

Solubility and colloid formation of Th(IV) in concentrated NaCl and MgCl₂ solution

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Summary. The solubility of crystalline ThO₂(cr) and amorphous hydrated Th(IV) oxyhydroxide ThO_n(OH)_{4-2n}·xH₂O(am) has been measured in dilute to concentrated NaCl and MgCl₂ solutions equilibrated with magnesium hydroxide or hydroxychloride at 22 ± 2 °C. The contributions of colloids to the total thorium concentrations observed in both over- and undersaturation experiments with amorphous Th(IV) precipitates have been analysed by ultracentrifugation. The solubility increasing effect of long-time stable Th(IV) eigencolloids, previously investigated in 0.5 M NaCl solutions, is also observed in concentrated 5 M NaCl. Ionic strength and chloride concentration have no effect on the stability of these hydrophilic Th(IV) oxyhydroxide eigencolloids, which are the predominant species in solution. They cause relatively high total thorium concentration in neutral to alkaline steady state solutions, independent of ionic strength: $\log[\text{Th}]_{\text{tot}} \approx \log[\text{Th}]_{\text{coll}} = -6.3 \pm 0.5$. In concentrated MgCl₂ solutions saturated with magnesium hydroxychloride colloids, the formation of pseudocolloids, *i.e.*, Th(IV) sorbed onto Mg₂(OH)₃Cl·4H₂O(coll), leads to a further increase of the total thorium concentration up to 10⁻⁵ M. The present results are discussed with regard to maximum Th(IV) and Pu(IV) concentrations in performance assessment calculations.

1. Introduction

In a series of recent papers of our laboratory [1–3] thorium was used as a surrogate for other tetravalent actinides to investigate the solid-liquid equilibria and the effect of colloids on the solubility of An(IV) oxides/hydroxides. These investigations (in 0.5 M NaCl solution) and the solubility studies of numerous other authors [4–10] have been performed in solutions of low and moderate ionic strength ($I < 1$ M). The only hitherto available study on the solubility of Th(IV) in concentrated NaCl and MgCl₂ solutions [8] is limited to the acidic pH range.

The present investigations have been focussed on concentrated chloride solutions with regard to nuclear waste disposal in underground salt mines, *i.e.*, to natural aquifer systems saturated predominantly with NaCl or MgCl₂. In

this context brucite has been proposed as additive to back-fill materials for the Asse salt mine in Germany [11]. The capacity of Mg(OH)₂(cr) to buffer pH and to scavenge carbonate (due to the limited solubility of magnesium carbonate solids) is considered to minimise actinide solubilities. Because of discrepancies in the frequently used thermodynamic databases for the computer codes EQ3/6 and Geochemist's Workbench, we have recently re-investigated the thermodynamics of brucite and magnesium hydroxychloride in the system Mg-Na-H-OH-Cl-H₂O (25 °C) [12]. In the present work the solubility of Th(IV), in particular the quantification of contributions from colloids and investigation of their stability, is studied in NaCl and MgCl₂ solutions saturated with Mg(OH)₂(cr) or Mg₂(OH)₃Cl·4H₂O(cr), which is formed in MgCl₂ solutions above 1.8 molal [12].

2. Experimental

2.1 Chemicals and analytical methods

Crystalline, anhydrous ThO₂ (99.99%) was obtained from Alfa Aesar and additionally heated at 750 °C for 8 hours. The preparation and characterisation of the amorphous Th(IV) hydrous oxide or hydroxide is described in [1]. Carbonate-free NaOH solution (Baker) was purchased from Baker, Th(NO₃)₄·5H₂O (p.a.), MgCl₂·6H₂O (p.a.) and NaCl (p.a.) from Merck. The stoichiometric composition, *i.e.* the water content of the MgCl₂·6H₂O was confirmed by chloride analysis. Crystalline Mg(OH)₂(cr) (purity ≥ 99%) was obtained from Fluka. In 2.5 and 4.5 M MgCl₂, Mg(OH)₂(cr) completely converted into magnesium hydroxychloride, identified and characterised as Mg₂(OH)₃Cl·4H₂O(cr) [12]. All solutions were prepared with purified water from a Milli-Q-academic apparatus (Millipore).

Thorium concentrations were determined by ICP-MS (ELAN 6100, Perkin Elmer). The background is found to be 0.001–0.002 ppb Th-232. Depending on the NaCl and MgCl₂ concentration the aliquots for ICP-MS analysis have to be diluted 1 : 10 to 1 : 100 and acidified (2% HNO₃). Accordingly, the detection limit for thorium in the original solutions varies from 10⁻¹⁰ to 10⁻⁹ mol/l.

