



Modelling the release of Mo, Tc, Ru and Rh from high burnup spent nuclear fuel at alkaline and hyperalkaline pH

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Abstract

The present work shows experimental data on the release of some radionuclides that are forming the so-called ϵ particles in the spent nuclear fuel (SNF): Mo, Tc, Ru and Rh. The leaching experiments were carried out with a $60 \text{ GWd}\cdot\text{t}^{-1}$ burnup SNF at two different pH values, 8.4 and 13.2, and under oxidizing conditions. The modelling of the data showed that the higher release of Mo, Tc, Ru and Rh at pH 13.2 could be due to the higher dissolution rate of the ϵ -particles.

Introduction

The composition of the spent nuclear fuel (SNF) is not homogeneous. On one hand, some radionuclides might migrate to the gap between the fuel and the cladding, to the gap between two pellets or to the grain boundaries [1–3]. On the other hand, other radionuclides are present in the nuclear fuel as metallic inclusions segregated from the fuel matrix. In particular, inclusions formed by Mo, Tc, Ru, Rh and Pd have been identified and studied in the last years and are usually called ϵ -particles [4, 5]. The metallic inclusions are expected to have a low solubility and a low dissolution rate and might have an important role during the dissolution of the spent fuel because they are believed to catalyse the reduction of a number of radionuclides by hydrogen radiolytically formed on the fuel surface [6, 7].

The release of the radionuclides would be different depending on the location of the radionuclide in the fuel: (1) radionuclides mainly embedded in the UO_2 matrix will be congruently released with uranium; (2) radionuclides preferentially enriched in the gap or grain boundaries would show a higher initial release, not congruent with the release

of uranium; and (3) radionuclides in the metallic inclusions would show a lower release than expected considering the dissolution of the matrix.

The evaluation of the release of each radionuclide from SNF leaching experiments is challenging because the radionuclides concentrations measured in solution are the sum of the moles of radionuclide released from their different locations in the fuel. In this sense, the application of the Segregated Radionuclide Identification and Quantification (SERNI) model to leaching data of some radionuclides has permitted to start to establish the actual influence of each location on the radionuclide release [1].

In particular, the model has been fitted to Mo data on SNF leaching experiments at alkaline and hyperalkaline pH [8]. The results of the fitting indicated that at hyperalkaline pH, Mo measured in the solution also came from ϵ -particles, whose dissolution seemed to be favoured at high pH because of a higher oxidation of the metal favoured by the hydroxyl anion.

The main objective of this work is to corroborate the dissolution of the metallic particles at high pH by studying the dissolution of three other radionuclides contained in the ϵ -particles: Tc, Ru and Rh.

Experimental data

The experimental data from this work were obtained from the leaching of a $60 \text{ GWd}\cdot\text{t}^{-1}$ SNF at two different pHs, 8.3 and 13.2. The characteristics of the fuel are already published in Iglesias et al. [9] and García-Gómez et al. [8],

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where the experimental procedure is also described. The experiments were made with a full replenishment of fresh solution after each measure.

Some of the experimental data were already published for uranium, technetium, and ruthenium [9] as well as Mo [8]. Data from rhodium were not previously published.

The SERNI model

The SERNI model assumes that the moles of a radionuclide measured in the solution in SNF leaching experiments are the sum of the moles released from the different sources of the radionuclide in the SNF. The release from each source follows a first-order kinetics [1].

For example, in the case of uranium, there are two different sources of uranium in the SNF: pre-oxidized phases or fines on the SNF surface and uranium in the UO_2 matrix and then, the mathematical expression of the model might be written as follows:

$$\text{mol}U_t = \text{mol}U_{\text{ox},\infty} \cdot (1 - e^{-k_{\text{ox}}t}) + \text{mol}U_{\text{ma},\infty} \cdot (1 - e^{-k_{\text{ma}}t}), \quad (1)$$

where $\text{mol}U_t$ is the number of cumulative moles of uranium released at time t , $\text{mol}U_{\text{ox},\infty}$ and $\text{mol}U_{\text{ma},\infty}$ are the number of moles contained in the oxidized phase and in the matrix, respectively, whilst k_{ox} and k_{ma} (both in d^{-1}) are the rate constants for the release of uranium from the oxidized phases and the matrix, respectively.

