Plutonium
An overview
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Overview

Plutonium

<table>
<thead>
<tr>
<th>Plutonium</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>silvery white</td>
<td></td>
</tr>
</tbody>
</table>

General properties

<table>
<thead>
<tr>
<th>Name, symbol, number</th>
<th>plutonium, Pu, 94</th>
</tr>
</thead>
</table>
| Pronunciation | /pluːˈtoʊniəm/  
ploo-toe-nee-əm |
| Element category | actinide |
| Group, period, block | n/a, 7, f |
| Standard atomic weight | (244) g·mol$^{-1}$ |
| Electron configuration | [Ra] 5f$^6$ 7s$^2$ |
| Electrons per shell | 2, 8, 18, 32, 24, 8, 2 (Image) |

Physical properties

| Phase | solid |
| Density (near r.t.) | 19.816 g·cm$^{-3}$ |
| Liquid density at m.p. | 16.63 g·cm$^{-3}$ |
| Melting point | 912.5 K, 639.4 °C, 1182.9 °F |
| Boiling point | 3505 K, 3228 °C, 5842 °F |
| Heat of fusion | 2.82 kJ·mol$^{-1}$ |
| Heat of vaporization | 333.5 kJ·mol$^{-1}$ |
| Specific heat capacity | (25 °C) 35.5 J·mol$^{-1}$·K$^{-1}$ |

Vapor pressure
<table>
<thead>
<tr>
<th>$P$/Pa</th>
<th>1</th>
<th>10</th>
<th>100</th>
<th>1 k</th>
<th>10 k</th>
<th>100 k</th>
</tr>
</thead>
<tbody>
<tr>
<td>at 7/K</td>
<td>1756</td>
<td>1953</td>
<td>2198</td>
<td>2511</td>
<td>2926</td>
<td>3499</td>
</tr>
</tbody>
</table>

**Atomic properties**

- **Oxidation states**: 7, 6, 5, 4, 3 (amphoteric oxide)
- **Electronegativity**: 1.28 (Pauling scale)
- **Ionization energies**: 1st: 584.7 kJ·mol$^{-1}$
- **Atomic radius**: 159 pm
- **Covalent radius**: 187±1 pm

**Miscellanea**

- **Crystal structure**: monoclinic
- **Magnetic ordering**: paramagnetic
- **Electrical resistivity**: (0 °C) 1.460 µΩ·m
- **Thermal conductivity**: (300 K) 6.74 W·m$^{-1}$·K$^{-1}$
- **Thermal expansion**: (25 °C) 46.7 µm·m$^{-1}$·K$^{-1}$
- **Speed of sound**: 2260 m/s
- **Young's modulus**: 96 GPa
- **Shear modulus**: 43 GPa
- **Poisson ratio**: 0.21
- **CAS registry number**: 7440-07-5

**Most stable isotopes**

<table>
<thead>
<tr>
<th>iso</th>
<th>NA</th>
<th>half-life</th>
<th>DM</th>
<th>DE (MeV)</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}$Pu</td>
<td>syn</td>
<td>87.74 y</td>
<td>SF</td>
<td>204.66</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>α</td>
<td></td>
<td>5.5</td>
<td></td>
<td>$^{234}$U</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>trace</td>
<td>2.41 × 10$^4$ y</td>
<td>SF</td>
<td>207.06</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>α</td>
<td></td>
<td>5.157</td>
<td></td>
<td>$^{235}$U</td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td>syn</td>
<td>6.5 × 10$^3$ y</td>
<td>SF</td>
<td>205.66</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>α</td>
<td></td>
<td>5.256</td>
<td></td>
<td>$^{236}$U</td>
</tr>
<tr>
<td>$^{241}$Pu</td>
<td>syn</td>
<td>14 y</td>
<td>β$^-$</td>
<td>0.02078</td>
<td>$^{241}$Am</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SF</td>
<td>210.83</td>
<td>—</td>
</tr>
<tr>
<td>$^{242}$Pu</td>
<td>syn</td>
<td>3.73 × 10$^5$ y</td>
<td>SF</td>
<td>209.47</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>α</td>
<td></td>
<td>4.984</td>
<td></td>
<td>$^{238}$U</td>
</tr>
<tr>
<td>$^{244}$Pu</td>
<td>trace</td>
<td>8.08 × 10$^7$ y</td>
<td>α</td>
<td>4.666</td>
<td>$^{240}$U</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SF</td>
<td></td>
<td>—</td>
</tr>
</tbody>
</table>
Plutonium ( /ˈpluːtəniəm/ ploo-tuh-nee-əm) is a transuranic radioactive chemical element with the chemical symbol Pu and atomic number 94. It is an actinide metal of silvery-white appearance that tarnishes when exposed to air, forming a dull coating when oxidized. The element normally exhibits six allotropes and four oxidation states. It reacts with carbon, halogens, nitrogen and silicon. When exposed to moist air, it forms oxides and hydrides that expand the sample up to 70% in volume, which in turn flake off as a powder that can spontaneously ignite. It is also a radioactive poison that accumulates in bone marrow. These and other properties make the handling of plutonium extremely dangerous.

Plutonium is the heaviest primordial element (see also primordial nuclide), by virtue of its most stable isotope, plutonium-244, whose half-life of about 80 million years is just long enough for the element to be found in trace quantities in nature.\(^3\) Plutonium is also a byproduct of nuclear fission in reactors: Some of the neutrons released by the fission process convert uranium-238 nuclei into plutonium.\(^4\)

The most important isotope of plutonium is plutonium-239, with a half-life of 24,100 years. Plutonium-239 is the isotope most useful for nuclear weapons. Plutonium-239 and 241 are fissile, meaning the nuclei of their atoms can split when bombarded by neutrons, releasing energy, gamma radiation and more neutrons. These neutrons can sustain a nuclear chain reaction, leading to applications in nuclear weapons and nuclear reactors.

Plutonium-238 has a half-life of 88 years and emits alpha particles. It is a heat source in radioisotope thermoelectric generators, which are used to power some spacecraft. Plutonium-240 has a high rate of spontaneous fission, raising the neutron flux of any sample it is in. The presence of plutonium-240 limits a sample’s usability for weapons or reactor fuel, and determines its grade. Plutonium isotopes are expensive and inconvenient to separate, so particular isotopes are usually manufactured in specialized reactors.

Plutonium was first synthesized in 1940 by a team led by Glenn T. Seaborg and Edwin McMillan at the University of California, Berkeley laboratory by bombarding uranium-238 with deuterons. Trace amounts of plutonium were subsequently discovered in nature. Producing plutonium in useful quantities for the first time was a major part of the Manhattan Project during World War II, which developed the first atomic bombs. The first nuclear test, "Trinity" (July 1945), and the second atomic bomb used to destroy a city (Nagasaki, Japan, in August 1945), "Fat Man", both had cores of plutonium-239. Human radiation experiments studying plutonium were conducted without informed consent, and a number of criticality accidents, some lethal, occurred during and after the war. Disposal of plutonium waste from nuclear power plants and dismantled nuclear weapons built during the Cold War is a nuclear-proliferation and environmental concern. Other sources of plutonium in the environment are fallout from numerous above-ground nuclear tests (now banned).

**Characteristics**

**Physical properties**

Plutonium, like most metals, has a bright silvery appearance at first, much like nickel, but it oxidizes very quickly to a dull gray, although yellow and olive green are also reported.\(^5\) [6] At room temperature plutonium is in its alpha form (alpha). This, the most common structural form of the element (allotrope), is about as hard and brittle as grey cast iron unless it is alloyed with other metals to make it soft and ductile. Unlike most metals, it is not a good conductor of heat or electricity. It has a low melting point (640 °C) and an unusually high boiling point (3,327 °C).\(^5\)

Alpha decay, the release of a high-energy helium nucleus, is the most common form of radioactive decay for plutonium.\(^7\) A 5 kg mass of \(^{239}\)Pu contains about 12.5 × 10^24 atoms. With a half life of 24,100 years, about 11.5 × 10^{12} of its atoms decay each second by emitting a 5.157 MeV alpha particle. This amounts to 9.68 watts of power. Heat produced by the deceleration of these alpha particles makes it warm to the touch.\(^8\) [9]

Resistivity is a measure of how strongly a material opposes the flow of electric current. The resistivity of plutonium at room temperature is very high for a metal, and it gets even higher with lower temperatures, which is unusual for metals.\(^10\) This trend continues down to 100 K, below which resistivity rapidly decreases for fresh samples.\(^10\)
Plutonium

Resistivity then begins to increase with time at around 20 K due to radiation damage, with the rate dictated by the isotopic composition of the sample.\cite{10}

Because of self-irradiation, a sample of plutonium fatigues throughout its crystal structure, meaning the ordered arrangement of its atoms becomes disrupted by radiation with time.\cite{11} Self-irradiation can also lead to annealing which counteracts some of the fatigue effects as temperature increases above 100 K.\cite{12}

Unlike most materials, plutonium increases in density when it melts, by 2.5%, but the liquid metal exhibits a linear decrease in density with temperature.\cite{10} Near the melting point, the liquid plutonium has also very high viscosity and surface tension as compared to other metals.\cite{11}

**Allotropes**

Plutonium normally has six allotropes and forms a seventh (zeta, ζ) at high temperature within a limited pressure range.\cite{13} These allotropes, which are different structural modifications or forms of an element, have very similar internal energies but significantly varying densities and crystal structures. This makes plutonium very sensitive to changes in temperature, pressure, or chemistry, and allows for dramatic volume changes following phase transitions from one allotropic form to another.\cite{11} Densities of the different allotropes vary from 16.00 g/cm$^3$ to 19.86 g/cm$^3$.\cite{14}

The presence of these many allotropes makes machining plutonium very difficult, as it changes state very readily. For example, the α form exists at room temperature in unalloyed plutonium. It has machining characteristics similar to cast iron but changes to the plastic and malleable β form (beta) at slightly higher temperatures.\cite{15} The reasons for the complicated phase diagram are not entirely understood. The α form has a low-symmetry monoclinic structure, hence its brittleness, strength, compressibility, and poor conductivity.\cite{13}

Plutonium in the δ form normally exists in the 310 °C to 452 °C range but is stable at room temperature when alloyed with a small percentage of gallium, aluminium, or cerium, enhancing workability and allowing it to be welded.\cite{15} The delta form has more typical metallic character, and is roughly as strong and malleable as aluminium.\cite{13} In fission weapons, the explosive shock waves used to compress a plutonium core will also cause a transition from the usual delta phase plutonium to the denser alpha form, significantly helping to achieve supercriticality.\cite{16} The ε phase, the highest temperature solid allotrope, exhibits anomalously high atomic self-diffusion compared to other elements.\cite{11}
Nuclear fission

Plutonium is an element in which the 5f electrons are the transition border between delocalized and localized; it is therefore considered one of the most complex elements. It is a radioactive actinide metal whose isotope, plutonium-239, is one of the three primary fissile isotopes (uranium-233 and uranium-235 are the other two); plutonium-241 is also highly fissile. To be considered fissile, an isotope's atomic nucleus must be able to break apart or fission when struck by a slow moving neutron, and to release enough additional neutrons in the process to sustain the nuclear chain reaction by splitting further nuclei.

Plutonium-239 has a multiplication factor (k) larger than one, which means that if the metal is present in sufficient mass and with an appropriate geometry (e.g., a compressed sphere), it can form a critical mass. During fission, a fraction of the binding energy, which holds a nucleus together, is released as a large amount of electromagnetic and kinetic energy (much of the latter being quickly converted to thermal energy). Fission of a kilogram of plutonium-239 can produce an explosion equivalent to 21,000 tons of TNT. It is this energy that makes plutonium-239 useful in nuclear weapons and reactors.

The presence of the isotope plutonium-240 in a sample limits its nuclear bomb potential, as plutonium-240 has a relatively high spontaneous fission rate (~440 fissions per second per gram—over 1,000 neutrons per second per gram), raising the background neutron levels and thus increasing the risk of predetonation. Plutonium is identified as either weapons-grade, fuel grade, or power reactor grade based on the percentage of plutonium-240 that it contains. Weapons-grade plutonium contains less than 7% plutonium-240. Fuel grade plutonium contains from 7% to less than 19%, and power reactor grade contains 19% or more plutonium-240. Supergrade plutonium, with less than 4% of plutonium-240, is used in U.S. Navy weapons stored in proximity to ship and submarine crews, due to its lower radioactivity. The isotope plutonium-238 is not fissile but can undergo nuclear fission easily with fast neutrons as well as alpha decay.
Isotopes and synthesis

Twenty radioactive isotopes of plutonium have been characterized. The longest-lived are plutonium-244, with a half-life of 80.8 million years, plutonium-242, with a half-life of 373,300 years, and plutonium-239, with a half-life of 24,110 years. All of the remaining radioactive isotopes have half-lives that are less than 7,000 years. This element also has eight metastable states, though none are stable and all have half-lives less than one second.[7]

The isotopes of plutonium range in mass number from 228 to 247. The primary decay modes of isotopes with mass numbers lower than the most stable isotope, plutonium-244, are spontaneous fission and α emission, mostly forming uranium (92 protons) and neptunium (93 protons) isotopes as decay products (neglecting the wide range of daughter nuclei created by fission processes). The primary decay mode for isotopes with mass numbers higher than plutonium-244 is β emission, mostly forming americium (95 protons) isotopes as decay products. Plutonium-241 is the parent isotope of the neptunium decay series, decaying to americium-241 via β or electron emission.[7] [24]

Plutonium-238 and 239 are the most-widely synthesized isotopes.[8] Plutonium-239 is synthesized via the following reaction using uranium (U) and neutrons (n) via beta decay (β−) with neptunium (Np) as an intermediate:[25]

\[
^{238}_{92}U + ^1_0n \rightarrow ^{239}_{92}U \rightarrow ^{239}_{93}Np \rightarrow ^{239}_{94}Pu
\]

Neutrons from the fission of uranium-235 are captured by uranium-238 nuclei to form uranium-239; a beta decay converts a neutron into a proton to form Np-239 (half-life 2.36 days) and another beta decay forms plutonium-239.[26] Workers on the Tube Alloys project had predicted this reaction theoretically in 1940.

