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Homogeneous hydrolysis of thorium by thermal decomposition of urea

kinetics, powder characteristics and radium co-precipitation

Abstract: Thorium was precipitated homogeneously from a thorium nitrate solution by the thermal decomposition products of urea. The kinetics of the hydrolysis were studied at 90 and 100 °C by pH measurement during the initial 5 h and the precipitation efficiencies of thorium and radium were measured over a 24 h period. Precipitation of the radium daughters was closely followed with the aim of co-precipitation of radium with thorium. The CO₂ formed during urea decomposition dissolved in the solution, forming CO₃²⁻ during the experiment upon reaching a sufficiently high pH level (>7). This allowed radium to co-precipitate partially, thus reducing the activity of the filtrate. After filtration or centrifugation, the precipitate is composed of nanocrystalline thorium dioxide (crystallite size ~10 nm), with weakly bound H₂O and CO₂.

Keywords: thorium, urea, radium, homogeneous precipitation, ThO₂

1 Introduction

Thorium dioxide has long been considered as a fertile matrix for nuclear fuel and was deployed in several reactors in the 1950's to 1970's [1], and interest in ThO₂ has risen again in recent years. Though its high melting point makes ThO₂ a better matrix than UO₂ from a margin to melting safety standard, it poses a challenge for the sintering. The sintering temperature needed to reach sufficiently high densities ($\geq 95\%$ of the theoretical density) often exceed the temperatures achievable in standard commercial furnaces (1700-1750 °C). In past industrial scale production, high densities were reached only after milling a starting powder calcined from thorium oxalate [1]. ThO₂ calcined from oxalates keeps the layered platelet structure of the primary oxalates, which impedes packing and flowability. The milling is also undesirable due to the health risks introduced by airborne contamination, and alternative methods to improve sintering need to be explored. A better designed starting powder can circumvent the poor sinterability problem. The most important driving force for sintering is a small crystallite size starting powder. With finer starting powders, the thermodynamic driving force and sintering rate increases and the necessary sintering temperature drops correspondingly. Very small particle sizes, however, also have industrial disadvantages. Powders composed of small particles generally flow poorly and pack to form low density green pellets. These disadvantages can be avoided by organizing the small particles into larger agglomerates which flow and pack well, but still contain the small crystallites for efficient sintering.

A critical difference between ²³²Th and ²³⁸U lies in the half-lives of their decay products. Unlike ²³⁸U decay products, ²³²Th decay products are both short-lived enough to build up significantly during storage and too long-lived to be allowed to simply decay to acceptable levels of activity. The long-lived aspect lies with ²²⁸Ra (half-life of 5.7 years), though ²²⁴Ra (3.6 days) also contributes. Disposal of these isotopes with the liquid waste (at concentrations >1% of the original) is prohibitively expensive, because radioactive contamination raises the price of chemical waste by an order of 10⁴. To avoid this severe cost increase, a solidification method must be found. Moreover, the costs of disposing of solid radioactive waste could also be removed if the Ra is contained in the pellet product. Since ²²⁸Ra concentration reaches the same order of magnitude (>10% of equilibrium activity) after less than one year of storage, this does not significantly change fuel properties. Thus it would be ideal if the precipitation route would also co-precipitate radium with thorium. Pure hydroxide precipitation has long been used as a method for separating Ra from Th [2] and is therefore unsuitable.

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Both radium oxalate and carbonate are known to be insoluble, [2] though the exact solubility products are not well quantified. The solubility of oxalates and carbonates of barium, a good chemical analogue, differ by two orders of magnitude ($\text{p}K_{\text{sp}} = 6.61$ [3] and 8.56 [4] for the oxalate and carbonate respectively). This would suggest that a carbonate containing precipitation process would be more suitable than its oxalate equivalent for removing radium from solution.

