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Dissolution of spent nuclear fuel fragments at high alkaline conditions under H_2 overpressure

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ABSTRACT

The long-term behavior of the UO_2 fuel matrix under conditions of the Belgian “Supercontainer design” was investigated by dissolution tests of high burn-up spent nuclear fuel (SNF) in high alkaline solution under 40 bar of (Ar + 8%H_2) atmosphere. Four fragments of SNF, obtained from a pellet previously leached during two years, were exposed to young cement water with Ca (YCWCa) under 3.2 bar H_2 partial pressure in four single/independent autoclave experiments for a period of 59, 182, 252 and 341 days, respectively. After a decrease of the concentration of dissolved ^{238}U, which is associated with a reduction of U(VI) to U(IV), the concentration of ^{238}U in solution is constant in the experiments running for 252 and 341 days. These observations indicate an inhibition of the matrix dissolution due to the presence of H_2. A slight increase in the concentration of ^{90}Sr and ^{137}Cs in the aqueous solution indicates that there is still dissolution of the grain boundaries. These findings are similar to those reported for spent nuclear fuel corrosion in synthetic near neutral pH solutions.

INTRODUCTION

In Belgium, for spent nuclear fuel (SNF) and vitrified high active waste disposal, a specific engineered barrier system, the so-called “Supercontainer” concept, has been developed. With respect to SNF disposal, the “Supercontainer” comprises fuel assembly canisters in carbon steel overpacks, which are surrounded by an overpack of a Portland cement concrete buffer and an outer stainless steel envelope [1-3].After re-saturation of the engineered barriers, the pore water composition will be altered by interactions with concrete. The altered pore water can be simulated by a "young cement water with calcium (YCWCa)" solution (pH of 13.5) that represents the first degree of concrete alteration. Due to the slow corrosion of the steel canister under highly alkaline conditions [4], the SNF could come in contact with the evolved highly alkaline solution. In parallel, in these systems a certain H_2 partial pressure is built-up due to steel corrosion processes. Therefore, it is of interest to study the corrosion behavior of the SNF UO_2 matrix in YCWCa in presence of externally applied H_2 overpressure.

MATERIAL AND METHODS

Spent nuclear fuel

The SNF material was irradiated during four cycles and a total time of 1226 days in the Gösgen pressurized water reactor located in Switzerland. The SNF achieved an average burn-up of 50.4 MWd/kg_{HM} and the average linear power was 260 $W \cdot cm^{-1}$. The cooling time prior to the start of the experiments was of 22 years. A detailed description of the manufacturing and irradiation properties of the SNF rod segment is given in [5].

Sample preparation

The fragments of SNF were obtained by removing the Zr-cladding from a fuel segment, which was previously used and leached [6]. The cladded SNF segment was fixed in a sample holder. Then, the Zr-cladding was cut by means of a metal saw that was remotely handled with a manipulator. Finally, different SNF fragments were obtained selecting four of them with similar physical properties (i.e. similar size, shape and mass), and denoted as follows: K11F2, K11F3, K11F4 and K11F5. The weight of the samples was: (0.225 ± 0.001) g for K11F2, (0.174 ± 0.001) g for K11F3, (0.169 ± 0.001) g for K11F4 and (0.205 ± 0.001) g for K11F5. An example of a fragment obtained after decladding of the SNF segment is shown in figure 1.

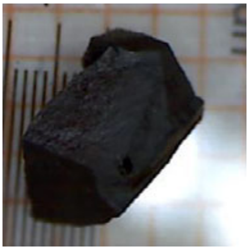

Figure 1. Fragment of SNF chosen to perform experiment K11F3 and obtained after removing the Zr-cladding from the cladded SNF segment.

Leachant solution (YCWCa)

The solution was prepared in an inert gas glove box according to the protocol provided by SCK•CEN (Studiecentrum voor Kernenergie - *Centre* d'Étude de l'énergie Nucléaire) [7]. The target composition of the YCWCa according to [7] is: 370 mM KOH, 136 mM NaOH, 2.0 mM Na_2SO_4, 0.4 mM $Ca(OH)_2$ and 0.3 mM $CaCO_3$. The measured pH is 13.5.

EXPERIMENTAL PROCEDURE

A total of four experiments were carried out.

Pre-leaching in YCWCa

The SNF fragments were placed into the autoclaves, which in turn were closed and flushed with Ar for about 30 min to remove completely air. Afterwards, each autoclave was filled with around (105 ± 5) mL of YCWCa under constant Ar flux to avoid air intrusion into the autoclave. The duration of the pre-leaching in the experiments was: 15 days for K11F2, 17 days for K11F3 and 41 days for K11F4 and K11F5. Once the pre-leaching was concluded, the complete solution was removed and analyzed. The pre-leaching was done to reduce the amount of the fraction of Cs inventory, which was expected to be fast released from open fresh grain boundaries originated during the samples preparation.

