USNRDL-TRC-85
26 September 1966

THE ELECTROCHROMATOGRAPHY OF SEAWATER CONTAINING DISSOLVED PLUTONIUM

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ADMINISTRATIVE INFORMATION

The work reported was part of a project sponsored by the Atomic Energy Commission, under Contract No. AT(49-5)-2084.

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ABSTRACT

Electrochromatographic techniques were used to determine the chemical form of plutonium in seawater. If either Pu (III), Pu (IV) or PuO_2^{++} was added to a 0.7M NaCl-0.0023 M Na_2CO_3 solution, it was found that in each case about 30 % of the plutonium would migrate to the anode and 70 % would not migrate. Similar results were obtained in solutions containing other anions found in seawater. Plutonium electromigration experiments using NaCl solutions containing varying concentrations of Na_2CO_3 indicated the presence of an anionic complex that is sensitive to carbonate ion concentration. This behavior was not found with other anions in seawater.

Plutonium from plutonium metal dissolved in seawater was found to migrate in the same way as Pu (III), Pu (IV) and PuO_2^{++}. This indicates that the same final chemical form is reached for both the dissolved metal and the added plutonium ions.

Plutonium from high fired PuO_2 beads dissolved in seawater was found to migrate about 23 % to the cathode and 22 % to the anode; 55 % did not migrate at all. This does not correspond to the migration behavior of the dissolved metal or the added plutonium ions; however, there is inconclusive evidence that the anionic fraction is the same carbonato-complex of plutonium.

SUMMARY

Problem

An evaluation of the hazard involved in the accidental release of large amounts of plutonium to a marine environment requires information on the final chemical form of the plutonium in seawater. Electrochromatographic techniques were used to acquire this information.

Findings

The results indicate that negatively-charged carbonato complex ions and a colloidal fraction are formed when soluble plutonium in any of its 3 oxidation states is added to seawater or when plutonium metal is dissolved in seawater. When high-fired PuO_2 beads are added to seawater, a positively charged plutonium complex ion forms in addition.

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INTRODUCTION

Increasing technological and industrial applications of plutonium as an energy source, which intensify its potentialities as a biological hazard, make it imperative that data be collected regarding its form and reactions in various natural environments. As a part of this effort, the nature of the soluble state of this element in seawater was investigated.

The published information regarding the behavior of plutonium in seawater is sparse. The pure metal dissolves spontaneously in commercial seawater (seawater concentrate + distilled water), giving as products a gas, a colloidal dispersion, and a black precipitate.[1] A gelatinous green solid also has been observed, reported to be plutonium hydroxide or plutonium dioxide.[2] Lai[3] has examined the nature of the reaction products formed when plutonium metal is dissolved in seawater. He observed over a period of a few hours the initial conversion of the metal to an oxide and an ionic species. The ionic species slowly precipitated from solution to form a green gelatinous solid. These solid reaction products over a period of a few weeks went into solution as complexed carbonate and sulfate ions. Goya[4] investigated several aspects of the behavior of plutonium dioxide in seawater, including the solubility characteristics when varying amounts of the salts of major anions in seawater are added to the solution.

Two methods for the gross assay for the soluble portion of Pu in seawater have been reported.[5,6]

A scheme for the separation of the oxidation states of certain actinides in aqueous solution, including seawater, has been proposed.[7] However, the nature of the oxidation states of plutonium found in an equilibrium seawater solution has not been studied directly.

Ideally, a method is needed by which one can determine the amounts of each oxidation state species in an equilibrium mixture and the charge on each ion, without disturbing the equilibrium concentration. Spectrophotometry is often suitable for this type of investigation but cannot be used in this case because of the combination of a very low solubility of plutonium in seawater (65-70 μg/ℓ) and very low extinction coefficients for the various soluble plutonium species.

The electrochromatographic method appears suited for the purpose. Ions migrate differentially from a narrow zone in a stabilized background electrolytic solution under the influence of the electric potential. The separation depends upon the applied potential, the solvent, the background electrolyte, the stabilization medium, and the electroosmotic flow of solution. Good separations of mixtures of various inorganic ions have been obtained by Sherma et al.[8] However reports concerning the efficacy of the method when applied to equilibrium mixtures of ions of a single element in various oxidation states are relatively scarce. Lingren and co-workers* studied the Fe(II)-Fe(III) system using this method and showed that the method appears to disturb only slightly the equilibrium concentrations of iron.

