# SPECIATION OF PLUTONIUM AND AMERICIUM IN GROUND WATERS FROM THE RADIOACTIVE WASTE MANAGEMENT COMPLEX, IDAHO NATIONAL ENGINEERING LABORATORY, IDAHO

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U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 93-4035

Denver, Colorado
1993

U.S. DEPARTMENT OF THE INTERIOR
MARCH 3, 1849

**U.S. DEPARTMENT OF THE INTERIOR**

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U.S. GEOLOGICAL SURVEY

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## CONVERSION FACTORS

| Multiply | By | To obtain |
|---|---|---|
| gallon (gal) | 3.785 | liter |
| foot (ft) | 0.3048 | meter |
| cubic foot | 0.02832 | cubic meter |
| gram (g) | 0.03527 | ounce |
| micrometer (µm) | .00003937 | inch |

# Speciation of Plutonium and Americium in Ground Waters from the Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho

*By* Jesse M. Cleveland and Ann H. Mullin

## Abstract

Speciation studies have indicated that plutonium and americium, with only a few exceptions, have generally low solubilities in waters from wells at the Radioactive Waste Management Complex (RWMC) at the Idaho National Engineering Laboratory (INEL). The solubility of plutonium, when added in the low-oxidation-state form [Pu(III) and (IV)], did not exceed 50 percent (of the amount added) in any of the waters from wells that penetrate the Snake River Plain aquifer, and was usually much less. In water from well 92, however, which is completed in a perched aquifer at a much shallower depth than the water table, 83 percent of Pu(III) and (IV) on figure 3 remained in solution 30 days after it was added. This water, which has contacted the buried waste, contains small concentrations of organic compounds that could reduce the plutonium to the more-soluble trivalent state, as well as possibly form soluble complexes. This water also has the highest concentration of carbonate (shown as alkalinity in table 1), which can form strong soluble complexes with plutonium (IV), a normally insoluble species. In experiments using the high oxidation states [Pu(V) and (VI)], virtually all the added plutonium remained in solution in the water from all wells, and remained in the relatively soluble high oxidation states. The solubility of americium was generally low in all waters, ranging from a high of 36 percent (of the amount added) to a low of 2 percent in water from well 92 after 30 days. The results indicate that although low-oxidation-state plutonium is generally insoluble in water from the Snake River Plain aquifer, it is more soluble in water from the perched aquifer and could, in time, be leached from the waste and ultimately reach the Snake River Plain aquifer.

## INTRODUCTION

From 1954 to 1970, approximately two million cubic feet of transuranic (TRU) waste, with an activity of approximately 253,000 curies (1 curie = 3.7 x $10^{10}$ disintegrations per second), was buried in the Subsurface Disposal Area at the Radioactive Waste Management Complex (RWMC) at the Idaho National Engineering Laboratory (INEL) in southeastern Idaho. In addition to the radioactive waste, the RWMC pits are estimated to contain approximately 222,000 gal of miscellaneous hazardous wastes, including about 24,000 gal of carbon tetrachloride and 31,000 gal of other organic compounds. Because most of this waste was contained in steel drums and wooden and cardboard boxes that have deteriorated or completely disintegrated, the potential exists for dissolution and migration of some of the transuranium nuclides in subsurface waters at the site. Of particular concern are plutonium and americium, the latter resulting from the decay of the considerable quantities of plutonium-241 (half-life = 15 yr) buried at the site.

The solubility - and hence mobility - of plutonium in ground waters depends on two characteristics of the waters, namely, their oxidation-reduction (redox) properties and their concentration of complexing anions. Of these two, redox properties generally are more important because of the great variation in plutonium solubility with oxidation state. Plutonium can commonly exist in aqueous solution in four different oxidation states [(III), (IV), (V) and (VI), the last two as the dioxo species $PuO_2^+$ and $PuO_2^{2+}$ ] (Cleveland, 1979, p. 11). The tendency towards hydrolysis and formation of insoluble hydroxides decreases in the order IV >> VI ≥ III > V (Cleveland 1979, p. 81); thus, for minimum solubility it is desirable that the plutonium be in the tetravalent state. Conversely, solubility will be higher in oxidizing waters, in which plutonium is converted to Pu(V) and (VI), and in strongly reducing waters, in which trivalent plutonium is formed.

