NEW RADIOACTIVE FACILITY FOR SPENT FUEL STABILITY STUDIES

Javier QUIÑONES[1], Sandra PEREZ-DE ANDRES, Eduardo IGLESIAS
Ciemat – Energy Department. Avda. Complutense, 22. E-28040-Madrid. SPAIN.

ABSTRACT
In this work a description of the new radioactive facility (Characteristics, scheme, projects involved, techniques, …) is presented. This facility was designed for performing R&D+i studies and/or projects related to characterize the physicochemical properties of the spent fuel, an its stability and behaviour under repository conditions.
Furthermore, this facility has the capability for carrying out chemical analysis with ICP-MS and HPLC techniques. Due to these reasons, nowadays, this laboratory is involved in several National and International projects related to spent fuel stability.
The paper reviews the manufacture and description of the laboratory, analytical techniques, the experimental work (leaching and coprecipitation experiments) and modelling performed for extrapolating to the repository conditions.

KEYWORDS **SPENT FUEL STABILITY, SPENT FUEL ANALOGUE, LEACHING STUDIES, COPRECIPITATION STUDIES**

1. INTRODUCTION

In order to make the Performance Assessment (PA) studies of the high-level waste (nuclear fuel) under deep geological storage conditions and for extrapolating to the long term, it is necessary to carry out experimental work (laboratory and/or natural analogues among others) and develop models (thermodynamic and/or kinetic) to determine the parameters that may be used to assess the safety of the waste in storage conditions. Some of the most important factors considered within the PA studies on the spent-fuel in the near field are: the dissolution rate of the spent-fuel matrix, the release rate of each radionuclide and the formation or not of secondary phases that can increase or decrease the spent-fuel stability in these conditions (Figure 1). The dissolution behaviour of the spent fuel matrix is the source term that will control the radionuclides release from the waste to the environment. Consequently, studies of the chemical stability of the fuel and the chemical behaviour of the released radionuclides are critical parameters for understanding the irradiated fuel behaviour under a repository conditions.

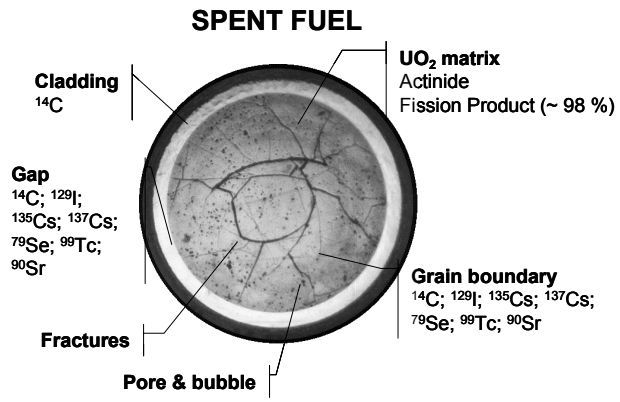

Figure 1. Scheme of a radionuclide distribution in a spent fuel pellet irradiated on a Light Water Reactor (LWR)

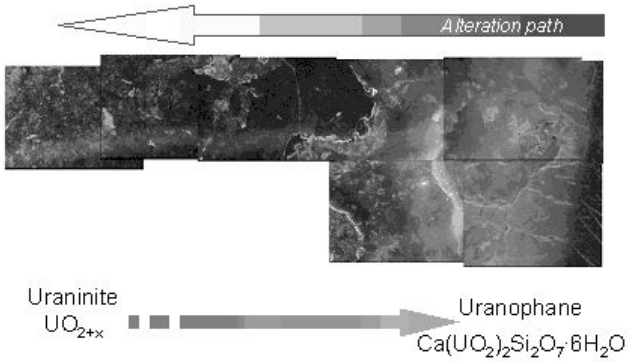

Figure 2. Micrograph of the uraninite weathering. Corrosion behaviour observed in the natural analogue.

Nowadays, the spent fuel available (in the whole world) has only a few decades of cooling time. As it is well known, the radionuclides decay might produce important changes on the physicochemical properties of the spent nuclear fuel. Therefore, the spent fuel can not reproduce the leaching behaviour that it will have after at least 1000 years of cooling time. As a result of the experimental studies done using different analogues materials as a function of the parameters studied, spent fuel and its chemical analogues as SIMFUEL[1] (natural UO_2 doped with non-radioactive elements simulating fission products), sinterized UO_2 (s) and mineral of uranium; for simulating repository conditions aqueous means, that try to simulate the chemical properties of groundwater (saline, granite and granite bentonite waters), are used.[2,3].