Combination pH electrodes (type ROSS, Orion Co.), calibrated against standard pH buffers (pH 1–10, Merck), were used to determine the H⁺ concentration ($-\log[\text{H}^+] = \text{pH}_c$) from the operational value pH_{exp} measured in NaCl and

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MgCl₂ solutions [12]:

$$-\log[\text{H}^+] = \text{pH}_{\text{exp}} + A.$$

The values of A were determined by measuring pH_{exp} in corresponding NaCl and MgCl₂ solutions containing 0.001–0.1 M HCl. They include the activity coefficient of the H⁺ ion and a contribution from the variation of the liquid junction potential when measuring diluted pH buffer solutions for calibration and NaCl or MgCl₂ test solutions. The measured H⁺ concentrations were confirmed by an independent method, *i.e.*, by a_{HCl} measurements using a cell without liquid junction. Details are given in [12].

2.2 Solubility measurements

The solubility of ThO₂(cr) and Th(OH)₄(am) was studied from the direction of undersaturation by adding an amount of about 20–50 mg of the Th(IV) solid to following matrix solutions equilibrated with solid Mg(OH)₂(cr) or Mg₂(OH)₃Cl·4H₂O(cr):

– 0.5 M NaCl, 5 M NaCl and 0.25 M MgCl₂ equilibrated with Mg(OH)₂(cr);

– 2.5 and 4.5 M MgCl₂ equilibrated with Mg₂(OH)₃Cl·4H₂O(cr).

For each of the matrix solutions, two experiments with Th(OH)₄(am) were performed in parallel. One sample contained about 20–40 mg of solid Mg(OH)₂(cr) or Mg₂(OH)₃Cl·4H₂O(cr). In the other sample the magnesium solid was removed by 450 nm filtration from the equilibrated matrix solution before Th(OH)₄(am) was added. All experiments were performed in polyethylene vials. The samples were stored at 22 ± 2 °C in an argon glove box. Thorium concentrations were measured after equilibration times of two weeks up to one year.

In order to measure the total thorium concentration ([Th]_{tot}) including colloids, aliquots of the supernatant were taken carefully in triplicate. For the separation of the aqueous solutions from solid and colloidal particles, numerous types of filter materials and filter pore sizes were tested. As neutral aqueous species show a high tendency towards sorption on the filter surface, the thorium concentration was measured in the filtrate and also after subsequent filtration of this filtrate, which must not lead to a further decrease of the thorium concentration. This test was successful when Gelman GHP Acrodisc 200 nm filters (polypropylene, hydrophilic) and Filtron Microsep TM 10 kD filters (polyethersulfone) were applied to concentrated MgCl₂ solutions. In this case, sorption sites on the filters are obviously saturated by Mg²⁺ ions. In the case of dilute solutions filtration was not successful. The thorium concentrations in filtered aliquots were usually at the background level of the ICP-MS, even after pre-equilibration of the filters.

Therefore, the thorium concentration was determined after ultracentrifugation (Beckman XL-90, rotor type 90Ti) using quick-seal centrifuge tubes (Vol. ≈ 4 ml). The removal of Th(IV) eigencolloids requires a large relative centrifugal force of about 1.5 × 10⁵ g (rotation velocities of 50 000 rpm). Increasing the rotation velocity from

50 000–90 000 rpm does not lead to a further decrease of the thorium concentration, indicating that the thorium species remaining dissolved are small aqueous species. The samples were routinely centrifuged for 60 minutes at 90 000 rpm, corresponding to a mean relative centrifugal force of about 5 × 10⁵ g.

In additional experiments, which were performed to quantify and specify the colloids formed in different media, Th(OH)₄(am) was precipitated in situ by adding carbonate-free NaOH (Baker) to 10^{−3} M thorium nitrate solutions in 5.0 M NaCl and in 0.5 and 4.5 M MgCl₂. Aliquots of these samples were centrifuged for 60 minutes at different rotation velocities.

3. Results and discussion

3.1 Solubility measurements with ThO₂(cr)

Solubility experiments with ThO₂(cr) were performed in 0.5 M NaCl, 5 M NaCl and 0.25 M MgCl₂ saturated with Mg(OH)₂(cr) and in 2.5 and 4.5 M MgCl₂ saturated with Mg₂(OH)₃Cl·4H₂O(cr). The thorium concentrations measured after equilibration times of 15–373 days are listed in Table 1. The values measured within the first 100 days were partly at or below the detection limit, the values measured after longer equilibration periods were found to be in the range of 10^{−10}–10^{−8} M. Similar as in our recent study in neutral to alkaline 0.5 M NaCl-NaOH solutions and in other studies discussed in [3], the measured thorium concentrations are comparable with experimental data for amorphous Th(IV) oxide/hydroxide. They are many orders of magnitude higher than the solubility calculated for the reaction ThO₂(cr) + 2H₂O ⇌ Th(OH)₄(aq) (log $K_{s,4}$ = −15.7 ± 1.5) from the known thermodynamic data for ThO₂(cr) and Th(IV) hydroxide complexes [13]. An effect of ionic strength cannot be observed from the widely scattered data.

