

# Post Irradiation Examinations of High Burnup Spent Fuel Samples: Corrosion Test Procedures, Sampling and Sample Treatment

Andreas Loida, Nikolaus Müller

Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgung (INE), P.O. Box 3640, D - 72021 Karlsruhe, Germany

## Abstract

Post Irradiation Examinations of spent fuel performed at FZK/INE are focused on the understanding of the overall corrosion behavior of this waste form under conditions, which are as close as possible to the geochemical environment possibly encountered in a repository after an assumed groundwater intrusion. This comprises corrosion tests using real spent fuel samples and near field materials, under the anticipated conditions. Because of the deficit of the spent fuel matrix in oxygen extreme small quantities of  $O_2$  are already sufficient to cause its very rapid oxidation upon the surface. Thus, in the case of preoxidation the  $UO_2$  matrix dissolution rate will be enhanced orders of magnitude, which will not reflect the behavior of spent fuel from an intact rod. High efforts are necessary, to protect (i) the fuel samples itself and (ii) the entire experimental corrosion test arrangement permanently against  $O_2$  uptake from air during the running time, and (iii) in particular during sampling of gases and solutions. To examine the impact of corrosion on solid materials very small particles are being separated by means of micromanipulator technique in association with light optical microscopy allowing steric view. Samples of interest are particles of fuel, new solid secondary phases, corroded container and backfill material. The dose rate of the separated samples is low enough to allow their handling outside the hot cell, but their size is sufficient large to carry out SEM, EDS, ESCA and XRD studies.

**KEYWORDS:** spent fuel, hot cells, remote operation, fuel oxidation, micromanipulator

## 1. Introduction

One important objective of Post Irradiation Examinations (PIE) of spent fuel is to study its overall corrosion behavior under conditions, which are as close as possible to the geochemical environment possibly encountered in a repository after an assumed groundwater intrusion. This comprises corrosion tests using real spent fuel samples and near field materials, under the anticipated conditions. Due to the high radioactivity of the fuel samples, all kind of experimental work focused on spent fuel is associated with a high extent of technical expenditure, because in any case it has to be carried out under remote operation in hot cells.

Under the assumption that the claddings remain intact during interim storage, preoxidation of the fuel, which enhances the matrix dissolution rate significantly [i] will not be expected. Hence, for experimental work high efforts are necessary to **protect the samples** of spent fuel and the entire experimental arrangements as well permanently **against oxygen uptake** from air atmosphere, which dominates generally the interior of the hot cell and the storage locations of the fuel samples.

All of the procedures to determine the progress of spent fuel dissolution and the associated release/retention of radionuclides require during every stage the **effective exclusion of air oxygen**. Related worksteps are primarily sampling and analyze of fission and radiolysis gases, sampling and analyze of leach solutions. Less concerned are worksteps after test termination to determine the amount of radionuclides retained in/on solid phases by various processes as (co)precipitation, formation of new secondary phases, or by sorption.

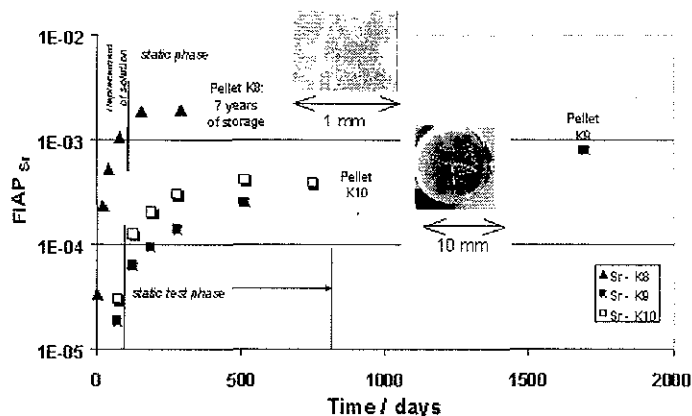
This communication describes in detail the experimental procedures performed at FZK/INE related to spent fuel sample preparation, accomplishment of corrosion tests, the associated sampling procedures for gases and solutions, preparation of solid samples of corroded high radioactive material, and practical experiences obtained during that work.

