the first 14 days after the incident (15 g boric acid per kg of water) and ≈4-4.5 (21 g boric acid per kg of water) in the remaining period, with measurements up to 1368 days. In the case of the leaking fuel, measurements up to 369 days are available. During the storage, the water purification system has led to periods of increasing and decreasing radionuclide concentrations. The dissolution rate was calculated in various ways for a series of isotopes, such as Cs, I and U isotopes.

An overview of the leach test matrix is given in **Tab. V**.

**Tab. V** Overview of the leach test matrix of WP3, with for each tested fuel the burn-up in GWd/t<sub>HM</sub> and the involved laboratory.

	<b>Cladded fuel segments</b>	<b>Opened cladding + fuel fragments</b>	<b>Fuel fragments (mm size)</b>	<b>Fuel powder</b>	<b>Cladding + adhering residues</b>	<b>Cleaned Cladding</b>
	Burn-up (GWd/t <sub>HM</sub> )	Burn-up (GWd/t <sub>HM</sub> )	Burn-up (GWd/t <sub>HM</sub> )	Burn-up (GWd/t <sub>HM</sub> )	Burn-up (GWd/t <sub>HM</sub> )	Burn-up (GWd/t <sub>HM</sub> )
<b>PWR</b>	50.4 (KIT) 50.5 (SCK) 56.6 (PSI)	50.5 (SCK)  54.4 (Stud)*	50.4 (KIT)  56.6 (PSI)	   70.2 (Stud)	50.4 (KIT)  56.6 (PSI)	56.6 (PSI)
<b>BWR</b>	42.2 (ITU) 50.2 (Stud) 54 (CTM) 54.8 (Stud) 57.5 (PSI)	57.1 (Stud) 59.1 (Stud) <sup>#</sup>	57.5 (PSI)	42.2 (ITU) <sup>†</sup>  54 (CTM) <sup>†</sup>		57.5 (PSI)
<b>MOX</b>			63 (PSI)			63 (PSI)

\*Gd doped; <sup>#</sup> Al/Cr doped; <sup>†</sup> separately for rim and core.

The exact experimental setup of the leach tests was different for the various laboratories. Some partners replace the solution completely after sampling (pseudo-dynamic experiments), other partners took samples aliquots without renewing the solution after sampling (static experiments).

The equipment and procedures were not standardised. The measured isotopes/elements determined by the dissolution based experiments are listed in **Tab. VI**.

**Tab. VI** IRFs of isotopes/elements determined by dissolution based experiments

	<sup>14</sup> C	Kr+Xe	<sup>79</sup> Se	Rb	<sup>90</sup> Sr	Mo	<sup>99</sup> Tc	Pd	<sup>129</sup> I	<sup>137</sup> Cs	U	Pu
KIT		x			x		x		x	x	x	
ITU				x	x	x	x	x		x	x	
PSI									x	x		
SCK-CEN	x				x	x	x	x		x	x	x
CTM				x	x	x				x	x	
Studsvik			x		x	x	x		x	x	x	

Analytical methods were developed and tested by several partners. JRC-ITU developed methods for the determination of pure  $\beta$  emitters (<sup>79</sup>Se, <sup>126</sup>Sn, <sup>135</sup>Cs, <sup>90</sup>Sr) based on sequential injection flow analysis coupled to ICP-MS [37, 39]. Studsvik developed a Laser Ablation ICP-MS technique for specific investigations of the selenium distribution in SNF pellets. PSI elaborated X-ray absorption near-edge structure ( $\mu$ -XANES) spectroscopy which allowed the determination of the chemical state of Se bound in the SNF. KIT installed an analytical setup in a glovebox for <sup>14</sup>C analytics.

#### 4.4.2 Results obtained in WP3

Until recently, the IRF of spent fuel was often related to its burn-up. With more data becoming available for high burn-up fuel, there is growing evidence that the fission gas release (FGR) and IRF depends much more on the linear power rating of the fuel than on the burn-up. The data gathered in FIRST-Nuclides give further convincing evidence for this. Hence, the linear power appears to be a more relevant operational parameter to predict the FGR than the burn-up is. This can be explained by the fact that the FGR depends on the temperature of the fuel pellet in the operator, and this temperature depends on the linear power, rather than on the burn-up.

The measurements of the FGR during the leach test by KIT have shown that FGR takes place also during the leaching of the fuel. The amount of fission gases released in this way appears to be higher than the amount of fission gases released in the plenum during the fuel operation.

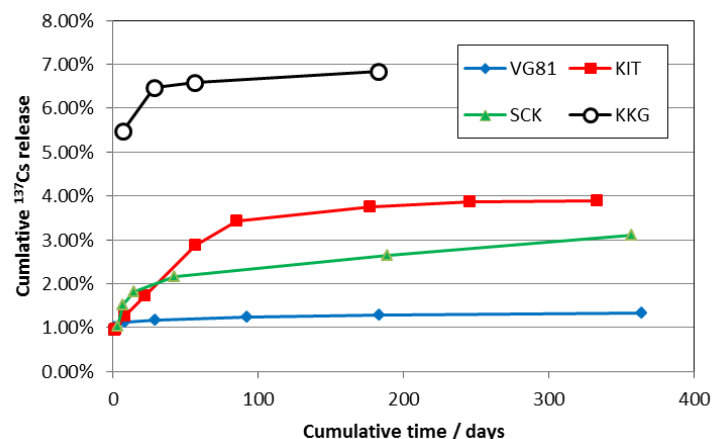
The cumulative IRF measurements for <sup>137</sup>Cs and <sup>129</sup>I determined for pellets and segments from PWR and BWR SNF samples obtained in FIRST-Nuclides are shown in **Fig. 14**, **Fig. 15** and **Fig. 16**. The characterization of the samples defined in the legend of the figures is listed in **Tab. III** and **Tab. IV**. The IRF values measured for Cs tend to be proportional to the FGR with a proportionality factor of 0.6. The IRF values measured for I tend to be proportional to the FGR with a proportionality factor of 1. The difference between the Cs or I release and FGR appears to increase in absolute terms with higher FGR, where the FGR increasingly overestimates the Cs or I release. To explain the increasing differences, a detailed analysis of each test needs to be performed. From the perspective of performance assessment, the upwards deviations (i.e. IRF >0.6 x FGR for caesium, or >1 x FGR for

iodine) are more relevant than the downwards deviations. To include all measurement points, both from FIRST-Nuclides and from older experiments, an extra term should be added.

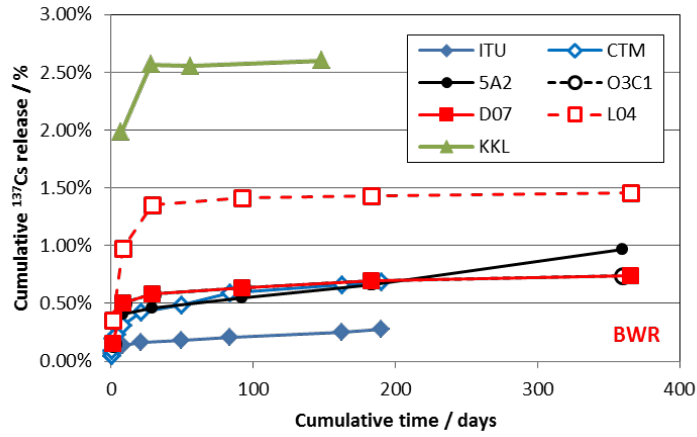
The IRF of Cs or I determined from differently prepared samples (clad segments, opened segments, fragments, powders...) are coherent. They depend on the exposed surface area and the nature of the exposed fuel structures (gap or grain boundaries). These data can be used further to estimate the relative contributions of the various fuel structures.

The Cs dissolution rate decreases with time in the leach tests. The net dissolution rates measured for the damaged and leaking VVER fuel (after subtraction of the  $\text{UO}_2$  matrix dissolution) are of the same order of magnitude as the rates determined in the leaching tests, and also decrease with time. Nevertheless, in almost all leaching experiments, a residual dissolution rate of Cs isotopes was measured for the longest test durations. This means that the measured IRF for the longest duration ( $\leq 1$  year) may not be the long-term maximum. The net Cs dissolution rates measured in the leach tests were all significantly higher than the expected long term  $\text{UO}_2$  matrix dissolution rate, even for the tests in reducing conditions by KIT. Extrapolation, preferably supported by modeling, is necessary to estimate the time required for the complete release of IRF nuclides. The long-term matrix dissolution rate, and the time it will take before the release of IRF radionuclides is controlled by this matrix dissolution, will depend on the redox conditions. In reducing conditions, the matrix dissolution rate will be much lower than in oxidizing conditions. Moreover, matrix oxidation tends to open grain boundaries and thus causes the continuous exposure of fresh grain boundaries with high concentrations of soluble IRF nuclides.

The IRF values measured in the leach tests can be compared with Performance Assessment oriented best estimate and pessimistic IRF estimations from a previous program (NF-PRO). It appears that Cs and I are confirmed as the most important IRF isotopes, and that the previous pessimistic estimates may still underestimate the IRF of fuels that have undergone a high linear power rating. The new IRF data available for  $^{14}\text{C}$  and Pd suggest that the previous estimations may be too pessimistic. The previous estimates for Sr and Tc are roughly confirmed by the new results. Se and Sn (left out as IRF nuclides in NF-PRO) may have small IRF contributions.

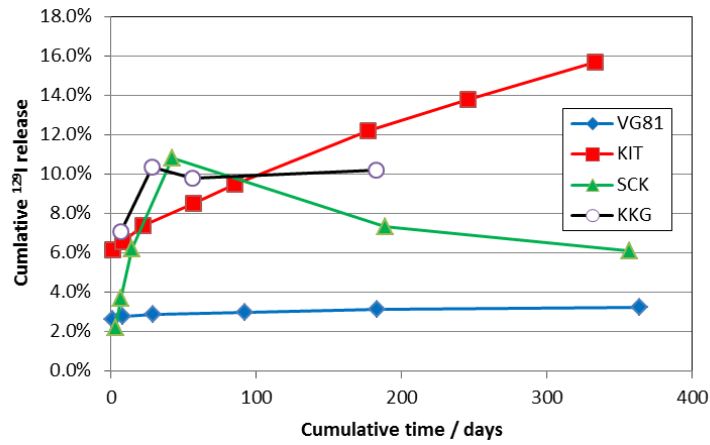


a) Cumulative IRF of  $^{137}\text{Cs}$  as function of time from PWR SNF pellets / segments

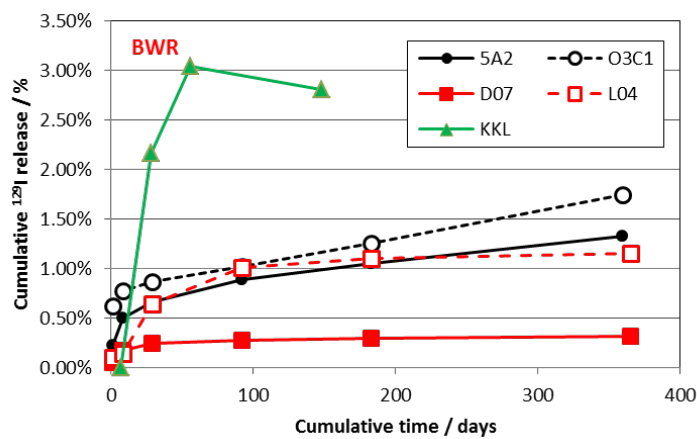


b) Cumulative IRF of <sup>137</sup>Cs as function of time from BWR SNF pellets / segments

**Fig. 14** Cumulative IRF of <sup>137</sup>Cs from various spent nuclear fuel samples investigated in FIRST-Nuclides



a) Cumulative IRF of <sup>129</sup>I as function of time from PWR SNF pellets and segments