Homogeneous and heterogeneous precipitation by the thermal decomposition of urea is a commercially and scientifically applied process for the precipitation of various transition metal oxides [5-7]. The urea in solution decomposes via ammonium cyanate to a mixture of ammonia and bicarbonate, according to the following overall reaction [7]:

Since the decomposition produces both ammonia and carbonates (if pH is high enough), the metal ions may precipitate both as a hydroxide and a carbonate and the precipitated product is often the kinetically rather than thermodynamically preferred compound [7, 8]. The rate of urea decomposition strongly depends on the temperature and some metals may also catalyze this process [7]. The process produces small primary particles, which are desired because they sinter more easily. As the pH evolution of the solution can be easily controlled, the primary particles can be easily agglomerated into larger spheres [8-10], which are expected to flow well.

Recently, several nuclear relevant elements have been studied using homogeneous precipitation with urea, with oxygen-rich complexing agents added to isolate and stabilize the precipitate shape. Using the urea method with polyethylene glycol, Ce^{3+} (a common Pu^{3+} analogue) precipitates as CeOHCO_3 , [11] while U^{4+} precipitates as $\text{UO}_2 \cdot n\text{H}_2\text{O}$, and UO_2^{2+} precipitates as a mixture of ammonium uranates, shoebite and metashoebite – hydrated U(VI) oxo-hydroxides [9]. Autoclave conditions with glycerol have also been used to precipitate thorium at a 1:2 urea:Th ratio as ThO_2 , with small amounts of ThOCO_3 [12].

Homogeneous precipitation has also been applied at a kg scale for the production of spherical agglomerates of ThO_2 powder, using the internal gelation process, where a mixture of hexamethylenetetramine and urea is decomposed in hot oil to form spheres of a hydrated gel [13]. More frequently, thorium was precipitated heterogeneously for the powder-pellet route.

This work seeks to determine the basic properties of the homogeneous precipitation of thorium with urea. The kinetics of the hydrolysis process were studied at 90 and 100 °C. The nature of the hydrolysis product was determined by means of solid state analysis. The co-precipitation of radium was followed by gamma-spectroscopy of the supernatant. This information can help to minimize manufacturing costs in terms of both reaction compounds and production waste. Additionally, the fresh precipitate was characterized in terms of shape and chemical form.

2 Experimental

A solution of 0.05 mol/l $\text{Th}(\text{NO}_3)_4$ in HNO_3 was prepared by diluting a solution of 1.9 mol/l $\text{Th}(\text{NO}_3)_4$ in 1.6 mol/l HNO_3 (confirmed as $\geq 99.95\%$ trace metal basis by ICP-MS, Solvay) with demineralized water. Solid urea (Reagent grade, Sigma-Aldrich) was dissolved in this solution to give the desired urea:Th molar ratios. The solution was maintained under reflux in an oil bath heated to 90 ± 2 °C or 100 ± 2 °C. Though urea decomposition proceeds at temperatures above 70 °C, the decomposition rate remains low even at the temperatures selected. A urea:Th ratio higher than the 1:2 reported by Wang et al. [12] is needed to neutralize the free HNO_3 present and then to precipitate all the Th^{4+} within a reasonable timeframe. Thus higher urea:Th molar ratios of 5, 25 and 50 were used.

The solutions were sampled every 20 min after reaching the desired temperature for pH measurement with a WTW pH 3100 pH/mV meter. These experiments were terminated after 5 h of total operating time or after a pH of 7 was reached. At both investigated temperatures, the solution did not boil, but bubbles were dislodged by the stirrer and during sampling, indicating the solution was supersaturated with CO_2 .

Additionally, the 25:1 urea:Th precipitation was further studied at 100 °C during an extended (24 h) decomposition time to characterize the Th and Ra precipitation efficiencies. Samples were taken at 1, 2, 3, 4, 8, 24 hours for pH measurement and dialysis. 5 ml samples were dialyzed 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 [14]. The final dialysate evaporated to ca. 40 ml during dialysis, which was then measured by γ spectrometry at least 4 weeks (8 half-lives or more of ^{224}Ra) after the dialysis, to allow the equilibrium between ^{228}Th and its daughters to establish. The precipitation efficiency of Ra was measured as ^{228}Ac in equilibrium with ^{228}Ra on its 338 keV emission line. ^{228}Th was used as a tracer for Th and it was measured on the 238 keV line of ^{212}Pb . Activities were measured using HPGe γ spectrometers (Canberra or Ortec).

