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Solubility of $PuO_2 \cdot xH_2O$ in Alkaline Hanford High-Level Waste Solution

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SUMMARY

The solubility of Pu(IV) hydrous oxide, $PuO_2 \cdot xH_2O$, in air-equilibrated, synthetic, Hanford high-level waste (HLW) solutions was determined as a function of NaOH, $NaAl(OH)_4$, $NaNO_3$, $NaNO_2$, and Na_2CO_3 concentrations. The solubility was found to increase with the square of the NaOH chemical activity. The components $NaNO_3$ and $NaNO_2$ increased $PuO_2 \cdot xH_2O$ solubility by increasing NaOH activity. Aluminate increased solubility by forming a 1:1 complex with the dissolved plutonium species, while carbonate increased solubility by forming a 1:2 plutonium-carbonate complex. Spectral, electrochemical, and solubility evidence points to the existence of hydroxide-complexed Pu(V) dissolved species.

INTRODUCTION

Acidic, plutonium-bearing, HLW solutions resulting from plutonium separation and waste processing operations at the U.S. Department of Energy's Hanford Site are made alkaline (>pH 12) with NaOH prior to discharge into underground waste storage tanks. Treatment of the acidic HLW with NaOH results in the precipitation of many sparingly soluble hydrous oxides including Fe(III) and presumably, Pu(IV) hydrous oxides. While scavenging (or carrier precipitation) reactions are well known for plutonium using Fe(III) carrier, the upper bound in plutonium concentration in alkaline solution will be established by the solubility of the compound formed by precipitation of Pu(IV) with NaOH solution. Knowledge of the solubility of plutonium compounds and the identities of the solid- and dissolved-plutonium species in the HLW are of interest in waste storage and processing operations at the Hanford Site.

Relevant studies on the chemistry of plutonium in alkaline solution are relatively few. Early investigation by Connick et al. (1949) of Pu(IV) and (VI) precipitates in 0.5M to 1M NaOH in air showed that in 1 to 2 days, negligible (IV) oxidized or (VI) reduced in either solution or precipitated solids. Reduction-oxidation (redox) potentials of dissolved plutonium species in NaOH solution that were determined by Peretrukhin and Alekseeva (1974) and Bourges (1972), using polarographic techniques, established oxidation state fields of stability. Studies of the solubility of plutonium compounds in highly alkaline solution are limited to the work of Perez-Bustamante (1965), who investigated dissolution of Pu(VI) hydroxide in solutions ranging from 0.11M to 10M in KOH. Those studies indicated plutonium concentration increased with the 0.5 power in hydroxide molar concentration.

A study by Delegard and Gallagher (1983) surveyed the effects of 12 major solution components of Hanford HLW on the solubility of the plutonium compound precipitating in simulated HLW. The study, based upon the nominal HLW composition given in table 1, indicated that increased NaOH, $NaAl(OH)_4$, and $NaNO_3$ concentrations significantly increased plutonium concentrations. Of the 12 components studied, $NaNO_2$ was the most effective in reducing plutonium solution concentration.

The present study was undertaken to investigate more fully the roles of NaOH, $NaAl(OH)_4$, $NaNO_3$, $NaNO_2$, and Na_2CO_3 on the solubility-limited concentrations of plutonium in air-equilibrated simulated HLW. Also investigated were the effects of plutonium oxidation state ((IV) or (VI)), undersaturation/oversaturation, and time on plutonium solution concentration. Redox potentials were measured, the solids controlling solubility were identified, and the oxidation states of the dissolved plutonium species were established. As a result, plausible dissolved plutonium species are proposed and mixed equilibrium constants for the identified solubility equilibria are evaluated.

Table 1. Typical Composition of Alkaline Hanford High-Level Waste Solution.

Component	Concentration ($\underline{M}$)
NaOH	4
$NaNO_3$	2
$NaNO_2$	2
$NaAl(OH)_4$	0.5
Na_2CO_3	0.05
Na_2SO_4	0.01
Na_3PO_4	0.01
NaF	0.01
Na_3HEDTA[a]	0.1
Na_4EDTA[b]	0.05
Na_3 citrate	0.03
Na glycolate	0.1

[a] HEDTA - N-2-hydroxyethyl ethylenediaminetriacetate.

[b] EDTA - ethlylenediaminetetraacetate.

MATERIALS AND METHODS

PREPARATION OF PLUTONIUM STOCK SOLUTIONS

To prepare Pu(IV) stock solutions, purified plutonium anion exchange eluate in nitric acid was concentrated through boiling to $\sim 1\underline{M}$ plutonium. The concentrated stock then was treated with 30% H_2O_2 at 50 to 60 °C to convert all plutonium to the (IV) state. Excess H_2O_2 was decomposed by reaction with HNO_3. Spectrophotometric analyses confirmed the existence of all plutonium in the (IV) state.

The Pu(VI) stock solution was prepared by ozonolysis of $\sim 0.06\underline{M}$ Pu(IV) in $0.25\underline{M}$ HNO_3. The ozone was produced from O_2 gas by an electrolytic ozone generator. About 40 hours of bubbling of the ozone through the plutonium solution was necessary to convert all plutonium to the (VI) state as determined by spectrophotometry. The stock produced was concentrated through evaporation by the flowing gas to $\sim 0.12\underline{M}$ plutonium in $\sim 0.5\underline{M}$ HNO_3.

The isotopic composition of the plutonium used in these studies was determined by mass spectrometry to be 0.034% ^{238}Pu, 90.9% ^{239}Pu, 8.4% ^{240}Pu, 0.54% ^{241}Pu, and 0.11% ^{242}Pu.

EXPERIMENTAL PROCEDURES AND METHODS

Test solutions were prepared from reagent grade chemicals and distilled water. Most of the solubility experiments were prepared by pipetting 50 μL of Pu(IV) stock ($\sim$0.05 mmol) into 10 mL of the appropriate test solution. The green Pu(IV) solids precipitated immediately. The suspensions, in polyethylene bottles, were double-wrapped in plastic bags and placed on reciprocal shakers. All experiments were conducted at room temperature (18 to 24 °C) in air. Separate experiments were conducted that indicated that plutonium solubility in $3\underline{M}$ to $5\underline{M}$ NaOH solutions was not appreciably affected by carbonate until carbonate concentrations exceeded $0.25\underline{M}$. Except for experiments in which Na_2CO_3 was added intentionally, carbonate concentrations in the experimental solutions were $<0.03\underline{M}$.

A small number of solubility experiments were conducted by adding Pu(IV) hydrous oxide solids to test solutions. The solids were prepared by adding NaOH solution rapidly, with stirring, to Pu(IV) stock. The resulting precipitate was separated from the supernatant solution by filtration, and the precipitate was washed several times with distilled water. The damp plutonium solids then were introduced to the 10 mL portions of test solutions.

Solubility experiments also were conducted using Pu(VI) stock solution; 350 μL of Pu(VI) stock ($\sim$0.04 mmol) were added to 10 mL of the appropriate test solutions. In the Pu(VI) experiments, precipitation was not immediately evident. After a few days to a few weeks, depending on the solution, brown, then green, solids appeared plated out on the vessel walls.

Samples of supernatant test solution were taken periodically, filtered, and the plutonium concentrations determined by liquid scintillation alpha counting. Filtration was accomplished using Amicon type-F50 Centriflo polysulfone membrane cones. The cones have nominal 3-nm pore sizes. Sequential filtering of selected plutonium-saturated test solutions through the membrane cones yielded experimentally identical plutonium concentrations, which indicated that negligible adsorption occurred on the filtration apparatus. Filtration of a 5M NaOH test solution through cellulose nitrate filters of nominal 10-, 100-, and 450-nm pore sizes yielded plutonium concentrations indistinguishable from the concentration obtained by using the 3-nm filters. Cellulose nitrate filters were not used in further tests due to their low stability in NaOH solutions. Direct or diluted portions of test solution filtrates were added to Packard Insta-gel liquid scintillation cocktail and the cocktail mixtures counted in a Packard Tri-Carb analyzer.

Redox potentials were measured with a coiled platinum-wire electrode referenced to a fiber-junction, saturated calomel electrode. A few potential measurements, using graphite and platinum electrodes referenced to a Ag/AgCl electrode, confirmed the calomel electrode-referenced data. Potential readings generally required 2 to 3 minutes to stabilize. The electrode measurement systems were calibrated against freshly prepared Fe(II)-Fe(III) solutions.

Dissolved plutonium oxidation states were identified by absorption spectrometry. Due to low molar extinction coefficients and low plutonium concentrations, direct spectral analyses of plutonium in the NaOH test solutions were possible only for the most concentrated solutions. Spectral analyses generally were performed on solutions acidified with 12.1M HCl. Again, however, plutonium absorption spectra were only evident for those solutions having higher plutonium concentrations. A spectral analysis technique developed by Swanson and Rai (1981), relying on the strongly absorbing Pu(IV)-arsenazo III complex, was used to determine plutonium oxidation states in lower concentration solutions. In the arsenazo III technique, various oxidants and reductants were used to determine Pu(IV), Pu(III) plus (IV), and total ionic plutonium concentrations. By subtraction, concentrations of Pu(III) and oxidized plutonium (in the (V) and (VI) states) could be determined.

The crystallinity and identity of the plutonium hydrous oxide solids were determined through X-ray diffraction. Plutonium solids were separated from the test solutions by filtration, washed by water, and air dried. The dried solids were suspended in an acrylic matrix, and the suspensions were pipetted and cured on a microscope slide. The slides were wrapped in Kapton film for contamination control, and the powder diffraction pattern was gathered using a Rigaku D/MAX-rA X-ray diffractometer.

RESULTS AND DISCUSSION

PLUTONIUM HYDROUS OXIDE IN NaOH SOLUTIONS

Plutonium concentrations in NaOH solutions in contact with Pu(IV) hydrous oxide varied with time at all NaOH concentrations studied (1M to 15M NaOH) (fig. 1). Except in 1M NaOH, plutonium concentrations initially increased with time from the first sampling at 2 days' contact. Other tests in 5M NaOH, which are not depicted here, showed that the plutonium concentrations increased from 30 minutes' contact time. The plutonium concentrations reached maxima, which occurred later as NaOH concentrations increased, before decreasing. The slopes of the descending log-log plots in figure 1 for the 1M to 10M NaOH experiments were all about -0.5. That is, the plutonium concentration decreased with $(\text{time})^{\frac{1}{2}}$. The increase then decrease in soluble species concentration with time is observed for other precipitation systems (Walton (1964)). The decrease in soluble plutonium concentration above Pu(IV) hydrous oxide solids with time has been observed by Rai and Ryan (1982) in pH 1 to 6 solutions, and was thought to be due to slow crystallization to a state they called PuO_2 (less crystalline).

None of the suspensions were at apparent equilibrium or steady state after more than 700 days' contact. However, extrapolating the above rates to a century's aging would result in less than a factor of 10 in further decrease in plutonium concentration. Studies to elucidate plutonium hydrous oxide solubility behavior in NaOH solutions were made at selected contact times (usually 8 weeks). Plotting plutonium molal concentration versus sodium hydroxide chemical activity at 8 weeks' contact time showed plutonium concentration rose with the square of NaOH activity (fig. 2). Greater contact times also showed the square dependence on NaOH activity. Sodium hydroxide activity coefficients were obtained from the compilation of Hamer and Wu (1972). The goodness of fit was high with no apparent difference noted between data from in situ-formed plutonium hydrous oxide (i.e., from oversaturation) and data from pre-formed solids (i.e., from undersaturation). The data presented in figure 2 may be expressed by the equation

$$\log [Pu] = 2.04 \log (NaOH) - 7.31 \tag{1}$$

In equation 1, and throughout this paper, activities are denoted by ( ) around the given species; molal concentrations are denoted by [ ].

