Reports

Plutonium Speciation in Water from Mono Lake, California

Abstract. *The solubility of plutonium in Mono Lake water is enhanced by the presence of large concentrations of indigenous carbonate ions and moderate concentrations of fluoride ions. In spite of the complex chemical composition of this water, only a few ions govern the behavior of plutonium, as demonstrated by the fact that it was possible to duplicate plutonium speciation in a synthetic water containing only the principal components of Mono Lake water.*

The enhanced solubility of plutonium and other actinides in the water of Mono Lake, California, has been addressed recently by Simpson *et al.* (*1, 2*) and Anderson *et al.* (*3*), who pointed out that the behavior of actinides in natural waters has great relevancy to the safe long-term storage of radioactive wastes. These investigators suggested that the relatively high solubility of plutonium in Mono Lake water is the result of CO_3^{2-} complexing in this very alkaline water; although this conclusion was quite plausible, it was supported by a minimum of experimental data and clearly needed additional confirmation. Moreover, as these researchers indicated, there were unanswered questions, such as the oxidation-state distribution of plutonium in Mono Lake water (*2*) and the possibility that other ligands are also important in solubilizing plutonium in this water (*3*).

We have studied the speciation of plutonium in Mono Lake water as part of a comprehensive investigation of transuranium-element chemistry in ground waters of possible relevance to radioactive waste disposal. One of the objectives of the program is to assess the effects of various anions on transuranium-element speciation; Mono Lake water, although not a ground water and certainly of only indirect relevance to waste disposal, was selected for study because of its high CO_3^{2-} concentration. In this study we have provided the needed data on plutonium oxidation-state distribution in Mono Lake water and have obtained results indicating that CO_3^{2-} does indeed enhance plutonium solubility in this water but that another anion, F^-, also has an effect. Moreover, we have obtained evidence that Pu(III), as well as the higher oxidation states, is stabilized by CO_3^{2-} complexing, a fact not addressed by the earlier investigators (*1–3*).

Rather than studying fallout plutonium in Mono Lake water, we added precisely known amounts of ^{239}Pu; in this way we could control the element's initial oxidation state and also be certain that it was in solution initially. A sample (50 liters) of water was obtained from the west shore of Mono Lake; before use this water was filtered through 0.45-μm Nuclepore (*4*) filters. The chemical composition of the water is shown in Table 1. A small volume (10 μl) of ^{239}Pu in 0.5*M* $HClO_4$ was added to 50-ml portions of the filtered water to achieve a plutonium concentration of $10^{-9}M$. (Because of the buffering capacity of the water, *p*H adjustment after addition of the $HClO_4$ was unnecessary.) To evaluate the effect of the initial oxidation state of the plutonium, we carried out two sets of experiments, one using predominantly reduced plutonium [Pu(III) and (IV)] and one using oxidized plutonium [Pu(V) and (VI)]. We also evaluated the effect of temperature by performing both sets of experiments at 25° and 90°C. The water samples containing added plutonium were placed in tightly capped Savillex Teflon containers and allowed to stand

