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Analogous materials for studying spent nuclear fuel: The influence of particle size distribution on the specific surface area of irradiated nuclear fuel

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ABSTRACT

Knowledge of the reactive surface that a given material presents to reactive species is one of the fundamental factors for the discussion of experimental data from the alteration of a solid at laboratory scale, or the extrapolation to different environmental conditions. The reactive surface depends on several factors such as the origin of the solid, for example, history of irradiation, the particle size distribution and the history of its reactive surface.

Here we discuss the relation between the particle size distribution and the specific surface area for different uranium oxides, namely, irradiated fuel, SIMFUEL and several fresh – non-irradiated – uranium oxides. The analysis is made comparing our own data with values reported in the literature. Our analysis strongly suggests that it is necessary to establish the surface area time evolution in order to model its behaviour in different scenarios where the alteration process will happen. Moreover, this is required in both, dry and wet conditions. A first step to get this function is the determination of the particle size distribution dependence of the specific surface area.

1. Introduction

Fuel elements used in nuclear power plants are composed of different materials. When they are extracted from the reactor, their physico-chemical characteristics are so special that it is difficult to describe them as concrete materials. Several works have studied the spent fuel chemical composition behaviour in the past. Nonetheless, there are still many unknowns regarding their complete characterisation due to the complex treatments currently used in hot cells, as well as the security protocols. In order to make a correct interpretation of the experimental data, a detailed analysis is thus necessary.

In our earlier review [1] we have demonstrated that microstructural modifications of the pellet set the behaviour of the spent fuel during the temporal storage (either wet or dry) previous to the definitive repository emplacement. As a consequence of the physico-chemical changes suffered in the reactor and a subsequent oxidation in its temporal storage, the structure of the materials under consideration is largely modified compared to the original. Major changes include grain growth and defect formations (cracks, fission gas bubbles), metallic precipitates and the migration of the volatile components, depending on their vapour pressure [2–5].

After irradiation in the reactor, the spent fuel is put in a wet disposal site, i.e. swimming pool. After this, and depending on the country, it is carried to a dry temporal storage. Finally, it is disposed into a definitive storage. If the country has chosen the fuel open cycle (and probably the closed too) the definitive storage consist of a deep geological repository (DGR). The mean life of this facility in the performance assessment studies is about 1 million years and the quickest way for the migration of the radionuclides to the biosphere is by water transport phenomenon (leachant). The water, which is often present in the repository host rock, will enter in contact with the spent fuel surface after around 10^4 years, when the container typically breaches. The exact time depends upon the environmental conditions and the different repositories designs employed in different countries.

The total surface area is usually expressed as the value that the fuel presents during its interaction with the leachant; this parameter will determine the evolution of the pellet alteration rate and, therefore, the evolution of the migration process of the radionuclides. This is directly related to the grain size distribution of the material and its type of porosity.

From the point of view of the crystalline structure, uranium oxides (UO_2) suffer a transformation from its original form to a

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multicomponent system as a consequence of the irradiation process. New elements appear and combine among themselves. Moreover, new solid solutions also appear, changing the old crystalline lattices into new ones [6]. The multicomponent structure consists of a UO_2 matrix, fission products (FP), actinides and activation products (AP). Therefore, the lost of the homogeneity experienced during irradiation transforms the preceding fuel physico-chemical characteristics (UO_2 mineral: uraninite and pechblenda, used as analogous). This leads to a more complex material from the chemical viewpoint due to the new components, as well as physical changes due to new cracks and the growth of a different type of porosity. A concrete description is, then, necessary in order to get a correct extrapolation for the large evaluation times used in the repository security studies (about a million years).

Due to the increasing pellet burnup >60 MWd kg^{-1} U [7] or 70–80 MWd kg^{-1} U [8] (over the standard burnup in Spanish nuclear power plants) a high burnup structure, called "rim"', appears at the edge of the pellet. This is a very thin strip of around 200 μm of thickness. As a consequence of the local burnup, a recrystallisation of this material produces grain sizes smaller than 1 μm (starting size of 10–20 μm). Furthermore, the porosity also increases. To the very best of our knowledge, none of the reported studies quantifies the way in which these modifications change the surface area of the pellet.

The sensitivity analysis of the Matrix Alteration Model (MAM) developed in CIEMAT shows that the specific surface area is a very important factor capable to roughly change the degree of the pellet alteration [4,10,17–21]. In order to explain this, experimental work was carried out at a laboratory scale. The evolution of the specific fuel surface area value (due to surface alteration process) can be explained for batch or slow flux experiments by the formation of alteration products on the surface of the specimen. This limits the contact between water and the matrix, which in return diminishes the available spaces for the oxygen (O_2) reduction [9] or adds radionuclides, retarding their release. However, for the dynamic experiments, where the saturation of solute (U) is never reached, this diminishing behaviour is also observed [3,10–13]. Often, the initial releases founded in the bibliography are explained by an oxidized layer on the fuel. Nonetheless, Serrano et al. [14] have demonstrated that this is a marginal effect (short), and cannot explain the continuing decreasing in time of the radionuclides release. In the context of the USA deep geological repository, Röllin et al. [15] has suggested that the falling in the matrix alteration rate is due to the corrosion of the stainless steel existing in the repository site near the pellet.

