Two-step alkaline thorium dioxide precipitation

A low waste method for highly sinterable ThO₂

T. Wangle^{1,2,3}, N. Peeters^{1,4}, N. Cautaerts¹, T. Delloye³, T. Cardinaels^{1,4}, J. Vleugels², M. Verwerft¹

¹ Belgian Nuclear Research Centre (SCK CEN), Institute for Nuclear Materials Science, Boeretang 200, B-2400 Mol, Belgium

² KU Leuven, Department of Materials Engineering, Kasteelpark Arenberg 44, P.O. Box 2450, B-3001 Heverlee, Belgium

³ Solvay, 85 Avenue des Frères Perret, 69190 St Fons, France

⁴ KU Leuven, Department of Chemistry, Celestijnenlaan 200F, P.O. Box 2404, B-3001 Heverlee, Belgium

Abstract: We precipitated thorium in a two-step process with ammonia and carbonates. In contrast to single step ammonia or carbonate precipitation, the two-step process precipitates >99.9% of Th and removes >99.5% of Ra alongside. Filterability is strongly affected by pH variations in the ammonia step, and under well-controlled conditions, the precipitated ThO₂ filters quickly and calcines to crystalline ThO₂ at low temperatures. As-precipitated ThO₂ contains significant quantities of adsorbed H₂O and CO₂, which are removed during calcination. The calcination temperature greatly affects the green density of produced pellets, but for all calcination temperatures investigated, the sintered densities are in excess of 96% with grain sizes within the range applied for nuclear fuels at 10-16 μm.

Keywords: ThO₂, permeability, radium removal, ammonia, carbonates

1 Introduction

Thorium has a long history in nuclear applications, with its first application considered in the 1940's [1] and deployed in reactors already in the late 1950's [2]. Unlike uranium, natural thorium lacks a fissile isotope and its consideration as nuclear fuel relates to the potential to breed fissile ²³³U in thermal and epithermal spectra. In theory, closed Th-²³³U fuel cycles are possible, but contamination with ²³²U and its fission products (primarily ²⁰⁸Tl) requires shielding and remote handling [3]. The technological challenges and the costs related to such a closed fuel cycle are huge. A closed Th-based fuel cycle still has to be initiated by the introduction of another fissile isotope, e.g. ²³⁵U or ²³⁹Pu. In spite of the huge technological challenges, diversifying and securing supply were the primary drivers for initiating research on thorium-based fuel cycles decades ago. Today they are still dominant factors to pursue research and development in the field. Besides diversifying supply, ThO₂ has a higher melting temperature [4] and better thermal conductivity [5, 6] than UO₂, which give ThO₂ a higher safety margin than UO₂. The higher thermal conductivity also means the fuel center line temperature is lower for identical linear power and fuel surface temperatures. In addition, the neutronics are also favorable for long term deployment. ²³²ThO₂-²³³UO₂ also has significantly better breeding characteristics in thermal and epithermal neutron spectra than ²³⁸UO₂-²³⁹PuO₂. The flattened reactivity curve [7]

and reduced rim effect [8] of ^{233}U breeding compared to ^{239}Pu breeding from ^{238}U in UO_2 fuels also increases the longevity of fuel.

Given these favorable characteristics, it is not surprising that the economics of thorium dioxide use in present water moderated nuclear reactors has been investigated. Largely these studies have focused on the costs of reprocessing and $(\text{Th}, ^{233}\text{U})\text{O}_2$ fuel manufacturing in a closed cycle [9]. ThO_2 has also been investigated for the once-through cycle [10-13], where costs associated with ThO_2 manufacturing become important. Continuous processes have higher material throughput than batch processes, which makes them more desirable at industrial scale. Unlike in batch processes, the constant inflow of materials creates a steady state in the reaction vessel. The manufacturing ThO_2 pellets from purified Th^{4+} solutions is associated with several cost factors related to filterability, thorium precipitation efficiency, wastewater activity and sinterability.

The greater the filterability and the thorium efficiency, the lower operating costs. The activity of wastewater from precipitation is a problem specific to ^{232}Th , whose daughters are more short-lived than those of ^{238}U , and can build up appreciably between Th^{4+} purification and powder precipitation. These daughters make wastewater from thorium precipitation expensive liquid radioactive waste. Wastewater can decay to free release levels quickly only if the longest lived isotopes are removed – most importantly ^{228}Ra (5.7 years), with minor contribution from ^{224}Ra (3.6 days) and ^{226}Ra (1600 years) decayed from ^{230}Th impurities. These can be precipitated alongside thorium or separated into solid radioactive waste. The poor sinterability of ThO_2 is a product of its otherwise desirable high thermal stability. For many powder processing routes, it proved to be difficult to achieve densities in the range 95-97% required for commercial water moderated reactors [14]. Commonly, sinterability is improved by metal doping [15-18], milling [19, 20], or powder process optimization [21]. Doping and milling are undesirable. Doping would complicate regulatory approval, while milling generates significant (radioactive) dust, which presents a serious health hazard.

Thorium has most often been precipitated with oxalates because an excellent thorium efficiency is guaranteed by the low solubility of thorium oxalate even in acidic conditions [22, 23]. Fast filtering has been demonstrated for thorium oxalate [24] and for crystallographically similar $\text{Np}(\text{C}_2\text{O}_4)_2$ [25]. With optimized process parameters, ThO_2 from oxalate has also been shown to reach satisfactory densities without milling [24, 26, 27]. Oxalate precipitation does not, however, achieve sufficient radium efficiency. Free release levels are only achieved if efficiencies are at least 99.9% for Th and 99.5% for Ra. The oxalate removes 99.9% Th, but only removes 95% of Ra [28], a measurement confirmed in this study.

Of the possible alternate CHON based precipitating agents required for fuel applications, only the oxalate, nitrate and carbonate form insoluble compounds of radium [29]. Early investigations showed thorium carbonate to sinter reasonably well both under conventional sinter-

ing [30, 31] and hot pressing [32], making this option also suitable from the sintering perspective. In addition, thorium oxycarbonate was shown to compact poorly, but to shrink very well, allowing it to outperform some oxalates [27].

Therefore, we investigated the suitability of a two-step, ammonia/carbonate-based precipitation process and compared it against our earlier thorium oxalate precipitation [24]. We adopted a two-step process to produce a fast-filtering precipitate which removes radium. By controlling pH outside of gel forming range, an easily filterable precipitate can be produced [33]. We then bound radium to the precipitate as carbonate by adding ammonium bicarbonate at high pH.

2 Experimental

2.1 Synthesis

ThO₂ pellets were prepared by a two-step, batch-wise precipitation in the same beaker, calcined and then sintered (see **Fig. 1**). In this first step (“hydroxide step”), Th⁴⁺ solution was added dropwise from a dropping funnel to a 0.5 mol/l NH₄NO₃ medium (BioXtra, Sigma-Aldrich). The Th⁴⁺ solution was prepared by diluting a solution of 1.9 mol/l Th(NO₃)₄ in 1.6 mol/l HNO₃ (confirmed as ≥99.95% trace metal basis by ICP-MS, Solvay) with demineralized water to 0.5 mol/l Th(NO₃)₄, no correction was made for excess HNO₃. Three batch sizes at 1:5 Th:NH₄NO₃ volume ratios were prepared (see **Tab. 1**).

Tab. 1: Batch sizes used during precipitation.

