Studies of the Influence of Water Radiolysis to the Spent Fuel Matrix Dissolution Process

Javier Quiñones and Joaquin Serrano

Ciemat. Departamento de Fisión Nuclear. Avda. Complutense 22, E-28040-Madrid. SPAIN

Abstract

The disposal of high level radioactive waste in geological deep repositories relies on the long term stability of spent fuel matrix, which must be assured for thousands of years. One of these factors considered within the studies of performance assessment on spent fuel under final repository conditions is the effect of the radiation on its leaching behaviour. Due to the radiation from spent fuel can modify some properties of both solid phase and leachant and therefore it would alter the chemical behaviour of the near field.

Particularising in the effect of the radiation on the leachant, it will cause generation of radiolytic species that could change the redox potential of the environment and therefore may bring on variations in the leaching process.

In this work, we compiled the leaching experiments performed in an irradiation facility (Nayade), in order to emulate γ radiation field of a spent fuel at different cooling times. Initial dose rate used was 0.014 Gy/s using source of [60]Co. The spent fuel chemical analogue utilised was SIMFUEL (natural UO_2 doped with non-radioactive elements simulating fission products) and the leachants selected were saline and granite bentonite waters both under initial anoxic conditions.

Preliminary results indicate that radiation produces an increase of the uranium dissolution rate, being the concentrations measured close to those obtained in oxic atmosphere without radiation field. In addition the solubility solid phases from experimental conditions were calculated, for both granite bentonite water and 5 m NaCl media.

On the other hand, a tentative approach to model the role of γ radiolysis in these SIMFUEL tests has been carried out as well.

Keywords: Radiolysis, uranium oxides, synthetic granitic groundwater; leaching experiments

1. Introduction

The long-term interactions between spent fuel and groundwater has to be understood in order to dispose the fuel in a safe final underground repository. With this goal in mind, and given the limitations related to the handling of irradiated fuel, spent fuel dissolution experiments combined with more detailed studies using non-irradiated chemical analogues are very useful for performance assessment (PA) studies.

One of the factors considered within the PA studies on spent fuel behaviour under final
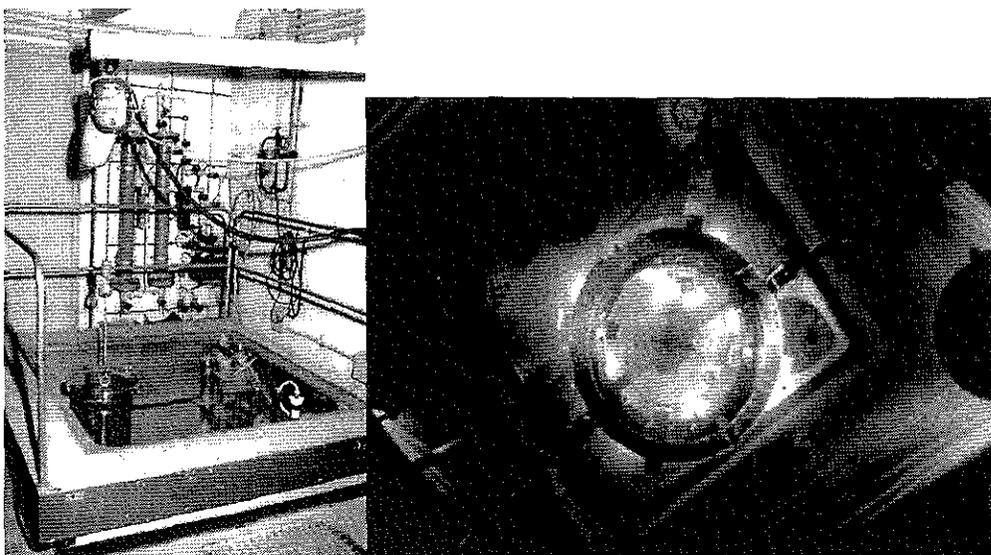
Figure 1 Gamma irradiation facility, Nayade, used for SIMFUEL leaching experiments.

underground repository conditions are the effect of the radiation on the leaching processes. The radiation emitted by spent nuclear fuel alters the properties of the solid and the leachant, in such way that it modifies the chemistry of the near field [1986SUN/SHO, 1990CHR, 1994LOI/GRA, 1999COB/RON and their references].

Radiolysis of the groundwater in contact with the used fuel produces oxidants for the oxidative dissolution of the nuclear fuel. The highest initial absorbed dose rate is generated by the β and γ radiation and after a long period the α radiation will be higher than those. Experimental measurements of the effects of radiolysis on the matrix dissolution rate are complicated by the fact that the effects of α, β and γ radiolysis cannot be separated.

