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ORIGINAL PAPER

Fission product release from spent nuclear UOX fuel dissolution: Comparison between anoxic and reducing conditions and impact of pH

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Abstract

Several clad segments from the same spent nuclear fuel rod were leached in a highly alkaline solution representative of the conditions expected in the current Belgian reference deep disposal design, and in presence of hydrogen. The results are compared with experiments that were conducted with clad and declad samples in a bicarbonate solution without presence of hydrogen. For the monitored radionuclides (^{238}U, ^{90}Sr, ^{137}Cs, ^{129}I, ^{99}Tc), a fast initial release was observed. Afterwards, the release depended on the experimental conditions (medium, redox conditions) for uranium, strontium and technetium, but not for cesium and iodine. The cumulated released fractions were quantified at the end of the experiment.

Introduction

The safe deep disposal of spent nuclear fuel (SNF) requires the determination of the critical parameters that influence the SNF behavior, taking into account the evolution of the engineered barriers and the interaction with the environment. In Belgium, the "Supercontainer design", involving a carbon steel overpack and a cementitious buffer, is the current reference design for the deep disposal of SNF [1]. After the failure of the overpack, a highly alkaline water is expected to come in contact with the SNF. Hydrogen, generated by corrosion of the iron-based materials, is known to decrease the dissolution rate of the UO_2 matrix. Experiments where thus performed in an alkaline solution and in the presence of two concentrations of dissolved hydrogen, the lowest value (2.4×10^{-4} mol(H_2) L^{-1}) was determined based on the expected corrosion rates of the iron-based materials [2], and using UOX clad fuel segments. A third experiment was performed in a bicarbonate solution. The results were compared with tests in the same bicarbonate solution without hydrogen, previously performed in the European program "FIRST-Nuclides" [3], where the influence of the exposed surface area in contact with the solution was also studied using a declad sample.

Materials and methods

The experiments were performed in glass columns closed with a piston (anoxic conditions) or in steel autoclaves with a titanium liner (reducing conditions). The alkaline leaching solution was a synthetic young cement water [4], denominated 'YCWCa' (Table 1). A complete description of the setups and the experimental conditions was reported in [5, 6].

The tested UOX fuel was irradiated in the PWR Tihange 1 reactor. It was initially enriched with 4.25 wt% of ^{235}U. The burnup at the sample location was 54.6 MWd $kg_{HM}{}^{-1}$, Fission Gas Release upon puncturing was 14.1%, and the average Linear Power Rate (LPR) was 321 W cm^{-1}. The test samples were about 2.4 cm long. Cutting was done at mid-pellet position using a tube cutter without cooling solution. This results in clad segments that contain one intact pellet enclosed by two half pellets. In one experiment under anoxic conditions performed for FIRST-Nuclides, the SNF was separated from the cladding. The separated pellets were broken and the fragments were leached together with the cladding to keep an equivalent amount of materials in all experiments. Table 1 gives the detailed experimental matrix and conditions.

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Table 1 Experimental matrices and leaching solution compositions

Exp.	Leaching solution and composition (mol L^{-1})	Sample	Atmosphere (gas composition, total pressure)	Concentration of dissolved H_2 (mol L^{-1})
40/1.6H	YCWCa	Clad	4% H_2/Ar, 40 bar	1.25×10^{-3}
40/0.3H	[Na] = 1.4×10^{-1} [Ca] = 3.8×10^{-4} [K] = 3.7×10^{-1} [CO_3^{2-}] = 3.0×10^{-4}	Clad	0.75% H_2/Ar, 40 bar	2.4×10^{-4}
40/0.3H—Bic	Bicarbonate	Clad	0.75% H_2/Ar, 40 bar	2.4×10^{-4}
0—Bic—Clad	[Na] = 2.0×10^{-2} [Cl] = 1.9×10^{-3}	Clad	Anoxic	–
0—Bic—Declad	[CO_3^{2-}] = 1.1×10^{-3}	Declad	Anoxic	–