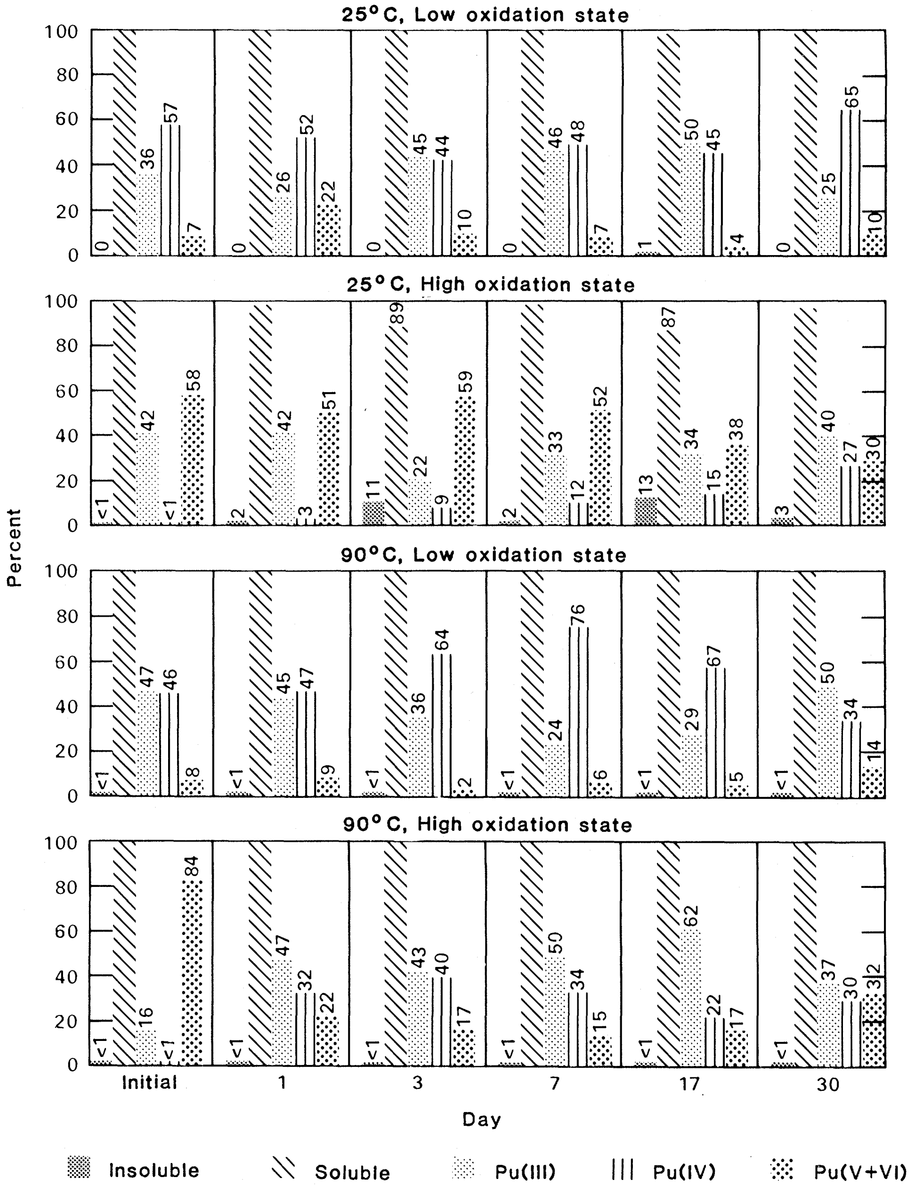

Fig. 1. Speciation of plutonium in Mono Lake water.

for 1, 3, 7, 17, or 30 days. At the conclusion of the specified time, the container was shaken, opened, and sampled. This sample was analyzed for total plutonium, which would include both dissolved and suspended plutonium.

The remainder of the water was filtered through a 0.05-μm Nuclepore filter and subjected to both a total-plutonium analysis and a series of PrF_3 carrier-precipitation and thenoyltrifluoroacetone solvent-extraction procedures (*5*) to establish the oxidation-state distribution of the dissolved plutonium. All samples were analyzed radiometrically. All experiments were performed in duplicate, and from material balance and reproducibility of the results we estimate the accuracy to be within ~ 20 percent of the given value (that is, 60 ± 2, not 60 ± 20). An exception may be values less than 10 percent, which may not be statistically different from zero.

Table 1. Chemical composition of the Mono Lake water sample.

Component	Concentration (mg/liter)
Alkalinity (as $CaCO_3$)	26,300
Calcium	12
Iron	1.0
Magnesium	23
Manganese	0.033
Potassium	1,300
Sodium	26,000
Strontium	0.029
Silica	13
Chloride	22,000
Fluoride	48
Phosphate	20
Sulfate	8,300
*p*H	10.0

The speciation results are shown in Fig. 1, with the percentages related to the amount that was added initially. Any plutonium not passing through the 0.05-μm filter is defined as insoluble and will consist of both sorbed and suspended plutonium. Soluble plutonium is defined as that passing through the filter, and, within experimental error, this value should equal the sum of the percentages of Pu(III), Pu(IV), and Pu(V + VI).

