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Sorption and coprecipitation of trace concentrations of thorium with various minerals under conditions simulating an acid uranium mill effluent environment [☆]

Edward R. Landa ^a, Anh H. Le ^b, Rudy L. Luck ^{c,*}, Philip J. Yeich ^{c,1}^a *US Geological Survey, 430 National Center, Reston, VA 22092, USA*^b *Naval Surface Warfare Center/Dahlgren Division, Materials Technology Branch R31, Silver Spring, MD 20903-5640, USA*^c *Department of Chemistry, The American University, 4400 Massachusetts Avenue NW, Washington, DC 20016-8014, USA*

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Abstract

Sorption of thorium by pre-existing crystals of anglesite (PbSO_4), apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$), barite (BaSO_4), bentonite ($\text{Na}_{0.7}\text{Al}_{3.3}\text{Mg}_{0.7}\text{Si}_8\text{O}_{20}(\text{OH})_4$), celestite (SrSO_4), fluorite (CaF_2), galena (PbS), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hematite (Fe_2O_3), jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), quartz (SiO_2) and sodium feldspar ($\text{NaAlSi}_3\text{O}_8$) was studied under conditions that simulate an acidic uranium mill effluent environment. Up to 100% removal of trace quantities of thorium (approx. 1.00 ppm in 0.01 N H_2SO_4) from solution occurred within 3 h with fluorite and within 48 h in the case of bentonite. Quartz, jarosite, hematite, sodium feldspar, gypsum and galena removed less than 15% of the thorium from solution. In the coprecipitation studies, barite, anglesite, gypsum and celestite were formed in the presence of thorium (approx. 1.00 ppm). Approximately all of the thorium present in solution coprecipitated with barite and celestite; 95% coprecipitated with anglesite and less than 5% with gypsum under similar conditions. When jarosite was precipitated in the presence of thorium, a significant amount of thorium (78%) was incorporated in the precipitate.

Keywords: Sorption; Coprecipitation; Thorium complexes; Mineral complexes

1. Introduction

Uranium-bearing ores are mined and milled as the first step in the nuclear fuel cycle. Milling consists of the mechanical and chemical processes that concentrate the uranium fraction from the ore. In conventional uranium milling, the ore is crushed and leached with either alkali or acid. Ores with limestone contents greater than 15% are generally leached under alkaline conditions using a mixture of Na_2CO_3 and NaHCO_3 , whereas other ores are leached with H_2SO_4 . The uranium extracted by the leaching solution is concentrated by solvent extraction or ion exchange, and subsequent precipitation (generally with NH_3) of a uranium concentrate (80–85% U_3O_8) which is referred to as 'yellow

cake'. The leached ore residues, 'tailings', are slurried with mill-waste solutions and pumped to an earthen retention pond. As the ores being exploited are typically low-grade, essentially all of the tonnage of ore processed at the mill is disposed of as tailings. The present inventory of uranium mill tailings (UMT) in the United States is about 200 million tons. Although about 90–95% of the uranium in the ore is extracted in the milling process, most of the uranium-daughter products remain with the tailings, and, this constitutes a low-level radioactive waste material.

The removal of solubilized radionuclides from solution by ore components or reaction products, during the milling of uranium ores may have both economic and environmental consequences. ^{230}Th extraction from sandstone ores during H_2SO_4 milling is typically about 90% [1,2]. Yet the ^{230}Th concentrations of samples taken at tailings piles are typically far less depleted in ^{230}Th (assuming initial secular equilibrium in the ore and using the ^{226}Ra concentration as a conservative

[☆] Dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

* Corresponding author.

¹ Deceased.

tracer of the initial uranium sales inventory) than a 90% extraction would produce [3–5]. It would appear that upon ‘aging’ in the tailings pond, the solubilized ^{230}Th becomes reassociated with the tailings solid. It is obvious that an understanding of the interaction of these radioactive wastes with common minerals is necessary in order to predict their mobility in the environment around disposal sites. In particular, the mobility of ^{230}Th is of importance because of the long half-life (7.7×10^4 years) and it is the source of other ^{238}U -decay series radionuclides, including ^{226}Ra ($t_{1/2} = 1602$ years) and ^{222}Rn ($t_{1/2} = 3.8$ days).