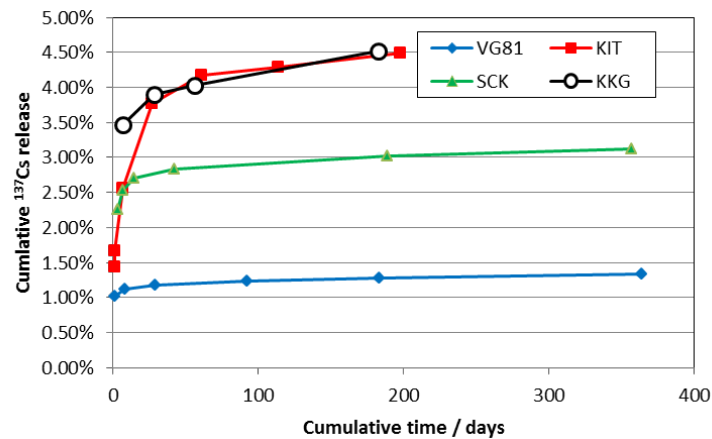


b) Cumulative IRF of <sup>129</sup>I as function of time from BWR SNF pellets and segments

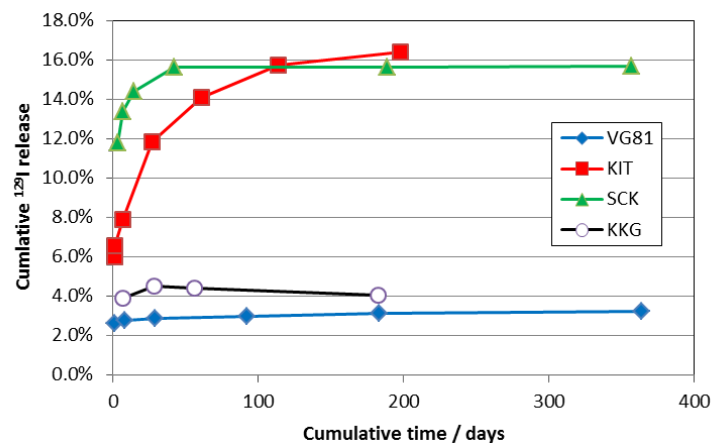
**Fig. 15** Cumulative IRF of <sup>129</sup>I from various spent nuclear fuel samples investigated in FIRST-Nuclides



The doping of  $\text{UO}_2$  with Al/Cr (O3C1) appears to have a favorable effect on the IRF, which is probably due to the fact that the larger grain size increases the distance over which Cs and I have to diffuse before they reach the grain boundary.



a) Cumulative IRF of  $^{137}\text{Cs}$  as function of time from PWR SNF fragments



b) Cumulative IRF of  $^{129}\text{I}$  as function of time from PWR SNF fragments

**Fig. 16** Cumulative IRF of  $^{137}\text{Cs}$  and  $^{129}\text{I}$  from various PWR fragment SNF samples

## 4.5 Modelling of migration/retention processes of fission products in the spent fuel structure

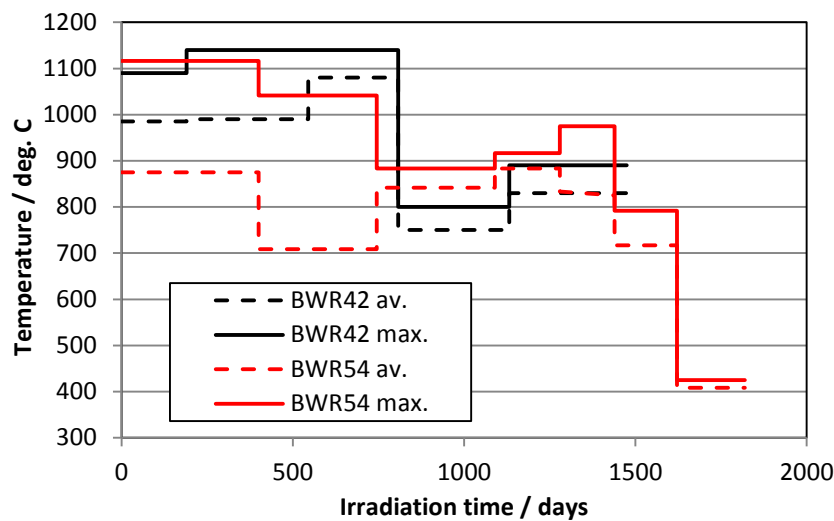
Modelling of migration/retention processes of fission products in the spent fuel structure was performed in WP 4 “**Modelling**”. The objectives of the WP 4 covered (1) determination of boundary condition of the SNF samples, (2) the initial speciation of fission products in LWR fuel, (3) multi-scale modelling of the migration / retention processes of fission products in the HBU spent fuel, in the cladding, and (4) the estimation of the fission product total release through the spent fuel rod. A

semi-empirical model was developed to predict fission product release to water from gap, grain boundaries and grains. This WP was led by Joan de Pablo, CTM.

Three institutions were involved in WP4: KIT, AMPHOS 21 and CTM-UPC. ITU provided for a contribution related to the use of the TRANSURANUS code for calculation of the centreline temperatures of the fuels BWR42 (JRC-ITU) and BWR54 (CTM).

INE-KIT focused its modelling on boundary conditions of the fuel samples investigated in WP 2 and 3, such as rod temperatures during irradiation in power plants, fission products diffusion as a function of the temperature during reactor operation as well as on the carbon ( $^{14}\text{C}$ ) compound formation based on thermodynamic calculations. AMPHOS 21 modelled water saturation of segmented fuel samples due to micro and macro-cracks. CTM-UPC developed and semi-empirical model from spent fuel leaching experiments to understand location of some relevant radionuclides in the fuel.

TRANSURANUS calculations were performed for the SNF BWR42 and BWR54 used by JRC-ITU and CTM, respectively. The calculations of the centreline temperatures at the position of the fuel samples (as maximum and average for each irradiation cycle) are based on data reported by the utility for BWR42, while the temperature profile of BWR54 was estimated from irradiation power history data using the TRANSURANUS code. The maximum temperature for both fuels was around  $1100^\circ\text{C}$ . In the first 1500 hours irradiation time the average was between  $\sim 700^\circ\text{C}$  to  $\sim 1000^\circ\text{C}$  [62].



**Fig. 17** Calculated centreline temperatures of BWR42 and BWR54 as function of the burn-up time

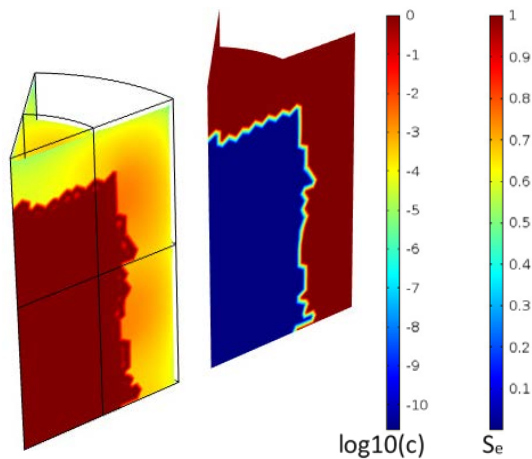
KIT performed calculations of burn-up, thickness and porosity of rim zone for initial and boundary conditions of a fuel sample with a burn-up of  $50.4 \text{ GWd}/t_{\text{HM}}$ , as well as Xe location in this zone [63]. Combined thermodynamic considerations with experimental investigation aimed on the speciation of  $^{14}\text{C}$  in the spent nuclear fuel matrix. Carbon-14 is a key radionuclide in the safety assessment and in disposal concepts it is assumed, that  $^{14}\text{C}$  bearing species are not retained.  $^{14}\text{C}$  is an activation product in spent nuclear fuel (SNF) showing low concentrations; its chemical speciation is widely unknown. After formation of  $^{14}\text{C}$  by a  $^{14}\text{N}(n,p)^{14}\text{C}$  reaction, the highly excited and charged carbon competes with available reactants within the fuel matrix and will likely form either oxides or in reactions with metals, carbides. In contact with water, these compounds react by forming carbonates or

hydrocarbons. The potential for the formation of oxides or carbides was investigated. Free energy of formation for some relevant carbides and oxides were provided. The results of thermodynamic considerations for  $^{14}\text{C}$  were compared with experimental gas measurements. According to the initial nitrogen concentration in the fuel between 4 and 11 ppm, the maximal nitrogen content of KIT's fuel rod sample was estimated to be  $2.1 \times 10^{-4}$  mol. Using the KKG operation characteristics, a formation of  $4.3 \times 10^{-6}$  mol  $^{14}\text{C}$  was expected whereas the measured amount of  $^{14}\text{CO}_2$  was only  $7.2 \times 10^{-7}$  mol, corresponding to 17% of the total measured  $\text{CO}_2$ . However, the speciation of  $^{14}\text{C}$  is not yet resolved [64].

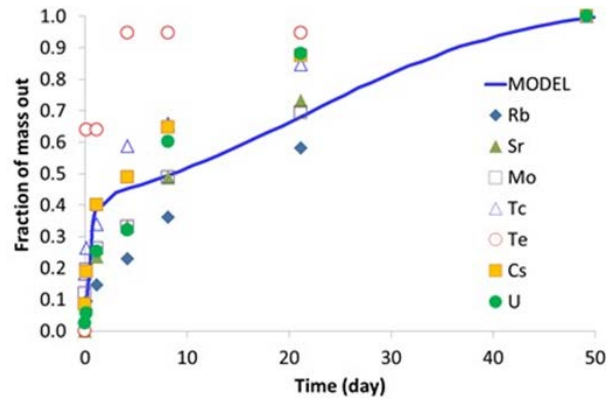
KIT also studied the behaviour of fission products on the fuel rod by modelling the temperature and diffusion coefficient of some radionuclides. Modelling was able to explain experimental LA-ICP-MS results. Some other results were shown from this modelling such as: i) Small gaps between the pellets or between pellet and cladding affect the temperature significantly; ii) Radial distribution of I, Xe, Se and Cs in a spent fuel pellet was modelled by assuming a temperature-dependent sorption; iii) The calculated total concentration in the colder region of the pellet corresponds to LA-ICP-MS measurements; iv) Calculated release of volatile radionuclides into the gap regions corroborate with the fission gas release (FGR) and v) After discharge from the reactor, diffusion processes of volatiles do not play any role due to the negligible diffusion coefficients at interim storage temperature [65].

AMPHOS 21 proposed a conceptual model that assumes that the rate of release for some radionuclides from a SNF pellet (or a fragment of it) upon contact with water is controlled by the wetting of surfaces of cracks present in the pellet. Calculations were carried out to quantify the mass (moles) of radionuclides released from the crack surfaces and accumulated in the external reservoir as a function of time. This allows direct comparison with data available from laboratory leaching experiments.

Modelling results indicate that wetting of crack surfaces present in a SNF pellet may quantitatively explain radionuclide release patterns observed in laboratory leaching experiments performed on SNF pellets or their fragments. Specifically, the time scales of initial fast radionuclide release and the later slower releases are on a scale comparable with the times calculated for complete saturation of the "macro" and "micro" crack systems. The proposed model is capable of capturing these general trends in a semi-quantitative manner. In order to increase the predictive capacity of the model further data on the statistical properties of cracks and on the distribution of radionuclides on the surfaces of cracks is needed [66-68].



**Fig. 18** Tracer concentration (left) and saturation with water (right) calculated in “macro cracks” for a 3 hours exposure time.



**Fig. 19** Modelling of experimental laboratory data of normalised radionuclide release from SNF pellet under the assumption that 40% of total tracer mass is initially associated with “macro cracks”.

Furthermore, a literature study was performed for models which are used by the utilities and other institutions for calculating the fission products release from spent nuclear fuel. The potential applicability for the CP FIRST-Nuclides was estimated [69].

