

Plutonium

An element at odds with itself



Plutonium is a physicist's dream but an engineer's nightmare. With little provocation, the metal changes its density by as much as 25 percent. It can be as brittle as glass or as malleable as aluminum; it expands when it solidifies—much like water freezing to ice; and its shiny, silvery, freshly machined surface will tarnish in minutes. It is highly reactive in air and strongly reducing in solution, forming multiple compounds and complexes in the environment and during chemical processing. It transmutes by radioactive decay, causing damage to its crystalline lattice and leaving behind helium, americium, uranium, neptunium, and other impurities. Plutonium damages materials on contact and is therefore difficult to handle, store, or transport. Only physicists would ever dream of making and using such a material. And they did make it—in order to take advantage of the extraordinary nuclear properties of plutonium-239.

Plutonium, the Most Complex Metal

Plutonium, the sixth member of the actinide series, is a metal, and like other metals, it conducts electricity (albeit quite poorly), is electropositive, and dissolves in mineral acids. It is extremely dense—more than twice as dense as iron—and as it is heated, it begins to show its incredible sensitivity to temperature, undergoing dramatic length changes equivalent to density changes of more than 20 percent.

Six Distinct Solid-State Phases of Plutonium

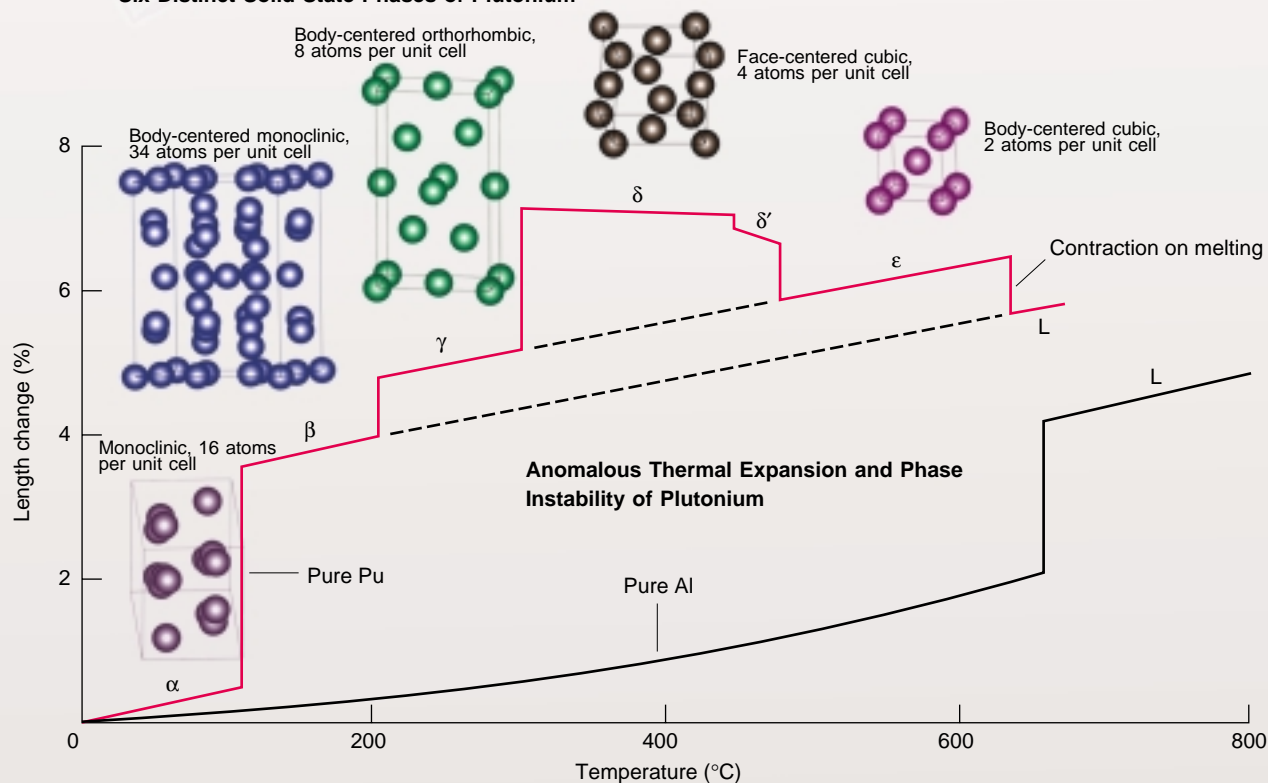


Table I. Physical Properties of Plutonium Compared with Other Metals

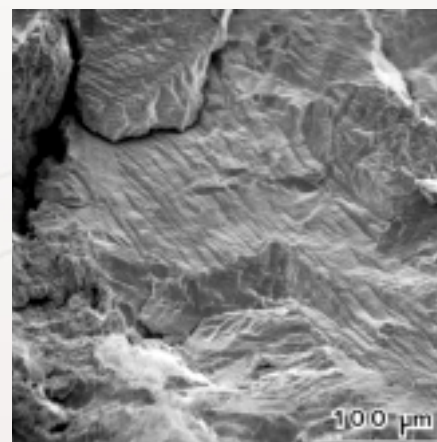
Metal	Thermal Conductivity (cal/cm·s·K)	Electrical Resistivity ($\Omega \text{ cm} \times 10^{-6}$)	Compressibility (GPa ⁻¹)	Young's Modulus (GPa)
Aluminum	0.530	2.9	0.015	70
Stainless Steel	0.036	70	0.0007	180
α -Plutonium	0.010	145	0.020	100
δ -Plutonium (Pu-Ga)	0.022	100	0.033	42

