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NEPTUNIUM CONCENTRATIONS IN SOLUTIONS CONTACTING ACTINIDE-DOPED GLASS

RADIOACTIVE WASTE
MANAGEMENT

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To help predict concentrations of neptunium leached from nuclear waste repositories in geologic environments, the solubility of neptunium in a neptunium-doped borosilicate glass, which simulates a high-level waste glass, was investigated. The concentrations of neptunium in solutions contacting the crushed doped glass were found to be controlled by a neptunium solid phase that is similar to crystalline(c)- NpO_2 in solubility. Thus, the maximum concentration of the neptunium leached from this waste form can be predicted from the solubility of $NpO_2(c)$. This conclusion is based on similar neptunium concentrations in solutions contacting neptunium-doped glass, neptunium-doped glass plus $NpO_2(c)$, and $NpO_2(c)$ alone, under controlled redox potentials and a range of pH values. The quinhydrone used in this study was found to be a very effective redox buffer (the approximate $pe + pH = 11.8$). The predictions based on the thermodynamic data and the solvent extraction tests showed $Np(V)$ to be the primary oxidation state in solution.

INTRODUCTION

One method to dispose of nuclear reactor wastes is to incorporate the waste into another material such as borosilicate glass and then to store the waste form in a deep geologic repository.¹ For this reason, the leachability of borosilicate glasses in aqueous solutions has been investigated.²⁻⁶ These studies relied primarily on static and/or flowing leach tests conducted at the expected repository temperatures and groundwater conditions. Although such tests may provide data for comparing different waste containment materials and for obtaining short-term

kinetic data for elemental releases, they do not identify the controlling mechanisms to allow long-range predictions of the leaching behavior of waste containment glasses in an aqueous environment. To understand the mechanisms of actinide releases from solid waste forms, experimental measurement and control of important solution parameters, such as redox potential, pH, and solution species, are needed.

In situations where the waste form is exposed to near static groundwaters, the solubility limits of many compounds will be reached. This is particularly true of compounds that have low solubilities, such as those of the lanthanides and actinides. It is, therefore, important to know the solubility limits and understand the mechanisms affecting the solubility of actinide compounds and their aqueous species. The experimentally determined solubility data for important actinide oxides in aqueous solutions are slowly becoming available.⁷⁻¹⁰ However, little is known about the solid phases of actinides and their solubilities when these actinide elements are incorporated in borosilicate glass.

Solubility studies were conducted on ²³⁷Np-doped Pacific Northwest Laboratory (PNL) 76-68 borosilicate glass to (a) determine the maximum concentration of dissolved neptunium (one of the important actinides in radioactive waste) and (b) develop a sound approach to predicting neptunium concentrations in solutions contacting a waste form in different geologic environments. These investigations were done under controlled redox potentials and over a range of pH values.

METHODS AND MATERIALS

The actinide-doped PNL 76-68 glass beads used in these experiments are representative of the family of borosilicate waste containment glasses.^{3,11} The

PNL glass was originally fabricated¹² to investigate the leaching characteristics of actinide isotopes from waste-containing glasses. The level of doping was designed to simulate concentrations normally found in high-level radioactive waste. Glass beads were chosen because of experimental convenience, good reproducibility, and homogeneity of the samples. The method of preparation of glass beads has been described by Bradley et al.¹² Briefly, the process involved wetting crushed glass with an HNO₃-HF solution containing ²³⁷Np and ²³⁹Pu. The wetted glass was then vacuum-dried and heated to 1050°C to remelt the glass. The glass melt was cooled, broken, and remelted in a bead fabricator. The beads were annealed at 500°C and slowly cooled. Autoradiographs of bead cross sections verified that a homogeneous radioisotopic distribution was achieved.¹²

Samples of PNL 76-68 glass beads were dissolved and analyzed by inductively coupled plasma (ICP) spectroscopy (Table I). These results are similar to those reported at Bradley et al.¹²