Plutonium-238 is synthesized by bombarding uranium-238 with deuterons (D, the nuclei of heavy hydrogen) in the following reaction:[27]

\[
^{238}_{92}U + ^1_2D \rightarrow ^{238}_{93}Np + ^1_0n \quad ; \quad ^{238}_{93}Np \rightarrow ^{238}_{94}Pu
\]

In this process, a deuteron hitting uranium-238 produces two neutrons and neptunium-238, which spontaneously decays by emitting negative beta particles to form plutonium-238.
Decay heat and fission properties

Plutonium isotopes undergo radioactive decay, which produces decay heat. Different isotopes produce different amounts of heat per mass. The decay heat is usually listed as watt/kilogram, or milliwatt/gram. In case of larger pieces of plutonium (e.g. a weapon pit) and inadequate heat removal the resulting self-heating may be significant. All isotopes produce weak gamma on decay.

Decay heat of plutonium isotopes\(^{[28]}\)

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Decay mode</th>
<th>Half-life (years)</th>
<th>Decay heat (W/kg)</th>
<th>Spontaneous fission neutrons (1/(g·s))</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu-238</td>
<td>alpha to U-234</td>
<td>87.74</td>
<td>560</td>
<td>2600</td>
<td>Very high decay heat. Even in small amounts can cause significant self-heating. Used on its own in radioisotope thermoelectric generators.</td>
</tr>
<tr>
<td>Pu-239</td>
<td>alpha to U-235</td>
<td>24100</td>
<td>1.9</td>
<td>0.022</td>
<td>The principal fissile isotope in use.</td>
</tr>
<tr>
<td>Pu-240</td>
<td>alpha to U-236, spontaneous fission</td>
<td>6560</td>
<td>6.8</td>
<td>910</td>
<td>The principal impurity of the Pu-239 isotope. The plutonium grade is usually listed as percentage of Pu-240. High spontaneous fission hinders use in nuclear weapons.</td>
</tr>
<tr>
<td>Pu-241</td>
<td>beta, to Am-241</td>
<td>14.4</td>
<td>4.2</td>
<td>0.049</td>
<td>Decays to americium-241; its buildup presents a radiation hazard in older samples.</td>
</tr>
<tr>
<td>Pu-242</td>
<td>alpha to U-238</td>
<td>376000</td>
<td>0.1</td>
<td>1700</td>
<td></td>
</tr>
</tbody>
</table>

Americium-241, the decay product of plutonium-241, has half-life of 430 years, 1.2 spontaneous fissions per gram per second, and decay heat of 114 watts per kilogram. As its decay produces highly penetrative gamma rays, its presence in plutonium, determined by the original concentration of plutonium-241 and the sample age, increases the radiation exposure of surrounding structures and personnel.

Compounds and chemistry

At room temperature, pure plutonium is silvery in color but gains a tarnish when oxidized.\(^{[29]}\) The element displays four common ionic oxidation states in aqueous solution and one rare one.\(^{[14]}\)

- Pu(III), as Pu\(^{3+}\) (blue lavender)
- Pu(IV), as Pu\(^{4+}\) (yellow brown)
- Pu(V), as PuO\(_2\)\(^{2+}\) (pink?)\(^{[30]}\)
- Pu(VI), as PuO\(_2\)\(^{2+}\) (pink orange)
- Pu(VII), as PuO\(_5\)\(^{3-}\) (green)—the heptavalent ion is rare

The color shown by plutonium solutions depends on both the oxidation state and the nature of the acid anion.\(^{[31]}\) It is the acid anion that influences the degree of complexing—how atoms connect to a central atom—of the plutonium species.

Metallic plutonium is produced by reacting plutonium tetrafluoride with barium, calcium or lithium at 1200 °C.\(^{[32]}\) It is attacked by acids, oxygen, and steam but not by alkalis and dissolves easily in concentrated hydrochloric,
Plutonium is a reactive metal. In moist air or moist argon, the metal oxidizes rapidly, producing a mixture of oxides and hydrides. If the metal is exposed long enough to a limited amount of water vapor, a powdery surface coating of PuO₂ is formed. Also formed is plutonium hydride but an excess of water vapor forms only PuO₂⁻.

With this coating, the metal is pyrophoric, meaning it can ignite spontaneously, so plutonium metal is usually handled in an inert, dry atmosphere of nitrogen or argon. Oxygen retards the effects of moisture and acts as a passivating agent.

Plutonium shows enormous, and reversible, reaction rates with pure hydrogen, forming plutonium hydride. It also reacts readily with oxygen, forming PuO and PuO₂ as well as intermediate oxides; plutonium oxide fills 40% more volume than plutonium metal. It reacts with the halogens, giving rise to compounds such as PuX₃ where X can be F, Cl, Br or I; PuF₄ is also seen. The following oxyhalides are observed: PuOCl, PuOBr and PuOI. It will react with carbon to form PuC, nitrogen to form PuN and silicon to form PuSi₂.

Crucibles used to contain plutonium need to be able to withstand its strongly reducing properties. Refractory metals such as tantalum and tungsten along with the more stable oxides, borides, carbides, nitrides and silicides can tolerate this. Melting in an electric arc furnace can be used to produce small ingots of the metal without the need for a crucible.

Cerium is used as a chemical simulant of plutonium for development of containment, extraction, and other technologies.

### Electronic structure

The anomalous behavior of plutonium is caused by its electronic structure. The energy difference between the 6d and 5f subshells is very low. The size of the 5f shell is just enough to allow the electrons to form bonds within the lattice, on the very boundary between localized and bonding behavior. The proximity of energy levels leads to multiple low-energy electron configurations with near equal energy levels. This leads to competing 5fⁿ7s² and 5fⁿ⁻¹7s²6d¹ configurations, which causes the complexity of its chemical behavior. The highly directional nature of 5f orbitals is responsible for directional covalent bonds in molecules and complexes of plutonium.

### Alloys

Plutonium can form alloys and intermediate compounds with most other metals. Exceptions include lithium, sodium, potassium, and rubidium of the alkali metals; and magnesium, calcium, strontium, and barium of the alkaline earth metals; and europium and ytterbium of the rare earth metals. Partial exceptions include the refractory metals chromium, molybdenum, niobium, tantalum, and tungsten, which are soluble in liquid plutonium, but insoluble or only slightly soluble in solid plutonium. Gallium, aluminium, americium, scandium and cerium can stabilize the δ phase of plutonium for room temperature. Silicon, indium, zinc and zirconium allow formation of metastable δ state when rapidly cooled. High amounts of hafnium, holmium and thallium also allows retaining some of the δ phase at room temperature. Neptunium is the only element that can stabilize the α phase at higher temperatures.

Plutonium alloys can be produced by adding a metal to molten plutonium. If the alloying metal is sufficiently reductive, plutonium can be added in the form of oxides or halides. The δ phase plutonium-gallium and plutonium-aluminium alloys are produced by adding plutonium(III) fluoride to molten gallium or aluminium, which
has the advantage of avoiding dealing directly with the highly reactive plutonium metal.\footnote{37}

- **Plutonium-gallium** is used for stabilizing the $\delta$ phase of plutonium, avoiding the $\alpha$-phase and $\alpha-\delta$ related issues. Its main use is in pits of implosion nuclear weapons.\footnote{38}

- **Plutonium-aluminium** is an alternative to the Pu-Ga alloy. It was the original element considered for $\delta$ phase stabilization, but its tendency to react with the alpha particles and release neutrons reduces its usability for nuclear weapon pits. Plutonium-aluminium alloy can be also used as a component of nuclear fuel.\footnote{39}

- **Plutonium-gallium-cobalt** alloy ($\text{PuCoGa}_5$) is an unconventional superconductor, showing superconductivity below 18.5 kelvin, an order of magnitude higher than the highest between heavy fermion systems, and has large critical current.\footnote{17} \footnote{40}

- **Plutonium-zirconium** alloy can be used as nuclear fuel.\footnote{41}

- **Plutonium-cerium** and **plutonium-cerium-cobalt** alloys are used as nuclear fuels.\footnote{42}

- **Plutonium-uranium**, with about 15–30 mol.\% plutonium, can be used as a nuclear fuel for fast breeder reactors. Its pyrophoric nature and high susceptibility to corrosion to the point of self-igniting or disintegrating after exposure to air require alloying with other components. Addition of aluminium, carbon or copper did not improve disintegration rates markedly, zirconium and iron alloys have better corrosion resistance but they disintegrate in several months in air as well. Addition of titanium and/or zirconium significantly increases the melting point of the alloy.\footnote{43}

- **Plutonium-uranium-titanium** and **plutonium-uranium-zirconium** were investigated for use as nuclear fuels. The addition of the third element increases corrosion resistance, reduces flammability, and improves ductility, fabricability, strength, and thermal expansion. **Plutonium-uranium-molybdenum** has the best corrosion resistance, forming a protective film of oxides, but titanium and zirconium are preferred for physics reasons.\footnote{43}

- **Thorium-uranium-plutonium** was investigated as a nuclear fuel for fast breeder reactors.\footnote{43}

### Occurrence

Trace amounts of at least two plutonium isotopes (plutonium-239 and 244) can be found in nature. Small traces of plutonium-239, a few parts per trillion, and its decay products are naturally found in some concentrated ores of uranium,\footnote{44} such as the natural nuclear fission reactor in Oklo, Gabon.\footnote{45} The ratio of plutonium-239 to uranium at the Cigar Lake Mine uranium deposit ranges from $2.4 \times 10^{-12}$ to $44 \times 10^{-12}$.\footnote{46} Even smaller amounts of primordial plutonium-244 occur naturally due to its relatively long half-life of about 80 million years.\footnote{47} These trace amounts of Pu-239 originate in the following fashion: On rare occasions, U-238 undergoes spontaneous fission, and in the process, the nucleus emits one or two free neutrons with some kinetic energy. When one of these neutrons strikes the nucleus of another U-238 atom, it is absorbed by the atom, which becomes U-239. With quite-short half-lives, U-239 decays to neptunium-239 (Np-239), and then Np-239 decays into Pu-239.

Since the relatively long-lived isotope plutonium-240 occurs in the decay chain of plutonium-244 it should also be present, albeit 10,000 times rarer still. Finally, exceedingly small amounts of plutonium-238, attributed to the incredibly rare double beta decay of uranium-238, have been found in natural uranium samples.\footnote{48}

Minute traces of plutonium are usually found in the human body due to the 550 atmospheric and underwater nuclear tests that have been carried out, and to a small number of major nuclear accidents. Most atmospheric and underwater nuclear testing was stopped by the Limited Test Ban Treaty in 1963, which was signed and ratified by the United States, the United Kingdom, the Soviet Union, and other nations. Continued atmospheric nuclear weapons testing since 1963 by non-treaty nations included those by China (atomic bomb test above the Gobi Desert in 1964, hydrogen bomb test in 1967, and follow-on tests), and France (tests as recently as the 1980s).

Because it is purposely manufactured for nuclear weapons and nuclear reactors, plutonium-239 is the most abundant isotope of plutonium by far.\footnote{34}

It is also hypothetically possible for minute quantities of plutonium to be produced by the natural bombardment of uranium ores with cosmic rays.
History

Discovery

Enrico Fermi and a team of scientists at the University of Rome reported that they had discovered element 94 in 1934. Fermi called the element **hesperium** and mentioned it in his Nobel Lecture in 1938. The sample was actually a mixture of barium, krypton, and other elements, but this was not known at the time because nuclear fission had not been discovered yet.

Plutonium (specifically, plutonium-238) was first produced and isolated on December 14, 1940, and chemically identified on February 23, 1941, by Dr. Glenn T. Seaborg, Edwin M. McMillan, J. W. Kennedy, and A. C. Wahl by deuteron bombardment of uranium in the 60-inch (150 cm) cyclotron at the University of California, Berkeley. In the 1940 experiment, neptunium-238 was created directly by the bombardment but decayed by beta emission two days later, which indicated the formation of element 94.

A paper documenting the discovery was prepared by the team and sent to the journal *Physical Review* in March 1941. The paper was withdrawn before publication after the discovery that an isotope of the new element (plutonium-239) could undergo nuclear fission in a way that might be useful in an atomic bomb. Publication was delayed until a year after the end of World War II due to security concerns.

Edwin McMillan had recently named the first transuranium element after the planet Neptune and suggested that element 94, being the next element in the series, be named for what was then considered the next planet, Pluto. Seaborg originally considered the name "plutium", but later thought that it did not sound as good as "plutonium." He chose the letters "Pu" as a joke, which passed without notice into the periodic table. Alternative names considered by Seaborg and others were "ultimium" or "extremium" because of the erroneous belief that they had found the last possible element on the periodic table.

Early research

The basic chemistry of plutonium was found to resemble uranium after a few months of initial study. Early research was continued at the secret Metallurgical Laboratory of the University of Chicago. On August 18, 1942, a trace quantity of this element was isolated and measured for the first time. About 50 micrograms of plutonium-239 combined with uranium and fission products was produced and only about 1 microgram was isolated. This procedure enabled chemists to determine the new element's atomic weight.

In November 1943 some plutonium trifluoride was reduced to create the first sample of plutonium metal: a few micrograms of metallic beads. Enough plutonium was produced to make it the first synthetically made element to be visible with the unaided eye.

The nuclear properties of plutonium-239 were also studied; researchers found that when it is hit by a neutron it breaks apart (fissions) by releasing more neutrons and energy. These neutrons can hit other atoms of plutonium-239 and so on in an exponentially fast chain reaction. This can result in an explosion large enough to destroy a city if enough of the isotope is concentrated to form a critical mass.
Production during the Manhattan Project

During World War II the U.S. government established the Manhattan Project, which was tasked with developing an atomic bomb. The three primary research and production sites of the project were the plutonium production facility at what is now the Hanford Site, the uranium enrichment facilities at Oak Ridge, Tennessee, and the weapons research and design laboratory, now known as Los Alamos National Laboratory.\[^{61}\]

The first production reactor that made plutonium-239 was the X-10 Graphite Reactor. It went online in 1943 and was built at a facility in Oak Ridge that later became the Oak Ridge National Laboratory.\[^{34}\]\[^{62}\]

On April 5, 1944, Emilio Segrè at Los Alamos received the first sample of reactor-produced plutonium from Oak Ridge.\[^{63}\]\[^{63}\] Within ten days, he discovered that reactor-bred plutonium had a higher concentration of the isotope plutonium-240 than cyclotron-produced plutonium. Plutonium-240 has a high spontaneous fission rate, raising the overall background neutron level of the plutonium sample. The original gun-type plutonium weapon, code-named "Thin Man", had to be abandoned as a result—the increased number of spontaneous neutrons meant that nuclear pre-detonation (a fizzle) would be likely.