At certain temperatures, the density changes are discontinuous as plutonium suddenly transforms into a new phase, or crystal structure. As it is being heated to its melting point at atmospheric pressure, plutonium will take on six distinct crystal structures; at higher pressures, it will take on a seventh structure. At room temperature and below, it is in the brittle α -phase, which has an unusual low-symmetry monoclinic structure typical of minerals. At 583 kelvins, it takes on the highly symmetric face-centered-cubic structure of the δ -phase, a close-packed structure typical of metals such as aluminum and copper.

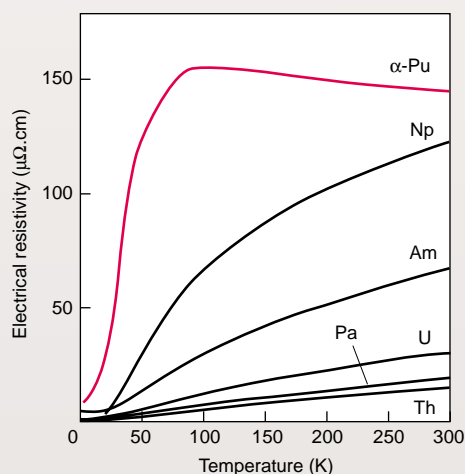
Even in a single phase, plutonium demonstrates unusual behavior—expanding when heated in the α -phase at a rate almost 5 times the rate in iron and contracting while being heated in the δ -phase. Then, at an unusually low 913 kelvins, plutonium melts. While melting, it contracts because the liquid is denser than the previous solid phase. In the liquid state, plutonium has a very high surface tension and the greatest viscosity of any element.

The table above compares plutonium with other metals. Like stainless steel, plutonium is a poor electrical and thermal conductor, and it is very soft, or compressible—even more so than aluminum. In addition, recent measurements have shown that the softening increases much more rapidly than expected with increasing temperature.

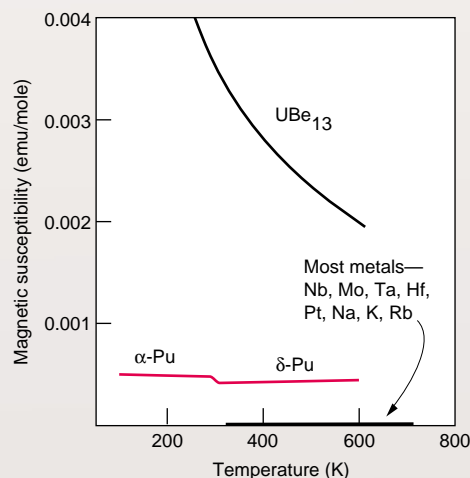
Cooling below room temperature brings out other atypical behaviors. Plutonium's electrical resistivity, already very high at room temperature, increases as the temperature is lowered to 100 kelvins. The energy required to heat plutonium (its specific heat) is 10 times higher than normal at temperatures close to absolute zero. Its magnetic susceptibility, also atypically high, remains constant with perhaps a slight increase as the temperature is lowered, indicating a tendency toward magnet-




The α -phase has undergone brittle fracture under torsion.