For the solubility experiments, three glass beads (~1 g) were crushed using a Diamonite® (U.S. Ceramic Tile Co., Canton, Ohio) mortar and pestle and added to 30 ml of 0.0015 M CaCl₂ solution containing 6 mg of quinhydrone per tube (~0.001 M). The individual suspensions were adjusted to different initial pH values with dilute NaOH or HCl solutions. Approximately 5 mg of 99.23% ²³⁷NpO₂ (c.c = crystalline) solid, as identified by radiochemical and x-ray diffraction techniques, was added to some of the tubes. All tubes were capped and placed on a shaker. At different times, the pH values were measured with a combination glass electrode and redox potentials (Eh, in volts) were measured with a platinum electrode. These Eh values were converted to pe values, because it is convenient to discuss the redox potential of a system in terms of the pe defined as -log₁₀ of electron activity. The pe value at 25°C is related to the Eh value by the following equation¹³:

$$pe = 16.9 Eh.$$

Aliquots of the filtered solution (0.015 or 0.0018 μm) were dried on cleaned stainless steel planchets and counted on surface barrier alpha detectors. These detectors were capable of resolving the different energies of the neptunium and plutonium alpha particles emitted from the sample. Aliquots of 200 μl or less were necessary to avoid excessive alpha peak tailing due to the dried salts present on the planchet. The calibrated overall efficiencies (count/dis) for these surface barrier detectors ranged from 0.22 to 0.25. After background subtraction, the counts for each aliquot were converted to the log of the concentration (mol/l).

Additional aliquots of the filtered solutions were made 1 M in HCl and extracted with 0.5 M of TTA to separate any Np(III) or Np(IV) species from the solution.¹⁴ The TTA-extracted oxidation states

TABLE I
Composition of PNL-76-68 Glass Beads (wt%)

Oxide	Bradley et al. (Ref. 12)	ICP Analysis ^a	
		Sample 1	Sample 2
Ag ₂ O	0.031		
Al ₂ O ₃		0.52	0.49
B ₂ O ₃	9.5	8.52	8.70
BaO	0.56	0.56	0.57
CaO	2.0	1.91	2.22
CdO	0.033	0.03	0.04
CeO ₂	1.19	1.28	1.35
Cr ₂ O ₃	0.40	0.95	0.88
Cs ₂ O	1.03		
CuO		0.09	0.10
Dy ₂ O ₃		0.01	0.02
Eu ₂ O ₃	0.070	0.08	0.08
Fe ₂ O ₃	9.6	12.9	12.9
Gd ₂ O ₃	0.050	0.06	0.07
K ₂ O		0.46	0.45
La ₂ O ₃	0.53	0.63	0.64
MgO		0.39	0.43
MnO ₂		0.12	0.11
MoO ₃	2.2	1.86	1.88
Na ₂ O	12.5	11.9	11.9
Nd ₂ O ₃	1.65	1.65	1.66
NiO	0.20	0.41	0.41
²³⁷ NpO ₂	0.46		
P ₂ O ₅	0.46	1.90	0.88
PdO	0.53		
Pr ₆ O ₁₁	0.53		
²³⁹ PuO ₂	0.046		
Rb ₂ O	0.13		
Rh ₂ O ₃	0.17		
RuO ₂	1.07	0.85	1.07
SiO ₂	40.0	38.2	38.8
Sm ₂ O ₃	0.32		
SrO	0.37	0.38	0.38
TeO ₂	0.26	0.25	0.30
TiO ₂	3.0	2.73	2.80
²³⁸ UO ₂	4.2	4.97	4.66
Y ₂ O ₃	0.21		
ZnO	5.0	4.06	4.22
ZrO ₂	1.7	1.51	1.51
Total	100.00	99.18	99.52

^aBecause of uncertainties in some of the measured values, the weight percent does not total to 100.

were then back extracted into 10 M HNO₃, which was evaporated onto a planchet and counted as described above. The portion of neptunium in the higher oxidation states (V and VI) was obtained by subtracting the TTA-extracted neptunium concentration from the total neptunium concentration in filtered solutions.

RESULTS AND DISCUSSION

Because neptunium is a multivalent element, the redox potential (or pe value) affects the nature of neptunium species and thus the solubility of neptunium solids. The effect of the redox potential on neptunium-hydroxy solution species was cal-

culated (Fig. 1) from the available thermodynamic data.¹⁵ A great degree of uncertainty exists in the thermodynamic data, especially in the neptunium hydroxo- and carbonato-complexes, because most of the data are estimated or extrapolated from other elements. Therefore, the boundaries of stability fields of neptunium-hydroxy complexes (Fig. 1) should be considered approximate at best. Although the uncertainty in the hydrolysis constants makes it difficult to discern the boundaries of individual stability fields, the data (Fig. 1) indicate that the species of Np(IV) and Np(V) oxidation states will predominate in the pH and pe range of environmental interest.¹⁶