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*W. E. Lingren, J. Reeck and R. Marson, "The Paper Electrophoresis of the Iron (II)- Iron (III) System", U. S. Naval Radiological Defense Laboratory, USNRDL-TR (in preparation).

It was thought that seawater, because of its electrical properties, would provide a satisfactory background electrolyte-solvent combination for separations using the electrochromatographic method.

EXPERIMENTAL

Reagents

All chemicals were reagent grade. The artificial seawater used in this work was made according to the directions of Lyman and Fleming.[9] The natural seawater was taken from a point about three miles off Neah Bay, Washington, at latitude 48°23'N and longitude 124°24'W. The pH of the sample was determined to be 7.8, the chlorinity 17.645, and the salinity 31.88.

Stock Solutions

Pu(III). A sample of aqueous plutonium was evaporated to dryness and dissolved in 0.6 M hydrochloric acid and hydroxylamine solution.

Pu(IV). A sample of aqueous plutonium was evaporated to dryness with hydroxylamine to insure that all the plutonium goes to Pu^{+++}, and the residue was dissolved in dilute nitric acid and sodium nitrite solution to oxidize the plutonium to Pu(IV).

PuO_2^{++}. A sample of aqueous plutonium was adjusted to a pH of 5, treated with 0.1 M HOCl, and heated for 15-20 min at 80°C.

Apparatus

The electrochromatography was done in a Gelman model no. 51325 chromatography chamber modified for this purpose. The electrode leads were inserted through a small hole drilled in the glass cover. The chamber could be filled with nitrogen whenever it was necessary to operate in an inert atmosphere. Both ascending and descending chromatography were employed.

The power supply was a 0-400 volts, 0-150 ma, Heathkit IP-32, unit.

Scans for radioactivity on the chromatograms were done using an end-window (1.4 mg/cm^2) Geiger tube, Nuclear-Chicago type 00-034, and a Nuclear-Chicago model 151A or model 186 scaler. Liquid scintillation counting, with a Tri-Carb 314A coincidence-type instrument, was used also.

Chromatographic Medium

The major portion of the work was done using Eastman "Chromagram," type K301R, a ready-made thin layer of silica gel on an inert polyethylene backing. Whatman 3MM paper was used in some experiments.

Experimental Technique

The technique was, in general, similar to that described by Sherma[8] et al. An appropriate amount of the plutonium solution to be examined was pipetted onto a piece of the thin layer material (or paper) which had been prepared for electrodes (holes about 2 cm apart punched along two parallel edges). The volume pipetted ranged from 50λ to 200λ. The spot containing the activity was placed beneath the Geiger tube and counted in duplicate for five minutes. The GM tube was positioned within 3 mm of the chromatogram but not allowed to touch the material. Some absorption of alphas by the thin-layer material occurred. The precision of the counting measurements was ± 2-3 %. The average of the measurements after correction for background was taken to be the total plutonium activity for the experiment. Background counts were about 35 ± 2 c.p.m. under these conditions. 18-gauge platinum wire electrodes were then threaded through the holes in the thin-layer material and the leads from the power supply attached. (Silver wire electrodes were used in some experiments but the silver tends to corrode badly.) The paper was placed in the Gelman unit which contained the eluant, the cover was replaced, and the potential was applied.

The applied potential rarely exceeded 10 volts/cm and the current was kept below 100 ma. If either of these limits were exceeded for any length of time, electrolysis products from the electrolyte (e.g. chlorine gas from seawater) would interfere with the separation or heat would produce a difficult-to-control evaporation problem. The operating time was varied but never exceeded four hours. A schematic drawing of a typical chromatogram is given in Fig. 1.

Upon completion of an experiment the thin-layer material (or paper) was removed, dried and divided into grids which were individually counted using the GM end-window tube. Each grid had approximately the same area (12.5 cm^2) as the GM tube and the tube was placed within 3 mm of the chromatogram for counting. Each grid was counted, in triplicate, for a period between five and ten minutes. The results of the three counts, after correction for background, were averaged and the value for the grid recorded. Count rates significantly above background (25 % or more) were taken to be evidence of the presence of plutonium. The minimum precision of these measurements was ± 20 %.

The total plutonium measured before migration occurred divided into the measured plutonium for a grid gives the fraction in the grid. The percentages reported in the succeeding tables of this report were computed from measurements of this type. An activity balance was determined for each chromatogram.