Count rates were converted to activity using calibrated efficiencies for each detector and emission yields collected on Laraweb [15]. Errors from Laraweb were used without modification, while 2.65σ was used for measurement errors. For comparison, the Ra precipitation efficiency was also measured in the same manner for thorium oxalate precipitated at 10 °C according to [16]. Precipitation was performed with 0.75 mol/l oxalic acid and the $\text{Th}(\text{NO}_3)_4$ in HNO_3 solution diluted to 1 mol/l.

The produced agglomerates of the precipitate were very soft and readily deformed on contact with another agglomerate. This posed a problem for separation and two different separation methods were used. The final suspension was centrifuged (5000 rpm, 5 min) or decanted, washed with demineralized water and again separated in the same way. The separated precipitate was dried at 70 °C and the agglomerates characterized by scanning electron microscopy. Scanning electron microscopy was performed on powder samples dispersed on carbon tape with a Jeol JSM 7100FA SEM field-emission microscope. SEM powder samples were coated with a 5 nm layer of Pt. Thermogravimetry (TGA) was performed on this 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). The TGA was performed under 100 ml/min Ar/0.4% O_2 to simulate calcination in air while limiting $^{14}\text{N}_2 - ^{12}\text{C}^{16}\text{O}$ interference in the mass spectrometer. TGA samples were measured in a Al_2O_3 crucible against an empty crucible blank using a type S thermocouple. The measurement included an initial 30 min holding period at 40 °C and then heating at 10 °C/min to 1000 °C, after 1 h of holding at 1000 °C, the sample was cooled at the same rate to 40 °C.

The form of the fresh precipitate was also characterized. A sample of the suspension after dialysis was pipetted onto a single crystal zero-background Si holder and dried in ambient conditions. X-ray diffraction was then performed on these samples with a Philips X'Pert Pro diffractometer with a Cu LFF tube, in a Bragg-Brentano para-focusing geometry and θ - θ configuration. Samples were measured from 10° to 130° 2θ with a step size of 0.008° with a position sensitive Real Time Multiple Strip detector (X'Celerator). The Cu K β was limited using a Ni filter in front of the detector. 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 [17]. Structural analyses were performed by the profile matching (Le Bail) method with the JANA 2006 software suite [18]. High resolution transmission electron microscopy of the fresh precipitate was performed on the suspension after dialysis dispersed on holey carbon grids and dried in ambient conditions on a Jeol 3010.

3 Results and discussion

3.1 Kinetics of Th^{4+} hydrolysis

The solution pH was monitored during hydrolysis of the Th^{4+} solution for different urea:Th molar ratios. The pH follows a similar trend for all experiments (see Fig. 1). For a 5:1 urea:Th ratio at 90°C, the pH slowly increased without reaching a plateau value. For the other experiments, the pH rose more quickly and reached a plateau near 4, where Th hydrolysis products are no longer soluble [19]. At this point the ammonia formed is used for successive thorium hydrolysis and the pH remains constant for a period of time. After some time at the plateau, during which the colloids grow both in size and amount, an opaque suspension is formed, likely composed of $\text{ThO}_2 \cdot n\text{H}_2\text{O}$ colloids, which form at this pH [20].

Fig. 1: Solution pH as a function of heating time at (a) 90 °C and (b) 100 °C for different urea:Th ratios. The arrows indicate the visual transition from clear solution to opaque colloidal suspension.

At 90 °C (a), the point at which colloids had grown sufficiently in size and amount to be visually observed occurred after roughly the same heating time (180-200 min after reaching the maximum temperature) for both 25:1 and 50:1 urea:Th solutions, which is supported by the close pH values (3.8-3.9 and 4.1-4.3) of the two hydrolysis plateaus.