Batch size	Th ⁴⁺ volume [ml]	NH ₄ NO ₃ volume [ml]
Small	5	25
Medium	15	75
Large	30	150

The addition of Th⁴⁺ was compensated by the on-line addition of NH₃ (Emsure, Sigma-Aldrich; 0.5 mol/l initially, rising to 1 mol/l after ca. half the Th⁴⁺ was added) to simulate the steady state of a continuous process and maintain the suspension pH in the 6-7 range. Th⁴⁺ rapidly forms a ThO₂ gel around pH 8, but as this gelation begins above pH 7, that was considered the upper pH limit. After all Th⁴⁺ was added, the suspension was brought to pH 6.5 and aged for 30 min. In the second step (“carbonate step”), RaCO₃ was bound to the permeable precipitate by the addition of a basic carbonate solution (2 mol/l NH₃ + 2 mol/l NH₄HCO₃; ReagentPlus, Sigma-Aldrich) dropwise from a dropping funnel. The basic carbonate solution was added until the suspension reached pH 9 and then aged for 30 min. The suspension was stirred from the moment of Th⁴⁺ addition until the end of the carbonate ageing step.

At the end of the second ageing, the precipitate was filtered and dried at 25 kPa at ambient temperature. As Mirza and Karkhanavala [34] reported carbonate loss from ThO₂·2H₂O·CO₂ during washing, washing was not performed. The agglomerates were broken up by shaking the

dried powder on a Turbula mixer at 60 rpm in a glass vial with one 9.5 mm PMMA bead and then calcined. Calcination was performed in a Nabertherm LT 9/13/P330 muffle furnace, heated at 3 K/min until the specified maximum temperature (673, 873, 1073, or 1273 K) for 2 h. Approximately 1 g of calcined powder was loaded without further manipulations into a stearic acid-coated, 6.9 mm-diameter steel die. The green pellets were uniaxially pressed with single side compaction in an Atlas Auto 8T semi-automatic press at 300 MPa. Sintering was performed in batches in a Linn HT 1800 Moly furnace with an alumina refractory matrix and molybdenum heating elements. The heating rate was 5 K/min and the atmosphere was Ar + 5% H₂ with a small admixture of Ar + 0.5% O₂, to give an oxygen potential of -420 kJ/mol at the maximum temperature of 2023 K, which was maintained for 8 h. Reducing atmosphere was chosen due to furnace requirements, though sintering-promoting point defects are produced in ThO₂ at high temperatures in both reducing and oxidizing atmosphere [35]. For pellets with closed porosity, the density was determined by immersion. For pellets with open porosity, the density was determined geometrically.

To compare the permeability, Th and Ra efficiency, oxalates were precipitated by adding 1 mol/l Th(NO₃)₄ (in HNO₃) to 0.75 mol/l oxalic acid at 283 K according to [24].

Fig. 1: Flowsheet of the solution to pellet production process. The products of the first and second step are referred to as the “hydroxide” and “carbonate” respectively.

2.2 Characterization

The permeability of the filtration cakes was monitored both after the hydroxide and after the carbonate step to determine the ease of processing. The permeability (κ) was expressed as:

$$\kappa = \frac{dV}{dt} \cdot \frac{L \mu}{A \Delta P}, \quad (1)$$

where dV/dt is the volumetric flow rate of the filtrate through the filtration cake, L is the cake thickness, μ the filtrate viscosity, A the filtration area and ΔP the difference in pressure. To measure the permeability, a suspension was first poured into a glass column atop a 0.22 μm cellulose ester filter (Millipore) mounted on a glass frit. The suspension was allowed to settle for 10 min and then filtered at reduced pressure ($\Delta P = 90$ kPa) into a volumetric cylinder (filtration times generally did not exceed 10 min). The flow rates were measured by recording time as a function of collected volume, with the volumetric flow rate in the linear section (where the solids are fully settled) reported. The wet cake thickness was measured in this linear section. The filtrate viscosity was measured with an Ostwald viscometer. The measured permeabilities were targeted to be within half an order of magnitude of the permeability of the oxalate. The oxalate permeability was measured to be $52 \cdot 10^{-15} \text{ m}^2$, and the threshold for good permeability was chosen as its $10^{-0.5}$ multiple: $16 \cdot 10^{-15} \text{ m}^2$.

The Th and Ra efficiency were measured by dialysis of 5 ml samples from the suspension (and from the 0.5 mol/l Th^{4+} solution) through Spectra/Por[®] 3 membranes (MWCO 3.5 kD) into 60 ml demineralized water for 24 h, at which point a high dialysis efficiency is reachable [36]. The final dialysate evaporated to ca. 40 ml during dialysis and was sampled into a vial whose geometry is calibrated. The dialysate sample in the vial was then measured by γ spectrometry at least 4 weeks (8 half-lives or more of ^{224}Ra) after the dialysis. This allowed the equilibrium between ^{228}Th and its daughters to be established. The efficiency of Ra was measured as ^{228}Ac in equilibrium with ^{228}Ra on its 338 keV emission line. The efficiency of Th was measured on the 238 keV line of ^{212}Pb in equilibrium with ^{228}Th . Please note, ^{228}Th is only used as a tracer and cannot be considered in equilibrium with ^{232}Th , as equilibrium was interrupted by purification in 1994. Activities were measured using HPGe γ -spectrometers of different efficiencies, dead times and backgrounds chosen according to expected activity (supplied by Canberra or Ortec). The detectors were calibrated using a solution of ^{241}Am , ^{51}Cr , ^{54}Mn , ^{57}Co , ^{60}Co , ^{65}Zn , ^{85}Sr , ^{88}Y , ^{109}Cd , ^{137}Cs , ^{113}Sn , ^{139}Ce standards. Corrections for efficiency transfer and summing were performed in EFFTRAN and activities were calculated with Genie2K. Count rates were converted to activity using calibrated efficiencies for each detector and emission yields collected on Laraweb [37]. Errors from Laraweb were used without modification, while 2.65σ was used for measurement errors. Volume transfer and sampling errors were estimated at 1%. For solutions with a high radium activity, the thorium activity was corrected for ^{228}Th buildup from ^{228}Ra . The Th and Ra efficiency was calculated from the activity normalized to the initial amount of Th^{4+} added to the suspension. Removal efficiencies were determined by dividing the

activity of the dialysate with the activity of the starting solution dialysate at equivalent Th loading. Th and Ra efficiency was also measured in the same manner for the oxalate.

For γ -spectrometry of solid samples, pellets were prepared to have a final height of around 3.5 mm in an effort to maintain similar geometries between different thermal treatments. These samples were then measured 4 weeks after the final thermal treatment under identical geometry and measurement times. No calibration standard was available for pure ThO₂, hence we chose to monitor two high energy lines (the 1620.7 keV line of ²¹²Bi for thorium and the 1630 keV line of ²²⁸Ac for radium) to study the Ra to Th ratio in solid pellets. In this way, biases in self shielding and detector efficiency were negligible.

Transmission electron microscopy (TEM) of the fresh precipitate was performed on a JEOL 3010. The suspension after dialysis was diluted in 2-propanol, dispersed on holey carbon grids and dried in ambient conditions.

Thermogravimetry (TGA) was performed on the dried precipitate using a Netzsch STA 449 F1 Jupiter. A fraction of the exhaust gas from the STA was diverted to a 403 D Aëolos quadrupole mass spectrometer (MS). Approximately 20 mg was used for DSC measurement, while approximately 2 g was used for TGA-MS. The TGA was performed under 100 ml/min Ar/0.4% O₂ to simulate calcination in air while limiting ¹⁴N₂ – ¹²C¹⁶O interference in the mass spectrometer. TGA samples were measured in an Al₂O₃ crucible against an empty crucible blank using a type S thermocouple. The measurement included an initial 30 min equilibration period at 313 K and then heating to 1273 K, after 1 h of holding at 1273 K, the sample was cooled at 10 K/min to 313 K. The heating rate for DSC measurements was 10 K/min, while for MS measurements it was 2 K/min.