The present results confirm the observations reported previously for ThO₂(cr) and UO₂(cr) [3, 13–15]. The solubility of crystalline An(IV) dioxides in neutral and alkaline solutions is not limited by the properties of the bulk crys-

Table 1. Thorium concentrations measured after ultracentrifugation in solubility experiments with ThO₂(cr) in the presence of solid brucite or magnesium hydroxychloride.

Medium	−log[H ⁺]	time (days)	log [Th]
0.5 M NaCl-NaOH ^a	11–13.5	71–112	−9.3 ± 0.8
		15–100	−9.1 ± 1.0
0.5 M NaCl ^b	10.4	269–373	−8.8 ± 0.2
		15–100	< −9.3 ^d
5.0 M NaCl ^b	10.8	269–373	−9.0 ± 0.6
		15–100	< −10 ^d
0.25 M MgCl ₂ ^b	9.0	269–373	−9.8 ± 0.4
		15–100	≤ −9.3
2.5 M MgCl ₂ ^c	8.9	269–373	−8.2 ± 1.3
		15–100	−9.0 ± 0.5
4.5 M MgCl ₂ ^c	8.8	269–373	−8.6 ± 0.6
		15–100	−9.0 ± 0.5

a: From [3];

b: Saturated with Mg(OH)₂(cr);

c: Saturated with Mg₂(OH)₃Cl·4H₂O(cr);

d: Below the analytical detection limit.

talline solids but given by amorphous fractions or surface layers.

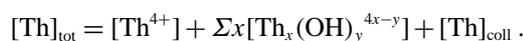
3.2 Effect of Th(IV) eigencolloids on the solubility of amorphous Th(IV) oxide/hydroxide

The available solubility data for X-ray amorphous Th(IV) oxide/hydroxide at $I = 0.1\text{--}0.6\text{ M}$ (NaClO₄, NaCl or KCl media) and 17–25 °C are widely scattered and differ by up 3 orders of magnitude in (Fig. 1). Most of these studies were performed with fresh precipitates only washed with water [4–9]. Solubility data determined at pH 3.5–5 with a solid dried at room temperature [1, 10] led to the values at the lower limit. The discrepancies may be explained with the fact that the experimental data do not refer to a well-defined unique solid phase but to hydrated oxyhydroxides ThO_n(OH)_{4–2n}·xH₂O(am), which may be called “Th(OH)₄(am)” or “ThO₂·xH₂O(am)”. The water content and molar Gibbs energy of formation (particle size in the range of 3–8 nm [16]) depends on the preparation method, pretreatment, and alteration.

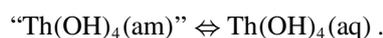
The important role of Th(IV) eigencolloids has been demonstrated by laser-induced breakdown detection (LIBD), ultrafiltration (1–2 nm), and extended X-ray absorption fine structure (EXAFS) spectroscopy [1, 2]. Careful coulometric titration of Th(IV) solutions in the range of pH 3–5 leads to hydrolysis of the Th⁴⁺ aquo ion and polynucleation up to the formation of amorphous oxyhydroxide colloids. Considering colloids as small solid particles, their formation indicates that the solubility is just exceeded during the titration. Hence the H⁺ and Th(IV) concentrations at the onset of colloid formation, which are consistent with the classical solubility data for the dried amorphous solid [1, 10], define the solubility of Th(OH)₄(am) excluding colloidal thorium species (lower limit line in Fig. 1) and yield a solubility product of $\log K_{\text{sp}}^{\circ} = -47.8 \pm 0.3$ [1].

At H⁺ and Th(IV) concentrations between the upper and lower calculated lines in Fig. 1, Th(IV) oxyhydroxide eigen-

colloids are the prevailing species [1, 2, 17]. They have the same structure as the amorphous precipitate formed at H⁺ and thorium concentrations above the upper limit in Fig. 1. The Th L₃ edge EXAFS spectra of these colloidal suspensions are similar to that of the amorphous precipitate [1, 17]. The long-time stability of the Th(IV) eigencolloids formed by coulometric titration at pH 3–5 was confirmed by LIBD and ultrafiltration [2]. Over the whole time period of investigation, up to more than 400 days, they did neither redissolve nor agglomerate to a precipitate. Neither the thorium colloid concentration nor the particle size changed noticeably. Moreover, pH changes measured as a function of time indicated that freshly prepared colloidal suspensions approach a steady state, where Th(IV) eigencolloids are in equilibrium with ionic species [2]. These observations support the assumption that hydrophilic oxyhydroxide eigencolloids formed by chemical polynucleation reactions are stable species and may be considered as large aqueous species contributing to the solubility of Th(IV):