Other tests were conducted in which Pu(VI) solutions were added to various concentrations of NaOH. With over 600 days' contact time, plutonium concentrations were approaching concentrations found for experiments beginning with Pu(IV) (fig. 3). In addition, the initially brown precipitates observed in the Pu(VI) experiments converted to the green color that was observed immediately in the Pu(IV) experiments.

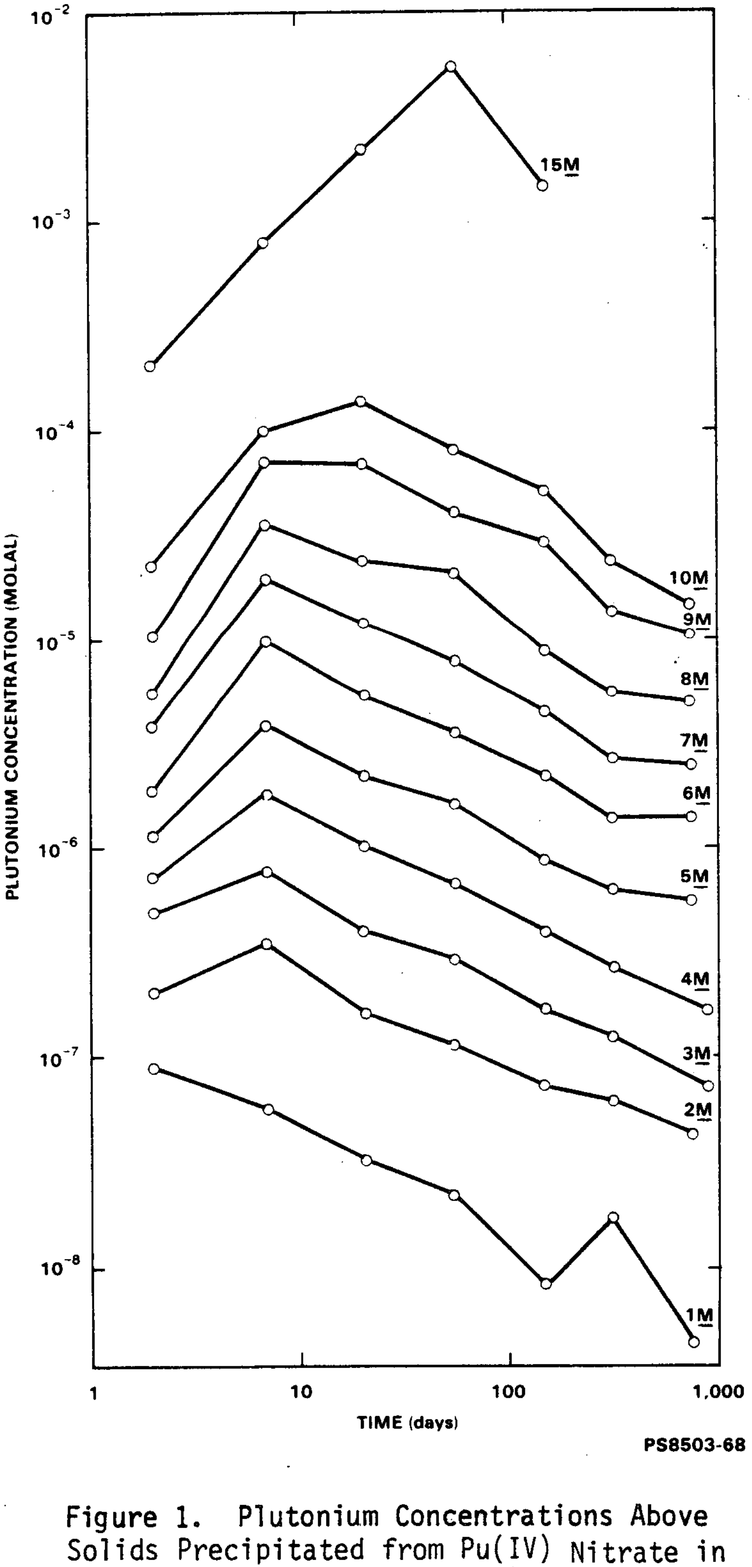

Figure 1. Plutonium Concentrations Above Solids Precipitated from Pu(IV) Nitrate in Various Concentrations of NaOH as a Function of Time.

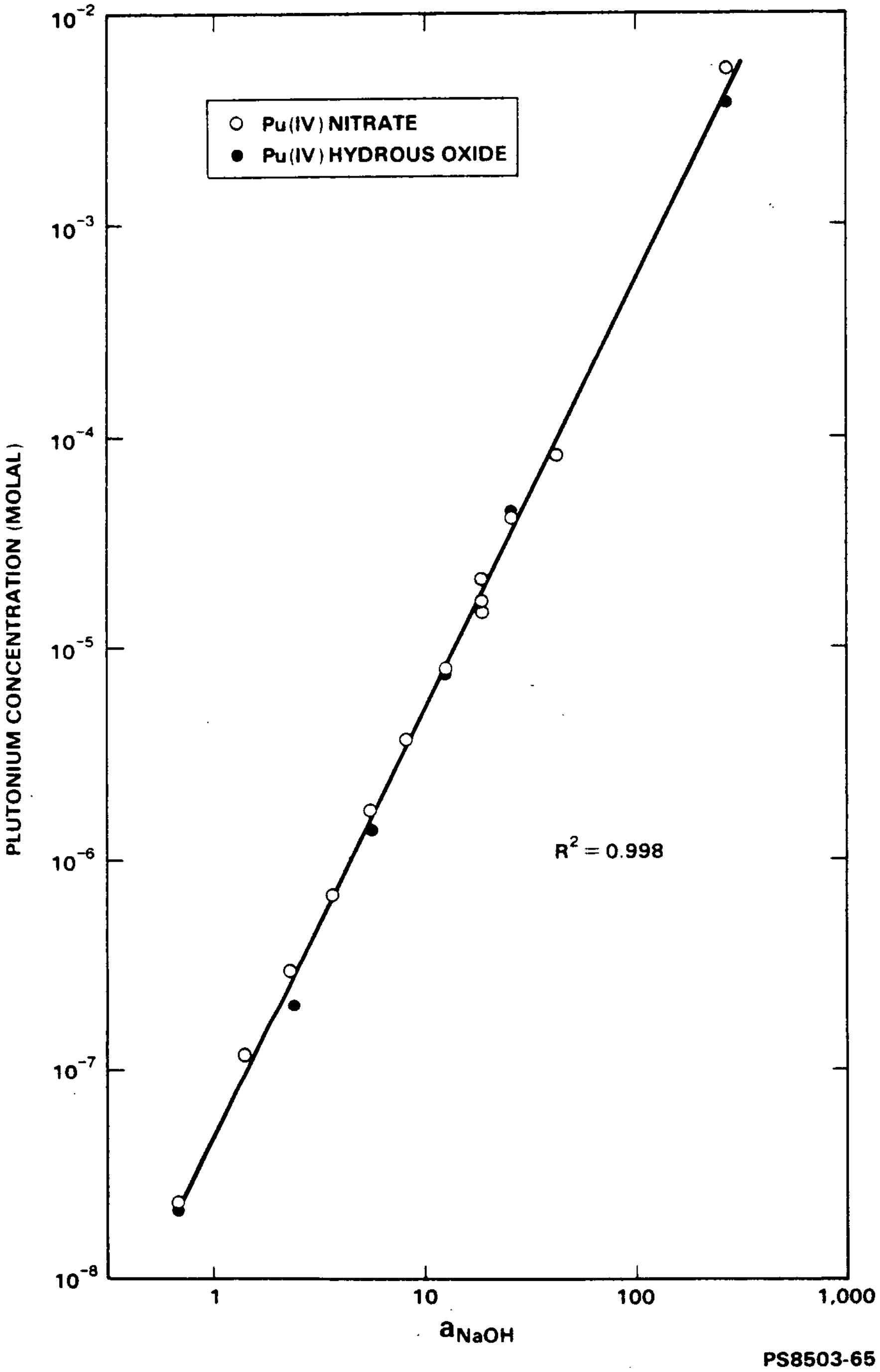

Figure 2. Plutonium Concentrations Above Solids Precipitated from Pu(IV) Nitrate and Above Pu(IV) Hydrous Oxide at 56 Days' Contact as a Function of NaOH Chemical Activity.

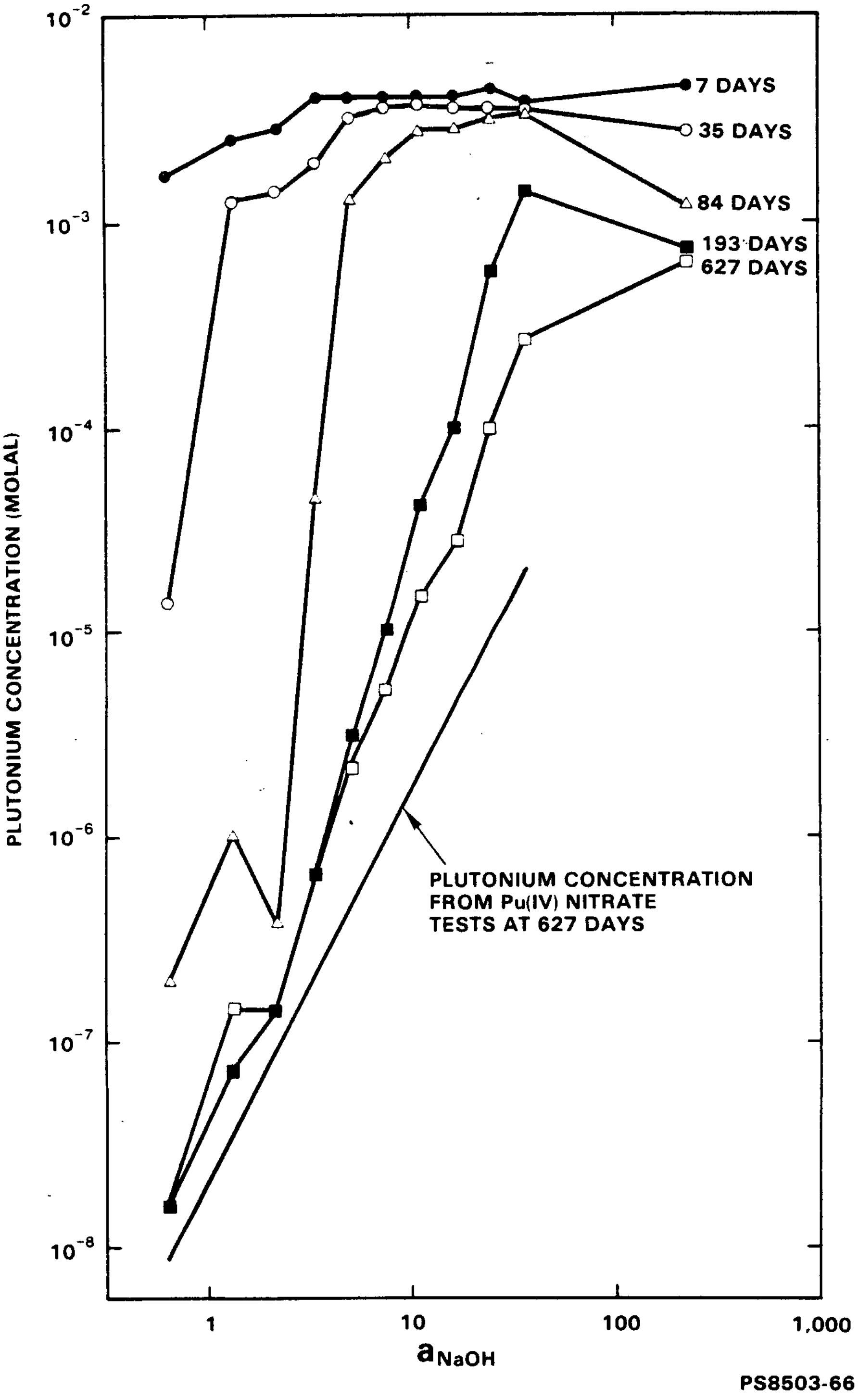

Figure 3. Plutonium Concentrations Above Solids Precipitated from Pu(IV) Nitrate at Various Contact Times as a Function of NaOH Chemical Activity.

