Mater. Res. Soc. Symp. Proc. Vol. 1124 © 2009 Materials Research Society 1124-Q02-02

Influence of the Specific Surface Area on Spent Nuclear Fuel Dissolution Rates

J. Quiñones*, E. Iglesias, N, Rodriguez, J. Nieto.
CIEMAT. High Level Waste Unit. Avda. Complutense, 22. 28040. Madrid.

ABSTRACT

This paper focuses on the influence of the evolution of the specific surface area during the alteration process of the spent nuclear fuel. We describe results of a spent fuel Matrix Alteration Model (MAM) that allows the alteration rate evolution to be predicted as a function of the host rock considered and evaluation time scale of interest.

The changes produced by the value of the UO_2 specific surface area on the MAM model (presented in a previous MRS conference) are here analyzed. The matrix alteration rates obtained with the MAM model (for granitic environment) are presented and compared to those performed for Spent Fuel Stability project (SFS). Furthermore, a sensitivity analysis study has been performed on the influence of the following variables: influence of the initial power size distribution and the initial oxidation state.

A strong dependence of the alteration rates of the spent fuel on the specific surface area is found. These results are presented for a specific scenario, but they could be extrapolated to different environments depending on the input file.

INTRODUCTION

The Matrix Alteration Model (MAM) developed by CIEMAT, UPC (Universidad Politécnica de Cataluña), ENVIROS, and financially supported by ENRESA (Empresa Nacional de Residuos) [1, 2] works in any scenario, depending on the environment of the final option for high level radioactive waste disposal (Deep Geological Repository: DGR). MAM predicts the matrix altered rate of the spent fuel pellet with a defined geometry under different environmental conditions. Model description and the considered hypothesis are detailed in [1-3]. There are still some processes not considered by the model [2], such as influence of precipitated secondary phases over the pellet; improvement is being developed by the MICADO coordinated action. Obtained values so far using MAM have been used in performance assessment studies for ENRESA [1] and the SFS project [3], in lab experiments for validation [4] and for long term extrapolation [2, 3]. The possibility of working with different host rocks (granite, clay and salt) and the capability for long term repository extrapolation gives the MAM a great versatility.

METHODS

At present, the model assumes that alteration of the spent fuel will start when the groundwater reaches and contact the solid surface and that only the radiolytic species of the groundwater (oxidants generated by α-radiation of spent fuel) produce the surface oxidation process and subsequent matrix dissolution. O_2, H_2O_2 and OH^- are the species that react with $UO_2(s)$ for oxidation of the pellet surface. The alteration process of the U surface sites is modeled in two steps: first, a surface co-ordination of the oxidized layer with aqueous ligands and, second, detachment (dissolution) of the product species. Taking this mechanism into account, the model gives the evolution of the spent fuel matrix alteration rate over periods as long as 1,000,000 years.

The MAM works in sequential steps. For different times in the mean life of the DGR, the dose rate of the radiation fields changes. This fact produces step-functions; the same happens for the chemical environmental. The results presented here are those corresponding to the following conditions.

The scenario is developed for just one pellet surrounded by water, simplifying the geometry. Only α-radiation fields are taken into account (Figure 1 and 2) because the water is assumed to come into the DGR after 10^3 years. Granite is the host rock and bentonite is the buffer material, so the concentration of chlorides and carbonates, and also the pH level, are changing while the calculations are running. The specific surface area for this scenario (base case) is $7\cdot10^{-3}$ m^2g^{-1} (best-estimated value: 90 % of the pellet is altered after 1 million y). The U site density value is 165 *sites*·nm^{-2}, obtained by de Pablo et al [5 and their references]. For solving differential equations the Maksima code [6] was used. In this scenario, three cases are taken into account depending on the origin of the specific surface area value: the empirical, theoretical and hybrid cases.

