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Accelerated Dissolution Process of the Spent Fuel (UO2) under Repository Conditions

Eduardo Iglesias, Javier Quiñones, and Nieves Rodriguez
Energy, CIEMAT, Avda. Complutense 22, Madrid, 28040, Spain

ABSTRACT

Nowadays, nuclear energy is one of the options for developed countries in order to maintain the demand of electric energy. One of the key problems associated with kind of energy generation is the residual waste formed after a fuel cycle (spent nuclear fuel). The thermal treatment received in the reactor and there composition renders these materials very difficult to characterize and thus exhaustive studies are required to obtain knowledge that will help to build a complete, reliable and very safety underground facility. In this way, the option known as the Deep Geological Repository (DGR) is under development by each country taking part in the nuclear energy industry.

The unique pathway for the migration to the biosphere of the radionuclide, actinide and lanthanides content in the spent fuel pellet (UO_2) after the closing of the deep geological repository is by a water transport phenomena. It is a fundamental question to know how much time they will spend on their trip and the first step is the rate of liberation of these radionuclides from the spent fuel pellet. In this way the matrix dissolution rate of the spent fuel pellet, which is not dependent on the specific surface area after normalization by the initial value is a key parameter to begin the performance assessment for any deep geological repository. The specific surface value is, following the Matrix Alteration Model (MAM) sensitivity analysis, one of the most important parameters controlling the radionuclides liberation.

In this way, several measurements were carried out to obtain values in different conditions for different sieves of UO_2 powder treated as fresh fuel. First of all, the specific surface area was measured with a multi-point isothermal procedure with N_2 and Kr for both.

The values obtained are presented in order to obtain a general law for the rate of evolution with the particle size. These data are part of a bigger project about the complete description of the spent fuel analogues, which are very useful for obtaining new dissolution rates for spent nuclear fuel under repository simulated conditions.

INTRODUCTION

The Matrix Alteration Model (MAM) has been developed at CIEMAT. It simulates the behaviour of the spent fuel under repository conditions[1,2] (Figure 1). This allows evaluating, from experimental results, the processes that will control the matrix dissolution (Figure 1) and the consistent radionuclides release to the biosphere. Taking into account that this fact will be the only one existing for the migration of the active radionuclides (actinides and lanthanides, the most of them), all the variables concerning to the matrix dissolution are very important regarding to the security of the performance assessment. As it can be seen in Figure 2, this model is very sensitive to the specific surface area initial conditions, in particular[2]. Nowadays, all the models developed work with this parameter as a constant, and it is very well known that this one depends strongly with the particle size[3]. In order to improve this model, several experiments are in process to describe exactly its behaviour with the particle size, oxidation degree, etc. This work carried out in CIEMAT laboratories is being developed with spent fuel analogous, because there are no hot cells necessary to work with active materials. In this way, the fresh fuel (UO_2) and SIMFUEL used, substituting the spent fuel, are previously treated to simulate the physicochemical appearance of the spent fuel after the reactor cycle in a nuclear power plant.

In this work, results of the variation of the specific surface area with the grain size of the UO_2 powder dissolved in different acid media in order to simulate the grains ageing with accelerated dissolution experiments, are presented. After the time steps designed in the experimental procedure, BET specific surface area will be measured in order to get the "time" evolution in an accelerated dissolution process and the percentage of altered mass will be presented to compare the different results obtained.

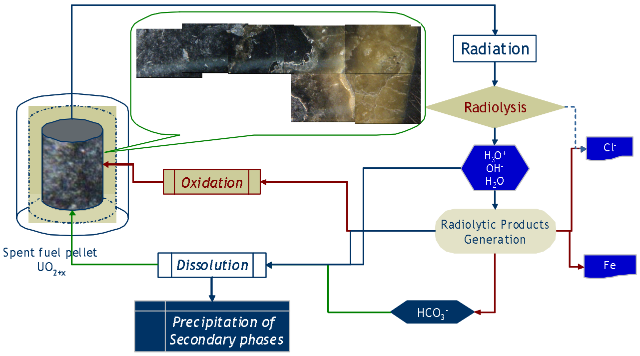


Figure 1 Diagram of the alteration process of the matrix alteration for the spent fuel pellet considered in MAM model [2,4]

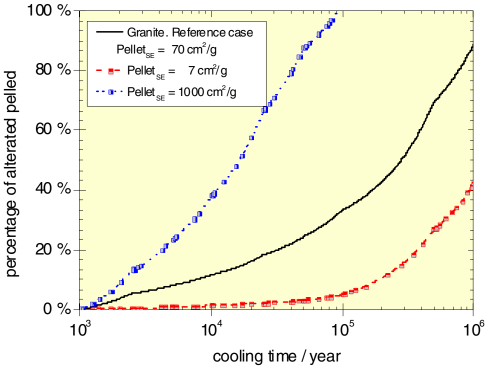


Figure 2 Influence of the specific surface area in the Matrix Alteration Model MAM [2]

EXPERIMENTAL PROCEDURE

The objective of the preparation phase is to simulate the cracks and size particle due to ageing –because of the corrosion and the temporal storage- previous to its definitive storage.

