

# Actinide Sorption by Fracture-Infilling Minerals

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## Abstract

A static batch method was used to determine sorption coefficients for uranium, neptunium and plutonium from synthetic solutions on fracture-infilling minerals common to granitic rock. The effects of mineralogy, total dissolved solids (TDS) content of the aqueous phase and two distinct redox/pH conditions on sorption were assessed. Differences in mineralogy were found to be most important in determining the relative sorption of these actinides from solution. In certain cases, sorption values for the actinides used here were found to vary inversely with TDS content, indicating that ion exchange may be a factor in the sorption process. The experimentally induced variation in redox/pH condition produced significant differences in sorption values obtained with certain mineral-radionuclide combinations. Precipitation of PuO<sub>2</sub> may be the primary mechanism for plutonium removal from solution under the experimental conditions used, although differences in mineralogy also appear to be of significance.

## 1. Introduction

The disposal of high-level radioactive wastes arising from the generation of electrical power by nuclear reactors is under study in virtually every country served by such facilities. In Canada, the concept of permanent disposal of used CANDU<sup>1</sup> fuel in stable plutonic rock is being studied through the Canadian Nuclear Fuel Waste Management Program [1].

One of the barriers to movement of dissolved radioactive materials from a disposal vault towards the biosphere is the host rock itself. In safety assessment, migration of dissolved radionuclides from the vault to the surface via groundwater passing through open fractures is being assessed. Sorption interactions between radionuclides in solution and fracture-lining materials will delay the arrival of contaminants at the surface. A number of studies, using various experimental techniques, have examined the sorption characteristics of granite, sediments and minerals exposed to several different actinides dissolved in a variety of solutions [2-10]. The present study was designed to determine the effect on sorption of two distinct redox/pH conditions, three distinct levels of total dissolved solids (TDS) content of the aqueous media and ten reference fracture-infilling minerals common

to granitic rock. Uranium, neptunium and plutonium were chosen for study since limited sorption data are available for these actinides on the minerals of interest. A preliminary interpretation of some of the data from this study was presented in an earlier communication [11]. Liquid-liquid extraction techniques were used to determine the oxidation states of the actinides in solution under these experimental conditions [12, 13]. The probable Np and Pu species existing under these conditions were identified through reference to Brookins [14]. The probable U speciation was estimated using the chemical equilibrium speciation program WATEQ4F [15].

## 2. Materials

### 2.1. Minerals

The ten minerals chosen for this study are representative of the most commonly occurring types of fracture-infilling minerals identified in granite formations at two separate research sites on the Canadian Shield [16, 17]. The sources of the minerals and the particle sizes used are given in Table 1. The specific surface areas and Na cation exchange capacities of the minerals are given in Table 2. Where necessary, the mineral samples were size-reduced using a crusher with tungsten carbide jaws and the size fraction for experimental use was isolated by wet-sieving. All minerals were analyzed by powder X-ray diffraction (XRD) and, with the exception of the illite, by X-ray fluorescence (XRF) to determine purity. The goethite was found to contain ~15% quartz as an impurity; the illite used was Sealbond clay, reported to consist of 40% illite, 30% quartz, 14% chlorite, 7.5% carbonate, 5% vermiculite and 3% feldspar [18]. All remaining minerals were found to be free of substantial impurities.

### 2.2. Solution compositions

Three saline solutions with different TDS concentrations were prepared for use with each radiotracer. A synthetic groundwater, WN-1M, typical of the 500 m level in the Whiteshell Research Area in southeastern Manitoba, Canada [19], was used as the reference solution. Initially, portions of the WN-1M were diluted to 1 and 10% of full strength. The radiotracers added to each solution were taken from acid stock

<sup>1</sup> CANada Deuterium Uranium. Registered trademark of AECL Research.

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Table 1. Fracture infilling

Mineral	Source	Particle size $\mu\text{m}$
Calcite <sup>a</sup>	Synthetic	<45
Chlorite <sup>b</sup>	Yancey County, North Carolina	106–180
Epidote <sup>b</sup>	Calumet, Colorado	106–180
Goethite <sup>b</sup>	Biwabik, Minnesota	106–180
Gypsum <sup>c</sup>	Synthetic	106–180
Hematite <sup>a</sup>	Synthetic	<45
Illite <sup>d</sup>	Ontario	<45
Kaolinite (KG1-a)	Source Clays Repository, The Clay Minerals Society	<45
Muscovite <sup>b</sup>	Unknown	106–180
Quartz <sup>b</sup>	Arkansas	106–180

<sup>a</sup> Fisher Scientific, Winnipeg, Manitoba.

<sup>b</sup> Ward's Natural Science Establishment, Rochester, New York.

<sup>c</sup> Prepared from plaster of paris at AECL, Research Company, Pinawa, Manitoba.

<sup>d</sup> Domtar Inc., Mississauga, Ontario.

Table 2. Specific surfaces areas and cation exchange capacities of common fracture-infilling minerals

Mineral	Specific surface area <sup>1</sup> $\text{m}^2 \cdot \text{g}^{-1}$	Cation exchange capacity <sup>2</sup> $\text{meq} \cdot 100\text{g}^{-1}$
Calcite	$0.69 \pm 0.13^*$	$0.184 \pm 0.022^*$
Chlorite	$2.38 \pm 0.07$	$1.699 \pm 0.139$
Epidote	$0.38 \pm 0.05$	$0.648 \pm 0.539$
Goethite	$1.35 \pm 0.01$	$1.026 \pm 0.085$
Gypsum	$1.44 \pm 0.16$	$10.95 \pm 0.861$
Hematite	$11.8 \pm 0.7$	$11.76 \pm 0.974$
Illite	$43^3$	16
Kaolinite	$8.38 \pm 0.19$	$13.99 \pm 1.079$
Muscovite	$5.2 \pm 0.6$	$8.99 \pm 0.75$
Quartz	$0.10 \pm 0.05$	$0.206 \pm 0.022$

<sup>1</sup> BET method except as noted (3) below.