CTM-UPC developed a semi-empirical model based on the experimental fitting by using three different first-order kinetic equations corresponding to different parts of the fuel: gap, cracks, external or internal grain boundaries, rim structure, and finally grains (matrix). This model was applied to different spent fuel samples: segmented vs. powder, 6 different burn-ups (42, 48, 52, 53, 54 and 60 GWd/t<sub>HM</sub>) and PWR fuel vs. BWR fuel [70-72]. The behavior of the following fission products was studied: Cs, Sr, Tc, Mo and Rb; moreover U was also studied as matrix dissolution indicator.

Normalized dissolution rate of caesium is always higher than for the rest of measured radionuclides, especially when looking at results obtained from cladded samples. For powder samples this trend is also observed except for Rb, which shows more similar release rates. This is also true for Sr rates obtained for PWR samples. This is assumed to be due to the degree of matrix segregation. The higher the fraction of a radionuclide is segregated, the higher is its release because it is supposed that this release is practically instantaneous as soon as the water gets in contact with them. In general, the percentage of radionuclide released is higher for powdered than for cladded samples, except in the case of Cs in PWR samples. It can be assumed that for Cs, its content in gaps and fractures is similar than its content in grain boundaries and micro fissures, which is not the case for the rest of radionuclides, that show greater content in grain boundaries due to their lower migration once segregated from the matrix. When comparing PWR and BWR fuel samples, clear differences in terms of normalized release rates are observed, being the values obtained for PWR fuels larger than for BWR fuels. Such differences become more significant when looking to Cs and Rb and to some extent to Sr, which are the ones expected to be segregated from the matrix in higher degrees. When looking at the percentages dissolved, they seem to be higher for pellets (higher availability to water) than for powders, except for Cs and PWR fuels.

## 4.6 WP 5 Knowledge, reporting and training

Documentation, dissemination of the generated knowledge and training activities were performed in WP5 “Knowledge, reporting and training”. This workpackage was led by Alba Valls, AMPHOS21.

Three different tasks were performed within this WP:

### 1. Dissemination activities

A high amount of dissemination activities has been performed and different ways of disseminate have been exploited. Some examples are listed below:

- Generic poster
- Newsletters
- Deliverables
- Web portal
- Annual workshops
- Presentation at international conferences
- Peer review publications

### 2. State of the Art report

The most important achievement in WP 5 was the report on the state-of-the-art before the CP FIRST-Nuclides, the interim and the final up-date of the state-of-the-art including the results obtained mainly in WP 3. The data discussed in the state-of-the-art reports are collected in an Excel based database including the fuel specific data collected in WP1 [2, 73].

More information on these database is provided in Section 5.7.

### 3. Training activities

The four main actions done with the aim of providing training and education to young scientist are briefly described below.

- Lab-Exchange meeting: 17 participants from four partner institutions (KIT-INE, JRC-ITU, Studsvik and PSI) have attended at this meeting organized by PSI on March 2013. The aim of the meeting was to serve as a discussion forum for experimentalists of the project to discuss analytical and technical experimental details.
- Organization of a training course: KIT-INE, JRC-ITU and AMPHOS21 organized a training course (9<sup>th</sup> - 10<sup>th</sup> July 2013, Karlsruhe). The course focused on the radionuclide release from LWR spent nuclear fuel (SNF), experimental methods available to quantify radionuclide release and relevant characteristics of LWR SNF. Twelve participants attended the course, from six project partners and three associated groups.
- Training mobility measures: The project has allocated resources for three training mobility measures, which consider the visit of one student from a participant institution to a different partner organization.

- 7 travel grants to attend the Final workshop: 7 PhD students have taken advantage of the travel grants. The grant covered travelling, accommodation and workshop fee expenses in order young people have the opportunity of attending the final workshop of the project.

## 5 Outcome and discussion of CP FIRST-Nuclides results

The outcome of the CP FIRST-Nuclides is documented in detail in the proceedings of the project workshops [37-39]. A series of conference contributions [3, 74, 75] reported the ongoing work of the project and publications covered specific investigations and results [55, 76]. In this chapter, the state of the art on the fast/instant release of radionuclides from SNF after finalization of the CP FIRST-Nuclides will be explained.

The WP3 “Dissolution Based Release Studies” covered the biggest part of the CP FIRST-Nuclides investigations. The SNF source term is described as a combination of radionuclide releases from three different inventories located in the fuel: radionuclides released (1) from the gaps between the pellets or between cladding and fuel, (2) from grain boundaries and (3) by co-dissolution with the UO<sub>2</sub> matrix (grains). Each release process successively prevails among the global radionuclide release. The first two fractions, the release from gaps and grain boundaries are combined in the so-called instant release fraction (IRF) [35, 77, 78]. The released radionuclide fraction is given by eq. 3 as function of time and can be different for different radionuclides:

$$F_{RN}^{total}(t) = F_{RN}^{gap}(type) + F_{RN}^{GB}(t, type) + F_{RN}^{matrix}(t, type, chemistry) \quad (\text{eq. 3})$$

$F_{RN}$ : fraction of radionuclide released                      t: time                      gap: accessible surfaces

type: type of fuel, burn-up, power rate, etc.                      GB: grain boundaries

chemistry: leaching conditions, groundwater composition                      matrix: UO<sub>2</sub> grains.

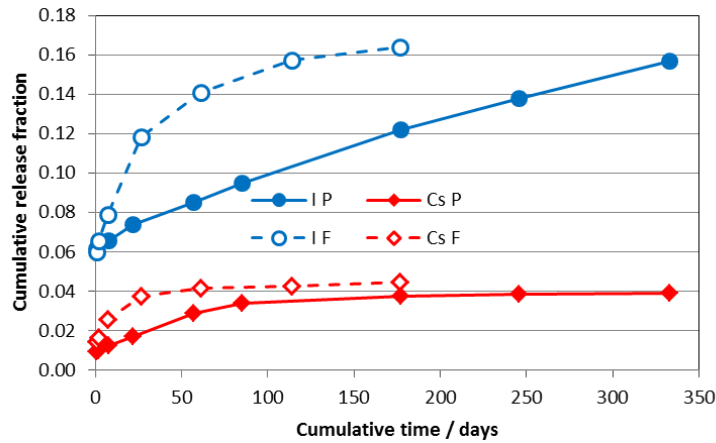
Johnson [77] published time dependencies for the release mechanisms for low burn-up Candu fuel.

### 5.1 Dependence of IRF on SNF sample properties

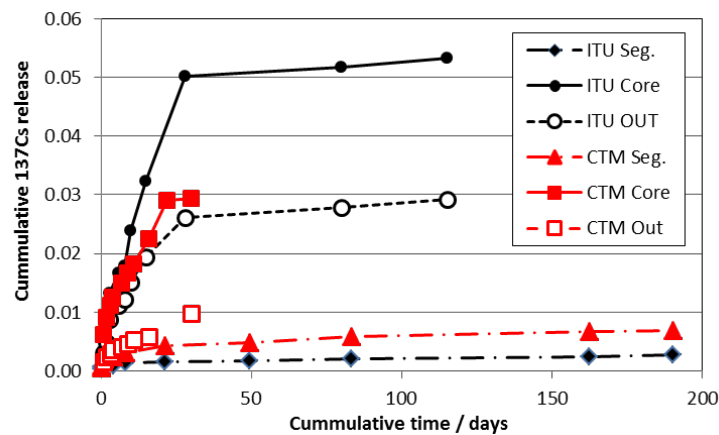
In safety analysis of nuclear waste disposals, a huge variety of different SNF needs to be considered. Some irradiation data of these SNF are available, such as the reactor type, initial enrichment, burn-up, the calculated FGR and partly the linear power rates. To estimate the total IRF of safety relevant radionuclides, correlations between measured IRFs and the irradiation data are desirable. For this reason, CP FIRST-Nuclides aimed on relating the IRFs with different parameters of the SNF under investigation. Another example for characteristic parameters are the size and preparation of SNF samples for leaching tests.

**Fig. 20** and **Fig. 21** show comparisons of IRF over the time for different sample preparations as an example for the dependency of the IRF from the size and preparation of a SNF sample. The graphs show IRF measured from pellets, segments, and powders. In **Fig. 20**, the cumulative IRF of Cs and I

leached from clad pellet and fragment of the same PWR SNF (KIT 50.4 GWd/t<sub>HM</sub>) is given, **Fig. 21** presents the Cs IRF for two BWR fuels (ITU: 45 GWd/t<sub>HM</sub>, CTM: 54 GWd/t<sub>HM</sub>) for segments cut through the middle of a pellet, and powders obtained by drilling in the core and in the rim region of a pellet.



**Fig. 20** Comparison of cumulative IRF of <sup>137</sup>Cs and <sup>129</sup>I leached from clad pellet (P) and fragment (F) of the same PWR SNF (KIT 50.4 GWd/t<sub>HM</sub>).



**Fig. 21** Comparison of cumulative <sup>137</sup>Cs IRF as function of time for 2 different BWR fuels (45 / 54 GWd/t<sub>HM</sub>) for segments (Seg.), powder drilled from the core and in the rim region.

The cumulative fraction of inventory of an element *i* released into the aqueous phase is given by the following equation which is the same as for the FIAP (Fraction of Inventory in the Aqueous Phase):

$$IRF(i) = \frac{m_{i,aq}}{m_{i,SNF}} = \frac{c_i \cdot V_{aq}}{m_{SNF} \cdot H_i} \quad (\text{eq. 4})$$

$m_{i,aq}$ : mass of dissolved RN<sub>i</sub>

$c_i$ : concentration of RN<sub>i</sub>

$m_{SNF}$ : mass of SNF in the test

$m_{i,SNF}$ : mass of RN<sub>i</sub> in the SNF

$V_{aq}$ : volume of leachant

$H_i$ : fraction of inventory of RN<sub>i</sub>

The same equation is used for the calculating the fission gas release into the gas phase during the leaching experiments by replacing  $m_{i,aq}$  by  $m_{i,gas}$  (mass in the gas phase). In the following chapters the instant release rate is used, which is the deviation of the IRF(i) with respect to the time  $\frac{d}{dt} IRF(RN_i)$ .

**Fig. 20** shows for Cs an IRF of about 4 % for the 50.4 GWd/ $t_{HM}$  sample in both kind of samples: pellet and fragment. In **Fig. 21**, the 2 segments cut from the middle of pellets reveal IRF(Cs) below 1 %. For the powders, the lower burn-up SNF (ITU) show a higher IRF after an initial phase of some 30 days in comparison to the 54 GWd/ $t_{HM}$  SNF (CTM). The reason is attributed to the different fines fractions of the powders due to different sieving procedures for the two materials [62]. However, **Fig. 17** shows a significantly higher temperature and stay at the elevated temperatures for lower burn-up fuel BWR 42.

The 50.4 GWd/ $t_{HM}$  samples indicate that the sample characteristic shows effect on the initial phase of a leaching experiment, only. **Fig. 20** and **Fig. 21** shows that the cumulative IRF(Cs) curves approach a maximum value which is different for the different SNF materials. In the case of iodine, it shows a continuous increase of the cumulative IRF(I) over a much longer period of time. The same release behavior is observed for the IRF(FG).