The entire plutonium weapon design effort at Los Alamos was soon changed to the more complicated implosion device, code-named "Fat Man." With an implosion weapon, a solid (or, in later designs, hollow) sphere of plutonium is compressed to a high density with explosive lenses—a technically more daunting task than the simple gun-type design, but necessary in order to use plutonium for weapons purposes. (Enriched uranium, by contrast, can be used with either method.)\[^{63}\]

Construction of the Hanford B Reactor, the first industrial-sized nuclear reactor for the purposes of material production, was completed in March 1945. B Reactor produced the fissile material for the plutonium weapons used during World War II.\[^{64}\]\[^{64}\] B, D and F were the initial reactors built at Hanford, and six additional plutonium-producing reactors were built later at the site.\[^{65}\]

In 2004, a safe was discovered during excavations of a burial trench at the Hanford nuclear site. Inside the safe were various items, including a large glass bottle containing a whitish slurry which was subsequently identified as the oldest sample of weapons-grade plutonium known to exist. Isotope analysis by Pacific Northwest National Laboratory indicated that the plutonium in the bottle was manufactured in the X-10 reactor at Oak Ridge during 1944.\[^{66}\]\[^{66}\]\[^{67}\]\[^{67}\]\[^{68}\]
Trinity and Fat Man atomic bombs

The first atomic bomb test, codenamed "Trinity" and detonated on July 16, 1945, near Alamogordo, New Mexico, used plutonium as its fissile material.[44] The implosion design of "the Gadget", as the Trinity device was code-named, used conventional explosive lenses to compress a sphere of plutonium into a supercritical mass, which was simultaneously showered with neutrons from the "Urchin", an initiator made of polonium and beryllium (neutron source: \((\alpha, n)\) reaction).[34] Together, these ensured a runaway chain reaction and explosion. The overall weapon weighed over 4 tonnes, although it used just 6.2 kg of plutonium in its core.[69] About 20% of the plutonium used in the Trinity weapon underwent fission, resulting in an explosion with an energy equivalent to approximately 20,000 tons of TNT.[70][71]

An identical design was used in the "Fat Man" atomic bomb dropped on Nagasaki, Japan, on August 9, 1945, killing 70,000 people and wounding another 100,000.[34] The "Little Boy" bomb dropped on Hiroshima three days earlier used uranium-235, not plutonium. Japan capitulated on August 15 to General Douglas MacArthur. Only after the announcement of the first atomic bombs was the existence of plutonium made public.

Cold War use and waste

Large stockpiles of weapons-grade plutonium were built up by both the Soviet Union and the United States during the Cold War. The U.S. reactors at Hanford and the Savannah River Site in South Carolina produced 103 tonnes,[72] and an estimated 170 tonnes of military-grade plutonium was produced in Russia.[73][74] Each year about 20 tonnes of the element is still produced as a by-product of the nuclear power industry.[14] As much as 1000 tonnes of plutonium may be in storage with more than 200 tonnes of that either inside or extracted from nuclear weapons.[34] SIPRI estimated the world plutonium stockpile in 2007 as about 500 tons, divided equally between weapon and civilian stocks.[75]

Since the end of the Cold War, these stockpiles have become a focus of nuclear proliferation concerns. In the U.S., some plutonium extracted from dismantled nuclear weapons is melted to form glass logs of plutonium oxide that weigh two tonnes.[34] The glass is made of borosilicates mixed with cadmium and gadolinium.[76] These logs are planned to be encased in stainless steel and stored as much as 4 km underground in bore holes that will be back-filled with concrete.[34] As of 2008, the only facility in the U.S. that is scheduled to store plutonium in this way is the Yucca Mountain nuclear waste repository, which is about 100 miles (160 km) north-east of Las Vegas, Nevada.[77] Local and state opposition to this plan has delayed efforts to store nuclear waste at Yucca Mountain. In March 2010, the Department of Energy withdrew its license application for the Yucca Mountain repository "with prejudice" and eliminated funding for the Office of Civilian Radioactive Waste Management, which had managed the Yucca Mountain site for 25 years.[78]
Medical experimentation
During and after the end of World War II, scientists working on the Manhattan Project and other nuclear weapons research projects conducted studies of the effects of plutonium on laboratory animals and human subjects.[79] Animal studies found that a few milligrams of plutonium per kilogram of tissue is a lethal dose.[80]

In the case of human subjects, this involved injecting solutions containing (typically) five micrograms of plutonium into hospital patients thought to be either terminally ill, or to have a life expectancy of less than ten years either due to age or chronic disease condition.[79] This was reduced to one microgram in July 1945 after animal studies found that the way plutonium distributed itself in bones was more dangerous than radium.[80]

Eighteen human test subjects were injected with plutonium without informed consent. The tests were used to create diagnostic tools to determine the uptake of plutonium in the body in order to develop safety standards for working with plutonium.[79]

The episode is now considered to be a serious breach of medical ethics and of the Hippocratic Oath. More sympathetic commentators have noted that while it was definitely a breach in trust and ethics, "the effects of the plutonium injections were not as damaging to the subjects as the early news stories painted, nor were they so inconsequential as many scientists, then and now, believe."[81]

Applications
Explosives
The isotope plutonium-239 is a key fissile component in nuclear weapons, due to its ease of fission and availability. Encasing the bomb's plutonium pit in a tamper (an optional layer of dense material) decreases the amount of plutonium needed to reach critical mass by reflecting escaping neutrons back into the plutonium core. This reduces the amount of plutonium needed to reach criticality from 16 kg to 10 kg, which is a sphere with a diameter of about 10 centimeters (4 in).[82] This critical mass is about a third of that for uranium-235.[8]

The "Fat Man"-type plutonium bombs produced during the Manhattan Project used explosive compression of plutonium to obtain significantly higher densities than normal, combined with a central neutron source to begin the reaction and increase efficiency. Thus only 6.2 kg of plutonium was needed for an explosive yield equivalent to 20 kilotons of TNT.[70] [83] (See also Nuclear weapon design.) Hypothetically, as little as 4 kg of plutonium—and maybe even less—could be used to make a single atomic bomb using very sophisticated assembly designs.[83]

Mixed oxide fuel
Spent nuclear fuel from normal light water reactors contains Plutonium, but it is a mixture of Plutonium-242, 240, 239 and 238. The mixture is not sufficiently enriched for efficient nuclear weapons, but can be used once as MOX fuel. Accidental neutron capture causes the amount of Plutonium-242 and 240 to grow each time the Plutonium is irradiated in a reactor with low-speed "thermal" neutrons, so that after the second cycle, the Plutonium can only be consumed by fast neutron reactors. If fast neutron reactors are not available (the normal case), excess Plutonium is usually discarded, and forms the longest-lived component of nuclear waste. The desire to consume this Plutonium and other transuranic fuels and reduce the radiotoxicity of the waste is the usual reason nuclear engineers give to make fast neutron reactors.
The most common chemical process, PUREX (Plutonium–URanium EXtraction) reprocesses spent nuclear fuel to extract plutonium and uranium which can be used to form a mixed oxide "MOX fuel" for reuse in nuclear reactors. Weapons grade plutonium can be added to the fuel mix. MOX fuel is used in light water reactors and consists of 60 kg of plutonium per tonne of fuel; after four years, three-quarters of the plutonium is burned (turned into other elements). Breeder reactors are specifically designed to create more fissionable material than they consume. MOX fuel has been in use since the 1980s and is widely used in Europe. In September 2000, the United States and the Russian Federation signed a Plutonium Management and Disposition Agreement by which each agreed to dispose of 34 tonnes of weapon grade plutonium. The U.S. Department of Energy plans to dispose of 34 tonnes of weapon grade plutonium in the United States before the end of 2019 by converting the plutonium to a MOX fuel to be used in commercial nuclear power reactors.

MOX fuel improves total burnup. A fuel rod is reprocessed after three years of use to remove waste products, which by then account for 3% of the total weight of the rods. Any uranium or plutonium isotopes produced during those three years are left and the rod goes back into production. The presence of up to 1% gallium per mass in weapon grade plutonium alloy has the potential to interfere with long-term operation of a light water reactor.

Plutonium recovered from spent reactor fuel poses a less significant proliferation hazard, because of excessive contamination with non-fissile plutonium-240 and plutonium-242. Separation of the isotopes is not feasible. A dedicated reactor operating on very low burnup is generally required to produce material suitable for use in efficient nuclear weapons. While 'weapons-grade' plutonium is defined to contain at least 92% plutonium-239, the United States have managed to detonate an under-20Kt device using plutonium believed to contain only about 85% plutonium-239, so called 'fuel-grade' plutonium. The 'reactor grade' plutonium produced by a regular LWR burnup cycle typically contains less than 60% Pu-239, with up to 30% parasitic Pu-240/Pu-242, and 10-15% fissile Pu-241. It's unknown if a device using plutonium obtained from reprocessed civil nuclear waste can be detonated, however such a device could hypothetically fizzle and spread radioactive materials over a large urban area. The IAEA conservatively classifies plutonium of all isotopic vectors as "direct-use" material, that is, "nuclear material that can be used for the manufacture of nuclear explosives components without transmutation or further enrichment".

Pu-241 has recently been suggested for use as a denaturing agent in plutonium reactor fuel rods to further limit its proliferation potential.

**Power and heat source**

The isotope plutonium-238 has a half-life of 87.74 years. It emits a large amount of thermal energy with low levels of both gamma rays/particles and spontaneous neutron rays/particles. Being an alpha emitter, it combines high energy radiation with low penetration and thereby requires minimal shielding. A sheet of paper can be used to shield against the alpha particles emitted by plutonium-238 while one kilogram of the isotope can generate about 570 watts of heat energy.

These characteristics make it well-suited for electrical power generation for devices which must function without direct maintenance for timescales approximating a human lifetime. It is therefore used in radioisotope thermoelectric generators and radioisotope heater units such as those in the Cassini, Voyager and New Horizons space probes.

The twin Voyager spacecraft were launched in 1977 with each containing a 500 watt plutonium power source. Over 30 years later each source is still producing about 300 watts which allows limited operation of each spacecraft.
Earlier versions of the same technology powered the ALSEP and EASEP systems including seismic experiments on the Apollo 14 Moon mission.\[^{34}\]

Plutonium-238 has also been used successfully to power artificial heart pacemakers, to reduce the risk of repeated surgery.\[^{93}\][^94] It has been largely replaced by lithium-based primary cells, but as of 2003 there were somewhere between 50 and 100 plutonium-powered pacemakers still implanted and functioning in living patients.\[^{95}\] Plutonium-238 was studied as way to provide supplemental heat to scuba diving.\[^{96}\] Plutonium-238 mixed with beryllium is used to generate neutrons for research purposes.\[^{34}\]

**Precautions**

**Toxicity**

Isotopes and compounds of plutonium are radioactive and accumulate in bone marrow. Contamination by plutonium oxide has resulted from a number of nuclear disasters and radioactive incidents including military nuclear accidents where nuclear weapons have burned.\[^{97}\] Studies of the negligible effects of these smaller releases, as well as of the widespread radiation poisoning sickness and death following the atomic bombings of Hiroshima and Nagasaki, have provided considerable information regarding the dangers, symptoms and prognosis of Radiation poisoning.\[^{98}\]

During the decay of plutonium, three types of radiation are released—alpha, beta, and gamma. Alpha radiation can travel only a short distance and cannot travel through the outer, dead layer of human skin. Beta radiation can penetrate human skin, but cannot go all the way through the body. Gamma radiation can go all the way through the body.\[^{99}\] Alpha, beta, and gamma radiation are all forms of ionizing radiation. Either acute or longer-term exposure carries a danger of unfavorable health outcomes including radiation sickness, cancer, and death. The danger increases with the amount of exposure.

Even though alpha radiation can not penetrate the skin, ingested or inhaled plutonium does irradiate internal organs.\[^{34}\] The skeleton, where plutonium is absorbed, and the liver, where it collects and becomes concentrated, are at risk.\[^{33}\] Plutonium is not absorbed into the body efficiently when ingested; only 0.04% of plutonium oxide is absorbed after ingestion.\[^{34}\] Plutonium absorbed by the body is excreted very slowly, with a biological half-life of 200 years.\[^{100}\] Plutonium passes only slowly through cell membranes and intestinal boundaries, so absorption by ingestion and incorporation into bone structure proceeds very slowly.\[^{101}\][^102]

Plutonium is more dangerous when inhaled than when ingested. The risk of lung cancer increases once the total radiation dose equivalent of inhaled plutonium exceeds 400 mSv.\[^{103}\] The U.S. Department of Energy estimates that the lifetime cancer risk from inhaling 5,000 plutonium particles, each about 3 microns wide, to be 1% over the background U.S. average.\[^{104}\] Ingestion or inhalation of large amounts may cause acute radiation poisoning and death; no human is known to have died because of inhaling or ingesting plutonium, and many people have measurable amounts of plutonium in their bodies.\[^{88}\]

The "hot particle" theory in which a particle of plutonium dust radiates a localized spot of lung tissue has been tested and found false—such particles are more mobile than originally thought and toxicity is not measurably increased due to particulate form.\[^{101}\]

However, when inhaled, plutonium can pass into the bloodstream. Once in the bloodstream, plutonium moves throughout the body and into the bones, liver, or other body organs. Plutonium that reaches body organs generally stays in the body for decades and continues to expose the surrounding tissue to radiation and thus may cause cancer.\[^{105}\]

A commonly cited quote by Ralph Nader, states that a pound of plutonium dust spread into the atmosphere would be enough to kill 8 billion people. However, the math shows that one pound of plutonium could kill no more than 2 million people by inhalation. This makes the toxicity of plutonium roughly equivalent with that of nerve gas.\[^{106}\]
Several populations of people who have been exposed to plutonium dust (e.g. people living down-wind of Nevada test sites, Hiroshima survivors, nuclear facility workers, and "terminally ill" patients injected with Pu in 1945–46 to study Pu metabolism) have been carefully followed and analyzed. These studies generally do not show especially high plutonium toxicity or plutonium-induced cancer results. There were about 25 workers from Los Alamos National Laboratory who inhaled a considerable amount of plutonium dust during the 1940's; according to the hot-particle theory, each of them has a 99.5% chance of being dead from lung cancer by now, but there has not been a single lung cancer among them.

Plutonium has a metallic taste.

**Criticality potential**

Toxicity issues aside, care must be taken to avoid the accumulation of amounts of plutonium which approach critical mass, particularly because plutonium's critical mass is only a third of that of uranium-235. A critical mass of plutonium emits lethal amounts of neutrons and gamma rays. Plutonium in solution is more likely to form a critical mass than the solid form due to moderation by the hydrogen in water.