The development of kinetic model based on the data obtained from studies of fuel matrix dissolution in presence of α and γ radiation could be useful for predict the evolution of oxidants generation and their impact on the stability of spent fuel under repository conditions [200QUI/SER].

Particularizing in the effect γ radiation, SIMFUEL leaching experiments with and without presence of external ^{60}Co sources in bentonitic groundwater (GBW) [5] and in 5 m NaCl were performed. In this paper the initial results obtained from these experiments are presented.

2. Experimental procedure

2.1. Characteristic of the irradiation facility

Leaching experiments were performed in a γ irradiation facility (NAYADE) situated at CIEMAT. This radioactive facility allows irradiating materials under water by γ emitter (^{60}Co).

Reactors leaching experiments were placed in a well-closed basket and this was immersed in the pool. The basket was encircled by γ sources.

Previously to start the experiments, Fricke dosimetry of the basket was performed, being the initial dose absorbed for the leaching vessel of 0,014 Gy/s [1997FUE]. This γ dose chosen is consistent with a 40

MWd/kg spent fuel after 20 years of cooling time.

2.2. Leaching experiments

SIMFUEL pellets used for these tests were supplied by AECL Research Chalk River Laboratories. The concentration of additives in SIMFUEL simulate the fission products representative of a burn up of 50 MWd/kg U. The percent of each element in UO_2 matrix and general characteristics of SIMFUEL are given elsewhere [1991LUC/VER].

Sampling and preparation of all leaching tests were performed inside of a globe box under anoxic conditions (N_2 atmosphere). The oxygen content in the globe box atmosphere was always lower than 1 ppm. SIMFUEL powder samples were conditioned as was described in previous report [1996GAR/SER]. They presented a specific surface of 0.04 m^2 g^{-1}. Leachants used were synthetic groundwater GBW [1996CIE] and 5 m NaCl.

Figure 2 Detail of the irradiation basket used for leaching experiments.

Parallel leaching experiments, inside a globe box under nitrogen atmosphere (without γ sources) and in the Nayade facility were performed. All the tests were got ready in N_2 atmosphere inside a glove box to avoid superficial oxidation before to start the experiments. Solutions were analyzed by ICP-MS and fluorimetric techniques.
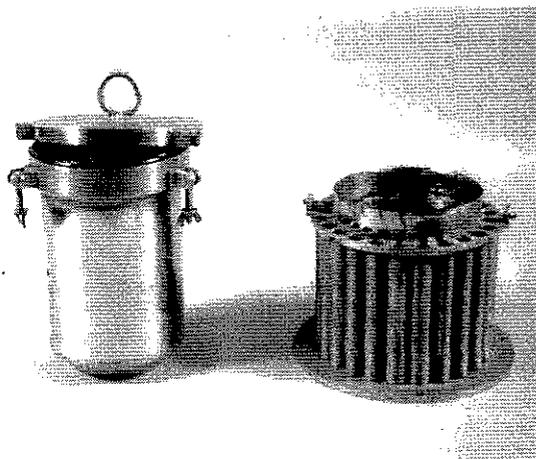
3. Results and discussion

Table I shows the U concentration from SIMFUEL after 190 days in N_2 atmosphere with and without presence of γ emitters (labeled *Nayade* and *Glove box*, respectively) in comparison with others obtained without external sources in air atmosphere [1998SER/QUI] for the same experimental time (labeled *Air*).

Table I U concentration after 190 d of experimental time in various conditions for both GBW and 5m ClNa: "Glove Box", nitrogen atmosphere; "Nayade", initial nitrogen atmosphere and presence of external γ source and "Air", air atmosphere.

Experiment	U (mol kg^{-1}) in GBW	U (mol kg^{-1}) in 5m ClNa
Glove box	4.6 10^{-8}	3.6 10^{-8}
Nayade	1.7 10^{-6}	2.2 10^{-6}
Air	3.2 10^{-6}	6.7 10^{-6}

It is observed that uranium concentrations measured in anoxic atmosphere (N_2 atmosphere) without irradiation (Glove box) both in GBW and in NaCl are lower than those obtained in the irradiation facility, Nayade (Fig. 3 and 4, respectively). From this it is reasonable to think that γ dose received by the leaching system is enough to alter SIMFUEL leaching behaviour, due to generation of oxidant radiolytic products.

