

The redox chemistry of Pu(V)O_2^+ interaction with common mineral surfaces in dilute solutions and seawater

WENDY L. KEENEY-KENNICUTT and JOHN W. MORSE

Department of Oceanography, Texas A&M University, College Station, Texas 77843

(Received November 8, 1984; accepted in revised form September 23, 1985)

Abstract—It has long been recognized that the Pu^{4+} ion can be readily adsorbed on solid surfaces, but it has been assumed that the generally more abundant Pu(V)O_2^+ ion should have little affinity for surfaces. Our results indicate that Pu(V)O_2^+ can be adsorbed from dilute solutions and seawater on goethite, aragonite, calcite, and $\delta\text{-MnO}_2$. Adsorption on $\delta\text{-MnO}_2$ is severely depressed in seawater, probably as a result of site competition with seawater cations.

The sorption behavior of PuO_2^+ is influenced by oxidation-reduction reactions occurring on the mineral surfaces. Adsorption on $\delta\text{-MnO}_2$ results in oxidation of adsorbed Pu(IV) and Pu(V) to Pu(VI) . However, adsorption on goethite results in a reaction in which Pu(IV) and Pu(VI) are formed on the mineral surface. The Pu(VI) is slowly reduced to Pu(IV) , leaving Pu(IV) as the dominant surface Pu species. This reaction can be photochemically catalyzed. PuO_2^+ adsorbed on carbonate minerals behaves similarly to Np(V)O_2^+ and undergoes little change in oxidation state after adsorption.

INTRODUCTION

THE PROCESSES RESPONSIBLE for the control of plutonium distribution and removal from natural aquatic systems have received increased attention in recent years. Research has focused on determining the distribution of Pu in different environments and, to a lesser extent, determining the rates at which it passes through or is sequestered in these environments. Numerous articles and books summarizing these findings are available (e.g., NAS, 1971; IAEA, 1976; FORSTER, 1976; LABEYRIE *et al.*, 1976; CLEVELAND, 1979; EDELSTEIN, 1981; SHOLKOVITZ, 1983; NELSON *et al.*, 1985). However, the actual chemistry involved in many of these processes and the pathways followed remained uncertain. Much of this uncertainty is the result of the extremely low Pu concentrations found in natural systems and the complex chemistry of Pu, which can simultaneously exist in at least three oxidation states (IV, V, and VI) in oxic waters. If further advances in our understanding of the behavior of Pu in natural systems are to be made, reliable data must be obtained about the chemical speciation of Pu and its interaction with organic materials and surfaces in natural waters.

A general observation has been that dissolved Pu in freshwater and seawater systems is found as a mixture of the oxidized and reduced forms (see NELSON *et al.*, 1985 for recent summary). The oxidized form is currently believed to be present mainly as a Pu(V)O_2^+ and to a much lesser extent as Pu(VI)O_2^{2+} (e.g., NELSON and ORLANDI, 1979; ASTON, 1980; BONDIETTI and TRABALKA, 1980; RAI *et al.*, 1980). Pu associated with sediments and particulate organic matter is reduced, with Pu(IV) probably being the dominant form (e.g., NELSON and LOVETT, 1978, 1981; SILVER, 1983; NELSON *et al.*, 1985). CHOPPIN and MORSE (1985) have summarized the currently available information on the chemical controls on the oxidation state of dissolved

Pu. They emphasize the importance of kinetic rather than equilibrium controls on dissolved Pu speciation in natural waters. A major question which has persisted concerns which pathway dissolved Pu in the oxidized form takes when transformed to adsorbed Pu in the reduced form. The two major choices are reduction of dissolved Pu followed by adsorption, or adsorption of the oxidized form followed by subsequent reduction on particle surfaces.

The direct removal of dissolved reduced Pu can be viewed as a "trickle down" in which a fraction of the Pu^{4+} is continuously lost to particle surfaces. In this situation, the dissolved Pu^{4+} is always at a higher concentration than is necessary for exchange equilibrium with the particle surfaces. Under such conditions, it has been contended, without verification, to parallel Th^{4+} behavior (e.g., SANTSCHI *et al.*, 1980; SANTSCHI, 1984; NELSON *et al.*, 1984). While this mechanism is almost certainly occurring in some systems, it is doubtful, based on recent laboratory studies (e.g., CHOPPIN and SAITO, 1984; SAITO *et al.*, 1985) of natural and artificial seawater, that the Pu^{4+} could be produced at sufficient rates to present a sufficient supply for removal by particles in environments other than those with extremely low suspended particle concentrations (e.g., the central Pacific Ocean).

The alternate possibility is that Pu is reduced after adsorption. The primary difficulties with this mechanism have been the assumption that the oxidized Pu should have a very low affinity for particle surfaces. The lack of Pu(VI)O_2^{2+} adsorption is largely based on analogy to the behavior of U(VI)O_2^{2+} , which does not interact strongly with surfaces in natural aquatic systems. It has also been argued (e.g., BONDIETTI and TAMURA, 1980; EDGINGTON, 1981) that Pu(V)O_2^+ should have even a lower surface affinity since it is a singly charged ion. However, KEENEY-KENNICUTT and MORSE (1984) have recently demonstrated that



ADMIN RECORD

2577 DOCUMENT CLASSIFICATION
REVIEW WAIVER PER
CLASSIFICATION OFFICE

SW-A-004586

Best Available Copy

(1977) Some peculiar rocks after mission Cratering (eds. MERRILL), pp. 343-
59) The relationship of data on the Ivory Coast 11-6815.
Program for computer detectors and other 19452, pp. 31. Univ.
The radioactivity of ion of the Bosumtwi Acta 33, 1101-1102. at Lake Bosumtwi trewnfield. National 1964 projects, 201-
URLEY P. M. (1966) umtwi crater area, Ivory Coast tektites.
and THOMAS H. H. nces in Ivory Coast r area. Ghana. Geo-
32) Age and prove- tes and possible im- Rb-Sr systematics.
xygen isotope studies asses from the Bos- -175.
ERON A. E. (1969) with lead in earth 33, 1045-1055.
4 degree field sheet ll. 30.
MULLER O. (1983) r tektites and crater sium. J. Radioan.
s of tektites. In Ra- 05.

Y12

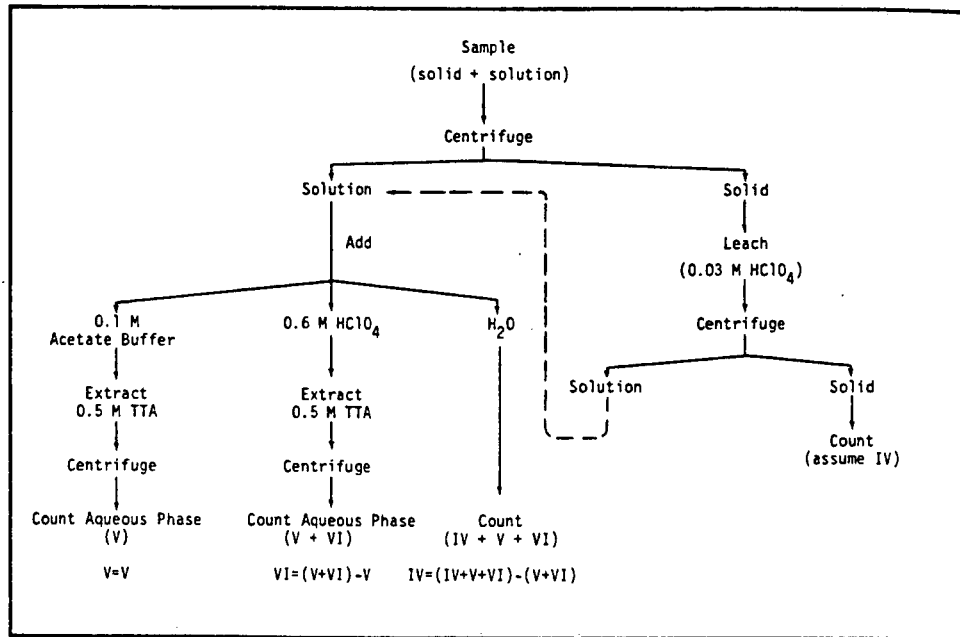


FIG. 1. Analytic "flow diagram" of methods used to determine Pu oxidation state. Note that the solution obtained from leaching the solid is analyzed separately from the solution obtained from the initial centrifugation.

Np(V)O_2^+ has a surprisingly high affinity for common mineral surfaces in both dilute solutions and seawater. While extensive adsorption of the Np(V) on mineral surfaces was found, there was no evidence for it being reduced after adsorption. Consequently, the central question of the ability of surfaces to cause Pu reduction remains, but it does seem possible that Pu(V)O_2^+ could be significantly adsorbed from natural waters.