Other radionuclides are released to the solution in SNF leaching experiments from additional sources, this is the case, for example, of caesium, which is released from the gap between the fuel and the cladding. In these cases, an additional term should be added:

$$\text{mol}Cs_{\text{seg},t} = \text{mol}Cs_{\text{seg},\infty} \cdot (1 - e^{-k_{\text{seg}}t}), \quad (2)$$

where $\text{mol}Cs_{\text{seg},t}$ are the moles released from this contribution at any time, $\text{mol}Cs_{\text{seg},\infty}$ are the total moles contained in the segregated phase, and k_{seg} is the kinetic constant (d^{-1}). The value of the parameter $\text{mol}RN_{\text{ox},\infty}$ is calculated from the value for uranium but considering the inventory of the radionuclide in the fuel, whilst k_{ox} and k_{ma} used are the ones obtained for uranium [1].

Results

Molybdenum and technetium

The fitting of the SERNI model to the release of Mo at alkaline and hyperalkaline pH was previously carried out [8]. The main results obtained showed that at hyperalkaline pH,

Mo moles released to the solution were much higher than at alkaline pH. This difference was attributed to the dissolution at hyperalkaline pH of the ϵ -particles. At alkaline pH, Mo released to the solution would mainly come from Mo(IV) in the UO_2 matrix whilst at hyperalkaline pH from both Mo(IV) in the matrix and Mo(0) from the ϵ -particles.

Technetium showed a similar pattern, with higher release at hyperalkaline pH. At $\text{pH}=8.4$, the Tc release during the first days of the experiment was found congruent with uranium, and at $t > 50$ d, Tc was released faster than uranium. At $\text{pH}=13.2$, Tc moles released to the solution are almost two orders of magnitude higher than at $\text{pH}=8.4$ (Fig. 1). As in the case of Mo, the SERNI model could not fit the results assuming a congruent release with uranium (see the solid line in Fig. 1). The fitting could only be carried out considering an additional source of Tc responsible of the Tc released to the solution, probably the ϵ -particles. Figure 1 shows the fitting of the model with this additional source.

The moles of Tc released to the solution from the ϵ -particles, $\text{mol}Tc_{\text{seg},\infty} = 9 \cdot 10^{-7}$, are 3 times lower than the moles of Mo, this could be related to the composition of the particles, with a 30% of Mo and 7% of Tc [6].

Ruthenium and rhodium

Ruthenium and Rhodium were expected to behave differently from Tc and Mo, because the only source of Ru and Rh in the SNF are the ϵ -particles, which have a low dissolution rate. As the matrix dissolves, although

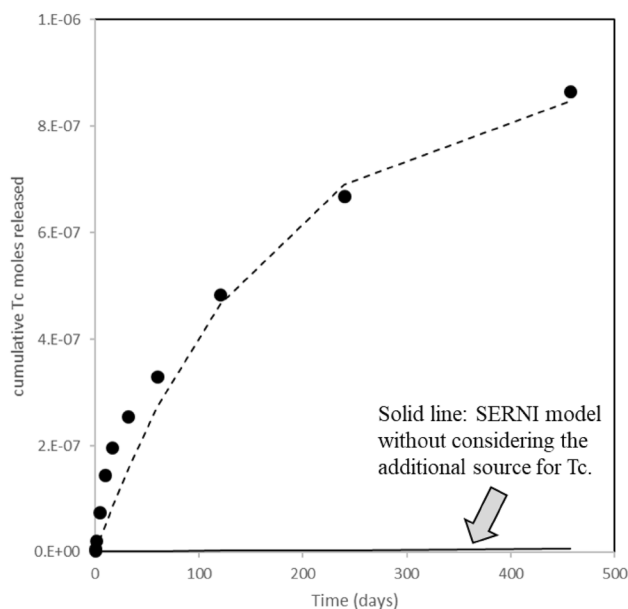


Fig. 1 Cumulative moles of Tc released to the solution in the experiment at $\text{pH}=13.2$. The black points represent the experimental data and the dotted line the SERNI model assuming that Tc is also released from the ϵ -particles

more ϵ -particles could be in contact with the solution, the release of both radionuclides would be relatively low because of the assumed slow dissolution of the particles. As it can be seen in Fig. 2, this was the behaviour observed in the experiment at pH = 8.4, Ru and Rh moles released to the solution were lower than the expected if congruent release with uranium was assumed.

($\text{molRu}_{\text{ox},\infty} = 8.1 \cdot 10^{-9}$; $\text{molRh}_{\text{ox},\infty} = 1.4 \cdot 10^{-9}$; $k_{\text{ox}} = 0.04 \text{ d}^{-1}$; $k_{\text{ma}} = 3.5 \cdot 10^{-7} \text{ d}^{-1}$).