At 100 °C (b), the pH rose quicker and the precipitation occurred significantly faster, causing the transition from clear solution to colloidal suspension to be observed earlier. Unlike at 90 °C, for 25:1 and 50:1 urea:Th the precipitation times (60 and 90 min) and plateaus (3.7-3.9 and 4.2-4.6) were also slightly different. At 25:1 urea:Th, the pH remains near the level of the plateau also for some time after the precipitation, even experiencing a slight dip. While at 50:1 urea:Th, the region of the plateau has a mild upward slope and the pH increases rapidly shortly after hydrolysis is finished.

The effect of temperature on the rate of pH increase is well known for pure urea solutions [7] and the present pH increase curves essentially follow those of pure urea solutions, except for the presence of the hydrolysis plateau. The rate increase from both the temperature and the urea concentration can in part be compensated by an increased Th^{4+} hydrolysis rate. For example, the hydrolysis plateaus for 25:1 urea:Th are at similar pH values for both temperatures (3.8-3.9 at 90 °C and 3.7-3.9 at 100 °C), but the plateau is significantly shortened from more than 240 min at 90 °C to 120 min at 100 °C. At 50:1 urea:Th, the rate of urea decomposition exceeds the rate of Th^{4+} hydrolysis and the pH rises even during the plateau.

As the pH was raised beyond the plateau, the precipitate formed a white suspension (after ca. pH 4). Sedimentation was observed to significantly increase when the pH rose to 7. If a sample of the suspension, taken at pH 3.9-4.2, was centrifuged and redispersed in demineralized water, the precipitate formed a stable colloidal suspension which could not be separated by further centrifugation. Passing the point of zero charge and the increased ionic strength due to urea decomposition clearly contributed to the agglomeration and subsequent sedimentation of the precipitates. In summary, it can be stated that the rate of the pH increase of the solution is proportional to both the amount of urea and the decomposition temperature.

3.2 Radium co-precipitation

The low temperature oxalate precipitation reported earlier [16] was repeated and yielded positive results from the efficiency standpoint, passing by which 99% Th^{4+} and 95% Ra^{2+} into the solid phase. At the high ionic strengths and acidities used, the solubility of both Th and Ra oxalates is expected to increase, [3, 21, 22] leading to a divergence in the solubilities of Th and Ra. This effect was not observed in this case. The amount of radium co-precipitated is still insufficient for free release (efficiencies $\geq 99\%$ desired), it would lead to significant cost reductions. While an excess of oxalate could increase the precipitation efficiency of Ra, the precipitation efficiency of Th decreases as the amount of excess oxalate increases. [23] This leaves little room to improve upon these precipitation efficiencies and a secondary solidification is needed.

In contrast to the batch results from oxalate precipitation, the precipitation efficiencies during urea hydrolysis can be followed over a period of time, during which the precipitation occurs. When the hydrolysis experiment of 25:1 urea:Th at 100 °C was repeated with a heating time of 24 h (Fig. 2 & Fig. 3), the pH evolution followed the same curve as in Fig. 1 (b), again showing a slowing of the pH evolution at pH 7.5, after this point it rose only slowly to reach a pH of 8.1 after 8 hours and pH 8.5 after 24 hours (see Fig. 2). The slowdown is likely due to the establishment of a $\text{NH}_3\text{-(NH}_4)_2\text{CO}_3$ buffer, which is efficient at pH 8-10.5 [24]. As the pH slowly evolves from acidic to basic, the precipitation kinetics of Th and Ra differ significantly.

Fig. 2: Solution pH for 25:1 urea:Th ratio during long heating times. After precipitation, the pH abruptly rose to 7 and increased slowly further.

Fig. 3: Activities of the dialysate from 25:1 urea:Th at 100°C. The thorium activity (and thus concentration) in solution drops to low value after the onset of precipitation (observed after 90 min), while the radium activity in solution only gradually decreases from the initial value and remains high even after 24 h.