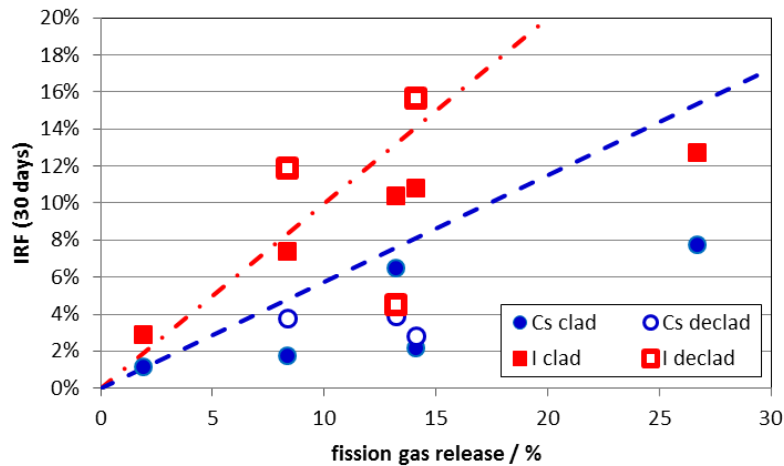
According to Walker [79, 80], the effective diffusion coefficients of Cs and Xe within irradiated  $UO_2$  grains are proportional:

$$D_{eff}^{Cs} = \varepsilon \cdot D_{eff}^{Xe} \quad (\text{eq. 5})$$

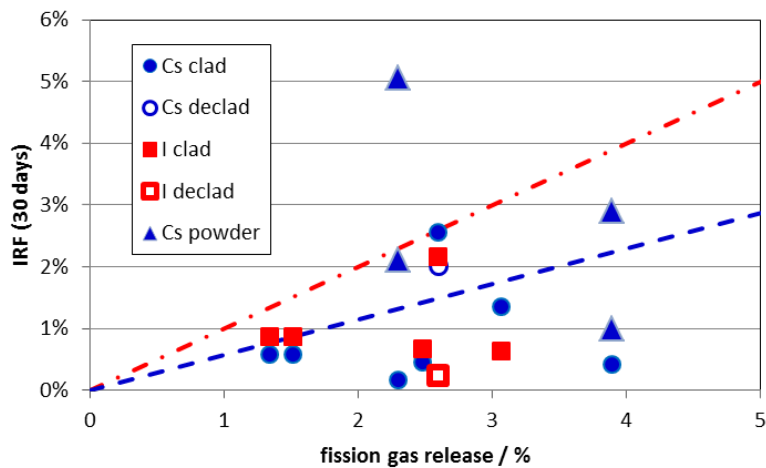
A factor  $\varepsilon = 0.33$  was fitted [81]. The fractional release  $f(t)$  from the grain to the grain boundary, i.e. the intragranular release is calculated by diffusion. Lassmann [81] showed a square root dependency of the diffusion coefficient for the mass of substance diffusing to the grain boundaries. Using eq. 5, the relation of the cumulative release fractions at time  $t$  for Cs and Xe depends on  $\sqrt{\varepsilon}$ . This relation was used in Johnson's discussion on the relation between IRF(Cs) and the FGR [25]. It was stated that due to Lassmann's analysis, the expected dependency of IRF(I) should be linear with the FGR, and the IRF(Cs) proportional to  $\sqrt{0.33} = 0.57$ . In both cases, the measured IRFs were mainly below the expected lines.

In order to test the IRF data obtained in FIRST Nuclides, the IRF(I) and IRF(Cs) are analyzed with respect to the reported rod FGR. **Fig. 22** shows the dependencies for cumulative IRFs after 30 days of leaching for PWR samples (**Fig. 22a**) and BWR samples (**Fig. 22b**) under investigations.





a) PWR



b) BWR

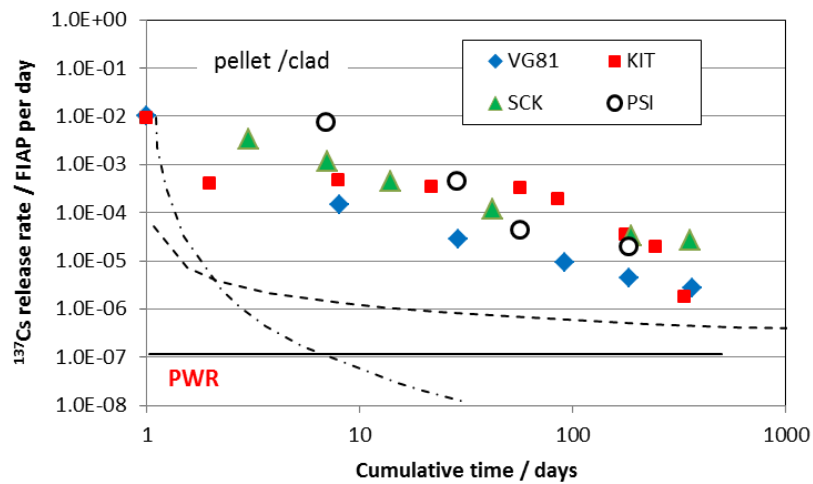
**Fig. 22** Cumulative IRF for Cs and I after 30 days leaching experiments as function of the rod fission gas releases for PWR and BWR fuel samples.

Squares: iodine, circles: caesium, triangles: powders (Cs only), Dashed lines indicate the proportionality and the  $\sqrt{0.33}$  lines.

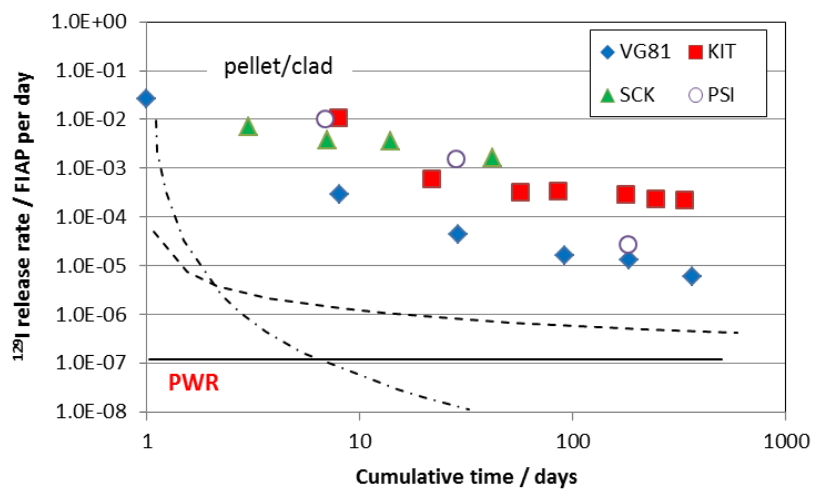
For PWR SNF samples, all IRF(Cs) are found below the  $\sqrt{0.33}$  line, independent on clad, declad or fragmented materials. In the case of iodine, most of PWR samples show IRF below the proportionality. Only for samples which experienced power rates above 300 W/cm, IRF above the proportionality were measured at 30 days. For BWR SNF, the determined IRF for iodine at 30 days is lower in comparison to the PWR samples. All data are recorded below the proportionality. The IRF(Cs) values of the BWR scatter around the  $\sqrt{0.33}$  line. The only outlier was found from a powder sample (BWR42) drilled from the core of a pellet which was irradiated at a relatively high power rate (**Tab. IV**). The described behavior for the IRF of iodine and Cs is found also for longer experimental periods for all kind of SNF.

## 5.2 Gap and grain boundary release

In the previous chapter, the measured cumulative fast / instant release of several nuclides are described. According to Johnson [77], the IRF can be described by a combination of radionuclide release from three different inventories in the SNF. To distinguish between the releases from the gap and grain boundary inventories, the time dependencies of the release mechanisms are analyzed. **Fig. 23** to **Fig. 25** show the release rates defined by differentiation of the measured cumulative IRF with respect to time. In this figures, the theoretical release rates of  $^{137}\text{Cs}$  and  $^{129}\text{I}$  defined by Johnson [77] are shown for comparison. The figures show the release rates from all PWR and BWR samples, clad and declad fragments as well as from SNF powders. In these figures, the time dependencies defined by Johnson are plotted (dash line: gap release, dash-dot line: grain boundary release and solid line: matrix contribution ).

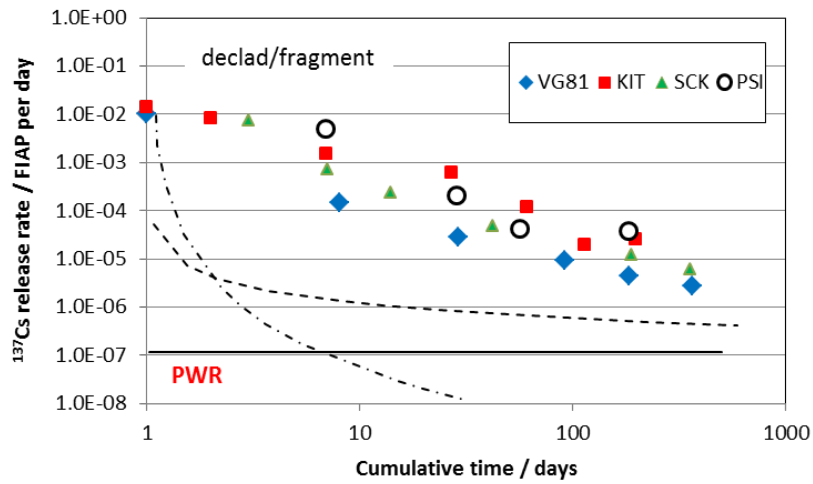


a) Release rate of  $^{137}\text{Cs}$  as function of time from PWR SNF pellets

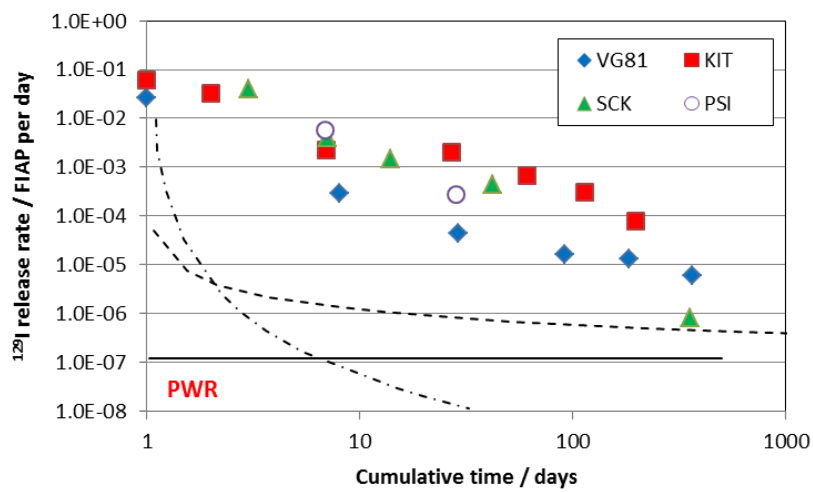


b) Release rate of  $^{129}\text{I}$  as function of time from PWR SNF pellets

**Fig. 23** Release rates of  $^{137}\text{Cs}$  and  $^{129}\text{I}$  from PWR SNF pellets

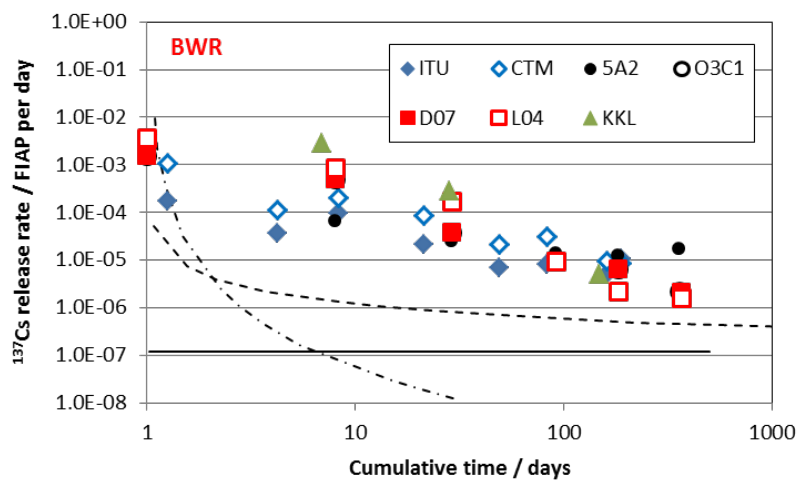


a) Release rate of  $^{137}\text{Cs}$  as function of time from PWR SNF fragments

