

# NUCLEAR AGE ELEMENTS

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## INTRODUCTION

In the fifth century BC, Democritus in Greece believed that the elementary substances of the ancient world: Earth, Water Fire and Air, were formed by minute "indivisible" particles or atoms. This became real between 1803 and 1808 when John Dalton determined the masses, or atomic weights of the elements relative to each other. William Prout in 1816, advanced the idea that all atomic weights are whole numbers and integral multiples of the atomic weight of hydrogen. This idea lost favor when elements such as chlorine were found to have non-integer atomic weights.

We now know better, and it is widely accepted that neutral atoms consist of N neutrons, Z protons and Z orbital electrons. The mass number A is equal to the sum of Z and N, or:

$$A = Z + N$$

and is a rounding of the actual atomic mass M expressed in atomic mass units. (amu), with Z designated as the atomic number. In this case:

$$1 \text{ amu} = 1.6605 \times 10^{-24} \text{ [gm]}$$

Isotopes are designated for any element X in the form:



Isotopes are nuclides with the same atomic number Z, but different neutron number N and consequently mass number A. For instance, hydrogen in nature consists of 2 isotope  ${}_1\text{H}^1$ , and  ${}_1\text{D}^2$  or deuteron, with a radioactive third isotope that minimally occurs in nature from cosmic ray interactions in the atmosphere. It is artificially produced, and is designate as:  ${}_1\text{T}^3$ , or tritium.

Information about the elements is nowadays compiled from a chemical perspective in the Periodic Table of the Elements, and from a nuclear and isotopic perspective in the Table of the Nuclides.

We consider here the elements of direct interest to nuclear applications, particularly, uranium, plutonium, neptunium, lithium, thorium, zirconium, and graphite or carbon.

## THE PERIODIC TABLE OF THE ELEMENTS

In his 1869 short note on: "The Correlation Between properties of Elements and Their Atomic Weights," Russian scientist Dmitri Mendeleev arranged the elements in rows

according to their atomic weights, starting from the lightest to the heaviest. Elements that appeared in the same vertical columns showed similarities in their chemical properties. For instance magnesium and strontium have similar properties to calcium, since they appear in the same column.

Mendeleev was able to predict the properties of then undiscovered elements such as gallium, scandium, and germanium, which were discovered later on.

Pair of elements such as nickel and cobalt, and iodine and tellurium, did not fit the periodic properties of their columns, and were interchanged. He argued that their atomic weights were in error.

We now know that it is the atomic number  $Z$  that determines the chemical properties of the elements, rather than the atomic weight  $A$ , as Mendeleev thought. The modern form of the Periodic Table of the Elements as shown in Fig. 1 displays the periodicity of the properties of the elements in terms of their atomic number. No wonder, since we now know that the number of electrons, which is equal to  $Z$ , as well as their configuration, determine the chemical properties of the elements.

The Periodic Table of the Elements displays the naturally occurring elements in nature up to uranium, with an atomic number of 92. There exist only 90 naturally occurring elements with the elements 43, or technetium, and 61 or promethium, as artificially created. Elements beyond uranium with  $Z = 92$  are also artificially created and are designated as the transuranics.

The Periodic Table enlarges at the element  $Z = 57$  or lanthanum with the Rare Earths, or the Lanthanide series. It also expands at the atomic number  $Z = 89$  or actinium with the Actinides series. All the elements in the Actinide and Lanthanide series have a complex atomic structure.

1	H	2	He																																		
3	Li	4	Be	5	B	6	C	7	N	8	O	9	F	10	Ne																						
11	Na	12	Mg	13	Al	14	Si	15	P	16	S	17	Cl	18	Ar																						
19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr		
37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe		
55	Cs	56	Ba	57	La	71	Ta	72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn
87	Fr	88	Ra	89	Ac	101	Unp	102	Unh	103	Uuh																										

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.91	144.24	(145)	150.4	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97

Lanthanides

90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.04	(231)	238.03	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(258)	(260)

Actinides

Figure 1. The Periodic Table of the Elements showing the Actinides and the Lanthanides series.

## THE ACTINIDES

The heavy actinides comprise americium through the end of the series. The lighter Actinides contain thorium, uranium, neptunium and plutonium. They also contain protactinium, which is not well studied because of its intense radioactivity, even in small quantities.

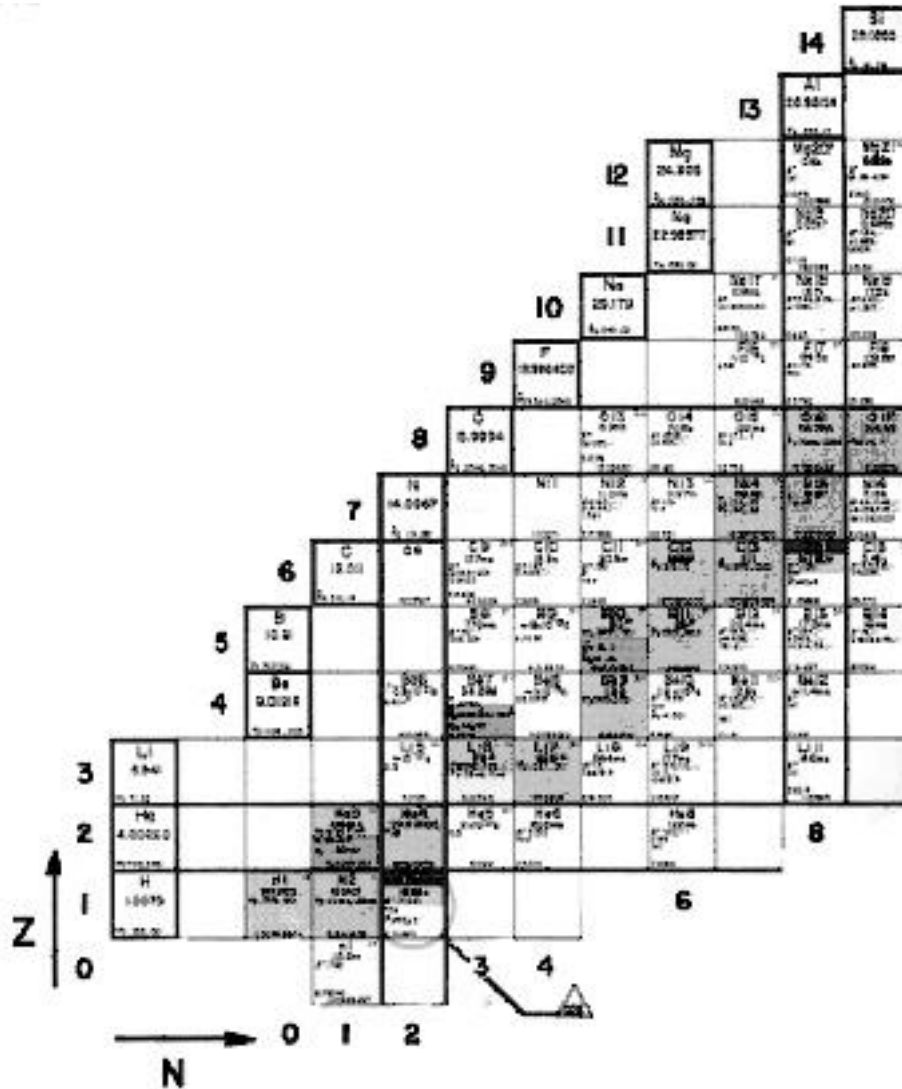


Figure 2. Table of the Nuclides or Chart of the Nuclides showing the atomic number Z against the neutron number N for the known natural and artificial nuclides.

In 2011, three new elements were added to the periodic table: Darmstadtium, Ds (110), Roentgenium, Rg (111) and Copernicium, Cn (112). The new elements were created through the process of “cross-bombardment,” in which particles are hurtled into one

another through an accelerator, such as zinc bombarding lead. Three elements, 113, 115 and 118, did not meet criteria for discovery. The discovery was achieved through a common effort by the Joint Institute for Nuclear Research in Dubna, Russia, and the Lawrence Livermore National Laboratory in Livermore, California. The International Union of Pure and Applied Chemistry reviewed the discovery of the new elements.

Two new elements 114 and 116 were also added in 2011. The researchers smashed calcium into plutonium to create element 114, and calcium into curium for element 116. Element 114 also resulted from the decay of element 116. Flerovium ( ${}_{114}\text{Fl}$ ) honors Flerov Laboratory of Nuclear Reactions, where super-heavy elements were synthesized by scientists. Georgiy N. Flerov, who passed away in 1990; a renowned physicist who discovered the spontaneous fission of uranium and was a pioneer in heavy-ion physics. Flerov founded the Joint Institute for Nuclear Research, but it was not until 1991 that the laboratory was named after Flerov: Flerov Laboratory of Nuclear Reactions (FLNR).

Livermorium ( ${}_{116}\text{Lv}$ ) honors Lawrence Livermore National Laboratory and the city of Livermore, California. Researchers from Lawrence Livermore National Laboratory (LLNL) and scientists at the Flerov Laboratory of Nuclear Reactions collaborated in Dubna on the synthesis of superheavy elements, including element 116. In 1989, Livermore scientists, Flerov and Ken Hulet, who passed away in 2010, brought scientists at LLNL and scientists at FLNR together. Flerov and Hulet's efforts eventually resulted in the synthesis of elements 114 and 116.

## **THE LANTHANIDES, RARE EARTHS**

The Lanthanides, or Rare Earths series of elements comprise elements 57 through 71 in the periodic table, or lanthanum through lutetium. These elements are nearly indistinguishable in their chemical behavior. Although they share the same outer electronic shell configuration, each element has a single extra electron than its next lighter neighbor. This additional electron is located deep within the electronic structure. It causes a smooth progression of the physical properties across the series, but has little effect on the chemical properties.

## **THE TABLE OR CHART OF THE NUCLIDES**

The Table of the Nuclides, or Chart of the Nuclides has normally an arrangement shown in Fig. 2, as suggested by Emilio Segré. It exists in many formats: wall chart, booklet, table, and an electronic World Wide Web accessible data warehouse format.

The atomic number  $Z$ , the number of protons, also equal to the number of electrons, is shown on the vertical axis. The neutron number  $N$  is shown on the horizontal axis. Each horizontal row thus shows an element and its isotopes as we move along the horizontal axis.

Heavy lines are shown at the "magic numbers" which constitute the number of protons or neutrons present when nuclear shells become closed at  $Z$  or  $N$  or both being equal to 2, 8, 20, 28, 50, 82, and 126. The most stable nuclear configurations correspond to the closed nuclear shells, such as  ${}_{20}\text{Ca}^{40}$ .

Spaces colored in gray, represent isotopes occurring in nature, and are considered stable. Each square in this case contains the atomic mass in atomic mass units (amu) on

the  $C^{12}$  scale, as well as the percent atomic abundance of each isotope. White or colored squares are artificially produced radio nuclides.

Some of the naturally occurring isotopes may be radioactive with very long radioactive decay half-lives, such as  $K^{40}$ ,  $V^{50}$ ,  $Rb^{87}$ ,  $Cd^{113}$ ,  $Te^{123}$ ,  $La^{139}$ , and  $Ce^{142}$ . In this case they are identified with a black rectangular area on top of a gray color in the square. Other naturally occurring isotopes have the black color with the rest of the square white or colored. Examples are  $Pu^{244}$ ,  $T^3$  and  $C^{14}$ , which are unstable nuclides with a sufficiently long half-life to have prevented the loss by decay of all atoms available at the time the nuclide was formed, or a short lived nuclide that is a disintegration product of the long-lived nuclide.

At the left hand side of each horizontal row, the chemical atomic weight of the element as found in nature as a mixture of its individual isotopes, is given. In this case, the atomic weight  $M$  is given as:

$$M = \sum_i \left( \frac{\gamma_i}{100} \right) \times M_i \text{ [amu]}, \quad (1)$$

where  $\gamma_i$  is the percent abundance of the  $i$ -th isotope,  
 $M_i$  is the atomic mass of the  $i$ -th isotope.

Isobars are those nuclides that have the same mass number  $A$ . They are connected by diagonal lines running from upper left to lower right. Nuclides with the same number of neutrons are called isotones.

Some of the values of the atomic abundance do not always add up to 100 percent, because of the relative accuracy of the values reported. The values reported refer to the naturally occurring elements.

In some laboratories, lithium with a depleted content of 3.75 percent in  $Li^6$  instead of the naturally occurring value of 7.5 percent can be found. This is lithium from which the  $Li^6$  isotope has been extracted to produce tritium for thermonuclear weapons. The depleted lithium was returned to the market place since chemically, it still behaves like lithium should.

Natural variations in the natural abundance of  $B^{10}$  from 19.8 to 20.1 percent have also been observed. This later discrepancy appears unexplained and merits further investigation as possibly being caused by cosmic radiation or by an Oppenheimer-Phillips neutron transmutation process with deuterium as discussed by Ragheb.

## URANIUM

### PROPERTIES

Uranium (U) is named after the planet Uranus. It is a heavy, silvery white metal, which is pyrophyric when divided into a fine powder. It is softer than steel, is malleable, ductile, and slightly paramagnetic and is attacked by water when it exists in a finely divided state. In air, a layer of oxide forms rapidly on its surface. It is not affected by alkalis, but acids dissolve the metal. Uranium moves from its alpha crystallographic form to the beta phase at  $667^\circ C$ , and to the gamma phase at  $772^\circ C$ .

It is a very dense metal at 18.9 gm/cm<sup>3</sup>. A major league baseball, which normally weighs 5.25 ounces, would weigh more than 8.5 pounds if made of uranium. A golf ball made of uranium metal would weigh 1.7 pounds.

It has fourteen natural and artificial isotopes, all of them radioactive. In nature, uranium contains the following atomic percentages of three isotopes:

U <sup>238</sup>	99.2746
U <sup>235</sup>	0.7200
U <sup>234</sup>	0.0054

Through radioactive decay chains they eventually transform into stable isotopes of lead. Uranium occurs in the following minerals: Pitchblende, Uraninite, Carnotite, Autunite, Uranophane, Davidite, Tobernite, Phosphate rock, Lignite and Monazite sands. It is more abundant than mercury, antimony, silver, cadmium, and is of the same abundance as arsenic or molybdenum. Some high grade ores contain up to 4 percent of uranium. Mining occurs at concentrations of 0.1 percent in uranium. About 4 billion tonnes of uranium are present in sea water at a concentration of 3 parts per billion (ppb).

The first uranium mining site was discovered in 1915 with 200 times the concentration of uranium in the ore as in other uranium deposits was located at Shinkolobwe in what was the Belgian Congo. The mined ore originated about 5 million years ago when it seeped upwards in a carbonate solution and became trapped in clays and granite. What was mined at the time was radium as a decay product in the uranium decay chain. It was originally used in the radiation treatment of cancer. At the time, it was extremely profitable with 30,000 times the price of gold at \$175,000 in 1915 dollars per gram of radium.

It can be prepared through the reduction of the uranium halides with alkali or alkaline earth metals, or by reducing the uranium oxides by calcium, magnesium, aluminum, or carbon at high temperatures. It can be produced by the electrolysis of KUF<sub>5</sub> or UF<sub>4</sub>, dissolved in a molten mixture of CaCl<sub>2</sub>+NaCl. Pure uranium is prepared by the thermal decomposition of uranium halides on a hot filament.

Much of the internal heat generation in the earth is attributable to the presence of uranium, thorium and potassium<sup>40</sup>. The age of igneous rocks is estimated by the presence of the U<sup>238</sup> isotope with a half-life of 4.51 x 10<sup>9</sup> years.

Uranium metal is used as a target for the production of high energy x rays. Uranium nitrate is used as a photographic toner. The acetate is used in analytical chemistry. Uranium salts have been used for producing yellow vaseline glass and glazes. The crystals of uranium nitrate are tribo-luminescent.

Uranium and its compounds are chemically and radiologically toxic. Its finely divided powder is pyrophoric presenting an explosion and fire hazard. The Maximum Permissible Concentration (MPC) of soluble uranium compounds in air based on its chemical toxicity is 0.05 [mg/m<sup>3</sup>]. It is set at 0.25 [mg/m<sup>3</sup>] for insoluble compounds. The maximum permissible body burden based on radio-toxicity is 0.2 microcurie (μCi) for soluble compounds, and 0.009 μCi for insoluble compounds. In air the MPC is 1.7 x 10<sup>-11</sup> [μCi /cm<sup>3</sup>].