At pH = 13.2, the moles released of both radionuclides were higher than at pH = 8.4. Fig. 3 shows the experimental data for both elements.

The results seem to corroborate the faster dissolution of the ϵ -particles at high pH. If a high release rate is assumed, the particles would be dissolved when the matrix is dissolved, and the release of Ru and Rh would increase with time. Figure 4 shows the fitting of the SERNI model to the Ru data considering that the release of Ru is related to the release of uranium. As it can be seen, during the first days, Ru moles released are higher than the expected considering

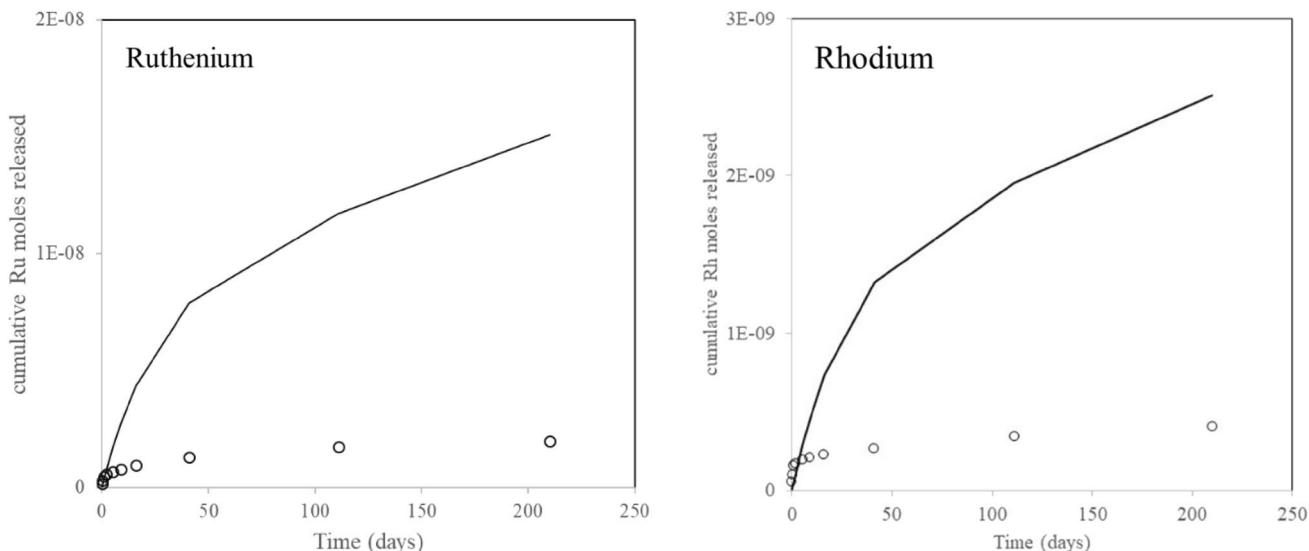


Fig. 2 Cumulative moles of Ru and Rh released to the solution in the experiment at pH = 8.4. The points represent the experimental data and the solid line the SERNI model assuming they are congruently released with uranium