Single point experiment

After the pre-leaching, the autoclaves were filled again with (200 ± 5) mL of fresh YCWCa solution in the same way as previously explained. A gas atmosphere of 40 bar Ar $+H_2$ (pH_2: 3.2 bar) was applied. At the end of the experiment, the whole solution was removed from the autoclave for further analyses.

pH and Eh measurements

The pH and Eh of the samples were measured at the end of the four experiments to avoid possible air intrusion that in the case of the Eh measurement would have given unrealistic values. The device and the procedure followed is the same as stated in [8]. At the end of each experiment the pH was 13.5 ± 0.2 and the $Eh_{(vs\ SHE)}$ was (-730 ± 50) mV.

RESULTS AND DISCUSSION

Concentration

The experiments were performed with four fragments with similar physical properties in order to achieve a comprehensive interpretation of the leaching/corrosion process. However, the results are statistically limited.

The results obtained for each single point experiment are plotted together in figure 2.

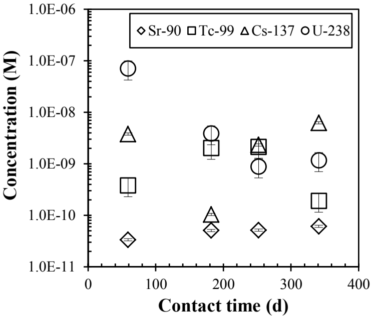

Figure 2. Concentration in solution of ^{90}Sr, ^{99}Tc, ^{137}Cs and ^{238}U as function of time in the four single point experiments: K11F2 (341 days), K11F3 (252 days), K11F4 (182 days) and K11F5 (59 days).

The aqueous concentration of ^{238}U in the single point experiments depends on the contacting time with the leaching solution. A relatively high concentration is observed in the short-term experiment K11F5 ((7 ± 3)x 10^{-8} M after 59 days), a considerably lower concentration in experiment K11F4((4 ± 2)x 10^{-9} M after 182 days). Relatively low concentrations are measured in the long-term experiments K11F3 ((9 ± 4)x 10^{-10} M after 252 days) and K11F2 ((1.2 ± 0.5)x 10^{-9} M after 341 days).

The decrease of ^{238}U concentration in solution as function of time is interpreted as a reduction of U from U(VI) to U(IV). The aqueous ^{238}U concentrations measured in the long-term experiments are in the range of those obtained in previous long-term spent nuclear fuel corrosion experiments under reducing conditions. For instance, the measured concentration of U at the end of an experiment under near neutral pH conditions was 2 x 10^{-9} M [5].

Taking into account the experimental conditions, in particular the measured pH (13.5 ± 0.2) and $Eh_{(vs\ SHE)}$ (-730 ± 50 mV) in solution, thermodynamic calculations predict $U(OH)_4(aq)$ as the predominant uranium species in solution and $UO_2{:}xH_2O(s)$ as the solubility controlling solid phase. Calculations were performed with thermodynamic data available in [9], giving U(IV) concentration of 3 x 10^{-9} M, which agrees well with the aqueous uranium concentration measured in the long-term experiments. Therefore, it is suggested that $UO_2{:}xH_2O(s)$ determines the uranium concentration in solution after 252 days of leaching.

The aqueous concentration of ^{99}Tc scattered with time. A maximum value of (2.1 ± 0.9) x 10^{-9} M was reached after 252 days (experiment K11F3). Tc is a redox sensitive element, and under the conditions of the present work the concentration of Tc in solution is expected to be controlled by $TcO_2{:}1.6(H_2O)(s)$ / $TcO(OH)_3^-$ equilibrium.

Based on the $TcO_2{:}1.6(H_2O)(s)$ equilibrium constant, a solubility limit of 3 x 10^{-6} M is calculated for pH 13.5 and $Eh_{(vs\ SHE)}$ of -730 mV. However, aqueous ^{99}Tc concentration measured in the four experiments (10−9-10−10 M) was far below the solubility of $TcO_2{:}1.6H_2O(s)$. Therefore, it is suggested that the ^{99}Tc concentration in solution might be limited by co-precipitation with U(IV) rather than by formation of $TcO_2{:}1.6H_2O(s)$. According to our interpretation the amount of Tc released from the fuel into solution was insufficient to form $TcO_2{:}1.6H_2O(s)$. Moreover, one can exclude the presence of per-technetate for such low Tc aqueous concentrations.

In the case of ^{90}Sr, the concentration in solution increased slightly from (3.3 ± 0.3)x 10^{-11} M, after 59 days (experiment K11F5), up to (6.3 ± 0.3) x 10^{-11} M, after 341 days (experiment K11F2). This concentration is too low to be limited by the solubility with $SrCO_3(s)$ (strontianite) or with $SrSO_4(s)$ (celestine).