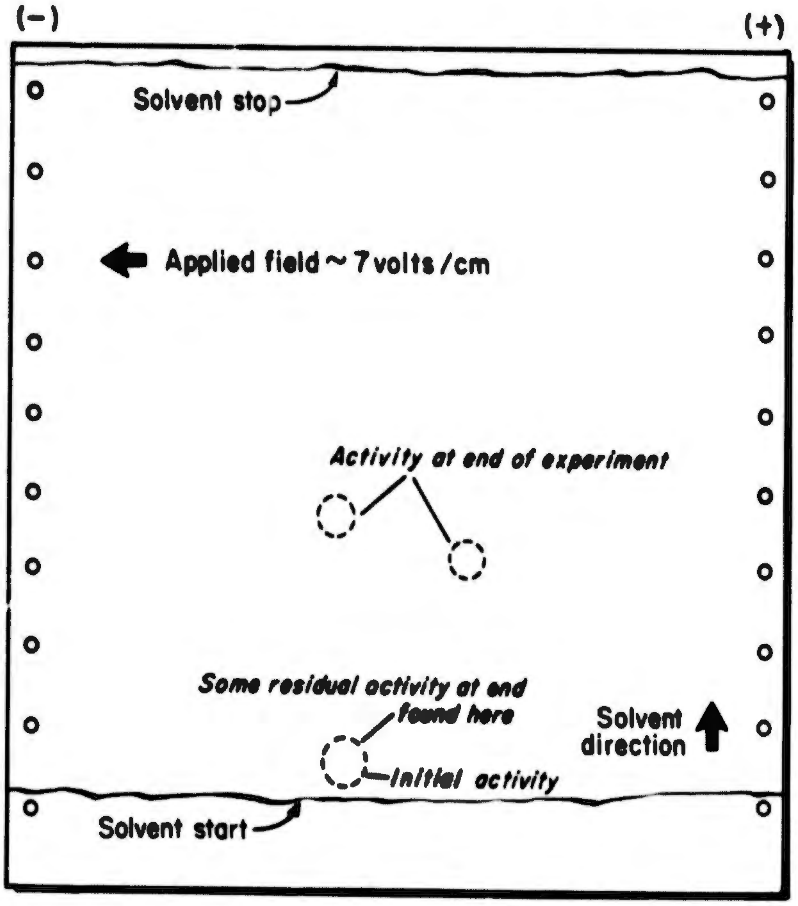

Fig. 1 Schematic Electrochromatogram

In some cases the chromatogram was cut into small squares approximately 1 cm on edge. These were placed in vials containing an organic scintillating agent (10 g of 2,5-diphenyloxazole and 0.5 g of 1,4-bis-2 (4-methyl-5-phenyloxazolyl-benzene per liter of toluene). The liquid scintillation samples were counted in quadruplicate for ten minutes. The average of the four, corrected for background, was taken as the experimental value for the square. The precision of these measurements was ± 7-9 %.

RESULTS

Table 1 contains the results of a series of experiments performed to test the capability of the electrochromatographic method. The stabilizing medium in this set was Whatman 3 MM chromatography paper, on which was placed 0.20 ml of plutonium in one of its oxidation states. The eluants were either HCl, H_2SO_4, or HNO_3.

These experimental results indicate that with this technique migration of plutonium species will occur. It is of interest to note that the negative plutonium-containing complex appears to predominate in the sulfate-containing solution. The results shown in Table 1 agree qualitatively with those summarized by Taube.[10]

Plutonium in each of its oxidation states (one at a time) was added to 10-ml seawater samples (both natural and artificial) in amounts sufficient to saturate the solution. The amount necessary for saturation, found by alpha-scintillation counting of the supernate over a hydrous precipitate, was that required to bring the Pu concentration in the final solution to 70 μg/ℓ. The pH was adjusted to 8, and the solutions were allowed to stand for several days before the electromigration experiment. In Table 2 are the results using 0.20 ml samples from these solutions.

TABLE 1

Electrical Migration of Pu(III), Pu(IV), and PuO_2^{++} Ions

Oxidation State of Plutonium	Acid	Plutonium Migrated (%)*	
		to Cathode	to Anode
III	1 M HCl	81 ± 5	19 ± 10
IV	2 M HCl	99 ± 4	-
IV	2 M HNO_3	98 ± 4	-
IV	0.5 M H_2SO_4	5	95 ± 4
VI	2 M HCl	100 ± 4	-
VI	2 M HNO_3	99 ± 4	-
VI	1 M H_2SO_4	24 ± 9	76 ± 5

*All the plutonium remained in solution and migrated.