Solids taken from tests begun by Pu(IV) nitrate addition were dissolved/suspended in 6M HNO_3 and analyzed spectrophotometrically. Only the characteristic spectrum of Pu(IV) polymer was obtained where spectra could be found. Other portions of the same solids were analyzed by X-ray diffraction at various contact times. The diffraction analyses at all contact times and NaOH concentrations studied gave peaks corresponding to the PuO_2 diffraction pattern. The peaks were broad, indicating that the solids were of low crystallinity. Solids taken from the Pu(VI) experiment at 1M NaOH also gave a pattern corresponding to the PuO_2 pattern, although this pattern indicated higher crystallinity than those shown by the Pu(IV) experiments. From these data, it was inferred that Pu(IV) hydrous oxide was the solid phase controlling plutonium concentration in the NaOH solutions.

Spectrophotometric analyses were used to determine the oxidation state of the dissolved plutonium species in tests begun by adding Pu(IV) to NaOH solutions. Direct spectral determination of the plutonium oxidation state was possible only for solution filtered from the 15M NaOH test. The spectrum closely matched the spectrum observed by Bourges (1972) for Pu(V) evolved electrochemically in 4M NaOH (fig. 4). Filtered solutions from the 5M and 10M NaOH tests were analyzed spectrophotometrically using the technique of Swanson and Rai (1981). The spectral analyses showed the plutonium present as plutonyl(V) or (VI) species. Solution from the 10M NaOH test, acidified with HCl, showed a peak at 830 nm due to the strongly absorbing Pu(VI). The height of this peak doubled when $KMnO_4$ solution was added indicating Pu(V) was present (Rai et al. (1980)).

Redox potential measurements were made for the air-equilibrated NaOH solutions both with and without the addition of Pu(IV) nitrate. The potentials were measured on a platinum electrode with reference to a saturated calomel electrode. The junction (or diffusion) potential existing between saturated KCl solution and NaOH solutions is significant and, together with the potential of the saturated calomel electrodes, must be included in calculations of potential versus normal hydrogen electrode (E_{NHE}). The diffusion potentials were obtained from the work of Fricke and Rohmann (1924) and the potential of the saturated calomel electrode used was 0.242 V. The E_{NHE} values were obtained by the equation

$$E_{NHE}, \text{ (volts)} = E_{meas} + 0.242 - E_{diff} \qquad (2)$$

where E_{diff} is the diffusion potential and E_{meas} is the measured potential. The E_{NHE} values are plotted versus the log of the NaOH activity (fig. 5). A comparison of the plots for the NaOH solutions both with and without Pu(IV) showed that the addition of plutonium reduced redox potential slightly. However, the NaOH solution chemistry seemed to be controlling redox potential in both systems. The redox potential, E_{NHE}, can be

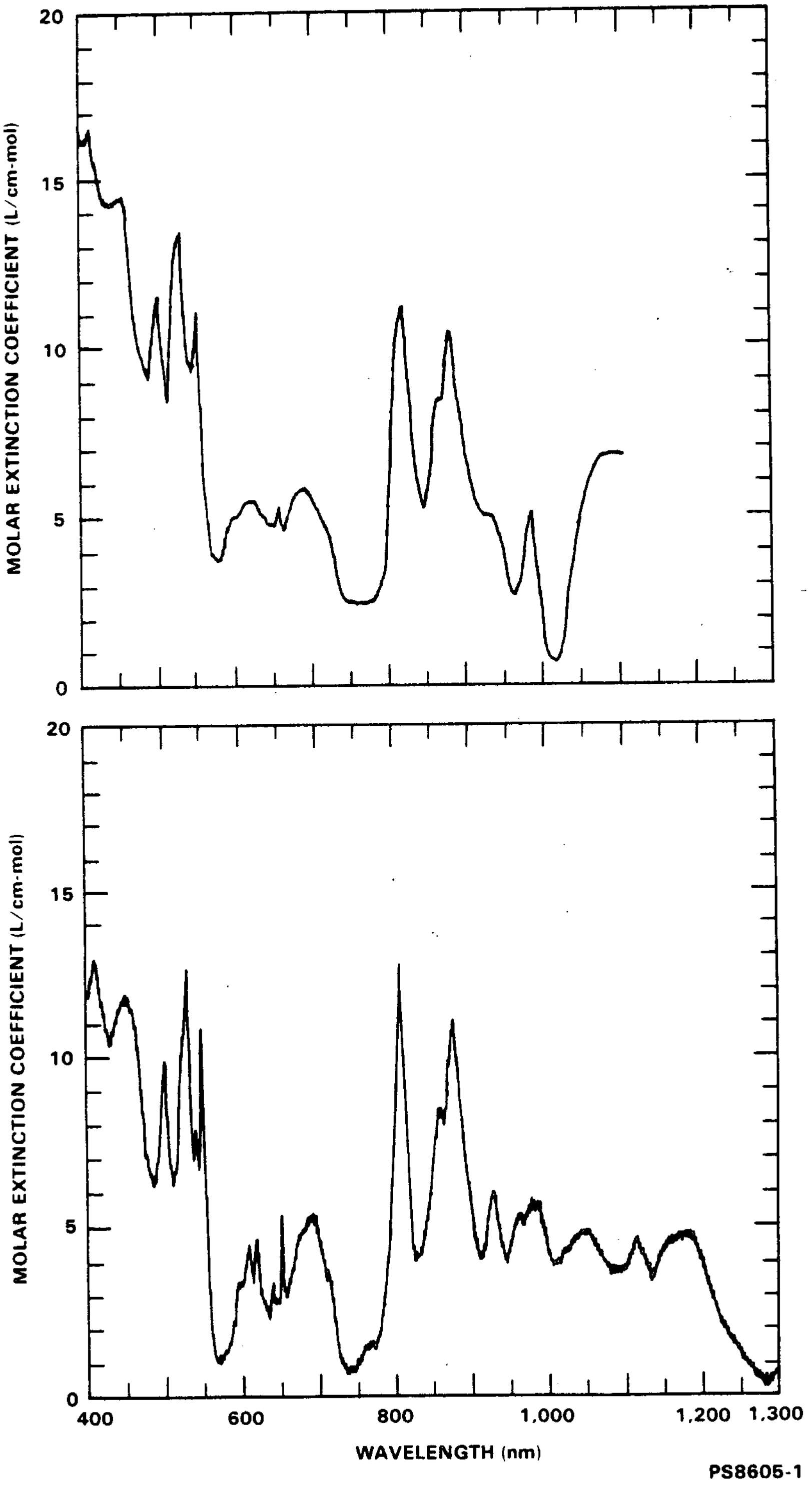

Figure 4. Absorption Spectra of Pu(V). TOP: Evolved Electrochemically in 4M NaOH (redrawn from Bourges (1972)); BOTTOM: 8.84 x 10^{-4} $\underline{M}$ Plutonium in 15$\underline{M}$ NaOH (from present work).

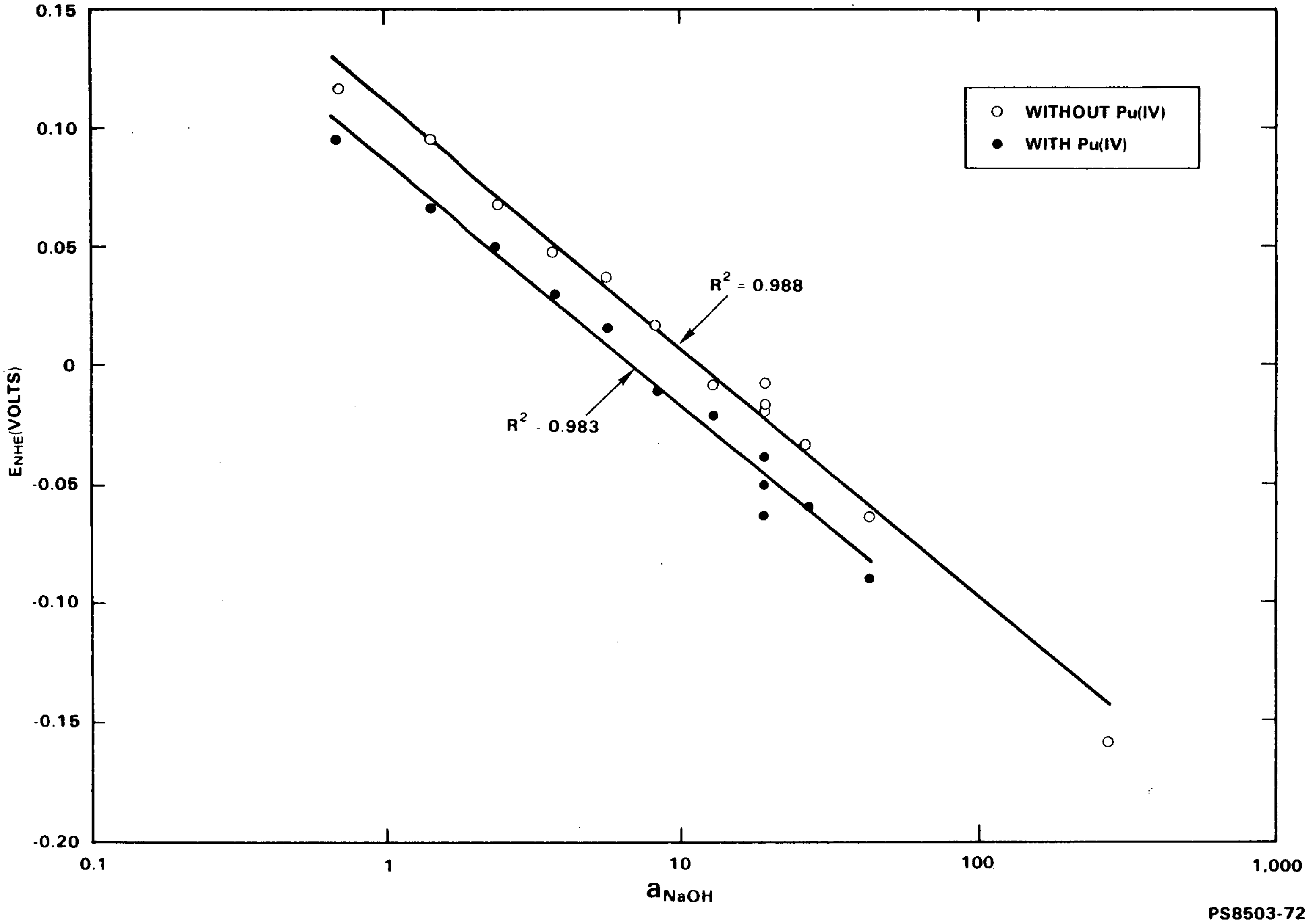

Figure 5. Electrode Potentials Versus the Normal Hydrogen Electrode for NaOH Solutions With and Without Pu(IV) Nitrate Addition as a Function of NaOH Chemical Activity.

converted to the negative logarithm of the electron activity, pe, by the equation pe = 16.9 E_{NHE}. The data presented in figure 5 for the NaOH system with plutonium may be expressed by the equation

$$pe = -\log(e^-) = -1.75 \log(\text{NaOH}) + 1.48 \quad (3)$$

Plutonium redox potentials in NaOH have been measured polarographically by Bourges (1972) and Peretrukhin and Alekseeva (1974) using calomel-referenced platinum electrodes. Plots of the polarographic data with the redox data from the present study (fig. 6) indicate Pu(V) to be the likely oxidation state in the air-equilibrated NaOH system. The redox data corroborate the spectrophotometric analyses that the dissolved plutonium species is in the (V) state.