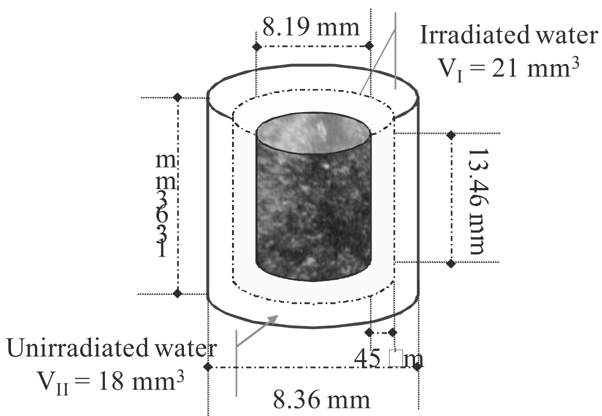

Figure 1. Pellet geometry considered in the exercise [1, 3].

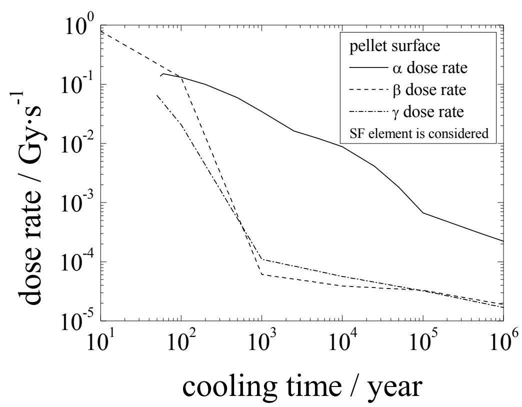

Figure 2. Dose rate evolution in the deep geological repository source [2].

The empirical value for the specific surface area comes from accelerated dissolutions tests carried out at CIEMAT [7]. It has been observed that, when the 10 weight percent of sample mass has been altered, the specific surface area becomes constant. The measured values have been called into question there are several reasons to support calculated values (geometric specific surface area) more than the measured values (BET surface area): different measurement methodologies; technical difficulties of the equipment during the measurement (dead time corrections), or just the fact that BET is not a good approach to the UO_2 specific surface area value. Two adsorbates gases are used to show the influence of the measuring process: N_2 and Kr. None of the measured values is the "real" one: water will be the real adsorbate in the DGR. At the moment, we cannot choose among any of the results obtained to give the "correct" one.

The theoretical approach for calculating specific surface area comes from calculations assuming cylindrical particles for the powder analyzed. This shape is linked to the corresponding value of 3.50 for the roughness factor (λ = 3.50): λ is a factor needed to make an idealized surface more realistic [8].

The hybrid case works in two steps. It begins with the theoretical results and it follows with the empirical ones (the calculations for the specific surface area are carried on taking into account the aforementioned roughness factor). The experimental values (10 and 0.10 $m^2 \cdot g^{-1}$, for N_2 and Kr respectively) substitute the theoretical primitive data when 10 % pellet alteration is reached (around $3.45 \cdot 10^5$ y for this case specific surface area value). It works better following these steps because the empirical values overestimate the alterarion rate. The whole pellet would be altered very early, and this work is devloped from the perspective of performance assessment studies for a DGR [7] .

RESULTS AND DISCUSSION

Empirical approach.

Figure 3 and Figure 5 show the weight percentage of pellet alteration depending on the measurement adsorbate as a function of the cooling time for the spent fuel in DGR conditions. The related matrix alteration rates are shown in Figure 4 and Figure 6. The starting values for the performance assessment study are 0.90 and 0.03 $m^2 \cdot g^{-1}$ for N_2 and Kr. In the models, 10 % of pellet mass is altered at 2500 y. The values for the specific surface area at this point are 10 and 0.10 $m^2 \cdot g^{-1}$ (results from accelerated leaching studies). For the N_2 case, after $2 \cdot 10^4$ y, the pellet has been corroded completely. However, for the Kr case, complete corrosion takes over 10^5 y. The values obtained are always higher than in the base case (SFS [2, 3]): the best estimated value for the SFS ($7 \cdot 10^{-3}$ $m^2 g^{-1}$) is very far from this empirical reality.