TABLE 2

Electromigration of Plutonium in Seawater*

Initial Oxidation State	Form of Seawater Eluant	Migration (%)		
		To Cathode	To Anode	Unmoved
Pu(III)	Natural	-	70 ± 7	29 ± 10
Pu(III)	Artificial	-	67 ± 7	31 ± 10
Pu(IV)	Natural	-	73 ± 7	25 ± 11
Pu(IV)	Artificial	-	69 ± 7	30 ± 10
PuO_2^{++}	Natural	-	73 ± 7	26 ± 11
PuO_2^{++}	Artificial	-	72 ± 7	27 ± 11

*Initial activity = 300 ± 15 cpm, background = 35 ± 2 cpm. PuO_2^{+} was not considered in these experiments because it is stable only in very acid solutions.

Closer examination of the Table 2 chromatograms showed two spots, sometimes poorly defined, in the migrating material. One, near the anode, constituted about 35 % of the migrating material; the other, near the chromatogram center-line, held about 65 %. Both spots clearly were moving towards the anode. There are several possible explanations for these results. The observed difference in migration behavior indicates that a difference in the magnitude of charge, a difference in mass, or a difference in both could account for the two spots. The only obvious conclusion is that both species have a common sign associated with their charges. The two spots were scraped off the chromatograms and analyzed spectrophotometrically, but the amounts of ligand were too small, even when several spots were added together, to permit identification.

Two samples of plutonium in seawater were also studied in which the plutonium was introduced in a much different manner than the known initial oxidation states in the series described in Table 2. In one, chips of plutonium metal were dissolved in seawater. In the other, beads of solid PuO_2 were dissolved. The behavior of these solutions is summarized in Table 3.

TABLE 3

Electromigration of Plutonium From Solid Sources Dissolved in Natural Seawater*

Source	Migration (%)		
	To Cathode	To Anode	Unmoved
PuO_2 Beads	23 ± 12	22 ± 12	55 ± 8
Pu Metal	-	69 ± 7	30 ± 10

*Initial activity = 285 ± 15 cpm, background = 35 ± 2 cpm.

Finally, experiments were performed in which plutonium ion was added to solutions which contained only the salts of selected anions found in appreciable concentrations in seawater. For example, plutonium was placed in a solution of NaCl in which the chloride ion concentration was equivalent to that found in seawater. The ionic strength was brought up to 0.7 M (seawater value) using $NaClO_4$. The tendency for ClO_4^- to form complexes is small. These solutions are listed in Table 4, along with the migration data.

R_f* values for the migration of plutonium in seawater and plutonium in the above solutions are collected in Table 5.

Attempts were made to determine the magnitude of the charge on the migrating species in seawater by coulometric means. These attempts were unsuccessful.

DISCUSSION

Consideration of the possible ionic forms of Pu in seawater must recognize that the element can exist in several different oxidation states:[11]

+2 state: This state is unimportant in this work since it apparently cannot exist in aqueous solution.

+3 state: This state appears to exist in aqueous solution as hydrated Pu^{+3} ion. In moderately acid solutions it is oxidized slowly. A precipitate of $Pu(OH)_3$ forms complexes with $CO_3^=$, $SO_4^=$, $C_2O_4^=$, Cl^- and NO_3^-.

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*R_f is the ratio of the distance the plutonium species traveled from the starting point to the distance the solvent front traveled from the starting point for a particular experiment.

TABLE 4

Electromigration of Plutonium in Solutions Containing only Selected Salts of Anions Found in Seawater
(Ionic strength = 0.7 M; pH = 8)
(Background= 35 ± 2 cpm)