The sample used in the laboratory was UO_2 powder, with a distribution size covering the range interval from minor than 20 µm to more than 500 µm. The powder was crashed and sieved in a jaws crusher with a dry manufacturing, and different sieves were obtained. Here it is presented the 500 - 315, 315 - 100 and < 20 µm, because the rest of the sieves have been used up in a bad experimental procedure design. However, these are enough to conclude what happens to the specific surface area when the particle size changes.

The procedure carried out was to measure the specific surface area of the samples in a chemi - physisorption equipment ASAP 2020, from MICROMERITICS, and the weight loss in a METTLER T200 balance. These samples were obtained extracting the solute -after different periods of time- from two different dissolutions: 0.1 % HNO_3 and 0.3 M $NaClO_4$. The solutions had been turning around in a wheel for 15 d periods of time -3 d for the < 20 µm-. Then the samples were extracted, dried, measured, and put back to the turning wheel again.

Before the BET measurement, each sample has been previously treated in order to clean the pores from the surface with a thermal treatment and a degasification process. So, a heating ramp from 10 to 50 °C with a evacuating rate of 10 mm Hg/s during 30 min, and another ramp to 300 °C during 100 min, were carried out. After the preparation, the measurements were done with N_2 and Kr, to be able to compare the results from different adsorbates.

RESULTS AND DISCUSSION

Here are presented only some figures as a representation of the results obtained and the data treatment followed.

The BET measurements of the different sieves (before leaching experimentation) are the following: $A_{BET\,(< 20\ \mu m)} = 7.6691 \pm 0.1094\ m^2/g$, $A_{BET\,(100-315\ \mu m)} = 0.1218 \pm 0.0075\ m^2/g$ y $A_{BET\,(315-500\ \mu m)} = 0.0517 \pm 0.0052\ m^2/g$ with N_2 and, for Kr, $A_{BET(< 20\ \mu m)} = 0.3641 \pm 0.0037\ m^2/g$, $A_{BET\,(100-315\ \mu m)} = 0.018 \pm 0.001\ m^2/g$, $A_{BET\,(315-500\ \mu m)} = 0.0117 \pm 0.0001\ m^2/g$. The uncertainties appearing are those calculated by the ASAP 2020 software.

In the following figures (Figure 3 to Figure 8), the data from the evolution of the BET specific surface area vs. the accelerated leaching time experiments are presented. Different adsorbates and different medias are indicated when it is necessary.

As it has been aforementioned, the leaching times for the < 20 µm sieved, are shorter than for the rest, as it can be seen in Figure 3 and Figure 4 (HNO_3 and $NaClO_4$ media, respectively). The data obtained with $N_2(g)$ are represented with squares, and circles are those representing data from Kr(g). As it can be seen in a first overview, the Kr values for the specific surface area are always lower than those obtained with N_2. This fact is common in adsorption experiments as it can be read in the literature; different characteristics as the molecule size and the affinity for the solid are involved to justify this behaviour [5].

In both cases, it has been observed for the sieved of **<** 20 µm, that the specific surface area remains almost constant. This fact can be explained due to the fine granulometry of the powder, because practically the whole grain surface is in contact with the leachant agent, so it exists a relation between the total area diminution and the lost of weight in this distribution of powder size. These experiments are still running to obtain the behaviour for this size for achieving longer periods of leaching time.

In the case of 100 – 315 µm (Figure 5 and Figure 6) and 315 – 500 µm fractions (Figure 7 and Figure 8), it is observed, independently of the media taken into account, that the specific surface values obtained with N_2 increase in almost 2 orders of magnitude, as a consequence of the leaching. However, for the Kr values of BET, the evolution detected was always under one order of magnitude. Moreover, for 100 – 315 µm fraction (Figure 5 and Figure 6), in the case of $NaClO_4$ media, a faster increment of the specific surface area is shown, as a consequence of a more aggressive attack from the acid. Nevertheless, the final value is similar for both solutions. The 315 - 500 µm fraction is the only one where an increment in that value obtained with Kr increases. This fact may be explained due to a larger particle size allowing preferential attacks of the particles –grain boundaries, for example- without its cracking, or division.