Based on the Np(V)O_2^+ results, we undertook the research presented in this paper to determine how extensively Pu(V)O_2^+ would adsorb on common mineral surfaces and if it could be reduced subsequent to adsorption. While we recognize that organic matter adsorbed on natural particle surfaces may significantly alter the chemical behavior of adsorbed Pu, we feel that it is necessary first to establish the behavior of Pu

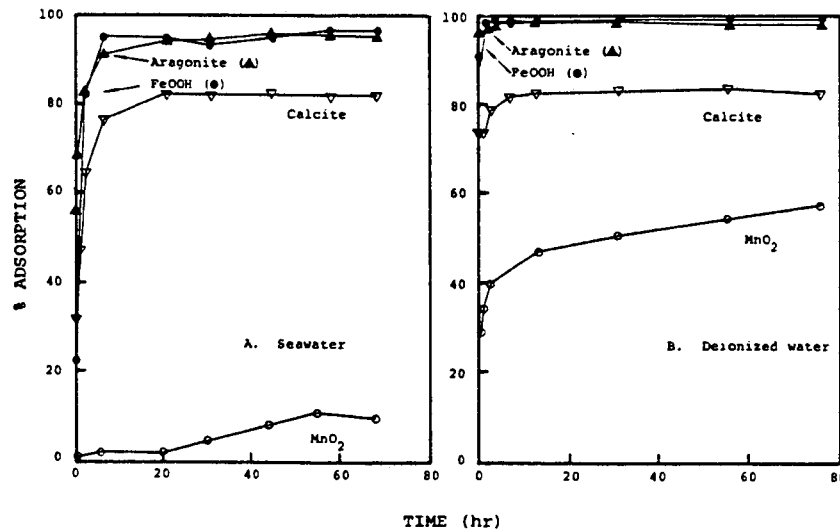


FIG. 2. Adsorption of $^{238}\text{Pu(V)O}_2^+$ at a concentration of 10^{-10} M in seawater ($S = 35$) and deionized water onto different solids at $5 \text{ m}^2 \text{ l}^{-1}$.

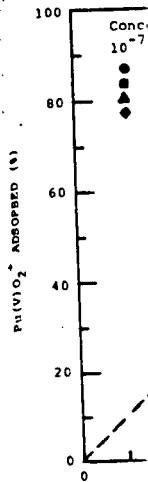


FIG. 3. A con onto carbonate ibrated with cal

with surfaces probable cor preting data : ganic matter.

M
Solids and sol

The solutio equilibrated wi and natural ne to a salinity of natural supers respect to calc at a $P_{\text{CO}_2} \approx 10$ ranged from

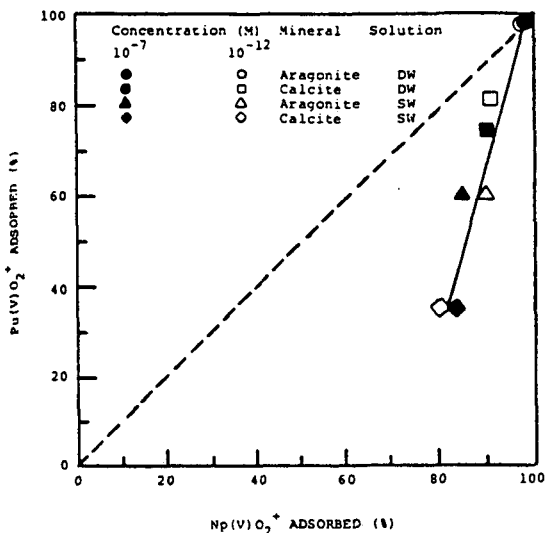


FIG. 3. A comparison of Pu(V)O₂⁺ and Np(V)O₂⁺ adsorption onto carbonate minerals (5 m² l⁻¹) in deionized water equilibrated with calcite (DW) and seawater (S = 35) (SW).

prevent the dissolution or precipitation of carbonate minerals during the adsorption experiments and to provide buffering capacity near pH 8 for the non-seawater solutions.

Pu adsorption experiments required three isotopes (²³⁶Pu, ²³⁸Pu, and ²³⁹Pu) with widely different half-lives to cover the Pu concentration range of 10⁻¹² M to 10⁻⁷ M used in this study. ²³⁹Np was used in some experiments. It was separated from ²⁴³Am as described by KEENEY-KENNICUTT and MORSE (1984). Pu(V)O₂⁺ and Np(V)O₂⁺ were prepared by the methods described by CHOPPIN and SAITO (1984) and SAITO *et al.* (1985).

The solids studied were goethite, calcite, and δ-MnO₂. Their preparation and characterization are described in detail by KEENEY-KENNICUTT and MORSE (1984).

Experimental procedures

The experimental design for the adsorption studies was similar to that employed by us previously (SHANBHAG and MORSE, 1982; KEENEY-KENNICUTT and MORSE, 1984). Counting of radioisotopes was performed with a Hewlett-Packard Model 3374 automatic liquid scintillation counter, using Liquiscint (National Diagnostics), a gel-forming scintillation cocktail. For a typical experiment, 50 ml of solution was pipetted into a 125 ml untreated borosilicate Erlenmeyer flask. An addition was made of approximately 0.1 ml of Pu(V)O₂⁺ or Np(V)O₂⁺ standard which did not significantly affect the pH or alkalinity of the solutions, and 1 ml of solution was withdrawn to determine the initial activity. The flask was shaken for 1 h to allow the isotope to equilibrate with the solution and the glass surface. Another 1 ml was withdrawn to determine any adsorption loss. No change in Pu or Np concentration was measured during this period. The solid substrate was then added at different solid to solution ratios (0.001 to 100 m² l⁻¹) and the flask was continuously shaken until the end of the experiment. At appropriate times, two aliquots were simultaneously withdrawn. One aliquot (3 ml) was centrifuged and the liquid phase was counted to determine the unadsorbed fraction of the isotope and a 1-ml aliquot was counted directly to determine the total radioisotope activity. The difference between the two measurements was equated to the adsorbed fraction. Solutions with no added solids were run as control experiments.

In experiments to study the kinetics and reversibility of adsorption-desorption reactions of Pu with δ-MnO₂, Pu(V)O₂⁺ was first adsorbed onto δ-MnO₂ at a concentration

with surfaces in organic-free systems before adding the probable complications to be encountered in interpreting data in more complex systems containing organic matter.

MATERIALS AND METHODS

Solids and solutions

The solutions used in this study were: deionized water equilibrated with calcite, 0.7 M NaCl equilibrated with calcite, and natural near surface Gulf Stream seawater weight diluted to a salinity of 35, either equilibrated with calcite or left at its natural supersaturation state of approximately 6 times with respect to calcite. All CaCO₃ equilibrations were performed at P_{CO2} ≈ 10^{-3.5} (atmospheric). The pH of these solutions ranged from 7.8 to 8.2. The solutions were equilibrated to

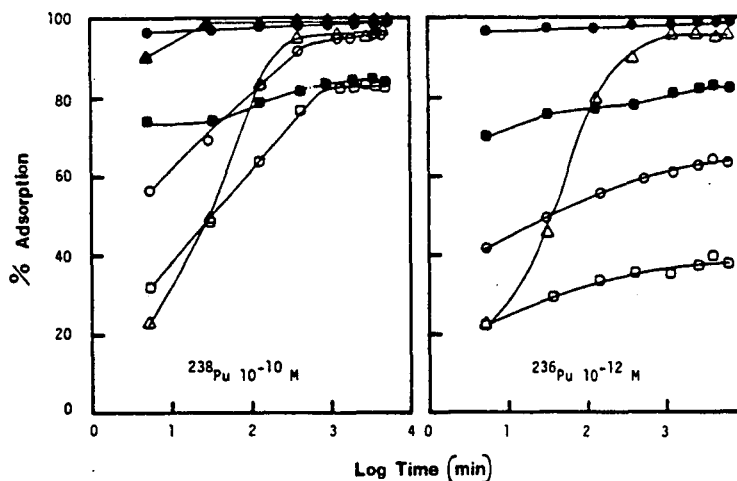


FIG. 4. Concentration dependence of Pu(V)O₂⁺ adsorption on aragonite, calcite, and goethite at 5 m² l⁻¹. ●, ○ aragonite; ■, □ calcite; ▲, △ goethite. Closed symbols: deionized water, open symbols: S = 35 seawater.