Criticality accidents have occurred in the past, some of them with lethal consequences. Careless handling of tungsten carbide bricks around a 6.2 kg plutonium sphere resulted in a fatal dose of radiation at Los Alamos on August 21, 1945, when scientist Harry K. Daghlian, Jr. received a dose estimated to be 5.1 Sievert (510 rems) and died 28 days later. Nine months later, another Los Alamos scientist, Louis Slotin, died from a similar accident involving a beryllium reflector and the same plutonium core (the so-called "demon core") that had previously claimed the life of Daghlian. These incidents were fictionalized in the 1989 film *Fat Man and Little Boy*.

In December 1958, during a process of purifying plutonium at Los Alamos, a critical mass was formed in a mixing vessel, which resulted in the death of a chemical operator named Cecil Kelley. Other nuclear accidents have occurred in the Soviet Union, Japan, the United States and many other countries.

**Flammability**

Metallic plutonium is a fire hazard, especially if the material is finely divided. In a moist environment, plutonium forms hydrides on its surface, which are pyrophoric and may ignite in air at room temperature. Plutonium expands up to 70% in volume as it oxidizes and thus may break its container. The radioactivity of the burning material is an additional hazard. Magnesium oxide sand is probably the most effective material for extinguishing a plutonium fire. It cools the burning material, acting as a heat sink, and also blocks off oxygen. Special precautions are necessary to store or handle plutonium in any form; generally a dry inert gas atmosphere is required.
Notes

Footnotes
[18] Stwertka 1998
[30] The PuO$_2^+$ ion is unstable in solution and will disproportionate into Pu$_{3}^{4+}$ and PuO$_2^{2+}$; the Pu$_{3}^{4+}$ will then oxidize the remaining PuO$_2^+$ to PuO$_2^{2+}$, being reduced in turn to Pu$_{3}^{4+}$. Thus, aqueous solutions of plutonium tend over time towards a mixture of Pu$_{3}^{4+}$ and PuO$_2^{2+}$.


[33] Miner 1968, p. 545

[34] Emsley 2001


[54] This was not the first time somebody suggested that an element be named "plutonium." A decade after barium was discovered, a Cambridge University professor suggested it be renamed to "plutonium" because the element was not (as suggested by the Greek root, barys, it was named for) heavy. He reasoned that, since it was produced by the relatively new technique of electrolysis, its name should refer to fire. Thus he suggested it be named for the Roman god of the underworld, Pluto. (Heiserman 1992)


[56] As one article puts it, referring to information Seaborg gave in a talk: "The obvious choice for the symbol would have been Pl, but facetiously, Seaborg suggested Pu, like the words a child would exclaim, 'Pee-yoo!' when smelling something bad. Seaborg thought that he would receive a great deal of flak over that suggestion, but the naming committee accepted the symbol without a word."


[59] Room 405 of the George Herbert Jones Laboratory, where the first isolation of plutonium took place, was named a National Historic Landmark in May 1967.

[60] Miner 1968, p. 540


[62] During the Manhattan Project, plutonium was also often referred to as simply "49": the number 4 was for the last digit in 94 (atomic number of plutonium), and 9 was for the last digit in plutonium-239, the weapon-grade fissile isotope used in nuclear bombs.


[64] The American Society of Mechanical Engineers (ASME) established B Reactor as a National Historic Mechanical Engineering Landmark in September 1976.


In August 2008, B Reactor was designated a U.S. National Historic Landmark.


[71] The efficiency calculation is based on the fact that 1 kg of plutonium-239 (or uranium-235) fissioning results in an energy release of approximately 17 kT, leading to a rounded estimate of 1.2 kg plutonium actually fissioned to produce the 20 kT yield. On the figure of 1 kg = 17 kT,


Much of this plutonium was used to make the fissionable cores of a type of thermonuclear weapon employing the Teller–Ulam design. These so-called ‘hydrogen bombs’ are a variety of nuclear weapon that use a fission bomb to trigger the nuclear fusion of heavy hydrogen isotopes. Their destructive yield is commonly in the millions of tons of TNT equivalent compared with the thousands of tons of TNT equivalent of fission-only devices. (Emsley 2001)


Gadolinium zirconium oxide (Gd_Zr O₂) has been studied because it could hold plutonium for up to 30 million years. (Emsley 2001)


Breakdown of plutonium in a spent nuclear fuel rod: plutonium-239 (~58%), 240 (24%), 241 (11%), 242 (5%), and 238 (2%). (Emsley 2001)


Voyager-Spacecraft Lifetime (http://voyager.jpl.nasa.gov/spacecraft/spacecraftlife.html)


Defunct pacemakers with Pu power source (http://www.orau.org/ptp/collection/Miscellaneous/pacemaker.htm)


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Plutonium


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References


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Allotropes of plutonium

Even at ambient pressure, plutonium occurs in a variety of allotropes. These allotropes differ widely in crystal structure and density; the $\alpha$ and $\delta$ allotropes differ in density by more than 25% at constant pressure.

Plutonium normally has six allotropes and forms a seventh ($\zeta$) under high temperature and a limited pressure range. These allotropes have very similar energy levels but significantly varying densities and crystal structures. This makes plutonium very sensitive to changes in temperature, pressure, or chemistry, and allows for dramatic volume changes following phase transitions. Unlike most materials, plutonium increases in density when it melts, by 2.5%, but the liquid metal exhibits a linear decrease in density with temperature. Densities of the different allotropes vary from 16.00 g/cm$^3$ to 19.86 g/cm$^3$.

The presence of these many allotropes makes machining plutonium very difficult, as it changes state very readily. For example, the $\alpha$ phase exists at room temperature in unalloyed plutonium. It has machining characteristics similar to cast iron but changes to the plastic and easy to work $\beta$ phase ($\text{beta phase}$) at slightly higher temperatures. The reasons for the complicated phase diagram are not entirely understood; recent research has focused on constructing accurate computer models of the phase transitions. The $\alpha$ phase has a low-symmetry monoclinic structure, hence its poor conductivity, brittleness, strength and compressibility.

Plutonium in the $\delta$ phase ($\text{delta phase}$) normally exists in the 310 °C to 452 °C range but is stable at room temperature when alloyed with a small percentage of gallium, aluminium, or cerium, enhancing workability and allowing it to be welded in weapons applications. The delta phase has more typical metallic character, and is roughly as strong and malleable as aluminium. In fission weapons, the explosive shock waves used to compress a plutonium core will also cause a transition from the usual delta phase plutonium to the denser alpha phase, significantly helping to achieve supercriticality. The plutonium-gallium alloy is the most common $\delta$-stabilized alloy.

Gallium, aluminium, americium, scandium and cerium can stabilize the $\delta$ phase of plutonium for room temperature. Silicon, indium, zinc and zirconium allow formation of metastable $\delta$ state when rapidly cooled. High amount of hafnium, holmium and thallium also allows retaining some of the $\delta$ phase at room temperature. Neptunium is the only element that can stabilize the $\alpha$ phase at higher temperatures. Titanium, hafnium and zirconium stabilize the $\beta$ phase at room temperature when rapidly cooled.
References


Plutonium (Pu) is an artificial element, except for trace quantities of primordial $^{244}$Pu, and thus a standard atomic mass cannot be given. Like all artificial elements, it has no stable isotopes. It was synthesized long before being found in nature, the first isotope synthesized being $^{238}$Pu in 1940. Twenty plutonium radioisotopes have been characterized. The most stable are Pu-244, with a half-life of 80.8 million years, Pu-242, with a half-life of 373,300 years, and Pu-239, with a half-life of 24,110 years. All of the remaining radioactive isotopes have half-lives that are less than 7,000 years. This element also has eight meta states, though none are very stable (all have half-lives less than one second).

The isotopes of plutonium range in atomic weight from 228.0387 u (Pu-228) to 247.074 u (Pu-247). The primary decay modes before the most stable isotope, Pu-244, are spontaneous fission and alpha emission; the primary mode after is beta emission. The primary decay products before Pu-244 are isotopes of uranium and neptunium (neglecting the wide range of daughter nuclei created by fission processes), and the primary products after are isotopes of americium.
Notable Isotopes

- Plutonium-238 has a half-life of 87.74 years\(^{[1]}\) and emits alpha particles. Pure Pu-238 for radioisotope thermoelectric generators which power some spacecraft is produced by neutron capture on neptunium-237 but plutonium from spent nuclear fuel can contain as much as a few percent of Pu-238, from either \(^{237}\)Np, alpha decay of \(^{242}\)Cm, or (n,2n) reactions.

- Plutonium-239 is the most important isotope of plutonium, with a half-life of 24,100 years. Pu-239 and Pu-241 are fissile, meaning that the nuclei of its atoms can break apart by being bombarded by slow moving thermal neutrons, releasing energy, gamma radiation and more neutrons. It can therefore sustain a nuclear chain reaction, leading to applications in nuclear weapons and nuclear reactors. Pu-239 is synthesized by irradiating uranium-238 with neutrons in a nuclear reactor, then recovered via nuclear reprocessing of the fuel. Further neutron capture produces successively heavier isotopes.

- Plutonium-240 has a high rate of spontaneous fission, raising the background neutron radiation of plutonium containing it. Plutonium is graded by proportion of Pu-240: weapons grade (< 7%), fuel grade (7–19%) and reactor grade (> 19%). Lower grades are less suited for nuclear weapons and thermal reactors but can fuel fast reactors. Pu-240 is not fissile, but is fertile material like U-238.

- Plutonium-241 is fissile, but also beta decays with a half-life of 14 years to americium-241.

- Plutonium-242 is not fissile, not very fertile (requiring 3 more neutron captures to become fissile), has a low neutron capture cross section, and a longer half-life than any of the lighter isotopes.

- Plutonium-244 is the most stable isotope of plutonium, with a half-life of about 80 million years, long enough to be found in trace quantities in nature. It is not significantly produced in nuclear reactors because Pu-243 has a short half-life, but some is produced in nuclear explosions.

Production and uses

Pu-239, a fissile isotope which is the second most used nuclear fuel in nuclear reactors after U-235, and the most used fuel in the fission portion of nuclear weapons, is produced from U-238 by neutron capture followed by two beta decays.

Pu-240, Pu-241, Pu-242 are produced by further neutron capture. The odd-mass isotopes Pu-239 and Pu-241 have about a 3/4 chance of undergoing fission on capture of a thermal neutron and about a 1/4 chance of retaining the neutron and becoming the following isotope. The even-mass isotopes are fertile material but not fissile and also have a lower overall probability (cross section) of neutron capture; therefore, they tend to accumulate in nuclear fuel used in a thermal reactor, the design of all nuclear power plants today. In
Isotopes of plutonium

plutonium that has been used a second time in thermal reactors in MOX fuel, Pu-240 may even be the most common isotope. All plutonium isotopes and other actinides, however, are fissionable with fast neutrons. Pu-240 does have a moderate thermal neutron absorption cross section, so that Pu-241 production in a thermal reactor becomes a significant fraction as large as Pu-239 production.

Pu-241 has a half-life of 14 years, and has slightly higher thermal neutron cross sections than Pu-239 for both fission and absorption. While nuclear fuel is being used in a reactor, a Pu-241 nucleus is much more likely to fission or to capture a neutron than to decay. Pu-241 accounts for a significant proportion of fissions in thermal reactor fuel that has been used for some time. However, in spent nuclear fuel that does not quickly undergo nuclear reprocessing but instead is cooled for years after use, much or most of the Pu-241 will beta decay to americium-241, one of the minor actinides, a strong alpha emitter, and difficult to use in thermal reactors.

Pu-242 has a particularly low cross section for thermal neutron capture; and it takes four neutron absorptions to become another fissile isotope (either curium-245 or Pu-241) and fission. Even then, there is a chance either of those two fissile isotopes will fail to fission but instead absorb the fourth neutron, becoming curium-246 (on the way to even heavier actinides like californium, which is a neutron emitter by spontaneous fission and difficult to handle) or becoming Pu-242 again; so the mean number of neutrons absorbed before fission is even higher than 4. Therefore Pu-242 is particularly unsuited to recycling in a thermal reactor and would be better used in a fast reactor where it can be fissioned directly. However, Pu-242's low cross section means that relatively little of it will be transmuted during one cycle in a thermal reactor. Pu-242's half-life is about 15 times as long as Pu-239's half-life; therefore it is 1/15 as radioactive and not one of the larger contributors to nuclear waste radioactivity. Pu-242's gamma ray emissions are also weaker than those of the other isotopes.

Pu-243 has a half-life of only 5 hours, beta decaying to americium-243. Because Pu-243 has little opportunity to capture an additional neutron before decay, the nuclear fuel cycle does not produce the extremely long-lived Pu-244 in significant quantity.

Pu-238 is not normally produced in as large quantity by the nuclear fuel cycle, but some is produced from neptunium-237 by neutron capture (this reaction can also be used with purified neptunium to produce Pu-238 relatively free of other plutonium isotopes for use in radioisotope thermoelectric generators), by the (n,2n) reaction of fast neutrons on Pu-239, or by alpha decay of curium-242 which is produced by neutron capture from Am-241. It has significant thermal neutron cross section for fission, but is more likely to capture a neutron and become Pu-239.

Transmutation flow between $^{238}\text{Pu}$ and $^{244}\text{Cm}$ in LWR. Transmutation speed not shown and varies greatly by nuclide. $^{245}\text{Cm}$ and $^{246}\text{Cm}$ are long-lived with negligible decay.
Isotopes of plutonium

Manufacture

Pu-240, Pu-241 and Pu-242
The activation cross section for \(^{239}\text{Pu}\) is 270 barns, while the fission cross section is 747 barns for thermal neutrons. The higher plutonium isotopes are created when the uranium fuel is used for a long time. It is the case that for high burnup used fuel that the concentrations of the higher plutonium isotopes will be higher than the low burnup fuel which is reprocessed to obtain weapons grade plutonium.

