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Leaching behaviour of unirradiated high temperature reactor (HTR) UO_2–ThO_2 mixed oxides fuel particles

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Abstract

The dissolution of different mixed oxide $(U, Th)O_2$ particles under reducing conditions has been studied using a continuous flow-through reactor. The U/Th ratio seems to have no or little influence on the normalised leaching rate of thorium or uranium, The release rate of uranium from the outer surface of a Th rich matrix seems to follow the behaviour of pure UO_2 even though U is a minor component in these phases and the dissolution rate of Th is much lower. After long time U concentrations will become depleted at the solids surface and it will be expected that U release rates will become controlled by the release rates of thorium (rates at neutral pH $< 10^{-6}\ g\ m^{-2}\ d^{-1}$). Under reducing conditions, the matrix of HTR fuel particles presents significant intrinsic radionuclide confinement properties.

1. Introduction

High temperature reactors (HTR) are considered as promising medium-term alternatives to present light water reactors. The specific advantages mainly result from inherent safety features, from the better energy conversion efficiency at high temperatures, from the reduction of wastes produced per unit of produced energy and from the very stable fuel design, which consists in embedding in a graphite matrix, the fissile material as actinide oxide in form of sealed-coated particles with particle diameters of about 0.5 mm. This concept allows achieving very high burn-ups. The fuel concept exhibits also certain advantages for the back-end of the fuel cycle. One of the back-end options is an open cycle with direct disposal of the spend fuel in a geological repository.

The behaviour of an HTR disposed spent fuel in a deep repository is based on the integrity of the coated particles. Indeed, it has been shown that no radionuclide can be released as long as the coating layers are intact [1,2]. However, if the coatings fails due to mechanical or chemical interactions, the long-term behaviour mainly depends on the chemical stability of fuel kernels.

Fuel kernel stability is probably a function of the redox conditions in the repository. In European repository concepts, oxidizing conditions may result only in the short-term from remaining post-closure oxygen traces or from radiolytic decomposition of water by α-irradiation, and this only, provided that hydrogen from container corrosion is absent. Due to the high radiation field, fresh spent fuel is known to create local oxidizing conditions at the surface, which are not representative in the long term. In contrast, a reducing environment is expected to prevail at the disposal location in the long

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term. In the present work, the behaviour of unirradiated fuel kernels is studied under reducing conditions. Unirradiated kernels are representative for the behaviour of the matrix of the fuel kernels in the long term, when α-radiolysis becomes negligible.

In previous work [3], we studied the leaching behaviour of unirradiated bare fuel mixed oxide (U, Th)O_2 particles of U/Th ratios, respectively 16.3%, 9.2% and 2.3%, in an oxidative environment using batch techniques. The pH ranged from 1.7 to 5.5. A selective release of uranium has been observed. However, no definitive conclusion has been made yet, for explaining the difference between the dissolution rates of U and Th. It was predicted that under constant conditions, more than 15 000 years would be necessary to completely dissolve uranium and more than 6 millions years for thorium.

In the present study, we used dynamic dissolution tests under reducing conditions (higher pH, synthetic clay water composition) to assess the leaching behaviour of fuel kernels under more realistic conditions. Dynamic leaching conditions where necessary to avoid saturation of dissolved U(IV) or Th in the reaction vessel.

2. Experimental procedure

2.1. Fuel particles characterization

Three types of coated HTR fuel particles have been obtained from Forschungzentrum Jülich (FZJ, Germany). These coated particles show the typical three layers TRISO structure. Three layers coat a fuel kernel, presented in Fig. 1: a SiC layer sandwiched between two pyrolitic carbon layers. The fuel material consists of a mixed oxides UO_2–ThO_2 solid solution with different U/(U + Th) mass ratio.

The SiC coating has protected the fuel kernels against oxidation or corrosion in humid laboratory atmosphere for well above 20 years. Prior to leaching experiments, the fuel kernels were isolated from their coating by breaking the coating by means of the tension imposed by the screw of a standard micrometer. The decoating process was performed under a protective nitrogen atmosphere and the bare particles were rapidly transferred (<10 min) into an inert environment. From SEM investigations of the kernels, we assume that (i) all of them present well-formed grains and (ii) there is no large open porosity. Compositions and geometrical properties of these kernels are reported in Table 1.