<sup>2</sup> Na exchange.

<sup>3</sup> Ethylene glycol method.

\* Errors at  $2\sigma$ .

solutions ( $12.1 \text{ mol l}^{-1}$  HCl for  $^{233}\text{U}$  and aqua regia for  $^{237}\text{Np}$  and  $^{238}\text{Pu}$ ). The pH of each solution was subsequently adjusted to  $7.5 \pm 0.5$  by NaOH additions. The chemical composition of each contacting solution after radiotracer addition and pH adjustment is given in Table 3.

### 2.3. Radiotracers

Individual bulk solutions of  $^{233}\text{U}$ ,  $^{237}\text{Np}$  and  $^{238}\text{Pu}$  were prepared in each of the three reference solutions. Each bulk radiotraced solution was filtered through  $0.4 \mu\text{m}$  polycarbonate filters prior to use. The solutions used under reduced oxygen conditions in the controlled atmosphere chamber were allowed to equilibrate with this environment for one week prior to filtration. To account for any losses of radiotracer from solution due to precipitation or vial wall adsorption, aliquots were taken from the bulk solutions for

radiometric analyses at times corresponding to the sorption period used in experiments described in 3.1. The radiotracer concentrations in solution determined from these analyses are given in Table 4 and were used in the calculation of the sorption coefficients.

## 3. Experimental method

### 3.1. Static batch sorption

Two distinct redox/pH environments were used in this study. Normal atmospheric  $\text{O}_2$  conditions were maintained for one mineral set with each solution composition. A second mineral set was exposed to the radiotracer solutions under reduced  $\text{O}_2$  conditions. The low  $\text{O}_2$  environment was maintained in a Vacuum Atmosphere Company chamber using high-purity  $\text{N}_2$  as the cover gas. Oxygen levels in the cover gas were maintained at  $<0.5$  ppm as measured by a Teledyne Analytical Instrument Model 317-1X trace  $\text{O}_2$  analyzer.

One-gram portions of each mineral except muscovite were placed in the individual polypropylene bottles used as reaction vessels. The limited supply of muscovite necessitated the use of 0.5-g portions of this mineral. All mineral samples in the low- $\text{O}_2$  environment study were allowed to stand in this atmosphere for at least one week prior to contact with the radiotracer solution.

Four millilitres of the appropriate radiotracer solution was added to each reaction vessel (2 ml in the case of muscovite) to produce a solution-to-solid ratio of 4. This ratio was chosen as a compromise between the low solution-to-solid ratios typical of natural settings and the need for adequate volumes of solution for analyses.

Three replicates of each solution-radionuclide-mineral-redox/pH combination were used. The pH of each contacting solution was measured prior to contacting and individual pH measurements were made on each radionuclide-mineral combination at sample time. The initial pH values measured for each radiotracer solution were 7.5–8.0 under oxic conditions and 8.0–8.5 under reduced  $\text{O}_2$  conditions. At the end of the sorption period, the measured pH under oxic conditions had increased to 8.0–8.5 for all solution-mineral combinations except for goethite and quartz (pH 7.0–7.5) and kaolinite (pH 6.5–7.0). Under reduced  $\text{O}_2$  conditions, all mineral-solution combinations had a final measured pH of  $9.5 \pm 0.5$ . Three replicates of each contacting solution were taken for radiometric analysis to determine the radionuclide concentration in solution with no mineral sorbing surface present (Table 4). Liquid scintillation counting was used for analysis of U and Pu; gamma spectrometry was used to analyze the Np-containing solutions.

A contact period ranging between 27 and 30 d was used in this set of experiments. Aliquots of solution were taken from each radionuclide-mineral combi-

Table 3. Solution compositions used in actinide-mineral sorption studies ( $\text{mg} \cdot \text{l}^{-1} \pm 5\%$ )

Constituent	Uranium contacting solutions			Neptunium contacting solutions			Plutonium contacting solutions		
	1300 TDS	2300 TDS	11800 TDS	1850 TDS	2830 TDS	12580 TDS	140 TDS	1120 TDS	10870 TDS
Na	500	670	2330	620	790	2450	30	200	1860
K	0.16	1.4	13.7	0.16	1.4	13.7	0.16	1.4	13.7
Mg	0.6	5.6	58.4	0.6	5.6	58.4	0.6	5.6	58.4
Ca	20	200	1940	20	200	1940	20	200	1940
Sr	0.2	2.3	23	0.2	2.3	23	0.2	2.3	23
Fe	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
SiO <sub>2</sub>	<0.6	0.6	10.5	<0.6	0.6	10.5	<0.6	0.6	10.5
F	0.02	0.2	1.7	0.02	0.2	1.7	0.02	0.2	1.7
Cl	770	1300	6650	700	1230	6580	70	600	5950
SO <sub>4</sub>	9.9	97	980	9.9	97	980	9.9	97	980
NO <sub>3</sub>				500	500	500	10	10	10
HCO <sub>3</sub> *	0.5	2	17.4	0.5	2	17.4	0.5	2	17.4
Initial pH	7.5±0.5	7.5±0.5	7.5±0.5	7.5±0.5	7.5±0.5	7.5±0.5	7.5±0.5	7.5±0.5	7.5±0.5

\* Actual value depends upon equilibrium with pCO<sub>2</sub> in the atmosphere at a given pH.