Javier.quinones@ciemat.es TEL.- +34 913466290. FAX - +34 913466233
In order to perform these projects a new facility was designed and manufactured. Nowadays, the facility consists of two radioactive laboratories, i.e., one dedicated to experimental work (leaching, coprecipitation and partitioning

experiments) and the second (chemical analysis) has accomplished the useful equipment for performing high quality analysis with ICP-MS and HPLC. Furthermore, in this facility, are placed 5 showcases and 3 glove boxes. Focussed on the showcases, two of them have the possibility of work with high corrosive gases (Cl_2(g) HCl(g)), with a special scrubber (model type AG 1800 l) for each line before entering in the ambient filters (air line out).
The ICP-MS room, has a special parameter control on several variables (depression, temperature, cleaning room). In order to keep a clean room, it is divided in two areas: Pc area, this was designed as the place for controlling the analysis equipment and also allows to monitor the analysis routine, equipment area has sited the ICP-MS (Perkin Elmer, ELAN – 6000) and HPLC (Perkin Elmer, 600 Series).The ambient temperature is fixed to 20 ºC, whereas the depressions either equipment and Pc area or Pc-area and the corridor are in the range of 2 – 3 mm of water column. In order to keep radiological safety during analysis the air extraction from torch and equipments warm-parts is directly connected to the filters.
Furthermore, and focussed on the applicability of ICP-MS studies to this field, in this work is reviewed how the knowledge of the isotopic distribution and mean life time of each radionuclide allows us to obtain important conclusions about oxidation, matrix dissolution processes, migration and transport of radionuclides that have been retained in a high-level repository conditions.

2. EXPERIMENTAL DETAILS

These studies have been carried out using ICP –MS as analytical technique. This analytical method is a very powerful tool that offers very low detection and quantification limits and broad elemental coverage with the additional capabilities of providing isotopic abundance information of fission products as well as actinides, measuring both stable and radioactive nuclides with similar sensitivity, and their absolute concentration. This fact is very useful for the main analytical applications (environmental, medical, biological, chemical,…). The problem is presented when it is applied to materials that come from nuclear fissions processes, because the isotopic relationship is not the same as the natural, and therefore, the result obtained has been discriminated according to different criteria.
The analysis of the samples obtained from the lixiviation and co precipitation experiments of the nuclear fuel analogues in different conditions were performed in a Perkin Elmer equipment model ELAN 6000. After the proportional sampling, filtration and ultra filtration (in sieves of 0.45 and 0.22 μm , respectively) were performed, they are acidified with 10% HNO_3 and then diluted. The dilution factors were in the range between 50 and 500, depending on the chemical composition of the initial solution to be analysed[2].

3. RESULTS

Figure 2 is a scheme performed using a micrograph of weathered uraninite (obtained with dark field optic microscopy), where the final result of this mineral corrosion can be observed. The left side of the Figure 2 shows the uranium material without corrosion "UO_2(s)" whereas on the right end there is a yellowish secondary phase of U(VI) (Uranophane "$Ca(UO_2)_2Si_2O_7{\cdot}6H_2O$") produced as a consequence of the groundwater alteration during thousands years. This micrograph is a clear example of the existence of an oxidation gradient. The model proposed in the exercise ENRESA – 2000[4], assumes that when groundwater reaches the spent fuel matrix, it is oxidised by the oxidants generated by the groundwater radiolysis and later dissolved. When the U concentration in solution achieves the solubility value the precipitation of schoepite will begin, with subsequent formation of other secondary phases of lower solubility. The chemical composition of this secondary phases will be a function of the geochemistry conditions.

$$UO_2(s) \rightarrow \text{oxidation (by radiolytic oxidants)} \rightarrow UO_{2.33}(s) \rightarrow \text{dissolution} \rightarrow \text{precipitation} \rightarrow UO_3{\cdot}2H_2O(s) \rightarrow Ca(UO_2)_2Si_2O_7{\cdot}6H_2O$$

The problem arises when the results of the experiments are extrapolated from laboratory to repository time scale. It is necessary to be careful because even so called "conservative" hypothesis and simplifications can lead to errors.
One of the issues related to the use of the natural analogues of the burned fuel is the chemical difference between them. Comparison of the mass spectra of a spent fuel with an average burnup of 40 MWd/kg U (Figure 3, spectra obtained by means of LA-ICP-MS of a polished surface)[5] with the spectrum obtained by ICP-MS analysis of an uraninite solution (Figure 4, uraninite from Oklo natural reactor)[6]suggests that the use of the isotopic dilution technique should allow to determine the contribution and origin of each isotope in a particular phase in different locations of the repository.

Figure 3 shows a normal distribution and it is in agreement with the fission yield produced in the light water reactors[7]. As proven by Garcia Serrano J., using these data one can calculate the fission yields that allow characterisation of the spent nuclear fuel.
Figure 4 shows a lot of heterogeneous behaviour. The differences between the spectra in Figures 3 and 4 is defined by the difference of the cooling period: the spent fuel has been cooling for a few years, whereas the natural material used was generated more than 1.74 billion years ago; and has already underwent the radioactive decay process.
From the experimental results obtained with ICP-MS, different behaviour patterns have been proposed for the different chemical elements of interest from the point of view of safety assessment of a repository. Modelling the results allows to define the behaviour of different elements of interest. In the case of Pu concentration in solution is proposed as a control of a pure secondary phase formation (Figure 5, granite bentonite media)[3]. This model is capable to predict the mentioned behaviour, however for other elements, i.e., Am (Figure 6, saline media)[1] a solubility control by coprecipitation of a secondary phase is proposed.