The Curie (Ci) is the unit of "activity," named to honor the discoverer of radium, Madame Curie. It corresponds to the number of radioactive transformations per unit time

undergone by a radionuclide, in the conventional system of units. This is equivalent to the activity in 1 gram of radium, particularly the Ra<sup>226</sup> isotope, which has a half-life of 1600 years, and represents:

$$1 \text{ Curie} = 3.7 \times 10^{10} \left[ \frac{\text{Transformations}}{\text{sec}} \right] = 3.7 \times 10^{10} \text{ Becquerels (Bq)},$$

with the Becquerel (Bq), being the unit of activity in the Système International (SI) of units, named after Henry Becquerel, the discoverer of radioactivity, where:

$$1 \text{ Becquerel} = 1 \left[ \frac{\text{Transformation}}{\text{sec}} \right].$$

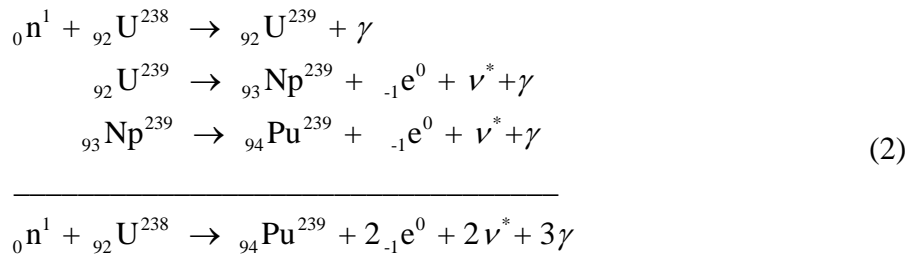
Notice that:

$$1 \text{ microCurie} = 1 \mu\text{Ci} = 10^{-6} \text{ Ci}.$$

## NUCLEAR ENERGY GENERATION

One pound of uranium, if totally fissioned, yields the equivalent energy of about 1,500 tons of coal. The most important isotope of uranium is U<sup>235</sup>, which is fissile with slow neutrons permitting the establishment of nuclear reactors using natural uranium with a moderator material that does not appreciably absorb neutrons, such as graphite (C) or heavy water (D<sub>2</sub>O).

If ordinary water (H<sub>2</sub>O) were used as a moderator and coolant, the absorption of neutrons in the nuclei of hydrogen would not provide enough neutrons to maintain a self-sustained fission chain reaction. A chain reaction can be maintained in ordinary water only if the uranium is enriched in the U<sup>235</sup> isotope from the natural abundance of 0.72 percent to a value of 3-5 percent or higher. This enrichment process can use gaseous diffusion, centrifugation and other physical processes. A result of the enrichment process is depleted uranium with about 0.25 percent U<sup>235</sup> instead of the natural 0.72 percent. This cannot be used for a self-sustained chain reaction. However, by a transmutation process, another fissile isotope Pu<sup>239</sup> can be bred from U<sup>238</sup> if subjected to a flux of neutrons in the following breeding reactions:



where  $\gamma$  is a gamma photon, and  $\nu^*$  is an antineutrino, a particle of practically zero mass associated with the conservation of momentum and parity in negative beta ( $_{-1}e^0$ ) or negative electron decay.

Metallic uranium was used in earlier reactors but has been replaced by ceramics, particularly uranium dioxide,  $UO_2$  as fuel for power reactors. Its melting point is  $2,750\text{ }^\circ\text{C}$  compared with  $1,130\text{ }^\circ\text{C}$  for uranium metal, which allows sustained operation at high temperature without phase change.

To achieve a self-sustained chain reaction, uranium must be configured into a critical mass. In this case the neutron generation is matched to the neutron absorption in the volume, and leakage through the surface of the assembly. One deals in this case with an effective multiplication factor  $k_{\text{eff}}$  as:

$$k_{\text{eff}} = \frac{\text{Number of neutrons in current generation}}{\text{Number of neutrons in previous generation}} \quad (3)$$

Three situations arise:

1. If  $k_{\text{eff}} = 1$ , the system is critical, and a self-sustained chain reaction occurs, as in an operational nuclear reactor.
2. If  $k_{\text{eff}} < 1$ , the system is subcritical, and the chain reaction is shut-down, like in the case of a reactor with its control rods inserted in.
3. If  $k_{\text{eff}} > 1$ , the system is supercritical, and the number of neutrons and the fissions increase exponentially, such as in the case of a nuclear explosion.

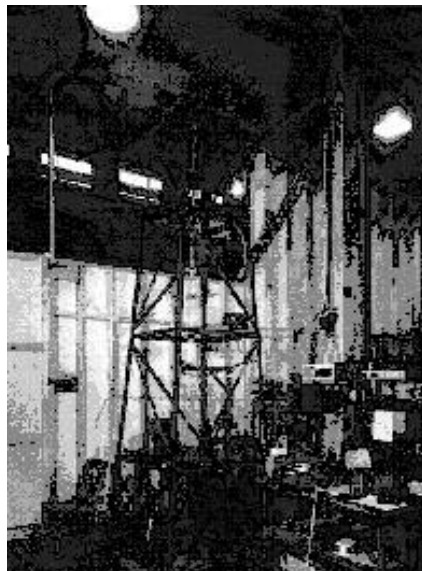


Figure 3. Guillotine mechanism where cylinders of uranium hydride were pulled through gravity down a wire between rings to estimate the critical masses.

Determining the value of the critical mass is calculated on high-speed computers, and is supplemented by critical experiments as shown in Fig. 3. Cylinders or blocks of



enriched uranium hydride are dropped along a wire in a guillotine experiment at Los Alamos National Laboratory, through rings of the same metal to experimentally determine the critical mass. The process was designated as “Tickling the dragon’s tail.” This became the basis of the Hiroshima weapon design where a subcritical cylindrical slug of enriched uranium was shot in a gun barrel through three subcritical rings of the same metal. The metal was surrounded by a reflector/tamper. And upon joining them, the combined rings and cylinder became highly supercritical resulting in the explosion.

## PLUTONIUM

### INTRODUCTION

Plutonium (Pu) is named after the planet Pluto. It exists in trace quantities in the naturally occurring uranium ores in the form of the primordial created  $\text{Pu}^{244}$  with a half-life of  $8.3 \times 10^7$  years. It also occurs in uranium ores as a result of the capture in  $\text{U}^{238}$  of neutrons from spontaneous fission and alpha-neutron ( $\alpha, n$ ) reactions. The concentration of plutonium is minute, as one part in  $10^{11}$  of the uranium present.

### PRODUCTION

The first synthetic plutonium was the  $\text{Pu}^{238}$  isotope first produced by the bombardment of uranium with 16 MeV deuterons from the University of California 60-in cyclotron in 1941.  $\text{Pu}^{239}$  was produced shortly thereafter by (d, n) reactions using the cyclotron accelerator.

The nuclear reactor produced isotope  $\text{Pu}^{239}$  is bred from  $\text{U}^{238}$  has a half-life of  $2.411 \times 10^4$  years as shown in Fig. 4. It transforms to the  $\text{U}^{235}$  isotope through the reaction:

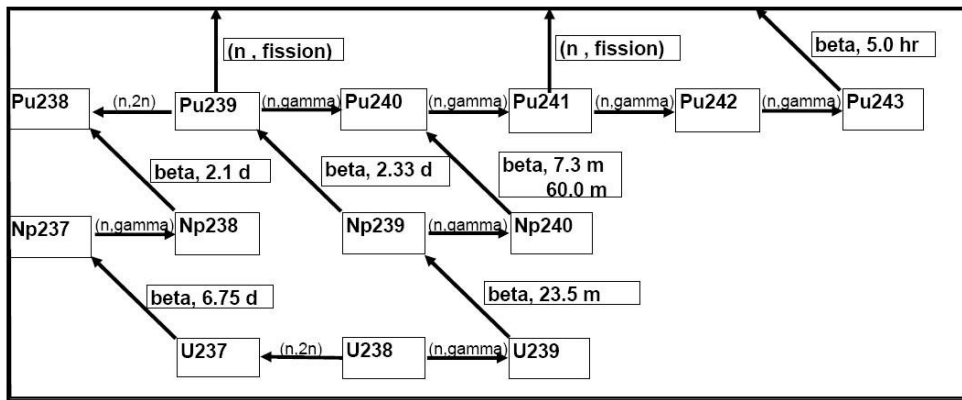


Figure 4. Production of  $\text{Pu}^{239}$  by neutron capture in  $\text{U}^{238}$  followed by beta decays, and production of  $\text{Np}^{239}$ . A fast-neutron (n, 2n) reaction results in the production of  $\text{Np}^{237}$ , which can be separated to produce upon neutron irradiation  $\text{Pu}^{238}$  used as a heat and electrical power in space power applications.

The isotopes  $\text{Pu}^{240}$ ,  $\text{Pu}^{241}$ ,  $\text{Pu}^{242}$ , and  $\text{Pu}^{243}$  are also formed from successive neutron captures. The short half-life of the  $\text{Pu}^{243}$  isotope essentially terminates the chain at the  $\text{Pu}^{242}$  isotope. Plutonium<sup>238</sup> is formed in small quantities from (n, 2n) reactions in  $\text{Pu}^{239}$  and  $\text{U}^{238}$ . The isotope  $\text{Pu}^{238}$  is a strong alpha emitter and is used as a heat source in power systems for space flight. It can be produced commercially for space applications heat and electrical sources from the neutron irradiation of the isotope  $\text{Np}^{237}$  separated from reprocessed nuclear fuel.

Plutonium<sup>240</sup> is also formed by neutron capture in the short-lived (2.3 days half-life) Neptunium<sup>239</sup>. The relative production of the  $\text{Pu}^{240}$  isotope from  $\text{Np}^{239}$  capture depends on the neutron flux level and becomes 1 percent of the total production rate of  $\text{Pu}^{239}$  at a flux of about  $4 \times 10^{14}$  [n/(cm<sup>2</sup>.sec)].

Fifteen radioactive artificial isotopes of plutonium are known. The  $\text{Pu}^{239}$  is fissile with neutrons of all energies, and is used in the breeder nuclear reactor concept in the form of the Mixed Oxide (MOX):  $\text{UO}_2 + \text{PuO}_2$ . It is also used in nuclear weapons devices.

Plutonium formed in a fast neutron spectrum is predominantly  $\text{Pu}^{239}$ , whereas significant quantities of the higher mass number isotopes may be present in plutonium from thermal or intermediate neutron spectrum reactors. In fact, the isotopic composition of plutonium depends on the design of the reactor and its operational history, as shown in Fig. 5.

Plutonium has been used as the starting point for producing other isotopes in nuclear reactors such as  $^{98}\text{Cf}^{252}$  and  $^{100}\text{Fm}^{255}$ . The Mike thermonuclear test in 1952, with its intense neutron flux, allowed the first time discovery of  $\text{Pu}^{244}$  with  $8.3 \times 10^7$  years half-life, and  $\text{Pu}^{246}$  with an 11 days half-life.

One pound of Pu has the energy equivalent content of about  $10 \times 10^6$  [kW.hr]. Other than its use in nuclear electrical power stations Pu has other power applications.

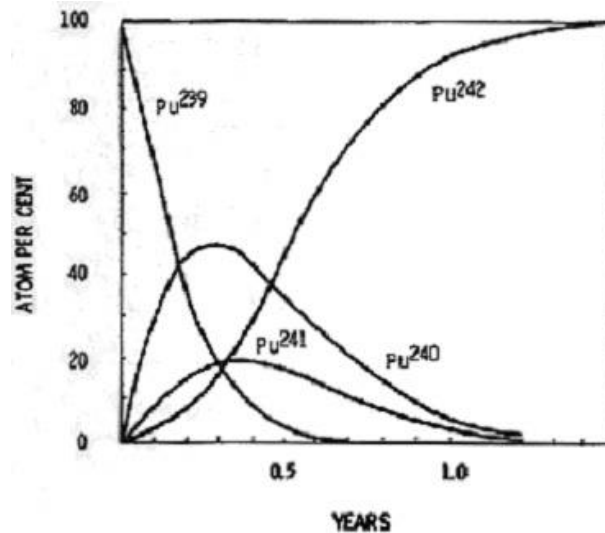


Figure 5. Isotopic content in  $\text{Pu}^{239}$  as a function of exposure to a thermal neutron flux of  $3 \times 10^{14}$  [n/cm<sup>2</sup>.sec].

## PLUTONIUM ISOTOPES

After a typical cycle of 50,000 megawatt-days of power production the irradiated fuel would contain the following plutonium isotopes:

1. Pu<sup>238</sup> is an alpha emitter but not fissile with thermal neutrons.
2. Pu<sup>239</sup> is the isotope of interest for weapons production. Weapons-grade Pu is 93 percent or higher in Pu<sup>239</sup>.
3. Pu<sup>240</sup> is formed in about 36 percent of all thermal-neutron capture events in Pu<sup>239</sup>. It is non fissile and has a very high rate of spontaneous fissions at 440 fissions / (gm.sec). This spontaneous fissions neutron emission from Pu<sup>240</sup> makes it unsuitable for weapons, causing them to fizzle and to pre-detonate and not produce a reliable yield.
4. Pu<sup>241</sup> is fissile. It is the radioactive parent precursor to Am<sup>241</sup>, used as an alpha particles source in smoke detectors.
5. Pu<sup>242</sup> is produced in about 25 percent of thermal neutron captures in Pu<sup>241</sup>. It is not fissile and has a low thermal neutron capture cross section, making it an end product of the chain.

## REACTOR VERSUS WEAPONS GRADE PLUTONIUM

All the isotopes of Pu are fissile in a fast neutron spectrum. The Pu in LWR fuel with a typical fuel burnup of 50,000 MW.day / tonne U, is about 56 percent Pu<sup>239</sup> and 27 percent Pu<sup>240</sup>.

The use of PWR reactor grade Pu in a weapon is so complex that no nuclear weapons nation has ever based its weapons program on it.

Nuclear weapons states have based their weapons programs on weapons-grade Pu<sup>239</sup> created from fuel rods irradiated for a short period in production reactors designed primarily for that purpose or enrichment using centrifugation of U<sup>235</sup> to weapons-grade levels.

A critical mass of about 10 kg of reactor grade Pu would contain about 2,700 gm of the undesirable isotope Pu<sup>240</sup>, emitting 2.7 million neutrons per second. The heat generation would make it glow red-hot affecting the surrounding chemical explosive as well as the crystal phase structure of the Pu itself, hence its density.

In comparison, 100 kgs of U<sup>235</sup> or about 2 critical masses in a speculated gun barrel approach emits just 1 neutron/sec.

Implementing an implosion system which can assemble a supercritical mass of reactor grade Pu before a chain reaction is initiated by spontaneous fission is difficult even with weapons-grade plutonium, unless an autocatalytic system with burnable poisons such as boron is used.

## PROPERTIES

Plutonium is the most complex known element. Before it liquefies it exhibits 6 solid material phases that vary considerably in density. A seventh phase may appear when the radioactive metal is under pressure.

Other anomalous properties include an almost complete absence of magnetism and a highly unusual resistivity.

The  $\text{Pu}^{238}$  isotope is an alpha particles emitter with a half-life of 87.74 years. It is available at an enrichment of 80-89 percent at about \$1,000 per gram. The heat released by the alpha decay process is significant making it warm to the touch, and a large enough piece of  $\text{Pu}^{239}$  is capable of boiling water if dropped into it. It has found usage in heat generation for warming the instrumentation in space probes. With thermoelectric and thermionic energy conversion, electricity can be produced. It has accordingly been used in heart pacers in medical applications and in Space Nuclear Auxiliary Power (SNAP) generators in various missions like the Apollo program on the Moon, the Cassini space probe to Saturn, and the Sojourner to Mars.

The plutonium metal can be produced by the reduction of its tri-fluoride with alkaline earth metals. It has a silvery appearance, is chemically reactive taking a yellowish tarnish, and dissolves in concentrated hydrochloric acid or perchloric acid forming the ion  $\text{Pu}^{+3}$ .

Extraction of plutonium is a complex industrial chemical process necessitating the use of remote control methodologies and radiation shielding in especially constructed hot cells. One such separation canyon designated as the Queen Mary as shown in Fig. 7.

Plutonium forms compounds with oxygen:  $\text{PuO}$ ,  $\text{PuO}_2$ , intermediate oxides with the halides:  $\text{PuF}_3$ ,  $\text{PuF}_4$ ,  $\text{PuCl}_3$ ,  $\text{PuBr}_3$ ,  $\text{PuI}_3$ , compounds with carbon:  $\text{PuC}$ , with nitrogen:  $\text{PuN}$ , with silicon:  $\text{PuSi}_2$ , and oxyl halides:  $\text{PuOCl}$ ,  $\text{PuOBr}$ ,  $\text{PuOI}$ .

