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Solubility measurements and sorption studies of thorium in cement pore water

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Abstract

Solubility experiments and sorption studies were carried out with microcrystalline ThO_2 and alkaline cement pore waters. For fresh pore water, a solubility of 10^{-9} M was found and for aged (portlandite, equilibrated) pore waters, 10^{-10} M, which is expected in aqueous systems with elevated pH-values. Sorption experiments were carried out at cement to pore water ratios of 0.5 g/l, 5 g/l and 50 g/l with fresh and aged cement pore waters. With aged pore water the thorium-concentration in the aqueous solution was below the detection limit of 0.01 μg/l thorium for the experiments using 5 g/l and 50 g/l, which resulted in a lower limit for the k_D-values of >48 m^3/kg and >4.8 m^3/kg, respectively. For the cement to pore water ratio of 0.5 g/l, the k_D-value was 83.31±0.04 m^3/kg. With fresh cement pore water the k_D-values for cement to pore water ratios of 5 g/l and 50 g/l were again below the detection limit and were about one order of magnitude smaller than for aged pore waters, i.e. >3.42 m^3/kg and >0.342 m^3/kg, respectively, and 19.5±0.6 m^3/kg for the cement to pore water ratio of 0.5 g/l. © 1998 Elsevier Science S.A.

Keywords: Cement; Pore water; Thorium; Solubility; Sorption

1. Introduction

For each ton of uranium burnt to produce 33 000 MWd, about 10 kg of actinides are produced by neutron capture followed by β-decay. Since the actinide isotopes produced have a very long lifetime and a high radiotoxicity, they are of major concern in the environment. Many studies have been performed to investigate the behaviour of actinide elements [1–3]. Most of these studies have focused on the solubility [4–6] and sorption behaviour [7–12] of actinides in natural waters, and the surrounding minerals.

Thorium is a naturally occurring actinide element which has a very stable tetravalent oxidation state, and can be used as an analogue for other tetravalent actinides. The only common natural thorium isotope is ^{232}Th, but ^{230}Th and ^{228}Th can also be found as radiogenic decay products. In sea water, a solubility of about 4.3×10^{-13} M has been found for thorium, with ThO_2 as the solubility-limiting solid [2]. However, earlier studies have found much higher solubilities in lakes with rather high pH-values [12,16,17]. This is due to the high concentration of carbonate in these waters and the formation of mixed thorium–hydroxo–carbonate complexes as well as thorium carbonate complexes [18–20].

This study concentrates on the interaction of the actinide element thorium with cement pore water, since cement is being evaluated as a possible waste matrix, container material, or engineered barrier by ANDRA (Agence Nationale pour la Gestion des Déchets Radioactifs, France). Cement pore waters are known to have pH-values in the range of 12.4 to 13.5 [21]. Due to their high $Ca(OH)_2$ content, little free carbonate is present in these waters, and a solubility lower than that in carbonate-rich waters is expected. Thorium shows a strong tendency to hydrolyze, which results in the formation of mono- and polynuclear hydrolysis products of Th^{4+}. In alkaline waters thorium is expected to form mainly $Th(OH)_4$ [12], and for pH values greater than 4 the solubility of thorium is about $10^{-9.5}$ M [22], depending on the crystallinity of the solubility-limiting solid. Besides the solubility of tetravalent thorium, its sorption behavior is also of interest, since it might have an influence on its mobility. Several investigations were already carried out to study the sorption behavior of thorium in the surrounding matrix from aqueous solutions [8–11]. With increasing pH value of the aqueous phase, the sorption tendency of thorium increases, which is also due to the hydrolysis of thorium, and the

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Table 1
k_D-values (m^3/kg) for the sorption behavior of thorium obtained in earlier experiments

Solid phase	Aqueous phase	Time	k_D-value (m^3/kg)	Reference
Concrete: 32% CLC 45 cement 68% sand	distilled water equilibrated with concrete, pH = 12.3	48 h	≥1000	[13]
Standard Portland cement	pore water, pH = 13.4	90 d	6	[14]
Standard Portland cement, French mixture	pore water, pH = 13.2	100 d	5	[15]

preferred sorption of hydrolysed species on surfaces [12]. Table 1 shows k_D-values measured in earlier experiments under similar conditions.