3

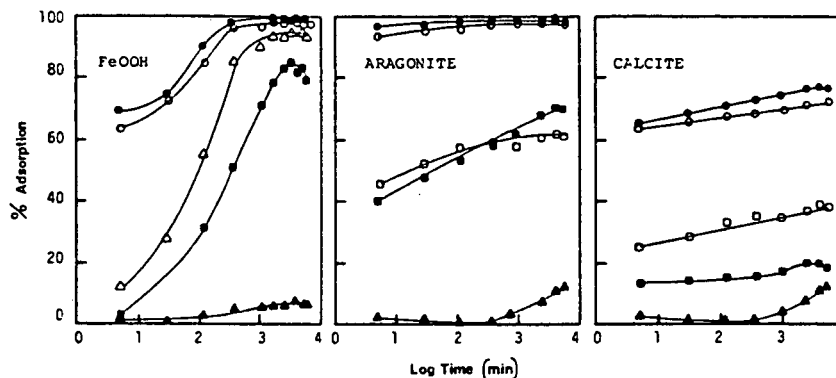


FIG. 5. Dependence of $^{239}\text{Pu}(\text{V})\text{O}_2^+$ adsorption (10^{-7} M) upon solution composition for goethite, aragonite, and calcite at $5 \text{ m}^2 \text{ l}^{-1}$. ●, ○ aragonite; ■, □ calcite; ▲, △ goethite. Closed symbols: deionized water; open symbols: seawater $S = 35$.

of $5 \text{ m}^2 \text{ l}^{-1}$ in deionized water equilibrated with calcite for 2 h, and the amount of adsorbed isotope was measured. Then a 5-ml aliquot of the suspension was centrifuged, 4 ml of supernatant was withdrawn and replaced with either deionized water equilibrated with calcite or seawater to restore the original volume and solid to solution ratio. The total and unadsorbed Pu concentrations were measured and compared with results from previous adsorption experiments.

Experiments to determine the influence of light were conducted in moderate room (fluorescent) light and in reaction vessels covered with Al foil to ensure dark conditions.

Pu speciation

The speciation of dissolved Pu and Np, which exist simultaneously in the IV, V and VI oxidation states, was determined

by the thenyltrifluoroacetone (TTA) solvent extraction method of BERTRAND and CHOPPIN (1984). This method is summarized in an analytic flow diagram in Fig. 1. Three 1 ml aliquots of analyte were added to 6 ml glass scintillation vials containing either 1 ml of 0.1 M sodium acetate/acetic acid buffer (pH = 4.7), 0.6 M HClO_4 or deionized water. The vial containing deionized water was counted for total concentration. The other two vials were shaken for 5 minutes in the dark with 2 ml of freshly prepared 0.5 M TTA in cyclohexane and centrifuged. One ml aliquots of the aqueous phases were pipetted into scintillation vials for counting. The buffered aqueous phase contained only the V oxidation state, while the acidified aqueous phase contained V and VI oxidation states. The concentration of the VI oxidation state was determined as the difference between concentrations in the acidified and buffered solutions, and the IV oxidation state concentra-

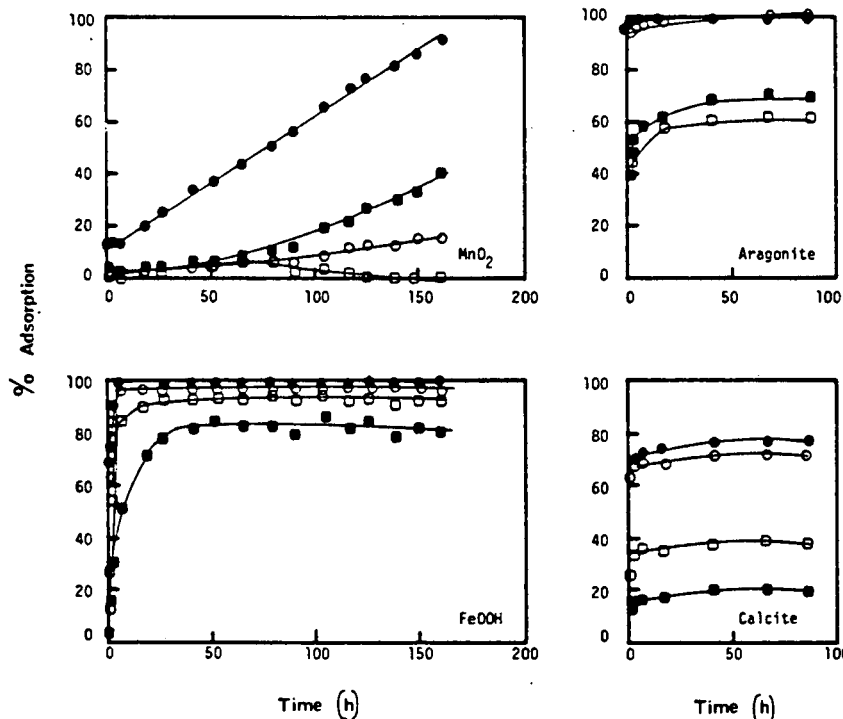


FIG. 6. Effect of solution composition on $^{239}\text{Pu}(\text{V})\text{O}_2^+$ adsorption (10^{-7} M) on $\delta\text{-MnO}_2$ and other substrates at $5 \text{ m}^2 \text{ l}^{-1}$. ●, deionized water; ○, 0.7 M NaCl; ■, artificial seawater; □, seawater.

at
0.

tion was de
water and
In the I
dissolved
sorvable P
for the ad
iment sam
and reduc
(e.g., NEL
potential
can not b
approach
In this
Fig. 1). T
gation and
removes c
optimum
1979). A
for total
solid by c
and the s
previousl
 CaCO_3 is
and the c
sequently
A major
which can

Table

Solut:

Defon:
equill:
with c

Seawa:

(a) Sc
1
(b) Sc
ec

4

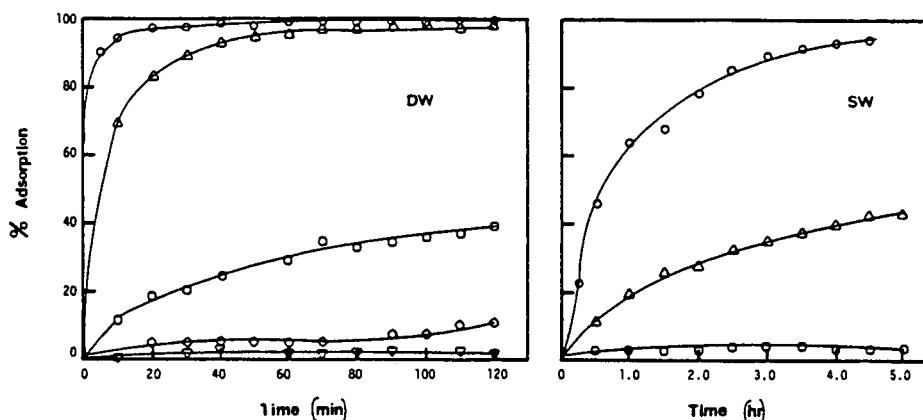


FIG. 7. Adsorption of $^{238}\text{Pu}(\text{V})\text{O}_2^+$ (10^{-10} M) on goethite in deionized water equilibrated with calcite (DW) and seawater ($S = 35$) (SW) at different solid to solution ratios. \circ , $5 \text{ m}^2 \text{ l}^{-1}$; Δ , $1 \text{ m}^2 \text{ l}^{-1}$; \square , $1 \text{ m}^2 \text{ l}^{-1}$; \diamond , $0.1 \text{ m}^2 \text{ l}^{-1}$; ∇ , $0.001 \text{ m}^2 \text{ l}^{-1}$.

tion was determined from the difference between the deionized water and acidified samples.

In the Introduction, the current generally held opinion that dissolved Pu exists in a mixture of oxidation states, while adsorbable Pu is in a reduced form, was presented. The evidence for the adsorbed Pu being in a reduced form is indirect. Sediment samples are leached with "dilute acid". Then oxidized and reduced forms in the leachate are separated with NdF_3 (e.g., NELSON and LOVETT, 1981). The overall efficiency and potential for oxidation state changes during such a procedure can not be readily evaluated. However, it remains the best approach currently available.

In this study we have used a similar technique (again see Fig. 1). The solid is separated from the solution by centrifugation and then leached with 0.03 M HClO_4 . This acid strength removes desorbable actinide from the solid and is within the optimum stability range for Pu(V) in HClO_4 (CLEVELAND, 1979). A mixture of the solid plus solution is then analyzed for total concentration. The solution is separated from the solid by centrifugation and is then analyzed for total actinide and the speciation of Pu in the solution determined by the previously described methods. In the experiments where CaCO_3 is used as the sorbate, the solid completely dissolves and the counting of the mixture and centrifugation are, consequently, not necessary.

A major assumption used in this study is that any actinide which can not be desorbed in HClO_4 is in the IV oxidation

state. In studies of natural sediments, information on the nondesorbable fraction of Pu has generally been lacking. While the fact that the nondesorbable fraction is in the IV oxidation state can not be independently confirmed, it does seem reasonable based on the high surface affinity of this oxidation state. It should also be kept in mind that no studies have been able to independently confirm that leaching does not alter oxidation state. Although these are major caveats, and the speciation results should consequently be viewed with caution, they are, hopefully, not unreasonable and, in any event, all that we could do at present. We hope in the future to be able to confirm these results using X-ray photoelectron spectroscopy.