The solubility in neutral to alkaline solutions is independent of pH. The data determined after ultrafiltration or ultracentrifugation are usually ascribed to the equilibrium



The large scatter of experimental solubility data is probably due to the varying success in removal of colloids by filtration or centrifugation. The mean value of the thorium concentrations measured at pH > 5 in [5–7] was calculated as $\log [\text{Th(OH)}_4(\text{aq})] = -8.5 \pm 0.6$ [13]. Considerably higher but less scattered thorium concentrations were measured in aliquots taken directly from the supernatant, without phase separation: $\log [\text{Th}]_{\text{tot}} = -6.3 \pm 0.5$ [1]. Solubility data at the same level were reported by Nabivanets and Kudritskaya [4] ($\log [\text{Th}] = -6.3$ at pH = 5.5–7 in 0.1 M NaClO₄, 17 °C) after centrifugation at only 10 000 rpm, which is not sufficient to remove small Th(IV) eigencolloids (c.f. Sect. 2.2 and 3.3, below). The observation that total thorium concentrations including colloids are well reproducible is a further indication that eigencolloids are in equilibrium with both, solid phase and mononuclear or oligomeric aqueous species.

The question whether this solubility increasing effect caused by the formation of Th(IV) eigencolloids occurs also in concentrated chloride solutions is investigated in the present study by measuring the solubility of amorphous Th(IV) oxyhydroxide from the direction of undersaturation, in 0.5 M NaCl, 5 M NaCl and 0.25 M MgCl₂ equilibrated with Mg(OH)₂(cr) and in 2.5 and 4.5 M MgCl₂ equilibrated with Mg₂(OH)₃Cl·4H₂O(cr). The total thorium concentrations [Th]_{tot} (including colloids) and the thorium concentration measured after ultracentrifugation at 90 000 rpm ($5 \times 10^5\text{ g}$) are listed in Table 2. They are mean values of different measurement performed after equilibration times of 20–100 days. The experimental data are shown in Fig. 2 together with comparable data measured recently in neutral to alkaline 0.5 M NaCl–NaOH [1].

The thorium concentrations measured in the NaCl and 0.25 M MgCl₂ samples containing 20–40 mg of brucite, are generally somewhat lower than those measured in the

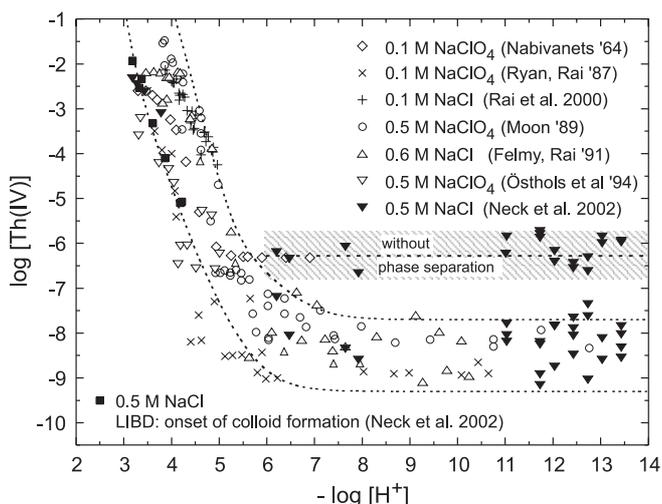


Fig. 1. Solubility of amorphous Th(IV) hydroxide or hydrous oxide at $I = 0.1\text{--}0.6\text{ M}$ and 17–25 °C (data from [1, 4–10]). The dashed curves represent lower and upper limits calculated with the solubility product ($\log K_{\text{sp}}^{\circ} = -47.0 \pm 0.8$) and hydrolysis constants discussed in a recent review [13]. The filled triangles in the hatched area show thorium concentrations measured without removal of colloids.

Table 2. Thorium concentrations measured in solubility experiments with $\text{Th}(\text{OH})_4(\text{am})$ in NaCl and MgCl_2 solutions saturated with brucite or magnesium hydroxychloride (from undersaturation, after 20–100 days).