2. Experimental

2.1. Chemicals and plasticware

All solutions were prepared using Millipore water. The uranium and thorium content of this water was below the detection limit of the ICP–MS.

Chemicals for the preparation of artificial ground water were obtained from Fluka, Switzerland, and were of MicroSelect quality.

Polyethylene or polypropylene containers were used to minimise sorption on surfaces and contamination by naturally occurring thorium, and were rinsed with concentrated nitric acid of Suprapur quality (Merck), followed by rinsing with Millipore water.

Microcrystalline thorium oxide/hydroxide was prepared according to Östhols [19].

2.2. Instrumentation

ICP–MS measurements were performed at SGAB (Svensk Grundämnesanalys AB) in Luleå, Sweden, detection limits are 0.01 μg/l, i.e. <43.1 pM Th and <42 pM U.

The pH-values were measured using a Radiometer Copenhagen PHM 64 Research pH Meter, with a pHG211 glass electrode for measurements at high pH-values in combination with a REF201 reference electrode. Calibration of the system was performed daily before every measurement and immediately after the measurement against 0.1 M NaOH and pH 10 buffer solution. The alkaline error for the glass electrode is approximately 0.03 pH at pH 13 in 0.1 M Na^+. This results in an estimated error of <0.05 pH for the measurements.

2.3. Cement samples

ANDRA has specified a hydraulic cement based on a simple Portland cement type, which contains at least 97% clinker. CPA 55 HTS (ciment Portland artificiel, haute teneur en silice) has been used in studies at the Commissariat à l'Energie Atomique (CEA) and is a French sulphate-resistant cement with a high silica content. To be comparable to the experiments performed at CEA, CEM I 42.5 HS cement was used, which is as close as possible to the properties to CPA 55 HTS.

Table 2 shows the chemical composition and characteristics of CEM I 42.5 HS.

Two different size fractions of the cement were used: the size fraction <0.01 mm was used to prepare fresh cement pore water (FPW) and a fraction 0.25–0.5 mm was used for the preparation of aged cement pore water (APW).

In the sorption studies the size fraction 0.25–0.5 mm was used.

Table 2
Chemical composition and other characteristics of CEM I 42.5 HS (*C = CaO, A = Al_2O_3, S = SiO_2, F = Fe_2O_3)

Matrix	%	Clinkers	%	Other properties	Value
SiO_2	19.4%	C_3A	1.8%	density	3.15 g/cm^3
Al_2O_3	4.4%	C_3S	64.5%	specific surface area	3900 cm^2/g
Fe_2O_3	6.1%	C_2S	20.0%	resistance towards compression	30 MPa (2 d) 52.8 MPa (28 d)
CaO	62.1%	C_4AF	5.3%	expansion	1.3 mm
Na_2O	0.5%	$CaSO_4$	6–7%	heat of hydration	150 J/g
K_2O	0.85%				
SO_3	2.7%				
Cl	0.04%				

Table 3
Composition of the artificial ground water (AGW)

Salt	Concentration (M)
$NaHCO_3$	5.7×10^{-4}
NaCl	3.3×10^{-2}
Na_2SO_4	3.1×10^{-2}
$CaSO_4$	5.8×10^{-3}
$MgSO_4$	5.2×10^{-3}
K_2SO_4	1.3×10^{-4}

2.4. Preparation of artificial ground water

For all sorption and solubility experiments an artificial groundwater was used (AGW). The composition of the AGW is as shown in Table 3.

Three batches of the AGW were prepared, the measured pH–values ranged from 7.68 to 8.06 in good agreement with a calculated pH–value of 7.94±0.15.