For 100 – 315 and 315 - 500 µm fraction, Figure 9, Figure 10, Figure 11 and Figure 12 (HNO_3 and $NaClO_4$ media, respectively) represent the measured values of the BET area evolution vs. the percentage of altered mass depending on the adsorbate used for measuring.

As a consequence of the leaching process, an increment in the BET area value is observed with independence of the media. This increment exceeds the diminution of the mass produced by the alteration process. Moreover, for the $N_2(g)$ case and for both media, an increment of more than 2 orders of magnitude is shown $\approx 10\ m^2/g$. Even the velocity when this value is achieved is larger in the $NaClO_4$ media. In the case of Kr, less than an order of magnitude is increased for both larger fractions in both media (Figure 9, Figure 10, Figure 11 and Figure 12). This increment reaches for lower alteration values in $NaClO_4$ than HNO_3 media (2 vs. 8 %, respectively). Using Kr for the same test, the increment is just of 1 order of magnitude in the case of the HNO_3 solution and of a factor of 4 in $NaClO_4$ media.

Attending to the lowest values, < 20 μm, it is discovered that until reaching to the 20 % of altered mass, the specific surface area remains almost constant (Figure 13 and Figure 14). This observation may be explained as the particle size distribution is so small that the changes in the total area due to the leaching are almost the same that the lost of mass from the solid, due to the dissolution process. So, the specific surface area remains constant.

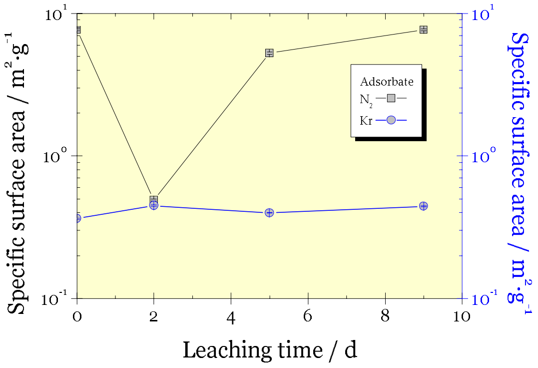


Figure 3 Specific surface area evolution of < 20 μm fraction (HNO_3 media).

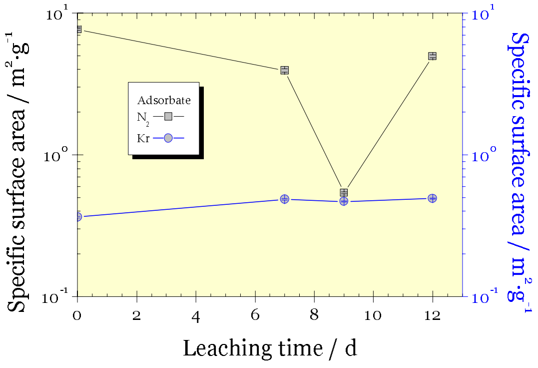


Figure 4 Specific surface area evolution of < 20 μm fraction ($NaClO_4$ media).

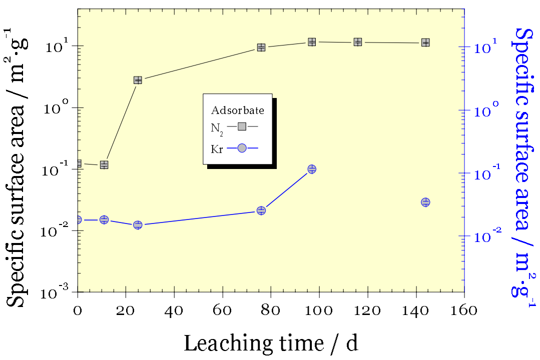


Figure 5 Specific surface area evolution of 100 - 315 μm fraction (HNO_3 media).

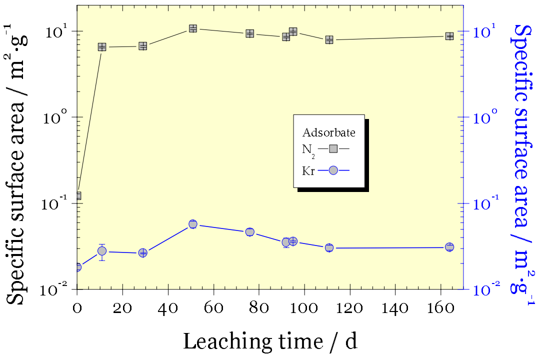


Figure 6 Specific surface area evolution of 100-315 μm fraction ($NaClO_4$ media).