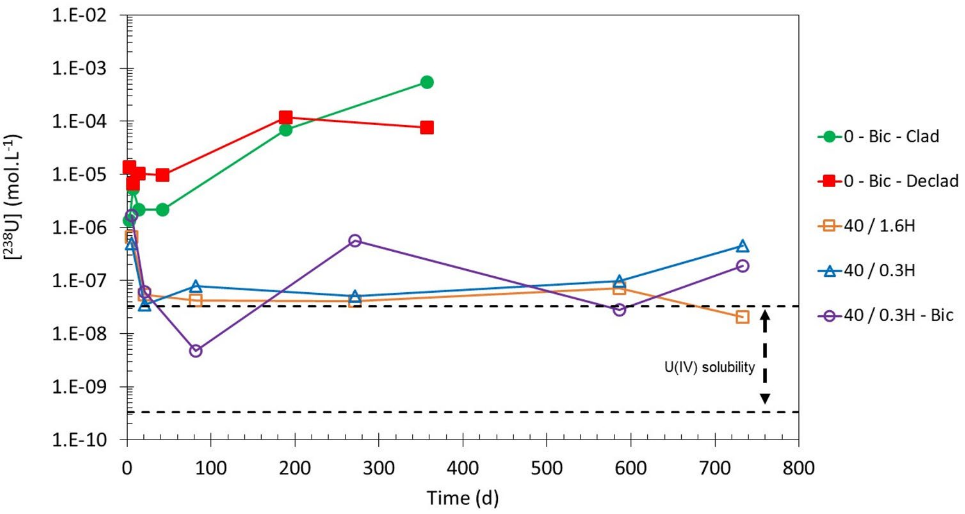
Regular samplings of the solution were performed to measure the release of a selection of radionuclides. In the experiments under anoxic conditions the solution was completely replaced by fresh solution after 7 and 14 days. In the experiments under reducing conditions the solution and gas phase in the autoclave headspace were renewed after 5 days. These renewals of solution and atmosphere were included to reduce the activity in the leachate and to lower the concentration of radionuclides that could be initially released from a pre-oxidized surface layer, and that may mask a smaller further release. The test duration was 357 days for the experiments under anoxic conditions and 733 days for the experiments under reducing conditions. The solution samples were analyzed by ICP-MS for the determination of ^{238}U, ^{99}Tc and ^{129}I, by gamma spectroscopy for ^{137}Cs and by LSC after several separation steps for the determination of ^{90}Sr. A complete description of the methodologies can be found in Mennecart et al. [6]. The uncertainties (2σ) are depicted in the figures as error bars; they are approximately as large as the symbols used.

Results

Figure 1 shows the evolution of the ^{238}U concentration as a function of the leaching time. In all experiments, there was a high initial release, followed by a decrease of the uranium concentrations due to the solution replacement. Under anoxic conditions, the uranium concentrations then stabilized shortly around to 10^{-6} to 10^{-5} mol L^{-1}, but between 42 and 82 days, they started to increase, reaching values about 10^{-3} to 10^{-4} mol L^{-1} after 1 year, probably as a result of air intrusion; a detailed discussion of this is given in Mennecart et al. [5]. In presence of H_2, the concentrations stayed around 10^{-7} mol L^{-1} for 2 years, with an important fluctuation in the bicarbonate solution. No obvious reason was identified to explain this fluctuation, but similar observations have already been reported in the literature [7, 8], and the lower value in the experiment 40/1.6H is likely a consequence of the general concentration variation.

Figure 2 shows the evolution of the total moles of ^{137}Cs released in the five experiments. In all leaching experiments, the most accessible fraction of cesium was released in less than 100 days, irrespective of the redox conditions or the

Fig. 1 Evolution of the concentration in solution of ^{238}U as a function of the leaching time and the range of the U(IV) solubility [9]