Table 4. Initial actinide concentrations in absence of sorbing minerals mol l<sup>-1</sup>

TDS	Normal O <sub>2</sub> atmosphere			Low O <sub>2</sub> atmosphere		
	U	Np	Pu	U	Np	Pu
Low	$1.35 \times 10^{-7}$	$8.84 \times 10^{-6}$	$1.49 \times 10^{-10}$	$1.50 \times 10^{-7}$	$9.54 \times 10^{-6}$	$7.62 \times 10^{-11}$
Mid	$1.55 \times 10^{-7}$	$8.84 \times 10^{-6}$	$2.05 \times 10^{-10}$	$1.53 \times 10^{-7}$	$9.38 \times 10^{-6}$	$1.19 \times 10^{-10}$
High	$1.62 \times 10^{-7}$	$9.05 \times 10^{-6}$	$3.58 \times 10^{-10}$	$1.61 \times 10^{-7}$	$8.96 \times 10^{-6}$	$3.05 \times 10^{-10}$

nation to determine the amount of sorption that occurred. Experimentally determined sorption values, expressed as  $R_d$  in units of  $\text{ml} \cdot \text{g}^{-1}$ , are calculated from

$$R_d (\text{ml} \cdot \text{g}^{-1}) = \left( \frac{V}{wt} \right) \left( \frac{C_0 - C_f}{C_f} \right)$$

where  $V$  is the volume of contacting solution in ml,  $wt$  is the weight of solid in g,  $C_0$  is the initial radiotracer concentration in  $\text{Bq} \cdot \text{ml}^{-1}$ , and  $C_f$  is the final radiotracer concentration in  $\text{Bq} \cdot \text{ml}^{-1}$ .

In a number of cases, the radioactivity in solution was at, or below, the detection limit at the end of the sorption period. In these situations the detection limit value was used to calculate the  $R_d$  value. This approach may underestimate the actual sorption that occurred.

With the exception of calcite, quartz and epidote, where gravity settling was considered adequate to separate the solid from the solution phase, each mineral-solution combination was centrifuged at approximately 2800 g for 15–20 min prior to removing a liquid aliquot for radiometric analysis. Since a centrifuge could not be placed in the controlled-atmosphere chamber, all samples requiring centrifugation were removed from the chamber. All reaction vessels remained sealed until aliquots were removed for analysis (to maintain the low O<sub>2</sub> atmosphere).

### 3.2. Oxidation state analyses

For each of the actinide solutions, a  $0.5 \text{ mol} \cdot \text{l}^{-1}$  solution of thenoyltrifluoroacetone (TTA) in xylene was used to extract the (IV) oxidation state from an equivalent volume of aqueous solution made  $1 \text{ mol} \cdot \text{l}^{-1}$  in HNO<sub>3</sub> [12]. For Np speciation, a second aqueous aliquot was made 1 M in HNO<sub>3</sub> and extracted with 10 vol% trioctylamine (TOA) in xylene to determine the fraction of neptunium present as Np(VI) in solution [13]. With the exception of the U contacting solutions under atmospheric O<sub>2</sub> conditions, where insufficient solution was available, aliquots of each radiotracer solution were subject to liquid-liquid extraction prior to initiating sorption. At the end of the sorption period, an aliquot was taken for each mineral-solution-redox/pH condition for both Np and Pu and extracted with TTA. A more limited number of U solution samples from the controlled atmosphere chamber were also taken through this extraction procedure. The aliquots taken from solutions under reduced O<sub>2</sub> conditions were returned immediately to the controlled atmosphere chamber for extraction.

### 3.3. Statistical analyses of data

Subsets of the data were tested to determine the significance of experimental variables on measured sorption using the Student's double-sided  $t$ -test. The data sets were compared on the basis of:

Table 5. Experimental sorption values under normal O<sub>2</sub> atmospheric conditions, ml · g<sup>-1</sup> (mean ± standard deviation)

Mineral	233 U			237 Np			238 Pu		
	1300 TDS	2300 TDS	11800 TDS	1850 TDS	2830 TDS	12580 TDS	140 TDS	1120 TDS	10870 TDS
Calcite	59 ± 7	75 ± 8	6.9 ± 1.0	49* ± 1	48* ± 1	6.5 ± 2.3	480 ± 100	93 ± 2	20 ± 1
Chlorite	1500* ± 0	400 ± 20	5.8 ± 0.3	57* ± 1	38 ± 4	12 ± 4	350 ± 100	400 ± 170	570 ± 30
Epidote	3.8 ± 0.3	2.5 ± 0.2	0.8 ± 0.1	2.2 ± 0.4	1.1 ± 0.4	0.6 ± 0.2	450 ± 330	180 ± 60	56 ± 6
Goethite	1500* ± 0	1700* ± 0	1400* ± 0	55* ± 5	39 ± 7	16 ± 3	400 ± 300	180 ± 20	280 ± 80
Gypsum	1.8 ± 0.1	2.0 ± 0.1	1.4 ± 0.1	1.2 ± 0.3	1.4 ± 0.7	0.6 ± 0.6	250 ± 10	130 ± 30	140 ± 20
Hematite	1500* ± 0	1700* ± 0	1800* ± 0	69* ± 2	68* ± 6	68* ± 2	2200* ± 0	3100* ± 0	550 ± 40
Illite	91 ± 1	87 ± 4	39 ± 1	57* ± 4	39* ± 11	7.8 ± 3.1	2200* ± 0	810 ± 110	5400* ± 0
Kaolinite	1500* ± 0	1700* ± 0	1800* ± 0	2.6 ± 1.2	1.4 ± 0.6	2.0 ± 0.5	1400* ± 700	150 ± 10	3100* ± 2100
Muscovite	1500* ± 0	89 ± 5	9.7 ± 0.4	1.6 ± 0.5	0.5 ± 0.8	0.9 ± 1.6	510 ± 90	69 ± 10	8.5 ± 0.3
Quartz	20 ± 8	3.9 ± 0.2	0.4 ± 0.1	0	0	0	39 ± 4	4.5 ± 0.5	3.0 ± 0.1

\* Based on detection limit values.

