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# Effect of the thorium oxide content on the leaching of a mixed thorium-uranium oxide fuel

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## Abstract

Leaching of uranium from uranium oxide fuel in contact with water can be a radiation hazard problem in the case of fuel cladding failure, either during nuclear reactor operation or in an interim storage, as well as in a final repository. One way to mitigate this is to reduce the solubility of the fuel matrix by the mixing uranium oxide with a compound which is less soluble but otherwise of similar properties. In this paper, the effect of thorium oxide content on the leaching of the uranium oxide matrix is investigated. The method was to study the leaching of the uranium oxide fuel matrix as a function of a varying content of thorium oxide, using materials manufactured by powder co-milling. It was found that the substitution of more than 25%  $\text{UO}_2$  with  $\text{ThO}_2$  reduces the matrix leaching by more than one order of magnitude in most of the different leaching solutions investigated. The substitution of 7%  $\text{UO}_2$  with  $\text{ThO}_2$  results in a reduction of matrix leaching by 10–90%, depending on the concentration of borate and dissolved oxygen in the leaching solution.

**Keywords** Nuclear fuel · Leaching · Solubility · Thorium oxide · Uranium oxide · Fuel cladding failure · Interim storage · Final repository

## Introduction

Nuclear fuels containing thorium are considered as a complement to the current uranium based nuclear fuels, see e.g. [1]. The substitution of uranium with thorium in nuclear fuels may have several advantages from the point of view of material properties, resource availability, minor actinide production and proliferation resistance [2]. Neutronic simulations have indicated that thorium dioxide  $\text{ThO}_2$  used as partial substitution for  $\text{UO}_2$  in normal uranium dioxide fuel may serve to reduce the needs of not only natural uranium but also burnable absorbers [3, 4]. In this context, it is also of interest to assess the potential benefits of  $\text{ThO}_2$  partial

substitution for  $\text{UO}_2$  from a chemical point of view.  $\text{ThO}_2$  is a highly insoluble compound, mainly due to the fact that ionic thorium only exists as the strong Lewis acid in the tetravalent oxidation state and, therefore, could potentially be able to protect the more redox sensitive and thus more soluble  $\text{UO}_2$  from oxidation from the tetravalent to the hexavalent state and, ultimately, its dissolution in water.  $\text{UO}_2$  is not *per se* more soluble in its tetravalent state than  $\text{ThO}_2$  but can be readily oxidised to the hexavalent state and then dissolve.

Dissolution of  $\text{UO}_2$  may be a problem under different scenarios, for example, during interim storage of spent fuel, in a final repository, and in the case of fuel cladding failure during normal reactor operations. It is assumed that groundwater could intrude in the repository, and one of the scenarios that have been evaluated by SKB (The Swedish Nuclear Fuel and Waste Management Co) for the proposed KBS-3 concept for spent fuel management, is that the assumed reducing conditions in the water-filled repository would change to oxidizing conditions [5]. Together with a scenario with defective fuel canisters, this would increase the dissolution rate of the deposited fuel, which would then be in direct contact with groundwater. The radioactivity release from such a worst-case scenario would possibly be mitigated by partial substitution of  $\text{UO}_2$  in the fuel

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with  $\text{ThO}_2$ . Under normal reactor operation, the dissolved oxygen content in the coolant medium is approximately 10 ppb, or  $3 \times 10^{-7}$  M, for PWRs (Pressurized Water Reactors) and 35 ppb, or  $1 \times 10^{-6}$  M, for BWRs (Boiling Water Reactors) [6]. Nevertheless, oxidizing conditions are prevailing during reactor shutdown. Hence, uranium dissolution rates under oxidizing conditions are also relevant for the cladding failure scenario, during reactor shutdown or interim storage.

In order to assess the effect of partial substitution of  $\text{UO}_2$  with  $\text{ThO}_2$  on the leaching behaviour, a series of experiments was devised, in which the leaching of uranium and thorium was quantified for four different materials; pure  $\text{UO}_2$ , and  $\text{UO}_2$  substituted with 7, 25 and 40 weight% of  $\text{ThO}_2$ , respectively. All materials were manufactured using a dry oxide powder co-milling route [7], which is deemed appropriate for up-scaling to industrial fuel manufacturing, but may result in a less homogeneous oxide ceramic than e.g. sol-gel manufacture techniques. The objective of the experiments was also to investigate how the dissolution behaviour in a reactor- or repository-like environment is affected by the  $\text{ThO}_2$  content of the fuel. Such effects on the dissolution behaviour of the leaching solution characteristics were addressed by the inclusion of dissolved oxygen and other possibly relevant species, such as  $\text{H}_3\text{BO}_3$  and  $\text{LiOH}$ , commonly used in PWRs for control of reactivity and pH, respectively.