2.5. Preparation of cement pore waters

For the preparation of FPW, 50 g, 100 g and 250 g of CEM I 42.5 HS size fraction <0.01 mm was mixed with 50, 100, and 250 g of AGW. After 6 days the FPW reached a stable pH-value of 13.22.

For comparison the mixture was then either filtered through 0.025-μm or 0.45-μm filters or centrifuged at 12 000*g* for 10 min. The chemical composition of FPW's was determined by ICP–MS and showed a constant composition for all three waters. The thorium and uranium contents are shown in Table 4.

For all following experiments filtration through 0.45-μm filters was chosen.

APW was prepared by leaching the cement (fraction size 0.25–0.5 μm) with AGW. A cement to AGW ratio of 1 to 5 was used. The supernatant was removed daily, the pH-value measured, and fresh AGW was added. A stable pH value of 12.45 was reached after about 1 month.

To obtain a defined composition and a good reproducibility the APW for the sorption experiments was simulated by saturating the AGW with $Ca(OH)_2$ (pH= 12.5).

Table 4
Determination of thorium- and uranium concentration in fresh cement pore-water samples with ICP–MS analysis

Sample	[Th] M	[U] M
Filtration with 0.025-μm filter	$9.3\pm1.0\times10^{-11}$	$1.5\pm0.4\times10^{-10}$
Filtration with 0.45-μm filter	$1.1\pm0.2\times10^{-11}$	$1.5\pm0.4\times10^{-10}$
Centrifugation at 12 000 g	$1.9\pm0.1\times10^{-10}$	$2.2\pm0.6\times10^{-10}$
AGW	$<4.31\times10^{-11}$	$7.2\pm3.9\times10^{-11}$
Millipore water	$<4.31\times10^{-11}$	$<4.2\times10^{-11}$

Separation of the solid and the liquid phase was obtained using 0.45-μm and 0.025-μm filters, and a centrifuge rotating at 12 000*g*. Analysis of AGW and Millipore water for comparison.

2.6. Solubility experiments

A small amount of the microcrystalline ThO_2 was contacted with 9 ml APW or FPW at 22°C and 55°C in polyethylene test tubes closed with screw caps and sealed with paraffin film. A constant temperature was obtained by using water baths.

Two series of experiments were performed, a short time experiment, where samples were taken after 5 h and after 120 h, and a long term experiment with sampling after 4, 11, 18, and 25 days. For reference one test tube was kept closed for the whole period of time (25 days) and only one sample was taken.

2.7. Sorption experiments

Sorption experiments were performed by contacting aged cement (size fraction 0.25–0.5 mm) with pore waters containing thorium of a known concentration at different solid/pore water ratios (0.5 g/l, 5 g/l, and 50 g/l). Again, the test tubes were closed with screw caps and sealed with paraffin film. The temperature was held constant at 22°C, and samples were taken after 5, 120 and 480 h.

The k_D-values were calculated from the concentration of thorium in the initial solution C_i, and of the solution after separation of the phases, C_f:

$$k_D = [(C_i/C_f) - 1]V/m\,[m^3/kg]$$

3. Results and discussion

3.1. Solubility experiments

During the short-time experiment, the solubility of thorium was found to be in the range of 3.8×10^{-9} M to 5.3×10^{-7} M.

In the second, long-term experiment, the solubilities of thorium found were considerably lower: for the experiments performed with FPW a solubility of about 10^{-9} M, with APW about 10^{-10} M was found (Fig. 1).

Table 5 compares the experimentally obtained solubilities and solubilities calculated using the MIN_SURF code.

3.2. Sorption experiments

The sorption experiments performed with FPW indicated an increasing k_D-value from 5 to 480 h for all solid/solution ratios. After 480 h the thorium concentration in the supernatant of the experiments performed at solid/solution ratios of 5 g/l and 50 g/l was below the detection limit indicating complete sorption of thorium.