Table 6. Experimental sorption values under low O<sub>2</sub> atmospheric conditions, ml · g<sup>-1</sup> (mean ± standard deviation)

Mineral	233 U			237 Np			238 Pu		
	1300 TDS	2300 TDS	11800 TDS	1850 TDS	2830 TDS	12580 TDS	140 TDS	1120 TDS	10870 TDS
Calcite	320 ± 80	220 ± 40	35 ± 2	66* ± 3	64* ± 3	15 ± 4	390 ± 30	200 ± 80	19 ± 2
Chlorite	560 ± 150	540 ± 110	69 ± 64	58* ± 3	13 ± 2	9.5 ± 3	150 ± 80	280 ± 70	150 ± 40
Epidote	52 ± 14	180 ± 60	86 ± 47	13 ± 3	9.1 ± 2	3.6 ± 0.2	150 ± 3	220 ± 20	38 ± 26
Goethite	860 ± 340	960 ± 100	590 ± 210	62* ± 6.2	47* ± 13	20 ± 8	210 ± 60	170 ± 130	170 ± 50
Gypsum	110 ± 70	97 ± 30	27 ± 14	5.1 ± 1.1	5.1 ± 1.0	3.0 ± 0.4	67 ± 9	82 ± 6	140 ± 40
Hematite	1100 ± 240	1000 ± 210	830 ± 210	84* ± 3	80* ± 6	72* ± 1	1100* ± 0	1800* ± 0	1400 ± 400
Illite	250 ± 140	370 ± 240	180 ± 80	79* ± 4	76* ± 7	25 ± 5	1200 ± 300	1700 ± 200	2300 ± 1200
Kaolinite	1000 ± 210	1300* ± 340	950 ± 100	4.1 ± 1.3	2.1 ± 0.3	2.6 ± 0.5	1500* ± 0	2400* ± 0	3600* ± 2200
Muscovite	710 ± 0	610 ± 220	730 ± 320	6.3 ± 0.8	5.3 ± 2.0	3.0 ± 1.4	67 ± 5	91 ± 38	12 ± 1
Quartz	120 ± 30	87 ± 17	41 ± 19	1.3 ± 0.2	0.8 ± 0.1	3.7 ± 1.1	23 ± 1	20 ± 1	9.2 ± 1.0

\* Based on detection limit values.

- i) mineral type;
- ii) redox/pH regime; and
- iii) TDS concentration in solution.

#### 4. Results and discussion

##### 4.1. Uranium

In the low-O<sub>2</sub> atmosphere 95–100% of the dissolved U, was found to be in the (VI) oxidation state. Liquid-liquid extractions could not be performed with U solutions under normal atmospheric conditions because of limited volumes of solution. However, U(VI) is expected to dominate under oxic conditions. Extractions completed on aliquots from selected mineral-solution combinations in the low O<sub>2</sub> atmosphere after the sorption period indicated that any remaining U existed in solution as U(VI).

Tables 5 and 6 contain a summary of sorption results obtained for this radionuclide.

##### 4.1.1. Effect of mineral type

Under normal atmospheric O<sub>2</sub> conditions, goethite, hematite and kaolinite lowered U concentrations to detection limits in all three solutions. Consequently,

no valid test for differences between the sorption results obtained with these minerals is possible. As well, detection limits were reached for U with chlorite and muscovite in the low-TDS solution. Therefore, tests for significance in results obtained with these minerals and those mentioned above are not possible for low-TDS solutions. Under the experimental conditions used, however, it appears that these minerals have similar, high sorption capacities for uranium. For the remaining mineral-solution combinations, *t*-test results indicated a significant difference at the 0.95 confidence level ( $P < 0.05$ ) between data sets for similar solution compositions in 110 of the possible 119 remaining combinations. These results illustrate that many fracture-infilling minerals have different sorption capacities for uranium under oxic conditions.

Under the reduced O<sub>2</sub> conditions, significant differences existed ( $P < 0.05$ ) in the data sets obtained for the minerals in 61 of the 135 possible cases. Illite sorption data showed no significant difference in 20 of the possible 27 combinations compared with sorption data sets obtained for the other minerals. No explanation is readily available except that measured sorption for this mineral fell roughly in a median range between the high and low values obtained with the minerals as a whole. No significant differences could

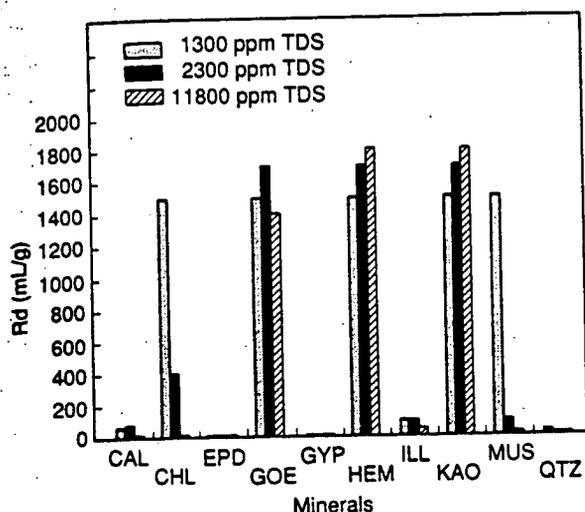


Fig. 1. Uranium sorption on fracture-infilling minerals as a function of TDS under normal O<sub>2</sub> atmosphere conditions.

be measured between data sets for the three minerals showing least sorption—quartz, epidote and gypsum. Similarly, comparison of the results for hematite, kaolinite and goethite, the minerals with the highest sorption values, showed no significant differences by the *t*-test.

Since sorption is a surface phenomenon, it might be expected that a direct correlation could be made between available surface area and sorption, regardless of mineral type. The goethite and gypsum used in this study have very similar BET surface areas (see Table 2) but are quite different in chemical composition. A comparison of the six data sets obtained for goethite with those obtained for gypsum indicates significant differences for all six cases at  $P < 0.1$  and 4 of the six cases at  $P < 0.005$ . Therefore, it would appear that available surface area was not of primary importance in determining the sorptive capacity of these two minerals for uranium.

The general effect of mineral type on measured sorption is illustrated in Figures 1 and 2.