Anomalous Resistivity



High Magnetic Susceptibility



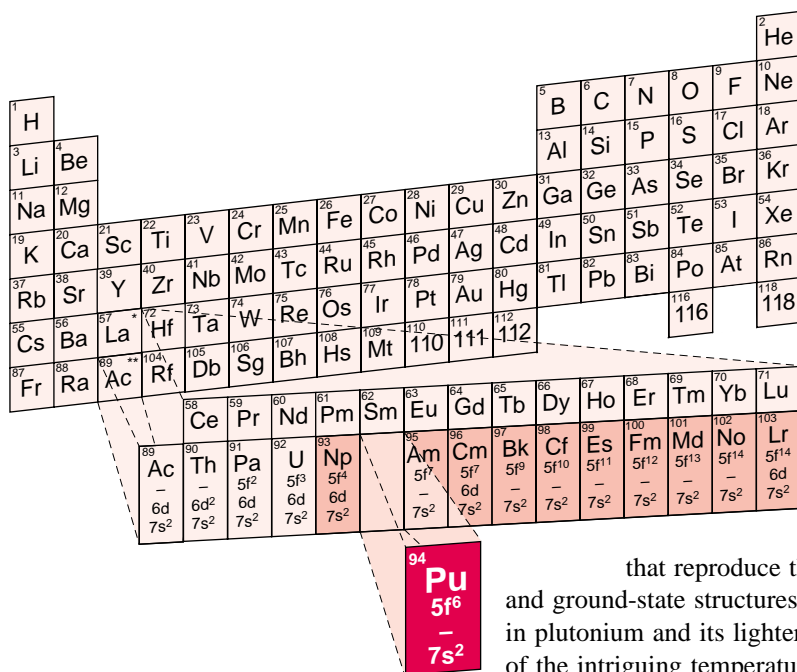
It's the 5f Electrons

together. In contrast, at americium, the 5f electrons start behaving like the 4f electrons of the rare earths, localizing at each lattice site and becoming chemically inert.

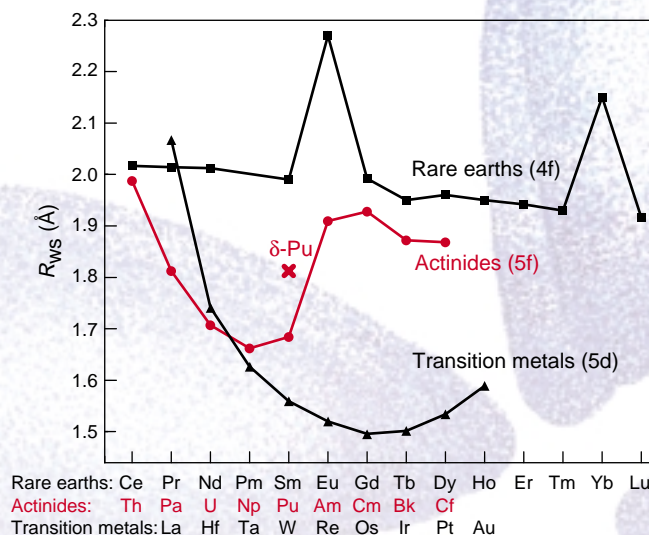
With no 5f contribution to bonding, the atomic volume suddenly increases at americium and contracts only slightly with increasing atomic number because the 5f electrons remain localized in the remainder of the series. The pattern of local magnetic moments confirms this picture. The light actinides show no local moments (as expected if all the valence electrons are in the conduction band), whereas the heavy actinides and the rare earths generally have local moments that are produced by their localized 5f and 4f electrons, respectively.

We now have rigorous first-principles calculations that reproduce the general trends in atomic volumes, local moments, and ground-state structures. These calculations also hint at the origin of instability in plutonium and its lighter neighbors. We can therefore begin to make sense of the intriguing temperature-composition phase diagram connecting all the actinides that was drawn almost 20 years ago (see the connected phase diagram on the opposite page).

The most important insight from calculations is that, in the early actinides, the 5f electrons from different atoms overlap—but just barely. They therefore



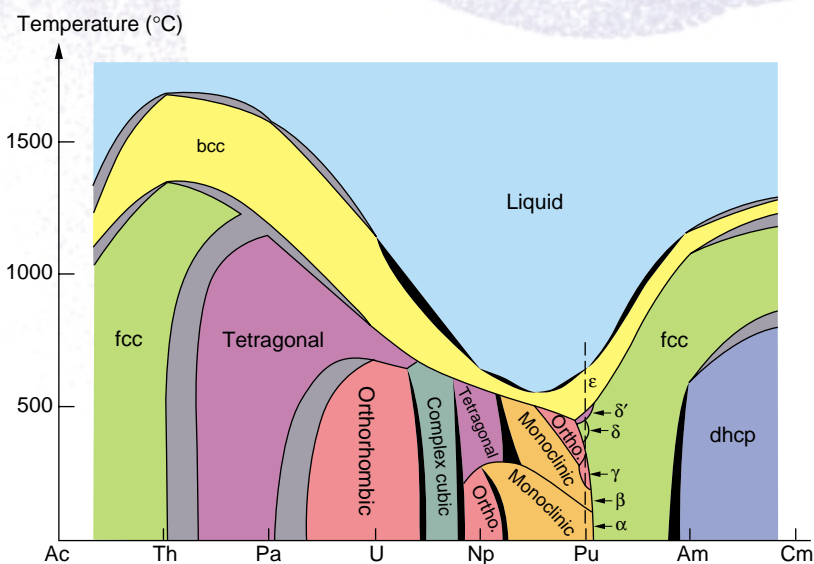
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The atomic radii of the actinide metals are compared with those of the rare earths and transition metals.