The presence of significant concentrations of complexing anions can also influence solubility

The presence of significant concentrations of complexing anions can also influence solubility because the complexes are likely to be soluble. The order of complex formation generally parallels that of hydrolysis, and in the presence of strongly complexing anions the solubility of even Pu(IV) may be enhanced. In most cases, however, hydrolysis predominates over complexation.

The chemistry of americium differs considerably from that of plutonium. Under environmental conditions americium will exist exclusively as the trivalent ion. For this reason, the redox properties of the water have no influence on its solubility; moreover, because americium forms relatively weak complexes, the presence of complexing ions also has less influence than in the case of plutonium. Hence, the solubility variations of americium cannot readily be correlated with the chemical properties of the ground water.

In this report, the results of a study of the chemical speciation of plutonium and americium in waters from a number of wells in and around the RWMC at INEL are presented. The approach taken is that of similar speciation studies of a number of ground waters from widely disparate locations (Cleveland and others, 1983a, 1983b, 1983c, 1985; Rees and others, 1984; Nash and others, 1988).

## EXPERIMENTAL METHODS DESIGN

The water samples used in this study were supplied by the staff of the U.S. Geological Survey Idaho Falls Project Office. The location of the sampled wells is shown in figure 1. With the exception of well 92, which is completed in a 2 ft-thick perched aquifer at a depth of about 215 ft and does not extend below this depth, all the wells are 625-675 ft deep; hence, they are completed in the Snake River Plain aquifer, which lies at a depth of approximately 580 ft, and they are open to the aquifer below the water level. The samples were analyzed for primary inorganic constituents; the results are shown in table 1. In addition to the inorganic ions shown in the table, water from well 92 contains small concentrations of carbon tetrachloride and chloroform, even smaller concentrations of a number of other chlorinated hydrocarbons, and trace concentrations of other organic compounds, including phenols, aromatic acids, azoles, alcohols, and alkanes.

The solubility and oxidation-state distribution of plutonium in the samples were determined by adding small aliquots of a stock solution of $^{239}$Pu (of known oxidation-state-distribution) in 0.5 molar (*M*) perchloric acid to measured volumes of each sample (unfiltered) in Savillex Teflon jars, to achieve a plutonium concentration of $\sim 10^{-9}$ *M*. After readjustment of the pH of each water sample to its original value, the jars were tightly capped and stored in darkness for the specified time period. Plutonium stock solutions with two different electrolytically prepared oxidation-state distributions were used: reduced [Pu(III) and (IV)] and oxidized [Pu(V) and (VI)]. Plutonium, in all oxidation states, and americium are soluble in 0.5 *M* perchloric acid.

**Table 1.** Results of chemical analyses of water from wells

[All concentrations in milligrams per liter, except pH, which is in standard units; -- indicates no data]

| Well | pH | Alkalinity (as $CaCO_3$) | Chloride | Fluoride | Sulfate | Sodium | Calcium | Magnesium |
|---|---|---|---|---|---|---|---|---|
| 87 | 8.0 | 134 | 12 | 0.3 | 26 | 10 | 40 | 13 |
| 88 | 8.2 | 92 | 92 | 0.3 | 70 | 44 | 32 | 22 |
| 89 | 8.1 | 80 | 3 | 0.4 | 40 | 20 | 27 | 15 |
| 90 | 8.2 | 130 | 14 | 0.3 | 29 | -- | -- | -- |
| 92 | 8.2 | 308 | 87 | 0.3 | 60 | 99 | 45 | 9 |
| 117 | 8.2 | 99 | 13 | 0.3 | 19 | 11 | 27 | 11 |
| 119 | 8.3 | 92 | 4 | 0.3 | 37 | 11 | 30 | 11 |
| 120 | 8.1 | 155 | 25 | 0.3 | 43 | 29 | 37 | 17 |
| RWMC | 8.1 | 142 | 15 | 0.2 | 28 | 9 | 45 | 14 |