The solubility of mixtures of  $\text{ThO}_2$  and  $\text{UO}_2$  has been studied previously. The conclusions of all the reported experiments were that the solubility decreased with increasing thorium content [8–13], and thorium migration towards the surface of the solid was observed to be one of the mechanisms behind this [8]. The reported experiments were in all cases performed on solid solutions prepared by wet routes resulting in an initially completely homogeneous composition. The formation of a protective thorium layer at the fuel surface can be expected to be less efficient in an inhomogeneous material where  $\text{ThO}_2$  and  $\text{UO}_2$  is located in separate grains. Furthermore, the previous experiments were performed in acidic leachate media, aiming to assess the dissolution characteristics relevant to reprocessing. This study rather aims to assess the characteristics relevant to inadvertent dissolution during reactor operation or in a final repository, under which pH values closer to neutral can be expected.

## Theory

The solubility of  $\text{ThO}_2$  is very low, as given by its standard state water solubility product ( $\log_{10}^*K_s^\circ = 1.8$  [14]). Since the tetravalent state is the only stable oxidation state of thorium, it cannot be oxidized further to a more soluble state.

Similarly, the solubility of the tetravalent uranium  $\text{UO}_2$  ( $\log_{10}^*K_s^\circ = 2.5$  [14]) is also low. However, uranium can readily be oxidised from its tetravalent state to the penta- or hexavalent states which will yield a considerably higher solubility. The presence of borate in the solution has been found to increase the solubility of uranium in its penta- or hexavalent states, whereas no significant effect of borate on the solubility of (tetravalent) thorium was observed [15].

The dioxides of thorium and uranium are isostructural, both with fluorite crystal structure (Face Centered Cubic, FCC structure, space group  $\text{Fm}\bar{3}\text{m}$ ), and mixtures thereof form an ideal solid solution [16]. When a ceramic oxide pellet of this material is immersed in water under oxidizing conditions, tetravalent uranium at the surface will be further oxidized to hexavalent uranium. The detailed chemical reactions describing this system are complex and still discussed in the literature [17, 18]. The end products, however, seem to be the mixed oxide  $\text{U}_3\text{O}_8$  and schoepite ( $\text{UO}_3$ ) in water. The schoepite then readily dissolves [19].

The purpose of adding  $\text{ThO}_2$  to the  $\text{UO}_2$  matrix, from a chemical point of view, would be that the  $\text{ThO}_2$  during oxidative dissolution eventually could form a layer at the surface, protecting the remaining  $\text{UO}_2$  from further oxidation and dissolution [8]. This could either be obtained by dissolution of  $\text{UO}_2$  at the phase boundaries leaving only  $\text{ThO}_2$  [9], or by migration of thorium atoms towards the phase boundaries. Whether this migration happens or not depends on whether the migration of O atoms into the material is faster than the migration of thorium atoms towards the surface. This in turn depends on structural properties of the material (lattice defects, detailed stoichiometry etc.) which are overly difficult to control, for which reason the matter has to be investigated experimentally. It has also been suggested that the inclusion of thorium stabilizes the fluorite structure by limiting inclusion of excessive oxygen in interstitial sites [19].

## Methods

Regarding the nuclear fuel performance during reactor operation, the neutronic simulations described in references [4] and [20] indicated that for BWR applications, the  $\text{ThO}_2$  content in the fuel should preferably range between zero and about 40 weight%. For PWR applications, a  $\text{ThO}_2$  content of 7 weight% was found optimal [21]. For this reason, three different fuel types were manufactured for the purposes of experimental verification of manufacturability and in-pile behaviour;  $\text{UO}_2$  fuel substituted with 7%, 25% and 40% thorium dioxide, respectively (all percentages referring to weight%  $\text{ThO}_2$  in total dioxide). In addition, pure  $\text{UO}_2$  fuel was manufactured to be used as a reference.