^{224}Th and ^{228}Ra were used as tracers for Th and Ra, respectively and the progression of activities in Fig. 3 mirror the behavior of the elements themselves. The age of the starting solution is such that ^{228}Ra , and thus ^{224}Th , are not in equilibrium with ^{232}Th , but ^{224}Th is in equilibrium with ^{228}Ra . Thus the activities of both isotopes in the sample at time zero are equal, but the activity of ^{224}Th serves only as a relative indicator of the concentration. Dissolved CO_3^{2-} can only be expected in appreciable amounts above pH 8 and the initial precipitation will be governed almost exclusively by hydrolysis. The substantially different solubility of $\text{Ra}(\text{OH})_2$ and $\text{Th}(\text{OH})_4$ (or $\text{ThO}_2 \cdot n\text{H}_2\text{O}$) implies that this early precipitation is almost exclusively of Th, and Ra passes into the solid phase only in small amounts. The negligible amount of CO_3^{2-} means it is likely that Ra is captured by mechanisms other than carbonate precipitation (such as adsorption, occlusion, or ion exchange). This is indeed the case and thorium can be seen to precipitate rapidly. Already after 2 h, which is during the plateau around pH 4, 93% Th is precipitated. After this point, the Th concentration in solution continues to fall gradually, reaching 99% Th precipitated after 24 h. In contrast to the thorium, the radium concentration in solution starts to gradually decrease only after the pH rises above 7 (after 3 h), eventually falling to 20% of the initial activity after 24 h. Through the complex mechanism of urea decomposition, both cations can be precipitated to an insoluble form, Th^{4+} by hydrolysis and Ra^{2+} by CO_3^{2-} at higher pH. The Ra co-precipitation efficiency is insufficient to significantly reduce costs because a separate waste solidification method is still required. As the pH remains largely unchanged during longer heating time, a heterogeneous addition of CO_3^{2-} and ammonia could also be used to further precipitate radium.

3.3 Nature of the separated precipitate

Since the precipitates from any of the precipitation conditions were composed of agglomerated colloidal particles, the separation method strongly affected its final shape. The results of two separation techniques are shown in Fig. 4. Compaction and “casting” by centrifugation (Fig. 4a) produced bulk pieces, while simple decantation (Fig. 4b) just consolidated the agglomerates while keeping their morphology. Shaping and agglomerate stability could be adjusted with the

addition of complexing agents or surfactants, such as those reported by Nkou Bouala et al. [9, 25], but that is outside the scope of this work.

Fig. 4: Urea precipitates separated by centrifugation (A) and decantation (B)

As with other actinides, hydrolysis of thorium leads to the formation of colloids. These colloids then grow to the precipitates whose microstructure is shown in Fig. 5. The product is composed of fine crystalline material. The crystal structure determined from both the electron (Fig. 5d) and X-ray (Fig. 6) diffraction patterns correspond to ThO_2 . The broad XRD peaks in Fig. 6 and diffraction rings in Fig. 5d confirm the nanometric size of the precipitates which can be seen in Fig. 5c. As might be expected from such fine cubic precipitates, the ThO_2 crystals are oriented randomly within the agglomerates. Comparing Figs. 5a and 5b shows that the size of the precipitates remains largely unchanged by the increased heating times after reaching pH 7, remaining nanometric. Indeed, the crystallite size calculated from XRD peak broadening shows a slight increase in size from 11 nm after 8 hours to 14 nm after 24 hours. This behavior is in line with the very slow crystallite growth during the aging at 90 °C of crystalline ThO_2 observed by Kobayashi et al. [26].

Fig. 5: Transmission electron microscopy of precipitates prepared from a 25:1 urea:Th ratio solution after heating for 8 h (A) and 24 h (B) at 100°C. Detail of particles collected after 24 h (C) and their corresponding electron diffraction pattern, with the most intense diffraction rings of ThO₂ indexed (D).