Oxidation State	Eluant	Migration (%)			Initial Activity, cpm
		to Cathode	to Anode	Unmoved	
		0.53 M NaCl-0.17 M $NaClO_4$			
Pu(III)	NaCl-$NaClO_4$	-	24	75	300 ± 15
Pu(IV)		-	20	79	260 ± 12
PuO_2^{++}		-	21	77	310 ± 15
		0.70 M NaCl-7 x 10^{-5} M NaF			
Pu(III)	NaCl-NaF	-	23	75	305 ± 15
Pu(IV)		-	19	80	275 ± 13
PuO_2^{++}		-	22	76	301 ± 15
		0.62 M NaCl-0.027 M Na_2SO_4			
Pu(III)	NaCl-Na_2SO_4	-	18	80	302 ± 15
Pu(IV)		-	20	79	280 ± 13
PuO_2^{++}		-	21	78	310 ± 15
		0.70 M NaCl-8 x 10^{-6} $NaNO_3$			
Pu(III)	NaCl-$NaNO_3$	-	20	78	307 ± 15
Pu(IV)		-	19	81	271 ± 12
PuO_2^{++}		-	20	69	311 ± 15
		0.69 M NaCl-4.2 x 10^{-4} H_3BO_4			
Pu(III)	NaCl-H_3BO_4	-	23	77	300 ± 15
Pu(IV)		-	25	74	278 ± 1[illegible]
PuO_2^{++}		-	24	76	301 ± 15

(continued)

TABLE 4 (Contd)

Electromigration of Plutonium in Solutions Containing only Selected Salts of Anions Found in Seawater
(Ionic strength = 0.7 M; pH = 8)
(Background = 35 ± 2 cpm)

Oxidation State	Eluant	Migration (%)			Initial Activity, cpm
		to Cathode	to Anode	Unmoved	
		0.70 M NaCl-trace Na_2HPO_4			
Pu(III)	NaCl-Na_2HPO_4	-	21	79	297 ± 15
Pu(IV)		-	20	80	271 ± 13
PuO_2^{++}		-	21	78	302 ± 15
		0.70 M NaCl-0.0023 M Na_2CO_3			
Pu(III)	NaCl-Na_2CO_3	-	27	70	300 ± 15
Pu(IV)		-	29	70	269 ± 12
PuO_2^{++}		-	30	69	311 ± 15

TABLE 5

R_f Values for Electromigrating Plutonium in Aqueous Solutions on Ascending Chromatograms (time = 2 hours; voltage = 4 volts/cm)

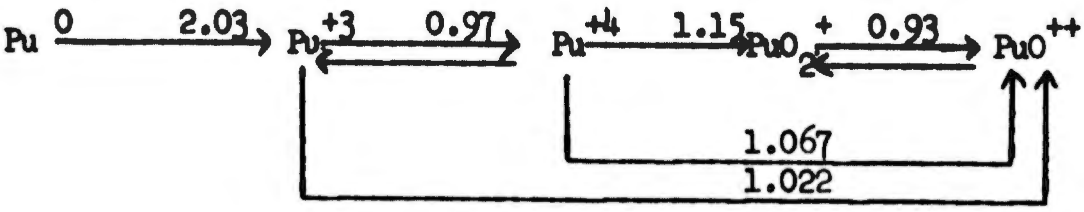
Solution	R_f
Natural Seawater	0.69
Artificial Seawater	0.65
NaCl-$NaClO_4$	0.53
NaCl-NaF	0.49
NaCl-Na_2SO_4	0.56
NaCl-$NaNO_3$	0.54
NaCl-H_3BO_4	0.49
NaCl-Na_2HPO_4	0.51
NaCl-Na_2CO_3	0.60
Seawater (Pu chip)	0.64
Seawater (PuO_2)	0.59 (anodic) 0.31 (cathodic)

+4 state: Unhydrolyzed Pu(IV) ion is believed to exist in aqueous solutions of 0.1 M hydrogen ion or greater. Precipitation of $Pu(OH)_4$, the end product of hydrolysis, begins at pH = 2 with 10^{-3} M solutions of Pu(IV). The solubility product of $Pu(OH)_4$ is 7×10^{-56}. In the intermediate stages of hydrolysis there is polymerization of the hydrolyzed forms of Pu(IV) through oxide or hydroxide bridges with the formation of colloidal aggregates.[12] Pu(IV) forms complexes with $CO_3^=$, $SO_4^=$, $SO_3^=$, $HPO_4^=$, $C_2O_4^=$, ClO_4^-, NO_3^-, F^-, Cl^-, Br^-, and I^-. The ion tends to disproportionate to an extent dependent upon the acidity of the solution and the complexing action of the negative ions present.

+5 state: In aqueous solution Pu(V) is believed to exist as PuO_2^+. It is fairly stable in the pH range 2 to 7. This ion has a lower tendency to form complexes than any other valence form of plutonium. Insufficient quantitative data make it impossible to state conclusively the relative tendency of anions from different acids to form complexes with it.

+6 state: It is thought that Pu(VI) exists as PuO_2^{++}, the plutonyl ion, in aqueous solution. This ion forms complexes with $CO_3^=$, $SO_4^=$, Cl^- and NO_3^-. The hydroxide of this ion is also relatively insoluble.