Medium		$-\log[\text{H}^+]$	$\log[\text{Th}]_{\text{tot}}$	$\log[\text{Th}]$
			without removal of colloids	after ultracentrifugation
0.5 M NaCl-NaOH ^a		6.5–13.5	-6.3 ± 0.5	-8.5 ± 0.6
0.5 M NaCl	(1) ^b	9.6	-6.8 ± 0.2	-8.3 ± 0.5
	(2) ^c	9.8	-7.3 ± 0.2	-9.1 ± 0.4
5.0 M NaCl	(1) ^b	9.8	-6.3 ± 0.2	-8.5 ± 0.6
	(2) ^c	10.4	-6.5 ± 0.5	-8.8 ± 0.6
0.25 M MgCl_2	(1) ^b	9.2	-6.5 ± 0.1	-8.5 ± 0.5
	(2) ^c	8.9	-7.0 ± 0.2	-9.1 ± 0.2
2.5 M MgCl_2	(1) ^b	8.9	-5.9 ± 0.2	-7.9 ± 0.5
	(2) ^d	8.8	-5.7 ± 0.2	-7.8 ± 0.2
4.5 M MgCl_2	(1) ^b	8.8	-4.7 ± 0.2	-6.6 ± 0.3
	(2) ^d	8.9	-4.7 ± 0.2	-6.4 ± 0.3

a: From [1];

b: The values from experiments (1) were obtained after removal of the magnesium solids from the matrix solution by 450 nm-filtration;

c: In the presence of solid brucite (20–40 mg in 50 ml solution);

d: In the presence of solid magnesium hydroxychloride (20–40 mg in 50 ml solution).

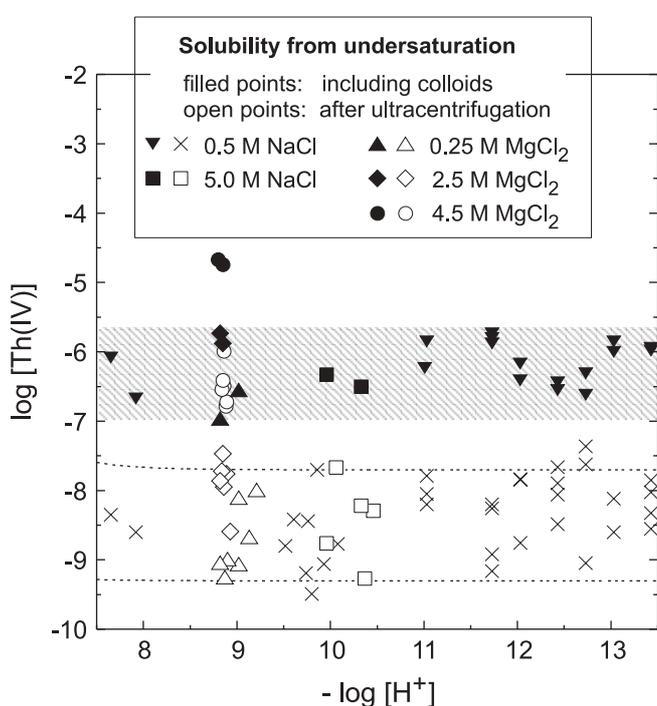


Fig. 2. Solubility of $\text{Th}(\text{OH})_4(\text{am})$ determined from undersaturation in 0.5 and 5.0 M NaCl and in 0.25, 2.5 and 4.5 M MgCl_2 . Filled points: Total thorium concentrations (including colloids), open points: thorium concentrations measured after ultracentrifugation at 90 000 rpm (5×10^5 g).

samples from which the solid $\text{Mg}(\text{OH})_2(\text{cr})$ was removed by 450 nm filtration before starting the experiment (c.f. Table 2). This indicates that $\text{Th}(\text{OH})_4(\text{aq})$ and $\text{Th}(\text{IV})$ eigencolloids may have a certain tendency towards sorption onto brucite.

3.2.1 Thorium concentrations measured after ultracentrifugation

The thorium concentrations measured after ultracentrifugation of the samples in 5 M NaCl and in 0.25 M MgCl_2 equilibrated with $\text{Mg}(\text{OH})_2(\text{cr})$ are found to be scattered within

the same range as those in 0.5 M NaCl-NaOH ($\log[\text{Th}] = -8$ to -9), while those obtained from the samples in 2.5 M MgCl_2 equilibrated with $\text{Mg}_2(\text{OH})_3\text{Cl} \cdot 4\text{H}_2\text{O}(\text{cr})$ are mostly at the upper limit of that range ($\log[\text{Th}] = -7.8 \pm 0.3$). There is no indication for a significant dependence on ionic strength or chloride concentration. (The considerably higher values of $\log[\text{Th}] = -6.5 \pm 0.4$ measured for the samples in 4.5 M MgCl_2 are not the result of an ionic strength effect but due to the formation of pseudocolloids, as confirmed by the value of $\log[\text{Th}] = -8.1 \pm 0.1$ measured after 2 nm ultrafiltration, c.f. discussion in Sect. 3.3.)

