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APPLICATION OF SPENT FUEL CHARACTERIZATION AND LEACHING STUDIES FOR VALIDATING ALTERATION MODELS

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ABSTRACT

From the Spanish point of view, one of the key issues related to the HLW performance assessment is knowing and predicting, or modelling, the behaviour of spent fuel under geological repository conditions. Taking into account this objective, several experiments have been performed in order to split and determine the influence of different variables on the final stability of the spent fuel matrix in the geological repository.

This paper presents some of the leaching results obtained with spent fuel and chemical analogues (UO_2, alpha doped – UO_2, SIMFUEL,) their application to extrapolate the corrosion behaviour for a long period of time and compare with corresponding data obtained using models. This procedure allows pointing out some of the uncertainties whose minimization is necessary to improve the models useful for performance assessment studies

INTRODUCTION

The Spanish HLW are generated as a consequence of the assumed 40-year lifetime of Spanish nuclear power plants for electricity production. They will consist of 6800 tU of irradiated fuel and 84 canisters of vitrified HLW from reprocessing Vandellos I NPP(GCR) spent fuel (the reactor currently is dismantled).

As established by the Spanish government, the Research & Development national programs rely upon ENRESA for financing and management; development and creation of experimental research external groups (universities, companies, institutions, etc…), and links to EU and international RDT programmes.

From 1986 up to 1999 ENRESA has implemented 3 R&D programmes. The main objective of those plans was the development of technologies for the final waste management based on deep geological disposal (AGP). Those plans were closely linked to the 3rd and 4th EU RDT programmes.

From 1999 - 2002 ENRESA 4th R&D plan was in force, linked to the 5th EU RDT programme, the main objective is to deepen knowledge and applications and verifications of the technological infrastructure created in previous plans, based on irradiated fuel as a waste form for disposal. The first management option is the storage of spent fuel (SF) in a repository. Partitioning and transmutation as a way of waste form volume and radiotoxicity reduction , will be studied, so that the decision that might be taken around year 2010, will be based on sound and feasible strategy. This strategy has been changed due to the government decision written down in the "VI Plan General de Residuos Radiactivos" [1]. In this document, it was chosen to build a Central Temporal Storage Facility for the HLW (spent fuel and vitrified waste) in dry condition.

A disposal concept for spent nuclear fuel and high level waste based on a deep geological repository has been defined. In the last years, a large range of activities has been devoted to the performance assessment of a generic repository, known as ENRESA 2000.

Spent fuel performance assessment requires evaluation of its long-term ability to isolate and immobilise individual radionuclides after the groundwater contact and it is necessary to know the waste behaviour under repository conditions.

The evolution of irradiated fuel under interim storage or deep geological conditions and the oxidation (O/M) rate before the water access to the fuel surface, are factors of great influence for enhancing dissolution.

Those studies have been undertaken by means of chemical analogues, real spent fuel and artificially aged irradiated fuel –experimental fuels-.

This work presents the guide lines followed in CIEMAT performed in close collaboration with previous Research & Development plans of ENRESA, and the activities in progress carried out specially on irradiated fuel, according to the 5th and 6th General Radioactive Waste Plan (GRWP) in force. The main part of the program is based on the use of chemical analogues of spent fuel, such as SIMFUEL and UO_2; due principally to its lower costs and because presently there are not hot cells facilities in operation for PIE fuel studies available in Spain. Besides, there is a collaboration agreement on spent fuel research with JRC-ITU, following the guidelines of the GRWP to promote international co-operation.

In this direction two new groups have been created in Ciemat to develop studies on hydrometallurgical and pyrometallurgical separation, joining the European projects in this area.

BACKGROUND AND EXPERIENCE

The objective of the different R&D projects done in CIEMAT is to support the performance assessment studies related to spent fuel final storage, both measuring the influence of several parameter of process and/or modelling the behaviour, and extrapolating to the interested cooling time.

This collaboration developes together with other Spanish group (UPC and ENVIROS) and international groups (EU Framework programs) [2]. The model used the knowledge obtained. Figure 1 schematically represents the way of working and how to proceed in order to obtain enough results and database to design, perform and validate a model to extrapolate the results obtained in the laboratory to those environment considered in performance assessment relevant to repository conditions.