The formation of \(^{240}\text{Pu}, ^{241}\text{Pu} and ^{242}\text{Pu}\) from \(^{238}\text{U}\)

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Thermal neutron cross section</th>
<th>Decay mode</th>
<th>Halflife</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Capture</td>
<td>Fission</td>
<td></td>
</tr>
<tr>
<td>(^{238}\text{U})</td>
<td>2.7</td>
<td>(\alpha)</td>
<td>(4.47 \times 10^9) years</td>
</tr>
<tr>
<td>(^{239}\text{U})</td>
<td>(\beta)</td>
<td></td>
<td>23 minutes</td>
</tr>
<tr>
<td>(^{239}\text{Np})</td>
<td>(\beta)</td>
<td></td>
<td>2.36 days</td>
</tr>
<tr>
<td>(^{239}\text{Pu})</td>
<td>270</td>
<td>(\alpha)</td>
<td>24,110 years</td>
</tr>
<tr>
<td>(^{240}\text{Pu})</td>
<td>289</td>
<td>(\alpha)</td>
<td>6,564 years</td>
</tr>
<tr>
<td>(^{241}\text{Pu})</td>
<td>362</td>
<td>(\beta)</td>
<td>14.35 years</td>
</tr>
<tr>
<td>(^{242}\text{Pu})</td>
<td>18.8</td>
<td>(\alpha)</td>
<td>373,300 years</td>
</tr>
</tbody>
</table>

Pu-239
Plutonium-239 is one of the three fissile materials used for the production of nuclear weapons and in some nuclear reactors as a source of energy. The other fissile materials are uranium-235 and uranium-233. Plutonium-239 is virtually nonexistent in nature. It is made by bombarding uranium-238 with neutrons in a nuclear reactor. Uranium-238 is present in quantity in most reactor fuel; hence plutonium-239 is continuously made in these reactors. Since plutonium-239 can itself be split by neutrons to release energy, plutonium-239 provides a portion of the energy generation in a nuclear reactor.
Isotopes of plutonium

A ring of weapons-grade electrorefined plutonium, with 99.96% purity. This 5.3 kg ring is enough plutonium for use in an efficient nuclear weapon. The ring shape is needed to depart from a spherical shape and avoid criticality.

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>Thermal neutron capture cross section (barn)</th>
<th>Thermal neutron fission Cross section (barn)</th>
<th>decay mode</th>
<th>halflife</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>238</td>
<td>2.68</td>
<td>5 \times 10^{-6}</td>
<td>α</td>
<td>4.47 \times 10^9 years</td>
</tr>
<tr>
<td>U</td>
<td>239</td>
<td>22</td>
<td>15</td>
<td>β</td>
<td>23 minutes</td>
</tr>
<tr>
<td>Np</td>
<td>239</td>
<td>30</td>
<td>1</td>
<td>β</td>
<td>2.36 days</td>
</tr>
<tr>
<td>Pu</td>
<td>239</td>
<td>271</td>
<td>750</td>
<td>α</td>
<td>24,110 years</td>
</tr>
</tbody>
</table>

**Pu-238**

There are small amounts of Pu-238 in the plutonium of usual plutonium-producing reactors. However, isotopic separation would be quite expensive compared to another method: when a U-235 atom captures a neutron, it is converted to an excited state of U-236. Some of the excited U-236 nuclei undergo fission, but some decay to the ground state of U-236 by emitting gamma radiation. Further neutron capture creates U-237 which has a half-life of 7 days and thus quickly decays to Np-237. Since nearly all neptunium is produced in this way or consists of isotopes which decay quickly, one gets nearly pure Np-237 by chemical separation of neptunium. After this chemical separation, Np-237 is again irradiated by reactor neutrons to be converted to Np-238 which decays to Pu-238 with a half-life of 2 days.
The formation of $^{238}\text{Pu}$ from $^{235}\text{U}$

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>Thermal neutron cross section</th>
<th>decay mode</th>
<th>halflife</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>235</td>
<td>99</td>
<td>$\alpha$</td>
<td>703,800,000 years</td>
</tr>
<tr>
<td>U</td>
<td>236</td>
<td>5.3</td>
<td>$\alpha$</td>
<td>23,420,000 years</td>
</tr>
<tr>
<td>U</td>
<td>237</td>
<td></td>
<td>$\beta$</td>
<td>6.75 days</td>
</tr>
<tr>
<td>Np</td>
<td>237</td>
<td>165 (capture)</td>
<td>$\alpha$</td>
<td>2,144,000 years</td>
</tr>
<tr>
<td>Np</td>
<td>238</td>
<td></td>
<td>$\beta$</td>
<td>2.11 days</td>
</tr>
<tr>
<td>Pu</td>
<td>238</td>
<td></td>
<td>$\alpha$</td>
<td>87.7 years</td>
</tr>
</tbody>
</table>

**Pu-240 as obstacle to nuclear weapons**

Pu-240 undergoes spontaneous fission as a secondary decay mode at a small but significant rate. The presence of Pu-240 limits the plutonium's nuclear bomb potential because the neutron flux from spontaneous fission, initiates the chain reaction prematurely and reduces the bomb's power by exploding the core before full implosion is reached. Plutonium consisting of more than about 90% Pu-239 is called **weapons-grade plutonium**; plutonium from spent nuclear fuel from commercial power reactors generally contains at least 20% Pu-240 and is called **reactor-grade plutonium**. However, modern nuclear weapons use fusion boosting which mitigates the predetonation problem; if the pit can generate a nuclear weapon yield of even a fraction of a kiloton, which is enough to start deuterium-tritium fusion, the resulting burst of neutrons will fission enough plutonium to ensure a yield of tens of kilotons.

Pu-240 contamination is the reason plutonium weapons must use the implosion method. Theoretically, pure Pu-239 could be used in a gun-type nuclear weapon, but achieving this level of purity is prohibitively difficult. Pu-240 contamination has proven a mixed blessing to nuclear weapons design. While it created delays and headaches during the Manhattan Project because of the need to develop implosion technology, those very same difficulties are currently a barrier to nuclear proliferation. Implosion devices are also inherently more efficient and less prone toward accidental detonation than are gun-type weapons.

**Table**

<table>
<thead>
<tr>
<th>nuclide symbol</th>
<th>$Z(p)$</th>
<th>$N(n)$</th>
<th>isotopic mass (u)</th>
<th>half-life</th>
<th>decay mode(5)</th>
<th>daughter isotopes (16)</th>
<th>nuclear spin</th>
<th>representative isotopic composition (mole fraction)</th>
<th>range of natural variation (mole fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>228$\text{Pu}$</td>
<td>94</td>
<td>134</td>
<td>228.03874(3)</td>
<td>1.1(+20-5) s</td>
<td>$\alpha$ (99.9%)</td>
<td>$^{224}\text{U}$</td>
<td>0+</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\beta$ (+.1%)</td>
<td>$^{228}\text{Np}$</td>
<td></td>
<td></td>
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<tr>
<td>229$\text{Pu}$</td>
<td>94</td>
<td>135</td>
<td>229.04015(6)</td>
<td>120(50) s</td>
<td>$\alpha$</td>
<td>$^{225}\text{U}$</td>
<td>3/2+##</td>
<td></td>
<td></td>
</tr>
<tr>
<td>230$\text{Pu}$</td>
<td>94</td>
<td>136</td>
<td>230.039650(16)</td>
<td>1.70(17) min</td>
<td>$\alpha$</td>
<td>$^{226}\text{U}$</td>
<td>0+</td>
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<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>$\beta$ (rare)</td>
<td>$^{230}\text{Np}$</td>
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<tr>
<td>231$\text{Pu}$</td>
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<td>137</td>
<td>231.041101(28)</td>
<td>8.6(5) min</td>
<td>$\beta$ (rare)</td>
<td>$^{231}\text{Np}$</td>
<td>3/2+##</td>
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<td></td>
<td>$\alpha$ (rare)</td>
<td>$^{227}\text{U}$</td>
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<tr>
<td>Mass Number</td>
<td>Protons</td>
<td>Neutrons</td>
<td>Atomic Mass</td>
<td>Stability</td>
<td>Decay Mode</td>
<td>Daughter</td>
<td>Energy</td>
<td>Lifespan</td>
<td></td>
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<td>232Pu</td>
<td>94</td>
<td>138</td>
<td>232.041187(19)</td>
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<td>EC (89%)</td>
<td>232Np</td>
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<td>α (11%)</td>
<td>228U</td>
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<td>233Pu</td>
<td>94</td>
<td>139</td>
<td>233.043000(5)</td>
<td>20.9(4) min</td>
<td>β⁺ (99.88%)</td>
<td>233Np</td>
<td>5/2+#</td>
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<td>α (.12%)</td>
<td>229U</td>
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<td>234Pu</td>
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<td>140</td>
<td>234.043317(7)</td>
<td>8.8(1) h</td>
<td>EC (94%)</td>
<td>234Np</td>
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<td></td>
<td></td>
<td></td>
<td>α (6%)</td>
<td>230U</td>
<td></td>
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<tr>
<td>235Pu</td>
<td>94</td>
<td>141</td>
<td>235.045286(22)</td>
<td>25.3(5) min</td>
<td>β⁺ (99.99%)</td>
<td>235Np</td>
<td>(5/2+)</td>
<td></td>
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<tr>
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<td></td>
<td></td>
<td>α (.0027%)</td>
<td>231U</td>
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<tr>
<td>236Pu</td>
<td>94</td>
<td>142</td>
<td>236.0460580(24)</td>
<td>2.858(8) a</td>
<td>α</td>
<td>232U</td>
<td>(various)</td>
<td></td>
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</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>SF (1.37×10⁻⁷%)</td>
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<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>CD (2×10⁻¹²%)</td>
<td>208Pb 28Mg</td>
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<td></td>
<td></td>
<td>β⁺β⁺ (rare)</td>
<td>236U</td>
<td></td>
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<tr>
<td>237Pu</td>
<td>94</td>
<td>143</td>
<td>237.0484097(24)</td>
<td>45.2(1) d</td>
<td>EC</td>
<td>237Np</td>
<td>7/2-</td>
<td></td>
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<td></td>
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<td></td>
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<td>α (.0042%)</td>
<td>233U</td>
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<tr>
<td>237m1Pu</td>
<td></td>
<td></td>
<td>145.544(10) keV</td>
<td>180(20) ms</td>
<td>IT</td>
<td>237Pu</td>
<td>1/2+</td>
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<tr>
<td>237m2Pu</td>
<td></td>
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<td>2900(250) keV</td>
<td>1.1(1) µs</td>
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<td></td>
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<tr>
<td>238Pu</td>
<td>94</td>
<td>144</td>
<td>238.0495599(20)</td>
<td>87.7(1) a</td>
<td>α</td>
<td>234U</td>
<td>(various)</td>
<td></td>
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<td>SF (1.9×10⁻⁷%)</td>
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<td></td>
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<td></td>
<td>CD (1.4×10⁻¹⁴%)</td>
<td>206Hg 52Si</td>
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<tr>
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<td></td>
<td>CD (6×10⁻¹⁵%)</td>
<td>180Yb 50Mg</td>
<td>28Mg</td>
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<tr>
<td>239Pu[8]</td>
<td>94</td>
<td>145</td>
<td>239.0521634(20) a</td>
<td>2.411(3)×10⁻⁴ a</td>
<td>α</td>
<td>235mU 1/2+</td>
<td>(various)</td>
<td></td>
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<td>SF (3.1×10⁻¹⁰%)</td>
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<td>239m1Pu</td>
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<td>391.584(3) keV</td>
<td>193(4) ns</td>
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<td>239Pu</td>
<td>7/2-</td>
<td></td>
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</tr>
<tr>
<td>239m2Pu</td>
<td></td>
<td></td>
<td>3100(200) keV</td>
<td>7.5(10) µs</td>
<td></td>
<td>(5/2+)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>240Pu</td>
<td>94</td>
<td>146</td>
<td>240.0538135(20)</td>
<td>6,561(7) a</td>
<td>α</td>
<td>236U</td>
<td>0+</td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>SF (5.7×10⁻⁶%)</td>
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<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>CD (1.3×10⁻¹³%)</td>
<td>206Hg 34Si</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Isotopes of Plutonium

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Protons</th>
<th>Neutrons</th>
<th>Mass Number</th>
<th>Half-Life</th>
<th>Mode(s) of Decay</th>
<th>Daughter Product</th>
<th>Decay Energy</th>
<th>Decay Half-Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{241}$Pu</td>
<td>94</td>
<td>147</td>
<td>241</td>
<td>14.290(6) a</td>
<td>$\beta^{-}$ (99.99%)</td>
<td>$^{241}$Am</td>
<td>5/2+</td>
<td>SF (2.4×10$^{-14}$%)</td>
</tr>
<tr>
<td>$^{241m1}$Pu</td>
<td>94</td>
<td>147</td>
<td>241</td>
<td>161.6(1) keV</td>
<td>SF (various)</td>
<td>$^{237}$U</td>
<td>1/2+</td>
<td></td>
</tr>
<tr>
<td>$^{241m2}$Pu</td>
<td>94</td>
<td>147</td>
<td>241</td>
<td>2200(200) keV</td>
<td>SF (various)</td>
<td>$^{237}$U</td>
<td>0+</td>
<td></td>
</tr>
<tr>
<td>$^{242}$Pu</td>
<td>94</td>
<td>148</td>
<td>242</td>
<td>3.75(2)×10$^{5}$ a</td>
<td>$\alpha$</td>
<td>$^{238}$U</td>
<td>0+</td>
<td></td>
</tr>
<tr>
<td>$^{243}$Pu</td>
<td>94</td>
<td>149</td>
<td>243</td>
<td>4.956(3) h</td>
<td>$\beta^{-}$</td>
<td>$^{243}$Am</td>
<td>7/2+</td>
<td></td>
</tr>
<tr>
<td>$^{243m}$Pu</td>
<td>94</td>
<td>149</td>
<td>243</td>
<td>383.6(4) keV</td>
<td>SF (various)</td>
<td>$^{243}$Am</td>
<td>1/2+</td>
<td></td>
</tr>
<tr>
<td>$^{244}$Pu</td>
<td>94</td>
<td>150</td>
<td>244</td>
<td>8.00(9)×10$^{7}$ a</td>
<td>$\alpha$ (99.88%)</td>
<td>$^{240}$U</td>
<td>0+</td>
<td>SF (1.23%)</td>
</tr>
<tr>
<td>$^{245}$Pu</td>
<td>94</td>
<td>151</td>
<td>245</td>
<td>10.5(1) h</td>
<td>$\beta^{-}$</td>
<td>$^{245}$Am</td>
<td>(9/2-)</td>
<td></td>
</tr>
<tr>
<td>$^{246}$Pu</td>
<td>94</td>
<td>152</td>
<td>246</td>
<td>10.84(2) d</td>
<td>$\beta^{-}$</td>
<td>$^{246m}$Am</td>
<td>0+</td>
<td></td>
</tr>
<tr>
<td>$^{247}$Pu</td>
<td>94</td>
<td>153</td>
<td>247</td>
<td>2.27(23) d</td>
<td>$\beta^{-}$</td>
<td>$^{247}$Am</td>
<td>1/2+#</td>
<td></td>
</tr>
</tbody>
</table>

[6] Abbreviations:
CD: Cluster decay
EC: Electron capture
IT: Isomeric transition
SF: Spontaneous fission
[7] Bold for stable isotopes
[8] Fissile nuclide
[9] Most useful isotope for nuclear weapons
[10] Primordial radionuclide
Notes

• Values marked # are not purely derived from experimental data, but at least partly from systematic trends. Spins with weak assignment arguments are enclosed in parentheses.