All four fuel compositions were manufactured at the IFE (Institute for Energy Technology) laboratory in Kjeller, Norway. ThO<sub>2</sub> powder (99.95%) was delivered from Solvay and UO<sub>2</sub> powder (99.9%) from AEP. Details on the manufacture procedures have been reported previously [7]. The pure oxide powders were co-milled, followed by pressing and sintering in a dry hydrogen atmosphere. Micrographs of polished cross sections at peripheral, intermediate and central positions in the pellets indicate that the porosity is homogeneously distributed in the radial direction. Densities are listed in Table 1, along with data on uranium enrichment. The pellets have a radius of 4.24 mm and a height of approximately 10 mm. All four compositions have been irradiated in instrumented test fuel rods in the research reactor in Halden, Norway [7] for assessment of the integral fuel performance under reactor conditions.

### Sample preparation

Two pellets of each type were obtained from IFE Kjeller. Each pellet was cut into three discs using a table saw (Buehler Isomet 1000) located in a glove box with N<sub>2</sub> atmosphere (<0.1% O<sub>2</sub>) which used a hydrotreated light petroleum oil as a lubricant during cutting to avoid unnecessary oxidation or hydrolysis. The discs had a radius of 4.24 mm and a height of approximately 3 mm. The discs were then transferred to another glove box with N<sub>2</sub> atmosphere (20 ppm O<sub>2</sub>) where the discs were washed with acetone and ethanol to remove oil residues from the cutting procedure. The discs were then washed five times with a deaerated 10 mM Na<sub>2</sub>CO<sub>3</sub> solution to dissolve and remove any hexavalent uranium on the fuel surface. The uranium concentration of the last (fifth) batch of carbonate solution used for washing was determined by ICP-MS to contain approximately 10<sup>-8</sup> M <sup>238</sup>U, i.e. significantly lower than the solubility of hexavalent uranium [8]. This washing procedure was repeated when the fuel discs from one leaching experiment, or pieces of the same material, was re-used in a subsequent experiment. Such fuel discs that were leached in one experiment (i.e. in PWR or BWR coolant analogue solution for >200 days), washed and subsequently used for another leaching experiment are referred to as “pre-leached” below

### Leaching solutions

Two different solutions were prepared - one analogue for a BWR coolant, and one analogue for a PWR coolant. Based

on the descriptions of light water reactor coolant chemistry in [6], the BWR coolant analogue was chosen simply to be purified (Milli-Q, Merck) water, since the noble metal additions that are sometimes used were deemed to be unimportant for the process of UO<sub>2</sub> leaching. The PWR coolant was modelled by purified water with 500 ppm B (corresponding to 46 mM H<sub>3</sub>BO<sub>3</sub>) by addition of H<sub>3</sub>BO<sub>3</sub> (Fluka, puriss p.A.). This being the typical average boron concentration over a PWR operating cycle. For the adjustment of pH, LiOH (LiOH·H<sub>2</sub>O, Sigma UltraGrade >99%) was also added to the solution. The pH at room temperature in the PWR solution was adjusted to 9±0.5, corresponding to a pH of 7.2±0.2 at a typical PWR operating temperature of 300°C [6]. The oxygen content in the solution was assumed to be in equilibrium with the atmosphere

After the cleaning procedure, the discs were weighed, and subsequently placed at the bottom of a 10 cm deep capped polypropylene container (50 mL, Brand) containing 50 mL of either the BWR or the PWR coolant analogue solution. The solution in each container was sampled 5–20 times at intervals deemed appropriate to follow the dissolution process. The samples taken out were always of a volume less than 0.6 mL, so that the volume of the solution in which the discs were immersed remained practically constant. The containers were not stirred during the experiment and samples were pipetted from the uppermost 1 cm, so by Stokes law [22], any particles with a diameter of less than 100 nm should have been removed by sedimentation from the sampled layer of fluid already at the time of the first sampling (5 days). Duplicate experiments were prepared for each fuel composition

### Leaching solution analysis

Each of the samples, taken from the leaching solutions during the leaching process, was diluted 1:10 with 0.5 M HNO<sub>3</sub> (Suprapur, Merck). As internal standards for the ICP-MS measurements, 1 ppb bismuth and 1 ppb zirconium made from 10 ppm standard solutions of bismuth (CPA Chem) and zirconium (VGA Labs) was added to both the samples and the external standards. External standard solutions were prepared to 0, 1, 5 and 10 ppb thorium and uranium made from 10 ppm standard solutions of thorium (Certipur, Merck) and uranium (CPA Chem). The mass intensities of <sup>209</sup>Bi, <sup>90</sup>Zr, <sup>232</sup>Th, <sup>235</sup>U and <sup>238</sup>U were measured with ICP-MS (iCAP Q, Thermo). The mass intensity signals were measured three times to give average and standard deviation and then the concentration was calculated from the standard series curves.