RESULTS AND DISCUSSION

Adsorption experiments

Initial adsorption experiments using $^{238}\text{Pu}(\text{V})\text{O}_2^+$ at a concentration of 10^{-10} indicated that in both seawater and deionized water equilibrated with calcite, the ranking of adsorbing substrate is goethite \cong aragonite $>$ calcite \gg $\delta\text{-MnO}_2$, when approximately equivalent surface areas are used (see Fig. 2). Adsorption equilibrium is rapid (<1 day) on goethite, calcite, and aragonite, but not reached until over 2 days or longer on $\delta\text{-MnO}_2$. While these adsorption experiments indicated that $\delta\text{-MnO}_2$ is a significant adsorbing substrate for $^{238}\text{Pu}(\text{V})\text{O}_2^+$ in dilute solutions, it was observed that in seawater, unlike the carbonate minerals and goethite, the adsorbing capability of $\delta\text{-MnO}_2$ is severely depressed when equivalent surface areas are used (see Fig. 2). These results are similar to those for $\text{Np}(\text{V})\text{O}_2^+$ adsorption on $\delta\text{-MnO}_2$ (KEENEY-KENNICUTT and MORSE, 1984).

$\text{Pu}(\text{V})\text{O}_2^+$ adsorption behavior on carbonate minerals is similar to that observed for $\text{Np}(\text{V})\text{O}_2^+$ (KEENEY-KENNICUTT and MORSE, 1984), but not as extensive (see Fig. 3 for comparison). At low Pu concentrations (10^{-12} M), solution composition (deionized water or $S = 35$ seawater) is more important than mineralogy

Table 1. First order rate constants for the initial adsorption of $\text{Pu}(\text{V})\text{O}_2^+$ onto $\alpha\text{-FeOOH}$.

Solution	Solid to Solution Ratio ($\text{m}^2 \text{ l}^{-1}$)	Solid	K (d^{-1})
Deionized water equilibrated with calcite	0.1	(a)	3.3
		(b)	3.0
	1.0	(a)	32.9
		(b)	26.0
Seawater	1.0	(a)	2.1
		(b)	1.5
	5.0	(a)	14.3
		(b)	14.6

- (a) Solid preequilibrated with deionized water for 1 year.
 (b) Solid preequilibrated for 6 d with deionized water equilibrated with calcite or seawater.

ethite, aragonite,
 sized water; open

TA) solvent extraction
 (1984). This method is
 diagram in Fig. 1. Three
 to 6 ml glass scintillation
 M sodium acetate/acetic
 or deionized water. The
 is counted for total con-
 shaken for 5 minutes in
 red 0.5 M TTA in cyclo-
 of the aqueous phases
 or counting. The buffered
 V oxidation state, while
 ned V and VI oxidation
 oxidation state was deter-
 concentrations in the acidified
 oxidation state concentra-

gonite
 100

100

other substrates

5

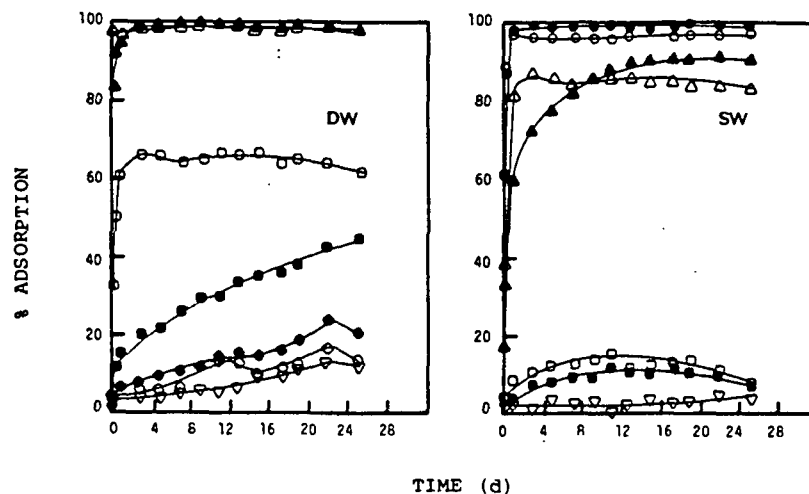


FIG. 8. Effect of room light and dark upon $^{238}\text{Pu}(\text{V})\text{O}_2^+$ (10^{-10} M) adsorption on goethite in deionized water equilibrated with calcite (DW) and seawater ($S = 35$) (SW) at different solid to solution ratios. Experiments were run in duplicate. \circ, \bullet $5 \text{ m}^2 \text{ l}^{-1}$; $\triangle, \blacktriangle$ $1 \text{ m}^2 \text{ l}^{-1}$; \square, \blacksquare $0.1 \text{ m}^2 \text{ l}^{-1}$; \diamond, \blacklozenge $0.01 \text{ m}^2 \text{ l}^{-1}$; $\nabla, \blacktriangledown$ $0.001 \text{ m}^2 \text{ l}^{-1}$. Open symbols: light; closed symbols: dark.

(calcite or aragonite) for the carbonates, but at higher concentrations (10^{-10} to 10^{-7} M) carbonate mineralogy becomes important (see Figs. 4, 5 and 6).

The adsorption kinetics of $\text{Pu}(\text{V})\text{O}_2^+$ on goethite were more rapid at lower Pu concentrations (10^{-10} , 10^{-12}) than higher (10^{-7}) concentrations and more rapid in deionized water than seawater (see Figs. 4 and 5). Adsorption kinetics in seawater are similar for Pu at 10^{-10} M and 10^{-12} M, indicating that the rate of adsorption may be independent of concentration below 10^{-10} M in seawater. Adsorption behavior differences between deionized water and seawater were not related to ionic strength changes, but are probably due to the presence of competing ions for sorption sites (e.g., Mg^{2+} and SO_4^{2-} ; BALISTRERI and MURRAY, 1981).

Pu adsorption on goethite at 10^{-10} M was studied in deionized water and seawater as functions of solid to solution ratio (Fig. 7). Adsorption in deionized water was much more rapid than in seawater at all solid to solution ratios. For example, at $5 \text{ m}^2 \text{ l}^{-1}$, 90% of $\text{Pu}(\text{V})\text{O}_2^+$ was adsorbed in 5 min in deionized water,

whereas in seawater 90% adsorption was not reached until 3 h.

Most of the adsorption experiments were done by equilibrating $\text{Pu}(\text{V})\text{O}_2^+$ in the solution, then adding goethite which has been stored since its preparation (>1 year) in deionized water. An experiment was done to see what effect preequilibrating the solid in the solution under investigation for several days would have on adsorption behavior. The solid was preequilibrated with the appropriate solution for 6 days. The $\text{Pu}(\text{V})\text{O}_2^+$ spiking solution was preequilibrated in a separate bottle in the same solution. Results (Table 1) indicate that the initial rate of adsorption was slower on the preequilibrated goethite, but the extent of adsorption was unchanged.

Figure 8 presents the results of experiments on the differences in $\text{Pu}(\text{V})\text{O}_2^+$ adsorption under room light and dark conditions on goethite at different solid to solution ratios (0.01 to $5 \text{ m}^2 \text{ l}^{-1}$). There are significant differences between the light and dark results. For example, in deionized water at $0.1 \text{ m}^2 \text{ l}^{-1}$, the percent adsorption in the light experiment rapidly reached its maximum level, whereas in the dark the percent adsorption increased more slowly with time. In all instances the initial rates (during first 2 hr) of adsorption were higher in the light (see Table 2). However, in some cases the final extent of adsorption was higher for experiments run in the dark.

The influences of Pu concentration, solution composition, solid to solution ratio, and solid preequilibration on $\text{Pu}(\text{V})\text{O}_2^+$ interactions with $\delta\text{-MnO}_2$ were investigated. A Pu concentration range of five orders of magnitude (10^{-7} to 10^{-12} , see Figs. 1 and 6) was studied in seawater and deionized water equilibrated with calcite at a $\delta\text{-MnO}_2$ concentration of $5 \text{ m}^2 \text{ l}^{-1}$. In deionized water, a period of rapid adsorption occurs

Table 2. First order rate constants for initial adsorption of $\text{Pu}(\text{V})\text{O}_2^+$ onto $\alpha\text{-FeOOH}$ in light and dark.

Solution	Solid to Solution Rate ($\text{m}^2 \text{ l}^{-1}$)	Rate Constants		$\frac{k_{\text{light}}}{k_{\text{dark}}}$
		k_{light}	k_{dark}	
Deionized water equilibrium with calcite	0.1	0.492, 0.068	0.398, 0.105	7.2 3.8
	1.0	3.58, 1.08	3.65, 1.77	3.3 2.1
Seawater	1.0	0.498, 0.122	0.484, 0.188	4.1 2.6
	5.0	2.55, 0.66	2.23, 0.94	3.9 2.4

FIG. 10. Co function of tin

within the ini
adsorption is
When the Pu
M to 10^{-10} M.

