

SORPTION OF U(VI) ON GRANITE

S. AKSOYOGLU

Hot-Labor, Paul Scherrer Institut, 5232 Villigen, (Switzerland)

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The sorption-desorption of uranium (VI) on Grimsel granite of Switzerland was studied under oxidizing conditions with an initial uranium concentration range of between $9.7 \cdot 10^{-7}$ and $4.5 \cdot 10^{-4}$ M, using a batch technique. The sorption coefficients varied between 8.0 and 0.4 ml/g and sorption was not fully reversible. The data could be fitted to a Freundlich isotherm. By fitting the data with the Dubinin-Radushkevich equation, a mean energy of sorption of 10.7 kJ/mol was calculated, which corresponds to the energy of ion exchange reactions. The kinetic data could be interpreted by assuming diffusion into the crushed granite particles. The calculated pore diffusion coefficient was between $2.0 \cdot 10^{-11}$ – $7.7 \cdot 10^{-11}$ m²/s.

Introduction

The disposal of radioactive waste in deep geological media requires a long-term safety assessment, which needs a thorough understanding of the migration behaviour of several radionuclides in the geological environment. The extent and rate of radionuclide transport to the biosphere must be considered because groundwater will eventually enter the vault, corrode the waste container and dissolve some or all of the waste material. Sorption due to the interaction of dissolved nuclides with the geological media is one of the most important factors in the retardation of the nuclide transport. Since uranium is an important constituent of nuclear waste, the prediction of its sorption behaviour is of great interest. In addition, uranium infiltration experiments into the bore cores have been performed¹ which can be modelled only when the isotherm is known. Uranium sorption is very dependent on redox conditions, temperature, pH and groundwater composition, since these factors strongly influence its speciation.^{2–10} Under oxidizing conditions uranium, as U(VI), is weakly sorbed on a number of geological materials.^{3,4} The experimentally established sorption coefficients of U(VI) on granitic rocks range from 0.4 to 10 ml/g.^{8,11,12}

Previous experiments on crushed granite with low uranium concentrations ($1.3 \cdot 10^{-7}$ M) showed that because of weak uranium sorption, a high rock to water

Table 1
Mineralogical analysis of Grimsel granite

Mineral	Abundance, %
Quartz	32.8
Potassium feldspar	34.1
Plagioclase	20.9
Biotite and chlorite	7.3
Mica	1.7
Epidote	2.3
Total	99.1

ratio must be used.¹¹ However, due to that high ratio, it was observed that more uranium was leached from the granite than was initially added to the system and therefore, the uranium concentration in the solution actually increased.¹¹ In this work, the sorption-desorption behaviour of uranium on crushed granite was studied under oxic conditions with high initial uranium concentrations of up to $4.5 \cdot 10^{-4}$ M. The kinetics and concentration dependence of sorption coefficients were investigated and data were fitted to FREUNDLICH and DUBININ-RADUSHKEVICH isotherms.

Materials and methods

As in the previous study, the granite was obtained from a borehole in Grimsel test site and characterized mineralogically and chemically.¹¹ The mineralogical composition is shown in Table 1. The granite was ground to obtain samples with particle size smaller than $300 \mu\text{m}$. These samples were then split to obtain homogeneous material for each batch.

The natural Saecingen groundwater (from Germany) used in this work is strongly mineralized and high in NaCl. This water was equilibrated to the ambient conditions before being used in the experiments. The composition of this water is given in Table 2. Before use, the water was filtered through $0.45 \mu\text{m}$ filters to remove calcite precipitates.

The solutions were prepared by adding sufficient ^{233}U and ^{238}U into the Saecingen groundwater, to give total uranium concentrations of $5 \cdot 10^{-6}$, $4.6 \cdot 10^{-5}$, $1.4 \cdot 10^{-4}$, $2.3 \cdot 10^{-4}$ and $4.5 \cdot 10^{-4}$ M. The uranium content of stock solutions was determined by mass spectrometry. The α -activity of ^{233}U was measured using a liquid scintillation counter.