X-ray diffraction was performed with a Philips X'Pert Pro diffractometer with a Cu LFF tube, in Bragg-Brentano parafocusing geometry and θ - θ configuration. Samples were measured from 10° to 130° 2 θ with a step size of 0.008° with a position sensitive Real Time Multiple Strip detector (X'Celerator). Cu K β radiation was limited using a Ni filter. The beam was adjusted using a copper beam mask (15 mm), a fixed divergence slit (1/2°), and a 0.02 rad Soller slit. The crystallite size together with the non-dimensional strain ϵ_0 was calculated using the Hall–Williamson formula [38]. Structural analyses were performed by the profile matching (Le Bail) method with the JANA2006 software suite [39].

Brunauer Emmett Teller (BET) specific surface area (SSA) analysis was performed on the calcined powders with a Micromeritics Tristar® II 3020. The powders were degassed at 523 K for 3 h in vacuum.

Dilatometry was performed in a Netzsch DIL 402/C/7. The heating rate was 5 K/min in an atmosphere of Ar + 5% H₂ with a small admixture of Ar + 0.5% O₂. The oxygen potential of the mixture was -420 kJ/mol at the maximum temperature of 1898 K, which was maintained for 1 h.

Scanning electron microscopy (SEM) was performed on etched pellets coated with Pt (5 nm) using a Jeol JSM 7100FA SEM field-emission microscope. The pellets were embedded

in Technovit 5071 and polished to a mirror finish. Afterwards, the resin was dissolved in acetone and the pellets were thermally etched for 3 h at 1723 K in synthetic air. These etched pellets were coated with Pt. All micrographs were obtained in secondary electron mode.

The grain sizes of etched pellets were calculated using the linear intercept method, where the grain size (G) was calculated from the number of grain boundaries (N) along a defined length of line (L) as $G = \frac{\pi L}{2 N}$. Several images from each pellet were used for calculation, with >500 intercepts used. The average grain size and its variations (reported as 2σ) were calculated from these data.

3 Results

3.1 Wet route optimization

An overview of permeability and efficiency tests is given in **Tab. 2** for various experiments. Samples are labelled according to the steps performed during precipitation: HH were precipitated only by addition of ammonia at pH 6-7 (i.e. first step only), HC were precipitated by addition of ammonia followed by the addition of a basic carbonate solution (i.e. the two-step process), and CC was precipitated with a single-step precipitation to pH 9 with 3 mol/l NH_3 and 1.5 mol/l NH_4HCO_3 . This last experiment was performed as a counter-example demonstrating that sequential addition is required. Discussion of the results is performed in following paragraphs.

Tab. 2: Overview table of permeability and efficiency values for various experiments.

Name		Batch size	ageing of step [h]		permeability [10 ⁻¹⁵ m ⁻²]	efficiencies [%]		Notes
			1 st	2 nd		Th	Ra	
Target			-	-	16	>99.9	>99.5	1.9 mol/l Th ⁴⁺
HH01	Medium	0.5	-	52	99.9 ± 0.2	<10		
HH02	Medium	2	-	28	-	-		
HH03	Medium	4	-	7	-	-		
HC01	Medium	0.5	0.5	16	99.96 ± 0.03	99.78 ± 0.06		
HC02	Medium	0.5	2	15	99.95 ± 0.03	99.85 ± 0.06		
HC03	Medium	0.5	4	15	99.87 ± 0.04	99.47 ± 0.08		
HC04	Large	0.5	0.5	46	99.94 ± 0.03	99.79 ± 0.09		
HC05	Large	4	0.5	31	-	-		
HC06	Large	0.5	0.5	55	99.98 ± 0.02	99.79 ± 0.17		
CC01	Medium	-	30	<1.1*	99.95 ± 0.02	>99.8**		

* The volumetric flow rate never reached a constant value as the cake was only settled at the end of filtration. The upper limit of 1.1 corresponds to a linear fitting of the final three points of the volumetric flow rate.

** No detected activity, minimum detectable activity reported.

3.1.1 The influence of suspension ageing after the hydroxide step

Surface chemistry changes were monitored during aging after the hydroxide step. The pH of the hydroxide suspension prepared in a small batch (5 ml Th^{4+} , see **Tab. 1**) was adjusted to 6.5 and then monitored over the course of 24 hours. As shown in **Fig. 2**, the pH of the suspension drops steadily over the monitoring time. This acidification is driven by the following reaction:

As the suspension ages, the surface charge on the ThO_2 particles will increase, expanding the electrical double layer and electrostatically stabilizing the suspension. This is expected to result in more homogeneously and more densely packed filtration cakes with a lower permeability.

Fig. 2: The change in pH during suspension ageing after the hydroxide step. The suspension pH decreased continuously from 6.5 as ageing proceeds, dropping below pH 6 after 4 hours.

The measured permeability of medium batches (15 ml Th^{4+} , see **Tab. 1**) followed the same trend as small-batch pH, gradually decreasing with ageing time (HH01-HH03 in **Tab. 2**). The permeability roughly halves from the previous value as ageing progresses from 0.5 to 2 to 4 hours (from HH01 to HH03), dropping below the threshold level after 4 hours. An ageing time of only 30 minutes was judged to be optimal.

3.1.2 Effect of carbonate addition on Th and Ra efficiencies

After preparing and ageing (30 min) the hydroxide precipitate, the suspension was sampled (without ageing) during carbonate addition for efficiency measurement. Carbonate addition was monitored by pH measurement. As shown in **Fig. 3**, the radium remains in solution below pH 9. The carbonate distribution equilibrium keeps CO_3^{2-} below 1% of the total carbonate content, which complicates RaCO_3 formation. At pH 9, the amount of CO_3^{2-} begins to reach significant levels and radium efficiencies are in excess of 95%. Above pH 9.5 the radium efficiency drops. After addition was ended at pH 9.7, the suspension completely re-dissolved within 30 minutes of ageing. This is likely due to the formation of soluble carbonate complexes of the $[\text{Th}(\text{OH})_n(\text{CO}_3)_m]^{4-n-2m}$ type which form from ThO_2 in carbonate solutions [40]. Later tests also showed redissolution at pH 9.5 after 30 min ageing. To take advantage of good efficiency, while avoiding re-dissolution at high carbonate content, pH 9 was chosen for further tests.

Fig. 3: The effects of carbonate added to the hydroxide precipitate on the activity of residual dissolved thorium and radium. At pH 9, thorium and radium efficiencies are >95%. Above this pH, the precipitate begins to re-dissolve after only a short ageing time, though without ageing the radium activity can fall below the detection limit at pH 9.7.

3.1.3 The effects of suspension ageing after the carbonate step

The pH scoping tests (as in section 3.1.1) were also performed for the second precipitation step. Hydrated ThO_2 was precipitated in a small batch and aged for 30 minutes. Then the $\text{NH}_3\text{-NH}_4\text{HCO}_3$ solution was added to bring the pH to 9 and the pH was measured during ageing. The pH remained unchanged over the length of the measurement, with variations within the measurement error. This lack of change is most likely the result of the ammonia-ammonium

carbonate buffer, which is effective at pH 9 [41]. The effect of ageing for 0.5, 2, and 4 hours at medium batch sizes was compared. The permeability of the carbonate falls to a lower value than of the starting hydroxide, reaching the threshold level (compare HC01, HC02 and HC03 in **Tab. 2**: Overview table). The permeability, like suspension pH, is not affected by ageing after carbonate addition.