• Uncertainties are given in concise form in parentheses after the corresponding last digits. Uncertainty values denote one standard deviation, except isotopic composition and standard atomic mass from IUPAC which use expanded uncertainties.

References

• Isotope masses from:

• Isotopic compositions and standard atomic masses from:

• Half-life, spin, and isomer data selected from the following sources. See editing notes on this article's talk page.
Compounds and mixtures

Plutonium borides

Several borides can be formed by direct combination of plutonium and boron powders in an inert atmosphere at reduced pressure.

PuB was reported to form at 1200 °C with a range of 40–70% boron. It supposedly has a Pu-B bond length of 2.46 Å and the NaCl structure, as do TiB, ZrB and HfB.\textsuperscript{[1]} The existence of PuB was contested later based on several arguments.\textsuperscript{[2]}

PuB\textsubscript{2} is formed at 800 °C and has similar structure as most other metal diborides (see Category:Borides).

At 1200 °C with 70–85% boron, mixtures of PuB\textsubscript{4} and PuB\textsubscript{6} are formed, with more of the latter as the temperature increases; PuB\textsubscript{4} has the tetragonal structure (same as UB\textsubscript{4}), and PuB\textsubscript{6} has cubic structure, same as all hexaborides (CaB\textsubscript{6}, LaB\textsubscript{6} etc.).\textsuperscript{[1]}

The most remarkable plutonium boride is arguably PuB\textsubscript{100}. Its existence \textsuperscript{[2]} demonstrates the importance of contamination in boride research as 1% of impurity is capable of changing the crystal structure.

References

Plutonium carbide

Plutonium carbide comes in several stoichiometries (PuC and Pu2C3).\[^1\] It can be used as a nuclear fuel for nuclear reactors in conjunction with uranium carbide. The mixture is also labeled as uranium-plutonium carbide (UPuC).

References

# Plutonium hexafluoride

<table>
<thead>
<tr>
<th>Plutonium hexafluoride[^1]</th>
<th>![Stereo structural formula of plutonium hexafluoride](Plutonium hexafluoride.svg)</th>
</tr>
</thead>
</table>

## Identifiers

- **CAS number**: 13693-06-6[^2] (✓)
- **PubChem**: 518809[^3]
- **ChemSpider**: 452599[^4] (✓)
- **Jmol-3D images**: Image 1[^5]

## Properties

### Molecular formula
- $\text{F}_6\text{Pu}$

### Molar mass
- 358.05 g mol$^{-1}$

### Exact mass
- 357.990 g mol$^{-1}$

### Appearance
- Dark red, opaque crystals

### Density
- 5.08 g cm$^{-3}$

### Melting point
- 52 °C, 325 K, 126 °F

### Boiling point
- 62 °C, 335 K, 144 °F

## Structure

- **Crystal structure**: Orthorhombic, $\alpha\text{P}2_1\text{b}2_1\text{b}2_1$
- **Space group**: $\text{Pnma}$, No. 62
- **Coordination geometry**: octahedral ($O_h$)
- **Dipole moment**: 0 D

## Related compounds

- Related fluoroplutoniums: Plutonium trifluoride, Plutonium tetrafluoride

[^1]: Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa)

Plutonium hexafluoride is the highest fluoride of plutonium, and is of interest for laser enrichment of plutonium, in particular for the production of pure plutonium-239 from irradiated uranium. This pure plutonium is needed to avoid premature ignition of low-mass nuclear weapon designs by neutrons produced by spontaneous fission of plutonium-240.

It is a red-brown volatile crystalline solid,[^1] the heat of sublimation is 12.1 kcal/mol[^7] and the heat of vaporization 7.4 kcal/mol[^7]. It is relatively hard to handle, being very corrosive and prone to auto-radiolysis.[^8][^9]
It is prepared by fluorination of plutonium tetrafluoride (PuF$_4$) by powerful fluorinating agents such as elemental fluorine.$^{[10]}$ [11] $^{[7]}$ $^{[12]}$

$$\text{PuF}_4 + \text{F}_2 \rightarrow \text{PuF}_6$$

Its further be obtained by fluorination of plutonium(III) fluoride or plutonium(IV) oxide.$^{[11]}$

$$2 \text{PuF}_3 + 3 \text{F}_2 \rightarrow 2 \text{PuF}_6$$

$$\text{PuO}_2 + 3 \text{F}_2 \rightarrow \text{PuF}_6 + \text{O}_2$$

Hydrogen fluoride is not sufficient$^{[13]}$; it is itself a powerful fluorinating agent.

Under laser irradiation at a wavelength of less than 520 nm, it decomposes to plutonium pentafluoride and fluorine$^{[14]}$; after more irradiation it decomposes further to plutonium tetrafluoride.$^{[15]}$

**Weblinks**

- webelements.com$^{[16]}$

**References**

5. http://chemapps.stolaf.edu/jmol/jmol.php?model=F%5BPu%5D%28F%29%28F%29%28F%29%28F%29
Plutonium hydride is the chemical compound with the formula PuH$_2$. It is one of two characterised hydrides of plutonium, the other is PuH$_3$. PuH$_2$ is non-stoichiometric with a composition range of PuH$_2$ – PuH$_{2.7}$. Additionally metastable stoichiometries with an excess of hydrogen (PuH$_{2.7}$ – PuH$_3$) can be formed. PuH$_2$ has a cubic structure. It is readily formed from the elements at 1 atmosphere at 100–200 °C:[4]

Pu + H$_2$ → PuH$_2$

Studies of the reaction of plutonium metal with moist air at 200–350 °C showed the presence of cubic plutonium hydride on the surface along with Pu$_2$O$_3$, PuO$_2$ and a higher oxide identified by X-ray diffraction and X-ray photoelectron spectroscopy as the mixed-valence phase Pu$^{IV}_3$–$x$Pu$^{VI}_x$O$_{6+x}$.[5] Investigation of the reaction performed without heating suggests that the reaction of Pu metal and moist air the production of PuO$_2$ and a higher oxide along with adsorbed hydrogen, which catalytically combines with O$_2$ to form water.[6]

Plutonium dihydride on the surface of hydrided plutonium acts as a catalyst for the oxidation of the metal with consumption of both O$_2$ and N$_2$ from air.[7]

References

Plutonium(III) chloride

<table>
<thead>
<tr>
<th><strong>Plutonium(III) chloride</strong></th>
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</thead>
<tbody>
<tr>
<td><img src="" alt="Image:UCl3.png" /></td>
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<table>
<thead>
<tr>
<th><strong>Identifiers</strong></th>
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<tbody>
<tr>
<td>CAS number</td>
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<tr>
<td>ChemSpider</td>
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<td>Jmol-3D images</td>
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<tr>
<th><strong>Properties</strong></th>
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<tbody>
<tr>
<td>Molecular formula</td>
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<tr>
<td>Molar mass</td>
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<td>Appearance</td>
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<tr>
<td>Density</td>
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<tr>
<td>Melting point</td>
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<tr>
<td>Boiling point</td>
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<table>
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<tr>
<th><strong>Hazards</strong></th>
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<tr>
<td>EU classification</td>
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<table>
<thead>
<tr>
<th><strong>Related compounds</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Other anions</td>
</tr>
</tbody>
</table>

(what is this?) (verify)[5]

Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa)

Plutonium(III) chloride is the chemical compound with the formula PuCl$_3$.

**Structure**

Plutonium atoms in crystalline PuCl$_3$ are 9 coordinate, and the structure is tricapped trigonal prismatic.[6]

**Safety**

As with all plutonium compounds, it is subject to control under the Nuclear Non-Proliferation Treaty. Due to the radioactivity of plutonium, all of its compounds, PuCl$_3$ included, are warm to the touch. Such contact is not recommended, since touching the material may result in serious injury.

**References**


**Plutonium(III) fluoride**

<table>
<thead>
<tr>
<th>Plutonium(III) fluoride</th>
<th>Unit cell, ball and stick model of plutonium(III) fluoride</th>
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</thead>
</table>

### Identifiers

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<tr>
<td>PubChem</td>
<td>139624 [2]</td>
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<td>ChemSpider</td>
<td>123138 [3]</td>
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<td>Jmol-3D images</td>
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### Properties

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<th>Molecular formula</th>
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<td>Molar mass</td>
<td>301.06 g mol$^{-1}$</td>
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<tr>
<td>Exact mass</td>
<td>300.995 g mol$^{-1}$</td>
</tr>
<tr>
<td>Appearance</td>
<td>Violet, opaque crystals</td>
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<tr>
<td>Density</td>
<td>9.3 g cm$^{-3}$</td>
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<tr>
<td>Melting point</td>
<td>1396 °C, 1669 K, 2545 °F [5]</td>
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<td>Boiling point</td>
<td>2000 °C, 2273 K, 3632 °F (decomposes [6])</td>
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### Related compounds

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<th>Plutonium(III) chloride</th>
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<td>Other cations</td>
<td>Samarium(III) fluoride</td>
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<tr>
<td>Related fluoroplutoniums</td>
<td>Plutonium tetrafluoride</td>
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<tr>
<td></td>
<td>Plutonium hexafluoride</td>
</tr>
</tbody>
</table>

Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa).

**Plutonium(III) fluoride** or **plutonium trifluoride** is the chemical compound composed of plutonium and fluorine with the formula PuF$_3$. It forms violet crystals. Plutonium(III) fluoride has the LaF$_3$ structure where the coordination around the plutonium atoms is complex and usually described as tri-capped trigonal prismatic. [7]
Reactions

A plutonium(III) fluoride precipitation method has been investigated as an alternative to the typical plutonium peroxide method of recovering plutonium from solution, such as that from a nuclear reprocessing plant. A 1957 study by the Los Alamos National Laboratory reported a less effective recovery than the traditional method, while a more recent study sponsored by the United States Office of Scientific and Technical Information found it to be one of the more effective methods.

Plutonium(III) fluoride can be used for manufacture of the plutonium-gallium alloy instead of more difficult to handle metallic plutonium.

References

Plutonium(IV) fluoride

<table>
<thead>
<tr>
<th>Plutonium(IV) fluoride[^1]</th>
</tr>
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<tbody>
<tr>
<td>![Image: Kristallstruktur Uran(IV)-fluorid.png](Image: Kristallstruktur Uran(IV)-fluorid.png)</td>
</tr>
</tbody>
</table>

**Identifiers**

- **CAS number**: 13709-56-3[^2]
- **ChemSpider**: 14074494[^3]

**Properties**

- **Molecular formula**: PuF₄
- **Molar mass**: 320 g/mol
- **Appearance**: reddish-brown monoclinic crystals
- **Density**: 7.1 g/cm³
- **Melting point**: 1027°C

**Structure**

- **Crystal structure**: Monoclinic, mS60
- **Space group**: C12/c1, No. 15

Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa)

**Infobox references**

---

Plutonium(IV) fluoride (PuF₄), as for all plutonium compounds, is subject to control under the Nuclear Non-Proliferation Treaty.

**References**


Metallic plutonium is produced by reacting plutonium tetrafluoride with barium, calcium or lithium at 1200 °C.
# Plutonium(IV) oxide

<table>
<thead>
<tr>
<th><strong>Plutonium(IV) oxide</strong></th>
<th><img src="Pudioxide.png" alt="Unit cell, ball and stick model of plutonium(IV) oxide" /></th>
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## Identifiers

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## Properties

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<td>Molecular formula</td>
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<td>Molar mass</td>
<td>276.06 g mol$^{-1}$</td>
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<td>Exact mass</td>
<td>275.990 g mol$^{-1}$</td>
</tr>
<tr>
<td>Appearance</td>
<td>Dark yellow crystals</td>
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<td>Density</td>
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<td>Melting point</td>
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## Structure

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<tr>
<td>Crystal structure</td>
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<td>Space group</td>
<td>Fm3m, No. 225</td>
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<td>Coordination geometry</td>
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## Hazards

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<tbody>
<tr>
<td>Main hazards</td>
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</tbody>
</table>

Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa).

Plutonium(IV) oxide is the chemical compound with the formula $PuO_2$. This high melting point solid is a principal compound of plutonium. It can vary in color from yellow to olive green, depending on the particle size, temperature and method of production. [5]
Structure
PuO$_2$ crystallizes in the fluorite motif, with the Pu$^{4+}$ centers organized in a face-centered cubic array and oxide ions occupying tetrahedral holes.\cite{6} PuO$_2$ owes utility as a nuclear fuel to the fact that vacancies in the octahedral holes allows room for fissile products. In nuclear fission, one atom of plutonium splits into two. The vacancy of the octahedral holes provides room for the new product and allows the PuO$_2$ monolith to retain its structural integrity.

Synthesis
Plutonium metal spontaneously oxidizes to PuO$_2$ in an atmosphere of oxygen. Plutonium dioxide is mainly produced by calcination of plutonium(IV) oxalate, Pu(C$_2$O$_4$)$_2$·6H$_2$O, at 300 °C. Plutonium oxalate is obtained during the reprocessing of nuclear fuel.

Applications
PuO$_2$ is used in mixed oxide (MOX) fuels for nuclear reactors. Plutonium-238 dioxide is used as fuel for several deep-space spacecraft such as the ‘New Horizons’ Pluto probe. The isotope decays by emitting α-particles which then generate heat (see radioisotope thermoelectric generator). There have been concerns that an accidental orbital earth re-entry might lead to the break-up and/or burn-up of a spacecraft, resulting in the dispersal of the plutonium, either over a large tract of the planetary surface or within the upper atmosphere.

Physicist Peter Zimmerman, following up a suggestion by Ted Taylor, demonstrated that a low-yield (1-kiloton) nuclear bomb could be made relatively easily from plutonium oxide.\cite{7}

Toxicology

See also, Plutonium Toxicity

Plutonium oxide is highly toxic to humans, especially via inhalation.\cite{8} As with all plutonium compounds, it is subject to control under the Nuclear Non-Proliferation Treaty. Due to the radioactive alpha decay of plutonium, all of its compounds, PuO$_2$ included, as well as plutonium metal, are warm to the touch.

References

Plutonium-gallium alloy

**Plutonium-gallium alloy (Pu-Ga)** is an alloy of plutonium and gallium, used in nuclear weapon pits – the component of a nuclear weapon where the fission chain reaction is started.