occupy a very narrow conduction (or energy) band, which has a very high density of states near the Fermi energy. As the number of 5f electrons populating that band increases, the specific properties of the band begin to dominate the bonding properties of the metal. For example, lattice distortions, or low-symmetry structures, are favored in narrow-band materials because they split the band in certain regions and thereby lower the total energy. Thus, the connected phase diagram shows that uranium, neptunium, and plutonium exhibit low-symmetry ground-state structures rather than high-symmetry structures, which are found in most metals. Before this new insight, the low-symmetry ground state of plutonium was attributed to directional or covalent-like bonding resulting from the angular characteristics of f electrons. Also, because the narrow 5f band overlaps the s, p, and d bands, a number of electronic configurations have nearly equal energy, leading to the multiple allotropic forms of uranium, neptunium, and plutonium and their great sensitivity to external influences.

Thus, many of the peculiarities of plutonium (anomalously low melting point, astonishingly high number of allotropes, and an unusual preference for low-symmetry crystal structures) are not part of a single anomaly but the culmination of a systematic trend in the early actinides resulting from the narrow 5f band. After plutonium, the 5f electrons are completely localized, and typical metallic structures and behaviors return. Right at plutonium, however, between the monoclinic α -phase, which is stable at room temperature, and the fcc δ -phase, which is stable at elevated temperatures, there appears to be a major transition in the 5f electronic structure from bonding to partial localization. It is that tendency toward partial localization that seems to contribute to plutonium's dramatic variability and sensitivity to external influences. The fundamental nature of the transition is at the research frontier of condensed matter physics. The consequences of the transition are critically important to the structural properties of plutonium—particularly to phase stability.



The connected binary-phase diagram of the actinides illustrates the transition from typical metallic behavior at thorium to complex behavior at plutonium and back to typical metallic behavior past americium.

Complex Chemistry of Plutonium



Each plutonium oxidation state has a characteristic color in solution.

The chemical behavior of plutonium, like its solid-state behavior, is controlled by its electronic structure. The lowest energy configuration of the valence electrons is nominally $5f^6 7s^2$, but the energy levels of the 6d and 5f orbitals are similar, and the $5f^6 7s^2$ and $5f^5 6d 7s^2$ electronic configurations compete. In fact, as one moves from thorium to plutonium in the periodic table, the orbital energies invert—the 5f orbitals become lower in energy than the 6d orbitals. Unlike the 4f orbitals in the lanthanides (rare earths), the 5f and 6d orbitals in the light actinides up to americium extend far enough to be accessible for chemical bonding. Consequently, the light actinides exhibit complex chemical behavior reminiscent of the d-transition elements. In the heavy actinides beyond americium, the 5f orbitals are pulled in and not involved in chemical bonding, and therefore the chemical behavior of those heavy actinides and the lanthanides are quite similar.

In the metal, multiple electronic configurations of nearly equal energy lead to multiple solid-state phases. In the atom, they produce a tendency to supply more bonding electrons in chemical reactions and thus to exhibit a very complex chemistry. A plutonium atom in aqueous solution will readily lose between three and seven of its outer electrons to form positively charged cations in five formal oxidation states ranging from Pu(III) to Pu(VII). Many different oxidation states, however,