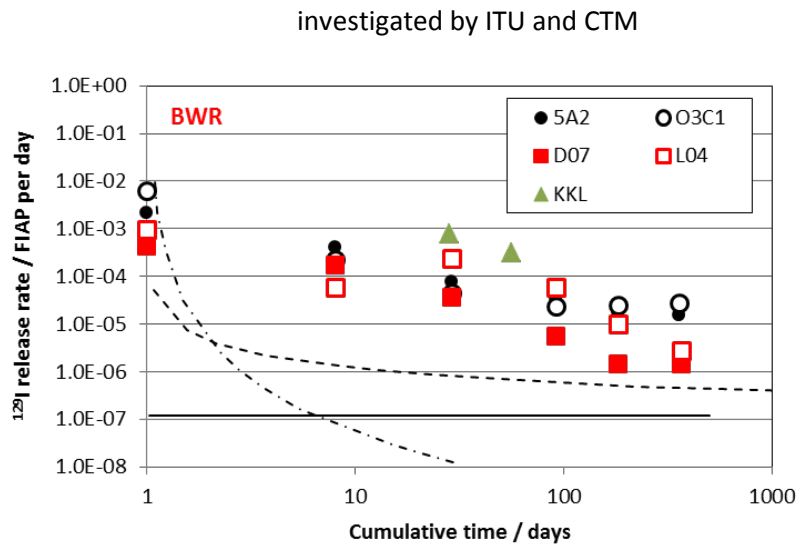


b) Release rate of  $^{129}\text{I}$  as function of time from PWR SNF fragments

**Fig. 24** Release rates of  $^{137}\text{Cs}$  and  $^{129}\text{I}$  from PWR SNF declad fragments

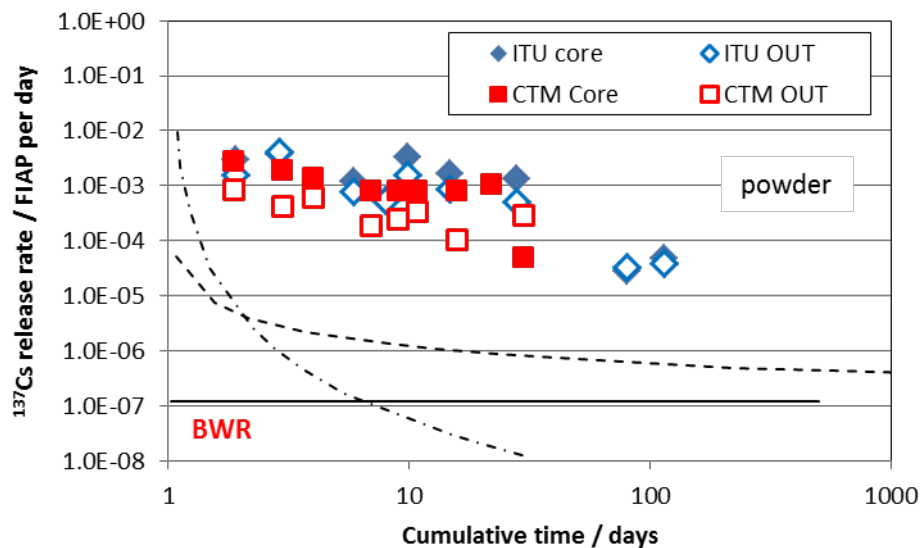


a) Release rate of  $^{137}\text{Cs}$  as function of time from BWR SNF fragments and the slices



b) Release rate of  $^{129}\text{I}$  as function of time from BWR SNF fragments

**Fig. 25** Release rates of  $^{137}\text{Cs}$  and  $^{129}\text{I}$  from various BWR SNF samples



**Fig. 26** Release rates of  $^{137}\text{Cs}$  as function of time for the CORE and OUT BWR powder samples investigated by ITU and CTM

The release rates of  $^{137}\text{Cs}$  determined for the CORE and OUT BWR powder samples show a slightly higher rate for the CORE powders from both SNFs. Significant differences for the two burn-ups and power rates are not obvious in **Fig. 26**.

The initial  $^{137}\text{Cs}$  and  $^{129}\text{I}$  release rates for Cs and I from all samples under investigation are found in the same range as reported by Johnson [77] who expected a quick decrease of the rates due to limited gap inventories. However, in the FIRST-Nuclides investigations, the observed IRF rated did not follow the expected decrease for both nuclides during the first days of the experiments (**Fig. 23 - Fig.**

25). In contrast, the shapes of the time-dependent release rate curves show a different tendency over some 100 days. For this reason, an exponential trend was tested (eq. 6).

$$\text{Release rate} = \frac{d}{dt} \text{IRF}(RN_i) = A \cdot t^{-b} \quad \text{eq. 6}$$

t: time in days

The factor A of eq. 6 corresponds to the initial release rate from the gap and b describes the time dependence.

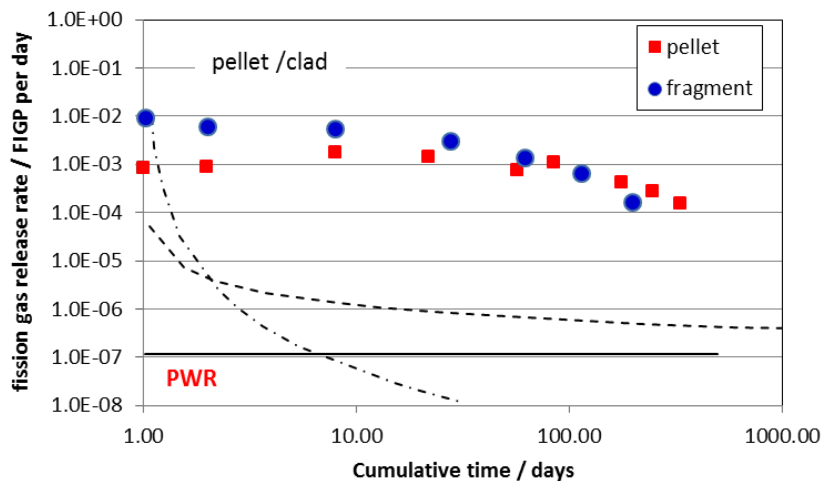
**Tab. VII** Test of linearity of the fast release rates IRF(<sup>137</sup>Cs) and IRF(<sup>129</sup>I).

Type		b(Cs)	Log <sub>10</sub> A(Cs)	b(I)	Log <sub>10</sub> A(I)
BWR	Segments	-0.95±0.06	-2.98±0.10	-0.93±0.12	-2.77±0.21
	Powder CORE	-0.98±0.14	-2.13±0.15		
	Powder OUT	-0.79±0.14	-2.61±0.14		
PWR	Clad Segment	-1.17±0.13	-2.10±0.22	-1.17±0.20	-1.51±0.34
	Declad segments	-1.35±0.10	-1.70±0.15	-1.53±0.18	-0.98±0.27

The decrease of the rates could be fitted for 100 days (and for the whole duration of the experiments) with reasonable coefficients of determination. Within the errors of the exponent b, the release rates of Cs and I could be considered linear with time (see **Tab. IV**). This linear release rate agrees perfectly with a modelling approach discussed in chapter 4.5 and 5.5.2 (Duro 2015, [68]). In this approach, the SNF pellet (fragment) was described in terms of a crack pattern, which allows water penetration. The penetration rate depends on the distribution of crack apertures. In the model “macro cracks” are considered according Oguma [82] relating mean pellet crack aperture (20 μm) and crack pattern with power rate applied to rod in the reactor. The “macro cracks” were represented as discrete fractures (with a defined geometry), while “micro cracks” were represented using the porous-equivalent approach. The saturated crack pathways exist for radionuclide transport. The model reproduce the observed experimental results in terms of their main two features: Fast initial release on the scale of a day, followed by slower rate of release during the remaining experimental period. The calculations result also in a linear dependency with time (see **Fig. 19**).

One of the important data provided by the utilities to the waste management organizations is the fission gas release (FGR) of SNF rods as function of the burn-up and other reactor operational parameters. The FGR measured by puncturing tests at the plenum of fuel rods (however, mainly calculated data) is considered to be similar to some extent to the gap inventory in the case of nonvolatile easily soluble elements. **Fig. 27** shows the fission gas released into the gas phase during the leaching experiments for a clad pellet and a SNF fragment (KIT, PWR fuel, 50.2 GWd/t<sub>HM</sub>, storage time 24 yrs.). For this SNF material, 8.35 % of the calculated sum of Kr and Xe inventory was found in the plenum of the rod after puncturing. In the case of the pellet, the initial gas release rate is lower by a factor of 10 in comparison to the fragment. This fact can be explained by the exposed surface to mass ratio which differs also by one order of magnitude. After some 100 days leaching experiment, the FGR rates are found in the same range.

The cumulative IRF(FG) and IRF( $^{129}\text{I}$ ) are found in the same range, however, the time dependencies of the FG and iodine are different. Unfortunately, FGR during the leaching experiments were measured by one partner, only. The observed time dependence of the initial IRF(Kr+Xe) values indicates a different time dependent behavior as in the case of the soluble elements iodine and cesium [83]. Up to about 100 days, the fission gas release rate into the solution is almost constant. After 100 days, a decrease of the release rate was found. This behaviour is different in comparison to the release rates of Cs or I where a linear decrease of the rates was observed (**Tab. VII**).



**Fig. 27** Fission gas release rate into the gas phase during a leaching experiment for a clad pellet and a SNF fragment (KIT, PWR fuel, 50.2 GWd/t<sub>HM</sub>, storage time 24 yrs.).

A time dependence of the gap release could not be determined. The gap release occurred within the first sampling period of the experiments. This observation indicates that the fast/instant release of Cs and I from clad or declad SNF samples are controlled by the structure of fractures of different apertures into the fuel sample, the penetration of water and the diffusive transport of radionuclides along these structures. This finding seems to be independent on the type of UO<sub>2</sub> fuel.

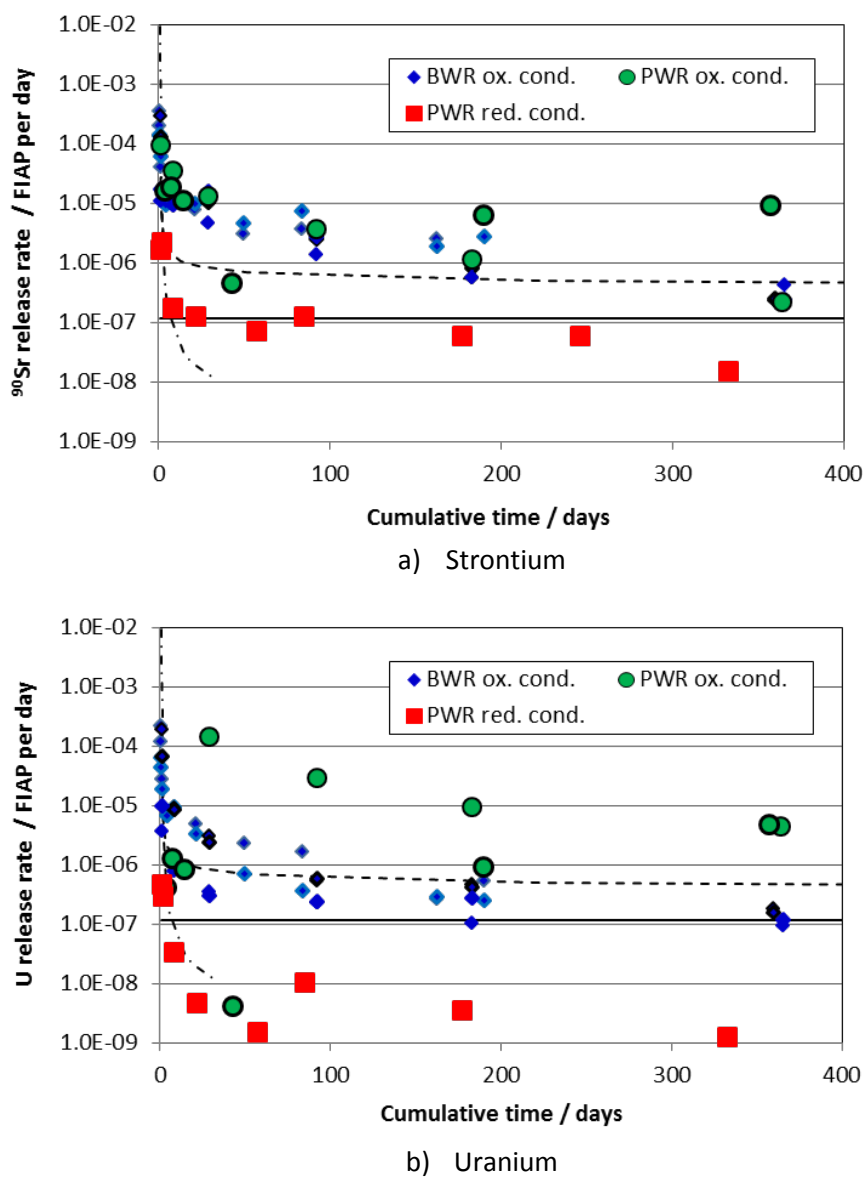
### 5.3 Grain boundary release under reducing conditions

In Johnson's definition of the instant release, the grain boundary release was not considered depending on the geochemical leaching conditions [77]. In this chapter, the fast release of  $^{99}\text{Tc}$  from BWR and PWR SNF as function of time is evaluated under oxidizing (BWR ox. cond., PWR ox. cond.) and PWR SNF under Ar/H<sub>2</sub> overpressure and related to the findings for the matrix elements Sr and U.