2.2. Leaching experiments

2.2.1. Experimental procedure

All experiments were performed under dynamic leaching conditions for about one year to 500 days. One hundred decoated kernels of each mixed oxide were put into a stainless steel reactor. These kernels were leached with a synthetic clay groundwater whose reduction potential was imposed by sodium sulphide. The composition of the water is given in Table 2.

The experimental set-up (Fig. 2) allows the removal of traces of oxygen of about 0.1 ppm in nitrogen gas, using the redox cycle presented in Table 3. The nitrogen gas, containing oxygen traces (<100 ppb), is splashed through a NH_4VO_3 solution containing a ZnHg amalgam. The vanadium solution is used as a colour indicator. When the amalgam is not efficient anymore, the green vanadium (II) is oxidized by oxygen to form red–brown peroxovanadium cation. The purified nitrogen gas is then saturated with water and bubbled through the synthetic groundwater to conserve O_2-free conditions. The oxygen free leaching solution was injected via stainless steel tubing into a stainless steel flow-through reactor of an active volume of about 1 mL. The fuel kernels were immobilized in the reactor between two 7 μm stainless steel filter membranes. The flow rate was varied ranging from 2 mL/h to 12 mL/h, using peristaltic pump, placed

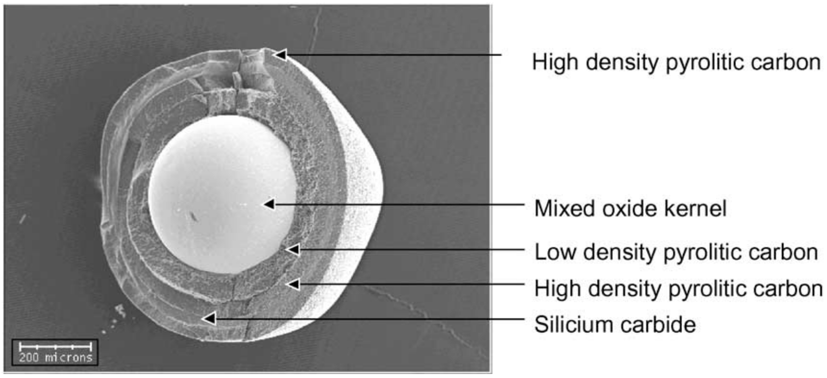

Fig. 1. SEM figure of a particle.

Table 1
Unirradiated HTR kernels properties

Sample	$Th_{0.837}U_{0.163}O_2$	$Th_{0.907}U_{0.093}O_2$	$Th_{0.977}U_{0.023}O_2$
Oxide (molar)	Mixed oxide 2.3% UO_2	Mixed oxide 9.3% UO_2	Mixed oxide 16.3% UO_2
Diameter, ±0.01 mm	0.49	0.58	0.38
Mass, ±0.02 mg	0.60	1.01	0.35
Geometric specific area, cm^2/g	12.34	10.46	13.2

Table 2
Leachant characteristics (pH = 7; $E = -145$ mV/ENH)

	NaCl	KCl	$CaCl_2$	$MgCl_2$	Na_2S
Concentration (mg/L)	600	5.5	190	90	25
Concentration (mmol/L)	10.27	0.07	1.71	0.95	0.32