The high non-dimensional strain values of 0.5%, as calculated from the Hall-Williamson formula, are typical of colloidal oxides prepared by hydrolysis, as reported for example for UO₂ [27]. The precipitate shows a good match with solids formed by precipitating Th⁴⁺ with other bases. While thorium precipitated by hydroxides is often amorphous [20, 26, 28, 29], crystalline ThO₂ is detectable by XRD when the suspension is heated [26, 28], similar to the precipitate in this work. Indeed, the formation of the hydrated oxide is generally in line with known results for tetravalent actinides precipitated from solutions of carbonates [20]. The hydrated oxide is the solubility limiting compound and it does not transform to crystalline solids containing the CO₃²⁻ group even in more carbonate rich solutions than those used here.

Fig. 6: X-ray diffraction pattern of the precipitate obtained from a 25:1 urea:Th ratio solution after heating for 24 h at 100 °C (GOF = 1.10, wRp = 11.06)

Nonetheless, the dried precipitate showed the release of two species during calcination: H_2O and CO_2 (Fig. 7). The release of these gases happened within a similar time-temperature frame, precluding quantification of their relative contributions. Nonetheless, the qualitative data from the mass spectrometer shows different release behaviors for the two gases. The release of H_2O began at 70 °C. Its release rate reached a maximum at 160 °C and then gradually decreased until 350 °C, where no signal was detected. The release of CO_2 could be detected over a similar temperature range of 150–375 °C, but the rate increased more gradually before dropping off sharply after a maximum at 300 °C. The weight loss proceeded further at a slow rate to a constant value at 1000 °C. The low amounts of gases released after ca. 350 °C are no longer detectable by mass spectrometry. The low release temperatures of both H_2O and CO_2 combined with the diffraction data suggest that both were bound quite weakly to a ThO_2 lattice. The amount of bound CO_2 probably remained quite low even for long heating times, however, this observation proves the presence of carbonates in the precipitates, either adsorbed on ThO_2 or co-precipitated, which might incorporate the radium stripped from the solution (Fig. 3). The TG curve quite closely resembles the dehydration curve of thorium precipitated with hydroxides reported by Dżimitrowicz et al. [29]. This hydroxide-like behavior has also been reported for the “oxycarbonate” (nominally $\text{ThOCO}_3 \cdot 2\text{H}_2\text{O}$) prepared by precipitating Th^{4+} with Na_2CO_3 by Mirza and Karkhanavala [30]. Their compound also contained weakly bound CO_2 which could be removed by washing or heating to only 350 °C. Chauvenet [31] showed that the solid formed by adding Na_2CO_3 to thorium solutions behaves identically to the one formed when a fresh hydroxide is exposed to high pressures of CO_2 , where both compounds released H_2O and CO_2 above 50 °C. CO_2 could be removed by calcination to 300 °C, while H_2O removal required 430 °C.

Fig. 7: Thermogravimetry and gas evolution for the precipitate from 25:1 urea:Th, 100 °C (200 min)

4 Conclusion

The effects of heating time, temperature, and urea concentration on the homogeneous precipitation of thorium by thermal decomposition of urea were assessed. With an increased bath temperature from 90 °C to 100 °C, the pH rose faster and the time to precipitation decreased by up to 70%. Increasing the urea:Th ratio in solution increased the rate at which the pH rose and decreased the precipitation time, but not as drastically as compared to a temperature increase. The process ensures a very efficient thorium precipitation, but the co-precipitation of radium is limited until heating times are increased beyond 8 h. About 80% of the Ra is incorporated in the solid phase during the 24 hours of heating at 100°C. The hydrolysis product is a colloid that forms at a pH of 3.5-4.0 and sediments upon a pH shift to 7.0. The precipitate is composed of nano-crystalline ThO_2 (11-14 nm from XRD peak broadening) with a large amount of bound water and a small amount of bound CO_2 . This bound CO_2 produces an 80% decrease in the Ra activity after 24 h of precipitation time, though this is insufficient for urea precipitation to be favorable in comparison with oxalate precipitation, where the precipitation efficiency at 10 °C is 95% for Ra.

