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EFFECTS OF SOLUTION pH AND COMPLEXING REAGENTS ON THE DESORPTION OF RADIONUCLIDES IN SOIL

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Introduction

In contaminated soils, radionuclides such as uranium and/or thorium may be associated with different chemical species on soil surfaces or inside soil grains with consequent differences in leachability and mobility. Chemical species in contacting solutions can react with soil contaminants by dissolution, ion exchange, or complexation to release contaminants from the soil to the solution. It is important to understand the effect of chemical species in solution for investigating the distribution of uranium and thorium between the soil and the solution under desorption conditions. In this work, the effects of the solution pH and the complexing reagents on the desorption of uranium and thorium under saturated equilibrium conditions were investigated.

Experimental Methods

Three surface soils -- Hazelwood A, Hazelwood B, and Weldon Spring -- were sampled, air-dried, and sieved (< 2 mm). Soil properties measured on the prepared material were pH (1:1 in water), cation exchange capacity (CEC),[1] amount of organic carbon,[2] saturated moisture content,[3] and concentrations of uranium and thorium.[4]

A kinetic study was performed to search for the equilibrium contacting time for the subsequent saturated batch experiments. In the kinetic study, 5-g samples of soil were each agitated with 200 ml of contacting solution, laboratory distilled deionized water with a pH of 6.08, or a potassium dihydrogen phosphate (KH_2PO_4) buffer solution with a pH of 6.50 for 30 minutes, 2 hours, 2 days, and 7 days. The soil and the solution were then separated by centrifugation at 2,000 rpm for 30 minutes. Activities of uranium and thorium in the solution phase were measured by alpha-spectrometry.[4]

The effect of the solution pH on the uranium and thorium desorption under batch extraction was investigated by adjusting the solution pH of 1 molar sodium acetate (NaOAc) solution to 4.00, 5.60, and 8.00. The effects of the complexing reagents were investigated under equilibrium batch extraction with 0.1 molar sodium nitrate ($NaNO_3$), 0.1 molar sodium sulfate (Na_2SO_4), 0.1 molar sodium bicarbonate ($NaHCO_3$), 0.1 molar diethylenetriaminepentaacetic acid (DTPA), and 0.15g/200 ml humic acid with a pH of 8.00.

Results and Discussion

Properties of the experimental soils are listed in Table 1. The soils are moderately alkaline, which suggests the presence of free carbonate. Uranium and thorium concentration measurements are summarized in Table 2. At both the Weldon Spring and Hazelwood sites, uranium concentrations vary from 19.74 to 325 pCi/g soil. Concentrations of thorium-230 in Hazelwood soils (451 and 2,260 pCi/g soil) are much higher than in Weldon Spring soil (2.83 pCi/g soil).

Results of the kinetic study, which are given in Table 3, indicate that the fractions of uranium and thorium desorbed approached a constant value after two days of agitation. Therefore, two days contacting time was used for the subsequent batch experiments. In Table 4, the fractions of total uranium and thorium activity desorbed by 1 molar NaOAc solutions at a different solution pH and the related distribution coefficients are summarized. As can be seen, the desorption of uranium and thorium increases

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by lowering the pH of the contacting solution. At a low solution pH, the predominant species tend to be uranyl (UO_2^{+2}), thorium(IV) dihydroxide ($Th(OH)_2^{+2}$), and thorium(IV) monohydroxide ($Th(OH)^{+3}$), which allow complex formations of uranium and/or thorium to form complexes with acetate. At a high solution pH, important uranium and thorium species tend to be uranyl tricarbonate ($UO_2(CO_3)_3^{-4}$) and thorium(IV) tetrahydroxide ($Th(OH)_4^0$), which appear to resist complexation with acetate.

Fractions of total uranium and thorium activity desorbed by the complexing agents investigated and related empirical distribution coefficients are summarized in Table 5. The results indicate the following:

1. The 0.1 molar $NaNO_3$ and 0.1 molar Na_2SO_4 solutions were not effective desorption or solubilizing agents for uranium and thorium, possibly due to low complex stability.