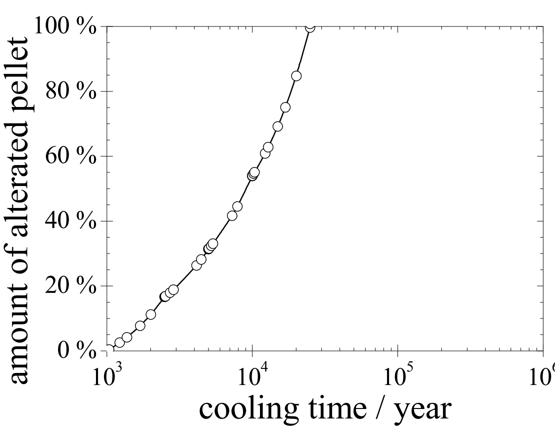

Figure 3. Alteration percentage of the spent fuel pellet in granite case, N_2 surface area.

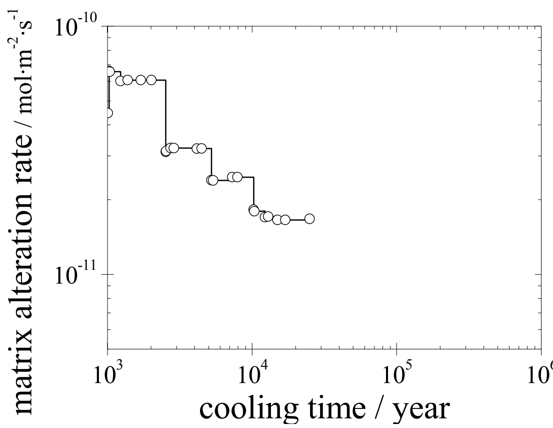

Figure 4. Alteration rate of the spent fuel pellet in granite case, N_2 surface area.

Theoretical approach: geometrical contribution.

Model values for the specific surface area are now calculated. The cylindrical shape of the particles and the correspondent value of 3.50 for the roughness factor [8] give a value ($2.1 \cdot 10^{-4}$ $m^2 \cdot g^{-1}$) that delays 10 % of alteration to $3.5 \cdot 10^5$ y. Results are presented in Figure 7 and Figure 8. After a million years the alteration of the pellet is about 30 % for the theoretical calculations versus a 90 % for the base case (SFS).

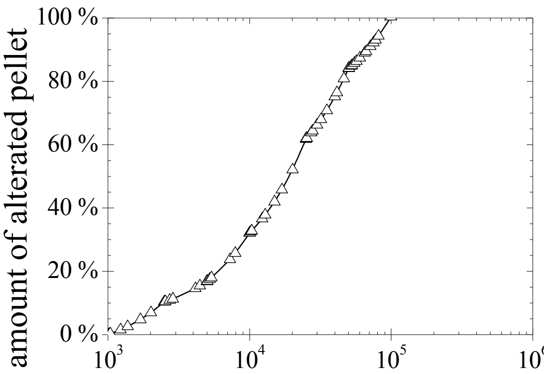

Figure 5. Alteration percentage of the spent fuel pellet in granite case, Kr surface area.

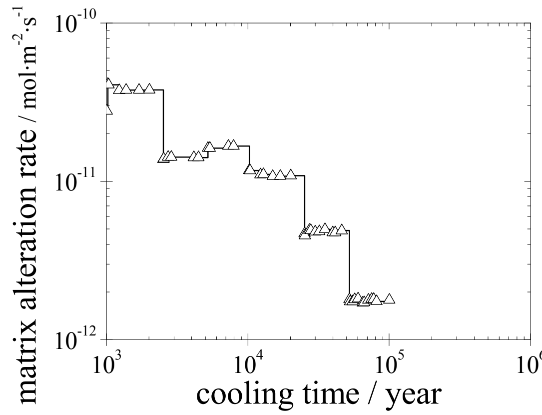

Figure 6. Alteration rate of the spent fuel pellet in granite case, Kr surface area.