It is difficult to measure and control redox potentials in unpoised solutions. Therefore, we

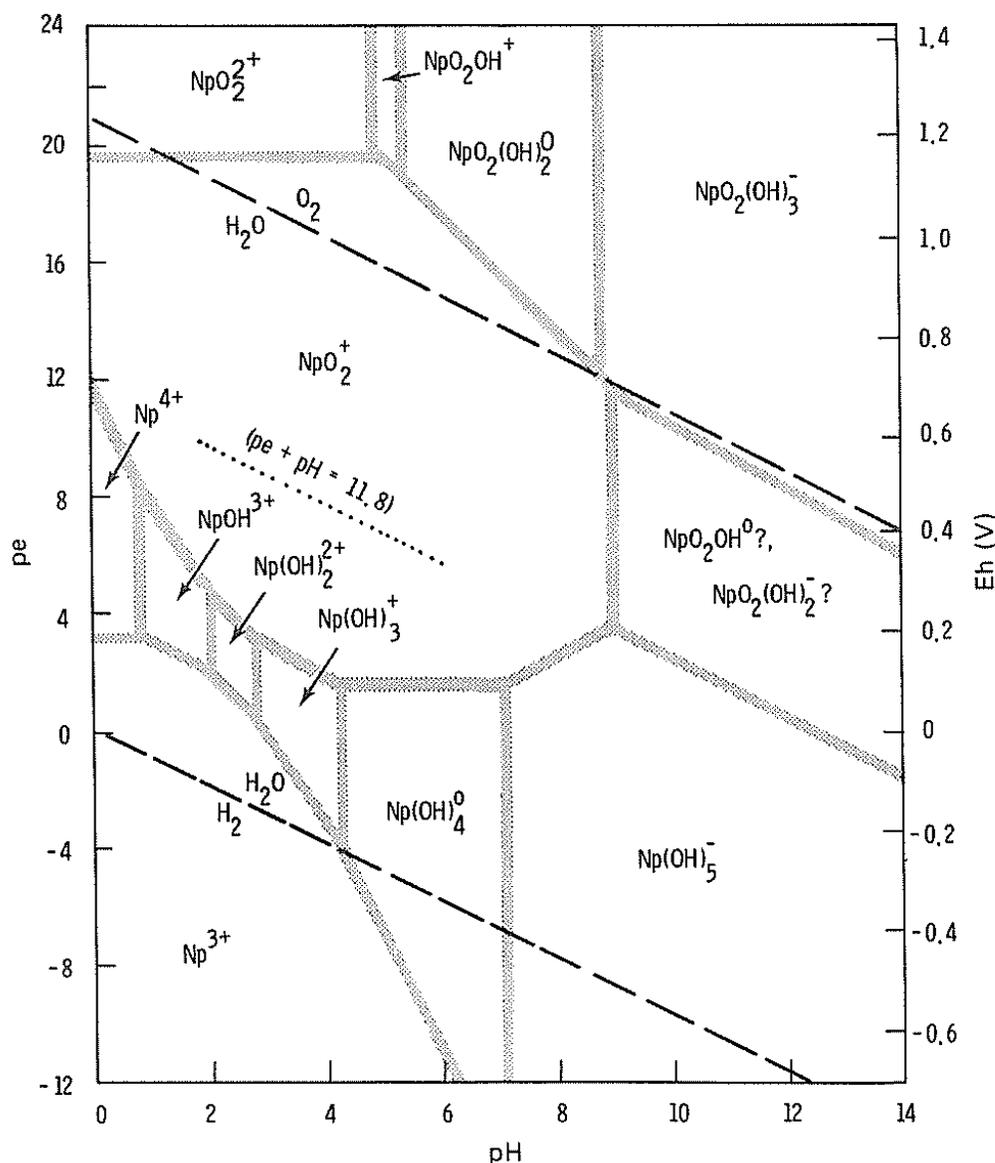
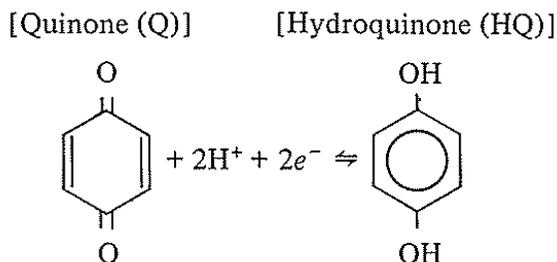