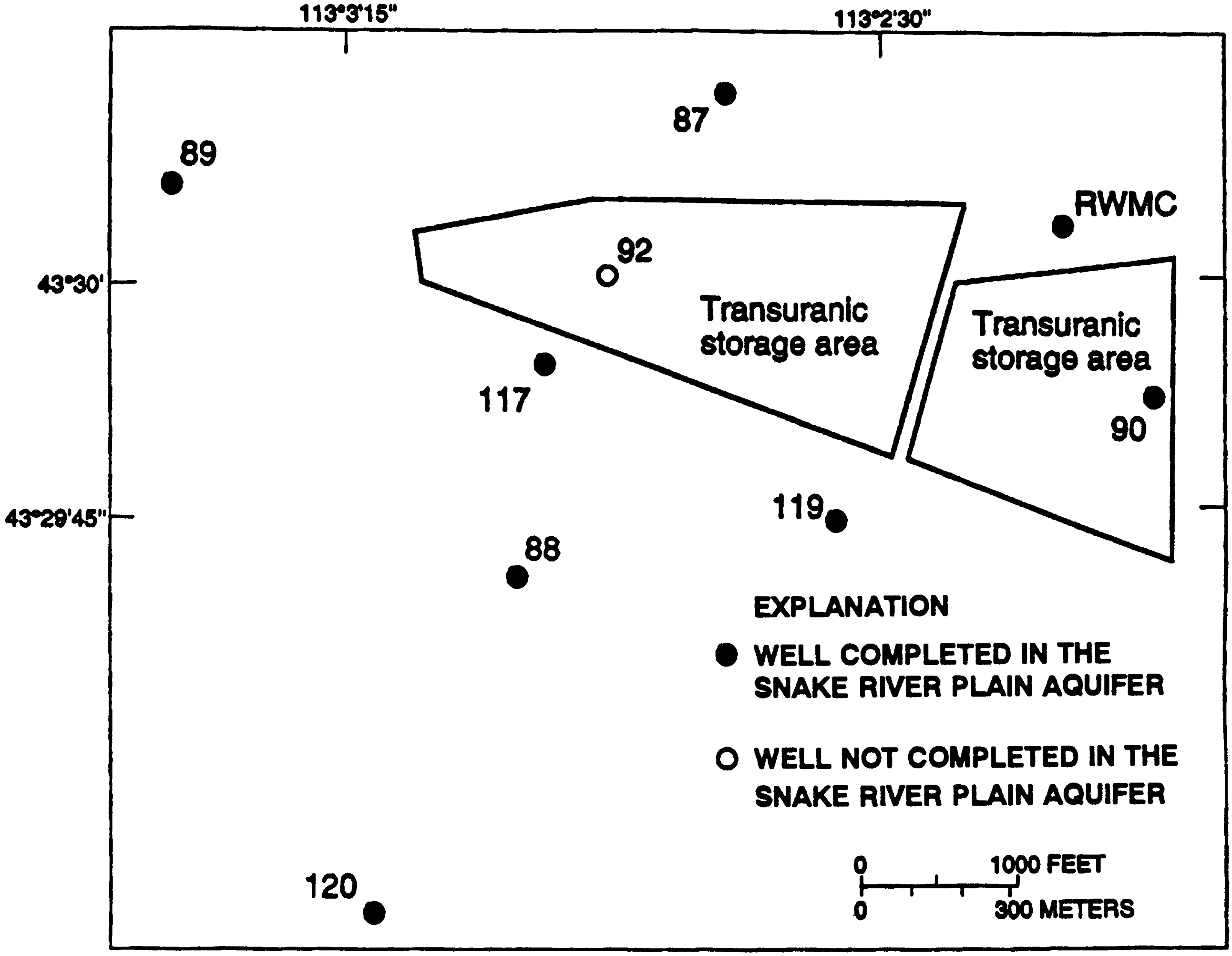

**Figure 1.** Location of the sampled wells at the Radioactive Waste Management Complex at the Idaho National Engineering Laboratory.