Efficiency, however, varied more than the permeability (see **Tab. 2**: Overview table). The thorium efficiency remains above the 99.95% threshold at short aging times (0.5 and 2 h) and drops to 99.85% at an aging time of 4 h. The radium follows the same trend. At short aging times, the efficiency is around 99.8 % and drops to slightly below 99.5% after 4 h aging.

3.1.4 The effects of pH stability, batch size and Th⁴⁺ loading

The downside of batchwise approximation of a continuous process is to introduce an unwelcome factor of operator error. In an effort to quantify these effects, we tested how much pH variation during hydroxide precipitation affects permeability. The stable permeability values in **Error! Reference source not found.** indicate that the pH stability requirements during carbonate addition are likely not very strict, but the variability for the hydroxide step indicates a possible pH sensitivity.

The outlying and regular operating pH values were recorded during the more pH-sensitive hydroxide step. As shown in **Fig. 4**, the pH during operation matters. Even when the pH remains (>95% of the time) within the 6-7 range, short term outliers can strongly influence the permeability. The early pH 7.0 outlier in the second repetition has no effect. Instead, the drop of pH well outside the range to 5.4 in the first repetition which accompanied final Th⁴⁺ addition, caused a significant drop in permeability despite subsequent correction to pH 6.5. A test involving a significant rise of the pH above 7 led to rapid gel formation above pH 7.3, which then led to a precipitate which did not filter, with a flow rate of only a few ml/h. The threshold for gelation moves to higher values as the amount of precipitate in suspension increases, affording greater margins as precipitation proceeds.

Overall, the pH window of 6-7 in which a good and stable permeability can be reached is reasonably wide. This provides a margin of error, which may be useful for potential minor changes in operating conditions, such as CO₂ absorption in the NH₃ solution.

Fig. 4: The effects of pH stability on permeability of the hydroxide step as a function of pH during precipitation, with the outliers also listed. Only the very low pH outlier in the first repetition reduced the permeability. High pH outliers cause the precipitate to gel and the permeability to drop by at least an order of magnitude.

Permeability of the end product was dramatically improved from the medium to the large batch when ageing 30 min after each step (compare the permeability, in **Tab. 2**, of HC01 with HC04). A large part of that is due to the ease of control, since the addition rate was kept constant while the batch size was increased. This means that the relative volume change is less, as is the pH change upon addition. Together with the larger number of crystallization centres in the early stages, these are contributing factors.

The final thorium loading of $\sim 0.05 \text{ mol/l ThO}_2$ is low by industrial standards. Therefore, it is important to know how well the process performs at a higher load. A large batch experiment (chosen for greater pH stability during precipitation) was performed with the undiluted $1.9 \text{ mol/l Th(NO}_3)_4$ in 1.6 mol/l HNO_3 (HC06). The pH fluctuations with each added drop of thorium solution were significantly more pronounced than at lower loads and required pH compensation with double the NH_3 concentration (1 mol/l , rising to 2 mol/l).

Higher thorium loading (compare HC04 to HC06 in **Tab. 2** which are equivalent except for Th loading) has little effect on the output parameters of the fresh powder. The permeability was even slightly better than the lower loading samples at an identical batch size, while the thorium and radium efficiencies were comparable.

3.1.5 Comparison with single step precipitation

The ammonia precipitate from the first step filters very well (the carbonate addition in the second step reduces the permeability, as discussed in section 3.1.3), but the ammonia precipitation removes little to no radium. This is not surprising since precipitation with ammonia has long been known as a process for separating radium from thorium [29].

A single step carbonate precipitation process was performed by adding the 2 mol/l + 2 mol/l $\text{NH}_3 + \text{NH}_4\text{HCO}_3$ solution to a Th^{4+} solution prepared by directly mixing 15 ml of 0.5 mol/l Th^{4+} and 75 ml 0.5 mol/l NH_4NO_3 . The precipitation proceeded smoothly, but the precipitate became less opaque and more gel-like above pH 7. After 15 minutes of ageing at pH 9, the suspension cleared as the precipitate redissolved. Because the carbonate was added from lower pH values, the total carbonate content is higher than in the two-step process. For the two-step process, dissolution occurred only at pH 9.7 (see section 3.1.2). With the higher $\text{NH}_3/\text{NH}_4\text{HCO}_3$ ratio (3 mol/l NH_3 + 1.5 mol/l NH_4HCO_3) the precipitate also gelled at pH 7, but did not re-dissolve at pH 9. The precipitate did not settle noticeably under gravitational forces ($\Delta P = 0$) over 30 minutes at the end of ageing. The precipitate slowly began to settle only at reduced pressure ($\Delta P = 90$ kPa) during filtering. The filtrate flow rate did not reach a constant value as the cake was only settled at the end of filtering. Therefore the steady state flow rate could only be estimated. Even with this overestimate, the permeability was a degree of magnitude lower than the target permeability. The Th and Ra efficiencies, however, were excellent. The thorium efficiency was as good as all the other precipitation methods, while the radium was removed to below the detection limit.

Each of the single-step processes has its advantages, as can be seen when comparing HC01, HH01 and CC01 in **Tab. 2**. The hydroxide filters quickly, at the price of nonexistent radium efficiency. The carbonate reaches near-total radium and thorium efficiency, but its permeability is very poor. The two-step precipitation is a compromise between the two. It maintains a majority of the permeability of the starting hydroxide precipitate in combination with the good radium efficiencies from the single-step carbonate process.

3.1.6 The fresh precipitate issued from the two-step process

As can be seen in **Fig. 5**, calcination of the hydroxide-carbonate precipitate showed a gradual mass decrease until ~ 620 K, when the mass begins to decrease more sharply. This is followed by a slow decrease in mass from 873 to 1273 K. Given the slower heating rate and larger powder mass in the TG-MS relative to the TG-DSC, peaks from TG-DSC are expected to be less well defined in the TGA profile.

Fig. 5: Profiles of thermogravimetry and calorimetry (below) and accompanying mass spectrometry (above, with masses and corresponding fragments) during calcination of the hydroxide - carbonate precipitate. Negative heat transfer values correspond to exothermic processes. The calcination begins quite early and continues until at least 873 K. The decomposition is accompanied by several releases of H₂O, CO₂, and various nitrogen compounds. The decomposition is largely endothermic, with one exothermic peak at 560-620 K. Please note, the calorimetry was performed at a different heating rate (10 K/min) than the TG-MS (2 K/min).

Energetically, DSC showed a large endothermic peak covering the area 313-570 K, with a maximum at 470 K. This was followed by a sharp exothermic peak at 600 K, likely from the decomposition of NH₄NO₃ formed during precipitation which covers the area 560-610 K. A final, endothermal, peak covers the area 610-873 K, with a maximum around 690 K.

Water and carbon dioxide are released at low temperatures, primarily up to 470 K, tailing off to 620 K. Fragments of NH₃, H₂O and nitrous oxides likely from NH₄NO₃ decomposition are observed from 620-720 K.

The XRD patterns of the precipitate, dried at ambient temperature, showed ThO₂ peaks, but with a very high degree of peak broadening (see **Fig. 6**). The calculated average crystallite size is 2.6 nm and the strain is 0.45%. The very small crystallites are very promising from a sintering

perspective, as nanometric powder generally has higher sinterability. The large amounts of adsorbed H_2O and CO_2 measured by TG-MS distort the lattice and contributes significantly to the strain.

Fig. 6: X-ray diffraction patterns, fitted patterns and differences between the actual and calculated pattern of: the fresh (dried) precipitate (blue square) and the same precipitate calcined at 673 K (red circles). The peaks show significant peak broadening due to small crystallites and significant strain. The calculated crystallite sizes and strains for the fresh and calcined powder respectively are: 2.6 nm and 0.45% and 3.9 nm and 0.1%.