Fig. 1. Equilibrium diagram of redox potential (pe or Eh) versus pH showing stability fields of different hydroxyl complexes. Dashed lines represent the upper and lower stability limits of water. The dotted line represents the pe-pH relationship of quinhydrone (see text). Stability fields are based on estimated thermodynamic data (Ref. 15).

investigated the use of quinhydrone (an equimolar ratio of quinone and hydroquinone) as a redox buffer. Equation (1) relates the equilibrium constant to the activities of the reactants and products of the following reaction¹⁷:



$$\log K = 23.65 = \log[(\text{HQ})/(\text{Q})] + 2\text{pH} + 2\text{pe} \quad (1)$$

When molar concentrations of hydroquinone and quinone are equal as in quinhydrone, $\text{pe} = 11.83 - \text{pH}$ [from Eq. (1)] at 25°C. This theoretical pe - pH relationship is plotted in Fig. 1 (dotted line).

The measured pe and pH of neptunium-doped glass suspensions containing quinhydrone are plotted in Fig. 2. The pe and pH values for four different equilibration periods (~5, 40, 80, and 300 days) were similar. The pH values of the solutions were observed to continuously decrease with time, presumably due to HNO_3 production by alpha radiolysis.¹⁸ Regardless of changes in pH values, the measured pe and pH values were close to the theoretical $\text{pe} + \text{pH}$ value (11.83) of quinhydrone [Eq. (1)], indicating that quinhydrone was an effective redox buffer for the neptunium-doped glass suspensions. The effect of quinhydrone on neptunium solubility was also investigated. To determine possible com-

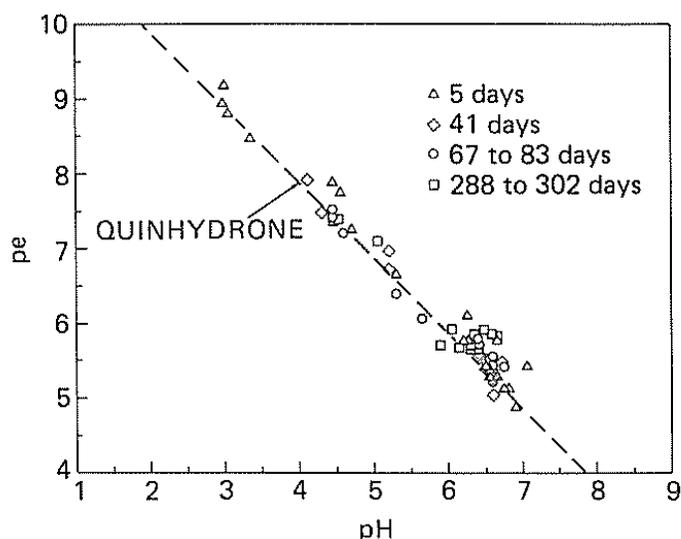


Fig. 2. Measured pe and pH values of neptunium-doped glass suspensions containing quinhydrone at different times during the experiment. The dashed line represents the pe - pH relationship for quinhydrone.

plexation effects, $\text{NpO}_2(\text{c})$ solubility measurements at pH values of 4 to 5 were conducted on a few samples containing between 0.01 and 0.0001 M of quinhydrone. It was concluded from these experiments that the quinhydrone species do not form significant complexes with neptunium solution ions because the observed neptunium concentrations in solutions containing between 0.01 and 0.0001 M of quinhydrone were similar.

For the solubility results to be meaningful, the solid material must be separated from solution. Centrifugation alone is generally not sufficient for this purpose.⁷ Therefore, we evaluated the effectiveness of fine membrane filters (0.015 and 0.0018 μm) to separate the solid from solution. Neptunium concentrations in unfiltered (centrifuged at 6000 rpm for 40 min) and filtered solutions (0.015 μm) were similar (Table II). Neptunium concentrations in solutions filtered through 0.015- and 0.0018- μm membranes were also similar (Fig. 3). These results (Table II and Fig. 3) indicate that significant amounts of particulate or polymeric neptunium species ($>0.0018 \mu\text{m}$) are absent from these solutions and that either of the two tested filters can be used for filtering the suspensions. However, to be reasonably sure of the absence of the colloidal particles, neptunium concentrations were determined using 0.0018- μm filtrates.