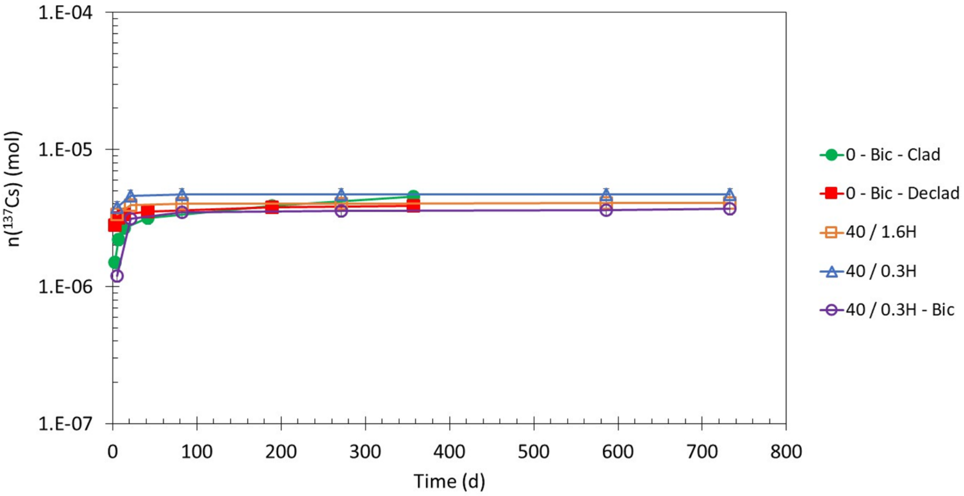


Fig. 2 Evolution of total moles of ^{137}Cs released as a function of the leaching time

solution composition. After 100 days, cesium continued to be released in solution but at a lower rate and the total amounts of cesium released at the end of the experiments were nearly the same in all experiments.

Iodine (^{129}I) followed the same trend as cesium, with a fast release in solution during the first 100 days and a much slower release until the end of the experiments, while no significant differences were observed between the various experimental conditions.

For ^{90}Sr, the release in solution depends on the experimental conditions (Fig. 3). The lowest release was found in the experiments under H_2. In YCWCa, the ^{90}Sr release almost stabilized and variation of the hydrogen partial pressure had no influence. In presence of bicarbonate, the ^{90}Sr release increased continuously, but the released amount was an order of magnitude smaller than in anoxic conditions.

In case of ^{99}Tc, the highest release was observed in the bicarbonate solution. The ^{99}Tc concentrations tend to be higher in anoxic conditions than in reducing conditions (the initial decrease for the clad segment in anoxic conditions is linked to the very high release after 7 and 14 days). In reducing conditions the concentrations are also higher in the carbonated medium than in YCWCa (Fig. S1, supplementary materials).

Discussion

Since the hot cell atmosphere was under air, it is likely that the results in the anoxic experiments were biased because of oxygen contamination resulting from radiation damage to the O-rings that should guarantee the airtightness. Under reducing conditions, the uranium concentrations were very close to the upper limit for the solubility proposed by Neck for amorphous U(IV); $[U] = 10^{-8.5\pm1}$ mol L^{-1} [9], which confirms that the SNF matrix was stabilized under these

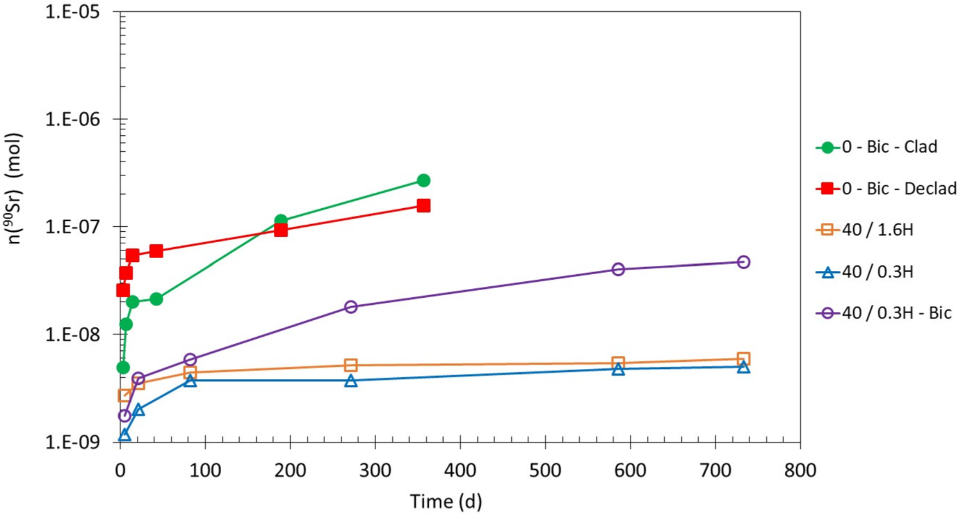


Fig. 3 Evolution of total moles of ^{90}Sr released as a function of the leaching time

reducing conditions and the absence of U(VI) as the uranium concentrations in bicarbonate solutions are equivalent to those in YCWCa. The variation in uranium concentrations for the tests with different H_2 concentrations is too large to conclude that there is a significant difference between these tests.