We report here a study comprised of two parts: a sorption section and a coprecipitation section. The conditions were chosen to simulate a sulfuric acid leach uranium mill effluent environment, and minerals chosen commonly are present in the uranium ore or at the disposal area or precipitate during the milling/waste disposal process. In the sorption section, anglesite (PbSO_4), apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$), barite (BaSO_4), bentonite (idealized formula $\text{Na}_{0.7}\text{Al}_{3.3}\text{Mg}_{0.7}\text{Si}_8\text{O}_{20}(\text{OH})_4$), celestite (SrSO_4), fluorite (CaF_2), galena (PbS), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hematite (Fe_2O_3), jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), kaolinite (idealized formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), quartz (SiO_2) and sodium feldspar ($\text{NaAlSi}_3\text{O}_8$) were individually placed in a solution of 0.01 N H_2SO_4 (pH 2) and 1.00 ppm Th (as $\text{Th}(\text{NO}_3)_4$ spiked with ^{234}Th) at 20 °C and sampled periodically over 30 days in order to determine Th uptake by the mineral. In the coprecipitation section, anglesite, barite, celestite, gypsum and jarosite were precipitated in a sulfuric acid solution (pH 2) and Th concentration of 1.00 ppm. In this case, the amount of Th removed from solution was determined initially and over a period of several weeks.

2. Experimental

The concentration of ^{232}Th carrier solution was adjusted using reagent grade $\text{Th}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Mallinckrodt 8170KADV). ^{234}Th was chosen as a tracer because it decays by beta emission which makes its detection by liquid scintillation analysis (LSA) very convenient and the short half-life (of 24 days) renders facile the disposal of reactant solutions. The ^{234}Th tracer was extracted from $\text{UO}_2(\text{NO}_3) \cdot 6\text{H}_2\text{O}$ (Mallinckrodt 8640KCAP) by ion exchange using the following method. Two grams of uranyl nitrate dissolved in 20 ml 8 N HCl were added to a 20 ml column containing Dowex 1X-8 ion exchange resin. The Th was eluted using three 20 ml portions of 8 N HCl while U is retained by the column. The eluent was then dried, and the ^{234}Th was brought up in 30 ml 0.01 N H_2SO_4 . The ^{234}Th solution was tested for U contamination using kinetic phosphorescence analysis (KPA) [6]. The ^{234}Th solution was used if the U concentration was below the KPA detection limit of 0.01 ng/ml. The tracer solution was also tested for radioactive contaminants by measuring by LSA the activity decrease over time. In every case the decay followed that of the theoretical decay for ^{234}Th (i.e. $t_{1/2} = 24$ days) and this suggests that the solutions consisted of that radionuclide.

2.1. Sorption studies

Minerals were weighed and placed in 50 ml poly-allymer centrifuge tubes. Table 1 lists the mineral origin or manufacturer and surface area (before experiment). In all cases 0.5000 ± 0.0006 g (one sigma) of mineral was used with the exception of apatite in which 0.2000 ± 0.0001 g (one sigma) was used due to the very

Table 1
Origin and surface area of the minerals

Mineral	Origin/manufacturer, lot no.	Surface area (initial) (m^2/g)
Anglesite, PbSO_4	synthesized	0.834
Apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	Fisher C-127, 851193	N/A
Barite, BaSO_4	Baker 1030-1, 528087 and 855838	6.59
Bentonite, $\text{Na}_{0.7}\text{Al}_{3.3}\text{Mg}_{0.7}\text{Si}_8\text{O}_{20}(\text{OH})_4^*$	Fisher B-235, 793684	24.00
Celestite, SrSO_4	synthesized	N/A
Fluorite, CaF_2	Fisher C-89, 783671	N/A
Galena, PbS	Alfa 88284, B08H	0.442
Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Fisher C-140, 720264	7.29
Hematite, Fe_2O_3	Baker 1-2024, 024405	6.991
Jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$	synthesized	1.35
Kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}^*$	Fisher K-5, 856142	8.54
Quartz, SiO_2	Ottawa sand (E.M. Science)	0.400
Sodium feldspar, $\text{NaAlSi}_3\text{O}_8$	NBS 99a, 583804	1.34