On the other hand, uranium concentrations obtained from Nayade experiments are in the same order of magnitude that those obtained in air atmosphere.

As it was expected, uranium concentration values obtained in NaCl and GBW are very close. However the ratio between U concentration measured in presence of not of γ field for tests performed in NaCl solution is almost double than in GBW. This fact could be related with the composition of the leachants, i.e. with the initial concentration of Cl⁻ and the subsequent generation of radiolytic species such us ClOH⁻, ClO_2^-, etc.

From experimental conditions of these tests (Eh, T, pH and leachant chemical compositions), and assuming the hypothesis that concentrations measured (Table I) reach the steady state, solubility control phases for U concentration in solution were calculated. The geochemical modeling codes used were EQ3/6 [1992WOL] for brine solutions (Pitzer data base "data0.pit.R2") and Phreeqc v.1.6 [1995PAR] for GBW tests supported by the thermodynamic data base NEA [1992GER].

Figure 3 shows the U concentration measured versus pH for the tests performed in GBW under irradiation, reducing and oxidizing conditions (Nayade, Glove box and Air tests, respectively). In this figure, the lines represent the uranium solubility

Figure 3 Uranium concentration vs. pH in GBW under irradiation, reducing and oxidizing conditions (Nayade, Glove box and air atmosphere, respectively). Lines correspond with the solubility solid phases calculated for Nayade conditions.

Figure 4 Uranium concentration vs. pH in NaCl under irradiation, reducing and oxidizing conditions (Nayade, Glove box and air atmosphere, respectively). Lines correspond with the solubility solid phases calculated for Nayade conditions.

calculated for each solid phase considered for the Nayade experimental conditions. As can be deduced, candidate solid phase for controlling uranium solubility in GBW under γ irradiation is Sklodowskite ($Mg(H_3O)_2(UO_2)_2(SiO_4)_2 \cdot 4H_2O$). In the case of the experiments carried out in 5m NaCl, Fig. 4, the controlling solid phase calculated, also for Nayade conditions, is Na_2UO_4 (α). In Table II, are summarized the controlling uranium phases in GBW and 5 m NaCl for the various chemical conditions studied.
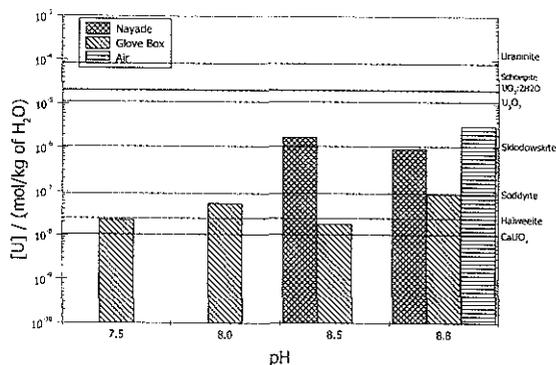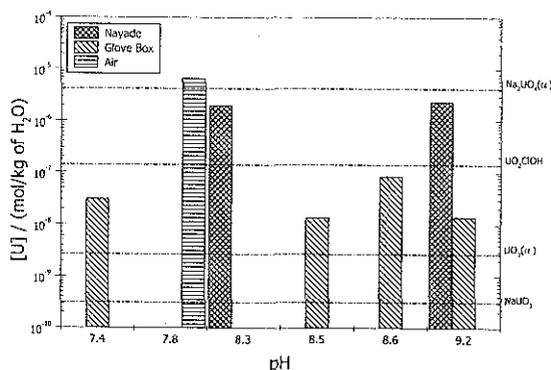
Table II Solubility controls on uranium concentration in GBW and 5 m NaCl for Nayade, Glove box and Air experiments. (Bold writing correspond with the expected controlling solids).