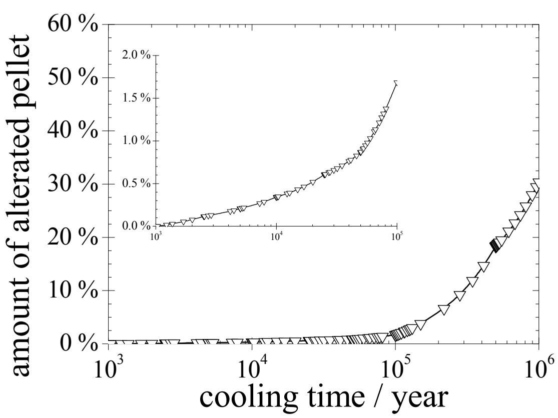

Figure 7. Evolution of pellet alteration in granite case with geometrical estimations.

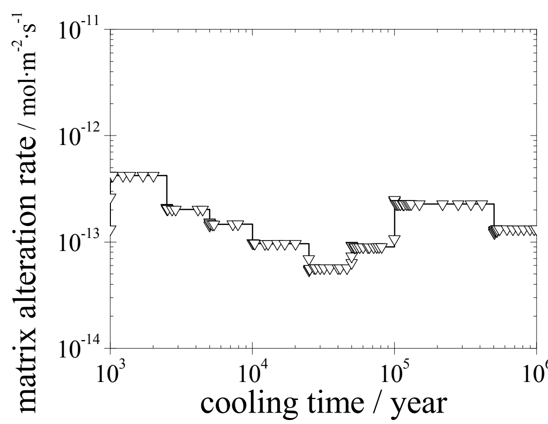

Figure 8. Alteration rate of the spent fuel pellet in granite case with geometrical estimations.

Hybrid approach. Coupled alteration rates: calculated and measured values.

Figure 9 to Figure 12 illustrate the hybrid model results. For the N_2 case the pellet is completely corroded by $9{\cdot}10^5$ y, but more gradually than the case that only takes the empirical values into account. However, for the Kr case, after a million of years, the pellet alteration will be around 90 % (similar to the base case).

Figure 13 and Figure 14 show all the models studied. The hybrid model is a very useful way of approximation to a very difficult unsolved problem. The result for the base case shown in Figure 13 runs between the results for the hybrid case. After that, the obtained values for the hybrid case lead to a similar final result in the case of Kr, despite considering even more realistic scenarios than the base case (updating the specific surface area value). Taking a look at the results here presented, from a performance assessment studies point of view, the empirical case is the most conservative, the theoretical one is the most optimistic and the hybrid approximation runs between them. It will depend on the scientific criteria of the researcher to choose the most suitable option for his work.

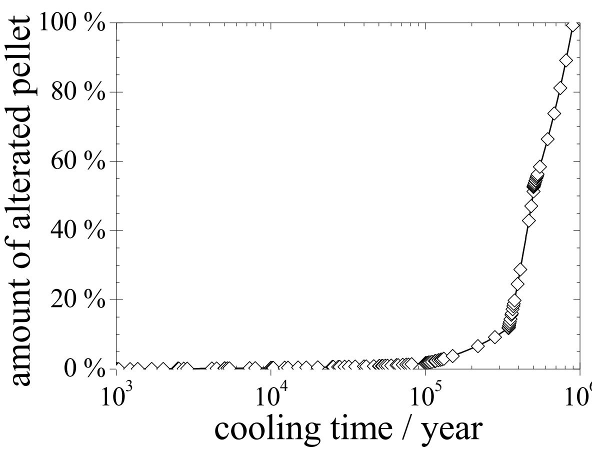

Figure 9. Evolution of pellet alteration in granite case, hybrid approach with N_2.