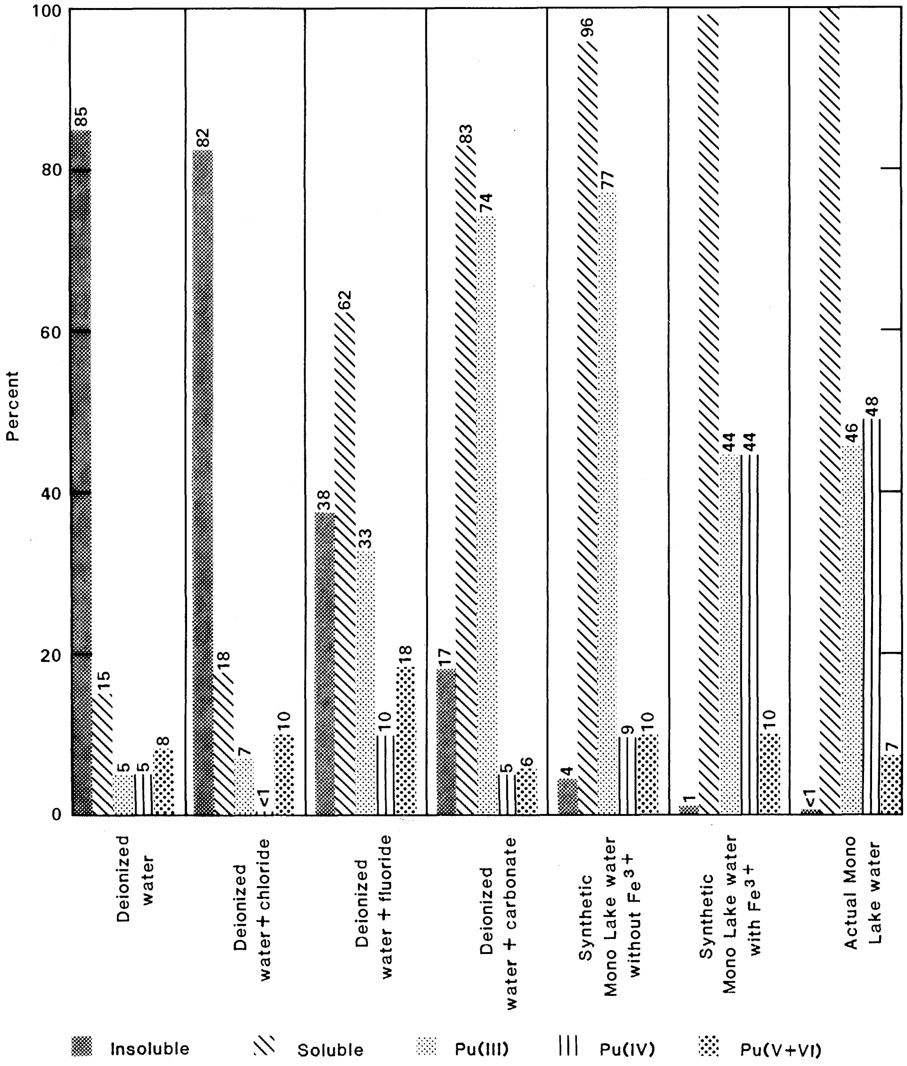

Fig. 2. Speciation of plutonium in synthetic solutions containing the principal components of Mono Lake water.

The plutonium is virtually completely soluble in Mono Lake water, regardless of initial oxidation state and temperature. Its oxidation-state distribution varies with conditions; however, all oxidation states are present in all cases. Regardless of temperature, in the two low-oxidation-state experiments there is little increase of Pu(V and VI) concentration in 30 days, whereas in the high-oxidation-state experiments the percentages of Pu(V and VI) decrease significantly. Eventually the oxidation-state distributions in the two sets of experiments would become virtually equal if the system were at equilibrium. The percentage of Pu(IV) increases significantly in the high-oxidation-state experiments but does not change much in the low-oxidation-state experiments. The most common oxidation state after 30 days in all but the 25°C low-oxidation-state experiments is Pu(III).

Most significant is the presence of appreciable concentrations of Pu(IV); earlier studies (*6*) have indicated that this oxidation state, because of its low solubility, is present in meaningful concentrations only in ground waters with relatively high concentrations of strong complexing agents (in that case, F^-). Thus, both the solubility of plutonium and its oxidation-state distribution suggest the presence of complexes.

Examination of Table 1 indicates that several ions are present in the water that might affect plutonium solubility through complexation, namely, CO_3^{2-} F^-, and Cl^-. [Earlier studies (*6*) have indicated that SO_4^{2-} does not enhance the solubility of plutonium in natural waters and in some cases may actually retard it.] To identify the complexes present, we performed a series of experiments using synthetic waters containing the various components of Mono Lake water. These auxiliary experiments involved only reduced plutonium [44 percent Pu(III) and 56 percent Pu(IV)] and were performed for only 7 days, because all the effects shown in Fig. 1 were obvious after that period. The results are shown in Fig. 2, in which the concentrations of all added ions are the same as in Mono Lake water.

The plutonium is virtually insoluble in deionized water and in deionized water containing Cl^-, indicating the absence of any significant effect from this anion. In the presence of F^-, however, plutonium solubility increases greatly; a similar effect is observed in the presence of CO_3^{2-}. In the presence of both of these anions, that is, in synthetic Mono Lake water either with or without added Fe^{3+}, the solubility of plutonium is virtually 100 percent, as in actual Mono Lake water. These results suggest that the solubility of plutonium in Mono Lake water is the result of complexation by both CO_3^{2-} and F^-. The overall stability constants of PuF^{3+} and PuF_2^{2+} are approximately 10^8 and 10^{14}, respectively (*7*), values that are not large enough to prevent hydrolysis at *p*H 10 (*8*). Although no reliable values exist for complexes of Pu(IV) and CO_3^{2-} (*7*), they are unquestionably large. Our data do not allow a conclusion as to whether mixed-ligand complexes or merely a mixture of single-ligand complexes are present.