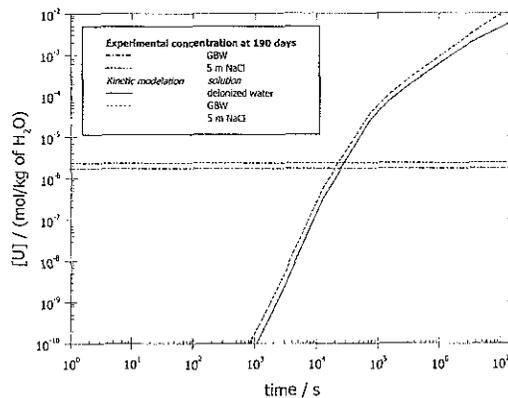|	GBW solid	U (mol kg^{-1})	NaCl Solid	U (mol kg^{-1})
Nayade	Shoepite	2.049 10^{-5}	Na$_2$UO$_4$(α)	4.2088 10^{-6}
	Haiweeite	2.46 10^{-8}	UO$_2$ClOH	1.4026 10^{-7}
	Skoldowskite	1.084 10^{-6}		
	U$_3$O$_7$ (β)	1.134 10^{-5}		
	UO$_3$ 2H$_2$O	2.125 10^{-5}		
	Uraninite	8.375 10^{-5}		
Air	Shoepite	1.975 10^{-5}	NaUO$_3$	7.1524 10^{-6}
	Skoldowskite	1.931 10^{-6}	UO$_2$ClOH	2.7987 10^{-8}
	Soddyite	8.503 10^{-8}		
	UO$_3$ 2H$_2$O	2.048 10^{-5}		
Glove box	Coffinite	3.994 10^{-9}	Na$_2$UO$_4$	6.6705 10^{-7}
	Rutherfordine	1.771 10^{-9}	UO$_2$ClOH	8.8500 10^{-8}
	U$_4$O$_9$	4.216 10^{-7}	UO3(α)	1.0705 10^{-9}

A tentative approach to model the role of γ radiolysis in these SIMFUEL tests was carried out. The kinetic model used [1999QUI/SER] is based on UO$_2$ matrix dissolution studies developed by Christensen et al. [1994CHR/SUN, 1999CHR]. Code applied for calculations was Maxim Chemist [1979CAR/HAN].

This model deems that UO$_2$ oxidation processes with O$_2$ and H$_2$O$_2$ can be reduced in two reactions taking into account experimental reaction constant values [1998BRU/CER and their references]. For chlorides, kinetics reactions used were taken from Kelm et al. [1998KEL, 1999KEL]. Retrodiffusion of O$_2$(g) and H$_2$(g) was considered.

Figure 5 Evolution of U concentration from the kinetic model used in this work.

Due to the special geometry of the experimental system (external γ source) it was assumed that all the radiolytic products generated in the whole leachant can react with the SIMFUEL powder surface. In addition, diffusion liquid-gas was taken into account.

The Fig 5 shows the experimental data of U concentrations measured at 190 d for both GBW and 5 m NaCl solutions (horizontal lines) and the U concentration evolution calculated considering various leachants: deionised water, GBW and 5 m NaCl. As can be observed the U concentrations values obtained in Nayade tests are much lower than those modelled for the same reaction time. This model achieves the experimental uranium concentrations in less than 3 hours. These high uranium concentrations calculated by the kinetic model can be related with the water layer in contact with water since as was aforementioned all the radiolytic products generated in the bulk leachant can react with the leachate.

As was expected, the evolution of U concentration from the kinetic model used for deionised water gives lower values than in GBW and 5 m NaCl due to the absence of chloride radiolytic products. When comparing the results calculated in the case of GBW and NaCl, the highest U concentration values were achieved for the brines.

Ongoing experimental work will provide data to try to obtain matrix alteration rates for various γ doses combining with groundwater chemistry by a more complex kinetic a thermodynamic model.

4. Conclusions

Enhanced U dissolution from SIMFUEL powder samples was observed by performing static leaching tests under anoxic conditions at room temperature in presence of external γ source in both GBW and in NaCl 5m solutions. After 190 days of leaching, the ratio between experiments performed with and without γ field was approximately 30 times for GBW and 60 times for 5 m NaCl.

Uranium concentrations obtained from the tests started under reducing atmosphere and underwent to a initial γ dose of 0.014Gy/s are comparable with others performed under oxic conditions (air atmosphere).

Solid phases candidate for controlling uranium dissolution in the tests performed in presence of γ sources were Skoldowskite for synthetic granite bentonite groundwater and $Na_2UO_4(\alpha)$ for 5m NaCl tests. Uranium concentrations calculated by the kinetic model were much higher than the measured values for both synthetic granite bentonite groundwater and 5m NaCl tests. These differences can be related with the water layer in contact with water since all the radiolytic products generated in the bulk leachant were assumed to be able to react with the leachate. Moreover, any restriction due to groundwater chemistry was taken into account.

A prediction of the role of γ radiolysis on SIMFUEL leaching, and in consequence for spent fuel dissolution behaviour tests pass to consider a combination of thermodynamic and kinetic aspects and of course accurate experimental data. On going SIMFUEL leaching tests with various geometries and dose rates will try to provide data for future calculations.

5. Acknowledgements

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