2. The 0.1 molar $NaHCO_3$ with a pH of 8.00 desorbed or solubilized 38% to 62% of total uranium activity from soils, possibly by the complex formation of UO_2^{+2} and carbonate. Equilibrium constants[5] showed that magnesium ions (Mg^{+2}) and ferrous ions (Fe^{+2}) have strong tendencies to precipitate with hydroxide ions (OH^-), and that UO_2^{+2} in the soil solution mainly competed with calcium ions (Ca^{+2}) for the available CO_3^{-2} for complexation.

3. The 0.1 molar DTPA with a pH of 8.00 desorbed 78% to 86% of total thorium activity from the soil by coordinating its nitrogen and oxygen atoms with thorium. The small ionic radius of thorium makes Th-DTPA complexes with a coordination number of 8 very stable in solution.[6] Conversely, the geometry of UO_2^{+2} and the low effective metal charge prevent UO_2^{+2} from forming stable complexes with DTPA.

4. Fractions of total uranium and thorium activity desorbed from the soils by 0.15g/200 ml humic acid ranged from 4.62% to 6.17% and 1.59% to 7.09%, respectively.

Conclusion

Three contaminated surface soils (Hazelwood A, Hazelwood B, and Weldon Spring soils) were used to investigate uranium and thorium desorption. A study of solution pH effect indicated that the fractions of total uranium and thorium activities released into the solution phase increased by lowering the solution pH. It is concluded that at a low solution pH, the major chemical species of uranium and thorium, UO_2^{+2}, $Th(OH)_2^{+2}$, and $Th(OH)^{+3}$, tend to form complexes with acetates in the solution phase. At a high solution pH, important uranium and thorium species, $UO_2(CO_3)_3^{-4}$ and $Th(OH)_4^0$, tend to resist complexation with acetate.

The presence of complexing reagents in solution can release radionuclides such as uranium and/or thorium from the soil to the solution by forming soluble complexes. Sodium bicarbonate and DTPA are strong complex formers that released 38% to 62% of total uranium activity and 78% to 86% of total thorium activity, respectively, from the soil samples investigated. Therefore, understanding solution chemistry is important for investigating the desorption of radionuclides. A computer model capable of predicting possible reactions between radionuclides in soil and chemical species in solution must be developed to investigate radionuclide mobility and transport.

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TABLE 1 Physical and Chemical Properties of Soil Samples

Soil Sample	pH	CEC meq/100g	Organic Carbon wt %	Saturated Moisture Content, wt %
Hazelwood A	8.47	43.59	4.28	37.5
Hazelwood B	8.35	45.89	5.77	47.0
Weldon Spring	8.14	69.28	3.80	64.0

TABLE 2 Uranium and Thorium Concentrations in Soil Samples

Radionuclide	Hazelwood A pCi/g	Hazelwood B pCi/g	Weldon Spring pCi/g
U-238	9.84 ± 0.47	114.9 ± 3.9	158.9 ± 5.9
U-235	0.11 ± 0.01	4.5 ± 0.2	6.7 ± 0.3
U-234	9.79 ± 0.47	118.3 ± 4.1	159.4 ± 5.9
Th-232	1.41 ± 0.06	2.27 ± 0.13	1.40 ± 0.07
Th-230	451 ± 18	2260 ± 140	2.83 ± 0.13
Th-228	0.94 ± 0.04	2.08 ± 0.12	1.57 ± 0.08

TABLE 3 Fractions (%) of Total Uranium and Thorium Activities Released into 200 ml Solution in Kinetic Study