#### 4.1.2. Effect of redox/pH

The low O<sub>2</sub> conditions imposed in the controlled-atmosphere chamber also result in increased pH in all solutions. It is unlikely that truly reducing conditions were achieved since O<sub>2</sub> remained detectable in the chamber atmosphere, albeit at low concentrations (<0.5 ppm). It is more probable that differences in solution pH account for any significant differences found in sorption on this suite of minerals in the low O<sub>2</sub> chamber as compared to sorption measured under normal atmospheric conditions.

A significant difference ( $P < 0.05$ ) exists in the data sets obtained with calcite in all three solutions. No significant differences were found for the hematite, illite or kaolinite data sets. The data sets for all remain-

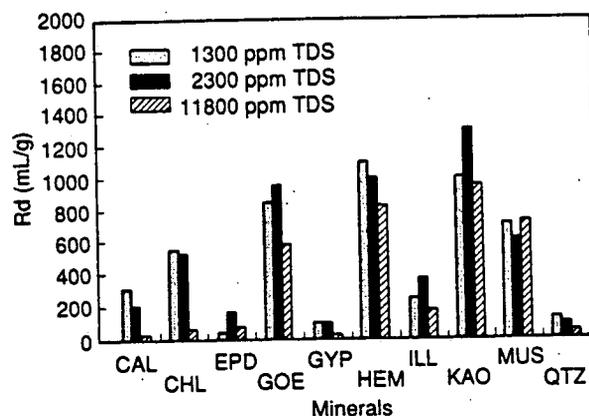


Fig. 2. Uranium sorption on fracture-infilling minerals as a function of TDS under low O<sub>2</sub> atmosphere conditions.

ing minerals indicate that differences exist at  $P < 0.10$  in 14 of the 18 remaining cases. In general, those minerals having the least affinity for U under normal atmospheric conditions (calcite, epidote, gypsum and quartz) showed an increase in sorption under the changed redox/pH conditions in the controlled-atmosphere chamber. Conversely, the measured sorption decreases somewhat under controlled-atmosphere conditions for the five minerals that showed the greatest sorption capacity under normal atmospheric conditions.

#### 4.1.3. Effect of TDS

The TDS content of each contacting solution influenced sorption for all minerals except goethite, hematite and kaolinite under normal atmospheric conditions. For these three minerals virtually all U was removed from each of the three solutions. In all other cases, an inverse relationship was generally found between sorption and TDS, with the highest sorption occurring from the lowest-TDS solution. Significant differences ( $P < 0.05$ ) existed in all three combinations of data sets for chlorite, epidote and muscovite. Data sets for calcite, quartz and illite were found to be significantly different ( $P < 0.05$ ) where the low- and medium-TDS solutions were compared with the high-TDS solution but not when data sets for the two lower-TDS solutions were compared with each other. These results indicate that relatively high levels of TDS in solution will result in competition for uranium sorption sites. The lack of sorption from the high-TDS solutions with chlorite and muscovite compared with the substantial sorption noted from low-TDS solutions may indicate that an ion exchange process is important for U sorption on these two minerals. However, increased TDS appears to result in a slight increase in U sorption with goethite, hematite and kaolinite under similar conditions.

The data sets were subject to regression analysis. Where the  $R^2$  value exceeded 0.90 for the quadratic

Table 7. Regression analysis coefficients to describe sorption as a function of TDS

Mineral	Atmo- sphere		Uranium				Neptunium				Plutonium			
			$R^2$	$b_0$	$b_1$	$b_{11}$	$R^2$	$b_0$	$b_1$	$b_{11}$	$R^2$	$b_0$	$b_1$	$b_{11}$
Calcite	Normal	O <sub>2</sub>	0.99	-23.36	14.9	-2.2					0.99	5.39	-1.45	0.11
Calcite	low	O <sub>2</sub>	0.97	-0.46	1.96	-0.41					0.97	1.01	1.51	-0.36
Epidote	normal	O <sub>2</sub>	0.98	4.65	-1.69	0.13								
Epidote	low	O <sub>2</sub>					0.92	8.3	-3.35	0.36				
Illite	normal	O <sub>2</sub>	0.99	-2.84	3.00	-0.47								
Muscovite	normal	O <sub>2</sub>									0.99	5.66	-1.49	-0.08
Muscovite	low	O <sub>2</sub>									0.93	-2.32	3.10	-0.56
Quartz	normal	O <sub>2</sub>	0.98	30.7	-15.0	1.81					0.99	8.03	-4.11	0.55
Quartz	low	O <sub>2</sub>									0.98	0.40	0.78	-0.16

fit, sorption of uranium could be described as a function of TDS by

$$\log R_d = b_0 + b_1 \log \text{TDS} + b_{11} \log^2 \text{TDS}$$

where  $b_0$  is the constant determined by linear regression,

$b_1$  is the coefficient determined in the first approximation for TDS,

and  $b_{11}$  is the coefficient determined in the second approximation for TDS.

The coefficients are listed in Table 7. Note, however, that extrapolation cannot be used to predict sorption values for TDS concentrations outside the experimental range.

Experimental results obtained in the controlled-atmosphere chamber showed significant differences due to TDS ( $P < 0.05$ ) for calcite and chlorite where data sets for the two lowest-TDS solutions were compared with those obtained with the high-TDS solution. In general, it appears that redox/pH differences outweigh TDS effects for uranium sorption.

The results obtained here with the iron minerals goethite and hematite are similar to those obtained by Ames *et al.* [4] who reported high sorption values for U in contact with amorphous ferric oxyhydroxide. Other studies [5, 6, 8] provide sorption values for illite, kaolinite and/or muscovite that are comparable to the results obtained in this study.

Sorption values reported for granites [8, 9] and basalts [3] are similar to the values obtained here for the low-sorption-capacity minerals, such as quartz, epidote and gypsum.