* Idealized formula

low bulk density of this material. 20.00 ml of ^{232}Th solution and 1.00 ml of ^{234}Th solution (both 0.01 N H_2SO_4) were added to the tubes containing each mineral giving an initial Th concentration of 1.00 ppm and an initial pH around 2. Reference tubes containing the same solution but with no mineral were also prepared. The tubes were immediately placed in a constant temperature shaker bath (155 rpm, 20.0 °C). Tubes were oriented horizontally in the shaker to ensure adequate mixing. The quantity of tubes prepared were sufficient to enable sampling of two tubes at the sampling points of 1 day, 1 week, 2 weeks and 4 weeks. The average %Th remaining in solution based on the two tubes is reported. Some studies were conducted keeping the pH constant at 2 by means of periodic monitoring and adjustment.

Sampling consisted of first centrifuging for 10 min at 8000 rpm, decanting and then filtering using a syringe mounted with a 0.2 μm pore size cellulose acetate filter. Two 1 ml aliquots of liquid were analyzed by LSA using 20 ml plastic scintillation vials and 14.0 ml Biosafe II (RPI) liquid scintillation cocktail. The pH of the remaining liquid was then measured. Data are reported in Table 2. The solids were air dried for 2–5 days and then placed in an oven at approximately 50 °C. Powder XRD was performed on selected solids to determine the mineral phases that were present. A Siemens D-500 diffractometer with a copper anode tube was used. Samples were ground using a mortar and pestle both made of alumina to a particle size approximately less than 20 μm . The power was then sprinkled on a single-crystal quartz zero background slide which had been pre-coated with a thin layer of petroleum jelly. Diffraction intensity was measured by a position sensitive detector on a Siemens θ - θ stationary sample diffractometer using Cu $K\alpha$ radiation at 30 mA and 40 kV in the angular range of 2θ from 10 to 70°, scanned at 2°/min. The powder diffraction spectra were compared to a NIST Crystal Data File (JCPDS) in order to identify the samples. The surface area of each mineral before and after experiment was determined by the one point B.E.T. N_2 gas adsorption technique [7,8]. In some cases scanning electron micrographs were made of the mineral after the experiment to give information on the surface characteristics. Occasionally, at the end of the sorption period, the solid was dissolved and the solution analyzed for ^{234}Th by LSA (as above) in order to verify if the total amount of ^{234}Th (i.e. associated with the solid and remaining in solution) was equal to the amount used initially. Invariably, there was good agreement with these two data.

2.2. Coprecipitation studies

For comparative purposes it was decided that the final conditions of the solution and the amount of solid

Table 2
Sorption of thorium with minerals

Mineral	Time (days)	^{234}Th remaining in solution ^a (%)	Final pH
Quartz	1	97.15	2.26
	7	95.99	2.28
	14	98.88	2.29
	30	97.95	2.31
Jarosite	1	97.07	2.24
	7	95.41	2.25
	14	95.88	2.25
	30	96.36	2.24
Gypsum	1	97.60	2.60
	7	95.29	2.57
	14	98.43	2.61
	30	95.00	2.60
Anglesite	1	89.98	2.27
	7	87.38	2.29
	14	86.86	2.25
	30	86.77	2.28
Barite	1	0.43	2.31
	7	0.34	2.31
	14	0.19	2.29
	30	0.23	2.31
Celestite	1	72.58	2.00
	7	66.74	2.01
	14	64.47	2.01
	30	62.23	2.01
Galena	1	73.51	2.40
	7	64.72	2.46
	14	59.40	2.57
	30	0.02	5.16
Hematite	1	86.50	2.27
	7	92.29	2.35
	14	93.29	2.31
	30	94.69	2.35
Sodium feldspar	1	75.47	2.54
	7	73.48	2.69
	14	66.29	2.75
	30	58.62	2.88
Kaolinite	1	36.28	2.35
	7	38.92	2.41
	14	38.49	2.42
	30	37.40	2.44
Bentonite	1	1.64	2.76
	8	1.32	2.93
	14	1.56	2.97
	30	1.25	3.04
Apatite	1	0.12	4.80
	7	0.14	N/A
	14	0.22	4.81
	30	0.49	4.75
Fluorite	1	0.06	2.06
	8	0.21	2.15
	14	0.33	2.14
	30	0.52	2.17