Finally, the concentration of ^{137}Cs increased slightly from 59 days ((3.8 ± 0.2) x10^{-9} M in experiment K11F5) to 341 days leaching time ((6.3± 0.4) x 10^{-9}M in experiment K11F2). However it has to be noted that the concentration in solution after 182 days (experiment K11F4) was one order of magnitude lower - this anomalous behavior is associated to an experimental artefact.

Based on the results obtained, the presence of H_2 indicates the suppression of UO_2 dissolution. However, aqueous concentrations of Sr and Cs increase slightly and thereby indicate that there is still dissolution of certain regions of the fuel fragments, most likely the grain boundaries.

SUMMARY

The leaching / corrosion behavior of spent nuclear fuel in highly alkaline Young Cement Water with calcium under H_2 overpressure was investigated. Four single-point experiments with SNF fragments in YCWCa solution were performed under a partial H_2 pressure of 3.2 bar. The concentrations in solution of ^{90}Sr, ^{99}Tc, ^{137}Cs and ^{238}U were determined

The U concentration in solution decreased until a steady state is reached after 252 days of leaching. The concertation decrease is related to the reduction from U(VI) to U(IV). Moreover, taking into account the measured concentration of ^{238}U, pH and Eh in solution and the solubility calculations performed in equilibrium with the used solution, it is concluded that the dissolved uranium was in equilibrium with the solid phase UO_2:xH_2O(s).

The measured aqueous concentrations of ^{99}Tc scattered with time. According to thermodynamic calculations, it is suggested that the ^{99}Tc concentration in solution might be limited by co-precipitation with U(IV) rather than by formation of TcO_2:1.6H_2O(s).

Finally, the measured aqueous concentrations of ^{90}Sr and ^{137}Cs slightly increased in the experiments.

According to these results the matrix dissolution associated to U release is inhibited in the presence of H_2. On the other hand, the slight concentration increase in solution of Sr and Cs observed during the experiments indicates that there is still dissolution of the grain boundaries.

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REFERENCES

1. J. Bel, A. Van Cotthem, C. De Bock. Document Construction, operation and closure of the Belgian repository for long-lived radioactive waste. Proceedings - 10th International Conference on Environmental Remediation and Radioactive Waste Management ICEM'05, Glasgow (UK), (2005), 1690-1696.
2. D. G. Bennett, R. Gens. *J. Nucl. Mater.* **379**, 1-8 (2008).
3. R. Gens, J. Bel, A. M. Pourbaix, M. Hélie, S. Wickham, D. Bennett. J. Phys. IV **136**, 13–23 (2006).
4. B. Kursten, B. Smailos, I. Azkarte, L. Werme, N.R. Smart, G. Marx, M.A. Cuñado, G. Santarini, Corrosion evaluation of metallic materials for long-lived HLW/spent fuel disposal containers: Review of 15-20 years research in: Nuclear Science and Technology, Euradwaste'04, Radioactive Waste Management - Community Policy and Research Initiatives, Proceedings of 6th European commission conference on the Management and Disposal of Radioactive Waste, Luxembourg 29-31 March 2004, ed. C. Davies, European Commission EUR 21027. (2004).
5. V. Metz, E. González-Robles, B. Kienzler, in *Proceedings of 7th EC FP – FIRST-Nuclides 2nd Annual Workshop, November 5th-7th, Antwerp, Belgium*, edited by B. Kienzler. V. Metz, L. Duro, A. Valls, KIT Scientific Reports, Karlsruhe KIT-SR 7676, pp. 55-60 (2014)

6. A. Loida, R. Gens, C. Bube, K. Lemmens, C. Cachoir, T. Mennecart, B. Kienzler. in *Scientific Basis for Nuclear Waste Management XXXV*, edited by R.M. Carranza, G.S Duffó, R.B. Rebak (Mater. Res. Soc. Symp. Proc. **1475,** Warrendale, PA, 2012) pp. 119-124.
7. C. Cachoir, P.De Cannière, F. Druyts, K. Ferrand, B. Kursten, K. Lemmens, T. Mennecart, E. Valcke, Preparation of Evolved Cement Water (ECW) and Young Cement Waters (YCW and YCWCa) for the Supercontainer experiments. IW.W&D.0099, (2006), 1-8.
8. A. Loida, R. Gens, V. Metz, K. Lemmens, C. Cachoir, T. Mennecart, B. Kienzler. in *Scientific Basis for Nuclear Waste Management XXXIII*, edited by B.E. Burakov, A.S. Aloy, (Mater. Res. Soc. Symp. Proc. **1475,** Warrendale, PA, 2009) pp. 597-604.
9. Guillaumont, R., Fanghänel, T., Neck, V., Fuger, J., Palmer, D. A., Grenthe, I., Rand, M. H. *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*. (Elsevier B.V. Amsterdam, Holland, 2003) p. 919.