EXTRAPOLATION STUDIES ON ADSORPTION OF THORIUM AND URANIUM AT DIFFERENT SOLUTION COMPOSITIONS ON SOIL SEDIMENTS

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Study on adsorption of Thorium and Uranium radionuclides by a soil sediment as a function of ionic composition of Ca, Mg and Na has been conducted. Experimentally conducted determined slopes representing an average of adsorption on soil sediments having different relative affinities for thorium, uranium, calcium and magnesium. Both thorium and uranium were found to be adsorbed to ion-exchange sites with calcium and magnesium cations as effective competitors. An extrapolated equation for distribution coefficient K_d was formed for each radionuclide thorium and uranium at the specified site where the soil sediments were sampled.

INTRODUCTION

There is a need for appropriate management of the disposal of low level radioactive wastes containing thorium and uranium. Adsorption studies are needed to estimate the rate of transport of thorium and uranium in the event of groundwater since there is a potential for contamination of drinking water. Information on adsorption mechanisms of thorium and uranium helps to understand controls on both radionuclides concentrations in groundwater, and to predict the risk of thorium and uranium release in leachates from mining activity and radioactive wastes.

Thorium is found in nature as a tetravalent cation. The element usually occurs in geologic materials as a trace constituent in solid solution in phosphate, oxide and silicate minerals, and sorbed onto clays and other colloids.¹ Previous studies shows that equilibrium adsorption of thorium by hydrous oxides goethite (α -FeOOH) and δ -MnO₂ in marine electrolytes is not affected by the major cations of Ca⁽²⁺⁾ and Mg⁽²⁺⁾, relative to NaCl electrolyte, while SO₄ decreased adsorption through competitive ion pairing with thorium in solution.² Studies were also conducted on the effects of pH, ionic strength and carbonate alkalinity on thorium adsorption by goethite in 0.1 M NaNO₃ electrolyte.³ Dissolved thorium is almost invariably complexed in natural water. This increases the solubility of thorium bearing heavy minerals below pH 8.⁴

The purpose of the present study is to examine the competitive effect of calcium and magnesium cations on thorium and uranium adsorption by laboratory experiments. The results and K_d values calculated through equations described below make it possible to understand trends in concentrations of thorium and uranium in groundwater at disposal sites.

EXPERIMENTAL

A series of batch adsorption experiments have been conducted to determine the thorium and uranium adsorption properties of soil sediments as a function of equilibrating solution composition.⁵⁻⁸ Experiments were conducted using soil sediments near a potential disposal site.

For experiment using thorium, eight (8) stock solutions of 500 ml were prepared with the concentrations of the major cations Ca, Mg and Na varying in the range 0.0 to 6.24×10^{-4} M, 0.0 to 2.50×10^{-4} M, and 0.0 to 1.65×10^{-4} M, respectively, (Table 1). The compositions of 9 stock solutions using uranium are listed in Table 2. The respective concentrations of the major cations Ca, Mg, Na are between 0.0 to 6.24×10^{-4} M, 0.0 to 2.5×10^{-4} M, and 0.0 to 1.65×10^{-4} M, respectively.

All of the solutions were spiked with the tracers respectively and the pH of each stock solution was adjusted to 6.70 - 7.00 with sodium hydroxide or hydrochloric acid. Each batch experiment was conducted in a 40 ml polycarbonate centrifuge tube. One (1) gram of the soil sediments were added into their respective tubes. Twenty (20) ml of spiked solution was then added into each tube. All the tubes were equilibrated for 14 days after being shaken at room temperature. After the equilibration period, all the tubes were centrifuged at 4000 rpm for 1 hour to separate the solid and the solution. Solution samples were filtered through a 0.2 μ m filter and then 1.0 ml were collected. It was then acidified by adding approximately 100 μ l of concentrated hydrochloric acid or nitric acid (6 M or 12 M) and then analysed for concentration of thorium and uranium by the neutron activation method. Solid sediments were removed from each tube by filtering through a 0.45 μ m filter and then the sediments were allowed to dry. The solid sediments were also analysed by the neutron activation method.