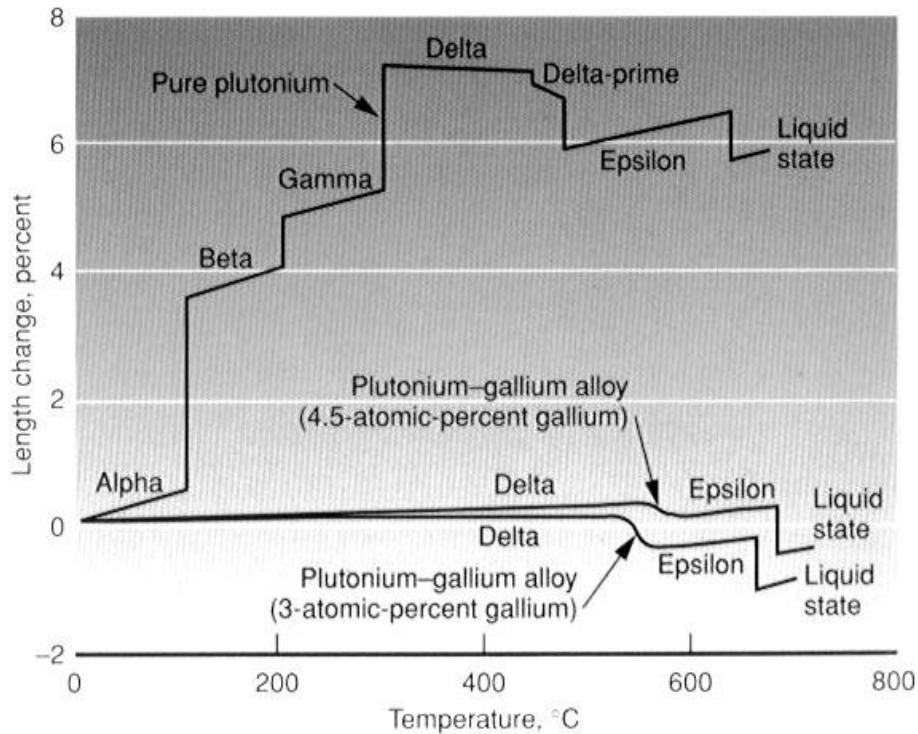


Figure 6. Different metallurgical phases of plutonium as a function of temperature. Pu can be stabilized in the delta phase at room temperature by alloying it with the rare earth element gallium.

## MANUFACTURE

A unique physical property of plutonium is that the pure metal exhibits six solid state phase transformations before reaching its liquid state. It passes from alpha, beta, delta, delta prime, to the epsilon phase. This is associated with large volume expansions and contractions between the stable room temperature alpha phase and the element's liquid phase. The different phases densities vary from 15.80 to 19.86 [gm/cm<sup>3</sup>].

Solid plutonium is most malleable in the delta phase. This phase is the most suitable for its fabrication. The delta phase of pure plutonium is stable only between 600 and 700 kelvin well above the 293 kelvin of room temperature.

The delta phase can be stabilized at room temperature with gallium, offering easier machinability, higher corrosion resistance and a melting temperature at 650 °C (Table 1).

Unalloyed plutonium melts at a relatively low temperature around 640 °C to yield a liquid of higher density than the solid form from which it melts. The elastic properties of the delta face centered cubic (fcc) phase of plutonium are highly directional or anisotropic. This means that the elasticity of the metal varies widely along different crystallographic directions by a factor of six to seven.

The delta fcc form of plutonium is stable at high temperatures and the highly symmetric fcc structure can be retained at room temperature by adding 2 atomic percent of an alloy rare earth metal such as gallium.

Table 1. Comparison of alpha and delta phase Pu<sup>239</sup>.

Allotropic Phase	Density [gm/cm <sup>3</sup> ]	Temperature range °C
α phase Pu <sup>239</sup>	19.5	20-115
δ phase Pu <sup>239</sup>	15.8	115-650
Gallium stabilized δ phase Pu <sup>239</sup>	15.8	20-650

## CHEMICAL AND RADIO TOXICITY

Because of its high alpha radioactivity and its seeking the bone marrow, Pu is radiotoxic like the other transuranics except for Np. The maximum permissible body burden, or the level that can be indefinitely maintained in an adult without significant injury, for Pu<sup>239</sup> is set at 0.04 microcurie or 0.6 microgram. Its Maximum Permissible Concentration (MPC) in air is 0.000,03 microgram / m<sup>3</sup>.

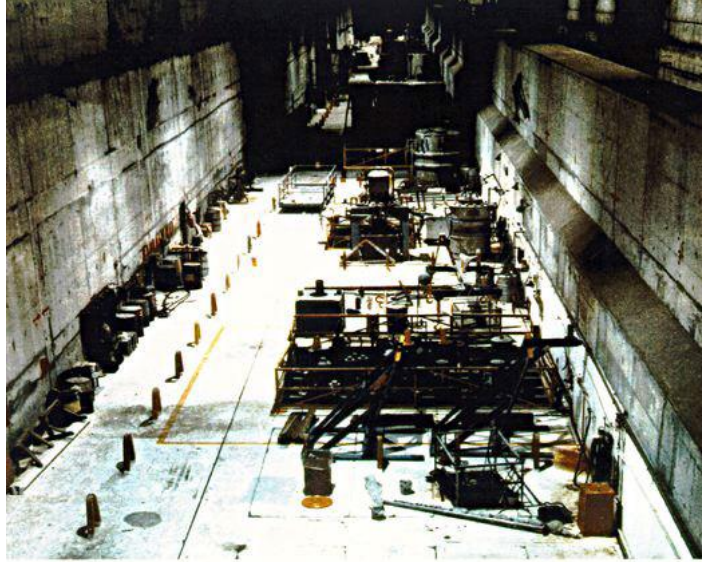


Figure 7. Queen Mary reprocessing canyon at Hanford.

## REACTIVITY EFFECTS

Low concentrations of plutonium enhance the reactivity of a reactor, and give a positive contribution to the temperature coefficient of reactivity, an undesirable feature. At high concentrations of plutonium, the sign of this contribution can reverse with a desirable negative temperature coefficient of reactivity. At concentrations of plutonium such that an appreciable amount of fission occurs in it, the control characteristics of the reactor are affected, since the delayed neutron fraction in Pu<sup>239</sup>, is one third that for U<sup>235</sup>.

## SPONTANEOUS FISSION SOURCE

The plutonium isotopes undergo a spontaneous fission process with the partial half-lives shown in Table 2, in comparison with the uranium isotopes.

To calculate the spontaneous fission neutron source we use the expression for the specific activity as:

$$\begin{aligned}
 \text{Specific Activity} &= \lambda N \\
 &= \frac{\ln 2}{T_{1/2}(\text{year}) \times 3.15 \times 10^7 \frac{\text{sec}}{\text{year}}} \frac{10^3 \frac{\text{gm}}{\text{kg}} A_v}{M(\text{amu})} \left[ \frac{\text{Bq}}{\text{kg}} \right] \\
 &= \frac{1.323 \times 10^{19}}{T_{1/2}(\text{year}) M(\text{amu})} \left[ \frac{\text{Bq}}{\text{kg}} \right]
 \end{aligned} \tag{5}$$

where: Avogadro's number  $A_v = 0.6023 \times 10^{24} \frac{\text{nuclei}}{\text{mole}}$

The neutron source from spontaneous fissions can be estimated by multiplying the specific activity by the average number of neutrons generated from fissions  $\nu$  as:

$$\begin{aligned} \text{Spontaneous fissions neutron source} &= \\ &= \frac{1.323 \times 10^{19} \nu}{T_{1/2}(\text{year})M(\text{amu})} \left[ \frac{\text{neutrons}}{\text{kg} \cdot \text{sec}} \right] \end{aligned} \quad (6)$$

### EXAMPLE

Taking  $\nu = 3$ , the partial spontaneous fission half-life for  $\text{Pu}^{242}$  is  $6.8 \times 10^{10}$  years, and its atomic weight is 242 amu. Thus:

$$\begin{aligned} \text{Spontaneous fissions neutron source} &= \\ &= \frac{1.323 \times 10^{19} \times 3}{6.8 \times 10^{10} \times 242} = 2.40 \times 10^6 \left[ \frac{\text{neutrons}}{\text{kg} \cdot \text{sec}} \right] \end{aligned}$$

Table 2. Comparison of half-lives and partial Spontaneous Fission (SF) half-lives of the plutonium and uranium isotopes

Isotope	Half life [years]	Partial Spontaneous fission half life [years]	Spontaneous fissions Neutrons emission [neutrons / (sec.kg)]
$\text{Pu}^{236}$	2.85	$3.50 \times 10^9$	
$\text{Pu}^{237}$	45.6 d	-	-
$\text{Pu}^{238}$	87.74	$4.30 \times 10^{10}$	
$\text{Pu}^{239}$	$2.411 \times 10^4$	$5.50 \times 10^{15}$	30.2
$\text{Pu}^{240}$	6,537	$1.22 \times 10^{11}$	$1.36 \times 10^6$
$\text{Pu}^{241}$	14.7	-	-
$\text{Pu}^{242}$	$3.76 \times 10^5$	$6.80 \times 10^{10}$	$2.40 \times 10^6$
$\text{Pu}^{243}$	4.956 h		
$\text{Pu}^{244}$	$8.3 \times 10^7$	$2.50 \times 10^{10}$	
$\text{U}^{233}$	$1,592 \times 10^5$	-	-
$\text{U}^{234}$	$2.44 \times 10^5$		
$\text{U}^{235}$	$7.04 \times 10^8$	$1.9 \times 10^{17}$	0.889
$\text{U}^{238}$	$4.468 \times 10^9$	$8.0 \times 10^{15}$	20.8
$\text{Np}^{237}$	$2.14 \times 10^6$	$> 10^{18}$	0.167

$\text{Pu}^{240}$  is the most stable among the even mass number isotopes and, being the most abundant among them in most samples, the  $\text{Pu}^{240}$  content can be assayed by spontaneous fission counting. The  $\text{Pu}^{238}$  content of normal reactor produced plutonium is frequently assayed by alpha energy analysis.

### REACTOR AND WEAPON CRADE PLUTONIUM

Plutonium<sup>239</sup> is the isotope used in atomic devices. In nuclear power reactors, the fuel is irradiated for over a year, and other isotopes of plutonium such as plutonium<sup>240</sup> are generated. The composition of nuclear fuel for different irradiation times is shown in Table 3.

Table 3. Comparison of the compositions of reactor, denatured, and weapons grade plutonium.

Composition Type	Fissile Pu <sup>239</sup> -Pu <sup>241</sup> [percent]	Pu <sup>240</sup> [percent]	Pu <sup>242</sup> [percent]
Typical thermal Light Water Reactor (LWR)	70	29	1
High burnup thermal Light Water Reactor (LWR)	50	40	10
Weapons grade Pu	94-99	1-6	-
High burnup denatured Pu	20	35	44
Very high burnup denatured Pu	5	13	82

The even numbered isotopes Pu<sup>240</sup> and Pu<sup>242</sup> are not fissile. These isotopes also undergo a spontaneous fission process, which generates a neutron source that would lead to the fizzling of a plutonium device using plutonium. High burnup fuel leads to denatured plutonium unsuitable for weapons manufacture. In addition the heavier plutonium isotopes are strong alpha emitters, leading to heat generation that would lead to expansion of the metallic core, and damage to the surrounding explosive material. On top of this, alpha neutron ( $\alpha$ , n) reactions with the trace light element impurities such as fluorine, oxygen and nitrogen introduced during chemical processing generate a neutron source. For all these reasons, reactor grade plutonium is unsuitable for making weapons without extremely sophisticated measures. These include the use of laser isotope separation for producing pure plutonium<sup>239</sup>. Tests have been conducted on reactor grade plutonium using burnable bubble poisons such as boron to control the neutron source until the plutonium core is fully compressed.

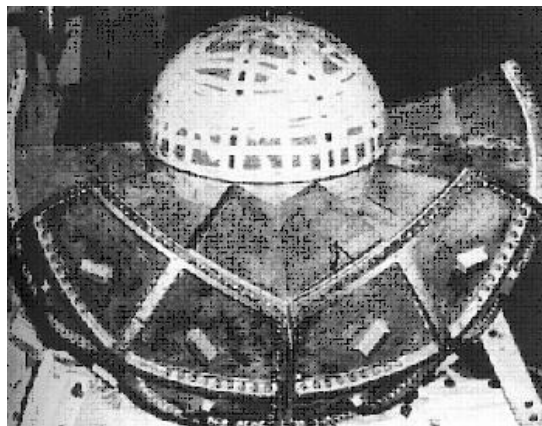


Figure 8. Early mockup of the plutonium implosion system, showing the explosive lenses and the uranium tamper.





Figure 9. Plutonium pit of trinity device being delivered to the test site.

Nations that built plutonium devices resorted to building special production reactors for this purpose. In this case, uranium is irradiated for a short period of time, around two weeks, to produce plutonium<sup>239</sup>, but not the other isotopes. Even with such pure plutonium<sup>239</sup> the existing neutron source precludes the use of a gun barrel concept like in the case of uranium<sup>235</sup>. Instead of the speed of a slug of uranium accelerated by a chemical charge, shock waves are used in the implosion process reaching the speed of sound at about 10 [km / sec]. This way, super criticality is obtained, and maintained for the metal after its compression. Figure 9 shows the pit of the Trinity first plutonium device being delivered to the test site.

Explosive lenses, as shown in the mockup of Fig. 8, are used to transform the spherically diverging shock wave from an initiator in a fast explosive, to a converging shock wave in a slow explosive. Different explosive materials are used in the explosive lenses such as Trinitrotoluene (TNT) and 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB). The properties of some explosive materials are shown in Table 4.

Table 4. Properties of some explosive materials.

	Compound B RDX/TNT 65/35	Hexogen RDX	Octogen HMX	TNT
Specific energy [kJ/g]	4.92	5.46	5.46	4.2

Density, $\rho$ [gm/cm <sup>3</sup> ]	2.333	2.376	2.533	
Adiabatic Coefficient, $\gamma$	2.776	2.908	3.004	
Detonation speed [km/sec]	7.956	8.75	9.10	
Generated pressure $p$ [Mbar]	0.287	0.338	0.398	
Chapman Jouguet Theory detonation speed, [km/sec]	2.107	2.214	2.273	
Sound speed $\sqrt{\gamma \frac{p}{\rho}}$ [km/sec]	5.649	6.425	6.827	

The convergent shock wave implodes a subcritical shell of low density plutonium at the center. A neutron source is positioned at the interior of the spherical shell, so that the nuclear reaction is only initiated upon total collapse of the shell with the first component of the neutron source, for instance polonium<sup>210</sup>, getting in contact with the second component such as beryllium. The alpha particles emitted by Po<sup>210</sup> would initiate an ( $\alpha$ , n) reaction with beryllium, releasing neutrons. Table 5 shows some possible neutron source combinations.

Instead of a static neutron source, ion accelerators can be used using the DD and the DT reactions. The reaction:



is exoergic with a Q value of 3.27 MeV. Its potential barrier is low and good neutron yields can be obtained with deuteron energies as low as 100 to 200 KeV.

In the DT reaction:



tritium is adsorbed on a zirconium or titanium target. The reaction has a strong resonance at 100 keV deuteron energy. It is exoergic with a Q value of 17.6 MeV, and the neutron energy is 14.06 MeV. At 200 keV, a neutron yield of 150 neutrons per 10<sup>7</sup> deuterons can be obtained.

Table 5. Alpha particles based static neutron sources.

Reaction	Q-value (MeV)	Neutron Energy (MeV)	Neutron Yield (per 10 <sup>6</sup> transformations)	Source Composition
${}^2_2\text{He}^4 + {}^4_4\text{Be}^9 \rightarrow {}^6_6\text{C}^{12} + {}^1_0\text{n}^1$	5.65	<13	460	${}^{88}\text{Ra}^{226} + \text{Be}$
${}^2_2\text{He}^4 + {}^4_4\text{Be}^9 \rightarrow {}^6_6\text{C}^{12} + {}^1_0\text{n}^1$	5.65	4-11	80	${}^{84}\text{Po}^{210} + \text{Be}$
${}^2_2\text{He}^4 + {}^5_5\text{B}^{10} \rightarrow {}^7_7\text{N}^{14} + {}^1_0\text{n}^1$	0.28	<6	180	${}^{88}\text{Ra}^{226} + \text{B}$
${}^2_2\text{He}^4 + {}^4_4\text{Be}^9 \rightarrow {}^6_6\text{C}^{12} + {}^1_0\text{n}^1$	5.65	<13	68.5	${}^{88}\text{Ra}^{226} \text{BeF}_4$
${}^2_2\text{He}^4 + {}^9_9\text{F}^{19} \rightarrow {}^{11}_{11}\text{Na}^{22} + {}^1_0\text{n}^1$				
${}^2_2\text{He}^4 + {}^4_4\text{Be}^9 \rightarrow {}^6_6\text{C}^{12} + {}^1_0\text{n}^1$	5.65	<11	60	${}^{94}\text{Pu}^{239} + \text{Be}$

### CRITICALITY CONSIDERATIONS

Plutonium presents a criticality hazard. If amounts exceed 300 grams are being handled a criticality danger exists. Criticality experiments must be associated with the handling of plutonium. Figure 10 shows the Jezebel bare plutonium critical assembly in its safe, half-assembled and critical configurations.