10^{-9}
 10^{-10}
 10^{-12}

$[\text{Pu}]_{\text{solid}} \text{ (mol m}^{-2}\text{)}$

FIG. 10. Co function of tin
ibration for Pu
ized water equ
 $\text{m}^2 \text{ l}^{-1}$; \square, \blacksquare 5
symbols: solid
bols: solid pre-

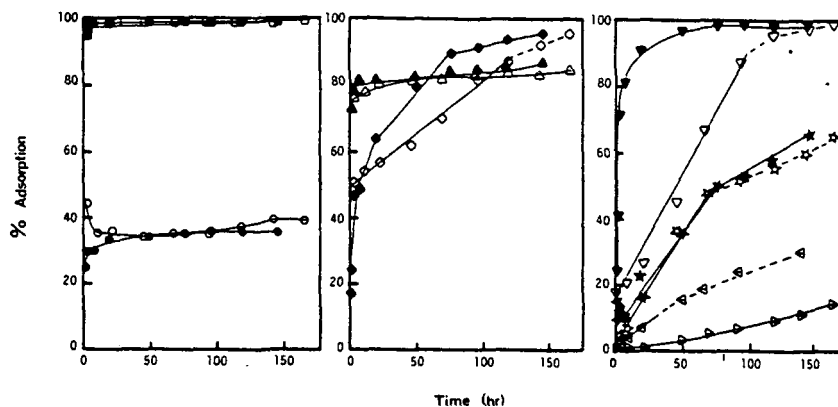


FIG. 9. Effects of solid to solution ratio and solid pre-equilibration upon ²³⁸Pu(V)O₂⁺ adsorption (10⁻¹⁰ M) on δ-MnO₂. ○, ● 100 m² l⁻¹ in seawater; □, ■ 100 m² l⁻¹ in deionized water; △, ▲ 20 m² l⁻¹ in deionized water; ◇, ◆ 5 m² l⁻¹ in deionized water; ▽, ▼ 1 m² l⁻¹ in deionized water; ☆, ★ 0.1 m² l⁻¹ in deionized water; ◁, ▷ 0.01 m² l⁻¹ in deionized water; ⋈, ⋉ 0 m² l⁻¹ in deionized water. Open symbols: solid not pre-equilibrated with solution; closed symbols: solid pre-equilibrated with solution for 6 days.

within the initial two hours of the experiment. This adsorption is enhanced at lower Pu concentrations. When the Pu concentration was decreased from 10⁻⁷ M to 10⁻¹⁰ M, the percent adsorption at 2 h increased

from 14% to 40%. However, the time required to reach the maximum extent of adsorption was approximately the same (150 to 200 h). In seawater, significantly less adsorption on δ-MnO₂ was observed at all Pu concentrations studied. Experiments at a Pu concentration of 10⁻⁷ M and solid to solution ratio of 5 m² l⁻¹ using deionized water equilibrated with calcite, 0.7 M NaCl, seawater (S = 35), and artificial seawater show that (see Fig. 6), unlike Pu adsorption on goethite, calcite, and aragonite, the adsorption of Pu on δ-MnO₂ is adversely affected by increasing ionic strength. Little adsorption occurred on δ-MnO₂ in 0.7 M NaCl. In fact, significant adsorption (30 to 50%) in seawater was only found at the high solid to solution ratio of 100 m² l⁻¹. The depression of Pu(V)O₂⁺ adsorption in seawater is possibly due to two processes: (1) flocculation of δ-MnO₂ at high ionic strength, thereby decreasing the total surface area available for adsorption, and (2) competition for adsorption sites by other ions.

The effects of solid to solution ratio and solid pre-equilibration upon Pu adsorption on δ-MnO₂ were also studied (see Figs. 9 and 10). Two trends were observed for 10⁻¹⁰ M Pu in deionized water equilibrated with

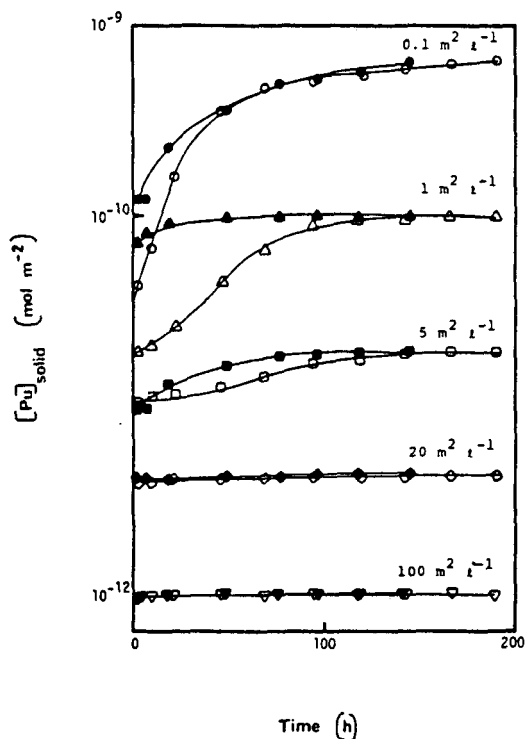


FIG. 10. Concentration of ²³⁸Pu(V)O₂⁺ on the solid as a function of time, solid to solution ratio, and solid pre-equilibration for PuO₂⁺ adsorption (10⁻¹⁰ M) on δ-MnO₂ in deionized water equilibrated with calcite. ○, ● 0.1 m² l⁻¹; △, ▲ 1 m² l⁻¹; □, ■ 5 m² l⁻¹; ◇, ◆ 20 m² l⁻¹; ▽, ▼ 100 m² l⁻¹. Open symbols: solid not pre-equilibrated with solution; closed symbols: solid pre-equilibrated with solution for 6 days.

Table 3. Speciation of dissolved actinide after 1 h.

Actinide	Concentration (M)	Solution	Method of V Preparation	% IV	% V	% VI
Pu	5 x 10 ⁻¹⁰	Deionized water	1	2.0	87.7	10.3
			1	2.1	90.9	7.0
		Seawater	1	0.9	93.9	5.2
			1	2.7	95.2	2.1
Np	1 x 10 ⁻¹³	Deionized water	1	14.7	77.2	8.1
			2	16.3	80.7	3.0
		Seawater	1	9.9	81.5	8.6
			2	12.9	84.4	2.7

1 = extraction of IV + VI with TTA in cyclohexane

2 = extraction of IV + VI with HDEHP in 2,2,4-trimethylpentane

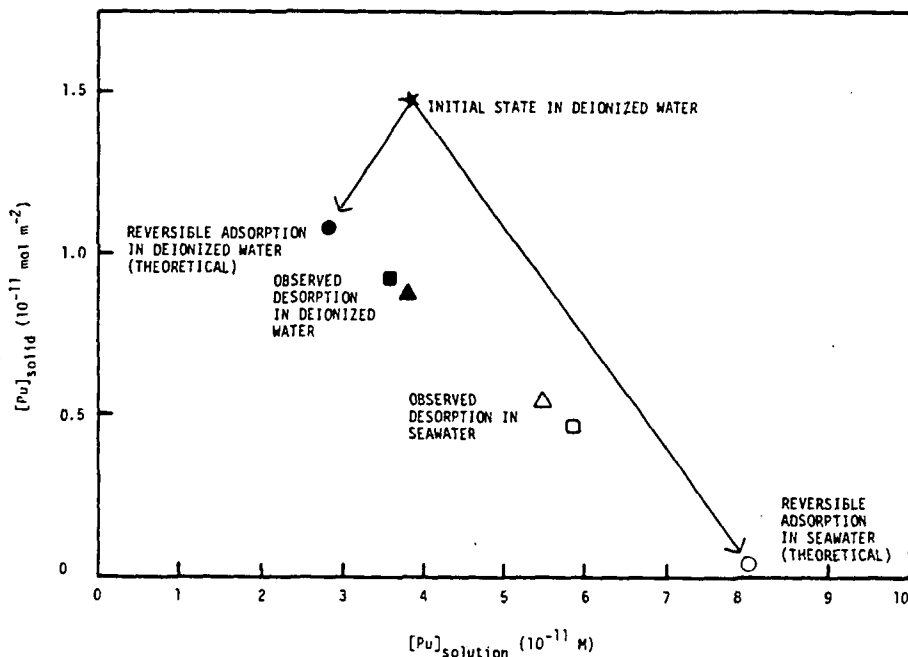


FIG. 11. Desorption of PuO_2^+ (10^{-10} M) from $\delta\text{-MnO}_2$ at $5 \text{ m}^2 \text{ l}^{-1}$. ●, ○ ideal reversibility; ▲, △ 30 min; ■, □ 2 h. Closed symbols: deionized water equilibrated with calcite; open symbols: seawater ($S = 35$).

calcite: (1) over the entire range studied (0.1 to $100 \text{ m}^2 \text{ l}^{-1}$), the initial percent adsorption measured at 2 h increases with increasing solid to solution ratio, and (2) in the intermediate solid to solution ratios (5 to $20 \text{ m}^2 \text{ l}^{-1}$), there is a decrease in the rate and extent of adsorption. For 1.0 , 5.0 and $2.0 \text{ m}^2 \text{ l}^{-1}$, 85% adsorption occurs at 90, 100, and 175 h, respectively. This is possibly due to increased flocculation at elevated $\delta\text{-MnO}_2$ concentrations (STUMM and MORGAN, 1981). The only observed difference attributable to the different methods was that the rate of adsorption for $1 \text{ m}^2 \text{ l}^{-1}$ in deionized water equilibrated with calcite was slightly enhanced for the preequilibrated system. The extent

of adsorption was unaffected. In seawater at a solid concentration of $100 \text{ m}^2 \text{ l}^{-1}$, the unpre-equilibrated sample had a 45% adsorption of Pu after 2 hr, which decreased with time to an equilibrium value of about 35%. This decrease was not observed for the preequilibrated sample, although the final extent of Pu adsorption in both samples were the same. The effects probably result from surface site competition by seawater ions and/or flocculation. Studies of $^{238}\text{Pu}(\text{V})\text{O}_2^+$ adsorption on $\delta\text{-MnO}_2$ under room light and dark conditions exhibited no differences at a range of solid to solution ratios of 0.001 to $100 \text{ m}^2 \text{ l}^{-1}$ in seawater and deionized water.