In order to obtain the results and define which are the key variables and processes that have a relevant influence on the alteration process of the spent fuel under repository conditions the following lines were evaluated:

i) Characterization of spent fuel composition and inventory (UO_2, fission products, activation products, actinides)[3, 4]
ii) Dissolution/alteration of UO_2 (dissolution mechanisms, redox conditions effect, pH effect, salinity and composition effect of leachants, SF physical state effect (such as flaws, cracks, distance between pellets and grain size)[5-8]
iii) Secondary phase formation [9, 10]
iv) Radiolysis influence [11-14]
v) Mobility of products dissolved (radiolysis effect, physical and chemical conditions effect, formation of complex and colloids, hydrodynamics conditions effect of environmental media.[15]
vi) Instant release of radionuclides [16].
vii) Modelling [2, 17-21]

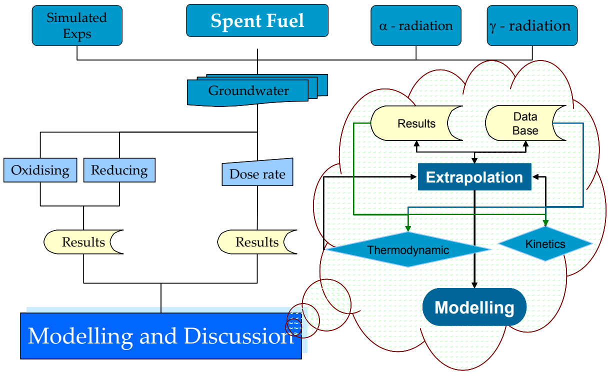

Figure 1 Scheme of research procedure

The principal objective is the study of radiolytic effect on spent fuel corrosion (α, β and γ) by means of alpha doped pellets dissolution studies, and external beta and gamma sources on SF matrix. The studies on real spent fuel were made in collaboration with ITU, by a collaboration contract on SF research signed in October 2000. The research on SF in the past was based on studies of analogues of spent fuel, like: uraninites, SIMFUEL (UO_2 matrix with stable nuclides simulating radioactive isotopes), and natural UO_2.

The instantaneous release of radionuclides during real spent fuel dissolution and the alteration/dissolution of real spent fuel in dynamic tests were studied in order to develop a model of the behaviour of SF in repository conditions.

The fraction of SF radionuclides inventory undergoing fast release -in premature or normal failure under repository conditions- is one of the key issues necessary to describe in a performance assessment study because they govern the doses released from SF under possible storage conditions. Nowadays, radionuclide release models used (ENRESA [22], SFS [23]) consider a conservative radionuclides inventory obtained from correlations with fission gas inventories.

Prediction of SF alteration rate is a difficult problem due to the sensitivity of uranium solubility to the redox conditions [24 and their references]. Although the SF matrix has a low solubility value ($< 10^{-11}$ mol·dm^{-3}) under reducing conditions, its solubility increases by some orders of magnitude under oxidizing conditions [7, 23]. Therefore, a prediction of the evolution of the SF alteration rate as a function of the repository environment considered (groundwater composition, radiation field, etc.) is necessary.

The initial scenario, in most performance assessment studies, considers that contact between groundwater and the SF matrix occurs after the failure of the disposal containers, designed for a minimum safety lifetime of thousands of years (the SF cladding is not considered in the performance assessment studies). The behaviour of a failed canister is complex and depends on a large number of factors [25]. As a consequence of this contact (groundwater vs SF matrix) a fast initial radionuclides release will be observed due to the dissolution of soluble phases deposited in the gap region and the grain boundary during reactor operation. This behaviour was collective labelled as “Instant Release Fraction”. However, a new definition for the process has been proposed by Werme et al. [26]. They suggested for a repository situation the term

"Rapid Release Fraction" as more appropriated for a better description since, "*although it may be considerably faster than the release of matrix-bound radionuclides, the release from the grain boundaries may well continue for an extended period of time*"[26].