**Table 1** Basic data on the four investigated fuel compositions

ThO <sub>2</sub> fraction [weight%]	0	7	25	40
Uranium enrichment [% <sup>235</sup> U in total uranium]	4.5%	4.96%	6%	7.6%
Density [% of theoretical density]	95	94.8	94.8	95.0

## Overview of experiments

Leaching experiments were carried out for four different leaching conditions, i.e. four different combinations of leaching solution (BWR- or PWR-coolant analogue), atmosphere (oxidizing or non-oxidizing) and material condition (fresh or pre-leached). The basic data of these four different conditions are listed in Table 2. In all four cases, leaching was performed with all four fuel compositions, i.e. with  $\text{UO}_2$  fuel with substitution of 0%, 7%, 25% and 40%  $\text{ThO}_2$  and in duplicates, which means 32 leaching experiments in total.

For the BWR-ox, PWR-ox and PWR-pl conditions, the experiments were carried out in a fume hood, i.e. in normal ambient atmosphere, which means that dissolved  $\text{O}_2$  in the leaching solutions was about  $3 \times 10^{-4}$  M, if one assumes equilibrium between the air and the solution [23]. In the PWR-no case, the experiment was performed in a  $\text{N}_2$  gas filled glove box with a slight over-pressure to ensure an  $\text{O}_2$  content a few ppm

The BWR-ox experiment was performed with intact fuel discs immediately after cutting. The PWR-no and PWR-ox experiments were performed with small fragments of broken discs that had previously undergone a brief period of leaching, i.e. with mostly fresh surfaces. The PWR-pl experiment was performed with intact fuel discs that had previously undergone a full leaching experiment of 225 days

## SEM and EDX measurements

The still intact discs that had undergone leaching for 225 + 537 days (PWR-pl) were investigated using an SEM (Scanning Electron Microscope, LEO Ultra 55) to assess surface inhomogeneity and, if possible, any signs of a thorium-enriched surface layer. Images were taken at an acceleration voltage of 15 kV, which corresponds to a maximum penetration depth of approximately  $0.5 \mu\text{m}$  in  $\text{UO}_2$  [24], and elemental fractions were assessed via EDX (Energy Dispersive X-ray analysis, Oxford Instruments). One disc of each composition was also polished to remove any surface layer affected by the leaching process and analysed similarly.

**Table 2** Basic data for the four conditions. Labels: ox = oxidizing, no = non-oxidizing, pl = pre-leached. The label indicates the type of leachant (coolant analogue) used.

Condition label	BWR-ox	PWR-no	PWR-ox	PWR-pl
Oxygen content [M]	$3 \times 10^{-4}$	~0	$3 \times 10^{-4}$	$3 \times 10^{-4}$
Material condition	fresh	fresh	fresh	pre-leached
Leaching time [days]	144	393	393	537

## Computer simulations

The dissolution behaviour was simulated using a simple model implemented in MATLAB [25] where the lattice of heavy metal atoms was represented by matrices, and the values of each element in the matrices indicated whether the corresponding position in the lattice was occupied by a uranium or a thorium atom, or if the position was empty. The positions occupied by oxygen atoms were not included in the model.

The progress of the dissolution was modelled by iterating over the matrices and updating the value of the matrix elements (empty, Th or U) according to a set of conditions on the neighbouring positions. Given the FCC lattice structure of the  $(\text{Th,U})\text{O}_2$  lattice, each position has four neighbours in the layer below, four in the same layer and four in the layer above. Different sets of conditions were investigated stating the number of neighbouring positions in each of the layers that should be empty for the atom in the considered position to go into solution. The conditions were set for thorium and uranium atoms separately. Similarly, different sets of conditions on the neighbouring positions in the different layers were investigated for a thorium atom in the considered position to migrate to a lower layer.