FIG. 1 and seaw

Investigation from $\delta\text{-MnO}_2$. behavior of Pu equilibrated with solution and also sorption for the second sorption affinity in deionized water in estuarine. Dilution with either in substantial decrease results in 100 minutes, then the second adsorption. Wh

Table 4. Speciation of adsorbed $^{238}\text{Pu}(\text{V})\text{O}_2^+$ ($^{238}\text{Pu}_{\text{total}} = 5 \times 10^{-10}$ M) on goethite ($5 \text{ m}^2 \text{ l}^{-1}$) in deionized water equilibrated with calcite and seawater ($S=35$).

Solution	Time	% Adsorp.	% Desorp.	Desorbable			Total Adsorbed		
				% IV	% V	% VI	% IV	% V	% VI
Deionized water (light)	1 min	79.8	92.5	30.2	23.5	46.3	35.4	21.8	42.8
	1 d	99.7	64.4	37.6	4.0	58.4	59.8	2.6	37.6
	7 d	99.6	52.2	54.4	8.3	37.3	76.7	4.3	19.0
	30 d	99.3	36.8	60.8	7.7	31.5	85.6	2.8	11.6
Deionized water (dark)	30 s	77.6	63.7	27.6	46.2	26.2	53.8	29.5	16.7
	1 h	96.0	74.0	27.9	17.9	54.2	46.7	13.2	40.1
	1 d	98.9	49.7	25.4	9.8	64.8	62.9	4.9	32.2
	7 d	99.0	44.1	39.5	5.6	54.9	73.3	2.5	24.2
Seawater (light)	30 d	99.9	20.0	52.0	7.5	40.5	90.4	1.5	8.1
	30 min	52.3	75.9	29.2	6.6	64.2	46.2	5.0	48.8
	1 d	95.5	72.1	35.9	6.2	57.9	53.8	4.5	41.7
	7 d	95.5	55.1	30.3	8.2	61.5	61.6	4.5	33.9
Seawater (dark)	30 d	97.7	32.8	47.2	7.5	45.3	82.6	2.5	14.9
	1 h	34.8	69.5	23.9	14.7	61.4	68.5	10.2	21.3
	1 d	98.4	71.6	21.7	6.6	71.7	44.0	4.7	51.3
	7 d	98.7	57.3	35.3	3.3	61.4	62.9	1.9	35.2
Seawater (dark)	30 d	99.1	34.7	35.2	5.8	59.0	77.5	2.0	20.5

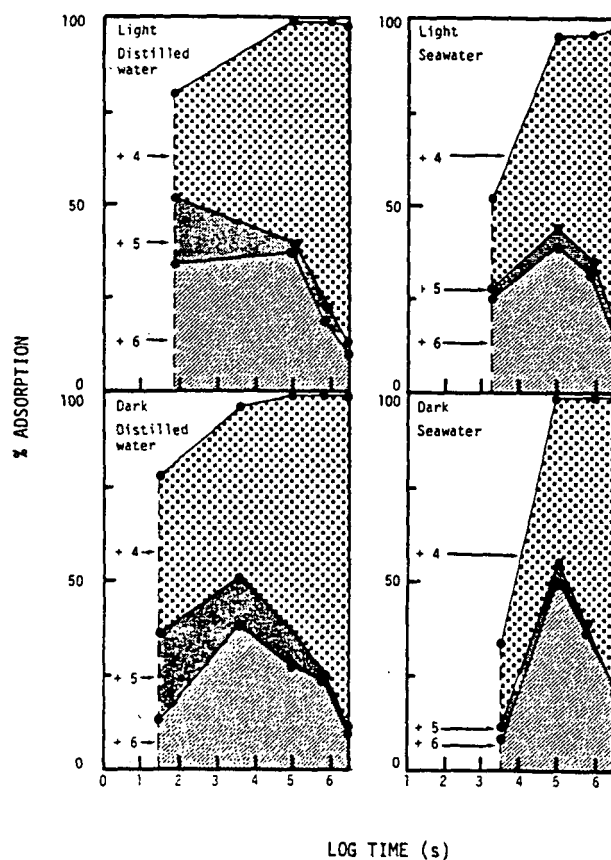


FIG. 12. Speciation of adsorbed ²³⁸Pu on goethite at 5 m² l⁻¹ in distilled water equilibrated with calcite and seawater (S = 35) in light and dark.

Investigations were made of desorption reactions from δ-MnO₂. The primary aim was to determine the behavior of Pu(V)O₂⁺ adsorbed in deionized water equilibrated with calcite upon dilution with the given solution and also upon mixing with seawater. The reason for the second objective was the large difference in sorption affinities of Pu(V)O₂⁺ for δ-MnO₂ surfaces in deionized water and seawater. The mixing experiment approximates the mixing of river water and seawater in estuaries. Results are summarized in Fig. 11. Dilution with either deionized water or seawater results in substantial desorption. Dilution with deionized water results in 100% desorption within the first five minutes, then the system approaches theoretical reversible adsorption. When diluting with seawater, approxi-

mately two-thirds of the desorption necessary to reach complete reversibility occurs.

Adsorbed Pu oxidation state

The speciation of both adsorbed Pu and Np on goethite under a variety of conditions was investigated to determine if redox reactions were important in controlling adsorption behavior. Np(V)O₂⁺ adsorption on goethite (KEENEY-KENNICUTT and MORSE, 1984) was extensive in deionized water and much lower in seawater. The comparison between Pu(V) and Np(V) was made because Np(V)O₂⁺ is less redox reactive than Pu(V)O₂⁺.

Table 5. Speciation of adsorbed Np (Np_T = 1 x 10⁻¹³M) on goethite (5 m² l⁻¹) after 1 h.

Solution	% Adsorp.	% Desorp.	Desorbed			Total Adsorbed		
			% IV	% V	% VI	% IV	% V	% VI
Deionized water	73.3	89.5	7.0	85.7	7.3	16.8	76.7	6.5
	79.1	89.4	10.7	81.1	8.2	20.1	72.5	7.4
Seawater	10.8	88.3	17.2	76.0	6.8	26.9	67.1	6.0
	12.0	85.9	10.9	77.8	11.3	23.5	66.8	9.7

EVERSIBLE
DSORPTION
N SEAWATER
THEORETICAL)

y; ▲, Δ 30 min;
er (S = 35).

In seawater at a solid
the unpre-equilibrated
f Pu after 2 hr, which
ilibrium value of about
erved for the preequi-
nal extent of Pu ad-
e the same. The ef-
face site competition
culation. Studies of
O₂ under room light
differences at a range
101 to 100 m² l⁻¹ in

5).
—
I
3
5
5
5
7
1
2
1
1
3
7
2
2
7
2
5

9

Table 6. Speciation of adsorbed $^{238}\text{Pu}(\text{V})\text{O}_2^+$ ($\text{Pu}_{\text{total}} = 5 \times 10^{-13} \text{ M}$) or $\delta\text{-MnO}_2$ in deionized water equilibrated with calcite and seawater.