The large scatter of experimental data is probably caused by incautious handling of the centrifuged vial, which may lead to re-suspension of colloidal particles. Because of these problems, the lower values at $\log[\text{Th}] \approx -9$ more likely represent the concentration of mononuclear $\text{Th}(\text{OH})_4(\text{aq})$. A very similar value is calculated by combining the solubility product of $\log K_{\text{sp}}^{\circ} = -47.8 \pm 0.3$, determined by Neck *et al.* [1] from the onset of colloid formation in the range of pH 3–4.5, and the formation constant $\log \beta_4^{\circ} = 39.0 \pm 0.5$ for the complex $\text{Th}(\text{OH})_4(\text{aq})$, derived from the solvent extraction study of Ekberg *et al.* [18]:

$$\log[\text{Th}(\text{OH})_4(\text{aq})] = -8.8 \pm 0.6.$$

3.2.2 Total thorium concentrations and contributions from eigencolloids

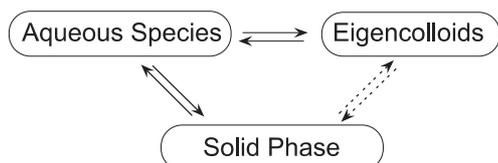
The total thorium concentrations measured from the supernatant are reasonably reproducible and systematically 2–3 orders of magnitude higher than those measured after ultracentrifugation. Similar as for the concentrations measured after ultracentrifugation, the values of $\log[\text{Th}]_{\text{tot}}$ show no dependence on the chloride concentration (again with the exception of the considerably higher concentrations in 4.5 M MgCl_2 , which are due to another effect that will be discussed below in Sect. 3.3). $\text{Th}(\text{IV})$ eigencolloids are the predominant species in the investigated chloride solutions. The complex $\text{Th}(\text{OH})_4(\text{aq})$ contributes less than 1% to the total thorium concentration. The mean value of $\log[\text{Th}]_{\text{tot}}$ calcu-

lated from all data at pH > 7 in 0.5 and 5.0 M NaCl and in 0.25 and 2.5 M MgCl₂ is

$$\log[\text{Th}]_{\text{tot}} \approx \log[\text{Th}]_{\text{coll}} = -6.3 \pm 0.5.$$

The high concentrations coming from Th(IV) eigencolloids in solubility studies from undersaturation were found to remain constant for investigation periods of more than a year [1]. These colloids are stable over a wide pH range (independent of the point of zero charge) and also in concentrated salt solutions, whereas the classical DLVO (Derjaguin–Landau–Verwey–Overbeek) theory predicts colloids to be meta- or instable towards agglomeration and precipitation, particularly in concentrated salt solutions. Therefore, it has to be emphasised that such hydrophilic oxyhydroxide eigencolloids must not be compared to colloids of crystalline oxides which may be formed by erosion of minerals or produced by special technical processes.

The pH titration of an aqueous Th⁴⁺ solution leads to the following continuous transition, (which of course depends on the total thorium concentration): The formation of mononuclear complexes Th(OH)_y^{4-y}(aq) with y = 1–4 is followed by polynucleation to oligomeric species Th_x(OH)_y^{4x-y}(aq) with x < 10 (e.g., dimers Th₂(OH)₂⁶⁺, Th₂(OH)₃⁵⁺ and Th₂(OH)₄⁴⁺, tetramers Th₄(OH)₈⁸⁺ and Th₄(OH)₁₂⁴⁺, and hexamers Th₆(OH)₁₄¹⁰⁺ and Th₆(OH)₁₅⁹⁺, as reported in [6, 10, 18] and other studies discussed in [1, 13] up to polymers with x > 100 (i.e., Th_x(OH)_y^{4x-y} colloids > 2 nm) and finally by the precipitation of amorphous “Th(OH)₄(am)”. These colloids formed by chemical condensation may be considered as small solid particles with physical properties similar to the bulk solid, but also as large aqueous species contributing to the total concentration in solution. Both, the bulk solid phase and colloidal particles are known to approach an equilibrium with aqueous species. Consequently an equilibrium between solid phase and eigencolloids should be approached as well.



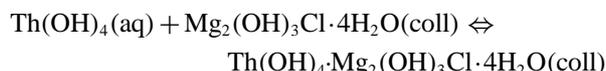
The quantification and modelling of contributions from eigencolloids to the total solubility of oxides/hydroxides of highly charged metal ions is also of particular interest for oxyhydroxide colloids of Fe, Al, and Si, because trace actinides may be sorbed onto or incorporated in these colloids and thus mobilised as pseudocolloids.

