New flow through reactor installed in the ITU Hot Cell laboratory to investigate the dissolution rates of the irradiated fuels

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Abstract

In order to study the dissolution rates for the different radionuclides, the effect of water radiolysis and to elucidate the dissolution mechanisms of the different radionuclides contained in the spent fuel matrix, irradiated spent fuel and UO_2 was used. This study is performed as a part of the collaboration programme "ENRESA – CIEMAT - ITU (EC DG/JRC)" to provide a source term for use in a performance assessment calculation.

For the determination of the dissolution rates a continuous flow through reactor specially designed for hot cell handling was built. This reactor allows the control in situ of different important parameters for leaching experiments such as, redox potential, pH and temperature.

These leaching experiments reported the effects of four important parameters (redox potential, pH, carbonate concentration and temperature) on the dissolution kinetics of the spent fuel matrix phase. The kinetic of dissolution of irradiated UO_2 fuel has been studied in synthetic granite groundwater under oxidizing conditions at room temperature. Preliminary results indicate that for spent fuel, dissolution rate depends on the burnup, being the dissolution rate calculated for the UO_2 LWR fuel with a burnup of 53 MWd/kg U of $2.66 \ 10^{-10}$ mol m^{-2} s^{-1} and of $6.77 \ 10^{-11}$ mol m^{-2} s^{-1} for the spent fuel of 29 MWd/kg U.

KEYWORDS: Spent fuel dissolution; radiolysis; dissolution rates; oxidising conditions; uranium oxides.

1. INTRODUCTION

The long term interactions between spent nuclear fuel and groundwater have to be understood in order to safely dispose the fuel in a final disposal. A final repository acts as a barrier against release of radionuclides to the biosphere.

For a repository performance assessment the rate of the spent fuel dissolution under different conditions is a very important parameter [i].

A review of dissolution experiments performed with UO_2 and spent nuclear fuel has already identified some of these inconsistencies [ii].

The understanding of the elementary processes of the mechanism reaction on the spent fuel in the repository conditions can be studied if some of the more important parameters (i.e. redox conditions) are controlled. Therefore, a good way to obtain information of these processes in solid dissolution reactions is the used of a continuous flow through reactor [iii, iv, v]. The experimental set up avoid the possibility of precipitation of dissolved reaction products because these products are being swept out of the experimental device by the flow before the dissolution becomes saturated with the non desirable products [vi].

This work is in the frame agreement between ENRESA/ITU and CIEMAT/ENRESA. The content of this publication is the sole responsibility of its publishers, and it in no way represents the views of the European Commission or its services.

2. EXPERIMENTAL

Figure 1 shows a schema of the dynamic leaching set-up built-up in a hot cell. The leaching reaction vessel is fitted with a quartz sample holder in the middle of the system. The reaction vessel with a total volume of 70 mL has a square section with a height of 10 cm and an adjustable top in order to exchange the samples at different experiments. The solid sample is held between two 100-μm quartz filters while the solution is circulated by a stirrer throughout the test to homogenise the solution. In order to avoid direct interaction between the sample and the stirring system, the sample is suspended in a quartz basket in the centre of the reaction vessel. The groundwater is introduced at the bottom of the reaction vessel by a dosing pump while the leached solution leaves the reaction vessel at the top. This concept assures that all of the groundwater is in contact with the spent fuel. The reaction vessel and the sampling part were installed into a hot cell while the rest i.e. feed solution, pump and electrical controllers for the pump, stirrer, pH, Eh and temperature were located outside (Figure 1). To follow the evolution of the reaction two combined glass electrodes (ph and Eh) and a thermo-couple are monitoring the conditions in the reactor during the experiment. A program database is monitoring the evolution of the experiment online and saves the data (pH, Eh and temperature) as function of the leaching time.