The log concentration of neptunium in solutions (filtered through 0.0018 μm) equilibrated with crushed glass beads for ~5, 40, 80, and 300 days versus the pe are plotted in Fig. 4. An approximate concentration of neptunium in solution at different pH values can also be obtained from Fig. 4, knowing the fact that the average $\text{pe} + \text{pH}$ is close to 11.8 (Fig. 2). In general, the concentration of dissolved

TABLE II
Comparison of Neptunium Concentrations from Filtered and Unfiltered Solutions

Sample	pH	pe	log Np (M)	
			0.0018 μm Filtered	Unfiltered
204	4.45	7.37	-5.48	-5.33
205	4.52	7.39	-5.41	-5.43
206	5.90	5.71	-5.76	-5.65
207	6.40	5.66	-5.71	-5.71
208	6.30	5.71	-5.73	-5.61
209	6.55	5.53	-5.69	-5.62
210	6.35	5.85	-5.69	-5.53
211	6.30	5.66	-5.69	-5.54
212	6.15	5.68	-5.68	-5.47
213	6.05	5.92	-5.80	-5.62

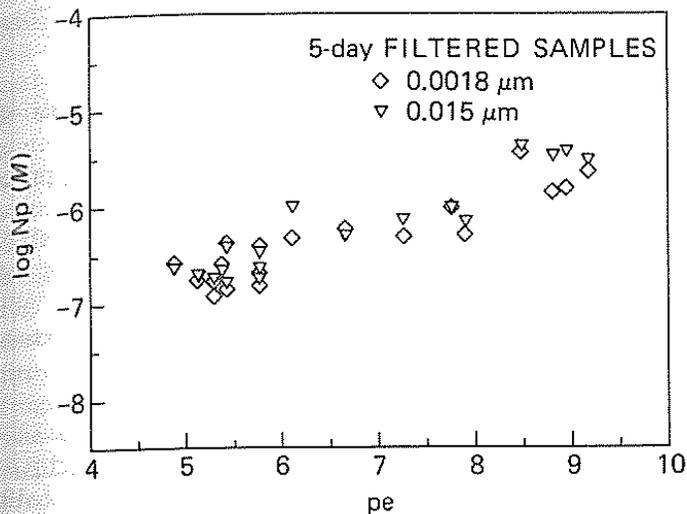


Fig. 3. Comparison of log Np concentrations in solutions filtered through 0.015- and 0.0018- μ m membrane filters.

neptunium appears to be nearly constant with changes in pe at the fixed pe + pH value of 11.8. Although the concentration of neptunium in solution tended to increase with time, the neptunium concentrations at ~80 and 300 days are similar, indicating that steady-state conditions had been reached in 300 days.

The addition of $\text{NpO}_2(\text{c})$ to the crushed neptunium-doped glass suspensions at a given pe and equilibrating period did not affect the neptunium solution concentrations (Fig. 4). If $\text{NpO}_2(\text{c})$ were more soluble than the neptunium compound in doped glass, then the neptunium solution concentration should have increased. These results indicate that the neptunium solid phase in doped glass is either similar to $\text{NpO}_2(\text{c})$ in solubility or is more soluble.

Because experimental $\text{NpO}_2(\text{c})$ solubility data were not available, we also determined the $\text{NpO}_2(\text{c})$ solubility under conditions similar to the neptunium-doped glass. The x-ray diffraction patterns of original