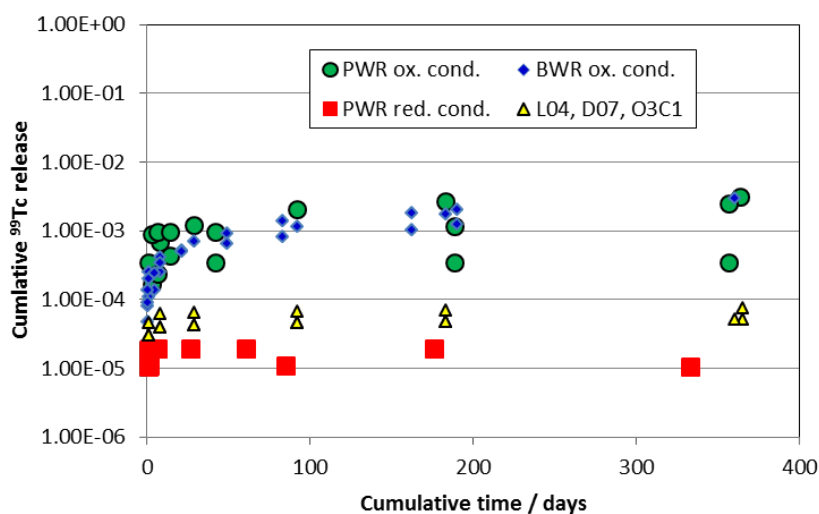
Before groundwater may come into contact with the SNF in a deep disposal, corrosion processes might have caused canister failure. The corrosion processes form H<sub>2</sub> gas up to high pressures. This processes were simulated in FIRST-Nuclides by IRF measurements under an Ar/H<sub>2</sub> overpressure ( $p_{\text{tot}} = 4 \text{ MPa}$ ). It is expected, that the presence H<sub>2</sub> provides reducing conditions and decreases the obtained rates of the IRF for uranium and other elements which are dissolved in the UO<sub>2</sub> matrix, such as strontium. The measured rates are shown in **Fig. 28**. BWR includes the measured data all partners of FIRST-Nuclides with BWR fuel (**Tab. II**) and PWR fuel (**Tab.I**), respectively, both under oxidizing

conditions. The **Fig. 28** shows the release rates for Sr and U. The release rate for Sr obtained under reducing conditions is about one order of magnitude below the rate obtained under oxidizing conditions, in the case of U, the release rate under reducing conditions is by two orders of magnitude below the rate under oxidizing environments.

**Fig. 29** shows the cumulative  $^{99}\text{Tc}$  release. Also in this case, the cumulated Tc release under reducing conditions is the range of  $10^{-5} \text{ day}^{-1}$ . Under oxidizing conditions, the total Tc release is by a factor of about 100 higher. Interestingly, the cumulative  $^{99}\text{Tc}$  of the Oskarshamn reactors OK1 (L04 and D07) and OK3 (O3C1) is slightly above the release under reducing conditions. Only for O3C1 additives are reported. The sample 5A2 which differs only in the initial enrichment (3.5 wt.%  $^{235}\text{U}$ ) fits with the PWR and other BWR fuel samples. In all cases, the  $^{99}\text{Tc}$  release rate in the time period after 20 days is very low ( $< 7 \times 10^{-6} \text{ day}^{-1}$ ).



**Fig. 28** Strontium and uranium release rates for the various types of SNF as function of time under oxidizing (BWR ox. cond., PWR ox. cond.) and PWR SNF under Ar/H<sub>2</sub> overpressure. PWR ox. cond.: VG81, SCK clad, SCK declad; BWR ox. cond.: 5A2, CTM slice, ITU slice; PWR red. cond.: KIT pellet, Kit fragment



**Fig. 29**  $^{99}\text{Tc}$  release rates for the BWR and PWR SNF as function of time under oxidizing (BWR ox. cond., PWR ox. cond.) and PWR SNF under Ar/H<sub>2</sub> overpressure.  
 PWR ox. cond.: VG81, SCK clad, SCK declad; BWR ox. cond.: 5A2, CTM slice, ITU slice;  
 PWR red. cond.: KIT pellet, Kit fragment

The cumulative release data can be compared to previous experimental data (**Tab. VIII**) obtained under oxidizing conditions in a similar (artificial) groundwater for high burn-up SNF [84]. The cumulative release data obtained within FIRST-Nuclides are in the same range. Similar cumulative release for Cs and Sr were observed for high burn-up SNF leaching experiments in high pH cement equilibrated water [85]. Under reducing conditions (presence of 3.3 bar H<sub>2</sub> overpressure, the release rates of Sr and Tc decreased and the cumulative releases were about two orders of magnitude lower [86]. In these experiments, the cumulative Tc release after 200 days was comparable to the data shown in **Fig. 29**.

**Tab. VIII** Published cumulative release fractions determined by leaching experiments under oxidizing conditions [84]

Sample	11-16		418-Q12		SUT3-00477		3V5-Q13	
Burn-up	48.8		58.2		61.4		66.5	
	1 yr.	2 yr.	1 yr.	2 yr.	1 yr.	2 yr.	1 yr.	2 yr.
Cs	$6.2 \times 10^{-3}$	$9.0 \times 10^{-3}$	$1.3 \times 10^{-2}$	-	$1.1 \times 10^{-2}$	-	$1.8 \times 10^{-2}$	$2.4 \times 10^{-2}$
Sr	$5.4 \times 10^{-4}$	$8.2 \times 10^{-4}$	$5.2 \times 10^{-4}$	-	$8.8 \times 10^{-4}$	-	$7.2 \times 10^{-4}$	$9.8 \times 10^{-4}$
Tc	$4.3 \times 10^{-4}$	$2.2 \times 10^{-3}$	$2.4 \times 10^{-4}$	-	$1.5 \times 10^{-4}$	-	$1.0 \times 10^{-4}$	$1.1 \times 10^{-4}$
U	$8.6 \times 10^{-5}$	$9.1 \times 10^{-5}$	$5.5 \times 10^{-5}$	-	$7.9 \times 10^{-5}$	-	$3.1 \times 10^{-5}$	$4.0 \times 10^{-5}$

The investigations on rim and grain boundary processes showed also that hydrogen has an inhibiting effect on the radionuclide release. The observed metallic precipitates are expected to increase the inhibiting effect of hydrogen. Such precipitates were completely missing on samples leached under aerobic conditions.



## 5.4 Investigation of specific elements

### 5.4.1 IRF of selenium

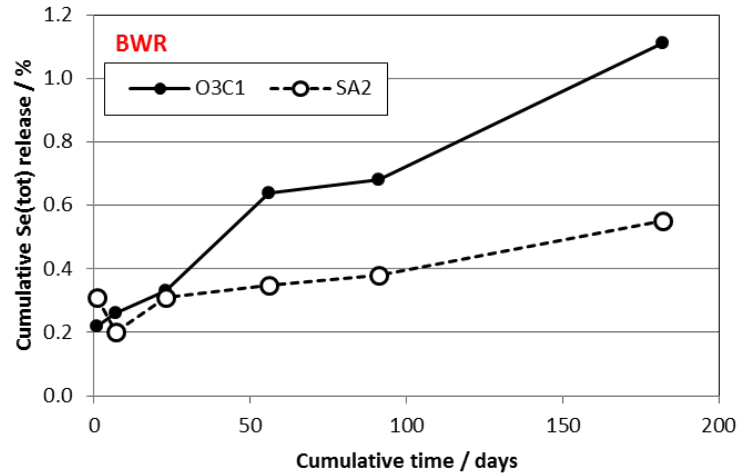
$^{79}\text{Se}$  is a long-lived safety-relevant nuclide (half-life  $3.3 \cdot 10^5$  yrs.) which is traditionally considered as a potentially significant Instant Release Fraction (IRF) contributor. Selenium has 6 stable isotopes<sup>2</sup>. It belongs to the volatile elements in the SNF. The boiling point of selenium in elemental form is  $684.9 \pm 1.0$  °C [87], of caesium 678.4 °C, of antimony 630.0 and of iodine 184.0 °C [88]. Oxidized selenium species are highly soluble in aqueous solutions. For these reasons, the behavior of selenium in the SNF gained specific priority within the CP FIRST-Nuclides.

Specific investigations have been performed on selenium. By means of Laser Ablation ICP-MS, the distribution of Se isotopes was determined in Studsvik's 5A2 and O3C1 pellets. Calculations resulted in total Se concentrations of 94 ppm for the 5A2, and 100 ppm for the O3C1 additive fuel. For the KIT SNF, 76 ppm was calculated. The isotopic abundance of Se produced by fission differs from the isotopic abundance of naturally occurring Se. Laser ablation analysis showed an increase of the Se concentration towards the rim of the pellets. The rim burn-up is higher by 33 % in comparison to the burn-up in the centre of a pellet [89]. A higher amount of  $^{239}\text{Pu}$  fissions in the rim region would not lead to a higher abundance of Se isotopes as the yield light FP decreases. For this reason, the Se concentration distribution over the diameter of a pellet seems to be influenced by transport/diffusion processes.

Cumulative  $^{79}\text{Se}$  release fractions were determined from the two leaching experiments using samples of the low enriched standard 5A2 and the  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  doped O3C1 SNF. The results are given in **Fig. 30** showing a cumulative  $^{79}\text{Se}$  release fraction evolution over 0-360 days of leaching. The Se release was slower than rapid release elements such as Cs, but higher than the matrix dissolution rate of U. After 360 days, the  $^{79}\text{Se}$  release fraction accumulated to 0.6% for 5A2 and to 1% for OK3C1 (178 days: 0.5% and 0.7%, respectively). The initial Se release fractions from the C1 sample (Al/Cr additive) followed the Mo release fraction up to 31 days. For longer leaching durations, the Se release was faster, approaching the Cs release fraction which was lower for the doped SNF sample in comparison to the standard  $\text{UO}_2$  sample. If this difference can be attributed to the effects of the additive such as Cr substitution in the  $\text{UO}_2$  matrix, larger grain sizes or the presence of Al-rich secondary phases could not be determined in this project. In Johnson's recent paper [25], a IRF( $^{79}\text{Se}$ ) of 0.22% after ~100 days was estimated based on a detection limit of 0.5 ng/g (0.5 ppt) in the leachant.