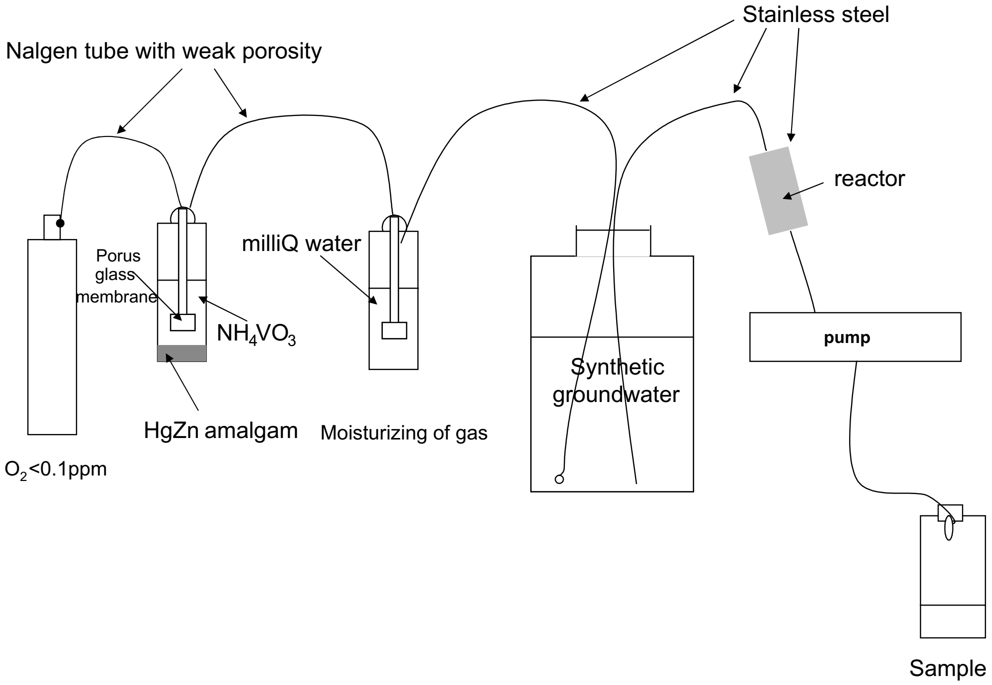

Fig. 2. Arrangement of the fuel kernels leaching experiment.

at some distance of the outlet of the flow though reactor to avoid oxygen contamination by diffusion through the associated plastic tubing. The collected sample volume in a given time interval was used to determine the average flow rate in this interval.

2.2.2. Solution analyses

The concentrations of uranium and thorium in the collected solution samples were found to be below ICP–MS detection limit. The solutions were concentrated by evaporation, but the resulting salt concentrations were very important and the analysis was neither possible by ICP–MS. Therefore, we have been developed a protocol allowing eliminating various salts. The solution was evaporated to dryness. U and Th were extracted from the salt rich residues using a DOWEX-2X8 resin filled column. The residue is taken up in a small volume of 7 M HNO_3, injected for Th and U fixation into a column, which was initially conditioned in the same media. The present various salts were eluted by 20 mL

Table 3
Purification of nitrogen gas from O_2 traces

Reducing cycle

$2VO_2^+(aq) + 4H^+(aq) + ZnHg \rightleftarrows 2VO^{2+}(aq) + Zn^{2+}(aq) + 2H_2\ O(l) + Hg$
green blue

$2VO_2^+(aq) + 4H^+(aq) + ZnHg \rightleftarrows 2V^{3+}(aq) + Zn^{2+}(aq) + 2H_2O(l) + Hg$
blue blue–green

$2V^{3+}(aq) + ZnHg \rightleftarrows 2V^{2+}\ (aq) + Zn^{2+}(aq) + Hg$
blue–green violet

Reducing cycle

$ZnHg + O_2(g) + 4H^+\ (aq) \rightleftarrows Zn^{2+}(aq) + 2H_2O(l) + Hg$
$V^{2+}(aq) + O_2(g) + 4H^+\ (aq) \rightleftarrows V^{3+}(aq) + 2H_2O(l)$
$V^{3+}(aq) + O_2(g) + \ 2H^+(aq) \rightleftarrows VO^{2+}\ (aq) + H_2O(l)$
$VO^{2+}(aq) + O_2(g) + 2H^+(aq) \rightleftarrows VO_2^+(aq) + H_2O(l)$
$2VO_2^+(aq) + O_2(g) + 4H^+(aq) \rightleftarrows 2VO_2^{3+}(aq) + 2H_2O(l)$
red–brown

of 7 M HNO_3. Thereafter, by using 0.1 M HCl, the fixed uranium and thorium were eluted. The eluate containing uranium and thorium with a recovery of more than 95%, was evaporated in the next step and the residue was taken up by HNO_3 2% for ICP–MS analysis. Uranium and thorium were not separated because their analysis can be performed simultaneously without interferency.

3. Results and discussion

In a dynamic test, the incremental dissolution rate of an element *i* from the solid for a given time interval can be described by a rate term R_H normalised to the sample surface area and to the fuel composition, using the following expression:

$$R_H(i) = \frac{C_i \times V}{S \times f_i \times t} = \frac{dN_L(i)}{dt} \tag{1}$$

with

C_i	aqueous concentration of the *i* element (g/L) in the collected sample
V	collected volume of the leachant in the interval t (L)
S	geometric surface area of the sample (m^2)
f_i	mass fraction of the element *i* in the fuel
t	duration of the leaching interval (days)
N_L	normalised mass loss (in g/m^2)

The $R_H(i)$ value (in $g\ m^{-2}\ d^{-1}$), can be divided by the density of the solid phase to obtain an equivalent corrosion rate (in $m\ d^{-1}$), or, in case of selective release the rate by which an elementary depletion depth progresses into the solid. In the same way, the division of the cumulative $N_L(i)$ value by the solids density gives an equivalent depletion depth of element *i* and/or a corrosion depth.