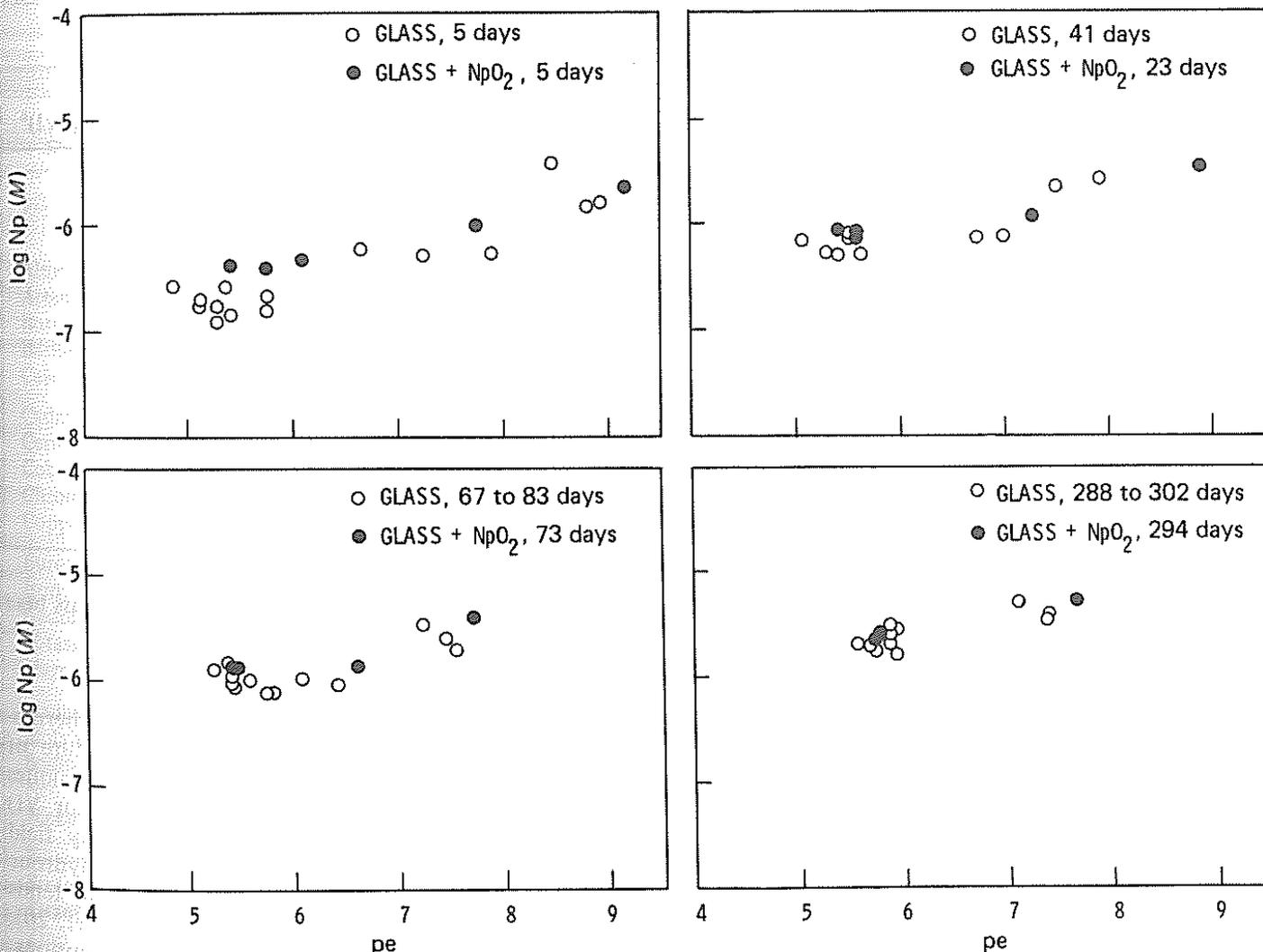


Fig. 4. Log Np concentrations of filtered (0.0018- μ m) solutions contacting neptunium-doped glass or neptunium-doped glass plus $\text{NpO}_2(\text{c})$.

NpO_2 and NpO_2 equilibrated in aqueous suspensions for 54 days showed patterns only of crystalline NpO_2 , indicating that $\text{NpO}_2(\text{c})$ was the only detectable neptunium-solid in these suspensions. The solubility of $\text{NpO}_2(\text{c})$ alone (Fig. 5) was similar to the solubility of neptunium-doped glass and the neptunium-doped glass plus $\text{NpO}_2(\text{c})$ (Fig. 4). These results indicate that the concentration of neptunium in solutions contacting doped glass is controlled by some neptunium compound similar in solubility to $\text{NpO}_2(\text{c})$. These results also indicate that the maximum concentration of the soluble neptunium leached out of the glass beads can be predicted from the knowledge of the $\text{NpO}_2(\text{c})$ solubility. Peters¹⁹ conducted static leach tests at 25°C on this neptunium-doped glass with distilled water and 0.015 *M* of NaHCO_3 solution under atmospheric conditions. His results cannot be directly compared with the present study because redox potentials (estimated to be slightly higher than those in our experiments) were not measured or controlled and the unfiltered neptunium concentrations included neptunium sorbed onto container walls. Nevertheless, his results showed steady-state neptunium concentrations, beyond 105 days, to be $\sim 2 \times 10^{-7}$ *M* in distilled water (pH of ~ 8) and 5×10^{-7} *M* in NaHCO_3 solutions (pH of ~ 9). These results are similar to results reported in Figs. 4 and 5 and substantiate the above conclusion that the information on $\text{NpO}_2(\text{c})$ solubility can be used to predict the maximum concentrations of neptunium that can be leached from glass beads.