The solubility and redox data may be combined to identify a plausible hydroxide-coordinated Pu(V) dissolved species and to determine the mixed equilibrium constant expressing the dissolution reaction. From identification of the solid phase and the oxidation state of the dissolved species, the redox reaction may be written

$$PuO_2 \cdot xH_2O \rightleftharpoons PuO_2^+ + x\,H_2O + e^-$$

where $PuO_2 \cdot xH_2O$ represents the poorly crystalline Pu(IV) hydrous oxide solid phase. In the high NaOH concentrations employed in the experiments, hydrolysis of the PuO_2^+ ion leads to the equilibrium

$$PuO_2 \cdot xH_2O + n\,OH^- \rightleftharpoons PuO_2(OH)_n^{(n-1)-} + x\,H_2O + e^-$$

Work by Musikas (1978) on Np(V) in NaOH solution suggests by analogy that at the low plutonium and high NaOH concentrations found in the present experiments, monomeric species are more likely than polymers. The $PuO_2(OH)_n^{(n-1)-}$ species is the dissolved plutonium species whose molal concentration was expressed as a function of NaOH activity in equation 1. Therefore, the dissolution and hydrolysis reaction stated above may be expressed in terms of the mixed-equilibrium constant

$$\log K_{m,OH} = \log [Pu] + \log(e^-) - n \log(\text{NaOH}) \quad (4)$$

The mixed-equilibrium constant is used rather than a true, or thermodynamic, equilibrium constant since the chemical activities of the dissolved plutonium species and of the hydroxide ion cannot be determined. The dissolved plutonium concentration, expressed in molality, is assumed to be proportional to the plutonium species chemical activity. Also implicit in equation 4 is the assumption that the chemical activity of the hydroxide ion is proportional to the chemical activity of NaOH.

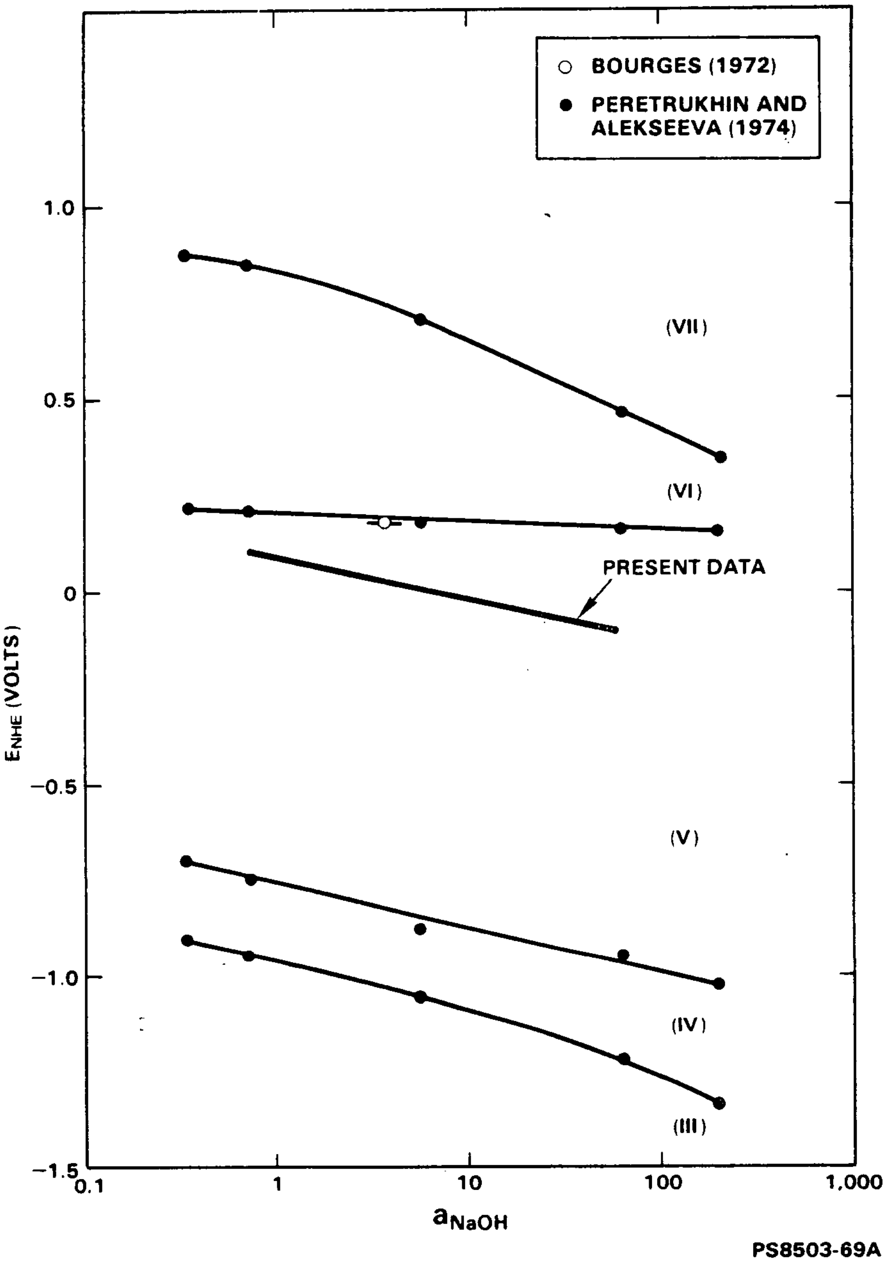

Figure 6. Dissolved Plutonium Oxidation State Fields of Stability as Found by Polarography and the Redox Measurements in the Present Study.

Substituting equations 1 and 3 into equation 4 yields the expression

$$\log K_{m,OH} = 3.79 \log (NaOH) - 8.76 - n \log (NaOH) \quad (5)$$

For log $K_{m,OH}$ to be a constant, n, the number of hydroxide ligands on the dissolved plutonium species, must be 3.79 ≈ 4. Therefore, the dissolved plutonium species appears to be $PuO_2(OH)_4{}^{3-}$, and equation 4 has the form

$$\log K_{m,OH} = \log [Pu] + \log (e^-) - 4 \log (NaOH) \quad (6)$$

Values of log $K_{m,OH}$ were determined using equation 6 for the experiments in which Pu(IV) nitrate was added to NaOH solution. For the 12 experiments, log $K_{m,OH} = -8.93 \pm 0.16$ at 1 standard deviation.

PLUTONIUM HYDROUS OXIDE IN $NaOH/NaNO_3/NaNO_2$ SOLUTIONS

After water and NaOH, $NaNO_3$ and $NaNO_2$ are the chemical components found in greatest concentration in Hanford HLW. The contributions of these components to the chemical activity of NaOH must be taken into account before further investigation is possible into their roles in plutonium hydrous oxide dissolution. The Debye-Hückel equation and its various extended versions have been used to determine activity coefficients in moderately concentrated, mixed-electrolyte solutions. However, most extended Debye-Hückel equations are applicable only at ionic strengths below 0.3 molal. Recently, an empirical method developed by Meissner (1980) has been applied to predict electrolytes' activity coefficients in highly concentrated electrolyte solution mixtures. This approach was used in the present study to identify the contributions of $NaNO_3$ and $NaNO_2$ to the NaOH activity.

Test solutions were prepared with NaOH concentrations in the range 4 to 7 molal, and $NaNO_3$ and $NaNO_2$ concentrations in the range 1 to 4 molal. Activity coefficient data for NaOH and $NaNO_3$ were obtained from the compilation of Hamer and Wu (1972); $NaNO_2$ activity coefficients were obtained from Staples (1981). The Meissner (1980) method then was used to evaluate the resulting NaOH activity coefficients in the $NaOH/NaNO_3$ and $NaOH/NaNO_2$ solutions. The calculations showed that up to twofold enhancement of NaOH activity occurred due to the contributions of $NaNO_3$ and $NaNO_2$.

Plutonium was added to the test solutions as Pu(IV) nitrate solution. The plutonium concentration data for the $NaOH/NaNO_3$ and $NaOH/NaNO_2$ experiments, obtained after 8 weeks' contact, were plotted versus the calculated NaOH activity and compared to results obtained in pure NaOH solution (fig. 7). Redox measurements of the test solutions with plutonium also made were and compared to results obtained for plutonium dissolved in pure NaOH solution (fig. 8).

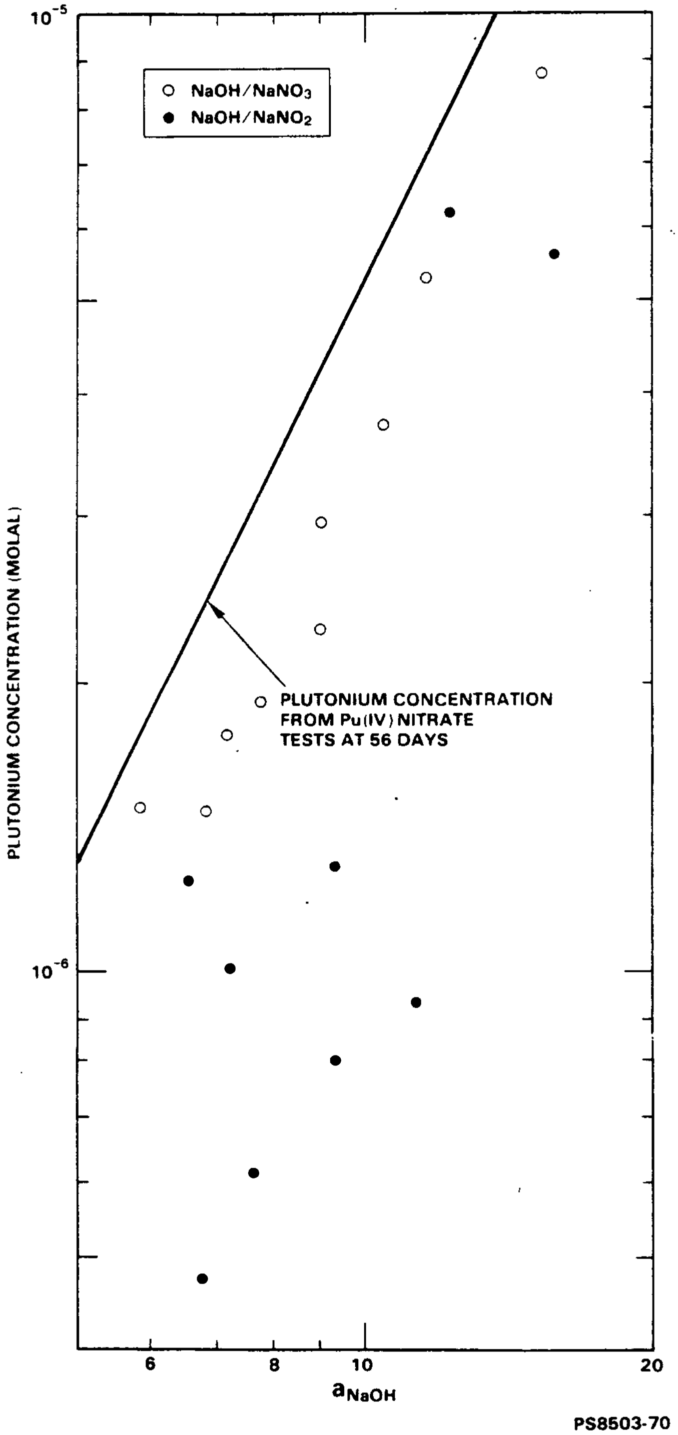

Figure 7. Plutonium Concentrations Above Solids Precipitated from Pu(IV) Nitrate in the NaOH/$NaNO_3$ and NaOH/$NaNO_2$ Systems.