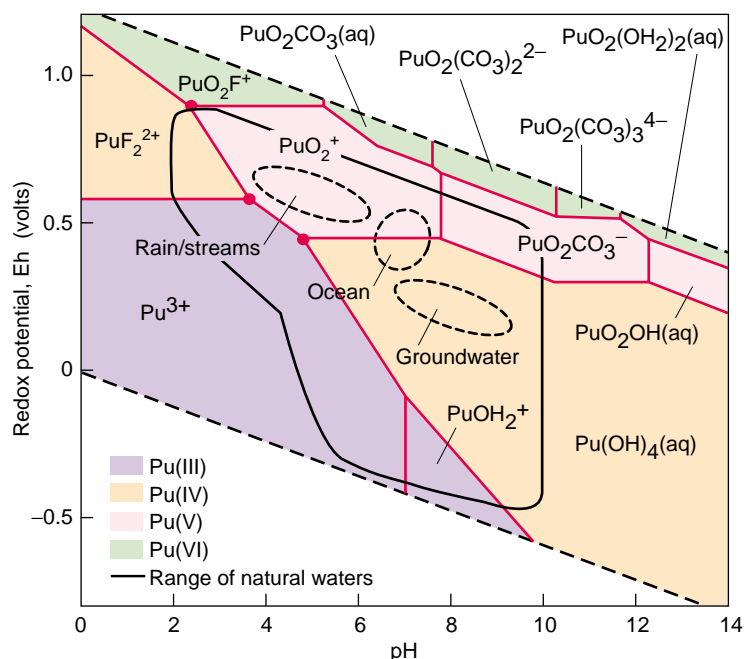
make solution chemistry very complex because each of them forms different compounds or complexes. The plutonium complexes span a broad range of structural motifs and typically have high coordination numbers (that is, the plutonium cation surrounds itself with many anions). Coordination numbers from 3 to 12 have been observed for various oxidation states.

Moreover, under acidic conditions, the energy needed to add or subtract electrons (the reduction-oxidation, or redox potential) and thereby change oxidation states is very similar (approximately 1 volt). Thus, plutonium will often change oxidation states in solution and follow several different chemical pathways simultaneously. It can also exist in several oxidation states within the same solution and, at very low pH, can even exhibit four oxidation states simultaneously. This last feature makes plutonium unique among the elements.

The shapes of 5f and 6d orbitals, in addition to their radial extents, affect molecular (not metallic) bonding. The f- and d-electron wave functions with three and two quanta of angular momentum, respectively, are nonspherical and have highly directional lobes, producing certain unique covalent

motifs. For example, in water, actinides in the (V) and (VI) oxidation state immediately bond with two oxygens to form the linear “actinyl” motif. Plutonyl $O=Pu=O$, uranyl $O=U=O$, and neptunyl $O=Np=O$ are examples. Once formed, other ligands bond in the equatorial plane bisecting the actinyl motif (see figure).

Each oxidation state can form various molecular complexes, each with a characteristic solubility and chemical reactivity. The instabilities of plutonium’s oxidation states, coupled with the creation of free radicals through its radioactive decay, yield solution chemistry that is constantly changing and affecting chemical processing operations, nuclear waste storage and treatment, and the reactivity and mobility of plutonium in the environment. Over the years, the redox states of plutonium have been controlled by complexation with various ligands. Some of these, such as



The range of plutonium complexes and oxidation states in water containing carbonate, hydroxyl, and fluoride ions is evident in the redox potential vs pH diagram. In many natural waters, plutonium will be in the relatively insoluble IV state. Redox reactions, however, will allow plutonium to assume any of the oxidation states III, V, and VI. Overall therefore, the environmental behavior of plutonium is extremely complicated. The red dots mark conditions under which plutonium can coexist in three different oxidation states simultaneously.

the nitrate anion, have played a historically critical role in the processing and purification of plutonium. Other ligands, such as the carbonate and hydroxyl anions, are ubiquitous in natural groundwaters and play an influential role in the transport of plutonium in the natural environment.