However, some assumptions are inherent in this approach:

- The geometric surface area should be equal to the effective surface area of fuel kernels. If this is not the case, the surface area term in the equation shall be multiplied by a factor accounting for surface roughness.
- The effective volume of the flow-through reactor shall be small compared to the collected volume *V*.
- The observed dissolution behaviour represents intrinsic kinetic parameters of the dissolution rate of the solids only if the concentrations of dissolved species in solution are lower than their solubility value. Otherwise the data rather represent thermodynamic constraints.

3.1. Mixed U, Th oxide dissolution under reducing conditions

Fig. 3 presents the cumulative normalised mass loss N_L(Th) and N_L(U) versus the cumulative time for the three different compositions of fuel kernels. A first fast transient release can be observed for both elements for whatever type of fuel kernels. This behaviour, which has been also observed previously [4,5] correspond probably to the dissolution of an oxidized layer UO_{2+x} dissolution, to the dissolution of unknown phases, segregated during the fabrication of solid solution formation or due to the detachment of high energy surface sites. The cumulative normalised mass loss of different fuel kernels correspond after 350 days to a depletion/corrosion depth of much less than one monolayer for thorium and to the depth of a unit cell of ThO_2 or UO_2 for uranium.

Considering a potential solubility control of normalised leaching rate, the value of the solubility constant is important. Indeed, the observed uranium and thorium

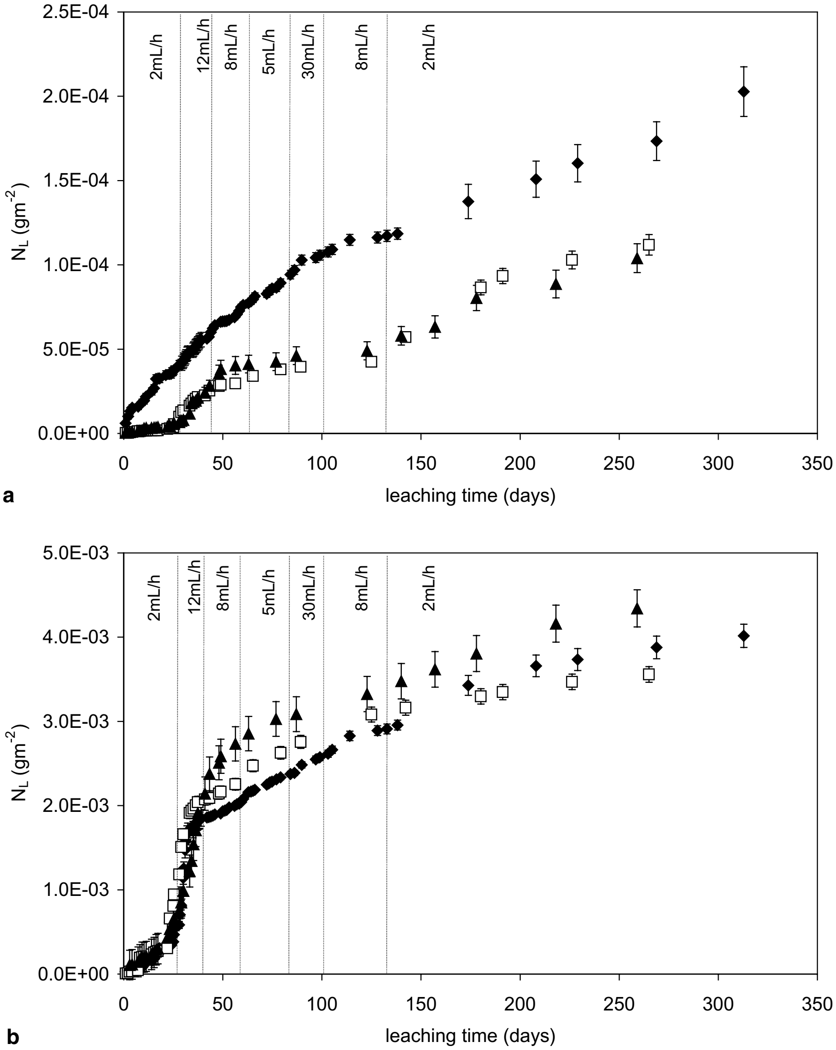

Fig. 3. Normalised leaching of (a) thorium and (b) uranium for different fuel kernels (♦) $Th_{0.837}U_{0.163}O_2$, (□) $Th_{0.907}U_{0.093}O_2$ and (△) $Th_{0.977}U_{0.023}O_2$ under reducing conditions (pH = 7; $E_h = -150$ mV/ENH).