3.3 Pseudocolloids: Th(IV) sorbed onto colloids of magnesium hydroxychloride

In order to investigate the reason for the high thorium concentrations in 4.5 M MgCl₂ (log[Th]_{tot} = -4.7 ± 0.2 and log[Th] = -6.5 ± 0.4 even after ultracentrifugation at 90 000 rpm) additional experiments were performed from the direction of oversaturation. Th(OH)₄(am) was precipitated in situ by adding appropriate amounts of NaOH to 10⁻³ M thorium nitrate solutions in 5.0 M NaCl and in

0.5 and 4.5 M MgCl₂. After one day, the thorium concentration resulting from suspended colloids was measured as a function of the centrifugal force (Fig. 3). In 5 M NaCl, the addition of NaOH leads only to the formation of solid and colloidal Th(OH)₄(am). Adding NaOH to 0.5 M MgCl₂ and 4.5 M MgCl₂ leads additionally to the precipitation of Mg(OH)₂(s) and Mg₂(OH)₃Cl·4H₂O(s), respectively. In particular, magnesium hydroxychloride forms small needle-like particles [12], i.e., the resulting suspension in 4.5 M MgCl₂ is also saturated with solid and colloidal Mg₂(OH)₃Cl·4H₂O(s).

The Th(IV) eigencolloids formed in 5.0 M NaCl and in 0.5 M MgCl₂ could be removed by ultracentrifugation at rotation velocities above 50 000 rpm (1.5 × 10⁵ g). The same can also be expected for Th(IV) eigencolloids formed in 4.5 M MgCl₂. Their density is not known but certainly much higher than the density of the 4.5 M MgCl₂ solution (1.302 g/cm³). However, the density of hydrous magnesium hydroxychloride colloids is expected to be similar to the density of this highly concentrated MgCl₂ solution. When Th(IV) is incorporated or sorbed onto these magnesium hydroxychloride colloids:



it is not possible to remove these colloids by ultracentrifugation, so that the thorium concentration remains at a high level of log[Th] = -5.7, also at increased rotation velocities (Fig. 3).

This explanation is supported by filtration experiments performed within the solubility study from undersaturation in 4.5 M MgCl₂ saturated with magnesium hydroxychloride (-log[H⁺] = 8.9). The thorium concentration measured after 200 nm filtration (Gelman GHP Acrodisc) was comparable with the concentration measured after ultracentrifugation (Table 3) and the application of 2 nm ultrafiltration (Filtron Microsep TM 10 kD polyethersulfone filters) led to a thorium concentration of log[Th] = -8.1 ± 0.1, which is

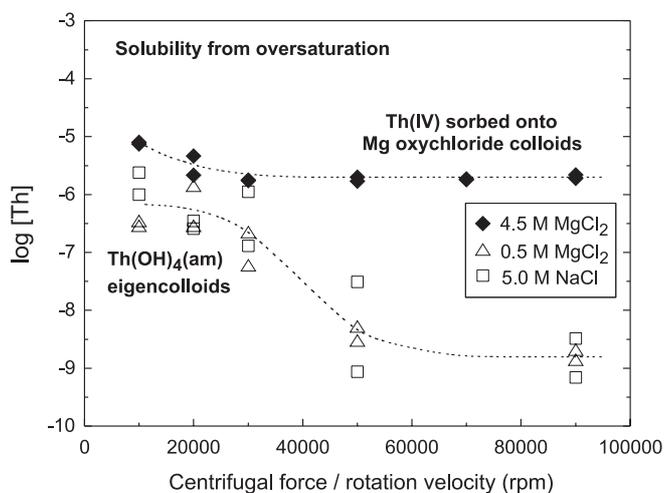


Fig. 3. Thorium concentrations measured after ultracentrifugation of colloidal suspensions of Th(OH)₄(am) precipitated in 5 M NaCl (pH_c = 11.8), 0.5 M MgCl₂ (pH_c = 9.0) and 4.5 M MgCl₂ (pH_c = 8.9) for 60 minutes at different rotation velocities.

Table 3. Thorium concentrations measured after 100 days in the solubility experiment from undersaturation with Th(OH)₄(am) in 4.5 M MgCl₂ saturated with Mg₂(OH)₃Cl·4H₂O(cr).

without removal of colloids:	$\log [\text{Th}]_{\text{tot}} = -4.8 \pm 0.2$
after ultracentrifugation (90 000 rpm):	$\log [\text{Th}] = -6.4 \pm 0.3$
after 200 nm filtration:	$\log [\text{Th}] = -6.7 \pm 0.1$
after 10 kD (2 nm) filtration:	$\log [\text{Th}] = -8.1 \pm 0.2$

in the range of experimental values ascribed to mononuclear Th(OH)₄(aq).

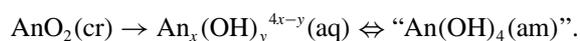
The high thorium concentrations from these pseudocolloids observed in the present laboratory experiments have not to be expected in real systems (Q-brine/brucite/magnesium hydroxychloride). The ratio of Th(IV) sorbed onto colloidal (mobile) and solid (immobile) magnesium hydroxychloride depends on the ratio of solution volume (saturated with Mg₂(OH)₃Cl·4H₂O colloids) and solid magnesium hydroxychloride. In our experiments, for practical reasons only 20–40 mg of the solid phase was added to 50 ml solution, whereas real systems contain large amounts of solid magnesium hydroxide/hydroxychloride (Sorel cement) and small volumes of aqueous phase. In NaCl or dilute MgCl₂ solutions, neither solid Mg₂(OH)₃Cl·4H₂O(s) nor its colloids are stable.