#### 4.1.4. Uranium speciation

The redox potential was measured for representative samples of the synthetic groundwater-mineral combinations using gold electrodes (Cole-Parmer Cat. No. N-05994-25). While it is recognized that measurement of a meaningful Eh value in poorly poised systems such as encountered here is difficult, the values obtained were used to indicate the redox potential achieved in these solution-mineral combinations. In this low-oxygen environment, an Eh of approximately

100 mV was obtained. A redox potential of 300 mV was assumed for normal atmospheric O<sub>2</sub> conditions. The aqueous speciation program WATEQ4F and the thermodynamic database referenced therein were used to estimate the predominant uranium species likely to exist in the solutions used in this study [15].

The total carbonate in solution is dependent upon the pCO<sub>2</sub> of the surrounding atmosphere and the pH of the solution. Under normal atmospheric conditions and a solution pH of 7, the carbonate concentration as HCO<sub>3</sub><sup>-</sup> would be approximately  $5 \text{ to } 8 \times 10^{-5} \text{ mol l}^{-1}$  [20]. The major uranium species in solutions calculated by WATEQ4F were UO<sub>2</sub>CO<sub>3</sub>, UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>, UO<sub>2</sub>(OH)<sub>3</sub><sup>-</sup> and UO<sub>2</sub>H<sup>+</sup>, independent of the TDS concentration of the solution. At the same pCO<sub>2</sub> and a pH of 8, the total carbonate in solution as HCO<sub>3</sub><sup>-</sup> would be approximately  $5 \text{ to } 8 \times 10^{-4} \text{ mol l}^{-1}$  [20]. WATEQ4F calculations for the three solution compositions at this pH and carbonate concentration estimated UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> and UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup> would dominate with UO<sub>2</sub>(OH)<sub>3</sub><sup>-</sup> as the third most abundant uranium species. The UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup> species was calculated to increase in abundance while the relative concentration of the UO<sub>2</sub>(OH)<sub>3</sub><sup>-</sup> species decreased as the TDS concentration in solution increased.

Under the N<sub>2</sub> atmosphere in the enclosed chamber, the total carbonate concentration in solution should decrease as the pCO<sub>2</sub> in this atmosphere and the solution pH reach equilibrium. However, this assumption requires further experimental work and could not be confirmed in the present study. Calculations were made with WATEQ4F where the total carbonate in solution as HCO<sub>3</sub><sup>-</sup> was input as  $10 \text{ mg l}^{-1}$  as an estimate for the low pCO<sub>2</sub> conditions. With an input Eh of 100 mV and a pH value of 9 the UO<sub>2</sub>(OH)<sub>3</sub><sup>-</sup> species was calculated to predominate in all three solution compositions used in this study. Surface interactions that are mineral-dependent appear to be the primary factor in U sorption in this study. Sorption of negatively charged species has been described by the triple-layer model [21, 22]. Results of the present study indicate that different minerals possess different numbers of protonated sites suitable for the sorption of the anionic species most likely to exist in these experimental solutions.

Based on the measured pH, calculations made with WATEQ4F indicate that precipitating U species should not form in these synthetic groundwaters. However, localized conditions that would promote precipitation may exist near the surface of the solids.

#### 4.2. Neptunium

Liquid-liquid extraction procedures on Np-traced solutions indicated that Np(V) was the most probable oxidation state under all conditions used in this study. The series of extractions conducted after the sorption period showed that any Np remaining in solution remained in the (V) oxidation state. This agrees with results obtained by other researchers [7], who extracted Np(V) from solutions under similar Eh-pH conditions.

Sorption values found for Np with each mineral under each set of experimental conditions are given in Tables 5 and 6.

##### 4.2.1. Mineral effects

Under normal atmosphere O<sub>2</sub> conditions, minimum detection limits for neptunium in solution were reached for all solutions in contact with hematite, in low- and medium-TDS solutions in contact with calcite and illite, and in the lowest-TDS solution in contact with chlorite and goethite. Consequently, no statistical comparisons can be made between these data sets and they can be considered to show similar high sorption capabilities. Of the remaining possible 120 combinations 93 showed significant differences due to mineralogy at the 0.95 confidence level.

Under the reduced O<sub>2</sub> and increased pH conditions in the controlled-atmosphere chamber, Np detection limits were reached for all solutions in contact with hematite, for the low- and medium-TDS solutions in contact with calcite and illite, and for the lowest-TDS solution in contact with chlorite and goethite. Again, statistical comparisons between these data sets were not possible. Of the remaining 122 combinations 85 showed statistically meaningful differences at the 0.95 confidence level and 100 comparisons were different at the 0.90 confidence level. As was the case for U sorption, it is clear that differences in individual mineral properties greatly influence Np sorption.

##### 4.2.2. Effect of redox/pH

No significant differences were determined between data sets for goethite and kaolinite due to redox/pH changes. Results obtained for epidote, gypsum and quartz showed significantly different sorption values ( $P < 0.05$ ) for all three solution types. Since detection limits for Np were reached in most cases for solutions in contact with calcite, hematite and illite, comparisons cannot be made for the sorption values obtained with these minerals. In the latter cases, sorption

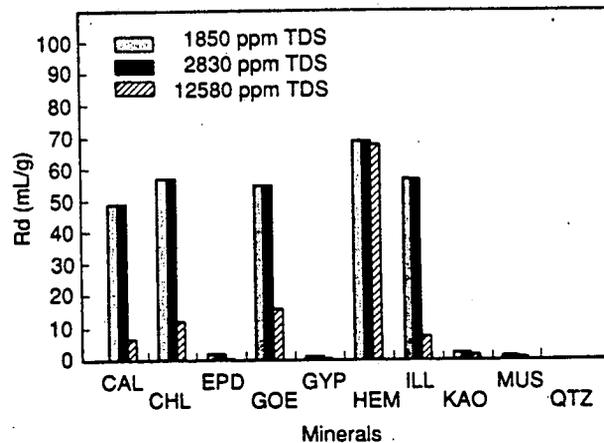


Fig. 3. Neptunium sorption on fracture-infilling minerals as a function of TDS under normal O<sub>2</sub> atmosphere conditions.

properties of the individual minerals appear to be of greater significance than any potential effects due to changes in the redox/pH conditions.