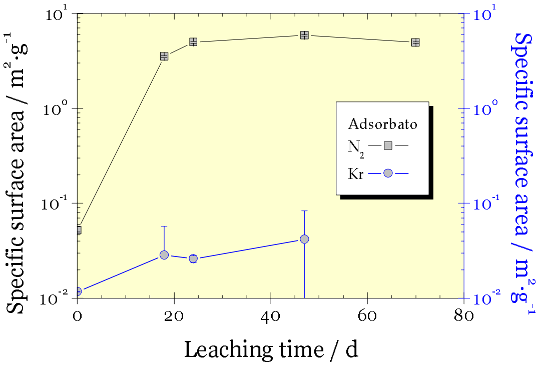


Figure 7 Specific surface area evolution of 315 - 500 μm fraction (HNO_3 media).

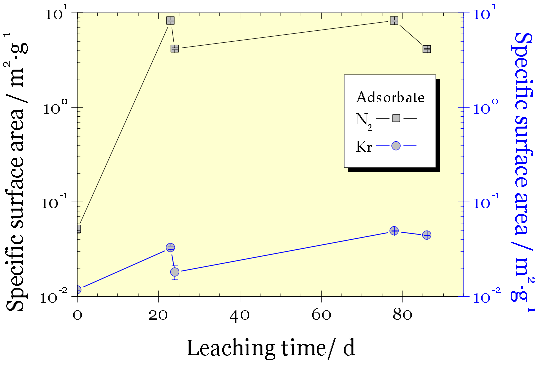
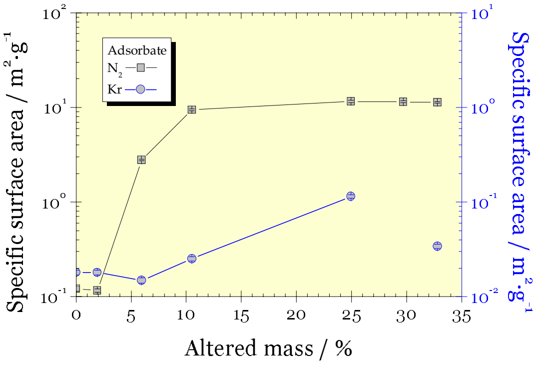


Figure 8 Specific surface area evolution of 315 - 500 μm fraction ($NaClO_4$ media).



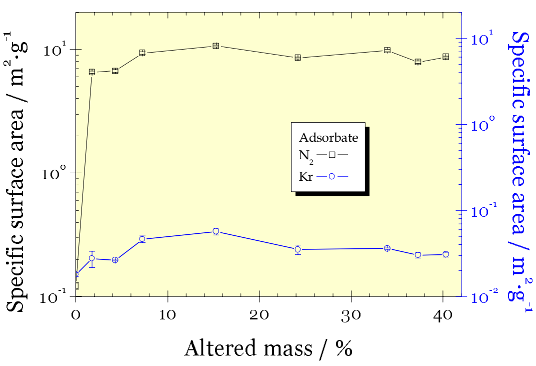
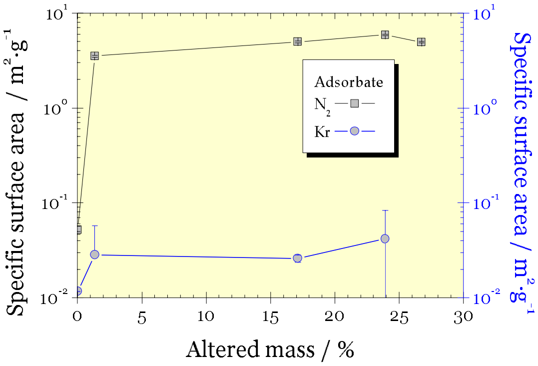


Figure 9 Specific surface area evolution in the UO_2 corrosion experiments for 100 – 315 µm in 0.1% HNO_3 media.

Figure 10 Specific surface area evolution in the UO_2 corrosion experiments for 100 – 315 µm in 0.3 M $NaClO_4$. media.