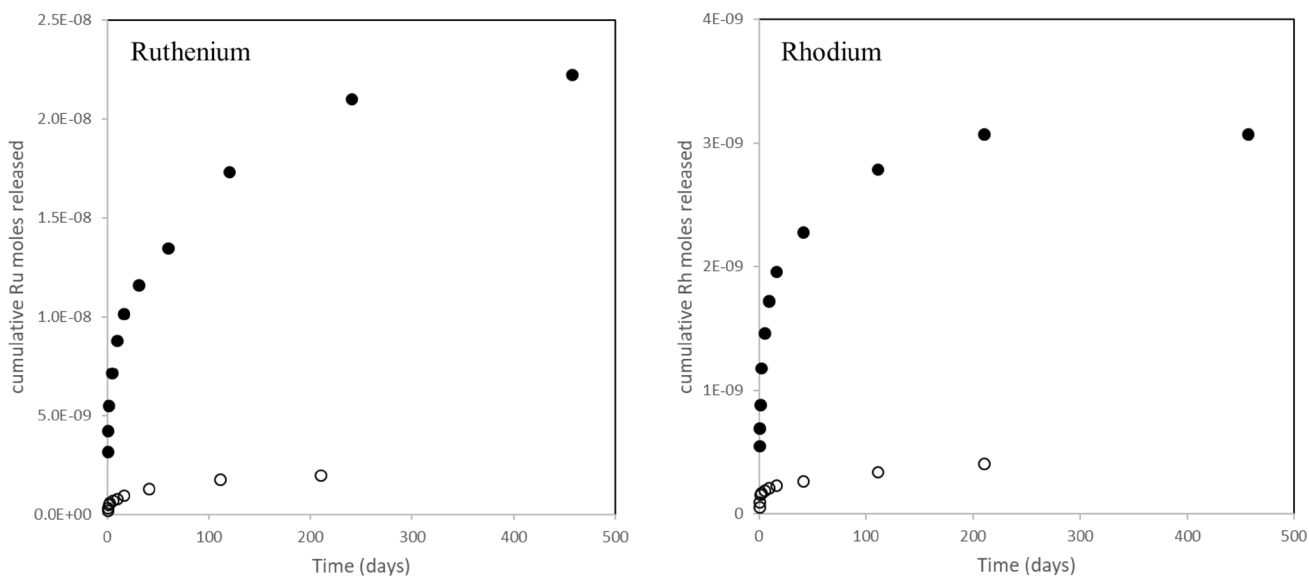


Fig. 3 Cumulative moles released to the solution: ● pH = 13.2 and ○ pH = 8.4

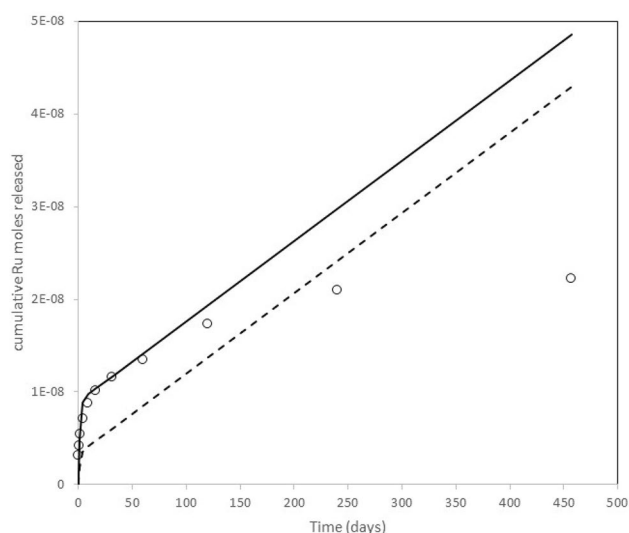


Fig. 4 Cumulative moles of Ru in the experiment at pH=13.2. The model assumed that Ru release was possible only as the fuel dissolved. The lines represent the model considering an accumulation of ϵ particles on the fuel surface (solid line) and not considering the accumulation (dotted line)

the dissolution of the pre-oxidized phases on the SF surface. This was not surprising because ϵ -particles accumulate on the surface of the fuel and in the grain boundaries. Solid line represents the model assuming an accumulation of such particles.

At higher contact times, moles of Ru were, however, lower than predicted by the model considering that the dissolution of the ϵ -particles was fast and Ru was released to the solution as the matrix was being dissolved. Actually, as it can be seen in Fig. 4, the moles released were almost constant after 100 days. One plausible reason is that Ru (and Rh, which showed a very similar behaviour) was precipitating in the conditions of the experiments, probably to form hydroxides or oxides [10–12], and the concentrations measured in the experiments in this range were $(6 \pm 2) \cdot 10^{-9} \text{ mol} \cdot \text{dm}^{-3}$ and $(4 \pm 2) \cdot 10^{-8} \text{ mol} \cdot \text{dm}^{-3}$ for Rh and Ru, respectively. In this sense, it is noticeable that Ru cumulative moles released from the ϵ -particles are 40 times lower than Tc although the content of both radionuclides in the ϵ -particles would be 40% and 7%, respectively [6], indicating that the access of the solution to the ϵ -particles is not the responsible of the low Ru and Rh moles measured, which could be the result of the precipitation of Ru and Rh secondary solid phases.

The results and the modelling showed that hyperalkaline pH favours the release of Ru and Rh to the solution and molybdenum experimental results showed that high pH solutions favoured the oxidation of the metal resulting in a faster release. In this sense, there are no data on the oxidation of Ru and Rh in the metallic inclusions; however, in Ru–Pt alloys, Ru can be oxidized to $\text{RuO}_2 \cdot \text{H}_2\text{O}$, more easily

dissolved than metallic Ru [13]. It is necessary to study both the oxidation of Ru and Rh metals as a function of pH in the alkaline-hyperalkaline region as well as the speciation in solution, in order to evaluate the possible precipitation of Ru and Rh at those conditions.