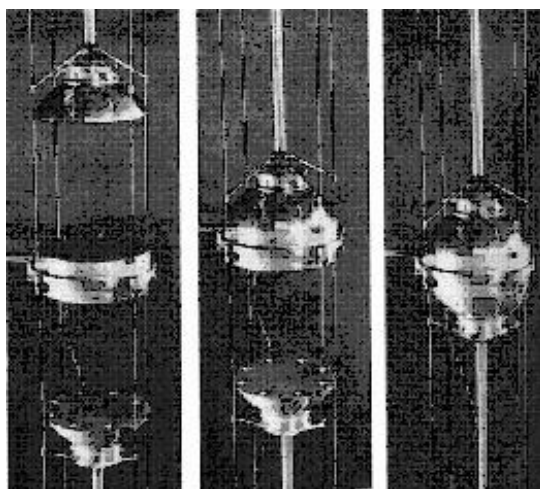


Figure 10. The Jezebel bare plutonium critical assembly in its safe, half-assembled and critical configurations.

Plutonium as a solid or in solution must be prevented from forming a critical mass like the accident in 1999 at the fuel reprocessing plant at Tokai-Mura, Japan. There, against safety rules, workers moved small amounts of a plutonium solution for reprocessing in small buckets, and exceeded the amounts that could be safely reprocessed at any given time possibly because of the ignorance of its criticality characteristics. It is more likely to form a critical mass when in liquid solution than when in solid form.

Since it is a strong alpha emitter, it must be handled in glove boxes since it is both chemically and radiologically toxic. Its radio-toxicity to the human system is twice that of radium. The maximum permissible body burden is 0.6 microgram.

### CHEMICAL SEPARATION

Three basic Pu chemical separations processes have been used on a production scale in the USA: the bismuth phosphate process, the REDuction OXidation (REDOX) process, and the Plutonium URanium EXtraction (PUREX) process.

### **Bismuth Phosphate Process:**

This batch process is based on the fact that plutonium will co-precipitate with bismuth phosphate in the +4 valence state, but not in the +6 valence state. Aluminum cladding was dissolved away from the fuel elements using a boiling sodium hydroxide solution. The bare uranium was then dissolved in concentrated aqueous nitric acid and plutonium was separated and concentrated by many cycles of precipitation and dissolution using bismuth phosphate. The bismuth phosphate process could only extract plutonium; the uranium remained in the high-level waste stream.

### **REDOX Process:**

The REDOX process was the first countercurrent, continuous-flow process for recovery of both plutonium and uranium. The heavy radionuclides Pu and U and fission products were separated in two liquid streams—an organic solution and an aqueous solution—which are not soluble in one another. REDOX began by de-cladding and dissolution of spent fuel and targets in nitric acid. An organic solvent is mixed with the resulting aqueous solution and the uranium and plutonium nitrates are transferred into the organic solvent; the fission products remain and are removed in the aqueous phase. Uranium and plutonium nitrate were then each separately reduced chemically and removed in the aqueous phase.

### **PUREX Process:**

The PUREX process is capable of recovering Pu, U, and other materials in separate cycles by countercurrent flow with organic solvents. The process begins with dissolution of the irradiated material in nitric acid. An organic solvent is introduced and the uranium and plutonium nitrates transfer into the organic solvent while the fission products remain and are removed in the aqueous phase. The desired materials—plutonium, uranium, and sometimes others, notably neptunium—are extracted and concentrated together in an organic solvent and then purified by chemical scrubbing with dilute nitric acid. Two further cycles of solvent extraction and scrubbing each result in separate, concentrated, and purified aqueous solutions of plutonium nitrate and uranium nitrate. When other materials are extracted, additional cycles of the nitrate solution are required.

## **NEPTUNIUM**

### **INTRODUCTION**

The element neptunium is named after the planet Neptune, which in turn is named after Neptune the Roman god of the sea. Neptunium (Fig. 11) was the first synthetic transuranic element of the actinide series discovered. Neptunium constitutes an artificial

decay chain with an end product as  $\text{Bi}^{239}$  (Fig. 12). It is designated by a recursive formula as the  $(4n + 1)$  chain.



Figure 11. Neptunium metal.

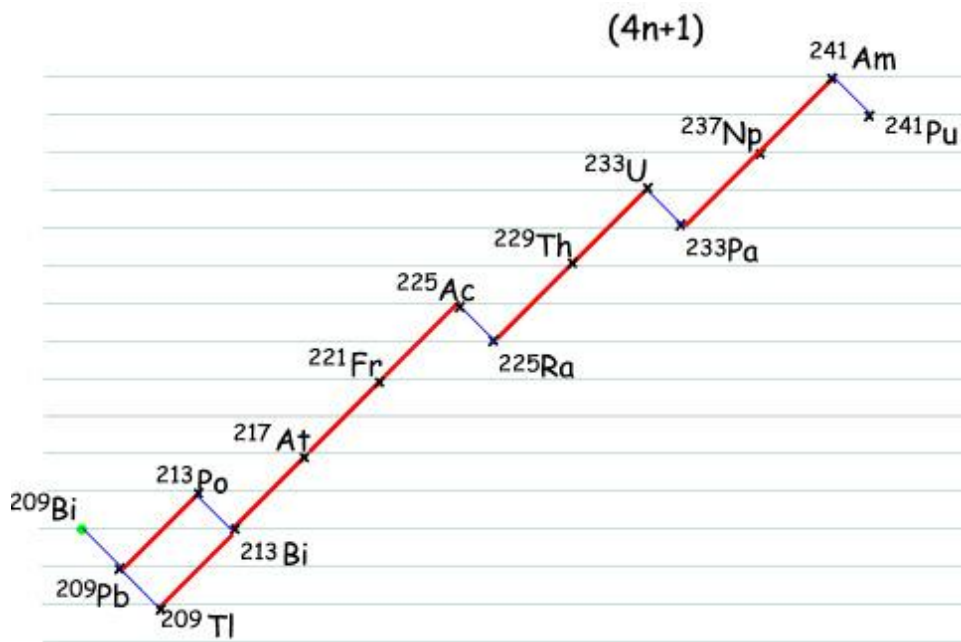


Figure 12. Neptunium decay chain.

Neptunium has fifteen isotopes. Oak Ridge National Laboratory (ORNL) had  $\text{Np}^{237}$  available for sale to its licensees and for export. It is used as a component in neutron detection instruments. It was offered for sale at a price of \$280/g as of 2002.

Working at the University of California, Berkeley, in 1940, Edwin M. McMillan bombarded a uranium target with cyclotron-produced neutrons. He noted that some unusual beta particles were emitted, indicating the presence of a new isotope. Philip H. Abelson, working with McMillan, proved in May 1940 that the beta particles came from a

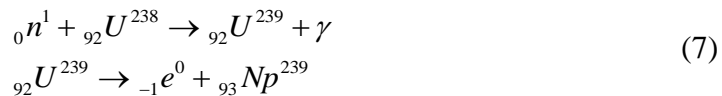
new element. They announced their discovery in a paper published in *Physical Review* later that year.

Because of national security concerns, research on neptunium continued in secret. In 1944, the first pure compound  $\text{NpO}_2$  was made using a few milligrams of the element. Scientists working toward a nuclear weapon found that plutonium was much better than neptunium for their purposes, so Np research moved to the back burner.

Sources differ on the number of isotopes neptunium has, but 17 is the most frequently given number, and they are all radioactive. McMillan and Abelson produced  $\text{Np}^{239}$ , which has a half-life of about 2.4 days. Among the isotopes, the range of stability is wide:  $\text{Np}^{232}$  has a half-life of 13 minutes, whereas for  $\text{Np}^{237}$  it is 2.14 million years.

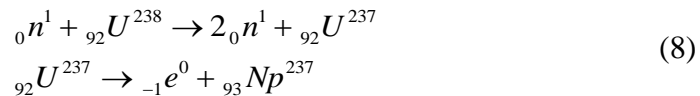
## PRODUCTION AND USE

The isotope  $\text{Np}^{239}$  was produced by McMillan and Abelson in 1940 at Berkeley, California, as the result of bombarding uranium with cyclotron-produced neutrons.



The isotope  $\text{Np}^{237}$  with a half-life of  $2.14 \times 10^6$  years and with minimal spontaneous fissions (partial spontaneous fission half-life  $> 10^{18}$  years), is currently obtained in gram quantities as a by-product from nuclear reactors in the production of plutonium.

In a fast neutron spectrum, with an (n, 2n) reaction with  $\text{U}^{238}$ , it is obtained on a short term basis from the reactions:



Even though the neutron capture reaction occurs practically over the whole energy range, the neutron multiplying reactions in  $\text{U}^{238}$  display a threshold behavior above about 6 MeV as shown in Fig. 13.

A typical 1,000 MWe Light Water Reactor (LWR) operating at an 80 percent capacity factor produces about 13 kgs of  $\text{Np}^{237}$  per year.

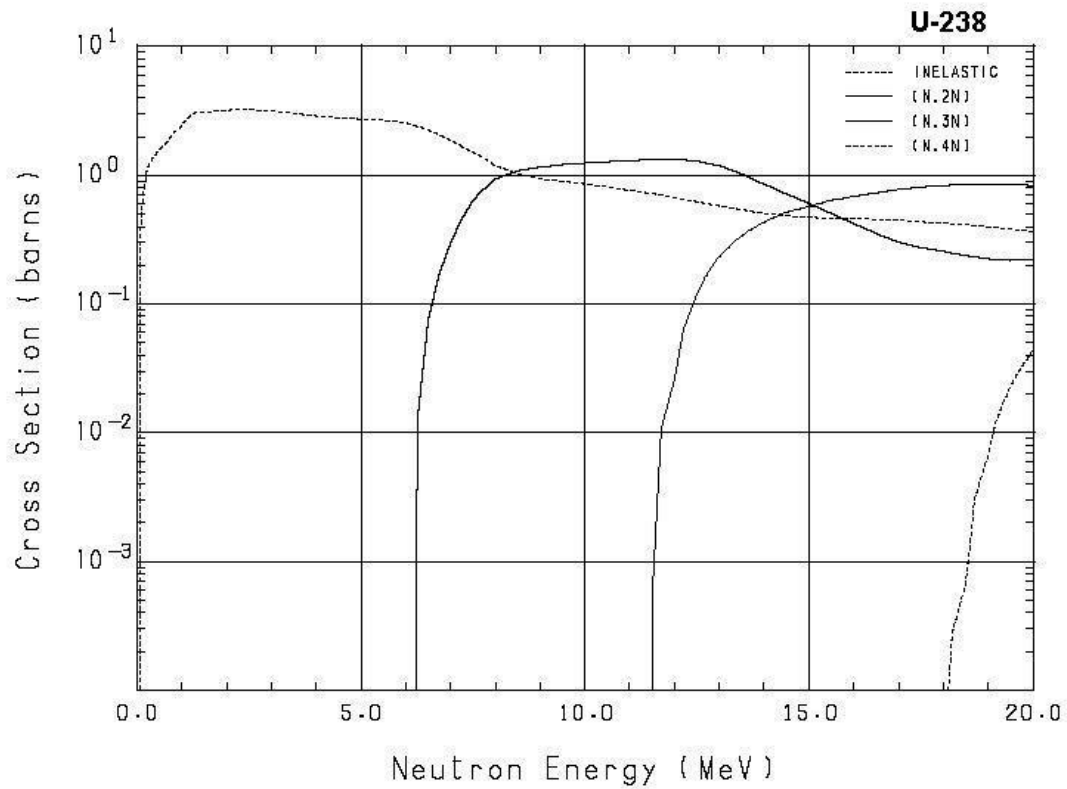
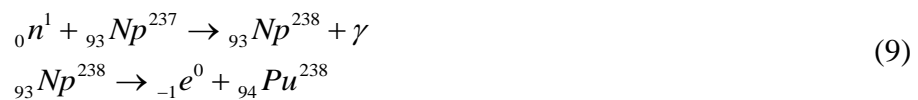
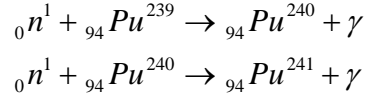


Figure 13. Inelastic and neutron multiplying threshold reactions in  $U^{238}$ .

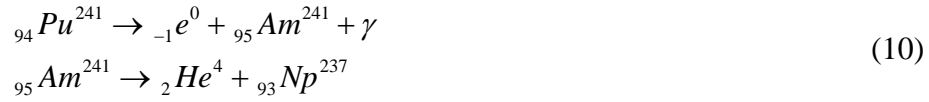
It is separated from irradiated nuclear fuel then placed in a neutron flux for the production of  $Pu^{238}$  which is used as a power source in space missions from the reaction:



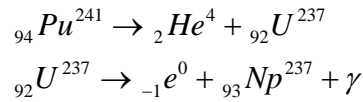
It is also produced in irradiated reactor fuel through the multiple neutron captures in  $Pu^{239}$  into  $Pu^{241}$ , then on a long term basis, through the two branches of beta or alpha decay of  $Pu^{241}$ :



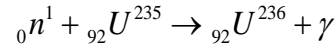
*beta decay branch:*



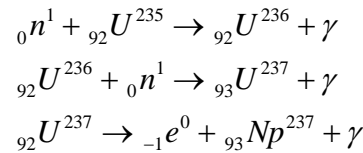
*alpha decay branch:*



In highly enriched fuels such as those used in naval reactors and fast reactors, the  $\text{U}^{235}$  isotope undergoes a radiative capture process leading to the production of the  $\text{U}^{236}$  isotope:



Its accumulation and appearance in reprocessed highly enriched fuels, being a fissionable but not fissile isotope, is an undesirable feature. Some highly enriched fuels have undergone a plasma separation process to decrease the  $\text{U}^{236}$  proportion and increase their  $\text{U}^{235}$  fraction, yielding isolated  $\text{U}^{236}$ . This can be another path for the production of  $\text{Np}^{237}$  through the reactions;



Being an odd numbered isotope, its occurrence in irradiated power reactor fuel is a safety hazard particularly in a fast spectrum, since its fission cross section in the thermal region is smaller than that of  $\text{U}^{235}$  or  $\text{Pu}^{239}$ . It may have caused criticality accidents in reprocessing wastes. It also poses a proliferation hazard even though it is produced as 1 gm of neptunium for each gram of plutonium.

The reason is that reactor grade plutonium is unsuitable for nuclear weapons manufacturing since it is a mixture of the  $\text{Pu}^{239}$ ,  $\text{Pu}^{240}$  and  $\text{Pu}^{241}$  isotopes. On the other hand, all the neptunium isotopes are short lived except for the  $\text{Np}^{236}$  and  $\text{Np}^{237}$  isotopes.  $\text{Np}^{236}$  does not occur substantially in irradiated fuel.  $\text{Np}^{237}$  in turn has negligible spontaneous fissions making it a so called “sweet” nuclear devices fuel. However, its 60 kgs unreflected or bare critical mass is larger than  $\text{U}^{235}$  critical mass of about 54 kgs, and  $\text{Pu}^{239}$  critical mass at 10 kgs.

## OCCURRENCE



Trace quantities of the element are found in nature due to transmutation reactions in uranium ores produced by the spontaneous fissions neutrons which are present. Neptunium is prepared by the reduction of  $\text{NpF}_3$  with barium or lithium vapor at about 1,200 °C.

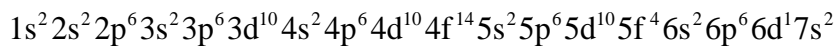
The neptunium metal has a silvery appearance, is chemically reactive, and exists in at least three allotropic forms: alpha-neptunium, orthorhombic, density 20.25 g / cm<sup>3</sup>, beta-neptunium, above 280 °C, tetragonal, density at 313 °C, 19.36 g / cm<sup>3</sup>, and gamma-neptunium, above 577 °C, cubic, density at 600 °C, 18.0 g /cm<sup>3</sup>.

Neptunium has four ionic oxidation states in solution: +3, +4, +5, and +6;  $\text{Np}^{+3}$  (pale purple) is analogous to the rare earth ion  $\text{Pm}^{+3}$ ,  $\text{Np}^{+4}$  (yellow green);  $\text{NpO}^{+}$  (green blue): and  $\text{NpO}^{++}$  (pale pink). These latter oxygenated species are in contrast to the rare earths which exhibit only simple ions of the (II), (III), and (IV) oxidation states in aqueous solution. In the +6 state, which is obtained with strong oxidizing agents, its properties are similar to hexavalent uranium, and it exists as the neptunyl ion in acid solution. In a basic medium, a dark brown precipitate:  $\text{NpO}_2(\text{OH})_2 \cdot x \text{H}_2\text{O}$ , forms. Neptunium hexafluoride is its only known hexahalide. The +5 state is stable in acidic aqueous media. In sulfuric acid it disproportionates to the +4 and +6 states since these states are complexed by sulfate ions.