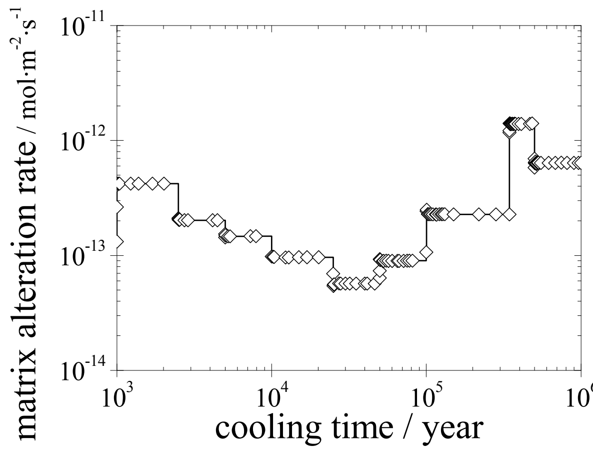

Figure 10. Alteration rate of the pellet in granite case, hybrid approach with N_2.

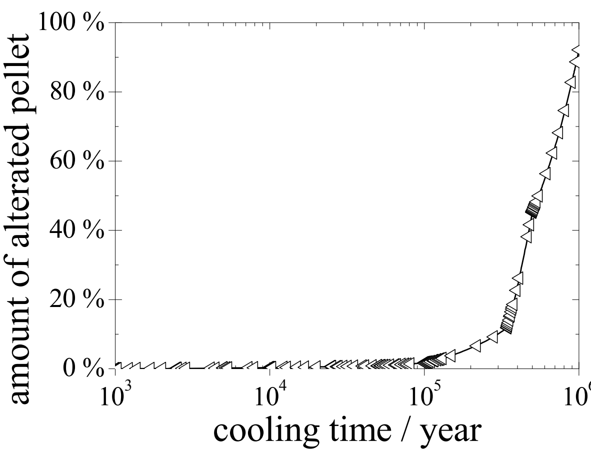

Figure 11. Evolution of pellet alteration in granite case, hybrid approach with Kr.

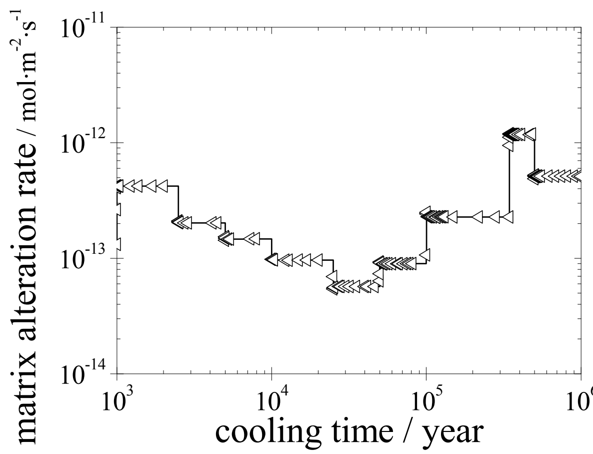

Figure 12. Alteration rate of the pellet in granite case, hybrid approach with Kr.

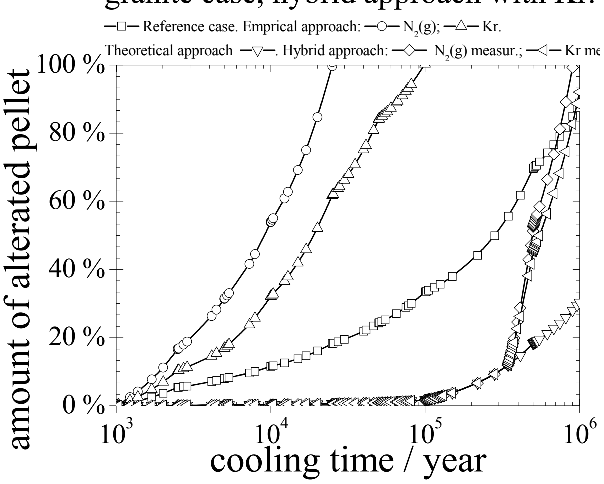

Figure 13. Evolution of the alteration in granite case. Summary of cases.