Transmission electron microscopy (see **Fig. 7**) of the fresh hydroxide - carbonate precipitate showed a precipitate composed of crystalline ThO_2 . Individual grains are mostly a few nanometers in diameter, and a small fraction of the grains grows to more than a hundred nanometers. The high degree of dilution during sample preparation isolates the individual grains, making observation easier, but obscures agglomeration information.

An additional coarse fraction was also observed in TEM. The coarser fraction was composed of larger crystalline ThO_2 about 200 nm in diameter. This coarse fraction is obscured in XRD by the fine phase.

Fig. 7: Transmission electron microscopy of the precipitate, showing the fine, nanometer-sized particles caught on the amorphous grid (left). TEM also showed coarser, fully crystalline fraction about two orders of magnitude larger than the fine fraction.

3.2 Dry route optimization

3.2.1 The effects of calcination temperature on sintering

As the powder was calcined (673-1273 K), the crystallites grew and the agglomerates coarsened, as illustrated in **Fig. 8**. The crystallite size of the powder calcined at 673 K (4 nm) is only slightly higher than the 2-3 nm of the precipitated powder, and even after calcination at 1273 K the crystallites are very small (24 nm). This is characteristic of the low thermal activity of ThO_2 which does not promote particle coarsening even at temperatures higher than those reported here [42, 43]. Nonetheless, neck formation eliminates surface area, decreasing SSA from the initial $18 \text{ m}^2/\text{g}$ with increasing calcination temperature. This gradual decrease in SSA with calcination temperature remains consistent, except for the lower SSA of the powder calcined at 1073 K as compared to that calcined at 1273 K. Yet the evolution of both the crystallite size and the sintering rate (see **Fig. 9**) are consistent with particle coarsening from 1073 to 1273 K.

The BET curves show hysteresis loops between the sorption and desorption curves. The loops indicate the presence of nanometric porosity ($< 2 \text{ nm}$) within the powder agglomerates. As calcination temperature increases, the grains within the agglomerates will sinter and eliminate the internal porosity. The hysteresis loops confirm this by gradually shrinking with increasing calcination temperature. At 1273 K the hysteresis loop, and thus also the internal porosity of the agglomerates, is almost completely eliminated.

Fig. 8: The effect of calcination temperature on the specific surface area and crystallite size of the ThO_2 . The specific surface area (squares) decreases while the crystallite size (circles) increases with increasing calcination temperature.

As shown by the dilatometer data in **Fig. 9**, this crystallite and particle coarsening is also shown in the sintering behaviour. The powder sinters in two steps, the first of which begins shortly above the calcination temperature of the powder and eliminates intra-agglomerate porosity. The second step eliminates inter-agglomerate porosity. It starts around 1273 K for all calcined powders and continues to high temperature. At higher calcination temperatures the first sintering step, was already partially (873 K) or completely (1073 and 1273 K) finished and only the second sintering stage remains.

The powder calcined at 673 K shows an additional three sintering rate peaks before the one common to all calcination temperatures, which starts at 1273 K. These additional peaks reach maxima at 430, 760 and 920 K. The first two contribute in short bursts, while the third is broader. The first, small peak covers the range 313-540 K and corresponds well with the release peaks of water and CO_2 on the fresh powder. Though H_2O and CO_2 are removed from the powder during calcination, ThO_2 has a high affinity for H_2O and CO_2 and readily adsorbs them from ambient atmosphere [24, 44-50]. This effect of adsorbed gasses is much more pronounced for the powder calcined at 673 K because of its significantly higher SSA. The maximum densification rate is reached during second peak. The temperature of the second peak corresponds well with the large gas release peaks shown in **Fig. 5**. As can be seen from **Fig. 5**, significant calcination continues to about 873 K, suggesting that sur-

face purification during gas release is the driving force for this maximum. The shape and position of the third, wider peak (at 920 K or 520 K above the calcination temperature) is consistent with intra-agglomerate sintering peaks of other calcined ThO_2 powders, such as the powder calcined at 873 K (maximum densification at around 1040 K) or oxalates (420-520 K above the calcination temperature from our previous research in [24]).

Fig. 9: The shrinkage rates of the hydroxide - carbonate powders calcined at 673, 873, 1073, and 1273 K. The first sintering rate peak appears just above the calcination temperature and is followed by a second densification peak whose maximum appears to lie beyond the maximum dilatometer sintering temperature of 1898 K.

The aforementioned disappearance of intra-agglomerate porosity is also reflected in the green densities after pressing at 300 MPa (see **Fig. 10**). As the calcination temperature increases, the green density quickly approaches the maximum density of 64% that is achievable with randomly packed spheres [51]. A maximum green density of 63% is reached for calcination temperatures above 1073 K, just as the first sintering rate peak disappeared (see **Fig. 9**). In all cases, the green pellets were geometrically very stable, without delamination or end capping.

Fig. 10: The effect of calcination temperature on the green and sintered density of pellets. As the calcination temperature increases to 1273 K, the green pellet density increases to a maximum of 63%, while the sintered density (2023 K) slightly varies in the 96-98% range. All green pellets were stable.

Upon sintering at 2023 K, the densities are all in the 96-98% range (**Fig. 10**). The higher calcination temperature pellets were slightly denser, and also had a higher sintered grain size (**Fig. 11**). Compared to the 673 K-calcined pellet, the average grain size of the 1273 K-calcined pellet is larger ($10.3 \pm 3.2 \mu\text{m}$ vs $16.5 \pm 9.6 \mu\text{m}$). Both the low and high calcination temperature pellets achieve closed porosity. The remaining porosity is distributed evenly across the polished surface and shows a large fraction of intragranular pores.

Fig. 11: Thermally etched polished surface of pellets sintered at 2023 K from powders calcined at 673 K (left) and 1273 K (right). The pellet from 673 K-calcined powder had a smaller average grain size of $10.3 \pm 3.2 \mu\text{m}$ vs the $16.5 \pm 9.6 \mu\text{m}$ of the pellet from 1273 K-calcined powder.

3.2.2 Fate of radium in the solid phase

The Ra/Th ratio was monitored to assess the fate of Ra bound during the carbonate step, throughout the powder processing route: directly after drying, calcined at 1273 K, after sintering for 8 hours at 1898 and at 2023 K under reducing atmosphere. The radium to thorium ratio gradually decreased with the heating process temperature (see **Fig. 12**). Some preferential release of radium can already be observed after calcination at 1273 K. This drop continues during sintering under reducing atmosphere.

Fig. 12: The relative evolution of Th and Ra in the solid phase in fresh dried powder, calcined at 1273 K (2 h) and sintered at 1898 and 2023 K (8 h), normalized to the ratio in the fresh powder. There is a preferential release of Ra from the solid phase, which increases with heat treatment temperature.

4 Discussion

The fresh precipitate after two-step precipitation is composed of hydrated, carbonated nanocrystalline ThO_2 . It shares many characteristics with hydrated ThO_2 precipitated by bases, which include nanometric grain sizes on precipitation [52-55], high SSA after calcination [54, 56] and dehydration curves [55, 56]. Due to the higher thermodynamic stability of ThO_2 than $\text{ThO}_x(\text{CO}_3)_{2-x}$ compounds [40] the precipitate remains as ThO_2 after carbonate addition. The extremely long dissolution times [57] and slow dissolution-precipitation [53] of ThO_2 maintain the good agglomeration characteristics imparted in the first precipitation step. In the second carbonate step, the high affinity for CO_2 [50] combined with its low binding energy [44, 58] implies $\text{ThO}_2 \cdot n\text{H}_2\text{O} \cdot m\text{CO}_2$ readily forms even from already precipitated ThO_2 (up to $m = 1$) if enough CO_2 is available [59]. The amount of CO_2 adsorbed on the ThO_2 surface cannot be estimated from the TG-MS data alone.