Many stable compounds are known in the tetravalent state. The element forms tri and tetrahalides such as  $\text{NpF}_3$ ,  $\text{NpF}_4$ ,  $\text{NpCl}_4$ ,  $\text{NpBr}_3$ ,  $\text{NpI}_3$ , and oxides for the various compositions such as are found in the uranium-oxygen system, including  $\text{Np}_3\text{O}_8$  and  $\text{NpO}_2$ . The hydroxide, oxalate, phosphate, and ammonium and potassium fluorides are insoluble. The tetrahalides and oxyhalides were identified.

The compounds of trivalent neptunium are not prepared in aqueous solution because of rapid atmospheric oxidation. They have been prepared by electrolytic reduction of the +4 state in dilute hydrochloric acid media at a mercury cathode. The trihalides were also synthesized.

The melting point of neptunium is 639.85 °C, and its boiling point is 3901.85 °C. Its electronic configuration is:



## CHEMICAL SEPARATION

In the separation of the actinides, the PUREX chemical separation process allows the separation of 99.8 percent of the uranium and the plutonium from reprocessed nuclear fuel. The use of the Tri Butyl Phosphate (TBP) during the same process also allows the separation of the neptunium without much modification to the actual technical installations.

This result is most important since  $\text{Np}^{237}$  is in effect present at a concentration of 430 gms per metric tonne of the irradiated  $\text{UO}_2$  fuel, and only under this isotopic form even in the case of the mixed oxide of uranium and plutonium, MOX.

The technetium<sup>239</sup> is similarly extracted by the same process. However, the result is only partial since this element is in effect present, not just in solution, but also in the form of solid residues representing a few ten percent that cannot be immediately separated.

Separating the  $\text{Np}^{237}$  alone is insufficient. In fact it is itself created by the decay of  $\text{Am}^{241}$ , the latter resulting from the decay of  $\text{Pu}^{241}$ . It is thus important in the reprocessing of nuclear fuel to extract those other elements, otherwise just the extraction of the neptunium would be useless.

## CRITICALITY

The fast criticality parameters for  $\text{Np}^{237}$  are shown in Table 6. It is characterized by a fission cross section in the fast region that is comparable to that of  $\text{U}^{235}$  and  $\text{Pu}^{239}$ , but has a comparatively low value in the thermal region. Thus it is primarily a fast neutrons only fissile material.

The estimates of its critical mass differ from one source to another as shown in Table 7.

Table 6. Fast spectrum data of a bare  $\text{Np}^{237}$  core assembly.

Quantity	Data
Density, $\rho$ [gm / cm <sup>3</sup> ]	20.45
Effective delayed neutron fraction, $\beta_{\text{eff}}$ [percent]	0.091
Capture cross section, $\sigma_c$ . [b]	0.385
Fission cross section $\sigma_f$ . [b]	0.896
Average number of fission neutron by fission cross section product, $\nu\sigma_f$ . [neutron.b]	2.687
Scattering cross section $\sigma_s$ . [b]	5.825
Transport cross section $\sigma_{\text{tr}}$ . [b]	6.952
(n, 2n) reaction cross section $\sigma_{n,2n}$ . [b]	$1.69 \times 10^{-3}$
Critical radius, $R_c$ [cm]	9.29
Critical mass, $M_c$ , [kg]	68.6
Criticality parameter, $(\rho R)_c$ [g/cm <sup>2</sup> ]	181.3
Product of effective delayed neutron fraction by inverse prompt neutrons lifetime, $\alpha_c = \beta_{\text{eff}}/\ell$ [sec <sup>-1</sup> ]	$- 0.29 \times 10^6$

Table 7. Critical mass estimates for  $\text{Np}^{237}$  configurations.

Composition	Critical mass [kg]		
	Bare core	Water reflected core	Iron reflected core
$\text{Np}^{237}$ metal	56, 60, 88	51, 55, 83	33, 58, 55
$\text{Np}^{237}$ O <sub>2</sub>	288	272	187

A criticality experiment with  $\text{Np}^{237}$  was achieved in late September 2002 at the Los Alamos National Laboratory (LANL) Technical Area 18 using a six kgs nickel clad  $\text{Np}^{237}$  sphere in combination with approximately 60 kilograms of enriched  $\text{U}^{235}$  (Fig. 14).



Figure 14. Nickel-clad  $\text{Np}^{237}$  in a critical experiment with enriched  $\text{U}^{235}$  shells.

The experiment was conducted using the Planet assembly device at the Los Alamos Critical Experiments Facility (LACEF). The neptunium and enriched uranium assembly was constructed at TA-18 Critical Assembly and Storage Area-One, and mounted on the Planet device (Fig. 15). The actual criticality was controlled remotely to assure the safety and security of the experiment.



Figure 15. Criticality experiment with  $\text{Np}^{237}$ .

Data from the experiment show the critical mass of  $\text{Np}^{237}$  is actually less than previously predicted at about 60 kgs. Prior to this experiment, the critical mass of neptunium was only estimated with computer models from data based on earlier

experiments using much smaller amounts of the element in less than optimal configurations.

The results of this experiment are of interest to scientists working in the fields of nuclear safeguards, nuclear nonproliferation and criticality safety. Neptunium has isotopes that are very short-lived, but  $\text{Np}^{237}$  has an extraordinary long half-life of two million years. The International Atomic Energy Agency approved monitoring neptunium in 1999.

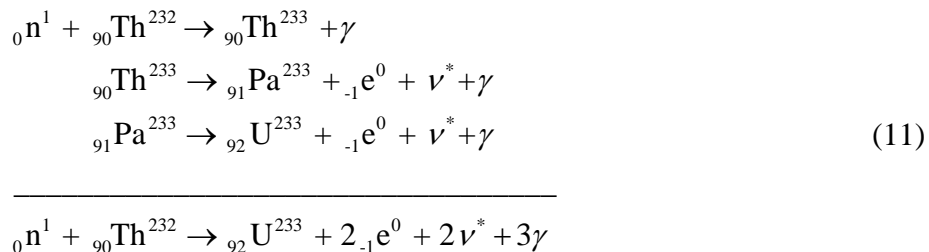
The work was done to support the DOE's Criticality Safety Program and the National Nuclear Security Administration's Nonproliferation and Emergency Response programs.

Bare criticality is achieved when sufficient mass of fissile material is present to sustain a nuclear chain reaction without any reflective materials. The neptunium criticality was achieved in a low power state where the overall radioactivity is kept relatively low, at about 300 mrem / hr, and no significant heat or fission byproducts are created.

Since the neptunium sphere alone was not of sufficient mass to sustain the nuclear reaction, it was placed in the center of several thin nested shells of enriched uranium configured in an upper and lower half, with the neptunium sphere located in the lower section. The uranium in this case helps drive the system aiding in the neptunium's ability to sustain the chain reaction. The two halves of the assembly were placed in the Planet device, one half above the other, a safe distance apart. During the experiment, measurements were taken as the lower section is raised and brought closer and closer to the upper section until sufficient mass of fissile materials is present and criticality is achieved. Since the reactivity of enriched uranium is well established, the critical mass of neptunium can be readily calculated from the experiment's data.

## THORIUM

Thorium (Th) is named after Thor, the Scandinavian god of war. It occurs in nature in the form of a single isotope:  $\text{Th}^{232}$ . Twelve isotopes are known for Th. It occurs in Thorite ( $\text{ThSiO}_4$ ) and Thorianite ( $\text{ThO}_2 + \text{UO}_2$ ). It is 3 times as abundant as uranium and as abundant as lead and molybdenum. It is commercially obtained from the monazite mineral containing 3-9 percent  $\text{ThO}_2$  with other rare-earths minerals. Its large abundance can make it in the future valuable for electrical energy generation with supplies exceeding both coal and uranium combined. This would depend on breeding of the fissile isotope  $\text{U}^{233}$  from thorium according to the breeding reactions:



Together with uranium, its radioactive decay chain leads to stable lead isotopes with a half-life of  $1.4 \times 10^{10}$  years for  $\text{Th}^{232}$ . It contributes to the internal heat generation in the Earth.

As  $\text{Th}^{232}$  decays into the stable  $\text{Pb}^{208}$  isotope, Radon<sup>220</sup> (Thoron) forms in the chain.  $\text{Rn}^{220}$  has a low boiling point and exists in gaseous form at room temperature. It poses a radiation hazard through its own daughter nuclei. Radon tests are needed to check for its presence in new homes that are possibly built on rocks like granite or sediments like shale or phosphate rock containing significant amounts of thorium. Adequate ventilation of homes that are over-insulated becomes a design consideration in this case.

Thorium, in the metallic form, can be produced by reduction of  $\text{ThO}_2$  using calcium or magnesium. Also by electrolysis of anhydrous thorium chloride in a fused mixture of Na and K chlorides, by calcium reduction of Th tetrachloride mixed with anhydrous zinc chloride, and by reduction with an alkali metal of Th tetrachloride.

Thorium is the second member of the actinides series in the periodic table of the elements. When pure, it is soft and ductile, can be cold rolled and drawn and it is a silvery white metal retaining its luster in air for several months. If contaminated by the oxide, it tarnishes in air into a gray then black color.

Thorium oxide has the highest melting temperature of all the oxides at 3,300 degrees C. Just a few other elements and compounds have a higher melting point such as tungsten and tantalum carbide. Water attacks it slowly, and acids do not attack it except for hydrochloric acid.

Thorium in the powder form is pyrophoric and can burn in air with a bright white light. In portable gas lights the Welsbach mantle is prepared with  $\text{ThO}_2$  with 1 percent cerium oxide and other ingredients. As an alloying element in magnesium, it gives high strength and creep resistance at high temperatures. Tungsten wire and electrodes used in electrical and electronic equipment such as electron guns in x-ray tubes or video screens are coated with Th due to its low work function and associated high electron emission. Its oxide is used to control the grain size of tungsten used in light bulbs and in high temperature laboratory crucibles. Glasses for lenses in cameras and scientific instruments are doped with Th to give them a high refractive index and low dispersion of light. In the petroleum industry, it is used as a catalyst in the conversion of ammonia to nitric acid, in oil cracking, and in the production of sulfuric acid.

## LITHIUM

### Discovery and occurrence

Lithium was discovered by the Swedish scientist Johan August Arfvedson in 1817. Lithium (Li) has its origin in Greek for stone: lithos. It has a soft silvery white appearance and is the lightest of the metals at a density of  $0.53 \text{ [gm/cm}^3\text{]}$ . It occurs as two isotopes in nature:

Isotope	Natural Abundance (percent)
${}_3\text{Li}^6$	92.5
${}_3\text{Li}^7$	7.5

It is found in a silicate mineral: spodumene ( $\text{LiAlSi}_2\text{O}_6$ ), in pegmatites, in brines, and in the world oceans. It is obtained through electrolysis of molten Li chloride. It is used in batteries, ceramics and lubricants and in pharmaceuticals.

Lithium's unique properties make it and its compounds attractive and versatile reagents in a broad spectrum of industrial applications. Milestones in lithium's history were the first preparations of the metal by Bunsen and Mathiessen in 1854 and those of the lithium organic compounds by Wilhelm Schlenk in 1917.

Lithium is not considered rare and can be found in all continents. The principal raw material sources are either ores, i.e. pegmatites such as the Li-Al-Si containing spodumene or salt lake brines. Recent estimates of the lithium known resources exceed 40 million tons of Li, corresponding to more than 210 million tons of lithium carbonate equivalents.

Prices for lithium are soaring as traditional demand from ceramics and glass manufacturers coincides with rising demand from lithium ion battery and electric vehicle manufacturers. Lithium prices rose from \$4,900 per tonne to \$5,900 per tonne in the year to October 2015, and since then the price has almost doubled to \$10,000 per tonne.

Lithium hydroxide and lithium carbonate are both consumed in battery cathodes. The high energy content and light molecular weight of lithium makes it an ideal energy source for transportation uses in electrical cars.

### **Geological Sources**

Brines, 61 percent: Lithium brine bodies in salt lakes, or "salars", are formed in basins where water that has leached the lithium from the surrounding mountainous rock is trapped and concentrated by evaporation. The process of extracting the lithium from brines involves pumping the brines into a series of evaporation ponds to crystallize other salts, leaving lithium-rich liquor. From shallow wells, the pumped liquor is further processed to remove impurities before conversion to either lithium carbonate or lithium chloride for further upgrading to lithium hydroxide

Hard Rock, 39 percent: There are three lithium minerals commercially mined today: spodumene, petalite and lepidolite. Spodumene is the most important commercially mined lithium mineral given its higher inherent lithia content. Both open-pit and underground mining methods are used to extract lithium minerals. Once extracted, the lithium mineral ore is crushed and subjected to a number of separation processes to upgrade the lithium content by removing waste materials.

### **Spodumene Mineral**



Figure 16. Spodumene mine, Greenbushes, Western Australia. Source: Albemarle.

Spodumene is a white to greyish mineral; chemically a lithium aluminum silicate  $\text{LiAl}(\text{Si}_2\text{O}_6)$  occurring in granite pegmatites. Milled and refined spodumene concentrates contain up to 7.5 percent lithium oxide or lithia, and have a low impurity profile. This characteristic makes them especially suitable as a clean lithia source for the glass and ceramics industry and for metallurgical applications.

One of the largest spodumene ore bodies is located in Greenbushes, Western Australia, where spodumene is mined from open pits. This ore body is unique not only in size, but also concerning the quality of the spodumene, which is very low in iron content. The ore, naturally containing up to 4.5 percent lithium oxide, is processed via gravity, heavy media, flotation and magnetic processes into a range of spodumene concentrates from 5.0 to 7.5 percent lithium oxide. Further operating modes are employed to make products that meet specific customer and application requirements.

### **Brine Sources**

Two raw material resources based on brine are located in the Salar de Atacama in Chile, and the other one in Clayton Valley near Silver Peak, Nevada in the USA. Spodumene mines are in Talison, Australia and in Kings Mountain, North Carolina, USA which is not currently in operation.

Clayton Valley Overview is located in south-central Esmeralda County, Nevada, approximately 190 miles northwest of Las Vegas, Nevada and the same distance southeast of Reno, Nevada. Clayton Valley is an anomaly in several ways. It is in the center of lithium-enriched rocks and waters related to rhyolitic volcanism and associated hot springs that occur over hundreds of square miles. It has been an intact basin receiving fluids for millions of years, and those fluids are still at shallow depths because the valley is a stable knot in the dynamic Walker Lane and Basin and Range tectonic terrain. There are geologic arguments that Li in this basin can be delivered via different processes to various reservoir rocks.

Clayton Valley is the site of the only lithium brine production operation in North America as of 2016; Albemarle's Silver Peak, which has been in production since 1966. The number of publicly acknowledged aquifers has grown from one to seven on the producing property.





Figure 17. Global Li resources, tons/ Li. Source: USA Geological Survey, Mineral Commodity Summary, 2014.



Figure 18. Salar at Silver Peak, Clayton Valley, Nevada, USA. Source: Albermarle.







Figure 19. The lithium resource at the Salar de Atacama, one of the driest deserts on earth in Chile is the most attractive in the world and in operation since the 1980s. Potash, for the manufacture of fertilizers, is also extracted. Source: Albemarle.

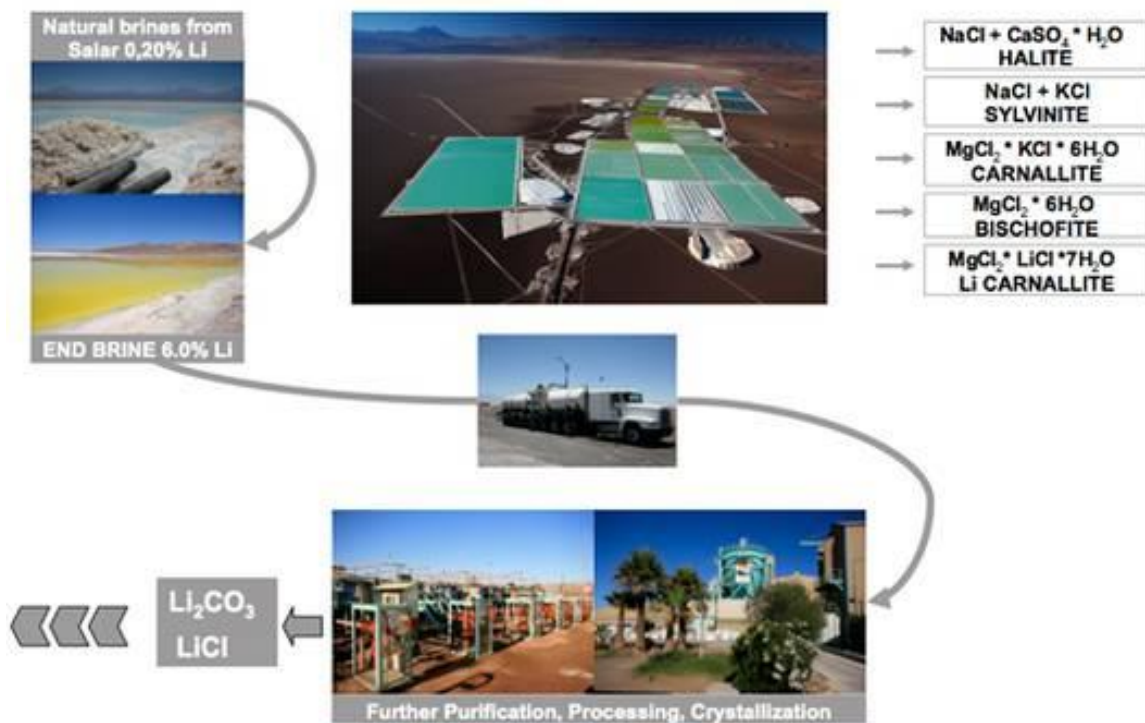


Figure 20. Li production process from carbonate brines in Chile. Source: Albermarle.