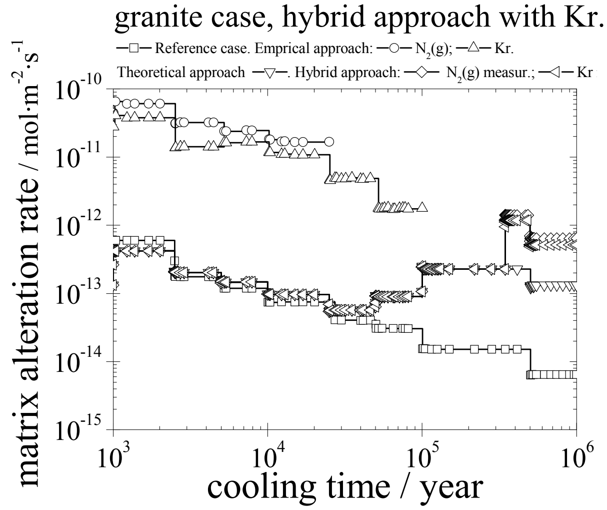

Figure 14. Alteration rate evolution in granite case. Summary of presented cases.

CONCLUSIONS

Different proposed approaches for MAM gave results capable of providing alternative pellet alteration rates for spent fuel pellet storage in a DGR. Results confirm that the specific surface area model, a controlling factor of the corroding process, can affect drastically the predicted rate of spent fuel pellet alteration.

The base case for Spain ($7\cdot10^{-3}$ m^2g^{-1}) shows that the pellet is altered 90 % after the mean life of the DGR (one million years): the alteration rate diminishes 2 orders of magnitude, achieving values under 10^{-14} mol $m^{-2}s^{-1}$. For the empirical approach here presented, in the N_2 (0.90 m^2g^{-1}) case, after $2\cdot10^4$ y the pellet has been completely corroded. For Kr (0.03 m^2g^{-1}), however, complete corrosion requires 10^5. For the theoretical approach ($2.1\cdot10^{-4}$ $m^2\cdot g^{-1}$), calculations assume cylindrical shaped particles combined with a roughness factor of 3.50: after a million years, 30 % of the pellet is altered. The hybrid model for N_2 (10 m^2g^{-1}) case shows that, with a cooling time of $9\cdot10^5$ y, the pellet is completely altered, but for the Kr (0.01 m^2g^{-1}), the alteration is about 90 % after one million years of cooling time. From the perspective of performance assessment studies of a DGR point of view, the hybrid approximation is the more realistic, while the empirical one is the most conservative. All the results show that the specific surface area is a controlling factor of the corrosion process.

ACKNOWLEDGEMENTS

This work has been financially supported under the agreement of ACACIAS project (ENRESA-CIEMAT framework).

REFERENCES

1. A. Martínez Esparza, et al., *Development of a Matrix Alteration Model (MAM)*, in *Publicaciones técnicas*. ENRESA. (2005).
2. J. Quiñones, et al. in *Scientific Basis for Nuclear Waste Management XXIX,* edited by P. Van Iseghem, (Mater. Res. Soc. Proc. **932**, Warrendale, PA, 2006) pp. 433-440.
3. C. Poinssot et al. Ed. CEA. Vol. CEA-R-6093. Saclay. (2005).
4. K. Spahiu et al., *D10. Contract Nº FIKW-CT-2001-20192 SFS. European Commission. 5th Euratom Framework Programme 1998-2002. Key Action: Nuclear Fission*. K. Spahiu (Editor) p. 63. (2004).
5. J. de Pablo et al., *Contribución experimental y modelización de procesos básicos para el desarrollo del modelo de alteración de la matriz del combustible irradiado*, in *Publicaciones técnicas*. ENRESA. Madrid, SPAIN. (2003).
6. M.B Carver, D.V. Hanley, and K.R. Chaplin, *Maksima Chemist. A program for mass action kinetics simulation by automatic chemical equation manipulation and integration by using Stiff techniques*. AECL: Chalk River, Ontario. (1979).
7. E. Iglesias, J. Quiñones, and N. Rodriguez Villagra in *Actinides 2008 - Basic Science, Aplications and Technology*, edited by D.K. Shuh, et al. (Mater. Res. Soc. Proc. **1104**, Warrendale, PA, 2008). pp. 101-105.
8. E. Iglesias and J. Quiñones. *Applied Surface Science*. **254** (21), 6890 (2008).