##### 4.2.3. Effects of TDS

Only the data sets for chlorite under normal atmospheric conditions showed significant differences ( $P < 0.05$ ) for all three comparisons based on TDS. Sorption values for minerals such as calcite, chlorite and goethite decreased substantially for the high-TDS solution compared with the two lower TDS solutions. It is noteworthy that of the 27 mineral data set comparisons discussed in section 4.2.1, where no significant differences between data sets were found based on mineralogy, 18 occurred with data sets for high-TDS solutions. It appears that the effect of TDS outweighs that of mineralogy in these cases.

As was the case for normal atmospheric conditions, 23 of the 37 comparisons under low O<sub>2</sub> conditions that showed no significant difference were data sets from the high-TDS solution. Calcite, chlorite, epidote and goethite had substantially lower sorption values from the high-TDS solution compared with the two lower-TDS solutions.

No statistical differences were found at the 0.95 confidence level for sorption with gypsum, kaolinite or muscovite under either normal atmospheric or low O<sub>2</sub> conditions. Results obtained for quartz showed no significant difference due to TDS under normal atmospheric conditions. Since detection limits for Np were reached for hematite and illite, comparisons of data sets could not be made.

The effect of both mineral type and TDS under normal and low O<sub>2</sub> conditions are illustrated in Figures 3 and 4. Sorption values of zero with quartz confirmed that vial wall sorption was not a factor for this radionuclide under these conditions. The minerals epidote, gypsum, kaolinite and muscovite show only slight affinity for neptunium. Hematite consistently shows the greatest ability to remove Np from solution

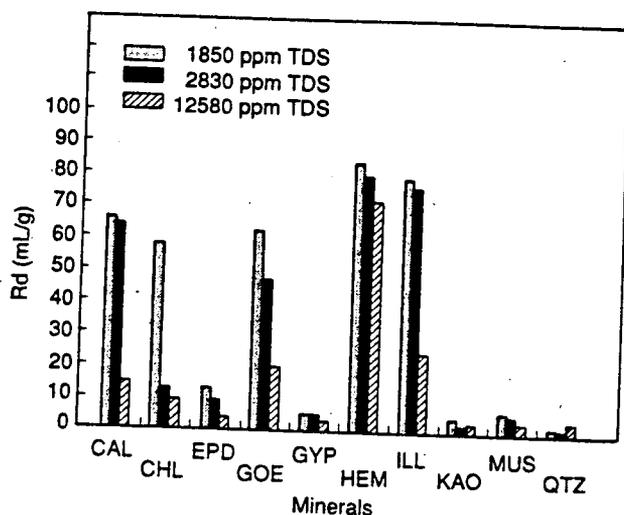


Fig. 4. Neptunium sorption on fracture-infilling minerals as a function of TDS under low  $O_2$  atmosphere conditions.

with all detectable Np removed from all three groundwaters under normal atmospheric conditions. Calcite, chlorite, goethite and illite removed all detectable Np from low- but not from high-TDS solutions. This demonstrates the inverse relationship between sorption and TDS for this element. In most cases, marginally higher sorption values were obtained under the low  $O_2$  conditions in the controlled atmosphere chamber, but the general trends noted from normal atmospheric  $O_2$  experimental conditions hold. Regression analysis on data sets allow sorption of Np to be expressed as a function of TDS. The coefficients for cases where  $R^2 > 0.90$  are given in Table 7.

Other researchers have also found that illite has a higher sorption capacity for Np than kaolinite [10]. However, significantly larger sorption values have also been reported for Np sorption with kaolinite [2]. Other data [8] suggest little difference in sorption capacity between three reference granites and illite.

#### 4.2.4. Neptunium speciation

Brookins [14] reports that  $NpO_2^+$  would likely predominate in solution under normal atmospheric oxygen conditions and the measured pH for the solutions used in this study. If  $NpO_2^+$  were predominant, it could be expected that Np sorption would correlate to the cation exchange capacity of the minerals. However, no such correlation is evident. Under reduced  $O_2$  conditions, and pH values of  $9.5 \pm 0.5$ ,  $Np(OH)_4$  would likely be the predominant Np(IV) species in solution [23]. However,  $NpO_2^+$  may persist in neutral or slightly basic solutions similar to those used in this study in the 0–100 mV range. This possibility is supported by the liquid-liquid extraction data, which indicated that Np was present as Np(V) in solution.

Other studies [7, 24] have indicated that Np will form carbonate complexes at  $Eh > 300$  mV when total carbonate exceeds about  $10^{-4}$  mol  $\cdot$  l $^{-1}$ . The  $NpO_2CO_3^-$  species could form in the high TDS solu-

Table 8.

Solution	Normal $O_2$ atmosphere		Low $O_2$ atmosphere	
	Pu(IV)	Pu(V, VI)	Pu(IV)	Pu(V, VI)
140 TDS	33	67	90	10
1120 TDS	51	49	55	45
10870 TDS	85	15	94	6

tion used in this work at a pH of  $\sim 8$  whereas it would be less likely to form in the low TDS solutions at pH values below 8.5 [25].

#### 4.3. Plutonium

Sorption values obtained for Pu with the suite of fracture-infilling minerals are shown in Tables 5 and 6. Results of the liquid-liquid extractions on Pu contacting solution aliquots are shown in Table 8. These extractions indicated that Pu(IV) dominated in the low-TDS solution under low  $O_2$  conditions and in the high-TDS solution under both atmospheric conditions. The medium-TDS solution appeared to have nearly equal distributions between the reduced and oxidized states, while the low-TDS solution contained substantially more Pu(V, VI) under normal atmospheric conditions. Where detectable Pu remained in solution after the sorption period, the results of liquid-liquid extractions generally indicated that the ratio of reduced-to-oxidized Pu in solution remained similar to that in the starting solution.