concentrations were more than one order of magnitude below the empirical solubility values compiled by Neck and Kim [6] from literature, however the solubility products of crystalline UO_2 or ThO_2 proposed by these authors correspond to a soluble concentration of U and Th of only 10^{-15} M. Hence, one cannot exclude that the solubility of the two elements controls their dissolution rate (dissolution rate = water flow rate times solubility limited concentration). In that case, the dissolution rate of either U or Th or of both should be a function of the flow rate. For the first 40 days of leaching, we can see a transient state of increasing dissolution rates just after an increase of flow rate for the different fuel kernels. During this transient state, the normalised leaching rate increases with the flow rate. However, after a cumulative time of about 40 days, the dissolution rate returned to a low value. Form the independency of the dissolution rates on water flow rate, we conclude that solubility constraints were absent after 40 days. The flow rate dependency at shorter times may correspond to the solubility controlled release of oxidised surface layers, high energy surface sites etc.

3.2. Leaching rate of thorium as a function of pH

The normalised dissolution rates were estimated for reducing conditions by linear regression of the experimental data (N_L versus cumulative time). The obtained steady state dissolution rates are presented in Fig. 4 including data previously [3] obtained under oxic conditions without Na_2S for pH between 2 and 5.5 and the new data obtained for reducing conditions at pH 7–8.

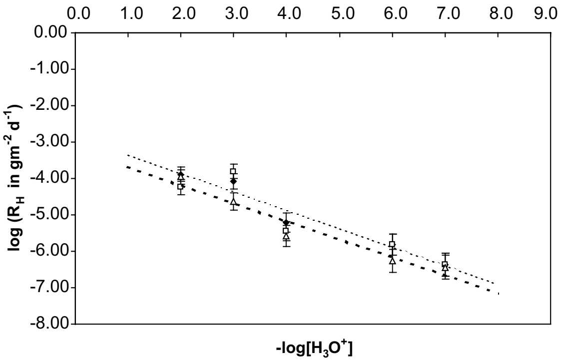

Fig. 4. Variation of $\log R_H$ (Th) versus $-\log[H_3O^+]$ for (♦) $Th_{0.837}U_{0.163}O_2$, (□) $Th_{0.907}U_{0.093}O_2$ and (△) $Th_{0.977}U_{0.023}O_2$.

The only factor of a certain influence seems to be the pH. Like Hubert et al. [7], we can explain our results by an empirical dissolution rate law using the expression

$$R_H(\mathrm{Th}) = k'_{T,Th}[H^+]^n, \quad n > 0. \tag{2}$$

Neither redox conditions (no effect of oxygen concentration), nor the water flow rate, or the presence of Na_2S as a potential complexing agent, or the U/Th ratio of the solid seem to have any measurable effect. According to this rate law, the logarithm of the normalised dissolution rate decreases linearly with increasing pH (Fig. 4) with a slope corresponding to the negative fractional reaction order of $n = 0.51 \pm 0.04$ with respect to the proton activity. This value is in good agreement with the results of Heisbourg et al. [8] even though these authors observed an effect of the U/Th ratio on the fractional reaction order. The fractional reaction order indicates that the detachment rate of thorium atoms from the surface is controlled by a sequence of reaction steps involving the formation of protonated activated surface complexes. The apparent normalised dissolution rate constant is equal to $\log k'_{T,Th} = -3.0 \pm 0.2$. This value is significantly higher than that measured by Heisbourg et al. The principal experimental difference is the about 1000 times lower specific surface area of 10^{-3} m^2/g in our study as compared to a value of 0.7–1.6 m^2/g in the case of Heisbourg et al. [8]. The estimation of surface area is of course a critical point. Measurements of surface area by BET is not suitable for fuel kernels since the error is large if gas adsorption is studied on a few particles of a few mm^2 surface area. However, when comparing our release rates of uranium as a function of dissolved oxygen concentration with literature data (see discussion below), it became evident that our normalised U release rates (or the dissolution rates of pure UO_2 kernels) are on the lower end of published dissolution rates. If the real rates would be even smaller, due to the underestimation of the effective surface area, the discrepancy with published rate data would become very large. For this reason we believe that the geometric surface area is a good estimation of effective surface area.