## 2. Influence of contamination by air oxygen

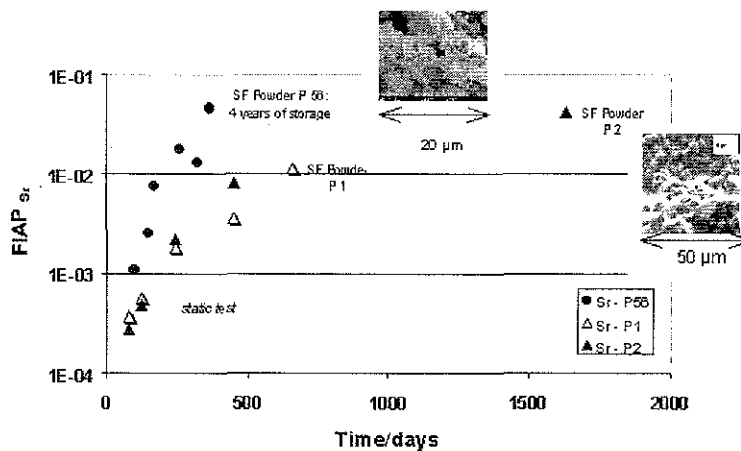
Because of the deficit of the spent fuel matrix in oxygen extreme small quantities of  $O_2$  are already sufficient to cause its very rapid oxidation upon the surface. Thus, the protection of the fuel samples and the entire experimental arrangement of the corrosion test as well is of vitally importance; otherwise, in the case of air contact and subsequent preoxidation the  $UO_2$  matrix the fuel dissolution rate will be enhanced orders of magnitude, which will not reflect the fuel behavior from an intact rod.

### 2.1. Effect of preoxidation of spent fuel samples during storage

The impact of air contamination on **spent fuel pellets** is demonstrated in Figure 1, where the matrix dissolution in terms of  $FIAP_{Sr}$  values (released fractions of Sr in solution) is plotted vs. the time, for both conditions, an oxidized (K8) and non oxidized pellets (K9, K10); related microscopic images are shown as well. A segment of high burnup  $UO_2$  spent fuel was cut in  $N_2$  atmosphere into various pellet sized segments. One part of these pellets was used immediately after cutting for a corrosion test in 200 ml 5M NaCl solution in the absence of carbonate. Detailed information on this test series is available in [ii]. The remaining pellets were sealed, at each case in "gas tight" stainless steel capsules, and at each case 3 capsules were packed into an aluminum capsule, and all of these capsules were placed into a 10 l tinplate drum, all work steps under inert ( $N_2$ ) atmosphere. However, the atmosphere inside the hot cell, where the **samples were stored for > 7 years**, was generally air. Despite several barriers against air intrusion significant effects were found. (1) During storage time a white layer was formed on the cut surface of the pellet, and (2) a significant increase of the matrix dissolution rate was observed. Both effects are shown in Figure 1, where the released fraction of Sr ( $FIAP_{Sr}$ ), which indicate the progress of matrix dissolution, is plotted as a function of corrosion time. Additionally, the pellet surfaces are shown for both conditions,