Samples were taken, after agitation, 17 and 30 days after plutonium addition and the pH of each was determined to ensure that it had not changed appreciably from its original value. Then the samples were analyzed for total plutonium concentration before and after filtration through 0.1-µm Micron Separations Inc. Cameo filters. The filtrate was considered to contain only soluble plutonium, and it was sampled for oxidation-state analysis by praseodymium fluoride carrier precipitation and thenoyltrifluoroacetone (TTA) extraction using methods described previously (Cleveland and others, 1983b). Carrier precipitations were performed on two aliquots of each filtrate. One was conducted in the presence of a small amount of sodium dichromate as holding oxidant to determine the combined concentrations of Pu(III) and (IV) in the filtrate; another was done after addition of sodium bisulfite reductant to reduce all plutonium to the lower oxidation states and yielded a value for the total soluble plutonium concentration in the water. A third aliquot was adjusted to 1*M* acidity and extracted with a 0.5-*M* solution of TTA in xylenes to determine the concentration of Pu(IV). From the analysis of the filtrate and the results of the carrier-precipitation and solvent-extraction determinations, it was possible to calculate the concentrations of plutonium in three different oxidation states: (III), (IV) and (V + VI). Five replicates were run for each set of conditions, and the results shown are the averages of these replicates.

Because americium would be present solely in the (III) oxidation state under the conditions of these experiments, it was not subjected to oxidation-state analyses. Instead, its solutions were sampled only before and after filtration through a 0.1-µm filter and from these values the percent of americium remaining in solution at the specified time period was calculated. Americium experiments involved four sampling periods: 3, 7, 17 and 30 days. Again, there were five replicates.

## SPECIATION OF PLUTONIUM AND AMERICIUM

Speciation results for experiments utilizing low-oxidation-state plutonium are shown in figures 2-4, where the percentages of plutonium displayed on the vertical axes are relative to the amount of plutonium originally added. Because plutonium is soluble in 0.5 *M* perchloric acid, the initial solubility in each case is 100 percent. Only three of these waters were able to retain in solution a substantial fraction of the added plutonium. By far, the highest plutonium solubility is in water from well 92. In this water, 90 percent of the plutonium was still in solution after 30 days, primarily as Pu(III), a significant fraction of Pu(IV), and only a small amount of Pu(V + VI). This water tends to reduce Pu(IV) to the more soluble (III) oxidation state, but even so, this is the only water from any of these wells that retains a significant percentage of the plutonium in the normally insoluble (IV) state.

The higher solubility of plutonium in water from well 92 results from the composition of this water. This well is the only one studied that is completed in a perched aquifer; hence, the water sample is from a much shallower depth than the other samples (215 ft as opposed to about 625 ft). This water has definitely contacted the buried waste, as evidenced by the results of chemical analyses (not given in this report) showing the presence of carbon tetrachloride and chloroform, as well as smaller concentrations of other chlorinated hydrocarbons and other organic compounds. The effect of the chlorinated hydrocarbons on plutonium solubility would be minor. These compounds would be unreactive with plutonium, and their hydrolysis would produce primarily chloride ions, which form only weak complexes with plutonium. Moreover, as table 1 indicates, the chloride concentration in this water is actually lower than that in water from well 88. Trace concentrations of other organic compounds are probably responsible for the reducing properties of this water, and some of these compounds, containing phenolic and carbonyl groups could form relatively strong complexes with plutonium, though to a limited extent at such low concentrations.

Water from well 92 contains a much higher concentration of carbonate (shown as alkalinity in table 1) - which forms strong complexes with plutonium, particularly the tetravalent species - than any of the other waters. Therefore, it is probable that the solubility of plutonium in water from well 92 is the result of the reducing action of the dissolved organic compounds along with complexing by carbonate ions, and possibly, to a much smaller extent, by dissolved trace organic compounds.

An obvious question is why, given the relatively high solubility of plutonium in water from well 92 and the fact that this water has contacted the waste, there is no appreciable concentration of plutonium in the water as sampled. To answer this question it must be remembered that the plutonium in these experiments was added to the water in a *soluble* form, whereas the plutonium in the waste is primarily present in less soluble forms, such as the dioxide. Nevertheless, to conclude that the plutonium in the waste would not leach into the ground water over a period of time is not warranted.