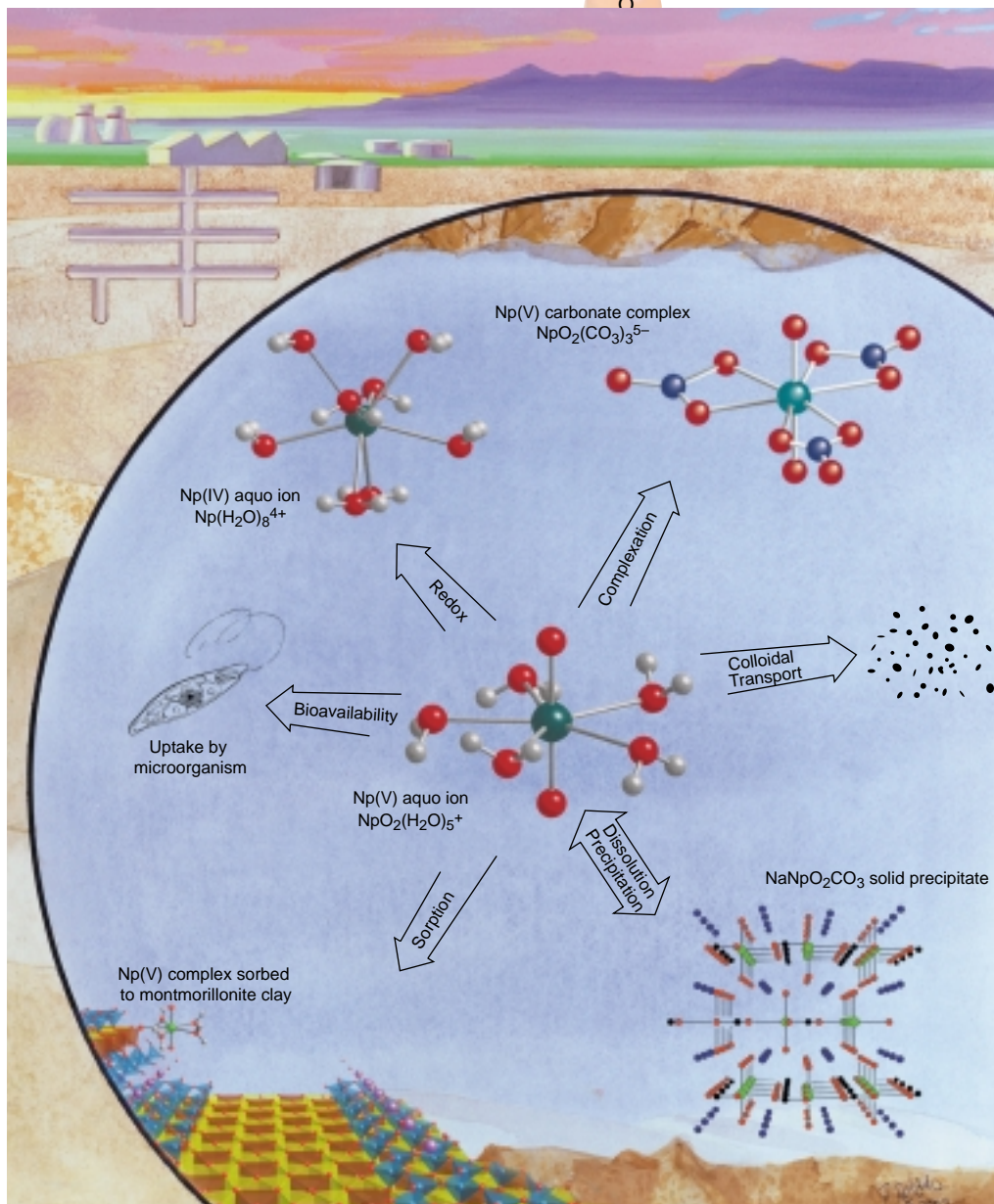
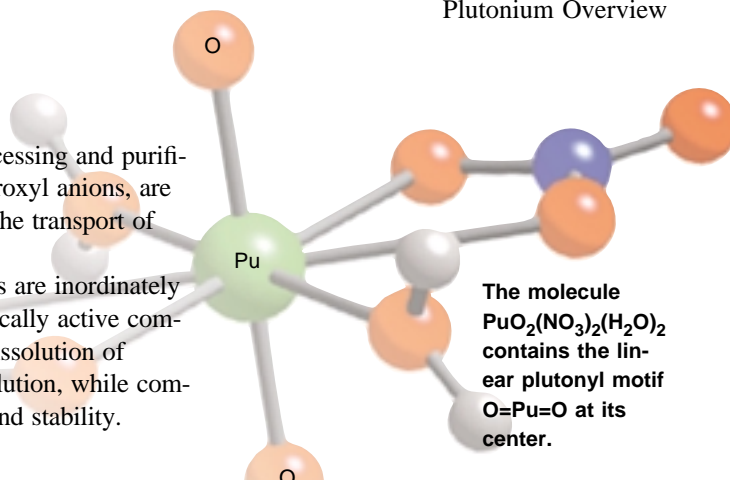
When actinides enter the environment, the chemical interactions are inordinately complex because, in addition to natural waters, hundreds of chemically active compounds and minerals exist in earth formations. Precipitation and dissolution of actinide-bearing solids limit the upper actinide concentration in solution, while complexation and redox reactions determine the species' distribution and stability.

The interaction of a dissolved species

with mineral and rock surfaces and/or colloids determines if and how those species will migrate through the environment. The prevalent oxidation state in groundwater is Pu(IV), whereas Pu(III), Pu(V), and Pu(VI) are also common in streams, brines, or bogs.

The light actinides, including plutonium, form the strongest, most stable complexes in the IV oxidation state. (See the article "The Chemical Interactions of Actinides in the Environment" on page 392.)