In addition, plutonium-couple oxidation potentials have been measured or calculated and a formal potential scheme has been compiled.[13]



These potentials, along with that of seawater which is calculated on the basis of the following half-reaction,

$$1/2 \qquad 2H^+ + 2e = H_2O; \qquad E = 1.229 \text{ volts,}$$

were used to compute the thermodynamic equilibrium constants for the redox couples in seawater. Assuming ideal conditions, the constants so calculated were used to predict which ions are most likely to be found in seawater. The calculations showed that, thermodynamically, PuO_2^+ and PuO_2^{++} are favored. The lower valence states are thermodynamically unstable in the oxidizing environment found in seawater. Of course, these calculations do not give any basis for predicting the rates of the redox reactions. As a case in point, Connick and coworkers[11] demonstrated that Pu(IV) is not converted into PuO_2^{++} in alkaline solutions (pH = 13) at an appreciable rate, although Pu(IV) is thermodynamically unstable with respect to PuO_2^{++} in such solutions. Furthermore, the rates of redox reactions are well known to be often influenced greatly by the presence of complex-forming ions.

The foregoing suggests that, although all the plutonium present in seawater may show the same oxidation state, it cannot be reasonably expected to. The evidence from this study is inconclusive on this point.

The ability of the different plutonium species to form complexes is directly related to the ionic potentials of these ions. A large ionic potential can be interpreted as reflecting a high tendency of the metallic ion to form stable complexes. Listed in Table 6 are the ionic potentials for the stable plutonium ions.

TABLE 6

Ionic Potentials of Plutonium in its Various Valence States

Cation	Crystal Radius (Å)	Cation Charge	Ionic Potential
Pu(IV)	0.90	+4	4.44
Pu(III)	1.03	+3	2.91
PuO_2^{++}	0.81	+2	2.47
PuO_2^+	0.87	+1	1.15

The tendency to form stable complexes as predicted by the ionic potentials in Table 6 is borne out, in general, by experimentation.[14] However, some experiments show that the structure and charge of the ligand often substantially affect the stability of the complexes.

The major anions in seawater which might act as ligands are listed in Table 7.

TABLE 7

Major Anions in Seawater[15]

Ion	Concentration (mg/l)
Cl^-	19,000
$SO_4^=$	885
Br^-	65
$CO_3^=$	28
$B(OH)_2O^-$	4.6
F^-	1.3
$NO_3^-(NH_3)$	0.5
$PO_4^{\equiv}(H_2PO_4^-, HPO_4^=)$	0.07
$IO_3^-(I)$	0.06

It should also be noted that at the pH of seawater, hydroxide complexes are significant for metal ions of oxidation number > 2. It can be shown that, if the chloride complex is to predominate, the difference $\log K_{Cl} - \log K_{OH}$ must be greater than -5.4, where the K's refer to the instability constants for the chloride and hydroxide complexes respectively. From a consideration of the constants available for Pu(IV),[16] it was calculated that this ion would not likely be present in seawater as the chloride complex. Similar calculations using instability constants for Pu(III)[17] and PuO_2^{++}[18] reveal that these species would probably not be found as chloride complexes in seawater. Only a few metals actually have been found[19] to exist as chloride complexes in seawater, and these are congregated near the middle of the periodic table, e.g., Ag^+ and Cd^{++}.

The negative plutonium species found in the $NaCl$-$NaClO_4$ solution of Table 4 is probably a hydroxy complex formed from a hydrolysis product of plutonium ions. The portion that did not migrate could be a precipitate of plutonium hydroxide, formed because of the evaporation of the solvent, or it could be a neutral complex. The presence of a negative chloride complex is ruled out primarily by the fact that the calculations used instability constants and that these complexes have been detected only in solutions of concentrated HCl. Little positive evidence has been found for perchlorate complexes of Pu(III), Pu(IV), or PuO_2^{++}.[14]

Bromide is a weaker ligand than chloride under most conditions; hence it would be surprising to see bromide complexes in these solutions. On the other hand fluoride could be expected to form very stable complexes with plutonium ions. However, experiments performed here with $NaCl$-NaF solutions indicated no change in migration behavior from that observed for the $NaCl$-$NaClO_4$ solutions; hence it is concluded that the fluoride ion, at the concentration found in seawater, was not competing successfully.