Table 2
Composition of Saecingen water (air-equilibrated)

Ion	Concentration, mg/l
Na	930
K	87
Mg	16
Ca	140
Fe	0.02
Mn	0.02
U	0.011
Cl	1675
SO ₄	248
HCO ₃	305
P _{tot}	0.02
F	3
SiO ₂	10
pH	8.1
Conductivity (20 °C)	4200 μ S/cm

The experiments were carried out in duplicate and in parallel with a blank series. About 150 g of split granite was mixed with 300 ml of the uranium solution in polyethylene bottles and the suspensions were shaken at 250 rpm. After various time intervals, 1–2 ml aliquots were sampled with a syringe and filtered through 0.2 μ m Acrodisc one-way filters and then mixed with Instagel scintillation cocktail. After sampling, the bottles were returned to the shaker. The total volume of all the aliquots taken during the experiments is smaller than 5% of the initial volume. After 14 days sorption, the solution was carefully decanted and the groundwater was added for a further 14 days of desorption. Adsorption on the containers and the filters were checked by leaching with HCl.

Results and discussion

Preliminary tests showed that under the conditions used the uranium solutions were stable over the whole experimental period and that losses of uranium on the container walls and filters were negligible (<1%). The speciation of uranium(VI) in the solutions was not considered in this work.

The sorption and desorption coefficients at steady-state (R_S and R_D respectively) are given in Table 3. The sorption coefficients obtained in this work are in the

Table 3
Sorption/desorption results

U_L^0, M	$R_S, \text{ml/g}$	$R_D, \text{ml/g}$
$9.7 \cdot 10^{-7} *$	8.0	—
$5.0 \cdot 10^{-6}$	2.3	8.4
$4.6 \cdot 10^{-5}$	1.0	3.8
$1.4 \cdot 10^{-4}$	0.6	2.6
$2.3 \cdot 10^{-4}$	0.5	2.1
$4.5 \cdot 10^{-4}$	0.4	2.0

*Taken from the previous work,¹¹ after correction for the leached uranium from granite.

range given by VANDERGRAAF¹³ and compatible with the values compiled by McKINLEY and HADERMANN.¹⁴ These values are lower than literature data^{3,15-16} which were measured at lower initial uranium concentrations.

Desorption coefficients were found to be higher than the corresponding sorption coefficients as also observed in other works.^{4,8,17} ERDAL et al.⁸ attribute this irreversibility to the diffusion of uranium into the solid.

Isotherms

The sorption isotherms are used in radionuclide transport models.^{18,19} Data obtained from sorption-desorption experiments carried out with uranium concentrations between $9.7 \cdot 10^{-7}$ and $4.5 \cdot 10^{-4} M$ (data for lowest uranium concentration was taken from the previous work¹¹), were fitted with FREUNDLICH²⁰ and DUBININ-RADUSHKEVICH²¹ isotherms.

Although the FREUNDLICH isotherm is regarded as empirical, there have been some attempts to get some information about surface heterogeneity from the empirical FREUNDLICH constants.^{22,23} Although this isotherm does not take the solid's finite capacity for adsorption at high concentrations of solute into account, it has been shown in many experimental studies that it can describe the experimental data well on a phenomenological basis.^{3,4,6,7,17} The linearized FREUNDLICH equation is:

$$\log X = \log K + N \log C \quad (1)$$

where

- X — amount of solute adsorbed per unit weight of solid (mol/g),
- C — equilibrium solute solution concentration (mol/l),
- K, N — constants.

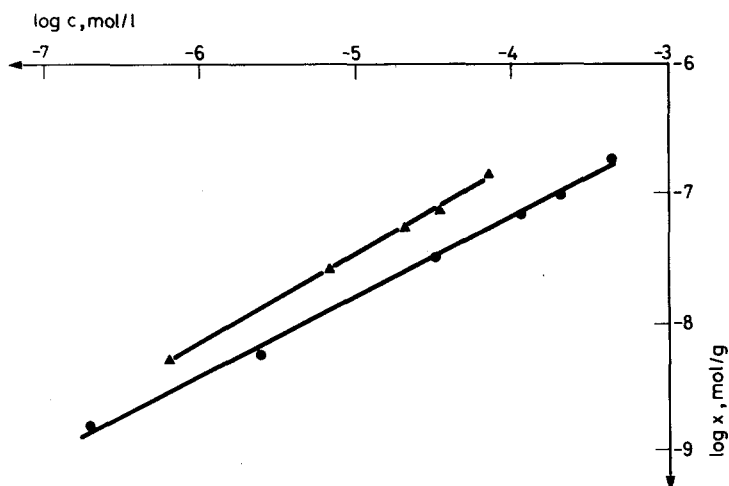


Fig. 1. FREUNDLICH plot of uranium sorption and desorption on Grimsel granite; ● sorption, ▲ desorption