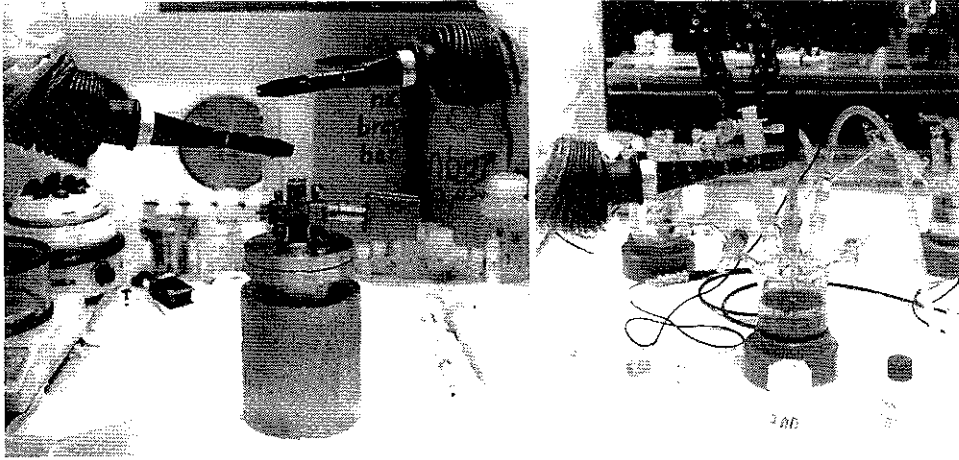
**Figure 1** Matrix dissolution of high burnup spent fuel pellets in 5m NaCl solution immediately after cutting (K9, K10), and after 7 years of storage (K8), indicated by released fractions of Sr as a function of time



**Figure 2** Matrix dissolution of high burnup spent fuel powder in 5 m NaCl solution immediately after cutting (P1, P2), and after 4 years of storage (P 56), indicated by released fractions of Sr as a function of time

immediately after cutting, and after 7 years of storage.

The influence of air contamination on **powdered spent fuel** with an average grain size of 5  $\mu\text{m}$  can be assessed from Figure 2. The necessary procedures as grinding, dust removal by washing, sieving and dividing into separate charges for various experiments were performed under  $\text{N}_2$  atmosphere. Two of these samples, P1 and P2 were used immediately in a corrosion test in 200 ml 5m NaCl solution. Details are also given in [ij]. The remaining powdered samples were sealed, packed and stored in an analogous manner as carried out with the pellet samples. However the storage time of the powder samples was only about 4 years. The related plot in Figure 2 illustrates that sample P56, which was stored over 4 years after



**Figure 3** Vessels for spent fuel leach tests under exclusion of air atmosphere: Ti/Pd lined stainless steel autoclave (500 ml) equipped with ball valves for Ar gas inlet and sampling on the lid (left) and quartz glass reaction vessel (300 ml) equipped with fittings to allow gas inlet and sampling (right).

preparation shows a significant higher matrix dissolution rate as the samples P1 and P2, as indicated by the associated released fractions of Sr. In contrast to pellet corrosion the effect of air contamination is probably more significant, because already after 4 years dry storage time the matrix dissolution rate of the oxidized samples is about 1.5 orders of magnitude higher than the non pre oxidized samples.

## 2.2. Oxygen Protection During Corrosion Test

Moreover, during the entire corrosion test, usually performed under anoxic conditions, the effective protection of the system "spent fuel – solution - gas phase" against air oxygen and carbonate is required. This is achieved by using gas tight reaction vessels as shown in Figure 3, either Ti/Pd lined stainless steel autoclaves (500 ml), or quartz glass vessels (ca. 280 ml). Both types of vessels are equipped with fittings, which allow: (1) the introduction of the desired atmosphere (mostly Ar), (2) to take samples of the gas phase, (3) to take samples of the solution under streaming Ar, and (4) to remove samples of solid particles during the test. The tightness of the system against air intrusion is verified by the results of the gas analysis, in particular by the amount of  $N_2$ , which belongs neither to the fission gases nor to the radiolysis gases.

The effect of air or of pure oxygen respectively, if they constitute the free gas volume of the vessel, on the release of radioelements is demonstrated in Figure 4. In the frame of a corrosion test, which was performed under  $N_2$  atmosphere so far in  $MgCl_2$ -rich salt brine (Q-Brine) at intervals of  $200 \pm 50$  days, the atmosphere was replaced by air for the next 208 days, and by oxygen only for the following 233 days. The diagram shows a strong increase at about a factor of 100 for the release of Sr, Cs and Sb, which can be used in that case as an indicator of the dissolution progress of the matrix; release values are similar under air and under  $O_2$  atmosphere. The releases of Eu, Am, Cm and Pu are also increasing, but at a lower extent (ca. factor 10), where the highest release can be observed under  $O_2$  atmosphere.