Strong complex formation of Pu(IV) and PuO_2^{++} in sulfate solutions has been reported,[14,20] while spectrophotometric data indicates that relatively weak sulfate complexing of Pu(III) occurs. The evidence in this work (Table 1) shows that for Pu(IV) and PuO_2^{++}, a negative species predominates in sulfate solutions. Although Sillen[19] observes that no ion has yet been discovered which exists chiefly as the sulfate complex in seawater, the possibility is not thus ruled out that plutonium might be the exception.

Table 4 shows that in the NaCl-Na_2SO_4 system a negative species is present. The effect of added sulfate on the migrating species was investigated, the data being listed in Table 8.

TABLE 8

Electromigration of Plutonium in Solutions of NaCl-Na_2SO_4
(Ionic strength = 0.7; pH = 8)

Conc. of $SO_4^=$ (M)	Migration (%)			
	To Cathode	To Anode	Unmoved	R_f
0.027	1	18	70	0.56
0.035	-	17	70	0.58
0.045	-	17	71	0.55

The data in Table 8 is interpreted to mean that the negative migrating species is not a sulfate-complex. In view of its R_f value it could easily be the same species as encountered in the NaCl-$NaClO_4$ mixture. The very small amount of cathodic material is not considered to be significant.

Nitrate apparently does not disturb the inorganic equilibria that are present in seawater,[19] which indicates that it cannot compete successfully with the chloride or hydroxide ligands. This statement cannot be taken to necessarily hold for plutonium since it is not yet involved to any great extent in the inorganic equilibria that presently exist in seawater. In addition the experimental evidence shows that for Pu(III) at least, nitrate is a better complexer than chloride. This does not appear to be true for Pu(IV) and PuO_2^{++}. In solutions where the ion ratio greatly favors the nitrate ion, anionic nitrate complexes of all three plutonium species are found. However, many cationic complexes, e.g. $Pu(NO_3)^{+3}$ and $Pu(NO_3)_2^{+2}$, exist in the solutions of lower nitrate concentration. Solutions containing various concentrations of nitrate ion were treated with plutonium and their electromigration behavior studied. The values obtained (Table 9) were observed no matter which oxidation state was placed in the solution initially.

TABLE 9

Electromigration of Plutonium in NaCl-$NaNO_3$ Solutions
(Ionic strength = 0.7 M; pH = 8)

Conc. $NaNO_3$ (M)	Migration (%) to Cathode	to Anode	not Migrating	R_f
8.1×10^{-6}	-	20	78	0.53
1.6×10^{-5}	1	19	80	0.54
3.0×10^{-5}	-	19	79	0.52

The ion ratio between plutonium and nitrate does not favor the formation of anionic complexes in seawater and the absence of appreciable cationic species can be taken to mean that there is no appreciable nitrate complexing. In fact it appears that the same species found in the chloride and sulfate test solutions is present here.

The behavior of plutonium towards phosphate as a ligand has not been studied as thoroughly as that of some of the other ions. From the scanty literature reports, phosphate forms complexes with Pu(IV) that are cationic except in concentrated phosphoric acid. The mole ratio of phosphate to plutonium in seawater is not great enough to favor the formation of anionic species. Electromigration experiments performed here on NaCl-Na_2HPO_4 solutions did not show the presence of any significant cationic species or any other unusual behavior.

Iodine is thought to be present as IO_3^-, which, combined with its low concentration, does not make it reasonable that plutonium would be present as iodo-complexes.

Borate possibly could behave as a ligand. However studies here of plutonium in solutions of NaCl-H_3BO_4 did not indicate that any such complex is present.

The remaining significant inorganic ligand in seawater is the carbonate ion. PuO_2^{++} tends to form strong complexes with carbonate in alkaline solution.[21] Qualitatively, at least, this would indicate that carbonato complexing is stronger than that of hydroxo; thus PuO_2^{++} could be reasonable expected to be in seawater as a carbonate complex. Similar evidence points towards a parallel tendency in Pu(IV). Electromigration experiments using plutonium as Pu(III) in NaCl-Na_2CO_3 solutions indicated here the presence of an anionic complex that is sensitive to carbonate ion concentration (cf. Table 10). Unfortunately, by this technique anionic complexes of Pu(IV), Pu(III) and PuO_2^{++} could not be distinguished from one another. These results are typical for any of the three oxidation states generally examined in this study.