Conclusion

Previous observations that metallic inclusions in the SNF would be dissolved at hyperalkaline pH seem to be confirmed when considering the release of other radionuclides contained in such particles: Tc, Ru, and Rh. The release of the three radionuclides increased at high pH and the fitting of the model to the experimental data indicated that this increase could be due to the radionuclides release from ϵ -particles.

In the case of Ru and Rh, the relatively high concentrations reached in solution could lead to the precipitation of secondary solid phases. In its present form, the SERNI model does not consider precipitation but only dissolution and indicates an interesting future development of the model.

The dissolution of the ϵ -particles at high alkaline pH might have important consequences on the redox environment of the fuel, because these particles are believed to catalyse reducing reactions by hydrogen.

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Data availability The raw data can be obtained on request from the corresponding author.

Declarations

Conflict of interest None.

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References

1. A. Espriu-Gascon, A. Martínez-Torrents, D. Serrano-Purroy, J. Giménez, J. de Pablo, I. Casas, Contribution of phases segregated from the UO_2 matrix to the release of radionuclides from spent nuclear fuel and duration of the Instant Release Fraction (IRF). *J. Nucl. Mater.* **532**, 152066 (2020)
2. D. Roudil, C. Jégou, V. Broudic, B. Muzeau, S. Peugeot, X. Deschanel, Gap and grain boundaries inventories from pressurized water reactor spent fuels. *J. Nucl. Mater.* **362**, 411–415 (2007)
3. L. Johnson, I. Günther-Leopold, J. Kobler Waldis, H.P. Linder, J. Low, D. Cui, E. Ekeröth, K. Spahiu, L.Z. Evins, Rapid aqueous release of fission products from high-burnup LWR fuel: experimental result and correlations with fission gas release. *J. Nucl. Mater.* **420**, 54–62 (2012)
4. J.I. Bramman, R.M. Sharpe, D. Thom, G. Yates, Metallic fission-product inclusions in irradiated oxide fuels. *J. Nucl. Mater.* **25**, 201–215 (1968)
5. H. Kleykamp, Post-irradiation examinations and composition of the residues from nitric acid dissolution experiments of high-burnup LWR fuel. *J. Nucl. Mater.* **171**, 181–188 (1990)
6. D. Cui, J. Low, C.J. Sjöstedt, K. Spahiu, On Mo–Ru–Tc–Pd–Rh–Te alloy particles extracted from spent fuel and their leaching behaviour under Ar and H_2 atmospheres. *Radiochim. Acta* **92**, 551–555 (2004)
7. A. Espriu-Gascon, J. Llorca, M. Domínguez, J. Giménez, I. Casas, J. de Pablo, Oxidation by $\text{H}_2\text{O}(\text{g})$ in the presence of $\text{H}_2(\text{g})$ of UO_2 doped with Pd nanoparticles. *J. Radioanal. Nucl. Chem.* **318**, 1201–1207 (2018)
8. S. García-Gómez, J. Giménez, I. Casas, J. Llorca, J. de Pablo, A. Martínez-Torrents, F. Clarens, J. Kokinda, L. Iglesias, D. Serrano-Purroy, Molybdenum release from high burnup spent nuclear fuel at alkaline and hyperalkaline pH. *Nucl. Eng. Tech.* (2023). <https://doi.org/10.1016/j.net.2023.08.024>
9. L. Iglesias, J. Kokinda, D. Serrano-Purroy, A. Martínez-Torrents, I. Casas, J. de Pablo, F. Clarens, J. Giménez, Dissolution of high burn-up spent nuclear fuel at high-pH. *Radiochim. Acta* (2023). <https://doi.org/10.1515/ract-2023-0178>
10. H. Shuto, T.H. Okabe, K. Morita, Ruthenium solubility and dissolution behaviour in molten slag. *Mater. Trans.* **52**, 1899–1904 (2011)
11. T.P. Luxton, M.J. Eick, K.G. Schekel, Characterization and dissolution properties of ruthenium oxides. *J. Coll. Interface Sci.* **359**, 30–39 (2011)
12. F. Villiard, G. Jerkiewicz, Comprehensive studies of formation and reduction of surface oxides at rhodium electrodes at 298K. *Can. J. Chem.* **75**, 1656–1665 (1997)
13. Y. Park, B. Lee, Ch. Kim, Y. Oh, S. Nam, B. Park, The effects of ruthenium-oxidation states on Ru dissolution in PtRu thin-film electrodes. *J. Mater. Res.* **24**, 2762–2766 (2009)

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