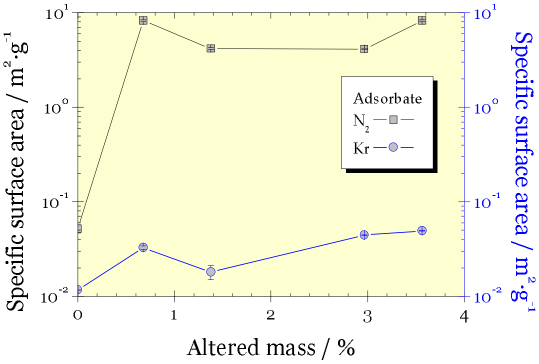
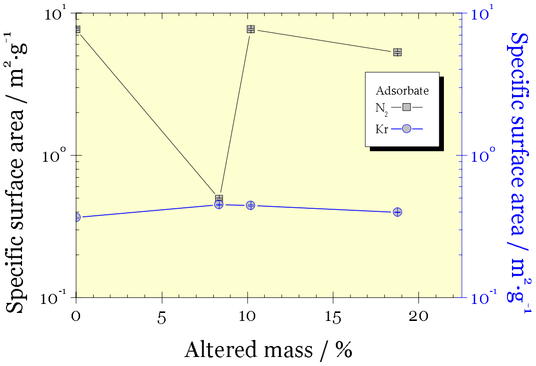


Figure 11 Specific surface area evolution in the UO_2 corrosion experiments for 315 - 500 µm in 0.1% HNO_3 media.

Figure 12 Specific surface area evolution in the UO_2 corrosion experiments for 315 - 500 µm in 0.3 M $NaClO_4$. media.



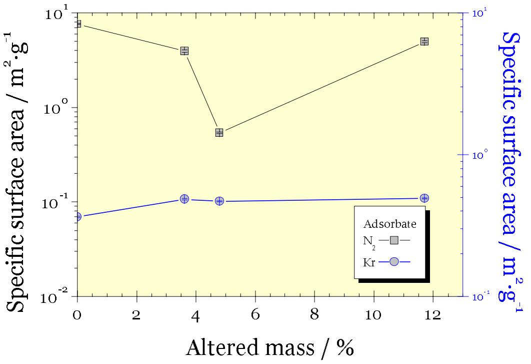


Figure 13 Specific surface area evolution in the UO_2 corrosion experiments for < 20 µm in 0.1% HNO_3 media.

Figure 14 Specific surface area evolution in the UO_2 corrosion experiments for < 20 µm in 0.3 M $NaClO_4$. media

It is not reasonable to think that the value of the specific surface area remains constant in the dissolution matrix process. As it can be seen, the uncertainties associated to the normalization of the dissolution rate to get a value specific for surface area none dependence will be a great source of error[3], because the changes in the initial value are in cases at least of 2 orders of magnitude. Taking into account these data in models, new values for matrix dissolution rates will be obtained, changing also the rate of radionuclides release to the biosphere.

CONCLUSIONS

Taking into account all of the results obtained so far and the fact that these types of experiments are still being run in order to obtain a definitive function describing the time dependence of the specific surface are, it can be concluded that with independence of the leaching media, this factor always increases in a dissolution process.

When $N_2(g)$ is used as adsorbate, the increment in the BET area is approximately 2 orders of magnitude greater. This is relevant regarding to the constant value supposed for this parameter in the models for all the evaluation times (until 10^6 y). Comparing the leachates used, it is observed that although almost the same value is reached, the process is faster in $NaClO_4$ media. Therefore in this media the higher value appears before than in the HNO_3, and in both cases it remains constant until a 40% of alteration.

If the grain size is bigger, the particle will spend more time dissolving itself, and the specific surface area will increase slower that one of the lower size particle. Taking into account these data in models, new values for matrix dissolution rates will be obtained, changing also the present rates of radionuclides release to the biosphere.

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REFERENCES

[1] Aurora Martínez Esparza, M.A. Cuñado, J.A. Gago et al., in *Publicaciones técnicas* (ENRESA, 2005), Vol. 1-05.

[2] Javier Quiñones, Eduardo Iglesias, Aurora Martínez Esparza et al., in *Scientific Basis for Nuclear Waste Management XXIX*, edited by Pierre Van Iseghem (Material Research Society., 2006), Vol. 932, pp. 433.

[3] B.D. Hanson, J.I. Friese, and C.Z. Soderquist, in *Scientific basis for nuclear wastw Management XXVIII*, edited by J. Hanchar, S. Stroes-Gascoyne, and L. Browning (MRS, San Francisco, 2004), Vol. 824, pp. 89.

[4] Javier Quiñones, Joaquin Angel Serrano, P. P. Díaz Arocas et al., (Ciemat, Madrid, 1999), Vol. DFN/RA-03/SP-99.

[5] T. Allen, *Particle size measurement*. (B. Scarlett, NY, 1981).