Water from well 120 has the second highest carbonate concentration (shown as alkalinity in table 1), and the second highest percentage of Pu(IV) (fig. 4),

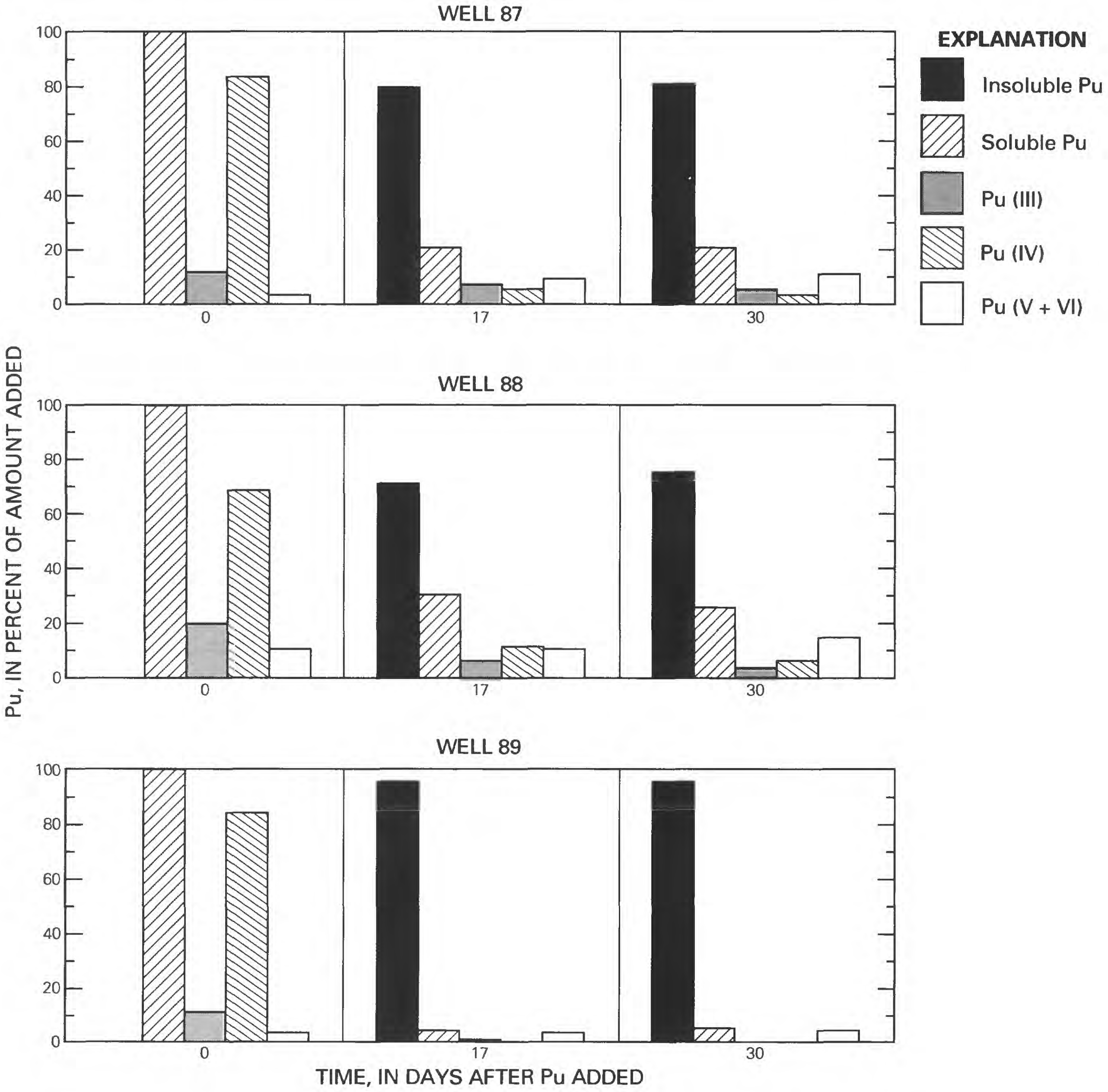

**Figure 2.** Speciation of plutonium (Pu) after its addition in low-oxidation-state form [Pu (III) and (IV)] to water from wells 87, 88, and 89.