Metallic plutonium has several different solid allotropes. The δ phase is the least dense and most easily machinable. It is formed at temperatures of 310 °C to 452 °C at ambient pressure (1 atmosphere), and is thermodynamically unstable at lower temperatures. However, plutonium can be stabilized in the δ phase by alloying it with a small amount of another metal. The preferred alloy is 3.0–3.5 mol.% (0.8–1.0 wt.%) gallium. This alloy was developed during the Manhattan Project.

Pu-Ga is stable between at least −75 to 475 °C, and has very low thermal expansion. The presence of gallium also significantly lowers the susceptibility of plutonium to corrosion, to 4% of corrosion rate of pure plutonium. The alloy is more dense in molten state than in solid state, which poses an advantage for casting as the tendency to form bubbles and internal defects is decreased.[1]

Stabilized δ-phase Pu-Ga is ductile, and can be rolled into sheets and machined by conventional methods. It is suitable for shaping by hot pressing at about 400 °C. This method was used for forming the first nuclear weapon pits. More modern pits are produced by casting. Subcritical testing showed that wrought and cast plutonium performance is the same.[2] [3] As only the ε-δ transition occurs during cooling, casting Pu-Ga is much less problematic than casting pure plutonium.[4]

δ phase Pu-Ga is still thermodynamically unstable, so there are concerns about its aging behavior. There are substantial differences of density (and therefore volume) between the various phases. The transition between δ-phase and α-phase Pu, occurs at a low temperature of 115 °C and can be reached by accident. Prevention of the phase transition and the associated mechanical deformations and consequent structural damage and/or loss of symmetry is of critical importance.

However, the phase change is useful during the operation of a nuclear weapon. As the reaction starts, it generates enormous pressures, in the range of hundreds of gigapascals. Under these conditions, δ phase Pu-Ga transforms to α phase, which is 25% denser and thus more critical.

Gallium tends to segregate in plutonium, causing "coring" – gallium-rich centers of grains and gallium-poor grain boundaries. To stabilize the lattice and reverse and prevent segregation of gallium, annealing is required at the temperature just below the δ-ε phase transition, so gallium atoms can diffuse through the grains and create homogeneous structure. The time to achieve homogenization of gallium increases with increasing grain size of the alloy and decreases with increasing temperature. The structure of stabilized plutonium at room temperature is the same as unstabilized at δ-phase temperature, with the difference of gallium atoms substituting plutonium in the fcc lattice.

Under 4 mol.% gallium the pressure-induced phase change is irreversible.

Plutonium in its α phase has a low internal symmetry, caused by uneven bonding between the atoms, resembling (and behaving like) more a ceramic than a metal. Addition of gallium causes the bonds becoming more even, increasing the stability of the δ phase.[5] The α phase bonds are mediated by the 5f shell electrons, and can be disrupted by increased temperature or by presence of suitable atoms in the lattice which reduce the available number of 5f electrons and weaken their bonds.[6] The alloy is more dense in molten state than in solid state, which poses an advantage for casting as the tendency to form bubbles and internal defects is decreased.[1] [7]
During the Manhattan Project, the maximum amount of diluent atoms for plutonium to not affect the explosion efficiency was calculated to be 5 mol.%. Two stabilizing elements were considered, silicon and aluminium. However only aluminium produced satisfactory alloys. But the aluminium tendency to react with α-particles and emit neutrons limited its maximum content to 0.5 mol.%; the next element from the boron group of elements, gallium, was tried and found satisfactory.[8][9]

There are several plutonium and gallium intermetallic compounds: PuGa, Pu$_3$Ga, and Pu$_6$Ga.

During aging of the stabilized δ alloy, gallium segregates from the lattice, forming regions of Pu$_3$Ga (ζ'-phase) within α phase, with the corresponding dimensional and density change and buildup of internal strains. The decay of plutonium however produces energetic particles (alpha particles and uranium-235 nuclei) that cause local disruption of the ζ'-phase, and establishing a dynamic equilibrium with only a modest amount of ζ'-phase present, which explains the alloy's unexpectedly slow, graceful aging.[10][11] The alpha particles are trapped as interstitial helium atoms in the lattice, coalescing into tiny (about 1 nm diameter) helium-filled bubbles in the metal and causing negligible levels of void swelling; the size of bubbles appears to be limited, though their number increases with time.

Addition of 7.5 wt.% of plutonium-238, which has significantly faster decay rate, to the alloy increases the aging damage rate by 16 times, assisting with plutonium aging research. The Blue Gene supercomputer aided with simulations of plutonium aging processes.[12]

Presence of gallium in plutonium signifies its origin from weapon plants or decommissioned nuclear weapons. The isotopic signature of plutonium then allows rough identification of its origin, manufacturing method, type of the reactor used in its production, and rough history of the irradiation, and matching to other samples, which is of importance in investigation of nuclear smuggling.[13]

For reprocessing of surplus warhead pits into MOX fuel, majority of gallium has to be removed as its high content could interfere with the fuel rod cladding (gallium attacks zirconium[14]) and with migration of fission products in the fuel pellets. In the ARIES process, the pits are converted to oxide by converting the material to plutonium hydride, then optionally to nitride, and then to oxide. Gallium is then mostly removed from the solid oxide mixture by heating at 1100°C in a 94% argon 6% hydrogen atmosphere, reducing gallium content from 1% to 200 ppm. Further dilution of plutonium oxide during the MOX fuel manufacture brings gallium content to levels considered negligible. A wet route of gallium removal, using ion exchange, is also possible.[15] Electrorefining is another way to separate gallium and plutonium.[16]

For weapons use, the plutonium pit parts have to be coated with a layer of another metal. The first attempts used galvanically deposited silver. Subsequent pits were coated with nickel, by exposing the plutonium parts to nickel tetracarbonyl gas, which reacts with the plutonium surface and deposits a thin layer of nickel. Evaporation coating with aluminium and electroplating with zinc were shown to not work.

Plutonium alloys can be produced by adding a metal to molten plutonium. However, if the alloying metal is sufficiently reductive, plutonium can be added in the form of oxides or halides. The δ phase plutonium-gallium and plutonium-aluminium alloys are produced by adding plutonium(III) fluoride to molten gallium or aluminium, which has the advantage of avoiding dealing directly with the highly reactive plutonium metal.[17]
References

MOX fuel

Mixed oxide fuel, commonly referred to as MOX fuel, is nuclear fuel that contains more than one oxide of fissile material. MOX fuel contains plutonium blended with natural uranium, reprocessed uranium, or depleted uranium. MOX fuel is an alternative to the low-enriched uranium (LEU) fuel used in the light water reactors that predominate nuclear power generation. For example, a mixture of 7% plutonium and 93% uranium reacts similarly, although not identically, to LEU fuel.

One attraction of MOX fuel is that it is a way of utilizing surplus weapons-grade plutonium, which would otherwise be stored as nuclear waste and might be stolen to make nuclear weapons. On the other hand, some fear that normalising the global commercial use of MOX fuel and the associated expansion of nuclear reprocessing will increase, rather than reduce, the risk of nuclear proliferation.

Overview

In every uranium-based nuclear reactor core there is both fission of uranium isotopes such as uranium-235 (\(^{235}\text{U}\)) and the formation of new, heavier isotopes due to neutron capture, primarily by uranium-238 (\(^{238}\text{U}\)). Most of the fuel mass in a reactor is \(^{238}\text{U}\). This can become plutonium-239 (\(^{239}\text{Pu}\)) and by successive neutron capture plutonium-240 (\(^{240}\text{Pu}\)), plutonium-241 (\(^{241}\text{Pu}\)), plutonium-242 (\(^{242}\text{Pu}\)) and other transuranic or actinide nuclides. \(^{239}\text{Pu}\) and \(^{241}\text{Pu}\) are fissile, like \(^{235}\text{U}\). Small quantities of uranium-236 (\(^{236}\text{U}\)), neptunium-237 (\(^{237}\text{Np}\)), and plutonium-238 (\(^{238}\text{Pu}\)) are formed similarly from \(^{235}\text{U}\). Normally, with the fuel being changed every three years or so, most of the \(^{239}\text{Pu}\) is "burned" in the reactor. It behaves like \(^{235}\text{U}\), with a slightly higher cross section for fission, and its fission releases a similar amount of energy. Typically about one percent of the spent fuel discharged from a reactor is plutonium, and some two thirds of the plutonium is \(^{239}\text{Pu}\). Worldwide, almost 100 tonnes of plutonium in spent fuel arises each year. A single recycling of plutonium increases the energy derived from the original uranium by some 12%, and if the \(^{235}\text{U}\) is also recycled by re-enrichment, this becomes about 20%. With additional recycling the percentage of fissile (usually meaning odd-neutron number nuclides) in the mix decreases and even-neutron number, neutron-absorbing nuclide increase, requiring the total plutonium and/or enriched uranium percentage to be increased. Today in thermal reactors plutonium is only recycled once as MOX fuel, and spent MOX fuel, with a high proportion of minor actinides and even plutonium isotopes, is stored as waste.

Re-licensing precedes the introduction of MOX fuel into existing nuclear reactors. Often only a third to half of the fuel load is switched to MOX. The use of MOX does change the operating characteristics of a reactor, and the plant must be designed or adapted slightly to take it. More control rods are needed. For more than 50% MOX loading, significant changes are necessary and a reactor needs to be designed accordingly. The Palo Verde Nuclear Generating Station near Phoenix, Arizona was designed for 100% MOX core compatibility but so far have always operated on fresh low enriched uranium. In theory the three Palo Verde reactors could use the MOX arising from seven conventionally fueled reactors each year and would no longer require fresh Uranium fuel.

According to Atomic Energy of Canada Limited (AECL), CANDU reactors could use 100% MOX cores without physical modification. AECL reported to the United States National Academy of Sciences committee on plutonium disposition that it has extensive experience in testing the use of MOX fuel containing from 0.5 to 3% plutonium.
**Current applications**

Reprocessing of commercial nuclear fuel to make MOX is done in the United Kingdom and France, and to a lesser extent in Russia, India and Japan. China plans to develop fast breeder reactors and reprocessing. Reprocessing of spent commercial-reactor nuclear fuel is not permitted in the United States due to nonproliferation considerations. All of these nations have long had nuclear weapons from military-focused research reactor fuels except Japan.

The United States is building a MOX plant at the Savannah River Site in South Carolina. The Tennessee Valley Authority and Duke Energy are interested in using the reactor fuel from the conversion of weapons-grade plutonium.[5]

**Thermal reactors**

About 30 thermal reactors in Europe (Belgium, Switzerland, Germany and France) are using MOX[6] and a further 20 have been licensed to do so. Most reactors use it as about one third of their core, but some will accept up to 50% MOX assemblies. In France, EDF aims to have all its 900 MWe series of reactors running with at least one-third MOX. Japan aimed to have one third of its reactors using MOX by 2010, and has approved construction of a new reactor with a complete fuel loading of MOX. Of the total nuclear fuel used today, MOX provides 2%.[4]

Licensing and safety issues of using MOX fuel include:[6]

- As plutonium isotopes absorb more neutrons than uranium fuels, reactor control systems may need modification.
- MOX fuel tends to run hotter because of lower thermal conductivity, which may be an issue in some reactor designs.
- Fission gas release in MOX fuel assemblies may limit the maximum burn-up time of MOX fuel.

About 30% of the plutonium originally loaded into MOX fuel is consumed by use in a thermal reactor. If one third of the core fuel load is MOX and two-thirds uranium fuel, there is zero net gain of plutonium in the spent fuel.[6]

All plutonium isotopes are either fissile or fertile, although plutonium-242 needs to absorb 3 neutrons before becoming fissile curium-245; in thermal reactors isotopic degradation limits the plutonium recycle potential. About 1% of spent nuclear fuel from current LWRs is plutonium, with approximate isotopic composition 52% $^{239}\text{Pu}$, 24% $^{240}\text{Pu}$, 15% $^{241}\text{Pu}$, 6% $^{242}\text{Pu}$ and 2% $^{238}\text{Pu}$ when the fuel is first removed from the reactor.[6]

**Fast reactors**

Because the fission to capture ratio of neutron cross-section with high energy or fast neutrons changes to favour fission for almost all of the actinides, including $^{238}\text{U}$, fast reactors can use all of them for fuel. All actinides, including TRU or transuranium actinides can undergo neutron induced fission with unmoderated or fast neutrons. A fast reactor is more efficient for using plutonium and higher actinides as fuel. Depending on how the reactor is fueled it can either be used as a plutonium breeder or burner.

These fast reactors are better suited for the transmutation of other actinides than are thermal reactors. Because thermal reactors use slow or moderated neutrons, the actinides which are not fissionable with thermal neutrons tend
to absorb the neutrons instead of fissioning. This leads to build up of heavier actinides and lowers the number of thermal neutrons available to continue the chain reaction.

**Fabrication**

The first step is separating the plutonium from the remaining uranium (about 96% of the spent fuel) and the fission products with other wastes (together about 3%). This is undertaken at a nuclear reprocessing plant.

**Dry mixing**

MOX fuel can be made by grinding together uranium oxide (UO$_2$) and plutonium oxide (PuO$_2$) before the mixed oxide is pressed into pellets, but this process has the disadvantage of forming lots of radioactive dust. MOX fuel, consisting of 7% plutonium mixed with depleted uranium, is equivalent to uranium oxide fuel enriched to about 4.5% $^{235}$U, assuming that the plutonium has about 60–65% $^{239}$Pu. If weapons-grade plutonium were used (>90% $^{239}$Pu), only about 5% plutonium would be needed in the mix.

**Coprecipitation**

A mixture of uranyl nitrate and plutonium nitrate in nitric acid is converted by treatment with a base such as ammonia to form a mixture of ammonium diuranate and plutonium hydroxide. This after heating in 5% hydrogen in argon will form a mixture of uranium dioxide and plutonium dioxide. The resulting powder can be converted using a base into green pellets using a press. The green pellet can then be sintered into mixed uranium and plutonium oxide pellet. While this second type of fuel is more homogenous on the microscopic scale (scanning electron microscope) it is possible to see plutonium rich areas and plutonium poor areas. It can be helpful to think of the solid as being like a salami (more than one solid material present in the pellet).

**Americium content**

Plutonium from reprocessed fuel is usually fabricated into MOX as soon as possible to avoid problems with the decay of short-lived isotopes of plutonium. In particular, $^{241}$Pu decays to americium-241 ($^{241}$Am) which is a gamma ray emitter, giving rise to a potential occupational health hazard if the separated plutonium over five years old is used in a normal MOX plant. While $^{241}$Am is a gamma emitter most of the photons it emits are low in energy, so 1 mm of lead, or thick glass on a glovebox will give the operators a great deal of protection to their torsos. When working with large amounts of americium in a glovebox, the potential exists for a high dose of radiation to be delivered to the hands.