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Bibliography

1. Hart, P.; Griffin, C.; Hsieh, K.; Matthews, R.; White, G.: ThO_2 -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, PNL-3064. National Technical Information Service, Springfield 1979 p. 174.

2. Salutsky, M.; Kirby, H.: The Radiochemistry of Radium, NAS-NS 3057. Federal Scientific and Technical Information, Springfield 1964 p. 210.
3. Qafoku, O.; Felmy, A.: Development of Accurate Chemical Equilibrium Models for Oxalate Species to High Ionic Strength in the System: Na—Ba—Ca—Mn—Sr—Cl—NO₃—PO₄—SO₄—H₂O at 25 °C. *J. Solut. Chem.* **36**, 81-95 (2007).
4. Millero, F.; Milne, P.; Thurmond, V.: The solubility of calcite, strontianite and witherite in NaCl solutions at 25°C. *Geochim. Cosmochim. Acta* **48**, 1141-1143 (1984).
5. Houšková, V.; Štengl, V.; Bakardjieva, S.; Murafa, N.; Tyrpekl, V.: Efficient gas phase photodecomposition of acetone by Ru-doped Titania. *Appl. Catal. B: Environ.* **89**, 613-619 (2009).
6. Tyrpekl, V.; Vejpravová, J.; Roca, A.; Murafa, N.; Szatmary, L.; Nižňanský, D.: Magnetically separable photocatalytic composite γ -Fe₂O₃@TiO₂ synthesized by heterogeneous precipitation, *Appl. Surf. Sci.* **257**, 4844-4848 (2011).
7. Soler-Illia, G.; Jobbágy, M.; Candal, R.; Regazzoni, A.; Blesa, M.: Synthesis of metal oxide particles from aqueous media: The homogeneous alkalization method, *J. Disper. Sci. Technol.* **19**, 207-228 (1998).
8. Soler-Illia, G.; Candal, R.; Regazzoni, A.; Blesa, M.: Synthesis of mixed copper-zinc basic carbonates and Zn-doped tenorite by homogeneous alkalization. *Chem. Mater.* **9**, 184-191 (1997).
9. Nkou Bouala, G.; Clavier, N.; Podor, R.; Cambedouzou, J.; Mesbah, A.; Brau, H.; Léchelle, J.; Dacheux, N.: Preparation and characterisation of uranium oxides with spherical shapes and hierarchical structures. *CrystEngComm* **16**, 6944-6954 (2014).
10. Šubrt, J.; Michálková, E.; Boháček, J.; Lukáč, J.; Gánovská, Z.; Máša, B.: Uniform particles formed by hydrolysis of acid mine drainage with urea. *Hydrometall.* **106**, 12-18 (2011).
11. Wang, S.; Gu, F.; Li, C.; Cao, H.: Shape-controlled synthesis of CeOHCO₃ and CeO₂ microstructures. *J. Cryst. Growth* **307**, 386-394 (2007).
12. Wang, L.; Zhao, R.; Wang, X.; Mei, L.; Yuan, L.; Wang, S.; Chai, Z.; Shi, W.: Size-tunable synthesis of monodisperse thorium dioxide nanoparticles and their performance on the adsorption of dye molecules. *CrystEngComm* **16**, 10469-10475 (2014).
13. van der Plas, T.; Kanij, J.; Noothout, A.; Hermans, M.: The KEMA sol-gel process, DPR 430. A.E.E. Winfrith, Winfrith 1966 p. 10.
14. Beydon, J.; Gratot, I.: Utilisation du recul nucléaire pour la séparation du ²²⁸Ra, du ²²⁴Ra et du ²³³Pa à partir d'hydroxyde de thorium colloidal, CEA-R-3493. Centre d'Etudes Nucléaires de Saclay, Gif-sur-Yvette 1968 p. 12.