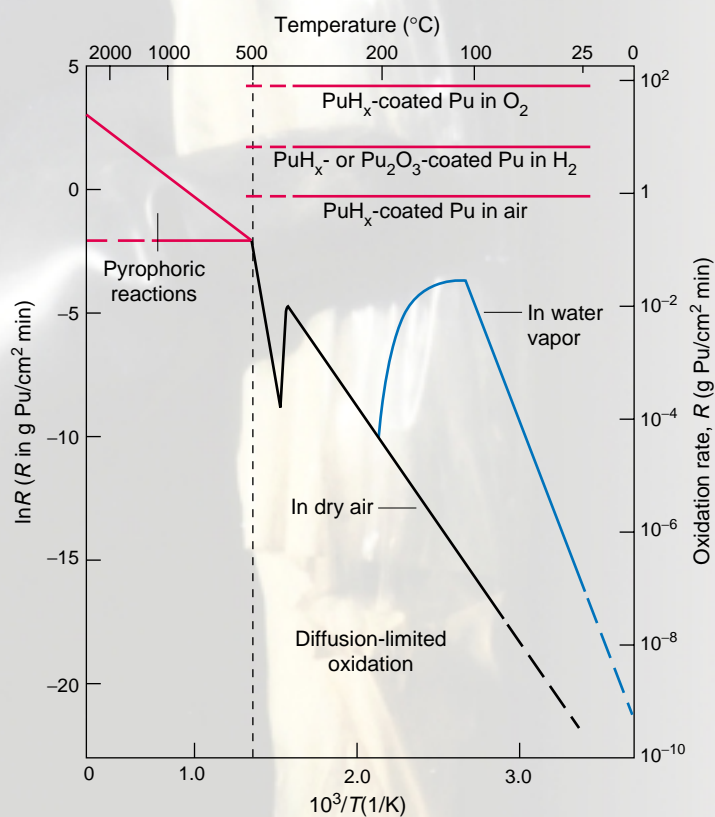
In general, actinide solubilities are so low in most natural waters—below micromolar concentrations—that only advanced spectroscopic techniques can detect the species present, a prerequisite for understanding environmental chemistry. Studies have shown that actinides in the V oxidation state have the highest solubilities; those in the IV state, the lowest. Actinides in the IV oxidation state also show the strongest sorption onto mineral and rock surfaces. The actinides' very low solubility and high sorption create two key natural barriers to actinide transport in the environment. Less-studied microorganisms represent a potential third barrier because plutonium binds with such organisms and their metabolic byproducts. However, recent observations at the Nevada Test Site showed that colloid-facilitated transport of plutonium in groundwater can play an important role in migration (see the box on page 490). Clearly, we must continue to apply modern chemical techniques to better understand the fundamental interactions of plutonium and the actinides in the environment.



This is an artist's rendition of the interactions that affect actinide mobility in the underground environment.

Plutonium Surfaces and Ceramics

Although plutonium is a very reactive metal, a protective surface layer of plutonium dioxide forms almost instantly in dry air (much as aluminum is protected by its oxide) so that further corrosion occurs at a miniscule rate of less than 0.2 micrometer per year. In moist air, however, the corrosion rate is 200 times faster at room temperature and 100,000 faster at 100°C. Rapid oxidation of plutonium is induced because water dissociates on the surface producing hydrogen and a plutonium hyperoxide (having more oxygen than the dioxide). The excess oxygen at the surface creates a high oxygen gradient across the oxide interface, enhancing the diffusion rate through the oxide layer and thus the rate of oxidation at the oxide/metal interface.



The graph above illustrates corrosion rates for plutonium metal. Surface hydrides and oxides can catalyze reactions with hydrogen, oxygen, and water vapor and make those reactions extremely fast. See the article “Surface and Corrosion Chemistry of Plutonium” on page 252.

Hydrogen reacts with plutonium metal at unprecedented rates. If the entire metal surface is covered with hydride, the reaction occurs very rapidly—at rates of 20 centimeters per hour linear penetration for hydrogen at atmospheric pressure, which is 10^{10} (ten billion) times faster than the reaction in dry air. We do not fully understand the fundamental physics and chemistry driving these surface reactions, but they likely involve the metallic bonding state of the substrate and the chemical bonding behavior of the surface in a certain environment.

Plutonium is also pyrophoric—it ignites spontaneously in air at 500°C. Plutonium particulates, such as powder or machining chips, ignite at temperatures as low as 150°C to 200°C. These potentially catastrophic surface reactions make it imperative that plutonium be protected from hydrogen or moisture in sealed containers.

Combining plutonium with nonmetallic elements, such as oxygen, in a bulk solid promotes a strong sharing of electronic charge between the plutonium cation and the oxygen anion. Hence, the oxide has a strong ionic character in contrast to the metallic character resulting from electrons in the conduction band of plutonium metal. The oxides are no longer dominated by the peculiarities of the 5f electrons. Plutonium oxides (as well as carbides and nitrides) are refractory—that is, heat resistant. Plutonium dioxide (PuO_2), the most important plutonium ceramic compound, melts at

2673 kelvins (plutonium metal melts at 913 kelvins), and is much less reactive than plutonium metal. The properties of these compounds are determined primarily by the type of crystal lattice (which is governed by the oxidation state and atomic sizes of cations and anions) and their defect structure. Consequently, plutonium ceramic compounds are still quite complex, but no longer the most complex.