## Results

### Leaching experiments

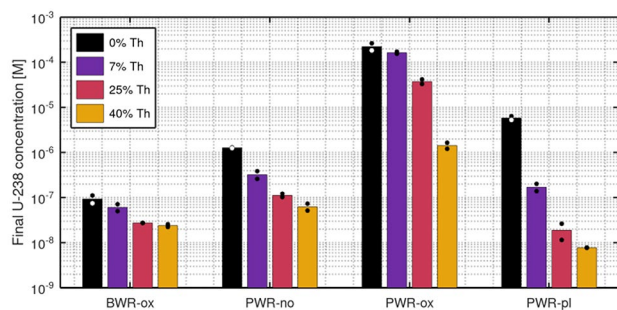
The measured concentrations in the leaching solutions confirm the expectation that the presence of  $\text{ThO}_2$  inhibits the leaching of the mixed oxide matrix since, in all cases, the final  $^{238}\text{U}$  concentration decreases significantly with increasing thorium content. The final  $^{238}\text{U}$  concentrations in the leaching solutions are shown in Fig. 1 for all four cases. Equilibrium was not reached in the PWR-pl and PWR-ox cases. Equilibrium was assumed to be reached when there was no apparent increase in  $^{238}\text{U}$  concentration in subsequent samplings. When constant (or decreasing) concentrations were measured, new samples were immediately (within a day) collected and analysed for confirmation.

The higher final  $^{238}\text{U}$  concentrations in the PWR-ox case (performed in an oxidizing environment) as compared with the PWR-no case (performed in a non-oxidizing environment) confirm that the dissolution is indeed an oxidative process, accelerated by an increased presence of oxygen in the leaching solution.

We also note that the final  $^{238}\text{U}$  concentrations are significantly higher in the PWR-ox case than in the BWR-ox case, which possibly indicates that a presence of borate in the leaching solution increases the solubility of the fuel matrix.

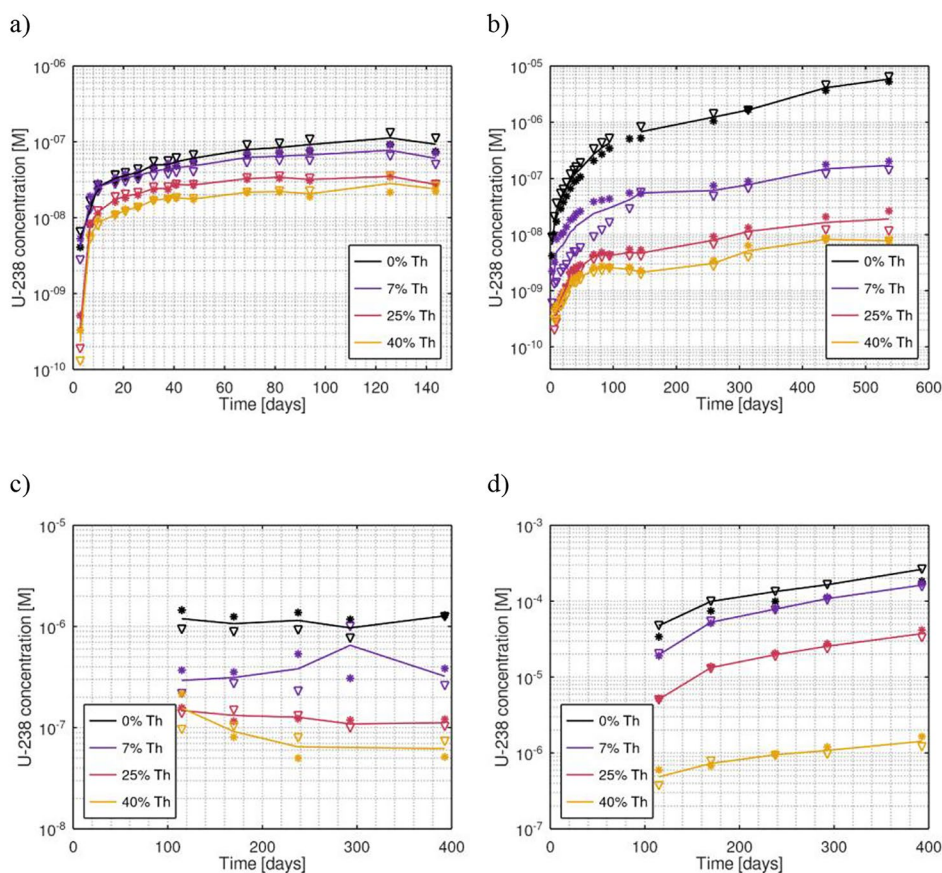


However, the PWR leachate was pH 9 compared with pH 7 for BWR leachate solution (pH measured by pH indicator paper sticks, Fisherbrand™), so increased hydrolysis may also contribute. However, using the thermodynamic data given in [14], the formation of anionic hexavalent uranium hydroxide species would only account for a factor of about three in solubility over this pH interval.