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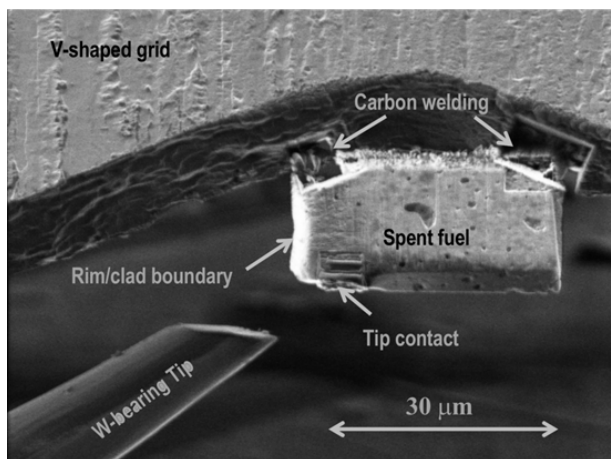
<sup>2</sup> Abundance of selenium isotopes:  $^{74}\text{Se}$ : 0.90 %,  $^{76}\text{Se}$ : 9.20 %,  $^{77}\text{Se}$ : 7.60 %,  $^{78}\text{Se}$ : 23.70 %,  $^{80}\text{Se}$ : 49.80 % and  $^{82}\text{Se}$ : 8.80 %.  $^{76}\text{Se}$  is not formed by thermal fission of  $^{235}\text{U}$  (JEFF-3.1 Library).



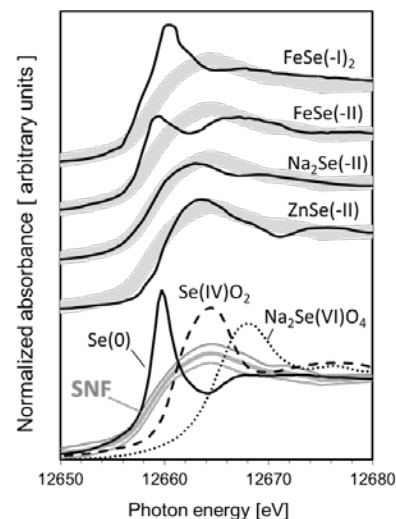
**Fig. 30** Cumulative IRF of total selenium from a doped and standard BWR fragment SNF samples

#### 5.4.2 Investigations of selenium binding state in SNF

Application of micro X-ray absorption near-edge structure ( $\mu$ -XANES) spectroscopy allowed the determination of the chemical state of Se in high-burn-up  $\text{UO}_2$  SNF. First measurements were performed using micro particles from Leibstadt SNF attached to adhesive Kapton tape [76]. Other experiments made use of chips ( $\mu\text{m}^3$  size) prepared from an Oskarshamn-3 SNF pellet by Focused Ion Beam (FIB) milling **Fig. 31**. The measurements were carried out at the  $\mu$ -XAS beamline, Swiss Light Source (SLS), Villigen, (Switzerland) with a microfocused X-ray beam. All measurements were performed in fluorescence mode, using a micro-focused monochromatic X-ray beam of about 2–3  $\mu\text{m}$  size in the energy ranges 12.6– 13.2 keV (Se-K edge and Se-K $\alpha$  fluorescence regions) and 17.2– 17.3 keV (U-La fluorescence). The energy calibration was carried out using a Se(0) reference.



**Fig. 31** FIB Sample ("RIM") of Oskarshamn SNF for XANES measurements.



**Fig. 32** Average smoothed Se K-edge  $\mu$ -XANES spectra from SNF (thick grey line) compared to the spectra of reference compounds.

The  $\mu$ -XAS beamline measurements at the Swiss Light Source (SLS), Villigen, (Switzerland) were performed in fluorescence mode, using a  $\mu$ -focused monochromatic X-ray beam of about 2–3  $\mu\text{m}$  size in the energy ranges 12.6– 13.2 keV (Se-K edge and Se-K $\alpha$  fluorescence regions) and 17.2– 17.3 keV (U-La fluorescence). The energy calibration was carried out using a Se(0) reference. All SNF spectra proved to be strikingly similar independently of the reactor origin and location in the pellet, suggesting a homogeneous chemical state of Se in the matrix of SNF from boiling water reactors. The XANES data were first evaluated by comparing the SNF spectra with those of reference compounds representing different oxidation states of Se (-II, -I, 0, IV, VI). The comparison suggests that Se occurs in the SNF either as a mixture of Se(0) and Se(IV), or entirely as Se(-II). Based on crystal-chemical arguments, the former option is considered to be unlikely. Occurrence as selenide is also supported by ab initio XANES calculations. The XANES data were fitted to theoretical (ab initio) spectra via geometrical optimization of atomic clusters around a central Se atom. Best fits were obtained assuming substitution of Se in occupied or vacant oxygen sites within the UO<sub>2</sub> lattice, with 20–25% local expansion. Based on these results and chemical arguments it is assumed that selenium <sup>79</sup>Se is stabilized to sparingly soluble Se(-II) in SNF [90].

This finding is not necessarily in contradiction to the IRF(Se) observed in the leaching experiments (**Fig. 30**) and to the increase of Se in the rim region of the pellets (see **Fig. 11**). The XAS data indicate unequivocally the same chemical environment of Se in the rim and in the core region of the pellet. The cumulative IRF(Se) shown for the samples 5S2 and O3C1 is much higher in comparison to earlier experiments where for KKL samples after 100 days leaching a cumulative IRF(Se) < 0.22 % was found [25]. This number was based on concentrations in the range of the detection limit for Se. The same KKL samples revealed a IRF(Cs) of about 2%. These discrepancies in the observations for selenium indicate the need for further investigation.

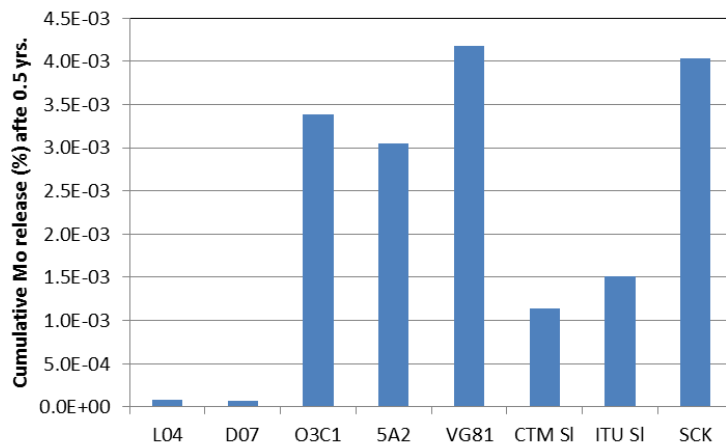
### 5.4.3 <sup>14</sup>C

KIT, PSI and Studsvik established analytical procedures for <sup>14</sup>C measurements. IRF of <sup>14</sup>C by leaching experiments was determined at SCK-CEN, only. The cumulative release fraction was in the range between 1 and 2 % for clad and declad samples showing no significant increase with time. At KIT, the <sup>14</sup>C concentration in the plenum gas was measured. The fuel rod segment investigated at KIT showed a total FGR of 8.35 %. According to the initial nitrogen concentration in the range between 4 and 11 ppm, a maximal amount of  $2.1 \times 10^{-4}$  mol nitrogen was present in KIT's rod segment. The total mass of <sup>14</sup>C was expected in the range of  $4.3 \times 10^{-6}$  mol. A comparison of this value with the measured data revealed, that 0.2 % of the <sup>14</sup>C inventory was present in the gas phase in the chemical form <sup>14</sup>CO<sub>2</sub> [64].

### 5.4.4 Other nuclides / elements

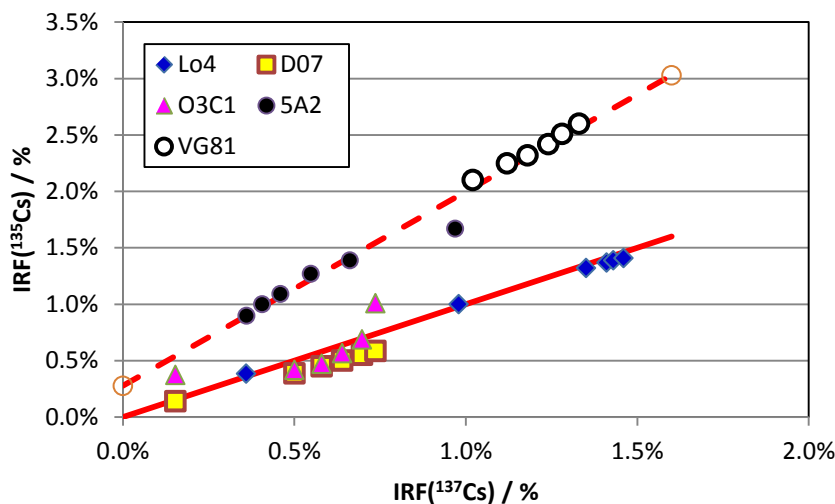
Molybdenum is not an element to be considered for the IRF. The cumulative yield of <sup>100</sup>Mo is 6.5 % with a half-life of  $9.9 \times 10^{18}$  yrs which may be considered stable. However, molybdenum can exist in several oxidation states which control the oxygen potential in the SNF. This fact may lead to different release properties of Mo. In **Fig. 33** the cumulative Mo release is shown after 0.5 yrs. The results from different SNF investigated by the partners are shown. Most results are found in the range of the

release fraction between 0.001 and 0.004 %. The ITU and CTM powders showed a release fraction up to 0.02 % within 30 days (not shown in **Fig. 33**). Two Swedish samples L04 and D07 revealed significantly lower releases. The available data do not allow an interpretation of this finding.



**Fig. 33** Cumulative Mo release at 0.5 yrs. from different SNF under investigation

Only Studsvik reported IRF of  $^{135}\text{Cs}$ . From the chemical properties  $^{137}\text{Cs}$  and  $^{135}\text{Cs}$  are expected to show the same release behavior. **Fig. 34** shows the release of  $^{135}\text{Cs}$  versus the release of  $^{137}\text{Cs}$  for the BWR and PWR SNF. For the PWR SNFs, the releases show a higher  $^{135}\text{Cs}$  release fraction in comparison to  $^{137}\text{Cs}$  (by a factor of 1.7). The reason cannot be explained, presently.



**Fig. 34** Cumulative release of  $^{135}\text{Cs}$  versus cumulative release of  $^{137}\text{Cs}$  for BWR and PWR SNFs

## 5.5 Modelling

A series of calculations were performed to provide for the initial and boundary conditions for the SNF sample under investigations. These calculations included the calculations of the inventories of fission products, actinides and activation product in the SNF. Parts of the burn-up and decay history

calculations were performed using the webKorigen software package [91]. Furthermore, the central temperature of a fuel rod under irradiation was calculated, as well as the rim zone thickness, the rim zone burn-up, and the Xe content and porosity of the rim zone.

### 5.5.1 Phenomenological model of the kinetics of IRF

Various modelling studies have been performed within FIRST-Nuclides. These covered the IRF modelling from spent fuel leaching experiments [72], relying on kinetic approaches.

$$m_{RN}(t) = \sum_{i=1}^N m_{RN,i\infty} \cdot (1 - e^{-k_i \cdot t}) \quad (\text{eq. 7})$$

$m_{RN}(t)$ : total cumulative released mass of RN     $t$ : time;  
 $m_{RN,i\infty}$ : total inventory in phase  $i$              $k_i$ : kinetic constant  
 $i = 1, \dots, N$ : specific phase

The kinetic model was fitted to the several measured data sets of fuels having different burn-up including data determined by experiments using cladded samples and powdered samples from the periphery of the pellets (OUT) and from the inner part (CORE) (**Tab. II**).

It was believed that the rate limiting step is the rate of water penetration starting with the gap, micro fractures and readily available exposed grain boundaries, latter to micro fissures and less exposed grain boundaries, and, finally, to the complete inventory present in the closed grain boundaries. Results obtained from cladded samples correspond to the release of the more rapidly areas accessed by water. Results obtained from powdered samples, correspond to the release from micro fissures and less exposed grain boundaries.