No effect of hydrogen nor the presence of bicarbonate was observed on the cesium and iodine release since the total moles were in the same range at the end of all the experiments.

Strontium behaved differently from iodine and cesium as its release in solution was found to depend on the experimental conditions. Under anoxic conditions, the high release of strontium was likely caused by the oxidation and dissolution of the SNF matrix by the traces of oxygen, not counteracted by the presence of hydrogen, and might thus be attributed to the release of strontium incorporated in the SNF matrix.

In presence of hydrogen, strontium was also continuously released in solution but the amount was one order of magnitude lower. At the end of the experiments, the ^{90}Sr concentrations were about 10^{-7} and 10^{-8} mol L^{-1} in bicarbonate solution and in YCWCa, respectively. The final concentrations were below the solubility limits of expected phases such as strontium carbonate [10]. The release of ^{90}Sr under reducing conditions also appears to be promoted by the presence of carbonates, in a similar way as for ^{99}Tc (see next paragraph). Like for uranium, the release of strontium was similar at low and at high hydrogen partial pressure YCWCa.

As a redox sensitive element, the technetium release could be influenced by the presence of hydrogen or air contamination. Indeed, reduced Tc(IV) is solubility limited, whereas oxidized Tc(VII) is not. The solubility of TcO_2(am,hyd) is $3.2 \pm 0.3 \times 10^{-6}$ mol L^{-1} determined in previous studies in 0.5 mol L^{-1} KCl–KOH solutions and in synthetic cement pore water at pH 13.3 [11, 12]. The data show that the ^{99}Tc concentration is effectively lower in the presence of hydrogen (in bicarbonate water and in YCWCa) than in anoxic conditions (in bicarbonate water). Moreover, in the experiments with hydrogen (YCWCa and Bic), the presence of bicarbonate appears to promote the ^{99}Tc release, but this is probably linked to the matrix dissolution rather than reactions between technetium and bicarbonate ions.

The cumulated released fractions for the considered radionuclides were calculated, subtracting the released uranium fraction. This can be considered as the Accessible Fraction of the Inventory (AFI), i.e., the fraction that is not incorporated in the UOX matrix. The values are in Table S1 (supplementary materials). The values for iodine are high, but this is because the tested fuel had been exposed to high temperatures during irradiation, resulting also in a high fission gas release. The AFI of cesium and iodine is similar in anoxic and reducing conditions. For ^{90}Sr and ^{99}Tc the AFI is larger in anoxic conditions. This is remarkable, because if the fuel was the same in both conditions, the accessible fraction should also be the same. The correction by the dissolved uranium to calculate the AFI probably does not give a correct image of the actual accessible fraction. This correction is done with the dissolved uranium, but this does not take into account the reprecipitated uranium.

Conclusion

Leaching experiments were performed with UOX fuel in a high pH solution (YCWCa, two H_2 partial pressures) and in a bicarbonate solution (anoxic/reducing conditions) to investigate the release of fission gases and a selection of actinides and fission products. The effect of hydrogen, to impose reducing conditions, strongly decreases the dissolution of the SNF and the release of radionuclides included in the matrix (^{90}Sr, ^{99}Tc). The lowest partial pressure, corresponding to a dissolved hydrogen about 2.3×10^{-4} mol L^{-1}, is enough to significantly inhibit the SNF dissolution. Nevertheless, the presence of bicarbonate enhances the release of ^{90}Sr and ^{99}Tc likely by promoting the dissolution/precipitation phenomena of the matrix. Cesium and iodine are not influenced by the redox conditions or leaching medium on this time scale. The results under reducing conditions were obtained during the first phase of a 1700-day experimental program. The results from the second phase still need to be processed, and in parallel a new leaching campaign was launched to increase the confidence of the results, among others by performing duplicate leaching experiments.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1557/s43580-024-00816-1.

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Data availability Data will be made available on request.

Declarations

Conflict of interest The authors declare no competing interests.

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