^a Values reported are averages of duplicate samples.

present should be as similar as possible to the conditions in the sorption phase of the study. In order to produce gypsum, celestite and barite, solutions were first prepared consisting of CaCl_2 , SrCl_2 and BaCl_2 , respectively, dissolved in 10 ml of 0.01 N HCl (solution A). For anglesite, $\text{Pb}(\text{NO}_3)_2$ was dissolved in 10 ml of 0.01 N

Table 3
Amount of material used keeping the theoretical yield of mineral at 0.5 g

Mineral	Solution A	Solution B in 0.01 N H ₂ SO ₄
Gypsum, CaSO ₄ ·2H ₂ O	0.322 g CaCl ₂ in 10 ml 0.01 N HCl	0.412 g Na ₂ SO ₄
Celestite, SrSO ₄	0.725 g SrCl ₂ ·6H ₂ O in 10 ml 0.01 N HCl	0.386 g Na ₂ SO ₄
Barite, BaSO ₄	0.523 g BaCl ₂ ·2H ₂ O in 10 ml 0.01 N HCl	0.304 g Na ₂ SO ₄
Anglesite, PbSO ₄	0.546 g Pb(NO ₃) ₂ in 10 ml 0.01 N HNO ₃	0.324 g Na ₂ SO ₄

Table 4
Coprecipitation of thorium with minerals

Mineral pH(i)=2.00 ^a T=21 °C ^b	[Th] (ppm)	Th remaining in solution following precipitation ^c (%)	Th remaining in solution at t=39 days ^c (%)
Gypsum CaSO ₄ ·2H ₂ O	1.00	95.12	94.61
Anglesite PbSO ₄	1.00	5.18	70.44
Barite BaSO ₄	1.00	0.26	0.54
Celestite SrSO ₄	1.00	0.81	1.79 (36 days)
Jarosite KFe ₃ (SO ₄) ₂ (OH) ₆ t=20 °C	1.00		22.1 (30 days)
Jarosite KFe ₃ (SO ₄) ₂ (OH) ₆ t=40 °C	1.00		33.9 (30 days)

^a This refers to the initial pH of the solution.

^b Room temperature.

^c Values reported are averages of duplicate samples.

HNO₃ (solution A). Another solution (solution B) was made of Na₂SO₄ in 11 ml 0.01 N H₂SO₄ and 1.00 ppm Th with ²³⁴Th tracer. The quantities of reagents used keeping the theoretical yield of the alkaline earth sulfate salt constant at 0.500 g are given in Table 3. Solution A was added either continuously to solution B at a rate of approximately 0.3 ml/min or dropwise using an additional funnel while, in both cases, stirring with a bar magnet at a rate sufficient to keep the precipitate suspended. Stirring of the suspension was continued for approximately 5 min after addition was completed. Some of the samples were placed in a constant temperature shaker bath (155 rpm, 20 °C) to be sampled later, while others were analyzed immediately. The same sampling procedure as above in the sorption studies was followed. Corrections for the slight differences in total volume in each solution were made by determining the total mass and density of the liquid.

In all cases, after sampling and drying (as above) the yield of the solid was determined.