**Fig. 1** Measured final concentrations of  $^{238}\text{U}$  for all four compositions in all four cases, labelled as in Table 2. The dots mark the final concentrations in each individual sample (duplicates) and the height of the bars correspond to the arithmetic mean.

**Fig. 2** Measured  $^{238}\text{U}$  concentration for (a) the BWR-ox, (b) the PWR-pl, (c) the PWR-no and (d) the PWR-ox cases. Triangles and stars represent each of the duplicates, lines follow the arithmetic mean value



Finally, the results displayed in Fig. 1 show that pre-leaching of the material slows-down the dissolution process. The final  $^{238}\text{U}$  concentration is significantly lower in the PWR-pl case than in the PWR-ox case. These cases are identical except for the fact that the material in the PWR-pl case had been subjected to 225 days of leaching prior to the start of the present experiment. The difference between the different fuel material compositions is also more pronounced in the PWR-pl case. It can also be noted that in the PWR-pl case, the leaching time was 537 days, as compared with 393 days in the PWR-ox case, so the lower final concentrations cannot be attributed to a shorter leaching period.

The time evolution of the measured  $^{238}\text{U}$  concentrations is shown in Fig. 2. In the BWR-ox (a) case and the PWR-no (c) cases, the leaching process is considered to have reached equilibrium. In the PWR-no (c) case, the concentrations do not change significantly with time. In the PWR-pl (b) and PWR-ox (d) cases, the concentrations are still increasing at the end of the experiment. The trends are similar, but the absolute values are lower in the PWR-pl (b) case, i.e. where the fuel fragments were pre-leached.

In the PWR-pl (b) case, and in particular for 7% Th, the difference between the two duplicates (represented by triangles and stars respectively) is likely due to slightly different surface areas of the leached fuel fragments, which affects

the reaction kinetics. The difference is most pronounced in the beginning of the leaching periods when the leaching rates are high and the difference between duplicates becomes insignificant after this initial phase.

### SEM and EDX analysis

The SEM/EDX images of the samples of the four different compositions showed that the samples were indeed homogeneous, despite the dry oxide powder co-milling manufacture route. No significant difference was observed between the polished and non-polished surfaces in this respect. As expected, the polished surfaces appeared smoother than the non-polished ones. SEM images of both polished and non-polished surfaces are shown in Fig. 3 for all four compositions. The EDX spectra collected with an acceleration voltage of 15 kV did not show that any of the leached (non-polished) surfaces had a higher thorium concentration than what would be expected, i.e., not higher than the polished reference cases. A reason for this could be that the acceleration voltage was too high and thus the signal was an average of the outermost layer and the bulk, thus diluting any higher thorium content in the outermost layers. An attempt was made to collect spectra at a lower acceleration voltage (6 kV), but this resulted in too bad statistics for significant results.

### Computer simulations

The dissolution behaviour was modelled using the simple computer model described above. The experimental result was most closely reproduced by the following:

The conditions for a uranium atom to go into solution (disappear from the lattice) were that (a) more than one of the neighbours in the atomic layer above were gone or (b) that more than three of the neighbours above and more than two of the neighbours in the same layer were gone or (c) all the neighbours in the layer below were gone. The conditions

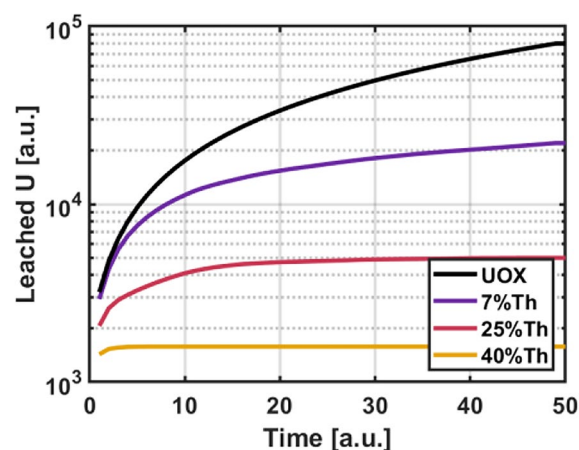
for a thorium atom to go into solution were much stricter, reflecting the lower propensity of a thorium atom to be oxidized; only if all neighbouring atoms were gone would the thorium atom also leave the lattice.