The specific surface area may be of influence on the normalised dissolution rate only if saturation effects in bulk solution or in the surface region are involved. Saturation effects are more likely to be of importance with high surface area powdered solids, than with low surface area fuel kernels.

3.3. Leaching rate of uranium (IV) as a function of pH

The normalised dissolution rates under dynamic reducing conditions were determined as previously for thorium. The release rates of uranium under reducing conditions (pH 7–8) are compared in Fig. 5 with reported data [3] for oxidizing static conditions in the pH range between 2 and 6. Under oxidizing conditions in carbonate free media, the first (fast) reaction step consists in the oxidation of the surface to a certain depth to an average oxidation state corresponding to U_3O_7. The U(VI) then becomes dissolved. Bruno et al. [9] showed that oxidized surface dissolution of UO_2 implies a rate expression according to:

$$R_H(\mathrm{U}) = k'_{T,U}[H^+]^n \quad n > 0. \tag{3}$$

Applying this law, we obtained a partial reaction order related to the proton activities equal to $n = 0.20 \pm 0.05$ and an apparent normalised dissolution rate constant equal to $\log k'_{T,U} = -2.80 \pm 0.30$. Considering the dissolution rate dependence on dissolved oxygen concentration, Fig. 6 gives a comparison of our data obtained under oxidizing and reducing conditions with literature values at other oxygen concentration. Within the large scatter of experimental data, the observed trend in the oxygen concentration dependency of the dissolution

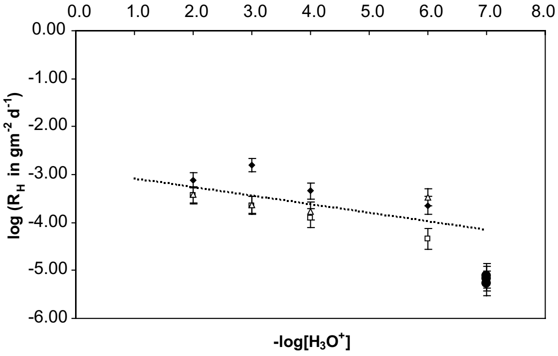

Fig. 5. Variation of $\log R_H(\mathrm{U})$ versus $-\log[H_3O^+]$ for (♦) $Th_{0.837}U_{0.163}O_2$, (□) $Th_{0.907}U_{0.093}O_2$ and (△) $Th_{0.977}U_{0.023}O_2$, including obtained for pH 2–6 under static oxidizing conditions published recently [3] and data generated in this paper at pH 7–8 under reducing conditions.

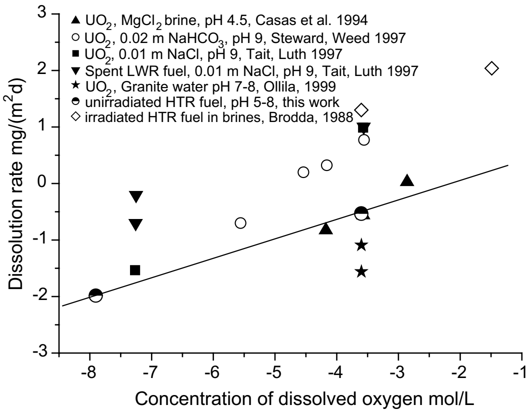

Fig. 6. Normalised dissolution rates of UO_2 from different studies at different dissolved oxygen concentration.

rates of HTR fuel particles and the absolute magnitude of the rate values are similar to the corresponding data from pure UO_2 or for LWR. A fractional reaction order with respect to the dissolved oxygen concentration of 0.31 of Torrero et al. [10] is consistent with our data. Fractional reaction orders both for H^+ and O_2 concentrations are due to the electrochemical nature of the UO_2 dissolution process and the build-up of corrosion potentials, which depend both on pH and on oxygen concentrations.