Although CO_3^{2-} and F^- are responsible for the solubility of plutonium, the oxidation-state distribution of plutonium appears to be determined by the dissolved iron. The solubility of plutonium in synthetic Mono Lake water containing no added Fe^{3+} is similar to that of the actual water, but the oxidation-state distribution differs greatly in that there is a much larger percentage of Pu(III). In the presence of added Fe^{3+} (as $FeCl_3$), however, both the solubility and the oxidation-state distribution of plutonium in the synthetic water are similar to those in actual Mono Lake water. This finding is consistent with our earlier conclusion (*6*) that ionic species, rather than dissolved oxygen, determine the oxidation-state distribution of actinides in solution. Moreover, the solubility of plutonium in synthetic Mono Lake water without added $FeCl_3$, despite the preponderance of Pu(III), is consistent with results in other waters (*6*) and suggests that Pu(III) is also stabilized by complexing.

This suggestion was further confirmed by the behavior of Am(III), a close analog of Pu(III) except for its existence in natural waters solely in the trivalent state, which also was soluble in Mono Lake water over the 30-day period of study. Reliable stability constants for CO_3^{2-} and F^- complexes of Pu(III) are lacking (*7*), but they do exist for Am(III). The overall stability constants of $AmCO_3^+$ and $Am(CO_3)_2^-$ have been reported as 6.5×10^5 and 5.2×10^9, respectively (*9*), and for AmF^{2+} as 310 (*10*), all at 1*M* ionic strength and 25°C. On the basis of stability constants and higher ligand concentration, the CO_3^{2-} complexes of Pu(III) would predominate strongly over the F^- complexes; a similar preponderance of Pu(IV)–CO_3^{2-} species would be expected if one assumes the same relative order of stability for complexes of the tetravalent ion.

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Van der Waals Surfaces in Molecular Modeling: Implementation with Real-Time Computer Graphics

Abstract. *A method is described for generating van der Waals molecular surfaces with a real-time interactive calligraphic color display system. These surfaces maintain their proper representation during bond rotation and global transformations, and an interior atom removal method yields a comprehensible picture of the molecular surface for large molecules. Both algorithms are faster than previous methods. This combination provides a powerful tool for real-time interactive molecular modeling.*

Molecular modeling with interactive color computer graphics in real time is a powerful method for studying the structures of molecules and their interactions (*1–3*). Computer-generated skeletal models maintain a consistent representation during manipulations such as bond rotations and global transformations but have the disadvantage that they give no indication of the physical space occupied by the atoms. We describe here a method for representing molecular surfaces that, unlike previous methods, is suitable for real-time interaction and manipulation.

With raster graphics atomic surfaces may be represented by shaded colored spheres. The displayed molecular surface is constructed by removing hidden surfaces of intersecting and overlapping spheres (*4, 5*) and shows a molecule in a given orientation and conformation. To view the molecule from another angle or in another conformation, one must generate an entirely new surface. Because hidden surface elimination may take several minutes on present equipment, this representation is of limited use in real-time molecular modeling. Several methods based on line drawing displays are available for similar static hidden-line representations (*6*). Other methods are based on an original idea by Richards (*7*) in which a "solvent-accessible surface" is traced out by the inward-facing surface of a "solvent sphere" making contact with the van der Waals surface of atoms in the molecule. This was first developed for studies of molecular interactions by using an interactive monochrome display (*8*), and later extended (*9*) for an interactive color display by using dots to represent the exterior solvent-accessible surface and internal cavities. A similar molecular surface may be generated more rapidly by using a "bit" lattice (*10*). Although these surfaces (*8–10*) may be globally manipulated in real time, bond rotation still requires recalculation of the area affected by the change. Therefore, modeling with molecular surfaces of this variety and frequent changes in torsion angles is laborious.

We have developed a method that generates a molecular surface faster than the above method and which has the significant advantage that the space-filling representation is retained during interactive real-time bond rotation. The ability to change the conformation of the molecular surface in real time cannot be overemphasized (*11, 12*).

For each atom surfaced, we generate a set of points distributed uniformly over a sphere whose radius is the van der Waals radius of the atom. Each point is com-