Also, a thorium atom would jump to an empty position in the layer below if (a) more than two of the neighbours in the same layer were gone and (b) more than two of the neighbours in the layer above were gone and (c) there would be an empty neighbouring position in the layer below.

The resulting time evolution of the number of leached uranium atoms is shown in Fig. 4, for the four investigated compositions.

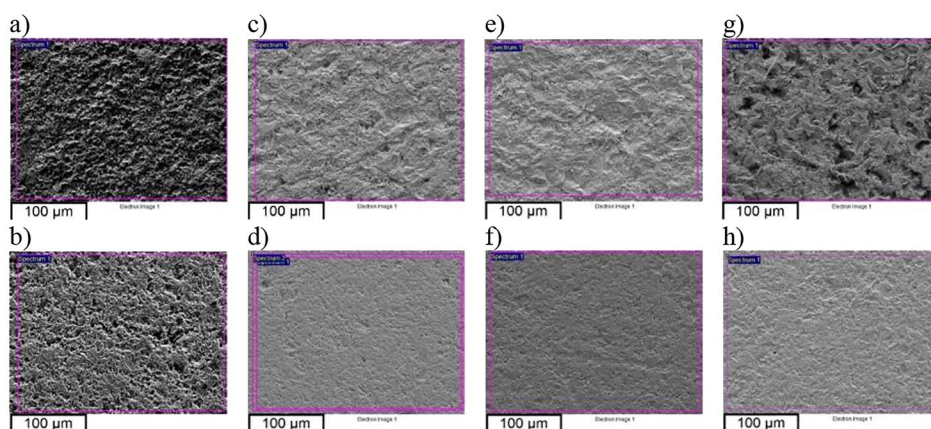
### Discussion

The results from the leaching of mixed oxide fuel material clearly indicate that the substitution with  $\text{ThO}_2$  for  $\text{UO}_2$  in



**Fig. 4** The number of leached uranium atoms as a function of time (both expressed in arbitrary units), as calculated by the described computer simulations. Compare with Fig. 2.

**Fig. 3** SEM images of surfaces of the discs with 0% (a, b), 7% (c, d), 25% (e, f) and 42% (g, h)  $\text{ThO}_2$  content. Upper row (a, c, e, g) leached (non-polished) surfaces, lower row (b, d, f, h) polished surfaces.



the fuel matrix lowers the effective solubility of the mixed oxide matrix. One proposed mechanism by which the substitution with  $\text{ThO}_2$  limits the dissolution of the mixed oxide is by formation of a protective layer enriched in thorium [8]. The layer thickness resolution of the EDX measurements was unfortunately too low for detecting the presence of such a layer, but we can also not exclude that it can be there. The fact that a pre-leached fuel surface showed much lower dissolution rates than fresh surfaces supports the theory that a protective surface layer is formed. Potentially, investigations using e.g. XPS could further elucidate this matter.

The proposed protective layer of thorium oxide may protect the  $\text{UO}_2$  matrix from dissolution in a manner similar to the protection of iron from dissolution by the addition of e.g. chromium in stainless steel. In stainless steel, some of the iron at the surface is oxidized and dissolved, which leaves the surface enriched in chromium atoms for oxidation. The chromium oxide thus formed has a significantly lower solubility and will thus eventually form a protective layer hindering further oxidation and dissolution of the matrix material [26]. This process is further enhanced by the chromium migration towards the surface and thus increasing the local concentration there helping the building of the protective layer [27].

Although  $\text{ThO}_2$  and  $\text{UO}_2$  have similar solubilities, the oxidation of uranium from the tetravalent- to the hexavalent state and the inertness of tetravalent thorium to further oxidation increases the solubility of  $\text{UO}_2$  significantly compared with  $\text{ThO}_2$ . In principle, the mechanism by which  $\text{ThO}_2$  addition protects  $\text{UO}_2$  from dissolution could be similar to the process which protects stainless steel.

The protective thorium layer, if present, is not thick enough to prevent alpha particles generated within the fuel to reach the aqueous phase and cause radiolysis [28]. However, these radiolytically produced oxidants will not have any effect on the protective thorium oxide layer and thus the fuel matrix dissolution. In spent fuel, the presence of fission products or fission product agglomerates could potentially affect the efficiency of the protective layer adversely.