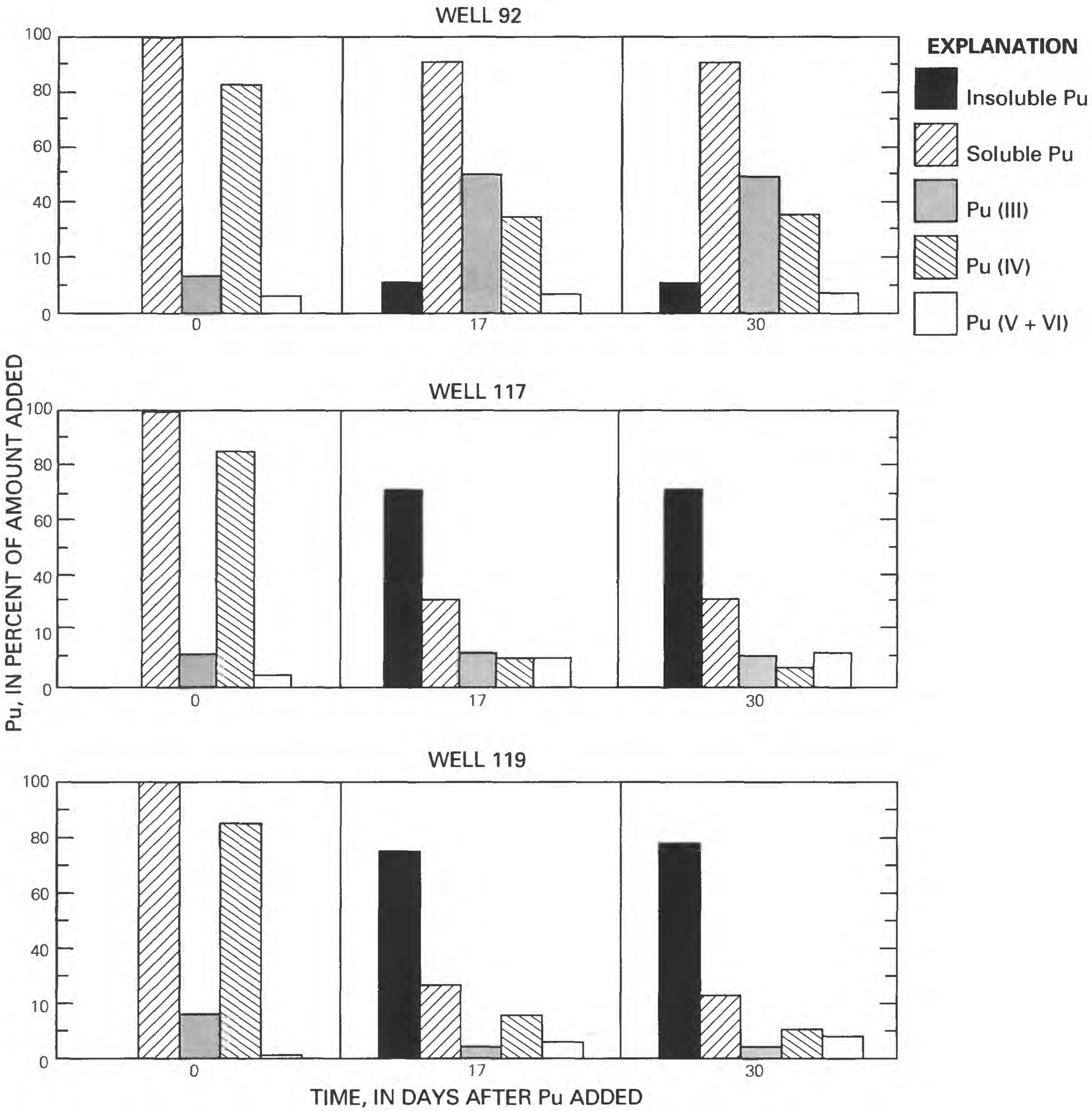

**Figure 3.** Speciation of plutonium (Pu) after its addition in low-oxiation-state form [Pu(III) and (IV)] to water from wells 92, 117, and 119.

