



EXTRAPOLATION STUDIES ON DESORPTION OF THORIUM AND URANIUM AT DIFFERENT SOLUTION COMPOSITIONS ON CONTAMINATED SOIL SEDIMENTS (MALAYSIA)

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Abstract

By means of batch desorption experiments the thorium and uranium desorption properties of contaminated soil sediments are investigated as a function of the effect of cations present in the groundwater. A phenomenological correlation between the desorption coefficient and the concentration of Ca and Mg in the water is determined.

$$K_{d_{\text{Thorium}}} = -0.15849 \pm 0.03237 \log (Ca + Mg) + 5.06715 \pm 0.09106$$

$$K_{d_{\text{Uranium}}} = -0.11984 \pm 0.03237 \log (Ca + Mg) + 2.99909 \pm 0.09105.$$

By these models the sorption/desorption behaviour of soils can be predicted phenomenologically as function of the groundwater composition.

INTRODUCTION

Significant quantities of ^{90}Sr radionuclides from Hanford sites burial sites, Washington, are seeping into groundwater and are entering into the Columbia river [1] The primary sources of groundwater contamination at the burial area are from certain disposal trenches. One of the reason for the observed increase in the concentration of the radionuclides is that the chemical composition of water flowing through the contaminated sediments has changed significantly and is now causing previously adsorbed radionuclides to desorb. Adsorption of the radionuclide is known to be quite sensitive to competing cations such as Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and H^+ . Studies conducted shows that ion exchange of Ca and Mg for previously adsorbed Sr is responsible for the increases in Sr in certain monitoring wells [2] Elevated Na concentrations in the groundwater is also likely to cause desorption of Ca and other certain radionuclides from soil exchange sites, resulting in elevated Ca concentrations and certain radionuclides in the groundwater.

Desorption 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/desorption 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.

The purpose of the present study is to gain a better understanding of the desorption properties of thorium and uranium from contaminated soil sediments and how changes in groundwater chemistry can effect this properties. The competitive effect of calcium and magnesium cations on thorium and uranium desorption were conducted in batch type 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. From the results of adsorption studies previously and present desorption studies, a radiological impact assessment on a potential repository can be conducted using the distribution coefficient K_d values which is a very important parameter as input in a computer model tool.

EXPERIMENTAL

A series of batch desorption experiments have been conducted to determine the thorium and uranium desorption properties of a contaminated soil sediments as a function of equilibrating solution composition [3–7]. The soil sediments used were obtained from a potential disposal site. Prior to the desorption experiments, contaminated soil sediments were obtained by conducting adsorption experiments using actual radioactive aqueous wastes containing thorium and uranium on the sampled soil sediments. Equilibrium period was allowed for 14 days, and the contaminated solid sediments were removed by filtering through a 0.45 μm . filter and collected and air dried to be used in the desorption experiments. The contaminated soil sediments contained both adsorbed thorium and uranium radionuclides.

For the desorption experiment, ten (10) 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 3.12×10^{-3} M, 0.0 to 2.5×10^{-3} M, and 0.0 to 3.12×10^{-3} M, respectively. All of the stock solutions its pH 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. Duplicate experiments were conducted for each soil sample used. All the tubes were equilibrated for 14 days after being shaken at room temperature of 26°C. 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 μm . filter and then 1.0 ml were collected. It was then acidified by adding approximately 100 μl of concentrated hydrochloric acid or nitric acid (6 M or 12 M).

Distribution coefficient K_d (desorption) were determined directly by measuring the concentration both in solution and in the sediment after the 14 day equilibrium period. The solutions were analysed for concentration (ppb) of thorium and uranium by using ICPMS method. Solid sediments were removed from each tube by filtering through a 0.45 μm . filter and then the sediments were allowed to dry. The solid sediments were analysed by the neutron activation method.

The distribution coefficient $K_d^{\text{Th, U}}$ was calculated as:

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

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

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

where m_i was the molality or concentration (m) of the i th species of charge z_i [8]. 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 [9, 10].

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:

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

EXTRAPOLATION METHOD

From the experimental results obtained in the desorption studies, graphs of $\log K_d$ (desorption of thorium) and (desorption of uranium) were plotted as a function of the sum of the equilibrium of calcium and magnesium concentration in solutions (moles/L) for the contaminated soil sediments. Detailed statistical regression and variance analyses were performed for each batch experiment to yield values for the extrapolated desorption coefficient K_d for thorium and uranium radionuclides.

Thorium and uranium concentrations and major ion concentrations (Ca and Mg) data can be obtained from a network of wells. The data can be used as input to the extrapolated desorption K_d coefficient equation and extrapolated adsorption K_d coefficient equation [11] (from previous studies) to calculate K_d values for each radionuclides at a specific site.