With the addition of carbonates and further ammonia, radium removal increases dramatically. The higher pH will increase the surface charge and thus ion exchange capacity of the precipitate surface. This should promote some removal of radium as cationic Ra^{2+} . Though Ra^{2+} has a lower sorption affinity for ion-exchange on oxides than hydrolysable divalent transition metals (Pb^{2+} , Cd^{2+} , etc.), it has the highest affinity of the alkaline earth metals [60]. Radium may also adsorb as RaCO_3 onto neutral parts of the surface. The adsorption process is not as rapid as precipitation and requires longer ageing times to reach optimal radium removal (see **Tab. 2**: Overview table). Because the radium is adsorbed on the surface of the ThO_2 , it is sensitive to any surface change and even re-dissolution. This may be the cause of reduced radium removal after ageing at 4 h. Carbonate loss from $\text{ThO}_2 \cdot n\text{H}_2\text{O} \cdot m\text{CO}_2$ has also been reported during washing or during digestion with hot water [34] and was therefore avoided in this exploratory study. The effect of washing needs to be evaluated further. A study of radium loss during washing with either water or ethanol would be desirable in the future. In addition, disproportionate radium loss was observed during calcination and sintering (see **Fig. 12**), as discussed below.

The as-precipitated nanometric ThO_2 contains considerable quantities of adsorbed H_2O , CO_2 . Various nitrogen compounds are precipitated alongside the compound as well. These and the adsorbed gasses are progressively released in the calcination step. Full release of adsorbents is achieved only around 873 K, not much different from the temperature at which oxalate decomposition is complete. For $m \leq 1$, the CO_2 degassing temperature does not depend on the binding mechanism. Whether bound by carbonate addition to an existing ThO_2 suspension (in this case), directly during precipitation with carbonates [34] or chemisorbed as gas on existing ThO_2 solids [44], the maximum degassing temperature is 623 K. CO_2 release above 623 K was reported only for $\text{ThO}_2 \cdot 2\text{CO}_2$ where the distinct initial release to 585 K is followed by a second CO_2 release to 800 K [61].

Regardless of the calcination temperature, compaction was straightforward, with good green pellet toughness for all calcination temperatures. Rather low green densities were obtained for

low-temperature calcined material, and levels off at 64% TD for calcination at 1073 K or higher. For all conditions, sintered densities in excess of 96% TD was achieved. The relative insensitivity of the precipitation and calcination steps of the present hydroxide-carbonate precipitation route to further powder and pellet processes is in stark contrast with the oxalate-derived process, where several processing routes resulted in brittle compacts and pellets prone to end-capping [24].

The two-step process is understood to bind Ra as carbonate (RaCO_3) by adsorption to the $\text{ThO}_2 \cdot n\text{H}_2\text{O} \cdot m\text{CO}_2$ precipitates, one may obviously question its fate during calcination and sintering. Assuming the crystallographic similarities of RaCO_3 and BaCO_3 [62] extend to thermal behavior, the volatilities of BaCO_3 and BaO can give clues to the thermal behavior of radium. BaCO_3 decomposes above 1373 K [63] and BaO is volatile above 1473 K [64]. Radium from carbonate is thus likely to evaporate at similar temperatures. Volatility differences are most likely determined by molecule size, which might push the volatilization to higher temperatures for larger Ra-containing molecules. The partial decomposition/volatilization of RaCO_3 is one of the few possible contributors to the early release at 1273 K and prior to 1898 K. The gases released during calcination may also serve to strip away surface radium. As part of future up-scaling investigations, the radioactivity and possibly the composition of off-gas need to be investigated. Balakrishna [65] reported partial sublimation of ThO_2 during sintering under reducing atmosphere at temperatures of 1873-1973 K and subsequent condensation on cooled furnace parts. This sublimating ThO_2 may strip the radium bonded on its surface and release it by physical evaporation. Near 2023 K, especially in reducing atmosphere, a slight under-stoichiometry as $\text{ThO}_{1.99}$ is expected, though sublimation takes place as ThO_2 [66]. Regardless of potential volatilization mechanism, the ThO_2 gasses and any radium species released are unlikely to be volatile at ambient temperature. Therefore colder parts of the furnace will likely be contaminated with ThO_2 or various Th decay products, including Ra-containing species. Where the evaporated species deposits will depend upon the specific furnace configuration and an aerosol filter will likely be sufficient to trap radium. Furnace contamination will increase disposal costs, but as these are incurred once at the end of life and are much less prohibitive than operational costs.

Overall, the two-step ammonia-carbonate precipitation produces comparably permeable precipitates to oxalate precipitation. ThO_2 calcined from both precipitates produces stable green pellets, which sinter to adequate density. This makes both precipitation routes suitable for producing ThO_2 for nuclear fuel applications. The primary difference lies in the reduced radioactive (radium-loaded) liquid waste production from the ammonia-carbonate precipitation. This makes the ammonia-carbonate process highly competitive in countries with high radioactive waste disposal costs.

5 Conclusions

The two-step ammonia-carbonate precipitation process reaches the goals of good permeability ($15 \cdot 10^{-15} \text{ m}^2$), radium efficiency of at least 99.5%, green pellet stability and sintering to closed porosity at 2023 K. For large batches the permeability is very good ($45 \cdot 10^{-15} \text{ m}^2$) and provides a good margin for process control. Unlike the two-step precipitation, single-step ammonia or carbonate precipitations provide either excellent permeability without radium efficiency (for ammonia precipitation) or excellent radium efficiency with poor permeability (for carbonate precipitation). The two-step ammonia-carbonate precipitate acts as hydrated ThO_2 , keeping the agglomerate and grain size characteristics given in the first step with additional adsorbed carbonate from the second step. Upon calcination, the powder sinters to the required >95% density at 2023 K at -420 kJ/mol within 8 h. With increasing calcination temperature up to 1273 K, the specific surface area of the powder decreased $2.2 \text{ m}^2/\text{g}$ and the crystallite size increased to 20 nm. The onset of sintering during calcination at higher temperatures reduces the sinterability available for subsequent sintering, but the shrinkage it causes in the agglomerates leads to higher green compact densities up to 63 %. Because of the higher green density, calcination temperatures over 1073 K lead to ca. 2% higher final sintered densities and larger grain sizes. Overall, the two-step ammonia-carbonate precipitation process shows promise as a powder source for ThO_2 nuclear fuel pellets, especially when waste disposal costs are a significant concern.

Acknowledgements

We would like to acknowledge Yves Heymans for polishing, Leen Verheyen and Magda Ooms for γ -spectrometry, Peter Dries and Koen Vanaken for assistance with dilatometry in particular and technical matters in general. This work was partially funded by Rhodia Operations under contract CO-90-15-3832-00.