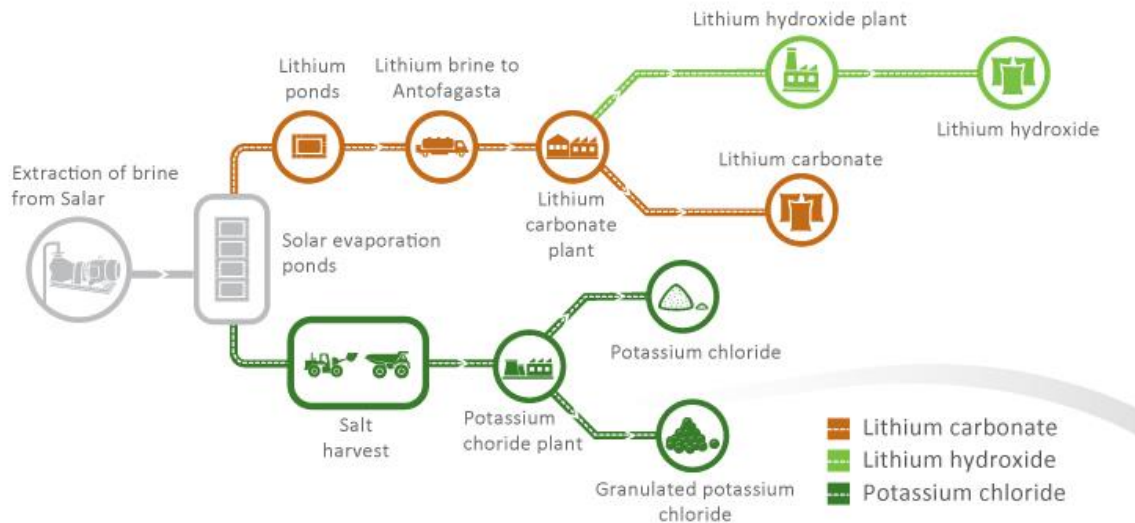


Figure 21. Production of Li carbonate, Li hydroxide and K chloride. Source: SQM.

### Industrial production

The lithium-containing brine is pumped out of the Salar de Atacama resource into evaporation ponds, concentrated, and then purified on its way through the system. The brine is pumped through a cascade of ponds where impurities or by-products are crystallized and removed. Main by-products are potash for the fertilizer industry and bischofite used for road paving. During the evaporation process, the lithium concentration is increased from about 2,000 ppm to up to 6% in the final brine. The final brine is transported to the Antofagasta plant for further purification and processing to yield lithium carbonate  $\text{Li}_2\text{CO}_3$  and lithium chloride  $\text{LiCl}$ .

Salar brines are located in the nucleus of the Salar de Atacama. They contain the largest lithium and potassium concentrations ever known, in addition to considerable sulphate and boron concentrations. From this natural resource lithium carbonate, potassium chloride, potassium sulfate, boric acid and magnesium chloride are produced.

The Salar de Atacama is a source of underground salar brines, formed through natural leaching from the Andes Mountains: throughout time, diverse minerals found under the salt surface crust have descended from the mountains, accumulating in increasing concentrations. Together with high concentrations of salar brines, the Salar de Atacama has a series of advantages: it enables low processing costs due to its reduced magnesium content; it has higher evaporation rates than other salt plains in the world and it is able to operate all year long due to the privileged weather conditions that favor it.

Salar brines are pumped from beneath the saline crust in two different areas of the salar. In one of them, extracted salar brines contain unprecedented concentration levels of potassium and lithium. In the other, salar brines obtained contain high concentrations of sulphate and boron.

After extraction, the salar brines are located in solar evaporation. The Atacama Desert is the driest place on earth, with a solar evaporation index of 3,200 millimeters and average precipitations of only 15 millimeters per year. This results in an extremely efficient process of solar energy concentration.

## **Industrial uses**

Otto Schott suggested the use of lithium compounds in the production of specialty glass as early as 1879, and C. M. Hall investigated their effects in aluminum electrolysis in 1886. Lithium derivatives were considered rather exotic for quite a long time, and were hardly used commercially until the 20th century.

Lithium's industrial use began with the first commercial production of lithium carbonate, lithium chloride and lithium metal by a German company, Metallgesellschaft/Chemetall now called Albemarle, in 1923. At that time the metal was used as an additive for a new antifriction alloy, "Bahnmetall" or "railway metal" in German, in the axle boxes of rail wagons.

Reliable sources of supply and new technological developments resulted in lower prices and larger and more diversified demand in the 1950s. Lithium carbonate came to be used widely in the aluminum, glass, enamel and ceramic industries. Lithium hydroxide became increasingly important in the production of high-performance lubricating greases. In the form of various salts, lithium carbonate for example is a highly effective medicine for the treatment of bipolar disorders or manic depression.

Lithium batteries have generated a lot of positive publicity because of their great efficiency. Lithium bromide has been used for many years in industrial absorption refrigerators. The most important application of butyl-lithium is as a polymerization initiator for the production of thermoplastic elastomers. Its applications in industrial pharmaceutical chemistry have developed most significantly.

Lithium specialties are versatile tools in synthetic organic chemistry. Lithium chemistry, characterized by flexibility and progress, is applied in many and diverse sectors of industry.

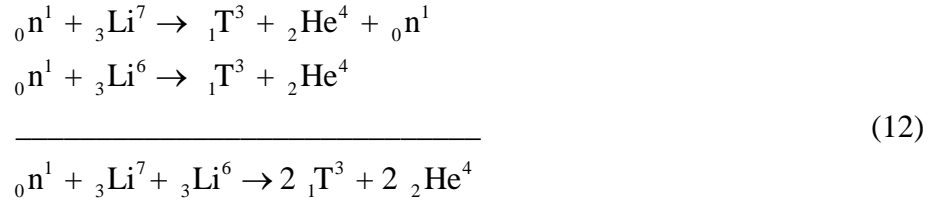
Lithium hydride is effective in the transportation of hydrogen. When 2 grams of the solid hydride is treated with water it produces 200 cubic feet of the gas. Because of this feature, it was employed during World War II in signal balloons and in air-rescue kits incorporating small antennae balloons.

Lithium is suggested as a neutron shielding material for space applications. This feature may become useful to store hydrogen for transportation purposes and fuel cell applications in a future hydrogen economy.

## **Fusion Energy Application**

The hydride with deuterium or  $\text{Li}^6\text{D}$ , lithium deuteride, was used in the form of a powder in thermonuclear weapons to breed tritium from the interaction of neutrons with the lithium<sup>6</sup> isotope, which would then fuse with deuterium at high temperatures through the DT fusion reaction.

Tritium, an isotope of hydrogen can be bred from natural Li with slow and fast neutrons for use in future fusion reactors as a coolant and tritium breeding material, through the reactions:



The first reaction is endothermic and proceeds with a fast neutron, then produces a triton and a neutron which in turn, as a slow neutron can produce a second triton through interaction with the  $\text{Li}^6$  isotope. For tritium used in thermonuclear devices Li is enriched into the  ${}^6_3\text{Li}$  isotope and only the second reaction is used to breed tritium with the neutrons being provided by fission reactors.

When lithium is bombarded with protons, very energetic gamma rays are emitted from the reaction:



The energy of these photons are 17.2 MeV, far higher than the 2.6 MeV photons which are the most energetic photons available from the natural radioactive nuclides. These photons can be used to photo-disintegrate other nuclei such as through the reactions:



Because it has a heat capacity three times that of sodium, it has been suggested as a coolant for future fusion reactors. It has, in its depleted  $\text{Li}^7$  form to avoid the formation of tritium from  $\text{Li}^6$  in a thermal neutron spectrum, been used in fission submarine reactors and in molten salt cooled reactors.

## CARBON AS GRAPHITE

Graphite is an allotropic form of carbon. Unlike diamond, it is an electrical conductor used in the electrodes of arc discharges. It is the most stable form of carbon that is hard to ignite. It is the highest grade of coal sometimes called meta-anthracite. It is named from the Greek “graphein” meaning “to draw, write” for its use in pencils “leads.” Thin flakes of graphite are flexible but inelastic. The mineral leaves black marks on hands and paper. It conducts electricity and shows superlubricity.

It was used as the moderator for the first nuclear reactor ever built: The Chicago Pile Number 1 or CP-1. It has also been used as a moderator for air cooled reactors for plutonium production, and in gas cooled reactors.

It is used as graphite fiber as a reinforcement for plastic.

Three ore deposits contain graphite. Crystalline flake graphite occurs as an isolated flat plate like particles with hexagonal edges if unbroken and when broken the edges could be irregular or angular. Amorphous graphite occurs as fine particles as a result of thermal

metamorphism of coal which is the last stage of coalification. Lump graphite or vein graphite is probably hydrothermal in nature and occurs in veins or fractures as massive fibrous or acicular crystalline aggregates.

Another form of graphite is pyrolytic graphite. The theoretical density of graphite ranges from 2.09 to 2.23 with an average value of 2.16 [gm / cm<sup>3</sup>]. Practically the evolution of gas from the pinch binder gives the material a porous structure with a lower density in the range of 1.6-1.8 [gm / cm<sup>3</sup>]. Pyrolytic carbon is used in the HTGR with a lower density that approaches the theoretical value. It is produced by deposition of carbon on the heated surface of a fuel particle in a fluidized bed, as a result of the thermal decomposition of a gaseous hydrocarbon such as methane gas. Pyrolytic carbon is highly anisotropic since the atomic sheets are aligned parallel to the surface on which the carbon is deposited. The impermeability of the material is remarkable, so that a 50 μm thick layer is impermeable to the gaseous fission products released in a fuel particle, a desirable safety feature. Figure 16 shows the triso graphite and silicon carbide coated particles fuel.



Figure 22. The Triso fuel particles contain 93 percent enriched U<sup>235</sup> or recycled U<sup>233</sup> as fuel in gas cooled reactors. The fuel particle is surrounded by pyrolytic carbon and SiC shells.

Another type of particle designated as the Biso particle contains Th<sup>232</sup> as a fertile fuel. The different layering between the triso and biso fuel particles allows them to be separated during reprocessing. At a given temperature the biso graphite layer can be burned, whereas the triso's SiC coating would not, separating the bred U<sup>233</sup> from the initial fuel loading. They are both manufactured either as graphite fuel element blocks as shown in Fig. 23 or as pebbles as shown in Fig. 24.

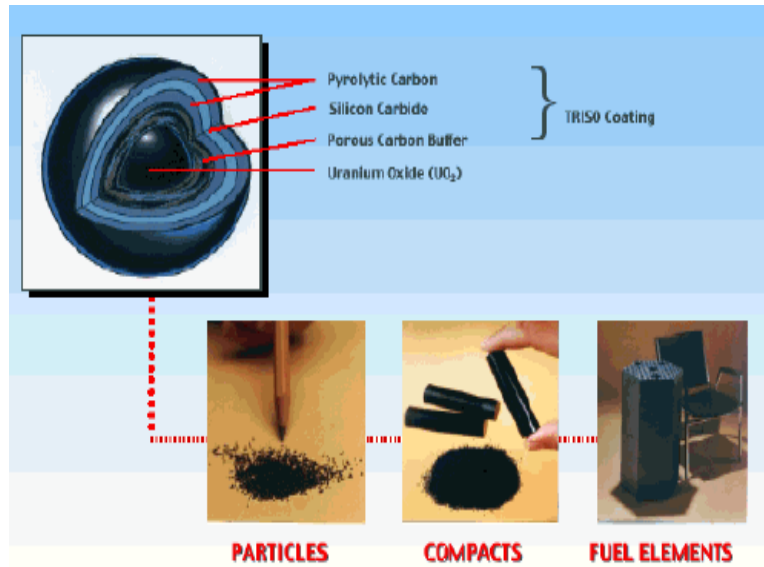


Figure 23. Fabrication of the Biso and Triso pellets into fuel elements blocks.

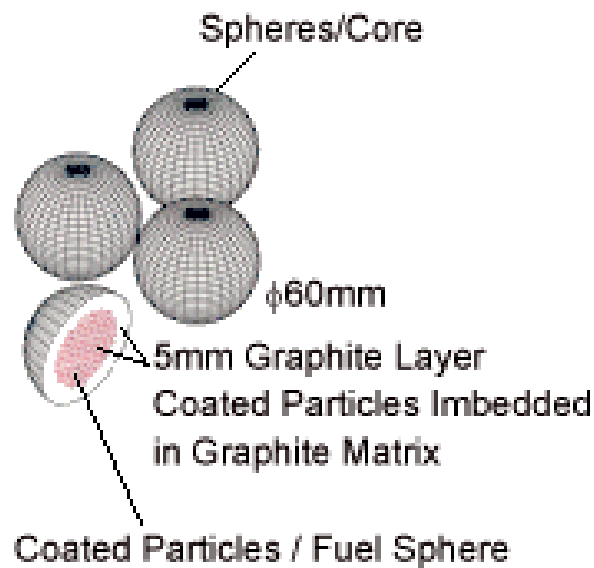


Figure 24. Fabrication of graphite pebbles from the triso and biso pellets embedded into a graphite matrix.

Graphite has a good moderating ratio, high thermal conductivity, good mechanical properties, and ability to operate at high temperature, is readily available and has high thermal inertia.

One of its limitations is its tendency to interact with oxygen and CO<sub>2</sub> at high temperature, which led to a fire at the Windscale accident in England, and later on in the Chernobyl accident of the RBMK-1000 design in the Ukraine. Its reaction with CO<sub>2</sub> can be controlled by the addition of some gas like methane to the coolant. Highly isotropic graphite must be manufactured to avoid dimensional changes under irradiation.

Graphite is produced commercially by graphitization of petroleum coke, which is a byproduct of oil refining. Ground coke is mixed with a pitch blender, the mixture is extruded, baked and graphitized at temperatures of 3,000 °C using electrical resistance heating. In this last stage, high purity graphite is produced, since any impurities are then volatilized.

Neutron irradiation below 300 °C produces an elongation perpendicular to the direction of extrusion, due to the displaced atoms coming to rest in the space between the atomic planes. A shrinkage occurs in the direction parallel to the extrusion. If operated at higher temperatures, self-annealing reduces the number of interplane defects. As the temperature goes above 300 °C, irradiation causes shrinkage in both directions. At temperatures in the range of 500-550 °C, a rapid growth rate occurs, thought to be caused by clustering of the vacancies or by increased porosity.

The extrusion process causes the anisotropy of the physical properties of graphite, with an alignment of the coke particles in the direction of extrusion. Graphite possesses a layered crystal structure with a hexagonal array in each sheet held together by covalent bonding. The bonding between one sheet and the other is by weak Van der Waals forces. As a result, the tensile strength is greater in the perpendicular direction to the planes. A similar anisotropy is shown in other physical properties such as electrical and thermal conductivity.

If graphite is an important structural element in the core, excessive change in direction can lead to slackness in the reactor structure. Misalignment can lead to difficulties in the refueling and control rod motion operations. Using keying on the graphite bricks, zirconium pins to keep the lattice pitch, isotropic graphite produced by a pressed mold method, have been approaches to minimize dimensional changes. A returning flow of cooler gas maintaining the graphite sleeve surrounding the fuel element at a temperature that minimizes dimensional changes is necessary.

An interesting result of atomic displacements of graphite under neutron irradiation is the “Wigner energy” effect. Upon irradiation at low temperature, the displaced atoms accumulate in interlattice positions, resulting in energy storage in the lattice. This energy can be released by raising the graphite to a level where the thermal agitation would cause the atoms to drop back to fill the lattice vacancies, or annealing the graphite. This annealing process has to be conducted in a controlled fashion at a suitable rate of temperature rise. If the process is uncontrolled, the process becomes self-accelerating because of positive feedback. It was an uncontrolled Wigner energy release caused by inadequate instrumentation which led to the Windscale(Sellafield) accident in the UK in 1957. A remedy for such situation is to operate graphite moderated reactors at such high temperature that self-annealing would occur.