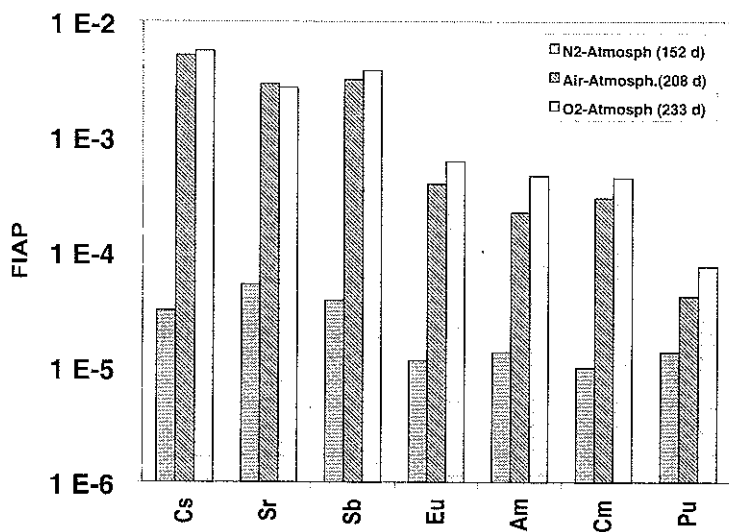


Figure 4 Effect of air and oxygen on the release of radioelements during spent fuel corrosion in Q-brine

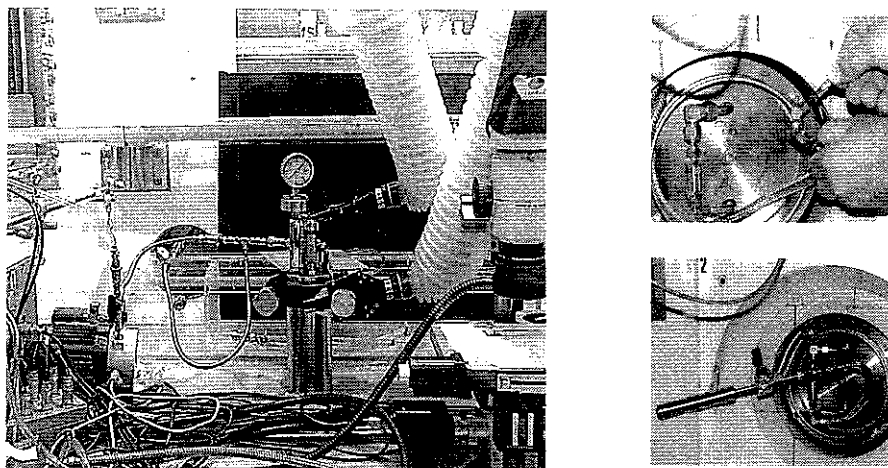


Figure 5 Sampling of fission and radiolysis gases: Arrangement inside (left) and outside the hot cell; mounting of a filter gasket (upper right), connection with the gas collecting cylinder (lower right)

### 2.3. Sampling of fission and radiolysis gases

The analysis of the gas composition from the free gas volume is an important work step for various reasons. (1) The encountered amount of N<sub>2</sub> indicate the extent of air contamination and allow the conclusion, if during the test run probably air could enter the system. Leakage within the plug-in-connectors may result in N<sub>2</sub> contents in the order of a few percent, which might however not be necessary an indication of air intrusion into the interior of the vessel. (2) The evolution of the gas composition in particular the

release of fission gases Kr and Xe is considered to be an additional independent indicator for the progress of matrix degradation, because they are not involved in any retention processes as sorption, precipitation or secondary phase formation.