Resrad computer code will be used to determine radiological impact assessment for the potential repository site using the most important parameters K_d values as input together with other site parameters. Appropriate use scenario and site specific parameters can be used so as to be realistic. The model will derive site specific guidelines for allowable residual concentrations of thorium and uranium in soil. Results from analyses of modelling will be able to calculate doses, risk and guidelines values. Performance and safety assessment of the repository system can be determined from the analyses and also used as an initial assessment to conduct screening assessment in order to determine a proper repository site.

RESULTS AND DISCUSSION

$K_d^{\text{Th, U}}$ (desorption) values for thorium and uranium were obtained for each of the batch experiments after examining desorption of thorium and uranium from the contaminated soil sediments at different solution composition. Experimental results proved to be reproducible and could be used with confidence to produce the K_d (desorption) equations for the soil sediments. The K_d (desorption) results were plotted in Figures 1 and 2 as a function of the sum of the equilibrium calcium and magnesium concentrations in solution for the soil sediments desorption of thorium and uranium, respectively. From both Figures, shows that thorium and uranium were desorbed from ion exchange sites and that Ca and Mg were effective competitors for these sites.

From the above short term experiments results, an extrapolated equation coefficient K_d for a specific site can be formed from different major ion (Ca and Mg) data, thorium and uranium concentrations. Table 1 lists the desorption coefficient K_d for soil sediments described by the associated best fit equations. Figures 1 and 2 show that good linear correlations can exist where the predicted data were used to calculate the associated best fit equations.

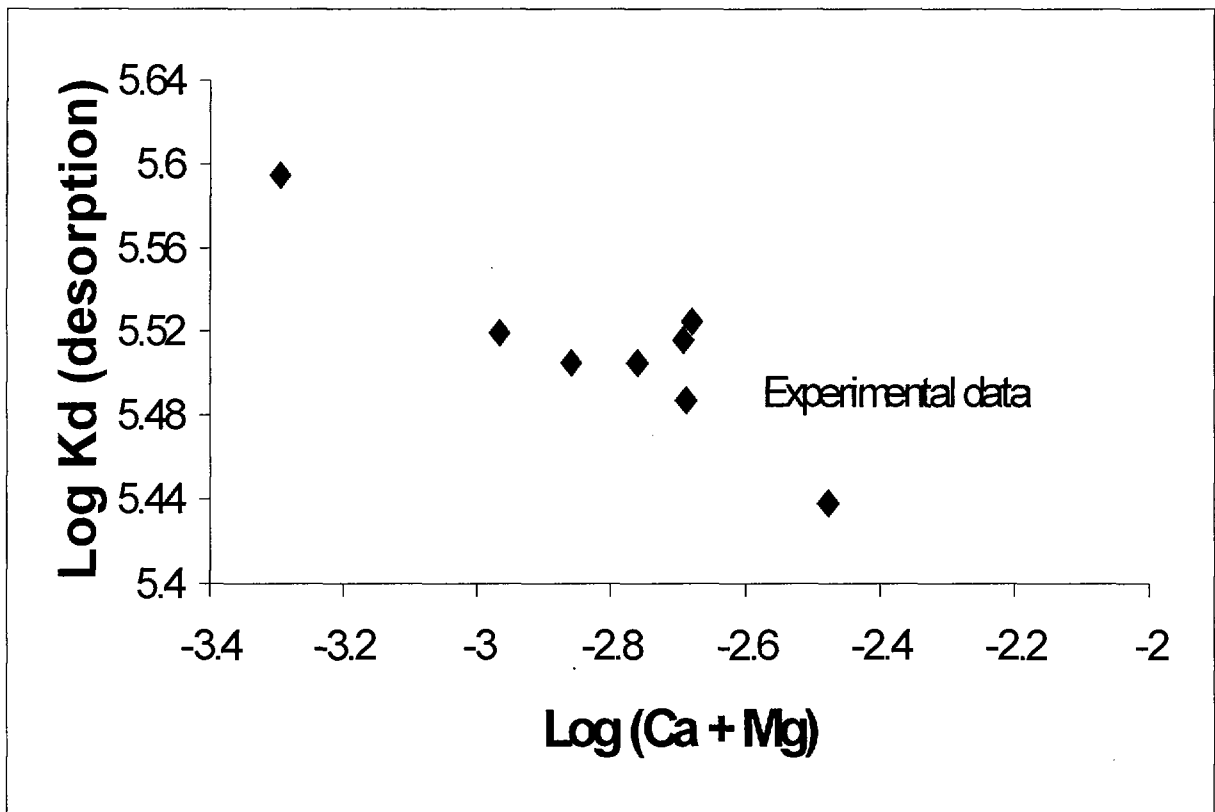


FIG. 1. Thorium K_d values as a function of the sum of the equilibrium Ca and Mg concentrations in solutions (moles/L) for the contaminated soil sediments.