Solution	Solid to Solution Ratio ($\text{m}^2 \text{ l}^{-1}$)	Time (d)	Adsorp.	Desorp.	Desorbable			Total Adsorbed		
					% IV	% V	% VI	% IV	% V	% VI
DW	5	0.042	48.7	100	1.8	82.1	16.1	1.8	82.1	16.1
		2	68.1	86.7	0.0	61.3	39.3	12.8	53.1	34.1
		8	98.4	77.6	0.6	56.8	42.6	23.0	44.0	33.0
		35	99.8	77.9	1.6	58.9	39.5	23.3	45.9	30.8
		64	99.4	71.6	0	78.5	22.3	28.4	55.8	15.8
DW	100	0.042	98.2	49.4	1.8	57.8	40.4	51.6	28.5	19.9
		2	99.2	36.7	0.9	99.1	0.0	63.7	36.3	0.0
		8	99.3	35.6	1.5	79.4	19.9	64.9	28.3	6.8
		35	99.7	51.7	0.8	60.5	38.7	48.7	31.3	20.0
		64	99.8	63.7	0	46.6	54.1	36.2	29.5	34.3
SW	100	0.042	56.4	64.8	35.9	57.8	6.3	58.4	37.5	4.1
		2	38.8	40.5	0.0	91.2	9.1	59.3	37.0	3.7
		8	45.8	46.1	0.0	90.0	10.7	53.6	41.4	5.0
		35	52.1	76.5	6.6	78.2	15.2	28.4	59.9	11.7
		64	51.7	91.5	0.6	82.9	16.5	9.0	75.9	15.1

The distribution of oxidation states for dissolved Pu and Np before the addition of goethite is presented in Table 3. The speciation of Pu adsorbed on goethite was followed as a function of time (Table 4 and Fig. 12). Pu(V) is both oxidized and reduced upon adsorption to Pu(VI) and Pu(IV) in seawater and deionized water. In the dark the extent of oxidation of Pu(V) to Pu(VI) was initially (first seconds to minutes) less than in the light, but similar values were obtained for light and dark conditions after 30 d (2×10^6 sec). Also, the percentage of adsorbed Pu that could be desorbed decreased with increasing time, indicating that a strongly bound form of Pu was being created. If the Pu which could not be desorbed is indeed Pu(IV), the speciation of Pu on the surface eventually becomes primarily Pu(IV).

These results are very different from what was found for adsorbed Np. Table 5 shows that Np speciation on goethite is primarily Np(V) after 1 h, indicating that

the Pu(V) is more susceptible than the Np(V) to oxidation/reduction processes which can occur at the solid-solution interface of goethite.

The same approach was used to study Pu(V) and Np(V) adsorption on $\delta\text{-MnO}_2$ as described for adsorption on goethite. The speciation of Pu adsorbed on $\delta\text{-MnO}_2$ was followed with time (Table 6 and Fig. 13). At the lower solid to solution ratio, $5 \text{ m}^2 \text{ l}^{-1}$, in deionized water, Pu is adsorbed primarily as Pu(V), with the initial distribution being about 80% Pu(V) and 20% Pu(VI). This is similar to adsorbed Np speciation on $\delta\text{-MnO}_2$ at $5 \text{ m}^2 \text{ l}^{-1}$ in both deionized water and seawater (Table 7). At a higher solid to solution ratio, $100 \text{ m}^2 \text{ l}^{-1}$, the initial adsorbed Pu speciation is 50% IV, 30% V, and 20% VI, and in seawater it is 60% IV and 40% V. With time the Pu is oxidized to V and VI. This can be observed in the growing percentage of Pu that can be desorbed. After two months (10^6 s), the percentage of adsorbed Pu existing as (V + VI) is

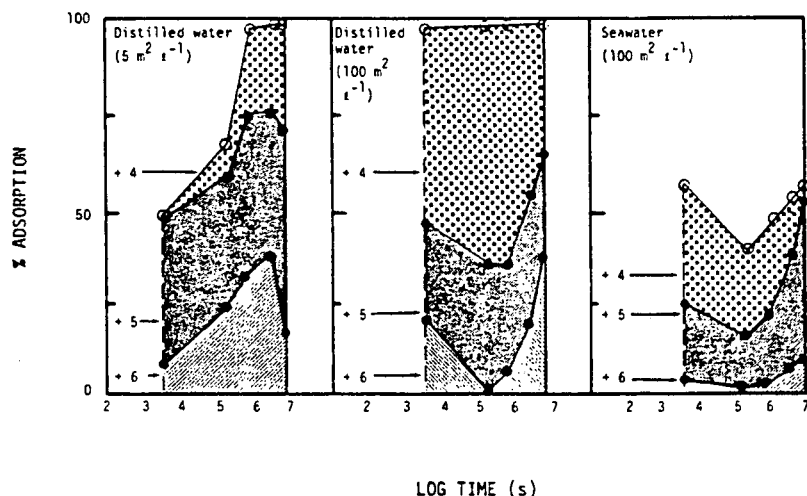


FIG. 13. Speciation of adsorbed ^{238}Pu on $\delta\text{-MnO}_2$ in distilled water equilibrated with calcite and seawater ($S = 35$).

64% and 91% for deionized water and seawater, respectively. This behavior is similar to observations of the oxidation of adsorbed metals (DILLARD, 1979; DILLARD, 1979). The speciation of Pu on carbonate minerals remained dominantly Pu(V) and Pu(VI). The difference between the speciation of Pu on carbonate minerals was observed in seawater, and larger differences were observed for

SUMMARY

Results indicate that Pu(V) is the dominant species interacting with carbonate surfaces in both deionized water and seawater. The interactions are complicated by the presence of goethite. The change in oxidation state of Pu(V) interacting with carbonate surfaces paralleled that of Np(V) and resulted in a net oxidation of Pu(V) to Pu(VI). The affinity of Pu(VI) for carbonate surfaces is much higher in deionized water than in seawater.

The interaction of Pu(V) and Pu(VI) with carbonate surfaces in the presence of goethite requires more research into the processes involved. Further

Table 8. The distribution of Pu(VI) on calcite and seawater.

Solid	None	None	Aragonite	Calcite	Aragonite	Calcite

Table 7. Speciation of adsorbed Np ($Np_T = 1 \times 10^{-13}$ M) on δ -MnO₂ after 1 h.

Solution	Solid to Solution Ratio ($m^2 l^{-1}$)	% Adsorp.	% Desorp.	Desorbable			Total Adsorbed		
				% IV	% V	% VI	% IV	% V	% VI
DW	5	12.6	100	10.3	80.2	9.5	10.3	80.2	9.5
	100	10.0	100	15.3	76.7	8.0	15.3	76.7	8.0
SW	5	95.1	53.1	12.4	83.3	4.3	53.5	44.2	2.3
	100	94.3	65.3	16.1	83.9	0.0	45.2	54.8	0.0
SW	5	5.1	95.2	15.2	84.2	0.6	16.7	82.7	0.6
	100	3.7	100	19.2	78.6	2.2	19.2	78.2	2.2
SW	5	33.3	55.2	13.0	82.4	4.6	53.9	45.5	0.6
	100	35.7	52.2	11.0	82.0	7.0	53.6	42.8	3.6

64% and 91% for deionized water and seawater, respectively. This behavior is consistent with other observations of the oxidizing nature of the δ -MnO₂ surface for adsorbed metals (e.g., HEM, 1978; MURRAY and DILLARD, 1979; DILLARD *et al.*, 1982, 1984).

Speciation measurements of Pu adsorbed on carbonate minerals indicated that the adsorbed Pu remained dominantly in the V oxidation state (Table 8). The difference between the percentage of Pu in the V oxidation state in solution and adsorbed on the carbonate minerals was larger in deionized water than seawater, and larger on aragonite than calcite. The average difference for all samples was 12%.

SUMMARY AND CONCLUSIONS

Results indicate that the Pu(V)O₂[±] ion is capable of interacting with carbonate and metal oxide mineral surfaces in both dilute solutions and seawater. The interactions between the Pu(V) and mineral surfaces is complicated by the redox reactivity of plutonium. Little change in oxidation state was observed for Pu(V) interacting with carbonate surfaces, where its behavior paralleled that of Np(V). Interaction of Pu with δ -MnO₂ resulted in a net oxidation of Pu(IV) and Pu(V) to Pu(VI). The affinity of Pu(V) for δ -MnO₂ surfaces was much higher in dilute solutions than in seawater.

The interaction with goethite was complex, with both Pu(IV) and Pu(VI) being formed on the goethite surface. The rate of the reaction was found to be faster in the presence of room light than in the dark. Although more research into the influence of light on these processes is needed, our results indicate it may be possible

that surface photochemical reactions play a role in controlling the rate of Pu removal from natural waters. Pu(VI) appears to be reduced with time at the goethite surface, leaving primarily reduced Pu(IV) on the mineral surface. This result is compatible with the recent observations of SANCHEZ *et al.* (1985), who also found that when Pu(V) was adsorbed on goethite surfaces it was reduced to Pu(IV).

These results indicate that Pu(V)O₂[±] may be removed from solutions similar to those of natural waters without first having to be reduced to Pu⁴⁺ ion. Thus, it is possible for Pu to be removed from solution in two different forms. Their relative importance will depend on such environmental variables as the dissolved Pu(IV) to Pu(V) ratio, concentrations of organic and particulate material and if adsorption is taking place in the photic zone. The fact that Pu(IV) can be oxidized to Pu(VI) on δ -MnO₂ surfaces provides a possible mechanism for remobilization of reduced Pu in sediments.