Table 4
Parameters of sorption isotherms

Isotherm	K	N	X_m , mol/g	K , mol ² /kJ ²	r
Freundlich sorption	$1.9 \cdot 10^{-5}$	0.62	—	—	0.998
Freundlich desorption	$8.9 \cdot 10^{-5}$	0.68	—	—	0.999
D—R sorption	—	—	$6.3 \cdot 10^{-7}$	$4.4 \cdot 10^{-3}$	0.990
D—R desorption	—	—	$1.6 \cdot 10^{-6}$	$4.8 \cdot 10^{-3}$	0.996

The sorption data of this work are well described by FREUNDLICH equation, with slopes less than one (Figure 1, Table 4). This means that the sorption of uranium(VI) on granite is concentration dependent, i.e. non-linear. The sorption and desorption isotherms show hysteresis probably because of diffusion into the particles. The site distribution function would be calculated using FREUNDLICH parameters, if some more information such as number of sorption sites were known.²² As an alternative to the FREUNDLICH isotherm, data can be fitted with a DUBININ—RADUSHKEVICH (D—R) isotherm.²⁴ The relationship between D—R and other type of sorption isotherms is shown by SOKOLOWSKA and SZCZYPA.²³ This isotherm is more general than the LANGMUIR isotherm,²⁵ since it does not assume a homogeneous surface or constant sorption potential. The D—R equation is:

$$X = X_m \exp(-K\epsilon^2) \quad (2)$$

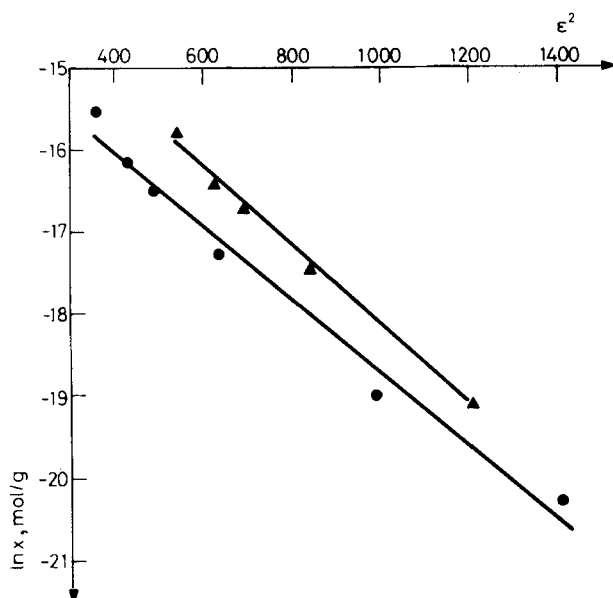


Fig. 2. DUBININ-RADUSHKEVICH plot of uranium sorption and desorption on Grimsel granite; ● sorption, ▲ desorption

where

$$\epsilon = RT \ln(1 + 1/C),$$

C — equilibrium solute solution concentration (mol/l),

R — gas constant (kJ/deg · mol),

T — temperature (K),

K — constant related to the sorption energy (mol^2/kJ^2),

X_m — sorption capacity of adsorbent per unit weight (mol/g),

X — amount of solute adsorbed per unit weight of solid (mol/g).

The linearized D-R equation is:

$$\ln X = \ln X_m - K\epsilon^2 \quad (3)$$

The plot of $\ln X$ against ϵ^2 is shown in Figure 2. The isotherm was calculated using a least squares method. The parameters X_m and K obtained from the intercept and the slope of this plot are given in Table 4. The correlation coefficients (r) for D-R and FREUNDLICH isotherms are comparable. By making certain assumptions,⁵ the mean energy of sorption, E, can be calculated. The mean energy of sorption is the free energy change when one mole of ion is transferred to the surface of the solid from infinity in solution and it is calculated from:^{26,27}

$$E = (-2K)^{-1/2} \quad (4)$$

The magnitude of E is useful for estimating the type of sorption reaction occurring. It was found to be 10.7 kJ/mol, which is within the energy range of ion-exchange reactions, 8–16 kJ/mol^{28,29} and it is very close to the literature values calculated from similar fittings.^{3,5}

Kinetics

Kinetic data were interpreted in two ways. The first is to assume that uranium sorbs on the surface of the particles according to a first order reaction and then the time dependence is given as:

$$R_{s,t} = R_{s,\infty}(1 - e^{-kt}) \quad (5)$$

where

$R_{s,t}$ – sorption coefficient at time t (ml/g),

$R_{s,\infty}$ – sorption coefficient at steady-state (ml/g),

t – time (s),

k – rate constant (s^{-1}).