##### 4.3.1. Effects of minerals

Of the 135 possible comparisons of sorption data sets under normal atmospheric conditions, 83 were found to be significantly different ( $P < 0.05$ ). In some solutions containing hematite or illite where the Pu detection limits were reached, comparisons were not possible. Under low  $O_2$  conditions, 79 of the possible 127 comparisons indicated that the data sets were significantly different ( $P < 0.05$ ). Of the minerals used in this work, quartz generally shows least sorption of Pu. Hematite, illite and kaolinite show the greatest affinity for Pu regardless of redox/pH condition or TDS content of each solution. Figures 5 and 6 illustrate sorption values obtained under both redox/pH conditions.

##### 4.3.2. Effect of redox/pH

Only data obtained with quartz showed significant differences due to changed redox/pH conditions in all three solutions. No differences were determined for calcite, epidote or goethite. Although comparisons are not strictly valid for hematite, illite and kaolinite since minimum detection limits for Pu were reached, it does not appear that experimentally induced redox/pH con-

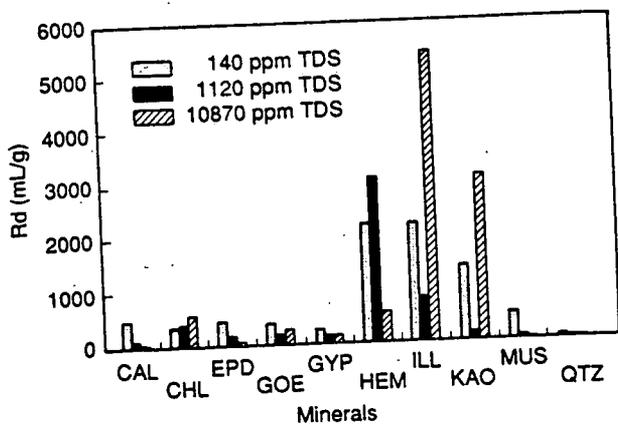


Fig. 5. Plutonium sorption on fracture-infilling minerals as a function of TDS under normal  $O_2$  atmosphere conditions.

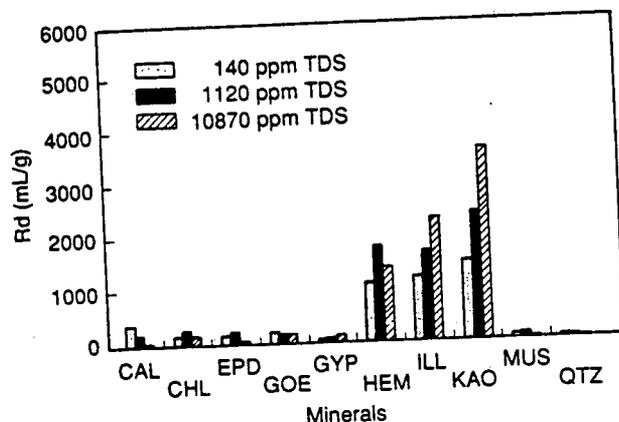


Fig. 6. Plutonium sorption on fracture-infilling minerals as a function of TDS under low  $O_2$  atmosphere conditions.

ditions significantly affected sorption. In general, the effect of the two redox/pH conditions imposed in this experiment appear to be minimal for Pu.

#### 4.3.3. Effect of TDS

Under normal atmospheric  $O_2$  conditions, data sets obtained for sorption on calcite, muscovite and quartz were significantly different for all three comparisons based on TDS. Under low  $O_2$  conditions, only the data sets with epidote were significantly different ( $P < 0.05$ ) for all three combinations. These data sets were subjected to regression analysis as described previously and equations were obtained to describe Pu sorption as a function of TDS where  $R^2 > 0.90$  (see Table 7). No significant differences could be seen for data sets involving chlorite, goethite, hematite, illite or kaolinite.

Torstenfelt *et al.* [8] reported sorption values for Pu in contact with three granites ranging from approximately  $60$  to  $250 \text{ ml} \cdot \text{g}^{-1}$ . As well, these researchers measured sorption values between  $150$  and  $200 \text{ ml} \cdot \text{g}^{-1}$  for an illite clay. These results indicate a relatively uniform amount of Pu sorption, whereas the present study found sorption values to range over two orders of magnitude depending on mineral type.

#### 4.3.4. Plutonium speciation

Brookins [14] suggests the insoluble species  $\text{PuO}_2$  would dominate in solution having compositions similar to those used here. Experimental sorption results indicate that some precipitation does occur from all solutions under both redox conditions. However, if sorption values for quartz ( $3-40 \text{ ml} \cdot \text{g}^{-1}$ ) are used as a conservative estimate of Pu removal due to precipitation rather than physical or chemical sorption, it would appear that other mechanisms for Pu removal from solution are important in these experimental systems.

## 5. Conclusions

This study provides data on the ability of fracture-infilling minerals common to granitic rock to remove actinides from solution. The data illustrate that mineralogy is one of the most important factors to consider in any assessment of a fractured geological formation as a potential site for radioactive waste disposal. The total carbonate concentration in solution is a major factor in determining actinide speciation. Further study is required to determine if anionic carbonate and hydroxide species have different sorption characteristics. The TDS of a solution will influence actinide speciation, which in turn may affect the ability of the solid to remove the actinide from solution. Further, competition for sorption sites as TDS increases may account for decreased actinide sorption on some mineral surfaces. The redox/pH conditions imposed on the experimental system also results in some variation in sorption. This can be attributed to changes in solution species as well as an increased tendency to precipitate formation under certain conditions. Solution pH, which varied with the atmosphere surrounding the solution in this study, also influences speciation and appears to play a role in the relative ability of minerals to sorb these actinides in some instances.

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<sup>2</sup> Unrestricted, unpublished report, available from SDDO, Atomic Energy of Canada Limited Research Company, Chalk River, Ontario KOJ 1J0.