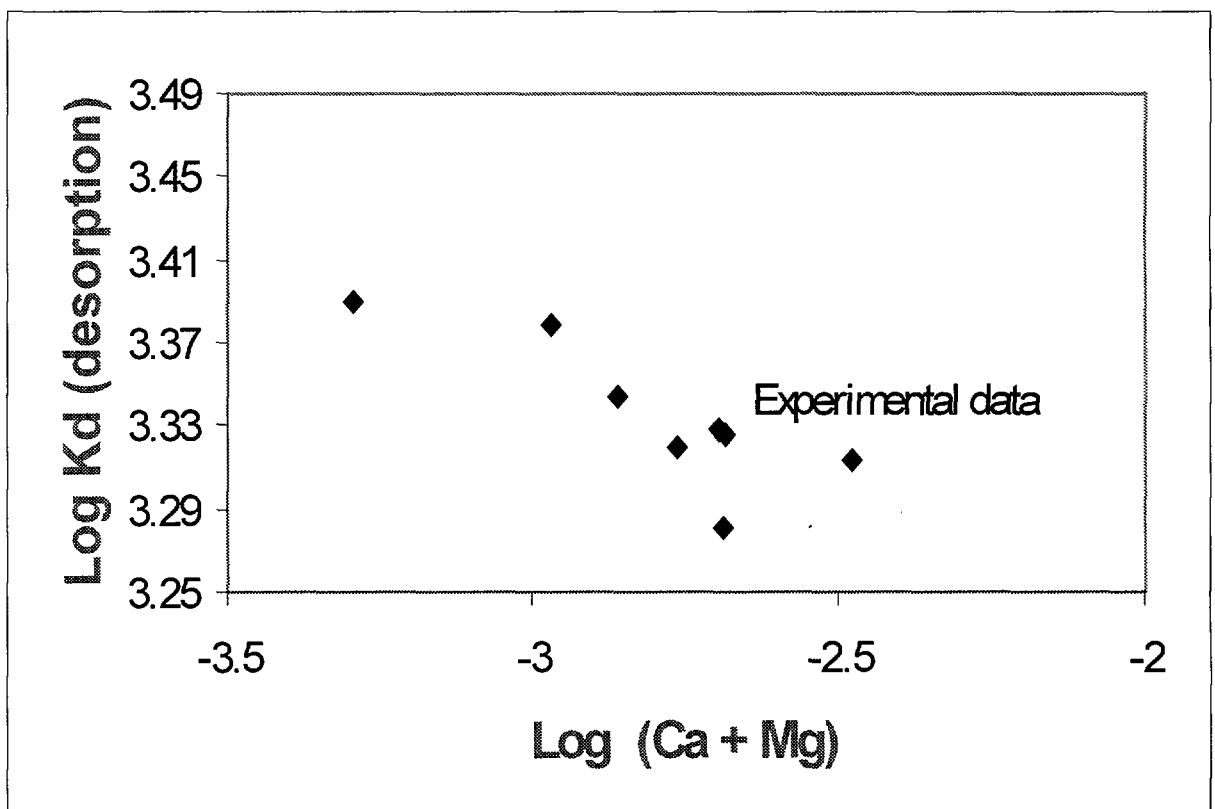


FIG. 2. Uranium K_d values as a function of the sum of the equilibrium Ca and Mg concentrations in solutions (moles/L) for the contaminated soil sediments.

Table 1. Desorption coefficient $K_d^{Th, U}$ equations for soil sediments

Radionuclide	Adsorption coefficient equation, log Kd	R square
Thorium	$-0.15849 \pm 0.03237 \log (Ca + Mg) + 5.06715 \pm 0.09106$	0.8
Uranium	$-0.11984 \pm 0.03237 \log (Ca + Mg) + 2.99909 \pm 0.09105$	0.7

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. Significant variation of the K_d values could occur if no resembles of the samples are used. This could result in serious errors in prediction of future thorium and uranium concentration within a contaminated burial sites.

CONCLUSIONS

Changes in groundwater chemistry can affect desorption properties of thorium and uranium from contaminated soil sediments. The competitive effects of calcium and magnesium cations on the desorption of thorium and uranium has been shown. Both thorium and uranium were found to be desorped from ion-exchange sites with calcium and magnesium cations as effective competitors. Ion exchange of Ca and Mg occurred for previously adsorbed thorium and uranium which was responsible for the increased in both radionuclides in the liquid solution. The combined cation concentration of calcium and magnesium in solution correlates linearly with the measured $K_d^{Th, U}$ desorption values. Thorium and uranium concentrations and major ion data can be obtained from a network of wells and can used as input to the extrapolated equation from the present desorption and previous adsorption studies [11] to calculate K_d values for a specific site.

For future works, Resrad computer code will be used to determine radiological impact assessment for the potential repository site using the most important parameters site specific K_d values as input together with other site parameters. By conducting the assessment by modelling, the performance of the repository site can be determined to isolate thorium and uranium radioactives wastes.

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