APW seems to have a similar effect on the sorption, in these experiments, the thorium concentration in the pore water was below the detection limit for the experiments

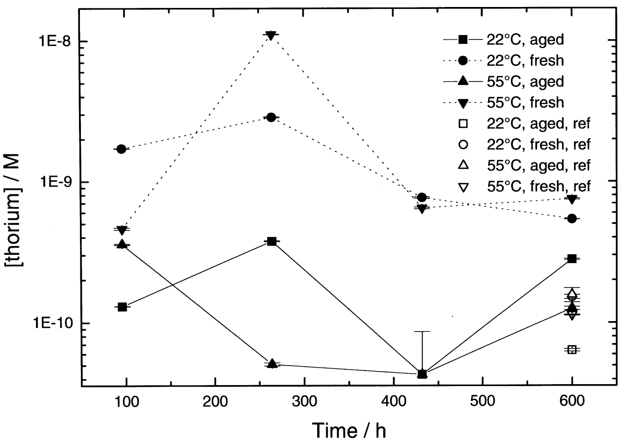

Fig. 1. Solubility of thorium in aged and fresh cement pore water at 22°C and 55°C.

performed at solid/solution ratios of 5 g/l and 50 g/l, indicating, that sorption of thorium on cement did take place. For a solid/solution ratio of 0.5 g/l sorption values of 98% were found for the whole experiment.

Table 6 shows the obtained k_D-values.

Table 6
k_D-values (m^3/kg) for the sorption of thorium on fresh and aged cement pore-water after 480 h

Solid/solution ratio	k_D(m^3/kg), APW	k_D(m^3/kg), FPW
0.5 g/l	83.31±0.04	19.5±0.6
5 g/l	>48	>3.42
50 g/l	>4.8	>0.342

For solid/solution ratios of 5 g/l and 50 g/l, the k_D is determined by the detection limit.

4. Conclusion

Both FPW and APW have pH-values greater than 12. In this carbonate-free environment, tetravalent thorium is expected to have a solubility of about $10^{-9.5}$ M, depending on the crystallinity of the solid phase. The first solubility experiment performed with FPW and APW, gave a solubility between 10^{-7} and 10^{-8} M, in contrast to the second series of experiments, which resulted in solubilities between 10^{-9} and 10^{-10} M, which are in complete agreement with the expected values and the values obtained in the model calculations. X-ray powder diffraction measurements showed, that the difference in the two experiments cannot be explained by an increased crystallinity of the thorium compound in the second experiment.

The sorption experiments indicated a high sorption tendency of thorium, although the k_D-values obtained in the experiments with APW are about one order of magnitude higher, than in the experiments performed with FPW. Again, these results are consistent with earlier experiments, which indicated, that tetravalent thorium sorbs strongly on surfaces, if the aqueous medium has a high pH-value and causes hydrolysis.

Thermodynamic calculations have shown, that FPW contains about ten times more dissolved carbonate (~8×10^{-5} M), than APW (~7×10^{-6} M). This may explain both, the higher thorium solubility in FPW, and the higher k_D-values for the sorption from APW on cement.

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Table 5
Solubility of microcrystalline thorium in cement pore waters: comparison of measured and calculated values

Pore water	Solubility (M)	Solubilities calculated with MIN_SURF (M)[a]
Fresh, 22°C	$1.36\times10^{-10}\pm4\times10^{-13}$	2.5×10^{-10} (pH=13.1, 25°C)
Aged, 22°C	$5.49\times10^{-10}\pm4\times10^{-13}$	2.5×10^{-10} (pH=12.45, 25°C)
Fresh, 55°C	$9.37\times10^{-11}\pm1.1\times10^{-12}$	1.8×10^{-10} (pH=13.1, 50°C)
Aged, 55°C	$1.26\times10^{-10}\pm7\times10^{-13}$	1.8×10^{-10} (pH=12.45, 50°C)

[a] Using the respective enthalphy data from the MIN_SURF data compilation [23].

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