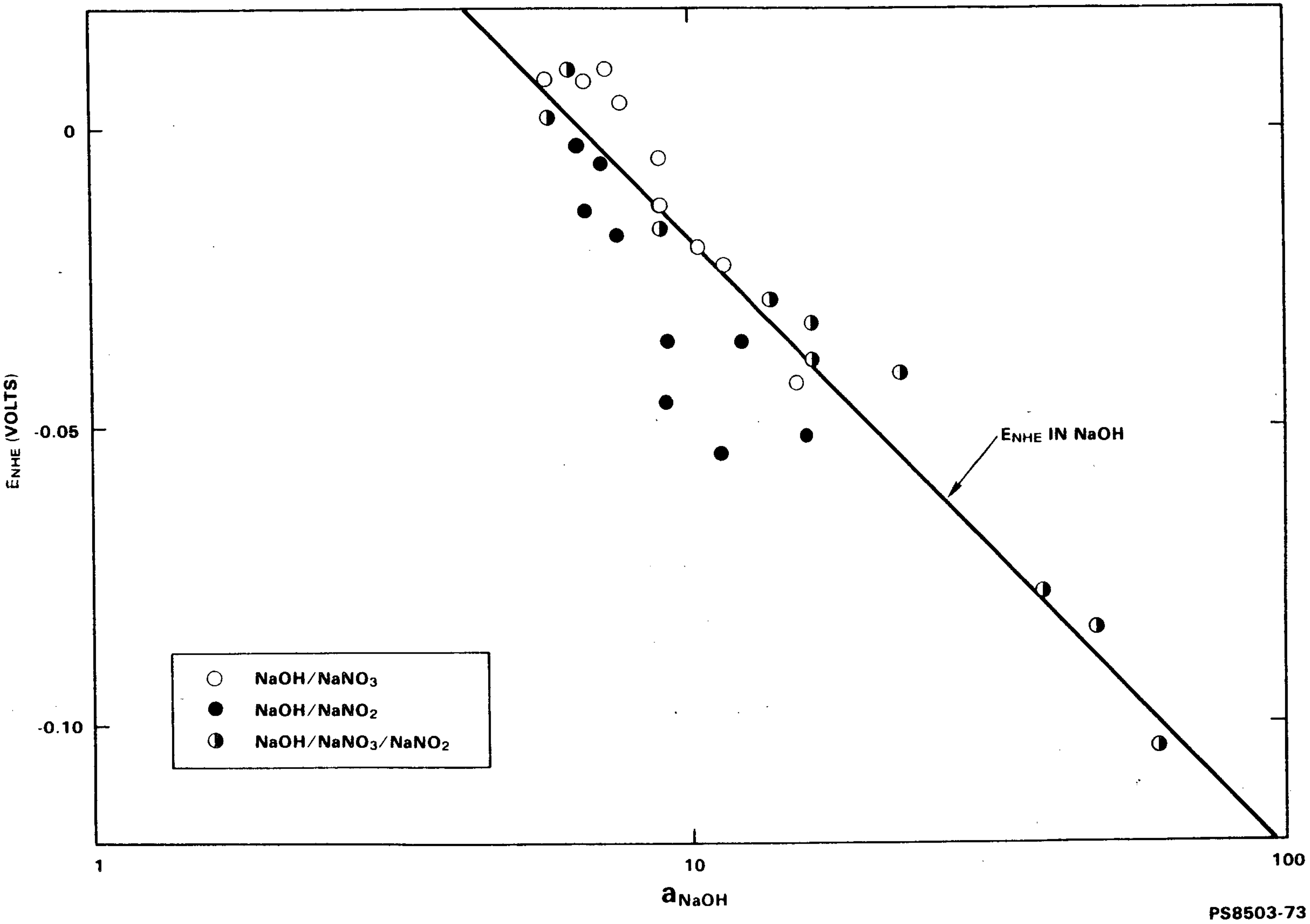

Figure 8. Electrode Potential Versus the Normal Hydrogen Electrode for the $NaOH/NaNO_3$, $NaNO_2$ Systems with Pu(IV) Nitrate Addition as a Function of NaOH Chemical Activity.

The plutonium concentration data for the $NaOH/NaNO_3$ system parallel and are slightly lower than those observed in the NaOH system. The redox potentials for $NaOH/NaNO_3$ are within 15 mV of the NaOH system measurements. The logarithm of the mixed equilibrium constant for the $NaOH/NaNO_3$ data, calculated using equation 6, was -9.20 ± 0.15 (1 standard deviation). At the 95% confidence level, the log $K_{m,OH}$ for the $NaOH/NaNO_3$ system is indistinguishable from the log $K_{m,OH}$ value in NaOH. Thus, $NaNO_3$ appears to enhance the solubility of Pu(IV) hydrous oxide solely through its contribution to the chemical activity of NaOH.

The plutonium concentration data for the $NaOH/NaNO_2$ system did not parallel the NaOH system data and were about 25% to 700% lower (fig. 7). Likewise, the redox measurements were, for the most part, lower than those obtained in the NaOH system (fig. 8). However, the plutonium concentration and redox values compensated each other. The logarithm of the mixed equilibrium constant for the $NaOH/NaNO_2$ system was -9.23 ± 0.18 (1 standard deviation), not significantly different than the log $K_{m,OH}$ value for the NaOH system. Earlier studies by Delegard and Gallagher (1983) showed $NaNO_2$ tended to decrease plutonium concentrations in synthetic Hanford HLW, although the effect was small. From the present solubility and redox data, $NaNO_2$ appears to act as a mild reductant, which prevents the Pu(IV) solids from oxidizing and dissolving as Pu(V).

The system $NaOH/NaNO_3/NaNO_2$ was also studied. Test solutions were prepared with NaOH concentrations in the range 1 to 11 molal and with $NaNO_3$ equal to $NaNO_2$ concentrations in the range 0.25 to 3 molal each. Using Meissner's (1980) methods, up to fourfold enhancement in NaOH activity was found to be contributed by the effects of $NaNO_3$ and $NaNO_2$.

Plutonium was added as Pu(IV) nitrate stock. Again, plutonium concentration data for 8 weeks' contact were plotted versus NaOH activity and were compared to data for the pure NaOH system (fig. 9). Redox measurements of selected solutions were made and plotted against NaOH activity (fig. 8).

The plutonium concentration data in the $NaOH/NaNO_3/NaNO_2$ system closely follow the concentration data in the pure NaOH system while redox potentials are within 12 mV of the NaOH system values. The logarithm of the mixed equilibrium constant, log $K_{m,OH}$, is -8.97 ± 0.16 (1 standard deviation) and is nearly identical to the value for the NaOH system. The solubility data indicate that when present together in alkaline solution, $NaNO_3$ and $NaNO_2$ increase plutonium hydrous oxide solubility by contributing to the chemical activity of NaOH.

PLUTONIUM HYDROUS OXIDE IN $NaOH/NaAl(OH)_4$ SOLUTIONS

Next to NaOH, $NaAl(OH)_4$ was the Hanford HLW component found to have the greatest effect on increasing plutonium hydrous oxide solubility (Delegard and Gallagher 1983). The contributions of $NaAl(OH)_4$ to the chemical activities of NaOH in the test solutions prepared for these experiments again were determined using the approach described by Meissner (1980).

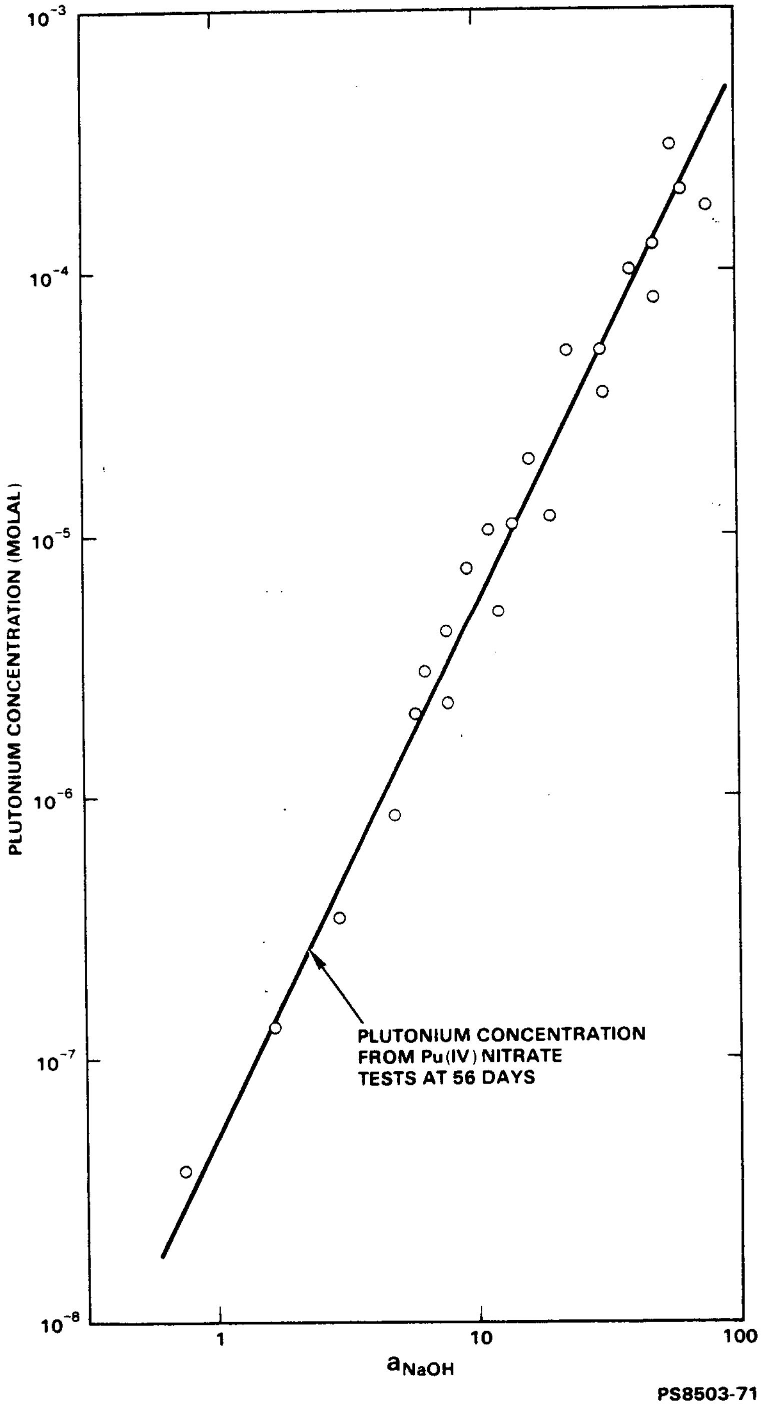

Figure 9. Plutonium Concentrations Above Solids Precipitated from Pu(IV) Nitrate in the NaOH/$NaNO_3$/$NaNO_2$ System as a Function of NaOH Chemical Activity.