15. Laraweb. <<http://www.nucleide.org/Laraweb/>>, (accessed 27.1.2017.).
16. Wangle, T.; Tyrpekl, V.; Cagno, S.; Delloye, T.; Larcher, O.; Cardinaels, T.; Vleugels, J.; Verwerft, M.: The effect of precipitation and calcination parameters on oxalate derived ThO₂ pellets. *J. Nucl. Mater.* **495**, 128-137 (2017).
17. Williamson, G.; Hall, W.: X-ray line broadening from filed aluminium and wolfram. *Acta Metall.* **1**, 22-31 (1953).
18. Petříček, V.; Dušek, M.; Palatinus, L.: Crystallographic Computing System JANA2006: General features. *Z. Kristall.* **229**, 345-352 (2014).
19. Neck, V.; Müller, R.; Bouby, M.; Altmaier, M.; Rothe, J.; Denecke, M.; Kim, J.: Solubility of amorphous Th(IV) hydroxide - application of LIBD to determine the solubility product and EXAFS for aqueous speciation. *Radiochim. Acta* **90**, 485-494 (2002).
20. Chemical Thermodynamics of Thorium. In: Chemical Thermodynamics (F. Mompean, ed.). OECD NEA, Issy-les-Moulineaux 2007.
21. Pazhukhin, E.; Smirnova, E.; Krivokhatskii, A.; Pazukhina, Y.; Kochergin, S.: Optimization of conditions of thorium oxalate precipitation. I. Solubility of thorium oxalate in the presence of like ions. *Radiokhim.* **27**, 606-611 (1985).
22. Kurnakova, A.; Shubochkin, L.: The solubility of Th(C₂O₄)₂·6H₂O in aqueous solutions of HNO₃ and H₂C₂O₄ at 25°C. *Zh. Neorg. Khim.* **8**, 1249-1254 (1963).
23. Ayers, A.: Precipitation of Thorium Oxalate from Nitric Acid Solutions, CC-2962. Iowa State College, Ames 1945 p. 4.
24. Perrin, D.; Dempsey, B.: Buffers for pH and Metal Ion Control, Springer Netherlands, Dordrecht, 1974 p. 176.
25. Nkou Bouala, G.; Clavier, N.; Léchelle, J.; Monnier, J.; Ricolleau, C.; Dacheux, N.; Podor, R.: High-temperature electron microscopy study of ThO₂ microspheres sintering. *J. Eur. Ceram Soc.* **37**, 727-738 (2017).
26. Kobayashi, T.; Sasaki, T.; Takagi, I.; Moriyama, H.: Effect of solid phase transformation on the solubility product of thorium hydrous oxide at 363 K. *J. Nucl. Sci. Technol.* **53**, 1787-1793 (2016).
27. Jovani Abril, R.; Eloirdi, R.; Bouëxière, D.; Malmbeck, R.; Spino, J.: In situ high temperature X-ray diffraction study of UO₂ nanoparticles. *J. Mater. Sci.* **46**, 7247-7252 (2011).
28. Götte, H.: Das Verhalten des Eisen(III)- und Thoriumhydroxyds in Abhängigkeit von der Vorbehandlung und Herstellung, untersucht nach der Emaniermethode von Otto Hahn. *Z. Phys. Chem. Abt. B* **40**, 207-230 (1938).
29. Dzimitrowicz, D.; Wiseman, P.; Cherns, D.: An electron microscope study of hydrous thorium dioxide ThO₂·nH₂O. *J. Colloid Interface Sci.* **103**, 170-177 (1985).
30. Mirza, E.; Karkhanavala, M.: On the Oxycarbonate of Thorium. *J. Indian Chem. Soc.* **40**, 903-904 (1963).
31. Chauvenet, E.: Sur les carbonates de thorium. *C. R. Séances Acad. Sci.* **153**, 66-68 (1911).