Efforts were made to determine the presence of the neptunium solid phase in the glass beads utilizing high resolution autoradiographic and x-ray diffraction techniques.¹² Autoradiographs showed no indication of segregation of the alpha-emitting phase. The x-ray diffraction patterns showed weak reflections of a spinel-type oxide estimated to range from 1 to 3 wt% of the doped glass.¹² Even if the plutonium and neptunium were present as crystalline phases, x-ray diffraction will not detect these phases because of their low potential weight percentage in the glass ($<0.5\%$). Therefore, neptunium solid phases must be submicron in size and evenly distributed if they exist. The use of a scanning transmission electron microscope (STEM) will be required to verify the existence of the fine oxide particles. Arrangements are currently under way to utilize the STEM on samples from the glass beads. However, the results presented above and the methods used to prepare neptunium-doped glass suggest the presence of $\text{NpO}_2(\text{c})$.

Characterization of the nature of solution species is important in understanding the dissolution mechanisms and in extrapolating the solubility results to other environmental conditions. Because of the low neptunium concentrations, a combination of

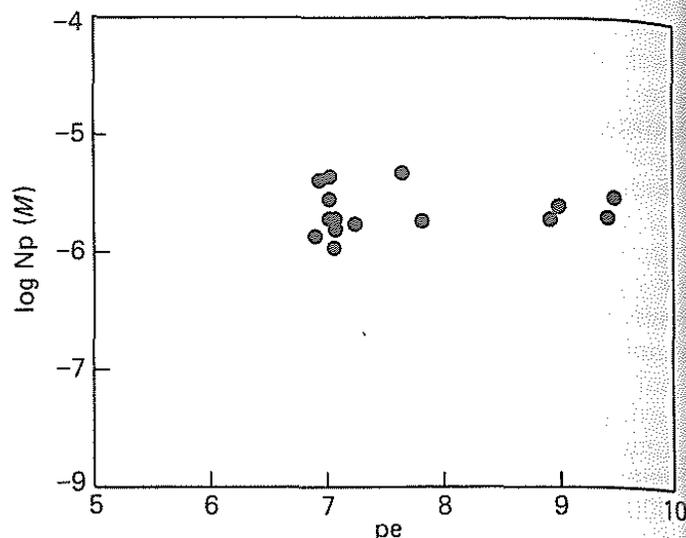


Fig. 5. Log Np concentrations of filtered (0.015- μm) solutions after contacting NpO_2 for 54 days.

TABLE III
Oxidation State of Neptunium in Solutions
Filtered Through 0.0018 μm

Number Sample	Equilibration Period (day)	pH	% Np(V) + Np(VI) ^a
219	18	4.6	93
221	18	6.8	95
214	23	3.2	94 ^b
217	23	6.7	97
219	67	4.6	99
221	67	6.6	97
214	73	4.3	94 ^b
217	73	6.6	99 ^b
204	82	4.5	99
208	82	6.6	98
204	293	4.5	93
208	293	6.3	96
217	294	6.5	97 ^b

^aShould primarily be Np(V), see text.

^bFive milligrams of $\text{NpO}_2(\text{c})$ added to neptunium-glass bead suspensions.

solvent extraction techniques and available thermodynamic data was used to estimate the nature of the neptunium species. Solvent extraction techniques indicated that, primarily, species of Np(V or VI) are present (Table III). Because the stability field of Np(VI) is far removed from the quinhydrone potentials (Fig. 1) and because quinhydrone tends to adjust all neptunium species to Np(V) (Ref. 20), species of Np(V) are expected in these solutions. These solutions are of low ionic strength (≈ 0.01 *M*) (glass dissolution products with 0.0015 *M* of CaCl_2)