### 5.5.2 Coupled saturation and transport model

Another modelling exercise dealt with the rate of saturation of the SNF structure with leachant during dissolution based determinations of the IRF. The release of the relevant radionuclides is only possible after wetting of the fuel's surfaces by water. The modelling approach covers three parts: (1) Saturation model, (2) Transport processes, and Comparison with Experimental Results. The model aims on comprising radionuclide instant release both with regard to laboratory experiments conducted with SNF and the release from SNF under repository conditions. The model [67] assumes that the rate of release for Cs and I from a SNF pellet (or fragment) after contact with water is controlled by the wetting of surfaces of cracks present in the pellet. During the irradiation of the fuel in nuclear power plants, cracks are formed in the fuel pellets. The cracks may vary in their aperture, geometry and inter-connectedness, depending on the specific properties of the fuel pellet and irradiation conditions [82].

The network of cracks in a pellet is conceptualised by the aperture, geometry and inter-connectedness. For modelling purposes, the complete cracks network was subdivided into two groups: "macro cracks" (the larger cracks with a mean aperture assumed to be equal 20  $\mu\text{m}$ ) and "micro cracks" (small cracks with a mean aperture of 0.1  $\mu\text{m}$ ). Modelling of water saturation involves solving equations describing variably-saturated flow of water. The simplest mathematical model for such a problem is based on the Richards equation [92]. The solution of the Richards equation must however be conducted simultaneously with a set of constitutive algebraic equations describing water

retention and relative permeability properties of the medium. In this study the commonly used van Genuchten model [93] is used in conjunction with the Richards flow equation.

A detailed description of this model is given in (Duro 2015), the application was demonstrated in chapter 5.2 "Gap and grain boundary release".

## 5.6 Non-standard SNFs

### 5.6.1 TRISO

The impact of burn up on the instant release fraction from very high burn up  $\text{UO}_2$  fuel ( $\sim 100$   $\text{GWd/t}_{\text{HM}}$ ) was studied. Such extreme burn-ups are not typical for LWR fuels, therefore TRISO (TRI-structural-ISO-tropic) particles were investigated. After cracking of the tight coatings  $^{85}\text{Kr}$  and  $^{14}\text{C}$  in the form of  $^{14}\text{CO}_2$  were detected in the gas fraction. Xe was not detected in the gas phase, this fission gas was accumulated in the buffer and inner pyrolytic coating of the particles. The  $\text{UO}_2$  fuel kernels were exposed to the standard synthetic groundwater both under aerobic (air) and anoxic/reducing ( $\text{Ar}/\text{H}_2$ ) conditions.

Under both redox conditions, the U concentration in the leachant was below the detection limit, indicating low matrix dissolution. Also, the concentrations of the actinides (Pu, Am, Np, Cm) in solution were below their detection limits. Under reducing conditions, the maximum of the cumulative IRF(Cs) was reached within the first 5 days (9% for  $^{137}\text{Cs}$ ) and no further significant release was observed. The leach tests were continued until 276 days. The contribution of  $^{90}\text{Sr}$  to the IRF was low (max. 0.2 %) and comparable to LWR spent fuel. In the case of aerobic conditions, the cumulative IRF( $^{137}\text{Cs}$ ) was only  $\sim 2\%$ .

ESEM investigations were performed to study the impact of leaching on the microstructure. Before leaching the surface of the fuel matrix showed a rough topography, few small pores (below  $2\ \mu\text{m}$ ) were visible and metallic precipitates appeared as hexagonal platelets. Independent on the redox conditions during leaching, a reduced roughness of the surfaces of the fuel matrix and of the grain boundaries was observed. Numerous small open pores were formed in oxic environment while under anoxic/reducing conditions these pores were filled with metallic precipitates. Independently of redox conditions The leaching under aerobic and reducing conditions influenced the microstructure of the  $\text{UO}_2$  matrix. However, the reason for the difference in the cumulative Cs release under aerobic and reducing conditions could not be explained.

### 5.6.2 Leaking VVER fuel assemblies

The isotopes dissolution of radionuclides from damaged and leaking VVER fuel assemblies during wet storage was analysed and the dissolution rates of several isotopes from leaking VVER fuel assemblies were determined for two pH in the coolant based on activity measurements at the Paks NPP in Hungary [94, 95]. Under the conditions of the storage pool, 1.8 % (71.5 kg) of the total mass (3969 kg) of the  $\text{UO}_2$  was dissolved during the four years of wet storage after the incident. The average dissolution rate of  $\text{UO}_2$  was estimated to 61 g/d ( $1.5 \cdot 10^{-4}$   $\text{day}^{-1}$ ). Over the initial period of 30 days

after the incident, the rates of the instant release fraction were estimated as follows:  $\frac{d}{dt} \text{IRF}({}^{137}\text{Cs}) = 1.3 \cdot 10^{-4} \text{ day}^{-1}$  and  $\frac{d}{dt} \text{IRF}({}^{131}\text{I}) = 5.8 \cdot 10^{-4} \text{ day}^{-1}$ . These rates correspond well with the measured release rates for standard high burn-up PWR fuels determined within FIRST-Nuclides.

## 5.7 Database

For application of data determined in FIRST-Nuclides in a Safety Case, extrapolations are needed which relate the measured data of single specific samples to the entirety of the disposed SNF. A close correlation between IRF, FGR and the in-reactor operation exists. For this reason, a database is needed allowing these kind of extrapolations. A uniform unambiguous data set for all samples should provide not only the information retrieved by the questionnaire but additionally information which allows relating the observed IRF to the complete rod. The additional information comprises the axial location of the sample in a rod, local burn-up and local axial power distribution as function of time. Furthermore, the uncertainty of measured IRF data needs to be documented, covering experimental uncertainties, uncertainties on the sample initial inventory inferred from code calculations and, local burn-up and power rates.

A database was developed within the project compiling all available data inclusively published data and data produced in FIRST-Nuclides. The database includes measured IRF and information related to these data. It is available in excel format and provides for plotting the results. The database is organized in 4 spreadsheets covering a summary table with information on basic material, experimental information and the results. The other spreadsheets contain graphic output, detailed information of each publication and the list of references. Plots can be created for selected samples, showing the IRF as function of the burn-up, fission gas release, and power rate. It can be selected according the type of samples (pellet, fragment, and powder), type of fuel, and the experimental conditions.

## 6 Summary

The CP FIRST-Nuclides aimed on providing for “instant release fractions (IRF)” for relevant radionuclides from High burn-up SNF supporting the needs of safety analysis for different host rocks but also for the variety of SNFs to be disposed of in each repository. To obtain added values on an European level, several prerequisites had to be met:

- In contrast to previous investigations, data of in-pile operation parameters have been made available for evaluation and interpretation of the result.
- Agreement between the experimentally working partners on a standard leachant.
- Use of different samples, sample sizes and preparations from PWR and BWR.
- Experiments under aerobic, anaerobic and reducing conditions.
- Analyses of a variety of elements/isotopes including redox sensitive elements.

The outcome obtained by the partners of the CP FIRST-Nuclides cover 12 different types of high burn-up LWR SNF, IRF measurements at 45 different time steps, for up to 3 sample preparations, and up to 20 isotopes. This huge amount of data provides an excellent basis for further detailed understanding of the processes summarized by fast/instant release.

- The determined rates of the gap and grain boundary releases do not confirm Johnson's approach [77]. The initial  $^{137}\text{Cs}$  and  $^{129}\text{I}$  release rates are found in the same range as reported earlier, the observed time behaviour of the IRF do not follow the expected decrease during the first days of the experiments. In contrast, the shapes of the time-dependent release rate curves showed a different trend.
- IRF of fission gas during the leaching experiments was observed. The initial gas release rate of a clad pellet is lower by a factor of 10 in comparison to a fragment, however, after some 100 days leaching experiment, the FGR rates are in the same range. The IRF(FG) and IRF( $^{129}\text{I}$ ) are also found in the same range after some time.
- The release rate for elements which remain in the  $\text{UO}_2$  matrix were analyzed. IRF(Sr) under reducing conditions is about one order of magnitude below the rate obtained under oxidizing conditions.
- For redox sensitive elements, such as U, the release rate under reducing conditions is by two orders of magnitude below the rate observed under oxidizing environments. The cumulated IRF(Tc) under reducing conditions is by a factor of 100 lower as in the case of oxidizing conditions. All cumulative IRF( $^{99}\text{Tc}$ ) of Swedish BWRs were found slightly above the IRF obtained under reducing conditions even if the experiments were not performed under hydrogen overpressure.
- Non-standard SNFs were investigated, such as extremely high burn-up TRISO and leaking VVER fuel assemblies stored in a pool. The release rates obtained from the leaking assemblies correspond well with the measured release rates for standard high burn-up PWR SNF.
- The IRF of selenium and  $^{14}\text{C}$  were determined only by one partner, each. For both elements, the IRF reached about 1% after one year.
- Application of micro X-ray absorption near-edge structure (I-XANES) spectroscopy on small samples allowed the determination of the chemical state of Se in high-burn-up  $\text{UO}_2$  SNF. Based on these results and chemical arguments it is assumed that selenium  $^{79}\text{Se}$  is stabilized to sparingly soluble Se(-II) in SNF. However, this finding is in disagreement to the IRF(Se) found by leaching experiments in the range of 1% after one year. IRF determination of  $^{36}\text{Cl}$  was not successful, up to now.
- A database was developed within the project compiling all available instant release data comprising earlier published data and data produced in FIRST-Nuclides. The database includes measured IRF and information related to these data. It is available in excel format and provides for plotting the results.
- The modelling approaches contributed to the interpretation of results. A model was developed to examine wetting of spent fuel fragments and the time behaviour of radionuclide release. The model suggests that transport in fractures is relatively rapid (within a few days) and that mass transport of soluble radionuclides out of fuel samples from micro-cracks should occur in less than 100 days.



There are still questions which could not be resolved within the three years Collaborative Project FIRST-Nuclides. These questions extend to:

- Fast radionuclide release from doped SNF and dependence of IRF of relevant RNs on the type and quantity of dopants.
- Quantification of dissolution based IRF under reducing conditions.
- Quantification of the FGR under dissolution based investigations and correlation with in-pile operational data.
- Quantification of the activation products  $^{14}\text{C}$  and  $^{36}\text{Cl}$  that arise from N and Cl impurities in fuel, and understanding the impurity level ranges in fuels from different suppliers.
- Special efforts have been made to obtain data on  $^{79}\text{Se}$  release and speciation in the  $\text{UO}_2$  matrix. However, the obtained results are contradicting to some extent. This contradiction needs to be elucidated.
- Open questions occur with some nuclides, such as  $^{135}\text{Cs}$  which shows a higher release in comparison to  $^{137}\text{Cs}$ .

From the position of the End-Users, the value of the studies performed in the Project FIRST-Nuclides appears to be high. The subject is highly relevant for all waste management organizations involved in repository development for which direct disposal of spent nuclear fuel is foreseen, as the Instant Release Fraction (IRF) contributes substantially to the peak releases after container breaching and to potential radiological consequences. Specifically, the results provided by CP FIRST-Nuclides include:

- Data from experimental determination of rapid release fractions for moderate and high burn-up  $\text{UO}_2$  fuels, including doped fuels, expected to be used much more by reactor operators in the future,
- An increased data base for release of Cs and I from high burn-up fuel and comprehensive comparisons of IRF with fission gas release (FGR), which are necessary in order to be able to estimate IRF data for a very large number of fuel rods and various reactor operation conditions,
- The improvement of analytical techniques for some difficult to measure radionuclides such as  $^{14}\text{C}$  and  $^{79}\text{Se}$ ,
- Improved data on fission product retention of TRISO fuel and
- Insights into mechanisms related to fission product release.

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