This equation is linearized as

$$\ln \left(1 - \frac{R_{s,t}}{R_{s,\infty}} \right) = -kt \quad (6)$$

The plot of $\ln(1 - R_{s,t}/R_{s,\infty})$ against t should be linear for a first order reaction.³⁰ The plots for different initial uranium concentrations are shown in Figure 3. As it is seen, the experimental points are not all on the straight lines drawn by least squares method and the slopes of the lines are randomly different. Therefore, the assumption of a first order reaction cannot be verified.

A second interpretation of the kinetic data treats the crushed particles as porous particles of spherical shape and of a single size and assumes that uranium diffuses into these micropores. The adsorption of solutes from solution by porous adsorbents involves 3 steps. The first step, bulk transport of solute in the solution is usually rapid because of mixing. The second step, film transport involves diffusion of the solute through a hypothetical film boundary layer. Except for a small amount of adsorption that occurs on the exterior of the adsorbent, the solute then diffuses within the pore volume of the adsorbent and/or along pore-wall surfaces to an active adsorption site (intra-particle transport). The actual adsorption of solute on interior surface sites is generally considered to be very rapid and hence makes an insignificant contribution to the overall adsorption rate.^{31,32,33} Film and intra-particle transport are thus the major factors controlling rates of adsorption from

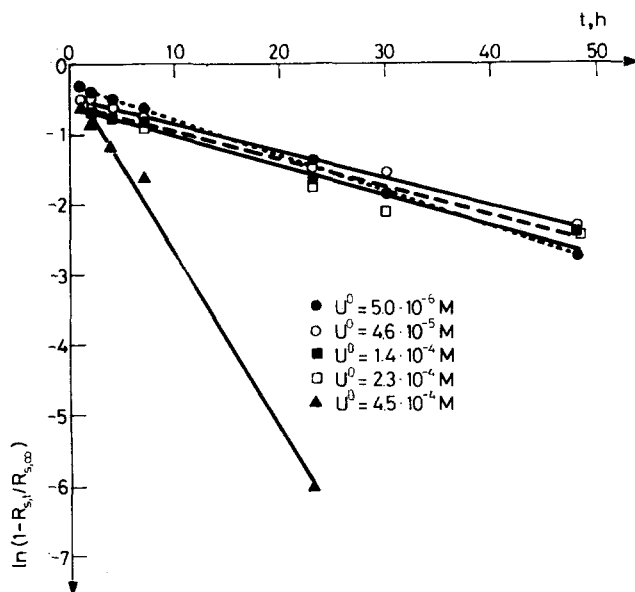


Fig. 3. Fitting of data to the first order sorption reaction kinetics

solution by porous adsorbents. The slower of the two steps is rate-limiting. At low concentrations and for the reactions controlled by film diffusion, the rate of reaction increases linearly with concentration, providing other conditions are unchanged.²⁹ When both film and intra-particle diffusion play a role in determining the rate, the relation is no longer linear. At high concentrations the rate reaches a limit where intra-particle diffusion is the rate-determining step and the rate is independent of concentration.

Assuming the time dependency of bulk sorption is governed by the intra-particle diffusion, the equation is:^{29,34}

$$R_{s,t}/R_{s,\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 D t / r^2) \quad (7)$$

where

- r – the mean radius of particles (m),
- D – apparent diffusion coefficient (m^2/s) $D = D_p/R$,
- D_p – pore diffusion coefficient (m^2/s),
- $R = 1 + (R_{s,\infty}\rho)/\epsilon$,
- ρ – density of the rock (g/cm^3),
- ϵ – porosity of the rock,
- $n = 1, 2, 3, \dots$