The materials used for this investigation were LWR UO_2 spent fuels. The samples were coming from pins with an average burnups of 56 and 29 MWd/Kg U. For the leaching experiments slice of rod fuel (including cladding material) weighted 2,07g and 2,574g for the spent fuels with a burnup of 29 and 53 MWd/kg U respectively. The preliminary microscopy characterisation showed a typical UO_2 spent fuel structure high density and formation of cracks in the surface (Figure 2).
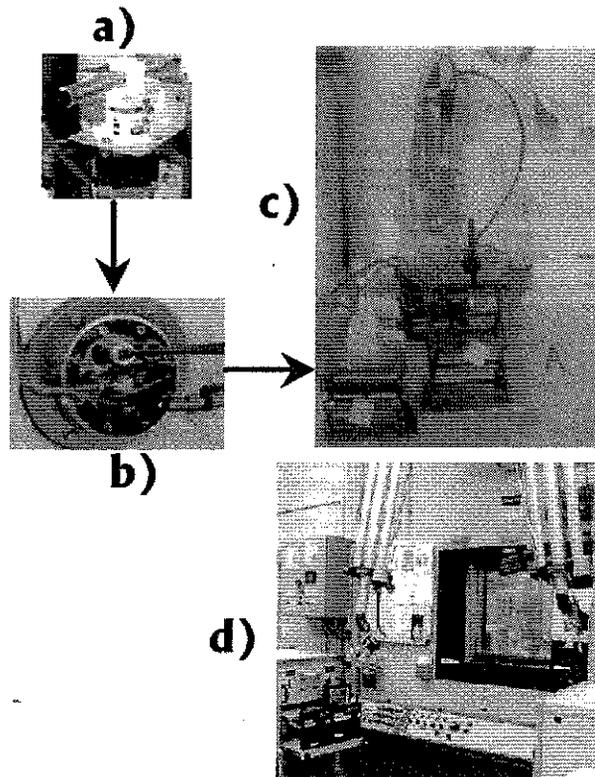
Figure 1 Flow Through reaction system used in the experiments reported here. a) Dose pump, b) Overpressure valve and feeding system c) Reaction vessel d) Control panels (Redox, pH, stirring system and pump control).
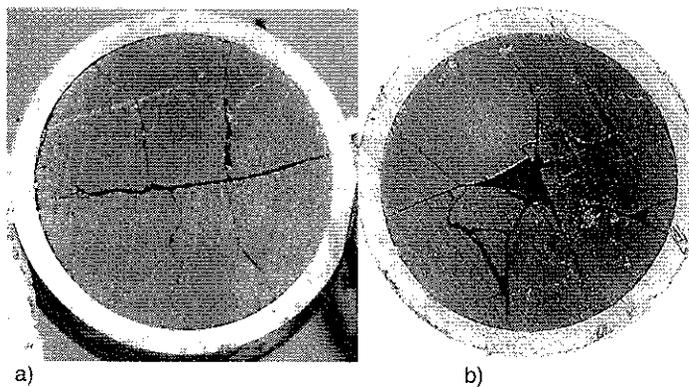

Figure 2 Microscopy characterisation for LWR UO_2 spent fuel a) burnup of 29 MWd/Kg U b) burnup of 53 MWd/kg U

3. RESULTS AND DISCUSSION

Experiments with spent fuel were carried out in a hot cell in granite groundwater under air atmosphere. Oxic conditions were obtained by equilibrating the leachant solution air at room temperature. The leachant used for these experiments was granite natural ground water (1mM [HCO_3^-]) the composition of this water is shown in the Table 1.

Table 1.- Composition of the granite natural ground water used in this investigation.

Specie	Concentration (mol/l)
Na^+	$4,09*10^{-4}$
K^+	$1,46*10^{-4}$
Mg^{2+}	$2,51*10^{-4}$
Ca^{2+}	$2,47*10^{-4}$
Cl^-	$2,37*10^{-4}$
Si	$4,99*10^{-4}$
SO_4^{2-}	$7,19*10^{-5}$
HCO_3^-	$1,07*10^{-3}$
F^-	$1,05*10^{-5}$
PO_4^{3-}	$1,04*10^{-7}$
Al^{3+}	$1,85*10^{-7}$
U_{total}	$2,32*10^{-9}$

The circulation rate of the leaching solution was maintained in the range of 0,1 to 0,001 ml/min. Working in this flow rate range ensures that the steady state conditions in these reactors are achieved, determined as in previous work [vii]. The dissolution rates determined using a continuo flow trough reaction vessel are based on the uranium concentration of the effluent at steady state. The rate of dissolution was calculated from the follow equation:

$$r_{dissolution} \equiv \frac{Q \times [U]}{S}$$

where Q is the flow rate (l/s) and the [U] uranium concentration at steady state (mol/L). These values were normalised with respect to the geometrical surface S (m^2) [iii].

Aliquots of 8 ml of leachants were taken at regular intervals and the uranium concentration was analysed. The leachants obtained were acidified with 1% HNO_3. The uranium analyses of spent fuel solutions were performed using a High Resolution Inductively Coupled Plasma-Mass Spectroscopy (HR-ICP-MS) from ThermoQuest Finnigan MAT (ELEMENT 2) modified to handle radioactive samples.

The dissolution rates were calculated applying the kinetic equation to the results obtained in the uranium dissolution of spent fuel. The results indicate that working in a flow rate between 0,025 and 0,15 ml/min the system avoid the precipitation of secondary phases. The preliminary results indicate that for spent fuel, dissolution rate depends on the burnup, being the dissolution rate calculated for the UO_2 LWR fuel with a burnup of 53 MWd/kg U of $2,66 \times 10^{-10}$ mol m^{-2} s^{-1} and of $6,77 \times 10^{-11}$ mol m^{-2} s^{-1} for the spent fuel of 29 MWd/kg U.

Spent fuel dissolution rates agree with the results obtained by Gray and Wilson [viii,ix] using similar conditions.

With this approach, the capabilities and performance of the flow-through reactor could thus be considerably improved.

Ongoing work will try to elucidate the mechanisms and the dissolution rates for the different radionuclides on the spent fuels used in this investigation and to extend this work to higher burn-up and different type of fuels (MOX).

4. References

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