References

- [1] D. Greneche, The Thorium Fuel Cycle: Past Achievements and Future Prospects, in: J.-P. Revol, M. Bourquin, Y. Kadi, E. Lillestol, J.-C. de Mestral, K. Samec (Eds.), Thorium Energy for the World, Springer International Publishing, Geneva, Switzerland, 2013.
- [2] P.E. Hart, C.W. Griffin, K.A. Hsieh, R.B. Matthews, G.D. White, ThO₂-based pellet fuels - their properties, methods of fabrication, and irradiation performance: a critical assessment of the state of the technology and recommendations for further work, 1979.
- [3] A.G. Croff, E.D. Collins, G.D.D. Cul, R.G. Wymer, A.M. Krichinsky, B.B. Spencer, B.D. Patton, ORNL Experience and Perspectives Related to Processing of Thorium and ²³³U for Nuclear Fuel, Nuclear Technology 194(2) (2016) 252-270.
- [4] D. Manara, R. Böhler, K. Boboridis, L. Capriotti, A. Quaini, L. Luzzi, F. De Bruycker, C. Guéneau, N. Dupin, R. Konings, The Melting Behaviour of Oxide Nuclear Fuels: Effects of the Oxygen Potential Studied by Laser Heating, Procedia Chemistry 7 (2012) 505-512.
- [5] T.R. Pavlov, M.R. Wenman, L. Vlahovic, D. Robba, R.J.M. Konings, P. Van Uffelen, R.W. Grimes, Measurement and interpretation of the thermo-physical properties of UO₂ at high temperatures: The viral effect of oxygen defects, Acta Materialia 139 (2017) 138-154.
- [6] T.R. Pavlov, T. Wangle, M.R. Wenman, V. Tyrpekl, L. Vlahovic, D. Robba, P. Van Uffelen, R.J.M. Konings, R.W. Grimes, High temperature measurements and condensed matter analysis of the thermo-physical properties of ThO₂, Scientific Reports 8 (2018).
- [7] S. Özdemir, E. Çubukçu, Once-through uranium thorium fuel cycle in CANDU reactors, in: V. Knapp, N. Čavlina (Eds.) Nuclear Option in Countries with Small and Medium Electricity Grids, Croatian Nuclear Society, Dubrovnik 2000, pp. 165-172.
- [8] Y. Long, Y. Yuan, E.E. Pilat, C.S. Rim, M.S. Kazimi, Modeling fission gas release in high burnup ThO₂-UO₂ fuel, 9. International Conference on Nuclear Engineering, Nice, France, 2001.
- [9] A.D. Mendoza España, B.P. Bromley, A Canadian Perspective of the Economic Issues Associated with Deploying Thorium-Based Fuel Cycles and Breeding in Heavy-Water Reactors, CNL Nuclear Review (2019) 1-22.
- [10] D. Kotlyar, G.T. Parks, E. Shwageraus, Thorium-based plutonium incineration in the I²S-LWR, Annals of Nuclear Energy 100 (2017) 68-75.
- [11] B.P. Bromley, High-Utilization Lattices for Thorium-Based Fuels in Heavy Water Reactors, Nuclear Technology 186(1) (2014) 17-32.
- [12] E.I. Vapirev, T. Jordanov, I. Christoskov, Conversion of highly enriched uranium in thorium-232 based oxide fuel for light water reactors: MOX-T fuel, WWER reactor fuel performance, modelling and experimental support, Bulgaria, 1994, pp. 241-243.
- [13] A.V. Colton, B.P. Bromley, Full-Core Evaluation of Uranium-Based Fuels Augmented with Small Amounts of Thorium in Pressure Tube Heavy Water Reactors, Nuclear Technology 196(1) (2016) 1-12.
- [14] Fuel Design Data, Nuclear Engineering International, 2015, pp. 30-37.
- [15] K. Ananthasivan, S. Balakrishnan, S. Anthonysamy, R. Divakar, E. Mohandas, V. Ganesan, Synthesis and sintering of nanocrystalline thoria doped with CaO and MgO derived through oxalate-deagglomeration, Journal of Nuclear Materials 434(1-3) (2013) 223-229.
- [16] A. Baena, T. Cardinaels, J. Vleugels, K. Binnemans, M. Verwerft, Activated sintering of ThO₂ with Al₂O₃ under reducing and oxidizing conditions, Journal of Nuclear Materials 470 (2016) 34-43.

- [17] A. Yayli, S. Kirtay, E. Oktay, A. Van, M.T. Aybers, L. Colak, Sintering properties of V_2O_5 , Ta_2O_5 and Nb_2O_5 doped ThO_2 powder under Ar-10% H_2 atmosphere, Key Engineering Materials 264-268(Pt. 1, Euro Ceramics VIII) (2004) 305-308.
- [18] K. Ananthasivan, S. Anthonysamy, C. Sudha, A.L.E. Terrance, P.R.V. Rao, Thoria doped with cations of group VB-synthesis and sintering, Journal of Nuclear Materials 300(2-3) (2002) 217-229.
- [19] R.B. Matthews, N.C. Davis, Fabrication of ThO_2 and ThO_2-UO_2 pellets for proliferation resistant fuels, Battelle Pacific Northwest Labs., 1979.
- [20] R.W. Jones, H.R. Lee, H. Hahn, J.F. Walker, A. Celli, Thoria Fuel Technology for CANDU-PHW Reactors, Transactions of the American Nuclear Society 27 (1977) 303-304.
- [21] D. Sanjay Kumar, K. Ananthasivan, S. Amirthapandian, A. Dasgupta, G. Jogeswara Rao, Citrate gel-combustion synthesis and sintering of nanocrystalline ThO_2 powders, Journal of Nuclear Materials 497 (2017) 16-29.
- [22] A.G. Kurnakova, L.K. Shubochkin, The solubility of $Th(C_2O_4)_2 \cdot 6H_2O$ in aqueous solutions of HNO_3 and $H_2C_2O_4$ at 25° , Zhurnal Neorganicheskoi Khimii 8(5) (1963) 1249-54.
- [23] E.M. Pazhukhin, E.A. Smirnova, A.S. Krivokhatskii, Y.L. Pazukhina, S.M. Kochergin, Optimization of conditions of thorium oxalate precipitation. I. Solubility of thorium oxalate in the presence of like ions, Radiokhimiya 27(5) (1985) 606-11.
- [24] T. Wangle, V. Tyrpekl, S. Cagno, T. Delloye, O. Larcher, T. Cardinaels, J. Vleugels, M. Verwerft, The effect of precipitation and calcination parameters on oxalate derived ThO_2 pellets, Journal of Nuclear Materials 495 (2017) 128-137.
- [25] D.T. Rankin, G.A. Burney, P.K. Smith, R.D. Sisson, Jr., Preparation and characterization of oxalate-based $^{237}NpO_2$ powder, Ceramic Bulletin 56(5) (1977) 478-483, 486.
- [26] E. Oktay, A. Yayli, Sintering properties of ThO_2 powder produced by ultrasonic agitation, Advances in Science and Technology 14(Ceramics: Getting into the 2000's, Part B) (1999) 761-766.
- [27] Y. Harada, Y. Baskin, J.H. Handwerk, Calcination and Sintering Study of Thoria, Journal of the American Ceramic Society 45(6) (1962) 253-257.
- [28] T. Wangle, V. Tyrpekl, T. Delloye, O. Larcher, J. Pakarinen, T. Cardinaels, J. Vleugels, M. Verwerft, Homogeneous hydrolysis of thorium by thermal decomposition of urea, Radiochimica Acta 106(8) (2018) 645-653.
- [29] M.L. Salutsky, H.W. Kirby, The Radiochemistry of Radium, 1964, p. 210.
- [30] S.K. Kantan, R.V. Raghavan, G.S. Tendolkar, Sintering of Thorium and Thoria, Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, pp. 132-138.
- [31] V.K. Moorthy, A.K. Kulkarny, S.V.K. Rao, Relation Between the Origin, Powder Characteristics, and Sintering Treatment on the Densification and Microstructures of Urania and Thoria, Third United Nations International Conference on the Peaceful Uses of Atomic Energy, United Nations, New York, 1964, pp. 386-392.
- [32] P. Murray, E.P. Rodgers, A.E. Williams, Practical and theoretical aspects of the hot pressing of refractory oxides, Transactions of the British Ceramic Society 53 (1954) 474-510.
- [33] T. Delloye, J.-L. Le Loarer, A. Leveque, Process for the treatment of soluble thorium compounds, and the thorium phosphate obtained, Rhone-Poulenc Chimie SA, Fr. . 1994, p. 8 pp.
- [34] E.B. Mirza, M.D. Karkhanavala, On the Oxycarbonate of Thorium, Journal of the Indian Chemical Society 40(10) (1963) 903-904.