Sampling of gases is carried out by connecting the reaction vessel and a pre-evacuated gas collection cylinder ( $1 \cdot 10^{-6}$  bar) with a vacuum pump and an Ar gas supply. To remove the air the connecting tubes are flushed with Ar and afterwards evacuated several times prior to open both the reaction vessel and the evacuated gas collection cylinder, which is plugged in by using a filter gasket on the connection tube outside the hot cell. Hence, no decontamination procedures are necessary before establishing the connection between the gas collection cylinder and the quadrupole mass spectrometer where the gas composition is being analyzed.

Figure 5 shows the experimental arrangement during sampling of gases. The left picture shows the interior of the hot cell, where the autoclave, the vacuum pump (bottom left corner), and the connecting flexible tubes, which are plugged in with the gas collection cylinder outside the hot cell. Both pictures on the right show the related place outside the hot cell: (1) The insert of a filter gasket to retain radioactive particles on the contact between gas collection cylinder and the flexible tube system inside the hot cell and (2) the connected gas collection cylinder during gas sampling. By means of smear tests all contact zones are always checked after disconnecting the gas collection cylinder, if they are free of any contamination.

#### 2.4. Sampling of solutions

Sampling of solution is performed by means of a syringe, which is connected by flexible Tygon tubes via a three port valve with the solution inside the vessel and an Ar gas supply. The connecting tube system is flushed with Ar prior to take the solution aliquot (ca. 8 - 10 ml) into the syringe. To avoid the uptake of fuel particles the solution sample will be filtered by using a  $0.45 \mu\text{m}$  filter. Afterwards an aliquot is filtered through a  $1.8 \text{ nm}$  filter. Both solution aliquots are analyzed radiochemically to identify the upper limit of possible colloid formation.

### 3. Preparing of high active solid material

Important information about the alteration processes, which pass during a test run can be obtained by the characterization of the solid materials present in a reaction vessel during spent fuel corrosion. Solid samples of interest are e.g. particles of spent fuel, reaction layers on the surfaces of the fuel, or of the liner, corroded Fe-powder, cladding and near field material. Primary objective is to study the corroded surfaces, the morphology of newly formed phases, their chemical composition and crystal lattice spacing. Because analytical equipment as SEM/EDX or XRD is not available inside the hot cells, it is necessary to select and send hot particles of interest to the desired equipment, under the assumption that they can be handled there. Reaction layers adhering on fuel surfaces will be removed by using a ceramic knife, and the obtained particle assemblage is saved on a sample holder. The micromanipulator technique enables the selection and the following separation of very small particles even from such assemblages. They are picked up by the micromanipulator needle, then they are moved and fixed upon a double coated carbon tape, which is adhering on a brass sample holder ( $\varnothing$  ca. 10 mm). The micromanipulator is associated with a reflecting light optical microscope (WILD M8), equipped with two video cameras instead of two oculars. The images from both cameras are sent outside the hot cell to an adapter unit, and eventually alternating (100 Hz) on a monitor screen, where they appear as a steric view (magnification 305x), if shutter glasses, which are controlled by the adapter unit (infrared) are used. The application of this technique enables an uncomplicated fast way to obtain particle or surface images of fairly good resolution. Specimens, which are isolated as described are characterized by a dose rate, which allows easily their transfer from the interior of the hot cell to the analytical equipment for further investigations (e.g. SEM, XPS, XRD). None of the investigated samples, spent fuel particles inclusive exceeded a dose rate of  $18 \mu\text{Sv/h}$ .