Acknowledgements—The authors thank G. R. Choppin, R. Roberts and E. R. Sholkovitz for their advice and comments. The research was supported by the U.S. Department of Energy, Office of Health and Environmental Research.

Editorial handling: E. R. Sholkovitz

REFERENCES

- ASTON S. R. (1980) Evaluation of chemical forms of plutonium in seawater. *Mar. Chem.* 8, 317-326.
- BALISTRERI L. S. and MURRAY J. W. (1981) The surface chemistry of goethite in major ion seawater. *Amer. J. Sci.* 281, 788-806.
- BERTRAND P. A. and CHOPPIN G. R. (1982) Separation of actinides in different oxidation states by solvent extraction. *Radiochim. Acta* 31, 133-137.
- BONDIETTI E. A. and TAMURA T. (1980) Physicochemical associations of plutonium and other actinides in soils. In *Transuranic Elements in the Environment* (ed. W. C. HANSON), pp. 145-164. DOE/TIC-22800.
- BONDIETTI E. A. and TRABALKA J. R. (1980) Evidence for plutonium(V) in an alkaline, freshwater pond. *Radioanal. Lett.* 43, 169-176.
- CHOPPIN G. R. and SAITO A. (1984) Reduction of neptunium and plutonium in photolyzed TTA-organic solvent systems. *Radiochim. Acta* 35, 149-154.

Table 8. The fraction of Pu (10^{-7} M) existing as Pu(V) in solution and adsorbed on calcite or aragonite ($5 m^2 l^{-1}$) after 87 h in deionized water or 5:35 seawater.

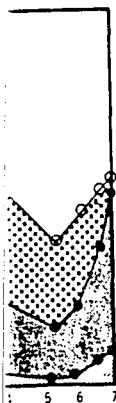
Solid	Solution	Percent Pu as Pu(V)	
		Solution	Solid
None	Deionized	97	--
None	Seawater	96	--
Aragonite	Deionized	100	88
Calcite	Deionized	96	72
Aragonite	Seawater	98	90
Calcite	Seawater	93	81

h calcite and seawater

bed
% VI
16.1
34.1
33.0
30.8
15.8
19.9
0.0
6.8
20.0
34.3
4.1
3.7
5.0
11.7
15.1

e than the Np(V) to oxi-
which can occur at the
ethite.

ed to study Pu(V)O₂[±] and
InO₂ as described for ad-
sorption of Pu adsorbed
with time (Table 6 and Fig.
solution ratio, $5 m^2 l^{-1}$, in
adsorbed primarily as Pu(V),
being about 80% Pu(V)
similar to adsorbed Np spe-
in both deionized water
a higher solid to solution
adsorbed Pu speciation is
and in seawater it is 60%
Pu is oxidized to V and
the growing percentage of
after two months ($10^{6.7}$ s),
Pu existing as (V + VI) is



11

- CHOPPIN G. R. and MORSE J. W. (1985) Laboratory studies of plutonium in marine systems. In *Symposium on Environmental Research for Actinide Elements* (in press).
- CLEVELAND J. M. (1979) Critical review of plutonium equilibria of environmental concern. In *Chemical Modeling in Aqueous Systems: Speciation, Sorption, Solubility, and Kinetics* (ed. E. A. JENNE), pp. 321-338. ACS Symposium Series 93.
- DILLARD J. G., CROWTHER D. L. and MURRAY J. W. (1982) The oxidation state of cobalt and selected metals in Pacific ferromanganese nodules. *Geochim. Cosmochim. Acta* 46, 755-759.
- DILLARD J. G., CROWTHER D. L. and CALVERT S. E. (1984) X-ray photoelectron spectroscopic study of ferromanganese nodules: Chemical speciation for selected transition metals. *Geochim. Cosmochim. Acta* 48, 1565-1569.
- EDELSTEIN N. M. (1981) *Actinides in Perspective*. Pergamon Press, 610 p.
- EDGINGTON D. N. (1981) A review of the persistence of long-lived radionuclides in the marine environments: Sediment/water interactions. In *Impacts of Radionuclide Releases into the Marine Environment*, pp. 67-91. Symposium Proceedings, 6-10 October 1980, Vienna. IAEA-SM-248/148.
- FORSTER W. O. (1976) Transuranic studies in the marine environment. In *Environmental Toxicity of the Aquatic Radionuclides: Models and Mechanisms* (eds. M. W. MILLER and J. N. STANNARD), pp. 11-27. Ann Arbor Science Inc., Ann Arbor, Mich.
- HEM J. D. (1978) Redox processes at surfaces of manganese oxide and their effects on aqueous metal ions. *Chem. Geol.* 21, 199-218.
- INTERNATIONAL ATOMIC ENERGY AGENCY (1976) *Transuranium nuclides in the environment*. Proceedings Series, 724 p.
- KEENEY-KENNICUTT W. L. and MORSE J. W. (1984) The interaction of Np(V)O_2^+ with common mineral surfaces in dilute aqueous solutions and seawater. *Mar. Chem.* 15, 133-150.
- LABEYRIE L. D., LIVINGSTON H. D. and BOWEN V. T. (1976) *Transuranium nuclides in the environment*, pp. 121-137. IAEA-SM-199/115.
- MURRAY J. W. and DILLARD J. G. (1979) The oxidation of cobalt(II) adsorbed on manganese dioxide. *Geochim. Cosmochim. Acta* 43, 781-787.
- NATIONAL ACADEMY OF SCIENCES (1971) *Radioactivity in the marine environment*. Prepared by the Panel on Radioactivity in the Marine Environment of the Committee on Oceanography, National Research Council, 272 p.
- NELSON D. M. and LOVETT M. B. (1978) Oxidation state of plutonium in the Irish Sea. *Nature (London)* 276, 599-601.
- NELSON D. M. and ORLANDI K. A. (1979) *Identification of Pu(V) in natural waters*, pp. 57-59. ANL-79-65, Argonne National Laboratory, Illinois.
- NELSON D. M. and LOVETT M. B. (1981) Measurements of the oxidation state and concentration of plutonium in interstitial waters in the Irish Sea. In *Impacts of Radionuclide Releases into the Marine Environment*, pp. 105-118. IAEA, Vienna.
- NELSON D. M., CAREY A. E. and BOWEN V. T. (1984) Plutonium oxidation state distributions in the Pacific Ocean during 1980-1981. *Earth Planet. Sci. Lett.* 68, 422-430.
- NELSON D. M., LARSEN R. P. and PENROSE W. R. (1985) Chemical speciation of Pu in natural waters. In *Symposium on Environmental Research for Actinide Elements* (in press).
- RAI D., SERNE R. J. and SWANSON J. L. (1980) Solution species of plutonium in the environment. *J. Environ. Quality* 9, 417-420.
- SAITO A., ROBERTS R. A. and CHOPPIN G. R. (1985) Preparation of solutions of trace level plutonium(V). *Anal. Chem.* 57, 390-391.
- SANCHEZ A. L., MURRAY J. W. and SIBLEY T. H. (1985) The adsorption of plutonium on goethite. *Geochim. Cosmochim. Acta* 49, 2297-2307.
- SANTSCHI P. H. (1984) Particle flux and trace metal residence time in natural waters. *Limnol. Oceanogr.* 29, 1100-1108.
- SANTSCHI P. H., LI Y.-H., BELL J. J., TRIER R. M. and LAWALUK K. (1980) Pu in coastal environments. *Earth Planet. Sci. Lett.* 51, 248-265.
- SHANBHAG P. M. and MORSE J. W. (1982) Americium interaction with calcite and aragonite surfaces in seawater. *Geochim. Cosmochim. Acta* 46, 241-246.
- SHOLKOVITZ E. R. (1983) The geochemistry of plutonium in fresh and marine environments. *Earth-Sci. Reviews* 19, 95-161.
- SILVER G. L. (1983) Comment on the behavior of the chemical forms of plutonium in seawater and other aqueous solutions. *Mar. Chem.* 12, 91-96.
- STUMM W. and MORGAN J. J. (1981) *Aquatic Chemistry* (2nd ed.). John Wiley and Sons, New York, 780 pp.

Role
G

Institu

Abstract—
River form:
and calcite
the results

A signifi
small or no
production
alone, and
at any sing
via a carb
effect, how
cracking, T
kerogen, w
of low mol
dioxide.

These re
and conde
examples c
mainly du

ORGANIC MATTER
buried in sediment
temperatures is g
and gaseous pro
duction (diagenes
form, followed b
molecular weight
(catagenesis), hy
pounds form in
petroleum (TISS
During the last t
in the understar
ratory pyrolysis
the laboratory th
in nature (TISS
WATARI *et al.*, 1
et al., 1980, 198
RILEY, 1984; ar
evolve under va
(HORSFIELD, 19
constituents of
condition, whe
present in produ
drous condition
1983).

* Publication
etary Physics, Ur
Present addre
Sugar Land, Tex

12/12