TABLE 10

Electromigration of Plutonium in NaCl-Na_2CO_3 Solutions
(Ionic strength = 0.7 M; pH = 8)

Conc. Na_2CO_3 (M)	Migration (%) to Cathode	to Anode	not Migrating	R_f
2.3×10^{-3}	1	27	70	0.60
4.7×10^{-3}	1	31	66	0.63
9.3×10^{-3}	-	38	59	0.59

All attempts to determine the magnitude of the charge on this negative migrating species and the number of ligands present proved to be fruitless.

Finally there remain the unknown seawater organic compounds of concentrations 10^{-5} to 10^{-6} M, which could be strong complex-formers with Pu ions. This factor cannot be assessed adequately because of the almost infinite variety of organic ligands which might be present in seawater. The similarity in migration behavior between artificial and natural seawater could have some bearing on this question, since no organics were added intentionally to the artificial seawater.

The evidence seems to point towards the presence of a carbonato-complex of plutonium in seawater; however there may be an appreciable amount of negative hydroxide complex present. The present set of experiments did not distinguish clearly between the possible oxidation states. It is of interest to note that in many of the experiments the behavior of the migrating ion was independent of the oxidation state of plutonium originally added. This could be interpreted to mean that only one state exists in seawater and that any different state added is immediately changed to the more stable one. The possibility seems small that the separation method itself is responsible for converting the plutonium into a single oxidation state. The work of Lingren, et. al.* seems to indicate that this is unlikely. Such results also could be due to several complexes of similar net charge but different metallic ion charge, e.g., $Pu(CO_3)_3^{=}$, $PuO_2(CO_3)_2^{=}$. These are very similar in mass and identical in charge and consequently very difficult to distinguish.

The samples from dissolved chips of plutonium (Table 3) behaved quite like those reported in Table 2. The conclusion is that the metal dissolved in this fashion reaches the same final form as does the Pu added to seawater in the ionic state.

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*W. E. Lingren, J. Reeck and R. Marson, "The Paper Electrophoresis of the Iron(II)-Iron(III) System," U. S. Naval Radiological Defense Laboratory, USNRDL-TR (in preparation).

The plutonium placed in seawater by dissolving the PuO_2 beads shows an appreciable amount of cationic species as well as an anionic species. This does not correspond to any migration behavior observed with solutions formed by introducing dissolved Pu. The R_f value for the anionic species lies near that for the value determined for carbonato-complexes of plutonium; however this in itself is not conclusive. The cation species could not be identified.

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DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) U.S. Naval Radiological Defense Laboratory San Francisco, California 94135	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

THE ELECTROCHROMATOGRAPHY OF SEAWATER CONTAINING DISSOLVED PLUTONIUM

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

5. AUTHOR(S) (Last name, first name, initial)

Lingren, Wesley E.

6. REPORT DATE 21 December 1966	7a. TOTAL NO OF PAGES 30	7b. NO OF REFS 21

8a. CONTRACT OR GRANT NO AEC Contract No. AT(49-5)-2084 b. PROJECT NO c d	9a. ORIGINATOR'S REPORT NUMBER(S) USNRDL-TRC-85 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. AVAILABILITY/LIMITATION NOTICES

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Atomic Energy Commission Washington, D.C. 20545

13. ABSTRACT

Electrochromatographic techniques were used to determine the chemical form of plutonium in seawater. If either Pu (III), Pu (IV) or PuO_2^{++} was added to a 0.7M NaCl-0.0023 M Na_2CO_3 solution, it was found that in each case about 30 % of the plutonium would migrate to the anode and 70 % would not migrate. Similar results were obtained in solutions containing other anions found in seawater. Plutonium electromigration experiments using NaCl solutions containing varying concentrations of Na_2CO_3 indicated the presence of an anionic complex that is sensitive to carbonate ion concentration. This behavior was not found with other anions in seawater.

Plutonium from plutonium metal dissolved in seawater was found to migrate in the same way as Pu (III), Pu (IV) and PuO_2^{++}. This indicates that the same final chemical form is reached for both the dissolved metal and the added plutonium ions.

Plutonium from high fired PuO_2 beads dissolved in seawater was found to migrate about 23 % to the cathode and 22 % to the anode; 55 % did not migrate at all. This does not correspond to the migration behavior of the dissolved metal or the added plutonium ions; however, there is inconclusive evidence that the anionic fraction is the same carbonato-complex of plutonium.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Plutonium Electrochromatography Carbonato-complexes SNAP Oxidation states						

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