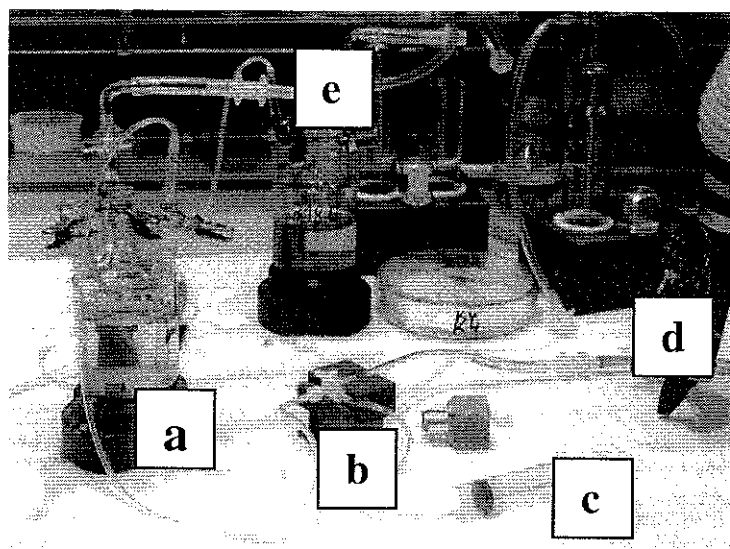


Figure 6 Sampling of solution under exclusion of air oxygen (a) glass vessel, (b) 3-port valve, (c) syringe, (d) Ar-supply, (e) fitting for gas sampling.

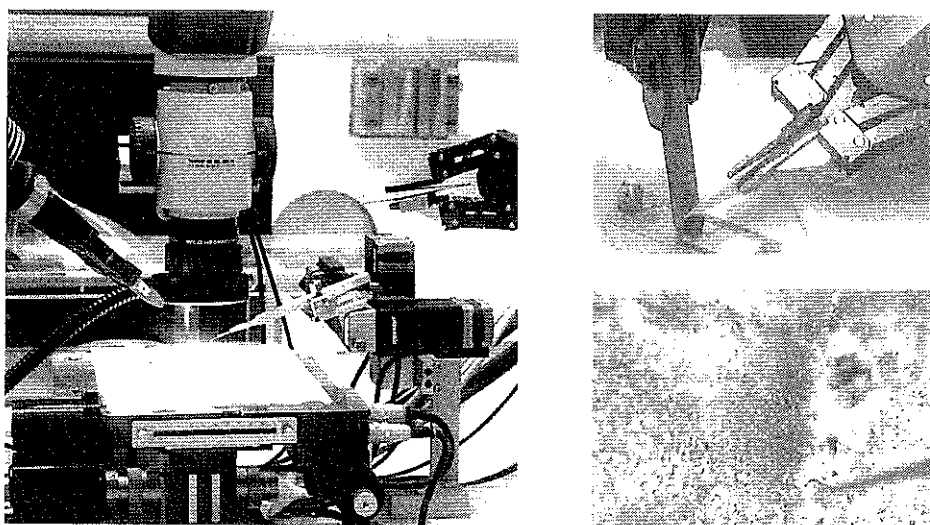


Figure 7 Micromanipulator, optical light microscope, reaction layer and reaction layer removal

Figure 7 shows the micromanipulator, the associated optical light microscope, the removal of reaction layers from a corroded fuel pellet by means of a ceramic knife, and a light optical micrograph of a reaction layer upon the cut surface of a corroded fuel pellet.

#### 4. Conclusions

Post irradiation examinations of spent fuel samples are performed at FzK/INE with emphasis on corrosion tests, focused on the understanding of the long-term behavior of the system "spent fuel – canister – backfill material – groundwater – gas phase". However, very small amounts of (air) oxygen contacting the fuel matrix prior to start the corrosion test, during the test itself and the associated gas and solution sampling procedures are sufficient to enhance the matrix dissolution rate significantly. In this context high efforts are necessary to avoid any (air) oxygen contact of the entire system, if the behavior of a fuel from an intact fuel rod shall be studied. To examine the impact of corrosion on solid materials very small particles are being separated by means of micromanipulator technique in association with light optical microscopy allowing steric view. Samples of interest are particles of fuel, new solid secondary phases, corroded container and backfill material. The dose rate of the separated samples is low enough to allow their handling outside the hot cell, but their size is sufficient large to carry out SEM, EDS, ESCA and XRD studies.

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#### 6. References

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