With the final aim of obtaining appropriate input data for modelling large evaluation times, it is therefore necessary to have a more accurate knowledge of the effects that the decrease in particle size has on the specific surface area (a dissolution process), so to be able to simulate the changes of this parameter.

There is no consensus in the scientific community about this topic. The main objective of this work is to get a good value for the specific surface area in order to be able to normalize the pellet dissolution rates. This action will give values for those rates non-depending on the surface area very useful for the performance assessment of final nuclear waste disposal studies of different national agencies for radioactive waste management. This would be more accurate if this operation could be substituted by a time dependence function for the specific surface area value, changing for different steps of the models.

2. Experimental procedure

In order to check the way in which the specific surface area of the fresh fuel (and analogous) works, the first step is to be able to describe their dependence on particle size. This was pursued by using different powders of a given material. The starting samples were UO_2 (from ENUSA) and SIMFUEL (supplied by AECL) in pellets. The surface area measurements were carried out with powder of different particle size distributions, as we explained below.

The pellets were crushed and sieved in a jaws crusher. This allows obtaining the required size without an excessive production of powder with a size lower than 20 μm. Then the powder was sieved to different size ranges (1.120 mm; 0.900 mm; 0.500 mm; 0.315 mm; 0.100 mm; 0.050 mm; 0.032 mm; 0.020 mm) following the standard "DIN4188". The rationale for this is to assimilate the different ranges of particle size to the different steps in the dissolution process of the mineral particles. The sieving was carried out in dry conditions. The remaining fines were separated via a 50 rpm 3D dry agitation.

The grain size, porosity and some possible defects existing in the original material (UO_2) due to the fabrication process, all have an influence on the measurements obtained, for the specific surface area values – and also on the leaching behaviour – in the dissolution process. For example, high porosity produces high specific surface area and a great increase in the contact area between leachant and solid. In order to characterize the properties

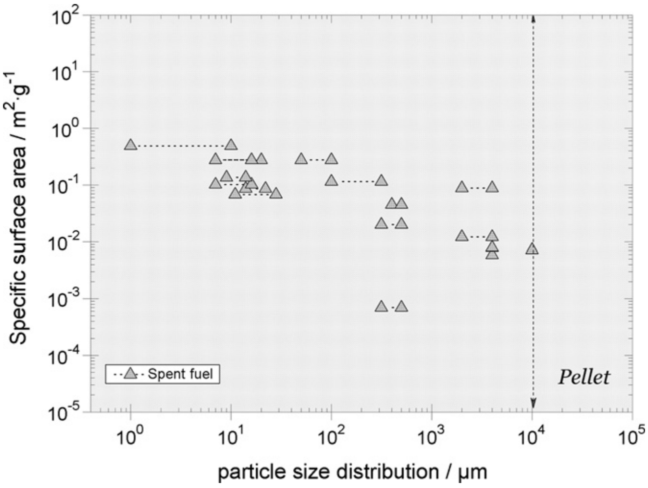

Fig. 1. Variation of the specific surface area of spent fuel with size (data from Table 1).

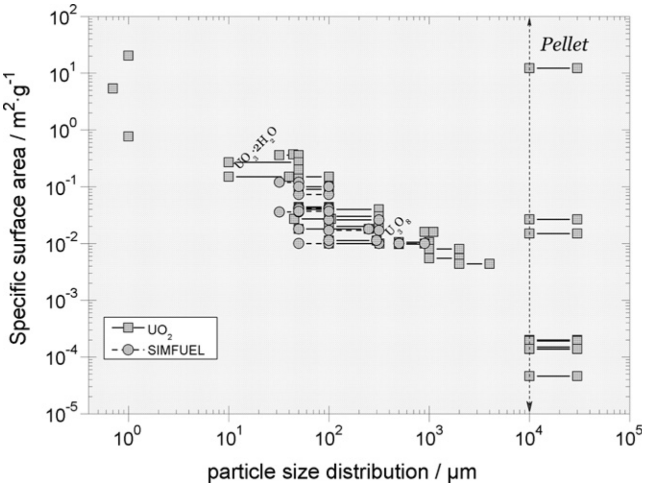

Fig. 2. Variation of the specific surface area of UO_2 and SIMFUEL with size (data from Table 1).