Also determined were the effects of NaOH on the $NaAl(OH)_4$ activities. Activity coefficient data for $NaAl(OH)_4$ were obtained from studies by Szita and Berecz (1975).

Test solutions were prepared with NaOH concentrations from about 5 to 10 molal. Concentrations of $NaAl(OH)_4$ ranged from about 0.3 to 2 molal. Plutonium was added to the test solutions as Pu(IV) nitrate; plutonium concentrations were determined after 8 weeks' contact. The plutonium concentrations plotted versus NaOH activity (fig. 10) were as much as 7 times higher than the values observed in the NaOH system. Since the effect of $NaAl(OH)_4$ on NaOH activity was taken into account, the possibility that the enhanced solubility was caused by complexation was investigated.

The general complexation reaction of the dissolved Pu(V) hydroxide complex with the aluminate ion may be written

$$PuO_2(OH)_4^{3-} + n\ Al(OH)_4^- \rightleftharpoons PuO_2(OH)_4(Al(OH)_4)_n^{(n+3)-}$$

The mixed-equilibrium constant describing the above reaction is

$$\log K_{m,Al} = \log [PuO_2(OH)_4(Al(OH)_4)_n^{(n+3)-}] - \log [PuO_2(OH)_4^{3-}] - n \log (NaAl(OH)_4) \qquad (7)$$

The mixed-equilibrium constant above uses molal values for the plutonium species concentrations and activity values for $NaAl(OH)_4$. Total plutonium concentration was obtained by measurement, while the concentration of the $PuO_2(OH)_4^{3-}$ complex was determined from equation 1. The concentration of the plutonium-aluminate complex was calculated as the difference between the total plutonium and the plutonium-hydroxide complex concentrations. Equation 7 may be rearranged to the expression

$$\log \frac{[PuO_2(OH)_4(Al(OH)_4)_n^{(n+3)-}]}{[PuO_2(OH)_4^{3-}]} = n \log (NaAl(OH)_4) + \log K_{m,Al} \qquad (8)$$

Equation 8 is of the form $y = mx+b$, in which n, the number of aluminate ligands, is the slope and $\log K_{m,Al}$ is the intercept.

The plutonium concentration data for the $NaOH/NaAl(OH)_4$ system were plotted following equation 8 and the slope was found to be near 1 (fig. 11). The data, therefore, are consistent with the formation of a 1:1 plutonium-aluminate complex and equation 7 becomes

$$\log K_{m,Al} = \log [PuO_2(OH)_4(Al(OH)_4)^{4-}] - \log [PuO_2(OH)_4^{3-}] - \log (NaAl(OH)_4) \qquad (9)$$

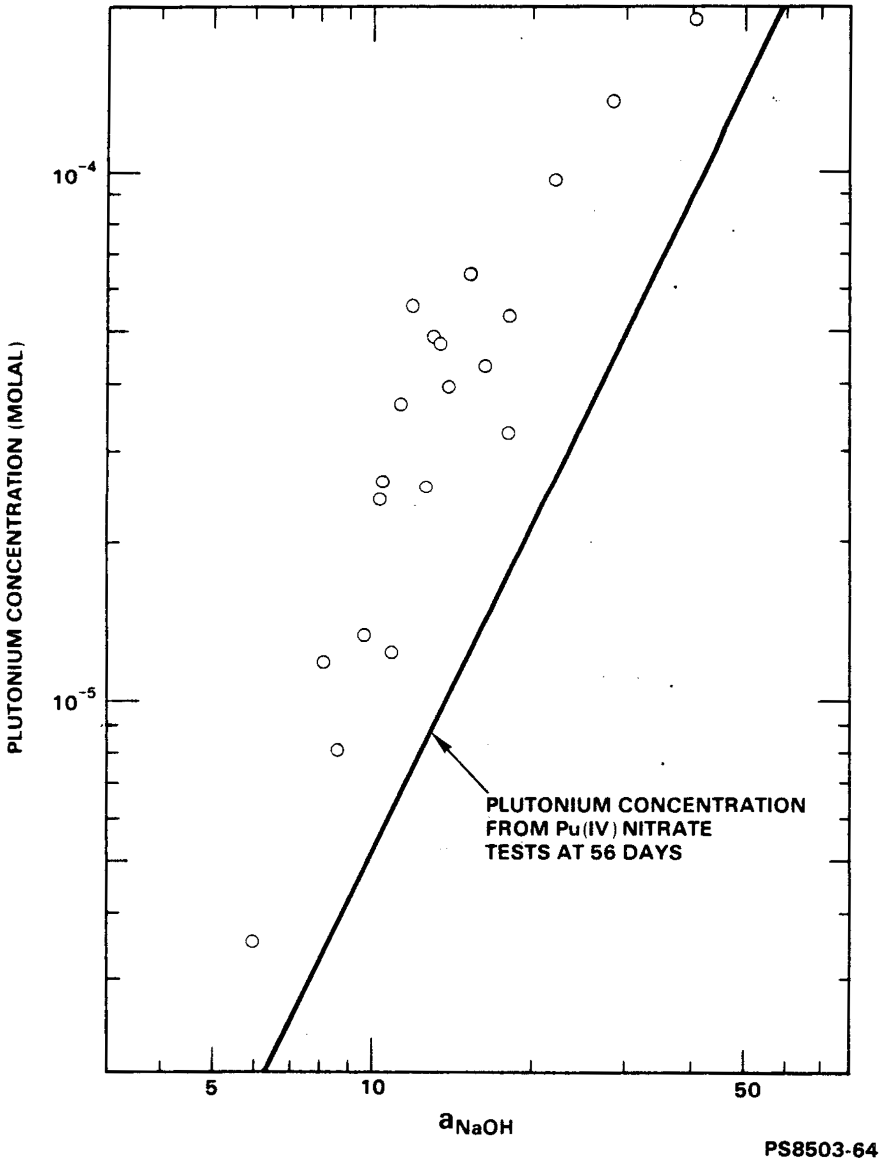

Figure 10. Plutonium Concentrations Above Solids Precipitated from Pu(IV) Nitrate in the NaOH/NaAl(OH)$_4$ System as a Function of NaOH Chemical Activity.

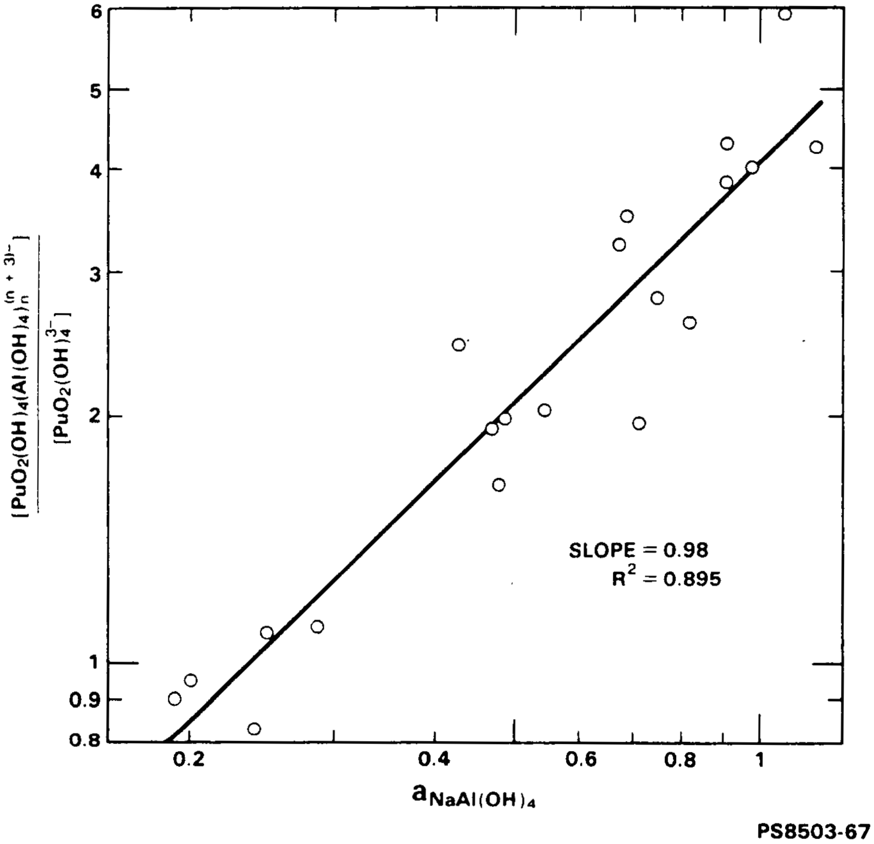

Figure 11. Plutonium-Aluminate Complex to $PuO_2(OH)_4^{3-}$ Concentration Ratios as a Function of $NaAl(OH)_4$ Chemical Activity.

Values of log $K_{m,Al}$ were determined for the 20 experiments conducted for the NaOH/NaAl(OH)$_4$ system. The average log $K_{m,Al}$ value was 0.62 ± 0.08 (1 standard deviation).

PLUTONIUM HYDROUS OXIDE IN NaOH/Na_2CO_3 SOLUTIONS

Earlier studies showed that at concentrations up to 0.05 molar, Na_2CO_3 had negligible effect on plutonium hydrous oxide solubility in simulated Hanford HLW (Delegard and Gallagher (1983)). Tests were conducted at higher concentrations of Na_2CO_3 in NaOH solution to determine if this behavior continued. The contributions of Na_2CO_3 to the activity of NaOH in the test solutions were determined, as before, following the approach of Meissner (1980). The same approach was used to determine the effects of NaOH on the Na_2CO_3 activities. Activity coefficient data for Na_2CO_3 were obtained from work by Goldberg (1981).

Test solutions were prepared with NaOH concentrations from ∽3 to 5 molal and Na_2CO_3 concentrations from ∽0.25 to 1 molal. The solubility of Na_2CO_3 in NaOH solution drops sharply above 5 molal NaOH. Plutonium was added as Pu(IV) nitrate solution. The dissolved plutonium concentrations were determined after 22 weeks' contact. The plutonium concentrations plotted versus NaOH activity (fig. 12) were up to 10 times higher than the values observed in the NaOH system at 22 weeks' contact. Enhancement of solubility caused by carbonate complexation was investigated.