In conclusion, from this work and from the work of Torrero et al. [10] for the partial order related to oxygen concentration, the dissolution rate of uranium (IV) oxide in carbonate free solutions can be described by the equation:

$$R_{\mathrm{H}}(\mathrm{U}) = k_{\mathrm{T,U}}[\mathrm{H}^+]^{0.33\pm0.06}[\mathrm{O}_2]^{0.31\pm0.02}.$$

4. Discussion of the relation between Th and U leaching rates

For the higher release rates of uranium when compared to thorium and for the independency of U release rates on the U/Th ratio, different explanations may be invoked: (1) A congruent dissolution and selective precipitation of Th can be excluded as explanation as it may only explain faster U release but it fails to explain the independency of the Th release rates of flow rate and the independency of U release rates of the U/Th ratio. (2) The fast dissolution of a potentially existing U rich segregated phase can also be excluded as explanation, since only explains the faster U release but it cannot explain the independency of normalised U release rates on the U/Th ratio (except in the unlikely case where the mass of segregated U rich phase would be proportional to the U/Th ratio). Moreover, this explanation decouples U and Th release behaviour entirely even thought Fig. 3 shows that U and Th behavior are strongly coupled. (3) Hence, the only possible explanation, consistent with all experimental observations is the selective detachment of U from a Th rich surface. This would only explain the independency of U release rates on the U/Th ratio if the detachment probability of U from the surface is independent on whether the neighbouring metal ions are U or Th atoms. This explanation applies to U atoms located at the outer surface plane and to the diffusion of U to the surface from beneath, provided that the diffusion rate is faster than the rate of Th detachment from the surface. This explanation implies the creation of a U depleted Th rich surface region. One can expect that after removal of all easily accessible U atoms from the surface, the release rate of U will approach the release rate of Th. In other words, the U release rates will become equal to Th release rates when the detachment of U atoms from sub-surface sites and the diffusion of these atoms through an U depleted surface region of ThO_2 is slower than or equal to the Th release rate. Under these long-term conditions, it is rather unlikely that normalised U release rates will remain independent of the U/Th ratio. This state has not yet been reached in our experiments. The U depletion depth after one year of reaction extents only to a unit cell. We conclude that the depletion of uranium from the surface to a depth of the size of a unit cell is not sufficient to slow down the release of uranium significantly. The detachement and diffusion of U atoms from the sub-surface region does still continue with a rate higher than the release rate of Th from the outer surface.

5. Summary and conclusion

The dissolution of Th rich mixed oxide $(U, Th)O_2$ particles under reducing conditions has been determined using a continuous flow-through reactor with hundred particles. Various water flow rates were used. The results were compared with published results obtained under oxidizing conditions.

The U/Th ratio seems to have no influence on the normalised leaching rate of thorium or uranium. The effect of flow rate on the dissolution rates was only of importance in the first 40 days. The dissolution rates for longer times are independent on flow rates. This confirms the kinetic control of fuel kernel dissolution rates.

The normalised release rate of uranium from a Th rich mixed oxide matrix seems to be similar to the dissolution rate of pure UO_2 even though U is a minor component in these phases and the dissolution rate of Th is much lower. The dissolution rates of uranium can be expressed by the equation:

$$R_{\mathrm{H}}(\mathrm{U}) = k_{\mathrm{T,U}}[\mathrm{H}^+]^{0.20\pm0.05}[\mathrm{O}_2]^{0.31\pm0.02} \quad \text{for } 2 < \text{pH} < 7.$$

The dissolution rate of thorium, is similar to that of pure $ThO_2(c)$. The dissolution rates can be explained with the equation:

$$R_H(\mathrm{Th}) = (1.00 \pm 0.58).10^{-3}[\mathrm{H}^+]^{0.51\pm0.04}$$
$$(1 < \mathrm{pH} < 7,\ \text{rate in g m}^{-2}\,\mathrm{d}^{-1}).$$

The data allow some preliminary conclusions on the potential performance under long-term repository conditions of the matrix of Th rich fuel kernels in the case of failure of the SiC coating. The observed dissolution rates of Th correspond to fuel particle life times of about 10^7 years, independent of the uncertainties concerning the estimation of the specific surface area. Hence, in the absence of radiolysis, HTR fuel particles seem to provide significant intrinsic confinement properties for repository relevant time periods. Nevertheless, for a complete analyses of fuel performance, irradiation effects, potential phase segregation, instant release fractions and burn-up effects will have to be investigated using irradiated fuel kernels.

Acknowledgements

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