In the case of jarosite coprecipitation, 1.96 g of Fe₂(SO₄)₃·5H₂O and 2.06 g K₂SO₄ were dissolved in deionized water following the published procedure [9]. The pH was adjusted to 2.0 using H₂SO₄, a Th solution containing ²³²Th and ²³⁴Th tracer was added and the total volume brought to 21.00 ml giving [Th]=1.00 ppm. Approximately 0.005 g of preformed jarosite (previously synthesized) was added as a seed to ensure jarosite formation and greater yield. The solution was shaken at a constant temperature for a minimum of 24 h and a maximum of 30 days. Again, the same sampling procedure as above was followed. The solids were dried and the yield determined. The results for the coprecipitation studies are listed in Table 4.

At the end of a sorption or coprecipitation experiment, surface area measurements and powder XRD (in order to verify the integrity of the sample) were conducted.

3. Results and discussion

3.1. Sorption studies

As is evident from the results tabulated in Table 2, quartz, jarosite and gypsum showed very little Th uptake with over 95% of the Th remaining in solution after 30 days. Anglesite removed 13% of the Th from solution in two weeks with no further removal thereafter. Kolthoff and Rosenblum [10] had reported that the rate of Th adsorption is dependent on the aging of PbSO₄. They found that freshly formed precipitate took up 96% of the Th from solution in 3 min while well-digested more perfect crystals took up only 3% of the Th. They attributed the large Th uptake of fresh precipitate to a large surface area due to very porous crystals and to some degree incorporation of Th into the crystal structure. In a subsequent publication, Kolthoff and Rosenblum [11] also reported that Th is distributed homogeneously throughout the PbSO₄ after 2–3 h of contact with crystals aged 1 and 40 min, respectively.

Barite took over 99% of the Th out of solution with a final pH of 2.3 (Table 2). In a separate experiment, with the pH of the solution maintained at 2.0, a similar uptake was noted. These results are supported by the work of Sill and Willis [12] who found that Th was readily taken up by preformed BaSO₄ crystals. It is interesting that celestite took up only 38% (pH 2.0) in 30 days. Since barite and celestite are chemically very similar and form a continuous solid solution from zero to 100% Ba–Sr substitution, [13], it was anticipated that Th would interact similarly with these minerals. The solubility of the sulfate minerals (based on a comparison of their solubility product constants [14]) used in this study from most soluble to least is: gypsum, anglesite, celestite, barite and it is interesting that the order of degree of Th sorption increases with decreasing solubility.

Galena gradually took up Th and after 30 days no Th remained in solution. There was also an increase in the pH noted from 2.40 to 5.16. Release of S^{2-} ions from the galena into solution with formation of H_2S may be responsible for the increase in pH noted. It is then possible that anglesite ($PbSO_4$) formed on the surface of the galena and, that the Th was incorporated into the anglesite structure; this will be the subject of further study.

Hematite was found to initially take up 13% of the Th at pH 2.27 and to release some of the Th back into solution (5% Th uptake after 30 days). It is intriguing that if the pH of the solution is kept at 2.00 by daily monitoring and adjustment, hematite was found not to absorb Th from solution, and, it is possible that the greater concentration of H^+ ions may be responsible for this effect.

Sodium feldspar gradually took up 41% of the Th from solution over 30 days. Here again it is conceivable that conversion of the mineral is taking place under our conditions and perhaps the sodium feldspar is being converted to kaolinite in the sulfuric acid solution. At a pH of 2.35, kaolinite took up just over 60% of the Th in 1 day and this changed very little over 30 days (Table 2). In a different study keeping the pH at 2.00, kaolinite absorbed only 21% of the Th from solution in 30 days. Bentonite removed approximately 99% of the Th from solution in 1 day, and, the Th remained associated with the clay.