The complexation reaction of the Pu(V) hydroxide complex with carbonate may be written

$$PuO_2(OH)_4^{3-} + n\ CO_3^{2-} \rightleftharpoons PuO_2(OH)_4(CO_3)_n^{(2n+3)-}$$

The mixed-equilibrium constant describing the above reaction is

$$\log K_{m,CO_3} = \log [PuO_2(OH)_4(CO_3)_n^{(2n+3)-}] - \log [PuO_2(OH)_4^{3-}] - n \log (Na_2CO_3) \quad (10)$$

where molal concentrations are used for the plutonium species and activity values are used for Na_2CO_3. Total plutonium concentration was obtained by measurement. The concentration of the $PuO_2(OH)_4^{3-}$ complex was determined using equation 1. The concentration of the plutonium-carbonate complex was calculated as the difference between total plutonium and the plutonium-hydroxide complex concentrations. Rearrangement of equation 10 yields

$$\log \frac{[PuO_2(OH)_4(CO_3)_n{}^{(2n+3)-}]}{[PuO_2(OH)_4^{3-}]} = n \log (Na_2CO_3) + \log K_{m,CO_3} \quad (11)$$

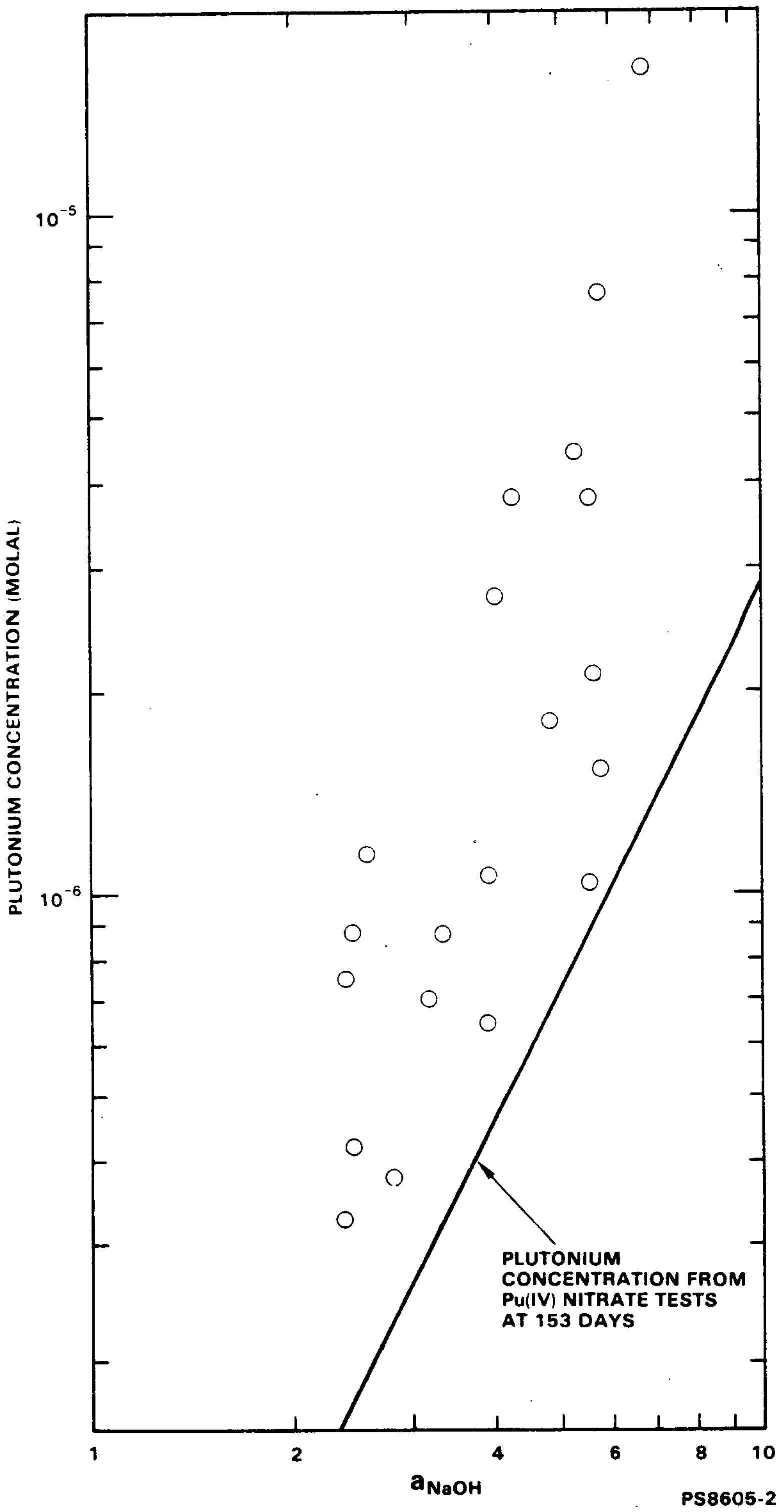

Figure 12. Plutonium Concentration Above Solids Precipitated from Pu(IV) Nitrate in the $NaOH/Na_2CO_3$ System as a Function of NaOH Chemical Activity.

Equation 11 is of the form y = mx+b, in which n, the number of carbonate ligands, is the slope and log K_{m,CO_3} is the intercept.

The plutonium concentration data for the $NaOH/Na_2CO_3$ system were plotted following equation 11. The 22-week data gave a slope near 2 (fig. 13). The data, therefore, are consistent with the formation of a 1:2 plutonium-carbonate complex and equation 9 becomes

$$\log K_{m,CO_3} = \log [PuO_2(OH)_4(CO_3)_2{}^{7-}] - \log [PuO_2(OH)_4{}^{3-}] - 2 \log (Na_2CO_3) \qquad (12)$$

Values of log K_{m,CO_3} were determined for the 20 experiments conducted for the $NaOH/Na_2CO_3$ system. At 22 weeks, the average log K_{m,CO_3} was 1.13 ± 0.20 (1 standard deviation).

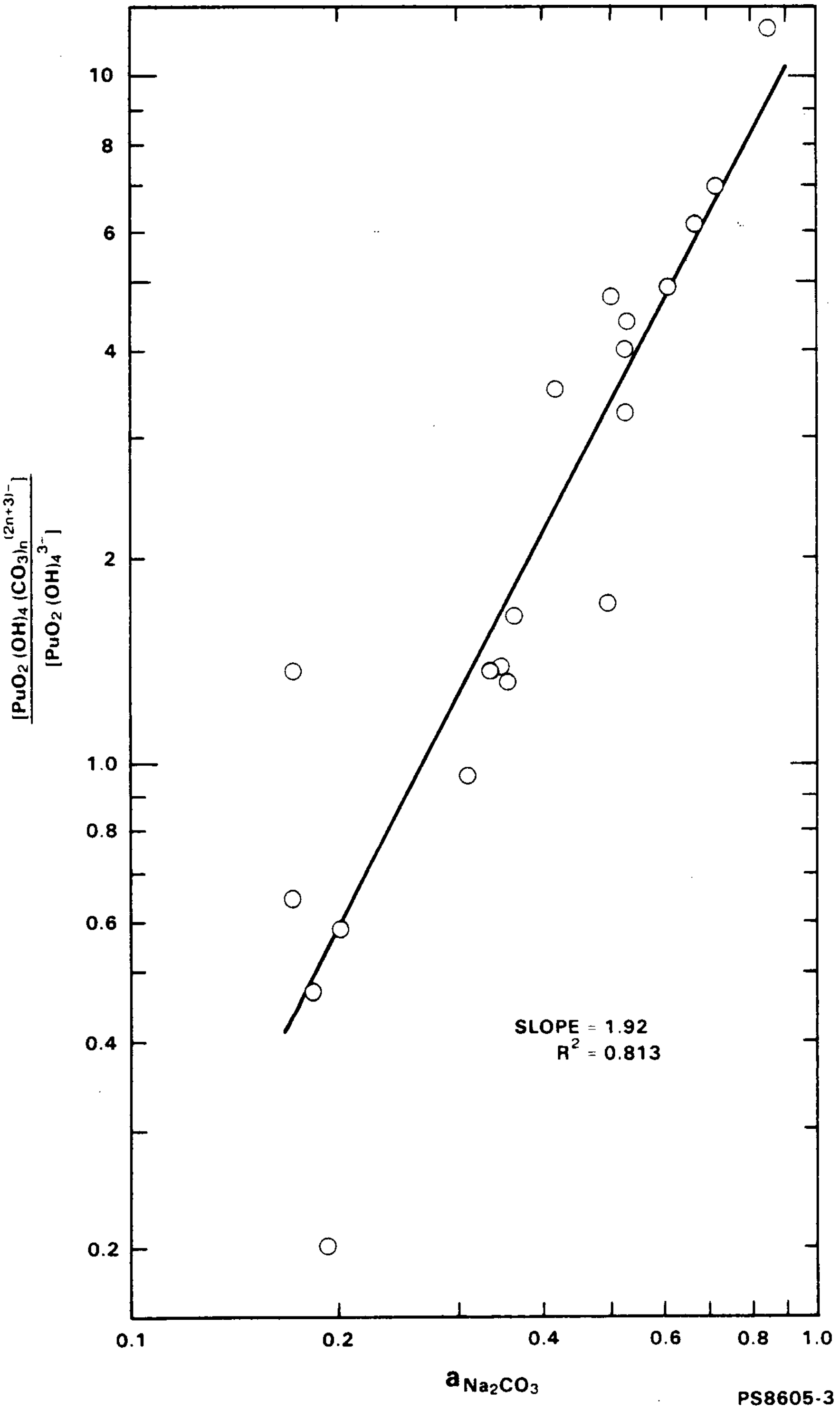

Figure 13. Plutonium-Carbonate Complex to $PuO_2(OH)_4^{3-}$ Concentration Ratios as a Function of Na_2CO_3 Chemical Activity.

CONCLUSIONS

Solids produced by precipitation of Pu(IV) in concentrated NaOH solution have been found to be Pu(IV) hydrous oxide of low crystallinity. The solubility of the Pu(IV) hydrous oxide precipitated from oversaturation matched the solubility of Pu(IV) hydrous oxide introduced to the NaOH solution as solids, and increased with the square of NaOH chemical activity in air-equilibrated solutions. The solubility of Pu(IV) hydrous oxide decreased with $(\text{time})^{\frac{1}{2}}$ in the concentration range $1\underline{M}$ to $10\underline{M}$ NaOH at contact times greater than about 3 weeks and continued at that rate to at least 700 days. With time, the solubility of solids produced by precipitation of plutonium initially in the (VI) state in concentrated NaOH solution approached the solubility of the Pu(IV) hydrous oxide. Solids found in aged Pu(VI) experiments also were identified as Pu(IV) hydrous oxide.

Direct and indirect spectrophotometric evidence showed the dissolved plutonium to be in the (V) oxidation state. Electrode potential measurements corroborated assignment of the dissolved species as Pu(V). Redox measurements of the NaOH solutions both with and without plutonium addition were similar and showed electron activity decreased approximately as the square of the NaOH activity. The redox and solubility data were combined to identify the plausible dissolved plutonium species as $PuO_2(OH)_4^{3-}$. A mixed-equilibrium constant was derived that related Pu(IV) hydrous oxide solubility to the NaOH and electron activities.

The contributions of $NaNO_3$ and $NaNO_2$ to the solubility of Pu(IV) hydrous oxide were explained by their contributions to the chemical activity of NaOH. With $NaNO_3$ absent from solution, $NaNO_2$ acted as a mild reductant, which decreased Pu(IV) hydrous oxide solubility by preventing Pu(IV) solids from oxidizing and dissolving as Pu(V). The mixed-equilibrium constants for Pu(IV) hydrous oxide solubility derived for the $NaOH/NaNO_3$, $NaOH/NaNO_2$, and $NaOH/NaNO_3/NaNO_2$ systems were statistically indistinguishable from the constant derived for the NaOH system.

The effect of $NaAl(OH)_4$ on the solubility of Pu(IV) hydrous oxide was greater than could be attributed to its contribution to the NaOH activity. The data were found to be consistent with formation of a 1:1 plutonium-aluminate complex. A mixed-equilibrium constant was derived that related the formation of the plutonium-aluminate complex to the chemical activity of the $NaAl(OH)_4$.