The oxidation of graphite if air is used as a coolant has led to the use of carbon dioxide as a coolant. The use of carbon dioxide is also limited by the reaction:



which leads to erosion of the graphite and a mass transport of the carbon to be deposited in other parts of the cooling circuit. For this reason, in newer gas cooled reactor designs such as the High Temperature Gas Cooled Reactor (HTGR), helium gas is used as a coolant.

## ZIRCONIUM

The inside of a nuclear reactor core needs the use of materials that have a low absorption for neutrons to ensure an adequate neutron economy for sustaining the chain reaction. Four potentially useful materials are Al, Be, Mg, and Zr. Their properties are shown in Table 8 as compared to steel as Iron.

Magnesium and aluminum appear to have low melting points, so that they can be used in low temperature reactors. Beryllium is a brittle metal, hard to fabricate, expensive and toxic. Zirconium stands out with high temperature operational capability as well as a low absorption cross section. It is also reasonably abundant in the “zircon” mineral from the Arabic “zarcoon”, has good corrosion resistance. It is thus used for the cladding enclosing the fuel in modern nuclear reactors, as well as the structure in the reactor core such as fuel spacers.

Zirconium, like stainless steel, forms a protective, invisible oxide film on its surface upon exposure to air. This oxide film is composed of zirconia or  $ZrO_2$  and is on the order of only 50 to 100 angstroms in thickness. This ultra-thin oxide prevents the reaction of the underlying zirconium metal with virtually any chemical reagent under ambient conditions. The only reagent that will attack zirconium metal at room temperature is hydrofluoric acid, HF, which will dissolve the thin oxide layer off of the surface of the metal and thus allow HF to dissolve the metal itself, with the concurrent evolution of hydrogen gas.

In manufacturing zirconium, care must be expanded in eliminating hafnium which occurs in nature with it, since it has a high neutron absorption cross section.

Alloying zirconium enhances the corrosion resistance and strength of zirconium. Zircaloy-2 has 1.2-1.7 wt percent of Tin, with minor amounts of iron, Chromium, and Nickel. Zircaloy-4 is similar, but without the Nickel. An alloy that offers improvement in strength is Zr- 2 1/2 percent Niobium.

Hot water is a highly corrosive substance at the typical operating temperature of 300 °C. In the range 300-360 °C the corrosion rate is slowed down by the formation of a thick zirconium oxide film:



that adheres to the surface. At this point further corrosion depends on further diffusion through this film. At a critical thickness, breakup of the film can occur with increased corrosion rates. Breakup can be accelerated by the presence of carbon and nitrogen in the zirconium. These impurities are countered by the alloying elements.

Table 8. Properties of materials used in nuclear reactor core structures.

Element	Thermal Absorption Cross Section(mb)	Melting point (°C)
Aluminum	233	660
Beryllium	8	1,280
Magnesium	63	651
Zirconium	184	1,851
Steel (Iron)	2,550	



Embrittlement of the Zircaloy-2 alloy can occur as a result of hydrogen pickup and formation of zirconium hydride. Exposure to fast neutron fluxes also increases the corrosion rate of Zirconium alloys, but not to the point where cladding corrosion becomes a life limiting factor of fuel elements.

Depending on fast neutron irradiation, stress from the rolling process and the time of exposure, an increase in the creep rate in Zircaloy pressure tubes is noticed.

## **HELIUM**

### **OVERVIEW**

Helium (He) is one of the noble or inert gases, which include argon, neon, and xenon. Its boiling point is  $-269\text{ }^{\circ}\text{C}$ , lower than any other element. It is present in small quantity in the atmosphere, but is extracted industrially from hydrocarbon deposits such as natural gas. Its origin in the stars is from the fusion process of the elementary hydrogen nuclei. In the Earth's crust, it results from the radioactive decay of heavy nuclides through the emission of alpha particles, which are helium nuclei. It is the second lightest element in the universe after hydrogen and had the lowest boiling point of any gas.

### **USES**

Helium is a vital gas for medical Magnetic Resonance Imaging (MRI) scanners that are the biggest consumers of this gas. It is used for cooling the super-conducting magnets in MRI scanners. It is used in making computer chips, in deep-sea diving, in welding tools, weather balloons and the manufacture of rocket fuel. Global demand may rise to about 300 million cubic meters (10.6 billion cubic feet) per year in 2030 from 175 million  $\text{m}^3$  / year in 2011.

Helium is a suitable coolant for gas cooled reactors substituting for the earlier used carbon dioxide and air coolants. The first advantage is that, being a noble gas, it does not easily form compounds with the other elements. The second advantage is that it does not activate into other radioactive products. When air is used, for instance, it contains argon by 0.94 in volume percent, whose  $\text{Ar}^{40}$  isotope, at a 99.6 atomic percent abundance, activates through neutron absorption into  $\text{Ar}^{41}$ , which is a negative beta emitter with a half-life of 1.83 hours.

With helium, it is possible to operate gas cooled reactors, which are moderated with graphite, at temperatures exceeding  $800\text{ }^{\circ}\text{C}$ , resulting in higher overall thermal efficiencies than light water, and heavy water cooled reactors. In addition, process heat applications can be attempted such as high temperature electrolysis of water to produce portable hydrogen fuel from water for future transportation needs with fuel cells replacing the internal combustion engine.



Figure 25. Liquid Helium.



Figure 26. Shenandoah, ZR-I, first USA He-filled dirigible.

The helium gas does not react with the reactor's structure, but great care must be expanded to prevent other gases from leaking into the coolant circuit such as steam from the heat exchangers, air through leaks in the circulators, and gases adsorbed on the graphite's surface.

As a remedy for an impending He shortage, other alternative gaseous coolants for nuclear reactors such as  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{N}_2\text{O}_4$  (as a dissociating gas) need to be investigated.

Russia, as a large producer of natural gas, could become the biggest supplier of He. While helium is the universe's most abundant element after hydrogen, supply on Earth is limited to natural gas reservoirs.

As helium is lighter than air it can be used to inflate airships, blimps and balloons, providing lift. Although hydrogen is cheaper and more buoyant, helium is preferred as it is non-flammable and therefore safer.

Helium's low boiling point makes it useful for cooling metals needed for superconductivity, from cooling the superconducting magnets in medical MRI scanners to maintaining the low temperature of the Large Hadron Collider at the CERN Laboratory, Switzerland, as well as future magnetic confinement fusion reactors..

Divers and others working under pressure use mixtures of helium, oxygen and nitrogen to breathe underwater, avoiding the problems caused by breathing ordinary air under high pressure, which include disorientation.

As well as being used to clean out rocket engines, helium is used to pressurize the interior of liquid fuel rockets, condense hydrogen and oxygen to make rocket fuel, and force fuel into the engines during rocket launches.

Helium can be used to estimate the age of rocks and minerals containing uranium and thorium by measuring their retention of helium.

He gas is used in solar telescopes to prevent the heating of the air, which reduces the distorting effects of temperature variations in the space between lenses.

## **SUPPLY**

The USA, the largest supplier, according to a 1996 law, decided to dispose of a federal stockpile maintained during the Cold War. The law stipulates that the USA National Helium Reserve, which is kept in a disused underground gas field, by far the biggest store of helium in the world, must all be sold off by 2015, irrespective of the market price. Global demand may rise 2 to 3 percent per year over the next years. The USA Bureau of Land Management raised the price for open market crude helium by almost 16 percent to \$75 a thousand cubic feet in 2011, after a review of how the policy affected USA interests and the global market. Russia is poised to increase its extraction in remote gas fields in Eastern Siberia that are helium rich and could hold a third of the world's remaining resources. Other suppliers are Algeria and Qatar, where the Exxon Mobil Corporation, and industrial gas producers Linde Group and Praxair Incorporated have invested in capacity.

Qatar could become the world's second-largest helium supplier after opening a second production facility in 2013. The Qatar Helium-2 Project plans sales of 1.3 billion cubic feet a year, almost double the first plant's capacity. The Qatari volumes will help replace withdrawal volumes from USA storage which are operationally capped at 2.1 billion cubic feet a year.

The world's present He supply is found within a 250-mile radius of Amarillo, Texas, the He Capital of the World. As a byproduct of billions of years of decay, it is distilled from natural gas that has accumulated in the presence of radioactive uranium and thorium deposits. If it is not extracted during the natural gas refining process, He simply soars off when the gas is burned, unrecoverable.

The USA federal government first identified helium as a strategic resource in the 1920s; in 1960 it began socking it away in earnest. Thirty-two billion cubic feet of the gas are bunkered underground in Cliffside, a field of porous rock near Amarillo, Texas. Industrial buyers use the He gas primarily for arc welding as He creates an inert atmosphere around the flame and leak detection since hydrogen has a smaller atom, but it usually forms a diatomic molecule, H<sub>2</sub>.

NASA uses He to pressurize space shuttle fuel tanks: The Kennedy Space Center alone uses more than 75 million cubic feet annually. Liquid helium, which has the lowest

melting point of any element (-452 degrees Fahrenheit), cools infrared detectors, nuclear reactors, wind tunnels, and the superconductive magnets in MRI equipment.

## **HELIUM SHORTAGE**

Helium is being depleted as an unprecedented rate and reserves could dwindle to virtually nothing within a generation. Nobel laureate Robert Richardson, professor of physics at Cornell University in Ithaca, New York, , who won his Nobel prize for his work on He<sup>3</sup>, discusses the issue at meeting of the Nobel Prize laureates in Lindau, Germany::

“In 1996, the US Congress decided to sell off the strategic reserve and the consequence was that the market was swelled with cheap helium because its price was not determined by the market. The motivation was to sell it all by 2015. The basic problem is that helium is too cheap. The Earth is 4.7 billion years old and it has taken that long to accumulate our helium reserves, which we will dissipate in about 100 years. One generation does not have the right to determine availability for ever. As a result of that Act, helium is far too cheap and is not treated as a precious resource. It is being squandered. They could not sell it fast enough and the world price for helium gas is ridiculously cheap. You might at first think it will be peculiarly an American topic because the sources of helium are primarily in the US but I assure you it matters of the rest of the world also. Once helium is released into the atmosphere in the form of party balloons or boiling helium it is lost to the Earth forever.”

He believes the price for helium should rise by between 20- and 50-fold to make recycling more worthwhile. He suggests that party balloons filled with He are too cheap, and they should really cost about \$100 (£75) to reflect the precious nature of the gas they contain.

NASA makes no attempt to recycle the He used to clean its rocket fuel tanks, one of the single biggest uses of the gas.

Soon after He mining was developed at the turn of the previous century, the USA established a National Helium Reserve in 1925. During the Second World War, helium was strategically important because of its use in military airships.

When the Cold War came along, it became even more important because of its uses in the purging of rocket fuel in intercontinental ballistic missiles. The national reserve was established in the porous rock of a disused natural gas field 30 miles north of Amarillo, which soon became known as the Helium Capital of the World.

A billion m<sup>3</sup>, or about half of the world's reserves are stored in this cluster of mines, pipes and vats that extend underground for more than 200 miles from Amarillo to Kansas.

In 1996, the USA passed the Helium Privatization Act which directed that this reserve should be sold by 2015 at a price that would substantially pay off the federal government's original investment in building up the reserve.

Professor Richardson co-chaired an inquiry into the impending He shortage convened by the USA National Research Council, an arm of the USA National Academy of Sciences. Its report recommends that the USA Government should revisit and reconsider its policy of selling off the USA national helium reserve.

At the current rate of consumption, the Cliffside site will likely be empty in 10 to 25 years, and the Earth will be virtually helium-free by the end of the 21st century.

An old party favorite is of breathing-in helium from a He-filled balloon, and then talking in squeaky voices as a result of helium's fast-moving atoms. This can cause dizziness, headaches and even death.

The United States is currently the world's biggest He supplier, with the bulk of it stored near Amarillo, Texas, in the national helium reserve which alone accounts for 35 percent of the world's supply. This was set up in 1925 as a strategic store for supplying gas to USA airships, while after World War II it provided coolant for missiles and rockets for the military and NASA. Since the mid-1990s, with growing civilian demand for helium in the manufacture of semiconductors and for MRI scanners, the USA has been clawing back the cost of storing the gas by gradually selling it off on the open market. The price of helium has doubled over the 2003-2013 period. Shortfalls in supply had anyway become routine.

The semiconductors industry in the USA in 2013 was receiving about 80 percent of the helium for which they have contracted. Legislation to avert a crisis in He supplies was passed by the USA Congress. While a "helium cliff" may have been averted, it is going to take time for other countries to be able to step into the market to supply the gas.

## **BERYLLIUM**

Beryllium takes its name from the Greek word “berullos” meaning beryl, the mineral from which it could be extracted:  $(3 \text{ BeO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2)$ , which is a beryllium aluminum silicate. This primary source is as a byproduct of feldspar, mica and lithium ores.

Be is simultaneously stiff and light, nonmagnetic and transparent to x-rays, with a modulus of elasticity almost 50 percent greater than steel, with only one-fourth the weight and an extremely high melting point of 2,349 °F. It has 30 percent the density of Al, six times the stiffness of steel, is non-magnetic and non-sparking.

The metal is of light, steely hue and is of fairly marked crystallinity. It is highly transparent to x-rays making it suitable for the design of laser fusion pellets and thermonuclear devices.

It is non-magnetic which makes it suitable for the construction of the body of gyroscopes in missiles.

Hydrogen does not attack the metal at any temperature, making it useful for the storage of tritium in yield-adjusted thermonuclear devices.

Beryllium in nuclear applications is used as a neutron reflector leading to a smaller critical mass for small reactor applications, by reflecting the neutron that would otherwise have leaked from the surface of the reactor. In Fig. 27, blocks of beryllium are surrounding smaller blocks of fissile materials in a subcritical experiment. Its absorption cross section for thermal neutron is small at 0.01 barn, and its scattering cross section is high as 7.0 barns.

It is also used as a neutron multiplier through the  $(n, 2n)$  reaction:



In this reaction, it appears to fission into helium nuclei while emitting two neutrons. Using alpha particles from radium, polonium, or plutonium, it can be used as a neutron source through the ( $\alpha$ , n) reaction:



Placing beryllium oxide (BeO) with silicon carbide cladding pellets with the uranium oxide will allow the nuclear fuel to burn more efficiently because it leads to an even heat distribution throughout the fuel rod.

Together with deuterium, it can be photo-disintegrated with gamma rays generated from the decay of natural radioactive substances. The deuteron,  ${}_1\text{D}^2$  having a binding energy of only 2.2 MeV, and the nuclide of  $\text{Be}^9$  in which one neutron is loosely bound with a Q value of -1.67 MeV undergo the photo-disintegration reactions:

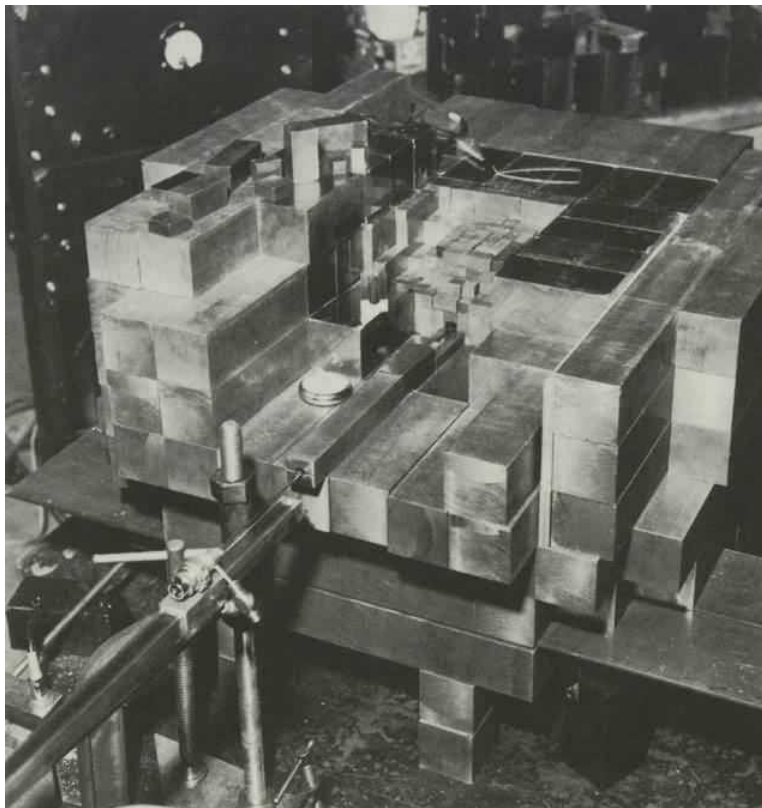


Figure 27. Beryllium blocks used as a reflector around fissile elements in a criticality experiment.