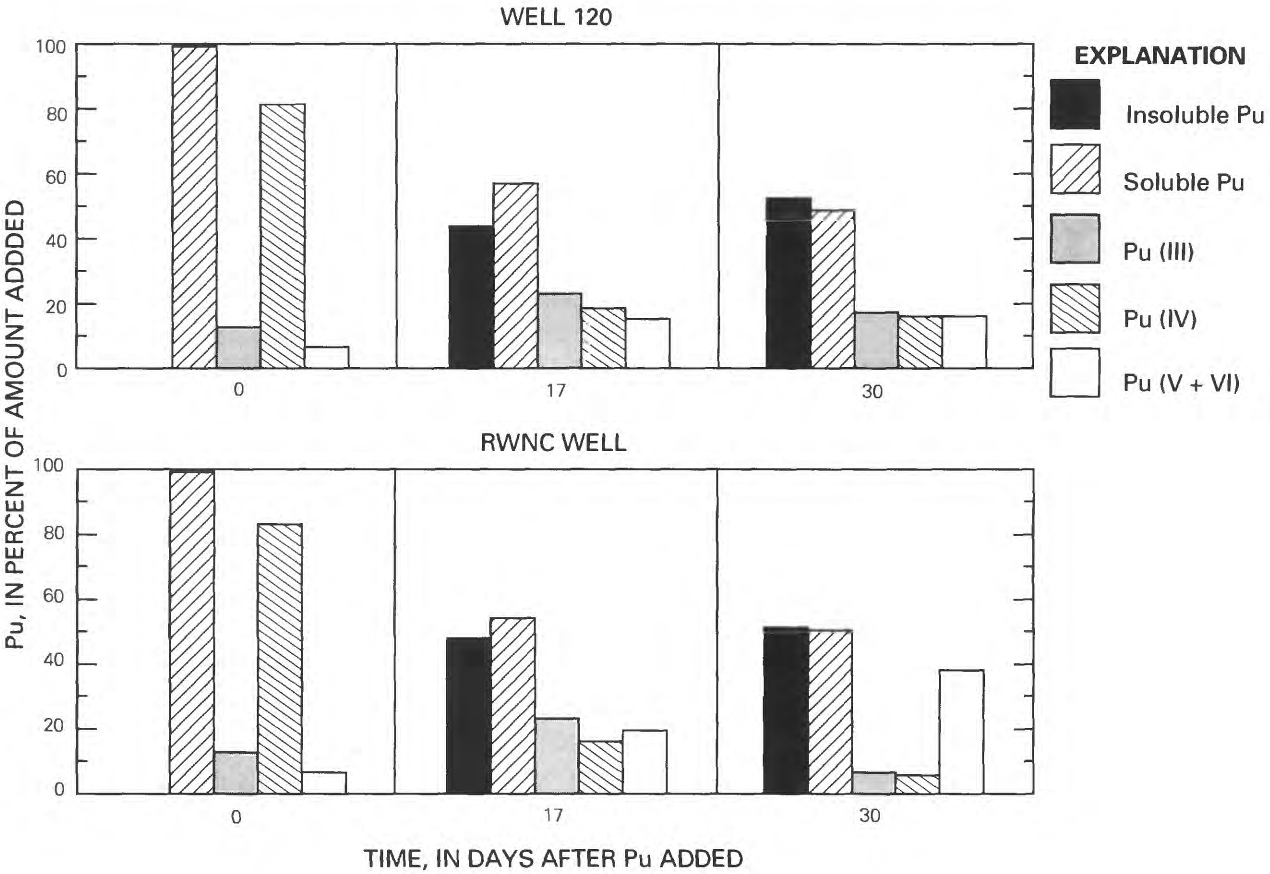

**Figure 4.** Speciation of plutonium (Pu) after its addition in low-oxidation-state form [Pu(III) and (IV)] to water from well 120 and RWMC well.

but the influence of carbonate complexation is probably less important, because the carbonate concentration is so much lower. Moreover, neither this water nor any of the others contains the organic species present in water from well 92. To the extent that plutonium is soluble in this water, it is probably the result of the disproportionation of the added Pu(IV) into the much more soluble (III) and (V + VI) species. And finally, the moderate solubility of plutonium in water from RWMC well, the production well for the RWMC complex, results from the ability of this water to oxidize part of the plutonium to the more soluble (V + VI) states.