Similarly, the effect of Na_2CO_3 on the solubility of Pu(IV) hydrous oxide in NaOH solutions was greater than could be attributed to its contribution to the NaOH activity. The data were consistent with formation of a 1:2 plutonium-carbonate complex. A mixed-equilibrium constant was derived that related formation of the complex to the chemical activity of Na_2CO_3.

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APPENDIX

DATA FOR MIXED-EQUILIBRIUM CONSTANTS AND FIGURES

The data used to derive many of the figures and all the mixed-equilibrium constants in this document are presented in tables A-1 to A-6.

Table A-1. Plutonium Concentrations Above Solids Precipitated from Pu(IV) Nitrate in Various Concentrations of NaOH as a Function of Time.

Concentration (M)	Concentration (g/L)	a_{NaOH}*	Negative log plutonium molal concentration							
NaOH	H_2O		2 days	7 days	21 days	56 days	56 days**	153 days	317 days	768 days
1.00	1001	0.673	7.039	7.240	7.483	7.650	7.680	8.086	7.767	8.345
2.00	1000	1.428	6.697	6.460	6.785	6.936		7.137	7.200	7.349
3.00	997	2.392	6.316	6.110	6.393	6.527	6.818	6.772	6.893	7.132***
4.00	992	3.694	6.141	5.733	5.983	6.164		6.397	6.569	6.774***
5.00	985	5.544	5.943	5.403	5.654	5.783	5.866	6.052	6.197	6.255
6.00	976	8.280	5.726	5.007	5.267	5.437		5.646	5.854	5.840
7.00	963	12.50	5.415	4.703	4.914	5.099	5.107	5.333	5.564	5.598
8.00	955	18.63	5.261	4.438	4.620	4.672		5.050	5.258	5.301
9.00	942	26.02	4.998	4.150	4.156	4.384	4.362	4.567	4.854	4.974
10.00	929	42.41	4.646	3.998	3.856	4.086		4.285	4.618	4.821
15.00	844	268.7	3.697	3.099	2.664	2.263	2.425	2.824	--	--

*Expressed in units of molality.

**Plutonium concentration above Pu(IV) hydrous oxide solids.

***At 877 days' contact.

Table A-2. Plutonium Concentrations Above Solids Precipitated from Pu(VI) Nitrate in Various Concentrations of NaOH as a Function of Time.

Concentration (M)	Concentration (g/L)	a_{NaOH}*	Negative log plutonium molal concentration				
NaOH	H_2O		7 days	35 days	84 days	193 days	627 days
0.95	1001	0.64	2.770	4.836	6.719	7.836	7.830
1.92	1000	1.35	2.592	2.896	5.983	7.145	6.848
2.88	998	2.25	2.544	2.856	6.459	6.865	6.866
3.85	993	3.45	2.403	2.714	4.334	6.206	6.193
4.81	986	5.1	2.399	2.491	2.896	5.585	5.685
5.78	978	7.6	2.389	2.440	2.688	4.987	5.285
6.75	969	11.3	2.393	2.434	2.555	4.378	4.885
7.71	958	16.5	2.400	2.452	2.550	3.996	4.567
8.68	946	24.5	2.356	2.451	2.491	3.253	3.993
9.64	934	36.5	2.424	2.446	2.481	2.857	3.571
14.48	853	225	2.337	2.561	2.917	3.130	3.208

*Expressed in units of molality.

Table A-3. Electrode Potentials for NaOH, NaOH/$NaNO_3$, NaOH/$NaNO_2$, and NaOH/$NaNO_3$/$NaNO_2$ Solutions with Pu(IV) Nitrate Addition.

Concentration (M)			a_{NaOH}*	Potential (millivolts)		
NaOH	$NaNO_3$	$NaNO_2$		E_{meas}	E_{diff}	E_{NHE}
1.00	0	0	0.673	-112	34	96
2.00	0	0	1.428	-131	44	67
3.00	0	0	2.392	-139	53	50
4.00	0	0	3.694	-148	63	31
5.00	0	0	5.544	-153	72	17
6.00	0	0	8.280	-172	80	-10
7.00	0	0	12.50	-173	89	-20
8.00	0	0	18.63	-181	98	-37
8.00	0	0	18.63	-206	98	-62
8.00	0	0	18.63	-194	98	-50
9.00	0	0	26.02	-195	106	-59
10.00	0	0	42.41	-213	118	-89
4.00	4.00	0	5.84	-161	73	8
5.00	1.00	0	6.78	-158	76	8
5.00	1.50	0	7.19	-155	77	10
5.00	2.00	0	7.79	-159	79	4
5.00	3.00	0	9.00	-173	82	-13
5.00	3.00	0	9.00	-165	82	-5
5.00	4.00	0	10.47	-177	85	-20
6.00	2.00	0	11.57	-177	88	-23
7.00	1.00	0	15.27	-191	94	-43
4.00	0	4.00	6.76	-180	76	-14
5.00	0	1.00	6.56	-170	75	-3
5.00	0	1.50	7.24	-171	77	-6
5.00	0	2.00	7.69	-182	78	-18
5.00	0	3.00	9.32	-205	83	-46
5.00	0	3.00	9.32	-195	83	-36
5.00	0	4.00	11.37	-207	90	-55
6.00	0	2.00	12.32	-189	89	-36
7.00	0	1.00	15.82	-200	94	-52
5.00	0.25	0.25	5.89	-167	73	2
5.00	0.50	0.50	6.39	-158	74	10
5.00	1.50	1.50	9.05	-177	82	-17
5.00	2.50	2.50	13.84	-179	92	-29
5.00	3.00	3.00	16.27	-180	95	-33
5.00	3.00	3.00	16.27	-186	95	-39
6.00	2.50	2.50	22.86	-181	102	-41
8.00	1.50	1.50	39.37	-205	115	-78
9.00	1.00	1.00	48.42	-206	120	-84
10.50	0.25	0.25	61.67	-220	126	-104

*Expressed in units of molality.

Table A-4. Plutonium Concentrations Above Solids Precipitated from Pu(IV) Nitrate in the NaOH/$NaNO_3$, NaOH/$NaNO_2$, and NaOH/$NaNO_3$/$NaNO_2$ Systems at 56 Days' Contact.

Concentration (M)			Concentration (g/L)	a_{NaOH}*	Negative log plutonium molal concentration
NaOH	$NaNO_3$	$NaNO_2$	H_2O		
4.00	4.00	0	850	5.84	5.830
5.00	1.00	0	915	6.78	5.833
5.00	1.50	0	903	7.19	5.757
5.00	2.00	0	880	7.79	5.719
5.00	3.00	0	845	9.00	5.532
5.00	3.00	0	845	9.00	5.644
5.00	4.00	0	810	10.47	5.431
6.00	2.00	0	890	11.57	5.274
7.00	1.00	0	915	15.27	5.062
4.00	0	4.00	854	6.76	6.326
5.00	0	1.00	941	6.56	5.907
5.00	0	1.50	917	7.24	5.999
5.00	0	2.00	912	7.69	6.216
5.00	0	3.00	873	9.32	5.893
5.00	0	3.00	873	9.32	6.097
5.00	0	4.00	834	11.37	6.032
6.00	0	2.00	892	12.32	5.207
7.00	0	1.00	911	15.82	5.253
1.00	1.00	1.00	926	0.76	7.426
2.00	1.00	1.00	926	1.68	6.876
3.00	1.00	1.00	926	2.96	6.465
4.00	1.00	1.00	916	4.87	6.078
5.00	0.25	0.25	972	5.89	5.684
5.00	0.50	0.50	953	6.39	5.524
5.00	1.00	1.00	906	7.69	5.370
5.00	1.00	1.00	906	7.69	5.636
5.00	1.50	1.50	869	9.15	5.127
5.00	2.00	2.00	822	11.31	4.975
5.00	2.50	2.50	785	13.84	4.967
5.00	3.00	3.00	758	16.27	4.710
5.00	3.00	3.00	758	16.27	4.710
6.00	1.00	1.00	896	12.04	5.290
6.00	2.50	2.50	775	22.86	4.307
7.00	1.00	1.00	876	19.30	4.928
7.00	2.00	2.00	797	30.52	4.298
8.00	1.00	1.00	856	31.21	4.457
8.00	1.50	1.50	819	39.37	3.987
9.00	1.00	1.00	846	48.42	3.896
9.00	1.00	1.00	846	48.42	4.103
10.00	0.50	0.50	878	57.01	3.513
10.00	1.00	1.00	826	77.31	3.757
10.50	0.25	0.25	892	61.69	3.686

*Expressed in units of molality.

Table A-5. Plutonium Concentrations Above Solids Precipitated from Pu(IV) Nitrate in Various Concentrations of $NaOH/NaAl(OH)_4$ at 56 Days' Contact.

Concentration ($\underline{M}$)		Concentration (g/L)	a_{NaOH}*	$a_{NaAl(OH)_4}$*	Negative log plutonium molal concentration
NaOH	$NaAl(OH)_4$	H_2O			
4.98	0.33	952	5.94	0.191	5.455
5.60	0.77	925	8.10	0.429	4.925
5.88	0.42	945	8.55	0.249	5.094
5.97	0.83	913	9.70	0.475	4.878
6.00	1.21	897	10.30	0.670	4.620
6.05	1.66	872	11.34	0.903	4.440
6.06	1.24	901	10.42	0.682	4.582
6.07	1.98	859	11.99	1.065	4.255
6.11	2.12	840	13.06	1.165	4.316
6.44	0.31	936	10.90	0.200	4.911
6.52	1.63	882	13.43	0.908	4.328
6.58	0.78	905	12.71	0.472	4.597
6.60	1.28	880	13.89	0.748	4.406
6.75	1.69	871	15.42	0.972	4.193
7.02	1.17	881	16.38	0.713	4.368
7.53	0.76	909	18.21	0.488	4.271
7.60	1.27	866	22.07	0.820	4.019
7.65	0.34	924	18.07	0.240	4.492
8.56	0.77	897	28.34	0.543	3.874
9.56	0.34	902	40.08	0.286	3.726

*Expressed in units of molality.

Table A-6. Plutonium Concentrations Above Solids Precipitated from Pu(IV) Nitrate in Various Concentrations of $NaOH/Na_2CO_3$ at 156 Days' Contact.

Concentration (M)		Concentration (g/L)	a_{NaOH}*	$a_{Na_2CO_3}$*	Negative log plutonium molal concentration
NaOH	Na_2CO_3	H_2O			
2.90	0.701	980	2.39	0.416	6.124
2.95	0.512	998	2.38	0.310	6.488
2.95	0.912	985	2.45	0.522	6.058
2.95	1.050	956	2.58	0.610	5.940
2.96	0.261	974	2.46	0.172	6.377
3.24	0.255	973	2.81	0.172	6.424
3.47	0.515	967	3.18	0.335	6.157
3.47	0.783	948	3.32	0.496	6.061
3.94	0.515	968	3.92	0.347	5.975
3.94	0.771	961	4.02	0.500	5.567
3.99	1.060	948	4.29	0.673	5.421
4.00	0.260	977	3.88	0.185	6.192
4.43	0.513	963	4.85	0.362	5.745
4.52	0.766	948	5.29	0.531	5.358
4.69	1.060	950	5.76	0.712	5.118
4.75	0.765	969	5.57	0.527	5.421
4.80	0.484	967	5.61	0.354	5.674
4.85	0.250	970	5.57	0.194	5.983
4.89	1.050	943	6.72	0.852	4.779
4.94	0.257	970	5.78	0.201	5.816

*Expressed in units of molality.