and do not contain significant amounts of complexing ligands other than perhaps the hydroxo- and carbonato-ligands in alkaline solutions (Table IV). It should also be noted that of all the oxidation states, Np(V) shows the least tendency to form complexes.²¹ The predictions based on estimated values for the formation constants of Np(V) with different ligands suggest that Np(V) species should be NpO_2^+ in these solutions (Wood and Rai²² and Fig. 1). However, if the solubility of NpO_2 were described in terms of NpO_2^+ [$\text{NpO}_2(\text{c}) \rightleftharpoons \text{NpO}_2^+ + e^-$], the predicted solution species, the solubility lines (Figs. 3, 4, and 5) should have had a slope of -1. The experimentally measured slope in these experiments was -0.25. This discrepancy between the predicted and the experimentally measured slope may be due to one or more of the following: (a) a solid phase other than $\text{NpO}_2(\text{c})$ may be controlling

the steady-state concentrations, (b) the estimated values of formation constants of NpO_2^+ with some key ligands may be in error, and (c) NpO_2^+ may form an as yet unidentified complex under these experimental conditions. Research is under way to check these various hypotheses. Regardless of which option is found valid, the solubilities discussed here appear to be associated with $\text{NpO}_2(\text{c})$ when it is equilibrated in aqueous suspensions under oxic conditions. It can also be stated that information regarding the $\text{NpO}_2(\text{c})$ behavior in aqueous suspensions can also be used to predict the neptunium concentrations in solutions contacting neptunium-doped glasses.

Note: While the manuscript was in press, the neptunium suspensions were analyzed again. The similarity of neptunium concentrations in solutions after 650- and 300-day contact with the neptunium-

TABLE IV

Concentrations of Elements in Different Solutions (0.0018- μm Filtrates) from Doped Glass Bead Suspensions Equilibrated for ~300 Days

Species	Detection Limits	Solution 1	Solution 2	Solution 3	Solution 4	Solution 5	Species	Solution 6	Solution 7
pH		4.45 (ppm)	5.90 (ppm)	6.30 (ppm)	6.35 (ppm)	6.15 (ppm)	pH	4.52 (ppm)	6.55 (ppm)
Aluminum	0.03	0.25	ND ^a	ND	ND	ND	F ⁻	3.0	2.65
Arsenic	0.08	ND	ND	ND	ND	ND	Cl ⁻	191	188
Boron	0.01	12.1	7.84	10.6	10.7	10.3	Br ⁻	153	ND
Barium	0.002	1.76	0.64	0.51	0.48	0.43	NO ₃ ⁻	ND	17.4
Calcium	0.01	50.4	43.2	38.1	36.3	34.3	SO ₄ ²⁻	1.9	1.2
Cadmium	0.004	0.12	0.031	0.018	0.020	0.026			
Cerium	0.04	0.26	ND	ND	0.04				
Cobalt	0.01	0.02	0.02	0.012	ND	ND			
Chromium	0.02	0.10	ND	ND	ND	ND			
Copper	0.004	0.07	0.02	0.017	0.018	0.03			
Europium	0.002	0.019	ND	ND	ND	ND			
Iron	0.005	8.11	0.28	0.25	0.25	0.38			
Gadolinium	0.01	0.02	ND	ND	ND	ND			
Potassium	0.3	32.9	7.26	7.8	8.7	6.7			
Magnesium	0.06	0.60	0.31	0.31	0.42	0.34			
Manganese	0.002	0.273	0.135	0.157	0.14	0.16			
Molybdenum	0.01	1.95	3.29	4.63	4.73	4.5			
Sodium	0.01	42.4	29.9	37.5	38.6	42			
Neodymium	0.02	0.34	0.03	0.07	0.07	0.06			
Nickel	0.02	0.80	0.341	0.37	0.35	0.39			
Silicon	0.02	61.4	37.6	42.8	43.8	45.1			
Strontium	0.02	1.42	0.79	0.84	0.84	0.76			
Titanium	0.002	0.04	0.017	0.017	0.016	0.027			
Zinc	0.02	14.9	7.07	5.67	6.55	7.47			
Zirconium	0.008	0.97	0.009	0.02	ND	0.039			

^aND = not detected. Calculations using the major components indicate that the ionic strength of the various solutions is ~0.01 M.

doped beads supports the earlier conclusion that steady-state neptunium concentrations were reached in 300 days. Although only 54-day equilibration data for NpO_2 solubility (Fig. 5) are plotted, results based on 5- to 700-day equilibrations show that steady concentrations were reached within 54 days.

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