In each of these low-oxidation-state experiments, the added plutonium was predominantly in the (IV) state. This oxidation state is generally insoluble in the absence of significant complexing, and only in water from well 92 is there any evidence of that. In the other waters, solubility depends on conversion of the Pu(IV) to a more soluble oxidation state, and only in the three wells discussed above did this occur to a significant extent. In the waters from wells 87, 88, 89, 117 and 119, oxidation or reduction of the Pu(IV) occurred to only a slight extent, resulting in low plutonium solubility in these waters.

Solubilities of plutonium when added in the high oxidation states to all of the waters in this study are not shown because of their uniformity. Invariably, more than 90 percent (and commonly more than 95 percent) of the oxidized plutonium added to these waters remained in solution after 30 days, most of it in the (V + VI) oxidation states, with only negligible amounts of Pu(III) and Pu(IV). These results not only confirm the relative solubility of the higher oxidation states, but also attest to the weak reducing properties of these waters.

Other than for well 92, there is no obvious correlation between well location and either water composition or plutonium solubility. Water from the RWMC well appears to be more oxidizing than the other waters, but there is no reason to attribute this to location. Well 120 is more isolated than the other wells, but there is no reason to expect the water there to differ from that of the other wells.

Under environmental conditions, americium will exist solely as the Am(III) species; hence, its solubility will not be influenced by the oxidation-reduction properties of the waters. Moreover, trivalent actinides are not as strongly complexed as the tetravalent species, thus limiting the extent of solubilization by this mechanism. Therefore, the americium solubility data, presented in table 2, are not readily correlated with water composition. In all cases, less than one-half the added americium remained in solution after 30 days, and it is perhaps noteworthy that solubility was lowest in water from well 92, in which plutonium was most soluble. One could speculate on whether carbonate could have an inhibiting effect on americium solubility, but the data are insufficient to address this question. The only conclusion is that americium solubility is influenced by secondary factors that are more difficult to assess than the more pronounced effects of redox

**Table 2.** Americium in solution, in percent of amount added to water samples, after selected time periods

| Well | Days after americium added | | | |
|---|---|---|---|---|
| | 3 | 7 | 17 | 30 |
| 87 | 33 | 27 | 16 | 16 |
| 88 | 14 | 14 | 14 | 9 |
| 89 | 19 | 17 | 14 | 18 |
| 90 | 35 | 37 | 35 | 36 |
| 92 | 7 | 4 | 3 | 2 |
| 117 | 42 | 30 | 24 | 24 |
| 119 | 10 | 6 | 6 | 5 |
| 120 | 49 | 42 | 46 | 31 |
| RWMC | 52 | 49 | 32 | 29 |

action and complexation that play such a large part in determining plutonium speciation.

## CONCLUSIONS

The experiments described in this report were conducted under specific conditions, using given concentrations of plutonium and americium; care must be exercised in interpreting the results in an actual environmental context, particularly over long periods of time. Nevertheless, some conclusions seem warranted. The results indicate that, although low-oxidation-state plutonium is generally insoluble in the water from the Snake River Plain aquifer, it is soluble in the water from the perched aquifer, and in time could be leached from the waste. Once dissolved, it could persist in solution and ultimately reach the Snake River Plain aquifer. Moreover, the generally higher solubility of high-oxidation-state plutonium indicates that any change in the redox properties of the water, such as might be caused by leaching of an oxidizing species from the waste, could also result in leaching and migration of plutonium from the waste. In addition, americium, although relatively insoluble and not subject to oxidation-state changes, could ultimately be leached from the waste to a small but radiologically significant extent.

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