- [35] I. Bransky, N.M. Tallan, Electrical Properties and Defect Structure of ThO₂, Journal of the American Ceramic Society 53(11) (1970) 625-629.
- [36] J. Beydon, I. Gratot, Utilisation du recul nucléaire pour la séparation du ²²⁸Ra, du ²²⁴Ra et du ²³³Pa à partir d'hydroxyde de thorium colloïdal, 1968, p. 12.
- [37] Laraweb. <<http://www.nucleide.org/Laraweb/>>, (accessed 27.1.2017.).
- [38] G.K. Williamson, W.H. Hall, X-ray line broadening from filed aluminium and wolfram, Acta Metallurgica 1(1) (1953) 22-31.
- [39] V. Petříček, M. Dušek, L. Palatinus, Crystallographic Computing System JANA2006: General features, Zeitschrift Für Kristallographie 229(5) (2014) 345-352.
- [40] M. Rand, J. Fuger, I. Grenthe, V. Neck, D. Rai, Chemical Thermodynamics of Thorium, OECD NEA, Issy-les-Moulineaux, France, 2007.
- [41] D.D. Perrin, B. Dempsey, Buffers for pH and Metal Ion Control, Springer Netherlands 1974.
- [42] G.I. Nkou Bouala, N. Clavier, J. Lechelle, J. Monnier, C. Ricolleau, N. Dacheux, R. Podor, High-temperature electron microscopy study of ThO₂ microspheres sintering, Journal of the European Ceramic Society 37(2) (2017) 727-738.
- [43] N. Clavier, R. Podor, L. Deliere, J. Ravaux, N. Dacheux, Combining *in situ* HT-ESEM observations and dilatometry: An original and fast way to the sintering map of ThO₂, Materials Chemistry and Physics 137(3) (2013) 742-749.
- [44] P. Pichat, J. Veron, B. Claudel, M.V. Mathieu, Étude de l'oxydation catalytique de CO sur la thorine par spectrométrie infrarouge, Journal de Chimie Physique 63(7-8) (1966) 1026-30.
- [45] M. Breyse, B. Claudel, M. Prettre, J. Veron, Catalytic properties of thorium oxide in the oxidation of carbon monoxide. I. Calorimetric confirmations of adsorption and catalysis processes, Journal of Catalysis 24(1) (1972) 106-16.
- [46] W. McLean, C.A. Colmenares, R.L. Smith, G.A. Somorjai, Chemisorption of carbon monoxide and carbon dioxide on gold-supported thorium oxide films, The Journal of Physical Chemistry 87(5) (1983) 788-793.
- [47] C.A. Colmenares, Oxidation mechanisms and catalytic properties of the actinides, Progress in Solid State Chemistry 15(4) (1984) 257-364.
- [48] H.F. Holmes, E.L. Fuller, Jr., C.H. Secoy, Gravimetric adsorption studies of thorium oxide. III. Adsorption of water on porous and nonporous samples, Journal of Physical Chemistry 72(7) (1968) 2293-300.
- [49] E.L. Fuller, Jr., H.F. Holmes, C.H. Secoy, Gravimetric adsorption studies of thorium oxide. II. Water adsorption at 25.00°, Journal of Physical Chemistry 70(5) (1966) 1633-6.
- [50] E.L. Fuller, P.A. Agron, Sorption of Water, Carbon Dioxide and Nitrogen by Sol-Gel Thorium Oxide, Journal of Colloid and Interface Science 57(2) (1976) 193-200.
- [51] S. Torquato, T.M. Truskett, P.G. Debenedetti, Is Random Close Packing of Spheres Well Defined?, Physical Review Letters 84(10) (2000) 2064-2067.
- [52] E. De Bona, O. Walter, H. Störmer, T. Wiss, G. Baldinozzi, M. Cologna, K. Popa, Synthesis of nanostructured ThO₂ pellets, Journal of the American Ceramic Society 102(7) (2019) 3814-3818.
- [53] T.V. Plakhova, A.Y. Romanchuk, D.V. Likhoshesterova, A.E. Baranchikov, P.V. Dorovatovskii, R.D. Svetogorov, T.B. Shatalova, T.B. Egorova, A.L. Trigub, K.O. Kvashnina, V.K. Ivanov, S.N. Kalmykov, Size Effects in Nanocrystalline Thoria, The Journal of Physical Chemistry C 123(37) (2019) 23167-23176.

- [54] W.S. Brey, B.H. Davis, P.G. Schmidt, C.G. Moreland, Preparation and properties of active thorium oxide from thorium hydroxide, *Journal of Catalysis* 3(4) (1964) 303-311.
- [55] D.J. Dzimitrowicz, P.J. Wiseman, D. Cherns, An electron microscope study of hydrous thorium dioxide $\text{ThO}_2 \cdot n\text{H}_2\text{O}$, *Journal of Colloid and Interface Science* 103(1) (1985) 170-177.
- [56] R.S. Mikhail, R.B. Fahim, Thermal treatment of thorium oxide gel at low temperatures, *Journal of Applied Chemistry* 17(5) (1967) 147-150.
- [57] T. Fanghänel, V. Neck, Aquatic chemistry and solubility phenomena of actinide oxides/hydroxides, *Pure and Applied Chemistry* 74(10) (2002) 1895-1907.
- [58] C.H. Pitt, M.E. Wadsworth, Carbon dioxide adsorption on thoria, 1958, p. 22.
- [59] E. Chauvenet, Sur les carbonates de thorium, *Comptes rendus des séances de l'Académie des sciences* 153 (1911) 66-68.
- [60] D.W. Shoesmith, The behaviour of radium in soil and in uranium mine-tailings, Atomic Energy of Canada, Pinawa, Manitoba, 1984.
- [61] S. Dash, A. Singh, P.K. Ajikumar, H. Subramanian, M. Rajalakshmi, A.K. Tyagi, A.K. Arora, S.V. Narasimhan, B. Raj, Synthesis and characterization of nanocrystalline thoria obtained from thermally decomposed thorium carbonate, *Journal of Nuclear Materials* 303(2-3) (2002) 156-168.
- [62] F. Weigel, A. Trinkl, Zur Kristallchemie des Radiums V. Diverse Radiumsalze anorganischer Anionen, *Radiochimica Acta* 19(4) (1973) 199-202.
- [63] R. Scarlat, E. Segal, G. Tomus, M. Constantin, The influence of titanium dioxides, alumina and calcium carbonate on the thermal stability of barium carbonate, *Thermochimica Acta* 61(3) (1983) 375-378.
- [64] A. Guntz, Sur la préparation du baryum put à la partir de son sous-oxyde, *Comptes rendus des séances de l'Académie des sciences* 143 (1906) 339-340.
- [65] P. Balakrishna, Fabrication of thorium and thorium dioxide, *Natural Science* 7(1) (2015) 10-17.
- [66] R.J. Ackermann, M. Tetenbaum, High-temperature thermodynamic properties of the thorium-oxygen system, *International colloquium on materials for high-temperature energy*, Toronto, Canada, 1979.