When the fraction of  $\text{ThO}_2$  in the mixture is too low for the thorium atoms to form an interconnecting web, only removal of superficial uranium will not ultimately result in a surface enriched in thorium. In this case, thorium atoms surrounded by only uranium atoms will disconnect from the lattice when all their neighbours are gone. Thus, this mechanism can likely be excluded.

The EDX measurements performed with an acceleration voltage of 15 kV penetrated approximately 1000 atomic layers into the material. If the proposed layer is formed by migration of thorium atoms towards the surface, the zone probed by the 15 keV electrons would likely cover both the thorium-enriched zone close to the surface and the

thorium-depleted layer below that, since the thickness of a typical protective oxide layer is only some tens of atomic layers [29], which means that the analysis method can neither exclude nor confirm this type of mechanism.

A third process which could result in formation of a thorium-enriched layer would be if thorium atoms at the fuel surface, having a very low solubility, migrate into empty vacated lattice positions rather than entering into solution. Thus, when a tetravalent uranium atom is oxidized to the hexavalent state and leaves the lattice, any thorium atom in a neighbouring, less tightly bound, position would “jump down” to occupy its place. The result would be that while a number of atomic layers are leached, the uranium atoms in these layers are dissolved, whereas the thorium atoms in these layers would accumulate at the surface, thus creating a thorium enriched surface layer. This is exactly the process that was modelled by the computer simulations and, when comparing Fig. 4 with Fig. 2b, the time evolution of the number of leached uranium atoms according to the model is qualitatively similar to the time evolution of the uranium concentration in the experiments. This suggests that a formation of a thorium-enriched layer through the proposed “jumping down” mechanism may be responsible for the observed protective effect of a thorium substitution of uranium in a mixed oxide.

The lower solubility, for all fuel compositions, in the BWR-ox case as compared with the PWR-ox case, indicates that the presence of borate increases the solubility of the fuel material, and more so for lower thorium content. This is expected since Hinz [15] found that the presence of borate ions increased the solubility of (penta- or hexavalent) uranium through complexation, but not the solubility of (tetravalent) thorium. Borate complexation of uranyl ions has been observed but the corresponding stability constants are too uncertain to make reliable speciation calculations with [15]. Thus, the dissolution of the uranium matrix would be accelerated whereas the propensity of thorium atoms to stay in the lattice would be unchanged. This also points towards the “jumping down” mechanism, since the presence of borate would affect this mechanism as described, but not the migration of thorium atoms within the lattice.

## Conclusions

The results from the leaching of mixed thorium/uranium oxide fuel indicate that the substitution of  $\text{UO}_2$  with  $\text{ThO}_2$  in a fuel matrix prepared by powder co-milling does indeed have a dissolution inhibiting effect on  $\text{UO}_2$  fuel. The lowering of the apparent solubility is around some tens of percent for 7%  $\text{ThO}_2$ , and exceeds an order of magnitude for 25% or 40%  $\text{ThO}_2$ . The effect seems to be due to the formation of a



protective  $\text{ThO}_2$  layer formed at the fuel surface. A simple computer model suggests that the mechanism behind the formation of this layer is that thorium atoms at the fuel surface move to occupy lattice positions vacated by dissolved uranium atoms, rather than leaving the lattice and entering into solution. However, we cannot exclude that thorium atoms in the lattice migrate towards the fuel surface and are thus responsible for all or part of the formation of the protective layer.

It should be noted that these experiments were performed at room temperature and the results are thereby not necessarily applicable to reactor conditions. Further experiments may be performed at high temperatures and pressures in autoclaves for an assessment of the dissolution behaviour under reactor conditions. The temperature at which the experiments were performed (18–20 °C) is however typical for interim storage conditions [30].

For final repository conditions in the longer time perspective, the temperature is likely to be below room temperature. A worst-case scenario envisaged is penetration of surface water into the repository, which would change the conditions from reducing to oxidizing. The experiment performed at oxidizing conditions with a BWR coolant analogue leaching solution (BWR-ox) is likely that which is most applicable to this scenario. The substitution of  $\text{UO}_2$  with  $\text{ThO}_2$  resulted in less dissolution, but the difference was less an order of magnitude for all investigated fractions of  $\text{ThO}_2$ . This indicates that the addition of  $\text{ThO}_2$  would not be an efficient means to improve fuel characteristics in a final repository.

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