As a result old reactor-grade plutonium can be difficult to use in a MOX fuel plant, as the $^{241}$Pu it contains decays with a short 14.1 year half-life into more radioactive $^{241}$Am which makes the fuel difficult to handle in a production plant. Within about 5 years typical reactor-grade plutonium would contain too much $^{241}$Am (about 3%). But it is possible to purify the plutonium bearing the americium by a chemical separation process. Even under the worst possible conditions the americium/plutonium mixture will never be as radioactive as a spent-fuel dissolution liquor, so it should be relatively straight forward to recover the plutonium by PUREX or another aqueous reprocessing method. Also, $^{241}$Pu is fissile while the isotopes of plutonium with even mass numbers are not (in general thermal neutrons will usually fission isotopes with an odd number of neutrons, but rarely those with an even number), so decay of $^{241}$Pu.

Pu to $^{241}$Am leaves plutonium with a lower proportion of isotopes usable as fuel, and a higher proportion of isotopes that simply capture neutrons (though they may become fissile isotopes after one or more captures). The decay of $^{238}$Pu to $^{234}$U and subsequent removal of this uranium would have the opposite effect, but $^{238}$Pu both has a longer half-life (87.7 years vs. 14.3) and is a smaller proportion of the spent nuclear fuel. $^{239}$Pu, $^{240}$Pu, and $^{242}$Pu all have much longer halflives so that decay is negligible. $^{244}$Pu has an even longer halflife, but is unlikely
to be formed by successive neutron capture because $^{243}_{94}$Pu quickly decays with a half-life of 5 hours giving $^{243}_{95}$Am.)

**Curium content**

It is possible that both americium and curium could be added to a U/Pu MOX fuel before it is loaded into a fast reactor. This is one means of transmutation. Work with curium is much harder than work with americium because curium is a neutron emitter, the MOX production line would need to be shielded with both lead and water to protect the workers.

Also, the neutron irradiation of curium generates the higher actinides, such as californium, which increase the neutron dose associated with the used nuclear fuel; this has the potential to pollute the fuel cycle with strong neutron emitters. As a result, it is likely that curium will be excluded from most MOX fuels.

**Thorium MOX**

MOX fuel containing thorium and plutonium oxides has also been studied. According to a Norwegian study, "the coolant void reactivity of the thorium-plutonium fuel is negative for plutonium contents up to 21%, whereas the transition lies at 16% for MOX fuel." The authors concluded, "Thorium-plutonium fuel seems to offer some advantages over MOX fuel with regards to control rod and boron worths, CVR and plutonium consumption."

**References**


**External links**

- Burning Weapons Plutonium in CANDU Reactors (http://www.ccnr.org/nas_mox.html)
- Program to turn plutonium bombs into fuel hits snags (http://www.shns.com/shns/g_index2.cfm?action=detail&pk=NUCLEAR-03-08-06)
Environment

Plutonium in the environment

*Part of the actinides in the environment series.*

**Plutonium in the environment** since the mid-20th century has primarily been due to human activity. The majority of plutonium isotopes are short-lived on a geological timescale.\(^1\) It has been argued that some natural plutonium (the very long lived \(^{244}\text{Pu}\) isotope) can be found in nature.\(^2\) This isotope has been found in lunar soil,\(^3\) meteorites,\(^4\) and in the Oklo natural reactor.\(^5\) But in general it is normally considered that the bulk of all plutonium is man made. According to one paper on marine sediments for plutonium in marine sediments, bomb fall out is responsible for the majority of the \(^{239}\text{Pu}\) and \(^{240}\text{Pu}\) (66% and 59% respectively of that found in the English Channel) while nuclear reprocessing is responsible for the majority of the \(^{238}\text{Pu}\) and \(^{241}\text{Pu}\) present in the sea (bomb tests are only responsible for 6.5 and 16.5% of these isotopes respectively).\(^6\)

**Bomb detonations**

About 3.5 tons of plutonium have been released into the environment by atomic bomb tests. While this might sound like a large amount it has only resulted in a very small dose to the majority of the humans on the earth. Overall the health effects of the fission products are far greater than the effects of the actinides released by a nuclear bomb detonation. The plutonium from the Pu fuel of the bomb is converted into a high fired oxide which is carried high into the air. It slowly falls to earth as global fallout and is not soluble, hence as a result it is difficult for this plutonium to be incorporated into an animal if taken by mouth. Much of this plutonium will become tightly absorbed onto sediments of lakes, rivers and oceans. However, about 66% of the plutonium from a bomb explosion is formed by the neutron capture of uranium-238; this plutonium is not converted by the bomb into a high fired oxide as it is formed more slowly. As a result this formed plutonium is more soluble and more able to cause harm when it falls to earth.\(^7\)

Some of the plutonium can be deposited close to the point of detonation. The glassy trinitite formed by the first atom bomb has been examined to determine what actinides and other radioisotopes it contained. A recent paper\(^8\) reports the levels of long lived radioisotopes in the trinitite. The trinitite was formed from feldspar and quartz which were melted by the heat. Two samples of trinitite were used, the first (left hand side bars) was taken from between 40 and 65 meters of ground zero while the other sample was taken from further away from the ground zero point.
The $^{152}\text{Eu}$ and $^{154}\text{Eu}$ was mainly formed by the neutron activation of the europium in the soil, it is clear that the level of radioactivity for these isotopes is highest where the neutron dose to the soil was larger. Some of the $^{60}\text{Co}$ is generated by activation of the cobalt in the soil, but some was also generated by the activation of the cobalt in the steel (100 foot) tower. This $^{60}\text{Co}$ from the tower would have been scattered over the site reducing the difference in the soil levels.

The $^{133}\text{Ba}$ and $^{241}\text{Am}$ are due to the neutron activation of barium and plutonium inside the bomb. The barium was present in the form of the nitrate in the chemical explosives used while the plutonium was the fissile fuel used.

It is interesting to note that the $^{137}\text{Cs}$ level is higher in the sample which was further away from the ground zero point. This is thought to be because the precursors to the $^{137}\text{Cs}$ ($^{137}\text{I}$ and $^{137}\text{Xe}$) and the caesium to a lesser degree are volatile. The natural radioisotopes in the glass are about the same in both locations.

In this paper a sample of the glass was digested and the plutonium extracted from it, and the mass ratio of the isotopes was calculated from the radiometric measurements. In light green the isotopic signature for the plutonium used for making the bomb is shown, and on the right in dark green the signature of the plutonium in the trinitite glass is shown. It is very clear that $^{239}\text{Pu}$ and $^{241}\text{Pu}$ were generated during the detonation, so it is reasonable to conclude that some $^{240}\text{Pu}$ was formed during the detonation.
As the $^{239}$Pu/$^{240}$Pu ratio only changed slightly during the detonation, it has been commented\cite{9} that this isotope ratio for the majority of atom bombs (In Japan the $^{239}$Pu/$^{240}$Pu ratio in soil is normally in the range 0.17 to 0.19)\cite{10} is very different than from the bomb dropped upon Nagasaki, so the forest soil\cite{10} and the lake sediment layer containing the local fallout from World War II bomb is very different from the layers due to global fallout from bomb tests conducted later.\cite{9}

**Bomb safety trials**

One form of release of plutonium into the environment has been safety trials in these experiments nuclear bombs have been subjected to simulated accidents or have been detonated with an abnormal initiation of the chemical explosives. An abnormal implosion will result in a compression of the pit which is less uniform and smaller than the designed compression in the device. Such an abnormal implosion could result from an accident which triggers one or more of the detonators which trigger the chemical explosive charges.

As a result of these experiments (where no or very little nuclear fission occurs) plutonium metal has been scattered around near the site of the experiment. While some of these tests have been done inside holes in the ground, other such tests were conducted in open air. A paper on the radioisotopes left on an island by the French nuclear bombs tests of the 20th century has been printed by the International Atomic Energy Agency and a section of this report deals with plutonium contamination resulting from such tests.\cite{11}
Other related trials were conducted at Maralinga, South Australia, where both normal bomb detonations and "safety trials" have been conducted. While the activity from the fission products has decayed away almost totally (as of 2006) the plutonium remains active. A report (warning it is very big) can be read at[12] while a smaller report can be seen at[13].

**Atomic batteries**

**Space**
Another potential source of plutonium being introduced into the environment is the reentry of artificial satellites containing atomic batteries. There have been several such incidents, the most prominent being the Apollo 13 mission. The Apollo Lunar Surface Experiment Package carried on the Lunar Module re-entered the atmosphere over the South Pacific. Many atomic batteries have been of the Radioisotope thermoelectric generator (RTG) type.

Chain reactions do not occur inside RTGs, so such a nuclear meltdown is impossible. In fact, some RTGs are designed so that fission does not occur at all; rather, forms of radioactive decay which cannot trigger other radioactive decays are used instead. As a result, the fuel in an RTG is consumed much more slowly and much less power is produced.

RTGs are still a potential source of radioactive contamination: if the container holding the fuel leaks, the radioactive material will contaminate the environment. The main concern is that if an accident were to occur during launch or a subsequent passage of a spacecraft close to Earth, harmful material could be released into the atmosphere. However, this event is extremely unlikely with current RTG cask designs.

In order to minimise the risk of the radioactive material being released, the fuel is typically stored in individual modular units with their own heat shielding. They are surrounded by a layer of iridium metal and encased in high-strength graphite blocks. These two materials are corrosion and heat-resistant. Surrounding the graphite blocks is an aeroshell, designed to protect the entire assembly against the heat of reentering the Earth's atmosphere. The plutonium fuel is also stored in a ceramic form that is heat-resistant, minimising the risk of vaporization and aerosolization. The ceramic is also highly insoluble.

The US Department of Energy has conducted seawater tests and determined that the graphite casing, which was designed to withstand reentry, is stable and no release of plutonium should occur. Subsequent investigations have found no increase in the natural background radiation in the area. The Apollo 13 accident represents an extreme scenario due to the high re-entry velocities of the craft returning from cislunar space. This accident has served to validate the design of later-generation RTGs as highly safe.

The Plutonium-238 used in RTGs has a half-life of 88 years, as opposed to the plutonium-239 used in nuclear weapons and reactors, which has a half-life of 24,100 years.
**Pacemakers**

Some heart pacemakers which are powered by RTGs using 238Pu have been made.

**Nuclear fuel cycle**

Plutonium has been released into the environment in aqueous solution from nuclear reprocessing and uranium enrichment plants. The chemistry of this plutonium is different from that of the metal oxides formed from nuclear bomb detonations.

One example of a site (military not civil) where plutonium entered the soil is Rocky Flats where in the recent past XANES (a X-ray spectroscopy) has been used to determine the chemical nature of the plutonium in the soil.\(^{[14]}\) The XANES was used to determine the oxidation state of the plutonium, while EXAFS was used to investigate the structure of the plutonium compound present in the soil and concrete.\(^{[15]}\)

![XANES experiments done on plutonium in soil, concrete and standards of the different oxidation states.](image)

**Chernobyl**

Because plutonium oxide is very involatile, most of the plutonium in the reactor was not released during the fire. (See also Chernobyl disaster.) However that which was released can be measured. V.I. Yoschenko et al. reported that grass and forest fires can make the caesium, strontium and plutonium become mobile in the air again. \(Journal of Environmental Radioactivity, 2006, 86, 143-163.\) As an experiment fires were set and the levels of the radioactivity in the air downwind of these fires was measured.
Nuclear crime

One case exists of a German man who attempted to poison his ex-wife with plutonium stolen from WAK (Wiederaufbereitungsanlage Karlsruhe). WAK was a small scale reprocessing plant where he worked. He did not steal a large amount of plutonium, just some rags used for wiping surfaces and a small amount of liquid waste. This man was sent to prison for his crime. At least two people (besides the criminal) were contaminated by the plutonium. Two flats in Rhineland-Palatinate were contaminated. These were later cleaned at a cost of two million euro.

For photographs of the case and details of other nuclear crimes see which was presented by a worker at the ITU. A general overview of the forensic matters associated with plutonium exists. The details of how the two flats in Landau were cleaned has been recorded. In addition it has been claimed that a house in Reading, Berkshire has been contaminated with plutonium.

Environmental chemistry

Overview

Plutonium like other actinides readily forms a dioxide plutonyl core (PuO$_2$). In the environment, this plutonyl core readily complexes with carbonate as well as other oxygen moieties (OH$^-$, NO$_2^-$, NO$_3^-$, and SO$_4^{2-}$) to form charged complexes which can be readily mobile with low affinities to soil.

- $\text{PuO}_2(\text{CO}_3)^{1-2}$
- $\text{PuO}_2(\text{CO}_3)^{2-4}$
- $\text{PuO}_2(\text{CO}_3)^{3-6}$

PuO$_2$ formed from neutralizing highly acidic nitric acid solutions tends to form polymeric PuO$_2$ which is resistant to complexation. Plutonium also readily shifts valences between the +3, +4, +5 and +6 states. It is common for some fraction of plutonium in solution to exist in all of these states in equilibrium.

Binding to soil

Plutonium is known to bind to soil particles very strongly, see above for a X-ray spectroscopic study of plutonium in soil and concrete. While caesium has very different chemistry to the actinides, it is well known that both caesium and many of the actinides bind strongly to the minerals in soil. Hence it has been possible to use $^{134}$Cs labeled soil to study the migration of Pu and Cs is soils. It has been shown that colloidal transport processes control the migration of Cs (and will control the migration of Pu) in the soil at the Waste Isolation Pilot Plant according to R.D. Whicker and S.A. Ibrahim, Journal of Environmental Radioactivity, 2006, 88, 171-188.

Microbiological chemistry

Mary Neu (at Los Alamos in the USA) has done some work which suggests that bacteria can accumulate plutonium because the iron transport systems used by the bacteria also function as plutonium transport systems.

Biology

Plutonium ingested by or injected into humans is transported in the transferrin based iron(III) transport system and then is stored in the liver in the iron store (ferritin), after an exposure to plutonium it is important to rapidly inject the subject with a chelating agent such as calcium complex of DTPA. This antidote is useful for a single one off exposure such as that which would occur if a glove box worker was to cut their hand with a Pu contaminated object. The calcium complex has faster metal binding kinetics than the zinc complex but if the calcium complex is used for a long time it tends to remove important minerals from the person. The zinc complex is less able to cause these effects.
Plutonium that is inhaled by humans lodges in the lungs and is slowly translocated to the lymph nodes. Inhaled plutonium has been shown to lead to lung cancer in experimental animals.

References


[18] (http://www.germnews.de/archive/dn/2005/02/24.html#16)


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