Aging of Plutonium—Alchemy at Work

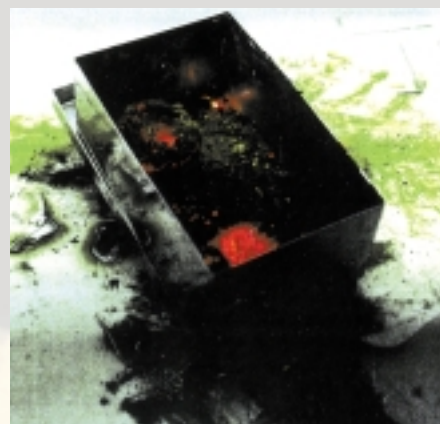
Like many other metals, plutonium ages from the outside in by corrosion. However, because of its radioactive nature, plutonium also ages from the inside out by self-irradiation damage. Plutonium-239 decays mainly by α -particle decay (emitting an α -particle, or He^{++} , and becoming a uranium nucleus), which damages the crystal lattice. The most severe damage occurs when a uranium nucleus recoils

from α -particle decay. The α -particles pick up electrons to become helium atoms, which can associate with crystal defects such as vacancies. Most of the roughly 5 million electron volts of energy released in each decay event is converted into heat, making plutonium noticeably warm to the touch.

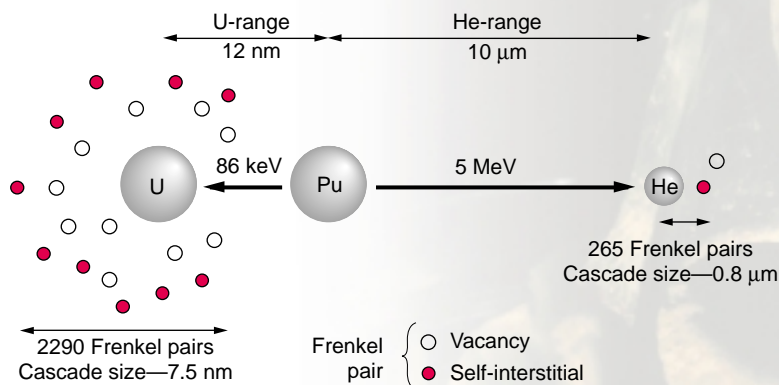
The relentless deposition of energy from the radioactive decay of plutonium damages its crystal lattice and transmutes some of the plutonium into other elements. For example, at standard temperature and pressure, 1 kilogram of plutonium accumulates almost 0.2 liter of helium in 50 years. Fortunately, much of the lattice damage is annealed out or “healed” at room temperature. Nevertheless, the defects resulting from the residual lattice damage and the changes in chemistry can affect plutonium’s delicate balance of stability with changes in temperature, pressure, or chemistry. Such defects may also influence diffusion rates and cause plutonium metal to swell.

Chemical and surface behaviors are also affected by radioactive decay. At high plutonium concentrations in solution, such decay can induce oxidation-state changes by radiolysis, even in the absence of redox agents. Radiolytic decomposition of the surrounding water can lead to the reduction of Pu(VI) and Pu(V) to Pu(IV) and Pu(III) and, consequently, to a change in the chemical behavior of plutonium over time. Radiolysis of hydrogenous materials in the vicinity of plutonium metal can also speed up surface corrosion dramatically by making hydrogen available. Therefore, it is especially important to avoid access to hydrogenous materials when storing plutonium. In geologic media, plutonium may also cause lattice damage and amorphization of the host solid leading to potentially increased leaching rates.

The plutonium challenges ahead—stockpile stewardship, nonproliferation, environmental issues, and nuclear power—require a better fundamental understanding of plutonium in metals or ceramics, on surfaces, in solution, and in the environment. ■



These glowing embers are small pieces of plutonium metal burning spontaneously in air under static conditions.



When a plutonium nucleus undergoes α -decay, the recoiling uranium and helium nuclei knock plutonium atoms from their lattice sites. Displaced plutonium atoms come to rest at interstitial sites and leave lattice vacancies behind. Each displaced plutonium atom creates a Frenkel pair—consisting of a vacancy and a self-interstitial. Each decay event creates more than 2000 Frenkel pairs. The cascade size is the space occupied by the Frenkel pairs created during a certain decay event.

Acknowledgments

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