The distribution coefficient $K_d^{Th, U}$ was calculated by :

$$K_d^{Th, U} = \frac{\mu\text{g/g (ppm) (Th, U) in solid form}}{\mu\text{g/ml (ppm) (Th, U) in liquid form}}$$

Ionic strength which measures the total concentration of charge in a solution was calculated by:

$$I = 0.5 \sum [m_i] z_i^2$$

where m_i was the molality or concentration (m) of the i th species of charge z_i .⁹ The ionic strength parameter (I) was used to calculate the activity coefficient of each solution. At higher concentrations less than 0.5 M, the Davies equation was used to calculate activity coefficient γ , as

this has been shown to better represent experimental data than other equations to be found in the literature.¹⁰⁻¹¹

Thus the activity coefficient γ was calculated as:

$$\ln \gamma_i = -1.17 z_i^2 [(\sqrt{I})/(1+\sqrt{I}) - 0.2I]$$

and activity was calculated by use of the expression:

$$\text{Activity (moles)} = \text{concentration (moles)} \times \text{activity coefficient } \gamma$$

Detailed statistical regression and variance analyses were performed for each batch experiment to yield values for the adsorption coefficient K_d .

RESULTS AND DISCUSSION

$K_d^{Th, U}$ values for thorium and uranium were obtained for each of the batch experiments after examining adsorption of thorium and uranium on the soil sediments at different solution composition. Table 1 and Table 2 shows the final pH of the solutions at the end of the equilibration period. Experimental results proved to be reproducible and could be used with confidence to produce the K_d equations for the soil sediments. Figure 1 and Figure 2, show K_d values as a function of the sum of the equilibrium calcium and magnesium concentrations in solution for the soil sediments adsorption of thorium and uranium, respectively. From both Figures, thorium K_d^{Th} values shows very high values compared to those for uranium. The results indicated that the soil sediments or some individual minerals components of the sediment selectively adsorbed thorium more than the uranium radionuclides.

Table 3 lists the adsorption coefficient K_d for soil sediments described by the associated best fit equations. Figure 1 and Figure 2, show that good linear correlations exist where the predicted data were used to calculate the associated best fit equations.

Table 3. Adsorption coefficient $K_d^{Th, U}$ equations for soil sediments

Radionuclide	Adsorption coefficient equation, log Kd	R square
Thorium	$-1.25532 \pm 0.299612 \log (Ca + Mg) + 1.823167 \pm 0.906504$	0.8
Uranium	$-0.19838 \pm 0.051125 \log (Ca + Mg) + 2.749482 \pm 0.153223$	0.7

From the high K_d values obtained indicated that both thorium and uranium radionuclides were adsorbed by the sediments as a function of the sum of the equilibrium calcium and magnesium concentrations in solution. This also indicated that ion exchange does exist in the soil sediments.

CONCLUSION

Changes in groundwater chemistry can affect adsorption properties of thorium and uranium onto soil sediments. The competitive effects of calcium and magnesium cations on the adsorption of thorium and uranium has been shown. The combined cation concentration of calcium and magnesium in solution correlates linearly with the measured $K_d^{Th, U}$ values. Thorium and uranium concentrations and major ion data can be obtained from a network of wells. Changes of the thorium and uranium concentrations with future major ion concentrations can be estimated if the aquifer material resembles the sedimentary material used in the experiments.

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Table 1. Experiment number and solution composition (molar concentration) using thorium ions

Experiment No.	Ca(NO ₃) ₂ 4H ₂ O	Na ₂ SO ₄	NaCl	MgCl.6H ₂ O	Final pH
1	0	0	0	0	6.79
2	0.000624	0	0	0	6.85
3	0	0.000165	0	0.0005	6.7
4	0.000624	0.000165	0	0.0005	6.75
5	0.000624	0.000165	0.000312	0.00025	6.8
6	0.00312	0	0.00156	0	6.85
7	0.00312	0.000823	0	0.0025	6.75
8	0.00156	0.000823	0.00156	0	6.86

Table 2. Experiment number and solution composition (molar concentration) using uranium ions

Experiment No.	Ca(NO ₃) ₂ 4H ₂ O	Na ₂ SO ₄	NaCl	MgCl.6H ₂ O	Final pH
1	0	0	0	0	6.6
2	0	0.000165	0	0.0005	6.9
3	0.000624	0.000165	0	0.0005	6.8
4	0.000624	0.000165	0.000312	0.00025	7.07
5	0.000624	0.0000823	0.000156	0	6.78
6	0.00312	0.000823	0	0.0025	6.7
7	0.00312	0.000823	0.00312	0	6.85
8	0.00156	0.000823	0.00156	0	6.88
9	0.00156	0.00165	0	0.00125	6.8

Sediments adsorption of Uranium

Fig 2. Kd values as a function of the sum of the equilibrium Ca and Mg concentrations in solution (mol/L) for soil sediments

Sediments adsorption of Thorium

Fig 1. Kd values as a function of the sum of the equilibrium Ca and Mg concentrations in solution (mol/L) for sediments)