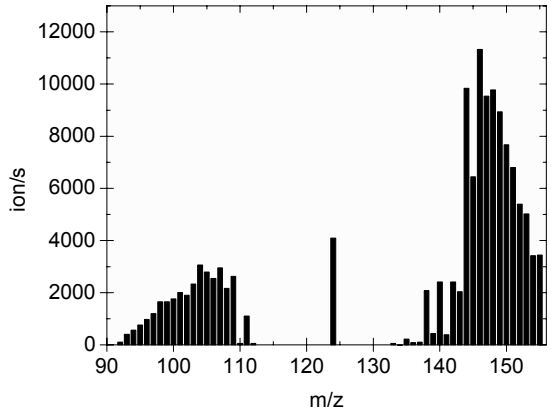

Figure 3. Mass spectrum of a spent fuel with an average burn up of 40 MWd/kg U.

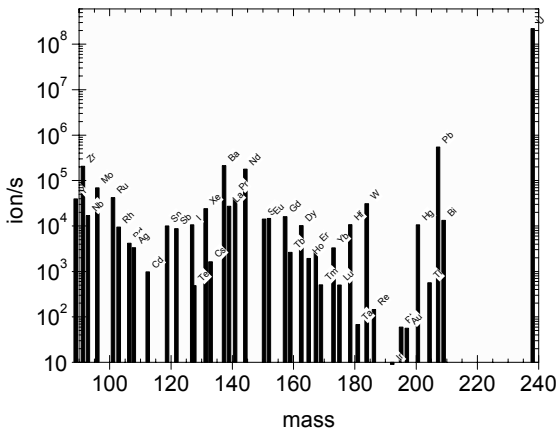

Figure 4. Mass spectrum of uraninite solution.

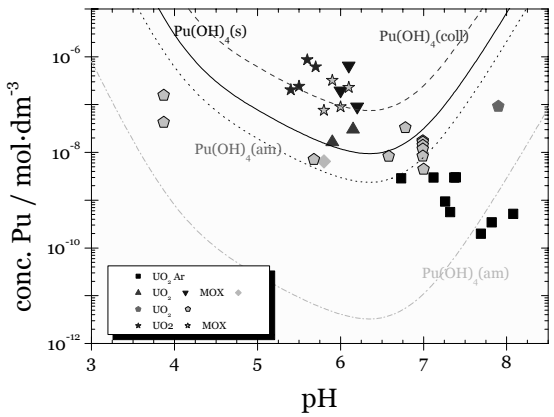

Figure 5. Modelling of the Pu solubility in granitic and granitic-bentonitic water. Comparison with experimental results of spent nuclear fuel as is described in [1].

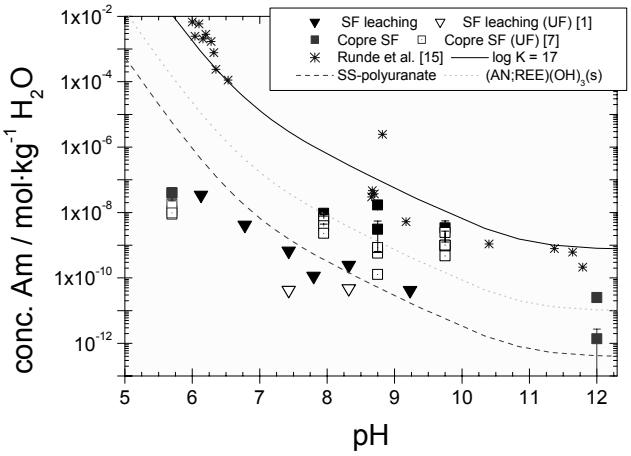

Figure 6. Modelling of the Am solubility in the saline repository conditions (Granite Bentonite medium, obtained from leaching and coprecipitation experiments [1]). Comparison with experimental result of spent nuclear fuel (SF). Points labelled with UF means ultrafiltered samples.

4. CONCLUSIONS

ICP-MS is a powerful tool for spent fuel stability studies under repository conditions. This technique allows to discriminate among different isotopes and the results obtained allow to develop models for extrapolation and prediction of the spent fuel behaviour at the time range useful for performance assessment studies.
Radioactive materials can have significantly differences to natural isotope ratios for many elements. This makes the use of isotope ratios difficult for analytical purposes. At the same time, isotope ratios allow to follow and predict the decay path in the system.

ACKNOWLEDGMENTS

Financial support for this research has been provided in the framework of the Ciemat – ENRESA agreement (2000 – 2003) related to "Spent Fuel technology. Characterisation techniques and modelling of the fission products leaching procedure". The authors gratefully acknowledge the contribution of Luis Gutierrez, Antonia Fariñas, Mª Jesús Tomas, José Manuel Cobo.

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