Contacting solution	Radionuclide	Contacting Time 0.5 Hr.	2.0 Hr.	48 Hr.	168 Hr.
DIW, pH = 6.08	Uranium	1.57 ± 0.02	2.20 ± 0.01	2.02 ± 0.01	2.03 ± 0.01
	Thorium	1.01 ± 0.01	1.18 ± 0.04	1.18 ± 0.02	1.09 ± 0.03
Buffer, pH = 6.50	Uranium	0.79 ± 0.02	1.65 ± 0.02	2.42 ± 0.06	2.24 ± 0.04
	Thorium	0.53 ± 0.01	0.78 ± 0.01	0.81 ± 0.01	1.06 ± 0.01

TABLE 4 Fraction (%) of Total Uranium and Thorium Activities Desorbed by 1 Molar NaOAc Solution with pH Adjusted to 4.00, 5.60, and 8.00, and Calculated Distribution Coefficients

Soil Sample	Solution pH	Uranium		Thorium	
		% Desorption	K_d, ml/g	% Desorption	K_d, ml/g
Hazelwood A	4.00	55.4 ± 3.2	32.2 ± 1.9	7.07 ± 0.10	526 ± 7
	5.60	16.3 ± 1.8	205.4 ± 22.7	0.081 ± 0.004	$(4.93\pm0.24)\times10^4$
	8.00	3.53 ± 0.66	1090 ± 200	0.04 ± 0.02	$(10.0\pm5.0)\times10^4$
Hazelwood B	4.00	67.7 ± 8.3	19.1 ± 2.3	23.9 ± 3.1	127 ± 17
	5.60	43.4 ± 2.7	52.2 ± 3.2	0.33 ± 0.05	$(1.21\pm0.18)\times10^4$
	8.00	7.37 ± 1.21	503 ± 83	0.06 ± 0.02	$(6.66\pm2.22)\times10^4$
Weldon Spring	4.00	37.2 ± 1.1	67.5 ± 2.0	36.9 ± 1.4	68.4 ± 2.6
	5.60	19.5 ± 3.4	165 ± 29	11.4 ± 2.5	311 ± 68
	8.00	5.41 ± 0.50	699 ± 65	3.82 ± 1.33	1010 ± 350

TABLE 5 Fraction (%) of Total Uranium and Total Thorium Activities Desorbed by Different Complexing Agents

Complexing Agents	Soil* Samples	Uranium		Thorium	
		% Desorption	K_d, ml/g	% Desorption	K_d, ml/g
0.1M $NaNO_3$ pH = 8.00	HWA	2.45±0.05	1590±40	0.048±0.020	$(10.1\pm4.4)\times10^4$
	HWB	1.91±0.33	2120±420	$(8.2\pm1.6)\times10^{-3}$	$(5.1\pm1.2)\times10^5$
	WS	5.95±1.16	658±134	4.90±3.88	1320±690
0.1M $NaHCO_3$ pH = 8.00	HWA	62.0±9.7	26.2±10.0	0.135±0.078	$(9.1\pm6.9)\times10^4$
	HWB	51.9±5.5	38.0±8.4	0.032±0.024	$(2.0\pm1.0)\times10^5$
	WS	38.0±3.2	67.0±7.7	5.13±3.19	1050±520
0.1M Na_2SO_4 pH = 8.00	HWA	2.42±0.23	1630±170	0.051±0.035	$(11.6\pm5.6)\times10^4$
	HWB	6.40±5.00	1080±700	0.011±0.003	$(3.80\pm0.9)\times10^5$
	WS	5.33±0.15	711±21	2.43±0.53	1700±440
0.1 M DTPA pH = 8.00	HWA	13.0±0.6	269±15	81.9±2.5	8.88±1.51
	HWB	13.0±0.3	269±7	85.9±3.0	6.62±1.64
	WS	8.72±1.40	432±79	78.1±11.8	12.5±8.6
0.15g/200ml Humic Acid pH = 8.00	HWA	5.90±0.86	651±96	1.59±0.22	2530±390
	HWB	6.17±0.38	610±38	2.29±0.52	1800±450
	WS	4.62±0.32	829±62	7.09±1.84	558±132

* HWA, Hazelwood A; HWB, Hazelwood B; and WS, Weldon Spring.

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