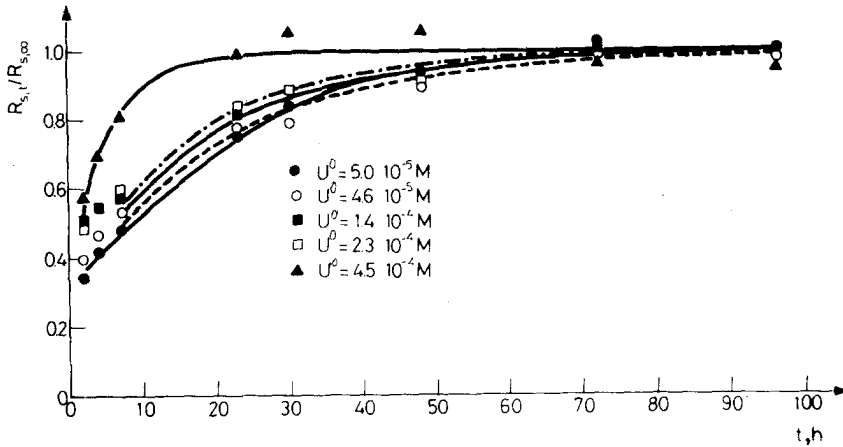


Fig. 4. Fitting of the experimental kinetic data to the diffusion model for uranium sorption on Grimsel granite. The points and lines are experimental values and calculated curves respectively

This expression neglects sorption on the outer surfaces of the particles, the distribution of the particle sizes and the effect of sorption non-linearity on the apparent diffusion constant. Kinetic data were fitted to the equation given above using the following assumptions: (1) the porosity of the rock is $1 \cdot 10^{-3}$,¹ (2) the mean radius of the particles is $1 \cdot 10^{-4}$ m,¹¹ and (3) the rock density is 2.5 g/cm^3 .

The best fits obtained by the least squares method are shown in Fig. 4 together with the experimental data, for each initial uranium concentration. In three cases, the fittings are not completely successful especially for the initial values. This could be because the solutions were not yet in equilibrium at the beginning of sorption. The first two experimental values for these three cases were therefore neglected in the fitting calculations. The pore diffusion coefficient, D_p was calculated from these fittings, for each concentration. Instead of yielding a single value for all initial concentrations, D_p was found to vary between $2.0 \cdot 10^{-11} \text{ m}^2/\text{s}$ and $7.7 \cdot 10^{-11} \text{ m}^2/\text{s}$. The reasons may be the neglects mentioned above, especially the assumption of a mean particle size. The smaller particles react more rapidly regardless of whether film or intra-particle diffusion is the slow step, because the ions have a shorter average distance to diffuse through the small particles. Particle size is quite important when the rate is controlled by intra-particle diffusion since r appears to the second power in Eq. (7). Another reason could be the combination of diffusion both in pores and in pore walls (surface diffusion). In systems having a nonlinear isotherm, concentration dependent coefficient of surface diffusion may be expected.³² Under

these considerations, the small variations of D_p from the fits are not very surprising. The pore diffusion coefficients calculated correspond to about 1–4% of the diffusivity in water, which is consistent with the expected values for granites.¹⁸

Conclusion

The sorption coefficients of uranium(VI) on Grimsel granite were found to change between 8 and 0.4 ml/g for the initial uranium concentration range of $9.7 \cdot 10^{-7}$ – $4.5 \cdot 10^{-4}$ M. Desorption coefficients were higher probably due to the diffusion of uranium into the particles. Data fitted to FREUNDLICH equation gave a non-linear isotherm with a slope of 0.62 for sorption and 0.68 for desorption. Sorption data was fitted to DUBININ–RADUSHKEVICH isotherm as well and the mean energy of sorption was calculated as 10.7 kJ/mol which is in the energy range for ion-exchange reactions. The fitting of experimental kinetic data to a first order rate equation for sorption was poor. Kinetic data were interpreted better by treating the crushed particles as porous spheres and assuming that uranium diffuses through the micropores, even though this approach was not perfectly successful probably due to the particle size effect, influence of sorption on outer surfaces and nonlinearity of the isotherm. The pore diffusion coefficients were calculated as $2.0 \cdot 10^{-11}$ – $7.7 \cdot 10^{-11}$ m²/s from the data fitting to diffusion equation in accordance with data from diffusion experiments.

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