From a safety point of view [23, 25-27] both are considered as an instant release from the SF matrix. Based on experimental evidences it is possible to affirm that the SF source term (radionuclide release from matrix) is usually described as a combination of these processes: i) Rapid release of radionuclides (Instant Release Fraction or Rapid Release Fraction) located in gap (gases or soluble precipitates) or in matrix grain boundaries; these areas are easyly leached when the matrix is reached by groundwater; ii) Slow radionuclide release. This process is directly related to SF alteration rate (i.e., oxidation and dissolution rate of the matrix).

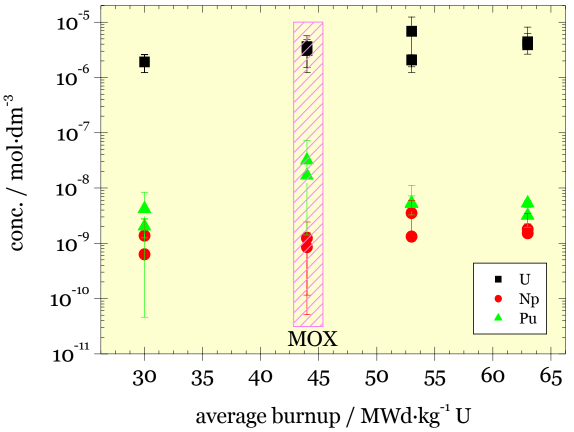

Figure 2 Influence of the SF burnup on the final concentration in solution achieved in leaching experiments in groundwater.

The experimental results obtained (Figure 2) show that at higher burnup, higher is the alteration of the SF; moreover, an increase in the mean concentration value of the radionuclides is observed. The differences observed between MOX and UOX SF specimens are related to the Pu concentration in solution (Figure 2). The highest Pu concentration was measured with MOX specimens, whereas in case of UOX, no influence on Pu concentration by the burnup was measured. The different behaviour and concentration in solution measured for Pu would be related to the microstructure of the specimens, which could produce a higher Pu dissolution rate in MOX than in UOX SF.

The evolution of the concentration in solution of these different radionuclides suggests the following explanation: i) U concentration in solution had not shown any influence, neither by burnup nor by type of fuel. The U concentration in solution is controlled by secondary phase formation, i.e., studtite. ii) In case of Np a slight increase of the concentration in solution is observed. The measured concentration in solution is always lower than the solubility of the pure phase iii) For both monovalent (Cs, Rb) and bivalent elements (Sr, Ba)an increase of the concentration in solution with burnup was observed. This behaviour indicated the presence in the system of a precipitation process (U secondary phase, i.e., studtite). iv). The concentrations in solution measured for redox sensitive elements (as Mo, Tc) show a clear increase with burnup. The type of fuel studied has no influence on the radionuclides studied. It is important to remark that the concentration values measured were always lower than the solubility of the pure phases. This behaviour increases the confidence on the studtite precipitation process.

From the results obtained and using the Matrix Alteration Model it is possible to extrapolate the evolution of the dissolution rate of spent fuel as a function of a defined environment. Figure 3 shows the MAM output data predicting the evolution of the matrix alteration rate as a function of alpha dose rate and groundwater evolution. A decrease in the alteration rate as a function of time is obtained.

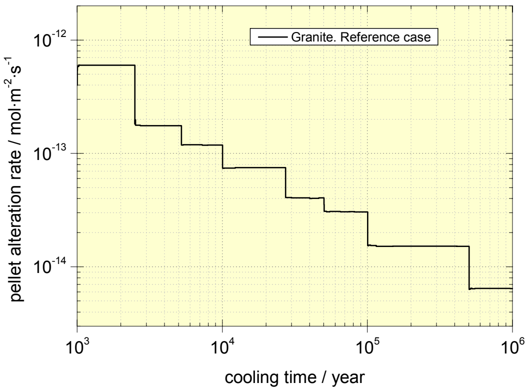

Figure 3 Evolution of pellet alteration rate in granite repository conditions [28]

The methodology applied allows us to define either the relevance of each variable or process considered and the necessity of new experimental work solving or clarifying the interdependence among several parameters. Throughout the aforementioned method (Figure 1), it is a recycled and interlinked structure rather than an open and stiff one. This allows to propose from experimental observation new implementation or changes in the model. At the same time, the experience coming from modelling, defines experiments, new lines of research or results in an increase in the accuracy of some parameter and process, leading even to discard or close experiments whose relevance in view of the final objective is not so high.

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