In the cases of apatite and fluorite, Th was taken entirely and very quickly out of solution and remained associated with the mineral over the entire 30 days. An increase in the pH to ~ 4.8 was observed for apatite. This could be rationalized in terms of acid hydrolysis of the OH^- group in apatite. Very insoluble species in thorium hydrogenphosphate ($Th(HPO_4)_2$) [15] and thorium fluoride (ThF_4) (for apatite and fluorite, respectively) are most likely being formed on the mineral and/or container surfaces. In a previous study, Gauglitz et al. [16] reported that apatite removed Th from a salt brine solution and attributed this to formation of a thorium phosphate precipitate. In a separate experiment here, 0.05 g of NaF was added to 21 ml of 0.01 N H_2SO_4 and $[Th] = 1.00$ ppm with no mineral present, and all the Th was removed from solution by first precipitation and subsequent filtration thus supporting the idea of the formation of an insoluble ThF_4 precipitate.

3.2. Coprecipitation studies

As the coprecipitation studies data in Table 4 based on Table 3 concentrations indicate, only about 5% of the Th coprecipitated with gypsum; this did not change with equilibration time. With barite and celestite, essentially all of the Th was coprecipitated with the

mineral and after 30 days was still associated with the solid. Coprecipitation of Th with $BaSO_4$ has been well documented [12,17]. Indeed it was suggested that $K_2Ba[Th(SO_4)_4]$ is formed in the presence of K^+ ions [17]. In our study K^+ ions were not present but Na^+ ions were present, and it is reasonable to assume that Na^+ could replace K^+ in the structure that Ambe and Lieser proposed [17].

As was previously discussed, anglesite, in the sorption section, took a relatively small amount of Th from solution, but in the coprecipitation section Th was readily taken out of solution when anglesite was precipitated, see Table 4. Interestingly enough, over time the Th was released back into solution. Sorption and coprecipitation are considered to be related such that in order for coprecipitation to occur, sorption to the surface of a forming solid occurs and the adsorbed species is then incorporated into the crystal structure. As time passes the crystal structure is perfected through a continuous dissolution/precipitation process and any species which causes a crystal to be unstable thermodynamically is typically released back into solution [18]. It is reasonable to attribute our coprecipitation results with anglesite to this reported phenomenon.

The ionic radii for the ions involved are given in Table 5 [14]. Based only on an ionic radii one would probably expect Th^{4+} to readily substitute into the gypsum structure. This does not happen. Th substitutes into barite and celestite forming what seems to be fairly stable structures even though the differences in ionic radii are considerable. The accepted limit for the formation of mixed crystals is 15% [16]. Note that although the ionic radius of Pb^{2+} is slightly closer to Th^{4+} than Ba, the Th/ $PbSO_4$ interaction is not as favored as that of Th/ $BaSO_4$, based upon our coprecipitation studies.

Finally, in the case of coprecipitation with jarosite, 78% of the Th ions were removed from solution at 20 °C and 66% at 40 °C (Table 4). This is in contrast to the sorption study where jarosite was found to effect very little Th uptake, as listed in Table 2. It appears as if incorporation of Th ions into the structure result as the mineral forms in solution. Finally, it appears that at higher temperatures, increased mineral dissolution may allow for the release of Th back into the solution media.

Table 5
Ionic radii for ions involved in coprecipitation studies [14]

Ion	Radius (Å)
Th^{4+}	1.02
Ca^{2+}	0.99
Sr^{2+}	1.12
Pb^{2+}	1.20
Ba^{2+}	1.34
Na^+	0.97
K^+	1.33

4. Conclusions

A wide variety of sorption and coprecipitation studies were carried out designed to investigate the removal of Th from solution in the presence of minerals. Essentially, fluorite and bentonite removed nearly all of the Th ions present in solution and the minerals quartz, jarosite, hematite, sodium feldspar, gypsum and galena removed less than 15%. Coprecipitation studies revealed that all of the thorium present in solution coprecipitated with barite and celestite, 95% precipitated with anglesite and less than 5% coprecipitated with gypsum under similar conditions. Release to solution of Th previously removed by PbSO_4 coprecipitation was noted over the course of a 39 day period. Finally jarosite coprecipitation resulted in a significant amount of thorium being removed from solution. Some of the studies produced interesting results and these (e.g. effect of pH with hematite) will be the subject of further investigations in our laboratories.

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