4. Conclusions for geochemical model calculations on maximum Th(IV) and Pu(IV) concentrations in natural aquifer systems

The results determined with Th(IV) as surrogate for tetravalent actinides are summarised below and used as analogues to estimate the corresponding behaviour of Pu(IV). In this context it is to note that model calculations on the solubility of PuO₂(s) in real systems must additionally account for aqueous Pu species at other oxidation states due to oxidation, radiolysis and disproportionation reactions.

Solubility limiting solid phase

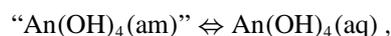
At very low pH, the thermodynamically stable crystalline dioxides AnO₂(cr) may actually represent the solubility limiting solid phase, in particular at higher temperature [3, 9, 15]. However, experimental solubility data in neutral and alkaline solutions are 6–7 orders of magnitude higher than the low values of $\leq 10^{-15}$ M calculated from the known thermodynamic data [13, 19] for AnO₂(cr) and An(IV) hydroxide complexes. At pH values above the onset of hydrolysis, the sorption or precipitation of monomeric or polynuclear hydroxide complexes An_x(OH)_y^{4x-y}(aq) on the surface of crystalline AnO₂(cr) will result in an amorphous solubility limiting surface layer:



Performance assessment calculations on the long-time behaviour of tetravalent actinides in natural systems must not take credit of the extremely low solubilities resulting from the thermodynamic data of the crystalline An(IV) dioxides.

Solubility of amorphous Th(IV) oxide/hydroxide: contributions from colloids

The solubilities determined in neutral and alkaline solutions after removal of colloids show no significant dependence on pH and chloride concentration or ionic strength. Ascribing these data to the equilibrium

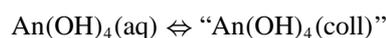


the experimental data for Th(IV) and those for Pu(IV) discussed in [13] yield:

$$\log [\text{Th(OH)}_4(\text{aq})] = -8.8 \pm 0.6,$$

$$\log [\text{Pu(OH)}_4(\text{aq})] = -10.4 \pm 0.5.$$

The total concentration measured without removal of colloids is found to be increased by 2–3 orders of magnitude. The solubility of amorphous Th(IV) oxide/hydroxide in near neutral to alkaline chloride solutions is dominated by Th(IV) eigencolloids. The reproducibility of these solubility data and the long-time stability of the Th(IV) eigencolloids support the assumption that these colloids should be considered as stable large aqueous species with a defined equilibrium concentration. The concentration of An(IV) eigencolloids may simply be modelled by the reaction



with $\log K = 2.5 \pm 0.8$ for An = Th(IV). As a first approximation this equilibrium constant may be adopted as well for Pu(IV), which results in the following solubility values in neutral and alkaline solution (again independent of pH and chloride concentration):

$$\log [\text{Th(IV)}]_{\text{coll}} = -6.3 \pm 0.5,$$

$$\log [\text{Pu(IV)}]_{\text{coll}} = -7.9 \pm 1.0.$$

This concentration of [Pu(IV)]_{coll} is in accord with a model on Pu(IV) polymer formation proposed by Fujiwara *et al.* [20]. According to this model, the concentration of $\log [\text{Pu(IV)}] = -9$ measured in 1 M NaClO₄ (pH 7–9) after 2 nm filtration is primarily caused by small Pu(IV) polymers, while $\log [\text{Pu(IV)}]_{\text{tot}}$ is expected to include also contributions from eigencolloids larger than 2 nm. The equilibrium concentration of monomeric Pu(IV) was calculated as $\log [\text{Pu(OH)}_4(\text{aq})] = -10.3 \pm 0.2$ [20]. Efurud *et al.* [21] investigated the solubility of PuO₂(am, hydr.) in Yucca Mountain groundwaters (pH 6–8.5). The authors also assumed that the concentrations in the range of $\log [\text{Pu(IV)}] = -7.3$ to -8.5 , measured after 4 nm filtration, include contribution from small colloids.

The high solubility observed in 4.5 M MgCl₂ due to the formation of pseudocolloids Th(IV)·Mg₂(OH)₃Cl·4H₂O (coll) has not to be expected in real systems where, contrary to the present laboratory experiments, the ratio of solution volume and solid magnesium hydroxide/hydroxychloride is very small so that sorption of Th(IV) onto solid (immobile) magnesium hydroxychloride will prevail over sorption onto (mobile) colloids. In this context it must also be emphasised that An(IV) eigencolloids, which cause relatively high solubilities, also show a high tendency towards sorption onto glass and mineral surfaces.

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