Figure 28. Beryllium neutron reflector being inserted into the University of Missouri Reactor (MURR) for the production of medical isotopes.

The last two reactions can be used as neutron sources if some naturally gamma emitting isotopes can be used such thallium<sup>208</sup>, a member of the thorium decay chain, with a gamma decay energy of 2.6146 MeV.

In addition to its use as a moderator, reflector, neutron multiplier and cladding material in nuclear applications, it can be used in the heat shields and structural members of missiles. Beryllium copper can be employed up to 2,000 degrees C, and the elevated temperature does not reduce its strength. It is used for recording instruments springs and for tools in the chemical, electrical and other industries where there is a risk of fire or explosion as a result of a sudden spark, since the alloy is non-sparking.

Any inhalation or ingestion of the metal or its compounds must be prevented. Dust, fumes and inadequate ventilation must be avoided. Handling with gloves, respirators, personal cleanliness, checking the surrounding atmospheres, and regular x-ray checking of those exposed are necessary. Beryllium oxide has not been found to be toxic so far.

## **BISMUTH**

Bismuth is a metallic element, which occurs in a native manner and as alloys with many metals such as antimony, arsenic and silver. The principal ores are the sulfide:  $\text{Bi}_2\text{S}_3$ , as well as the oxide and the carbonate.

The pure metal is soft and coarsely crystalline with a white color with a reddish tinge. It is one of the few metals which expand when cooled and its melting point is low. Its thermal conductivity is lower than any other metal except for mercury. Its electrical resistance is high.

It has been used as a coolant in some reactor designs applied to naval propulsion in the Russian fleet. It has also been alloyed with lead as a fast reactor coolant.

A major use of bismuth is in the form of salts for medicinal purposes and cosmetics preparations. The bismuth used for medicinal purposes must have a limit of less than 2 ppm of arsenic. These contain bismuth produced by electrolysis at 99.95 percent purity. The salts of bismuth are slightly antiseptic. When the subnitrate is taken internally, it

decomposes in the presence of water setting free strongly antiseptic nitric acid. In the product "pepto-bismol," it is used to treat diarrhea.

In powder form, it is slightly astringent. This subnitrate is valuable for dyspepsia and more so for diarrhea. The principal salts used are the carbonate, oxide, subnitrate, and the salicylate. It is a sedative in vomiting and an aid to x-ray diagnosis. As a dusting powder, it is used in cases of eczema and weeping skin conditions, being mixed with starch powder or zinc oxide, or both. With arsenic and penicillin, its finely powdered form is injected intramuscularly in the treatment of syphilis.

It is employed in the field of powder metallurgy because its electrical resistance increases in a magnetic field inversely with a change of temperature, and with a change of strength of the field. Consequently, composite bismuth alloys containing copper, silver, aluminum, tungsten and molybdenum, can be produced easily by pressing the mixed powders and sintering at a temperature higher than the melting point.

## **CADMIUM**

Cadmium gets its name from the Greek "kadmia," meaning Cadmean or Earth. It is a white metallic element crystallizing in the hexagonal form.

It has a relationship to zinc with which it is associated. There exists no ores of cadmium in the normal sense of the name. It is produced as a metallic byproduct in the production of zinc. Production is also from the flue dusts in the smelting of lead and copper ores. Zinc ores contain from 0.1-0.7 percent cadmium.

In nuclear applications it is used as a control rod material because of its affinity for neutrons. It has been also used as shielding against neutrons. It is used in control rods as a solid or as plating on graphite.

Cadmium is soft and will mark paper. It is harder than tin and softer but denser than zinc. It can accept a high polish and is resistant to alkalis. It is used as plating for protective purposes, mostly with ferrous metals, and also for copper and its alloys.

It is used in the production of cadmium lithopone, when it serves as paint for the detection of poison gas.

Cadmium forms amalgams with mercury and has been used in dentistry in the filling of cavities in teeth. It is permanent in dry air, but in moist air it becomes coated with an oxide surface film. When heated it burns to redness and forms a brown oxide. It can be easily dissolved in mineral acids to form the corresponding salts. Unfortunately both elements are toxic.

Cases of toxicity have arisen when cadmium has been used as plating in contact with mildly acidic foodstuffs. It should therefore not be used where it would come in contact with food or drink, certainly not in the human mouth like in dentistry.

Similarly as for beryllium, the fumes are harmful, and the proper measures must be taken to avoid its inhalation. Since heat is hazardous, in oxy-acetylene welding or spot welding on steel coated with cadmium, the type or plating or coating on the metal to be welded should be checked beforehand.

## **CESIUM**



Cesium is a metallic element in the first group of the periodic table and one of the alkali metals such as sodium. The Latin name “caesius” means sky-blue from the two bright lines in its spectrum.

It is found in nature in the mineral pollucite, which is a hydrated cesium aluminum sodium silicate. It is also found in minute amounts in the mineral carnallite: CsCl, which is found in a number of continental mineral springs.

Cesium<sup>137</sup> is a radioactive isotope recovered as a fission product in the reprocessing of uranium fuel. It could be released from the fuel under accidental conditions like the Chernobyl and Fukushima accidents, because of its low boiling point at 690 degrees C. Through fractionation, it would cool down and deposit itself around the accident site.

It was released from the nuclear testing in the atmosphere, particularly in the Marshall Islands, where it contaminated the soil and the food supply. There it would find its way through the food chain into the human body, particularly the muscle system, since it has chemical properties similar to sodium and potassium in the periodic table of the elements. It has a half-life of 33 years and a characteristic gamma ray of 0.66 MeV. Because of its half-life magnitude, once ingested in the body, traces of it would remain for a lifetime, and its ingestion should be avoided.

The strong gamma ray emission makes it suitable as a gamma-ray source in nuclear medicine application for the treatment of tumors, and in the gamma-ray sterilization of medical products and in the applications of food preservation by irradiation.

Cesium is used in ion propulsion engines of low thrust for spacecraft, and as a heat transfer medium in thermal applications.

It is the most strongly basic and electropositive metal known. It is light, silvery white in color and soft enough to be cut with a knife. It oxidizes rapidly and ignites in air and it decomposes water at ordinary temperatures. When interacting with water, it forms the hydroxide with the escaping hydrogen burning with a red violet flame.

As a reactive medium, better than lithium, potassium or sodium, it could be used for propulsion in a torpedo design that would work on the rocket principle.

Cesium is used in photoelectric cells. As light is projected on the cesium surface, negative electrons are emitted, which are collected on a positive electrode producing a current. The emission is affected by the frequency and intensity of the incident radiation, and can thus be used to measure its properties.

Because it ignites once exposed to air, and reacts explosively with water, it must be used with caution. The peroxides generated with its reaction with air are both explosive and sensitive to shock and is explosive. It must be stored in a vacuum or covered with an inert gas or in an anhydrous liquid hydrocarbon such as oil or kerosene.

## **COBALT**

Cobalt is a metallic element whose name originates from the German “kobold,” meaning a little goblin who haunts the mines. The term was given to certain substances that even though similar to metallic ores, gave no metal when smelted. It was applied later to cobalt, which gives glass a bluish taint. It is both magnetic and difficult to fuse.



Figure 29. Cobalt metal.

Cobalt ores are widely distributed in the form of complex sulphides and arsenides, generally associated with nickel, and often with iron, manganese, copper and silver, such as smaltite:  $\text{CoAs}_2$ , cobaltite:  $\text{CoAsS}$ , and cobalt bloom:  $\text{Co}(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ .

The metal is gray-white with a bluish cast, and is magnetic below 1075 degrees C. It will take a high degree of polish and resembles iron in its properties, but is harder and tougher. Like iron it acquires strength and hardness with the addition of carbon. It can be hammered and rolled when hot, but is brittle at room temperature. Its magnetism is greater than any other metal except iron making it a choice for high performance magnets. It presents great resistance to corrosion.

Initially it was used as a coloring agent in the glass and pottery industries. It has been used for catalysis in the production of oil from coal. Co-chrome is an alloy of 75 percent cobalt and 25 percent chromium is used instead of Nichrome for the heating elements of electric ovens and radiators.

Cobalt<sup>60</sup> is a radioactive isotope that can be used instead of Cesium<sup>137</sup>, radium and high voltage x-rays in the treatment of malignant tumors. It has a half-life of 5.27 years and characteristic gamma rays of 1.33 and 1.17 MeV. The strong gamma ray makes it suitable as a gamma ray source in nuclear medicine applications, in the gamma ray sterilization of medical products and in the applications of food preservation by irradiation. It is produced by the neutron irradiation in a nuclear reactor of the 100 percent naturally abundant isotope of cobalt: Cobalt<sup>59</sup>.



Steels used in nuclear applications where a coolant can be subjected to neutron irradiation must not use cobalt as an alloying element. This is so since the crud arising in the coolant by erosion and corrosion, would settle in pockets of the piping subjecting the maintenance personnel in a power plant to unnecessary exposure to the strong gamma radiation from  $\text{Co}^{60}$ .

Along the previous line, there was a suggestion that was never realized, of using a cobalt atomic device where the fission core would be surrounded by a cobalt blanket. The

Co<sup>60</sup> produced would interdict any access to the fallout zone for several half-lives to both friendly and enemy troops. The use of Na<sup>24</sup> from the 100 percent abundant sodium<sup>23</sup>, with a half-life of 15.02 hours, and the stronger gamma rays energies of 2.754 and 1.369 MeV, as sodium chloride or table salt would also produce another so-called “salted” dirty device with powerful gamma rays, but with a much shorter interdiction time. Other so called salting agents are listed in Table 9, including gold.

Table 9. Candidate Salting Agents.

Salting element	Percent abundance [a/o]	Product isotope From neutron capture (n, γ)	Half life T <sub>1/2</sub>
<sup>27</sup> Co <sup>59</sup>	100	<sup>27</sup> Co <sup>60</sup>	5.27 a
<sup>11</sup> Na <sup>23</sup>	100	<sup>11</sup> Na <sup>24</sup>	15.02 hr
<sup>30</sup> Zn <sup>64</sup>	48.6	<sup>30</sup> Zn <sup>65</sup>	243.8 d
<sup>73</sup> Ta <sup>181</sup>	99.998	<sup>73</sup> Ta <sup>182</sup>	115 d
<sup>79</sup> Au <sup>197</sup>	100	<sup>79</sup> Au <sup>198</sup>	2.696 d

## PALLADIUM

Palladium is a metallic element deriving its name from the French: “Pallas,” an asteroid. Obtained as a byproduct in the extraction of platinum, it is produced in a spongy state by the thermal decomposition of palladium dichlorodiamine.

Its main application is to contacts in electrical relays, where its freedom from tarnish makes it exceptionally trustworthy and gives transmission free from noise in voice circuits. It is also used as a catalyst in chemical engineering.

Palladium is renowned for its high affinity for hydrogen. It readily takes it up to the extent of about 800 times its own volume at room temperature. This makes it very valuable as a diffusion barrier for the production of small volumes of extremely pure hydrogen, deuterium and tritium. Septa or membranes of palladium are embodied in electrolytic cells for the separation of hydrogen isotopes by electrolytic migration.

Lately, there has been an interest in the possibility that low energy nuclear reactions can occur between deuterium and palladium through an Oppenheimer-Phillips process, as suggested by Ragheb. This would be so because of the low binding energy per nucleon at 1.12 MeV for the deuteron. A deuteron would lose a neutron to palladium releasing hydrogen through an exothermic low energy reaction. This suggestion replaces the hypothesis of cold fusion where deuterons are hypothesized to undergo fusion in the palladium lattice.

## POLONIUM

Polonium is a radioactive metal discovered by Pierre and Marie Curie (Fig. 30) in the pitchblende uranium ore. Its name comes from the Latin “Polonia” for Poland. Marie Sklodowska Curie, 1867-1934, received a Nobel Prize in Physics (1903) which she shared

with her husband Pierre Curie and Henri Becquerel, and a Nobel Prize in Chemistry (1911) for the discovery of the two elements polonium and radium. Marie and Pierre Curie coined the term: “radioactivity.”

The principal isotope is polonium<sup>210</sup>, which has a melting point of 254 °C and a half-life of 138.38 days or  $138.376/356.256 = 0.3788$  year, decaying into the stable lead isotope lead<sup>206</sup>, through alpha emission:



with energy of 5.3045 MeV with 100 percent relative intensity and a rare 4.51653 MeV alpha particle with 0.00122 percent relative intensity. Another rare gamma ray photon of energy 0.8031 MeV is emitted with a relative intensity of 0.00121 percent.

The most stable isotope of polonium is Po<sup>209</sup> with a half-life of 102 years and it alpha decays into Pb<sup>205</sup> :



Figure 30. Marie Skłodowska Curie, 1867-1934, obtained a Nobel Prize in Physics and a Nobel Prize in Chemistry for the discovery of the two elements polonium and radium.

Polonium is combined with beryllium to form a Po<sup>210</sup>-Be neutron source, used as a neutron source and initially as an initiator designated as an urchin in early design nuclear devices through the reaction:



This reaction is practically free from gamma rays.

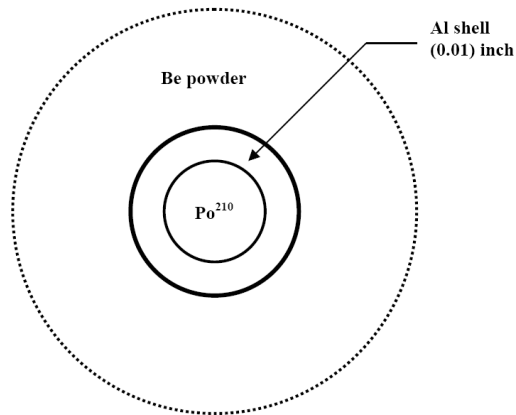


Figure 31. Polonium beryllium neutron source initiator.

### SPECIFIC ACTIVITY

Milligram quantities of polonium<sup>210</sup> can be produced by bombarding bismuth which occurs in nature as 100 percent as the isotope  $Bi^{209}$  with neutrons in a nuclear reactor or particle accelerators. This forms  $Bi^{210}$  through a neutron radiative capture process.  $Bi^{210}$  then decays into  $Po^{210}$  through negative beta decay with a half-life of 5.01 days:



Polonium<sup>210</sup> is a very strong alpha emitter. The specific activity or the activity of 1 gram of  $Po^{210}$  is large for an alpha emitter and can be calculated as:

$$\begin{aligned}
A_0' &= \frac{\lambda N_0}{g} \\
&= \frac{\lambda g A_v}{g M} \\
&= \frac{\ln 2 A_v}{T_{1/2} M} \\
&= \frac{0.6931}{138.376 \times 24 \times 60 \times 60} \frac{0.6 \times 10^{24}}{210} \\
&= 1.656 \times 10^{14} \left[ \frac{Bq}{gm} \right] \\
&= \frac{1.656 \times 10^{14}}{3.7 \times 10^{10}} = 4,476.6 \left[ \frac{Ci}{gm} \right]
\end{aligned} \tag{25}$$

This high specific activity implies that a minute amount of  $Po^{210}$  can produce a significant amount of activity. Thus to produce 1 mCi of activity a mass of just:

$$m(Po^{210}) = \frac{1}{4.4766} \frac{mCi}{Ci/gm} = \frac{10^{-3}}{4.4766} \frac{Ci}{Ci/gm} = 0.223 \times 10^{-6} = 0.223 \mu gm$$

is needed.

Since 1 Curie is by definition the activity of 1 gram of radium<sup>226</sup>:

$$\begin{aligned}
1 Ci &\equiv 1 gm \text{ of } Ra^{226} = 3.7 \times 10^{10} Bq \\
4,476.6 Ci &\text{ of } Po^{210} \rightarrow 1 gm \text{ of } Po^{210} \\
\frac{4,476.6}{1,000} Ci &\text{ of } Po^{210} \rightarrow 10^{-3} gm \text{ of } Po^{210}
\end{aligned}$$

thus a small amount of just 1 mg of  $Po^{210}$  produces as much activity as 4.4766 or about 4.5 full grams of  $Ra^{226}$ .

## RADIOTOXICITY

Radio toxicity results suggest that an ingestion intake of 3 mCi of  $Po^{210}$  could be potentially lethal to some individuals out of a large group that would survive it. This corresponds to:

$$3 mCi \text{ of } Po^{210} = 3 \times 0.223 \mu gm = 0.669 \mu gm$$

Thus in terms of radiotoxicity, ingestion of microgram level quantities of  $Po^{210}$  could be lethal.

If ingested, a significant proportion of  $Po$  is removed as excreta from the body. A significant amount can enter the body from the gastro intestinal tract and then concentrated in the filtering organs of the body such as the spleen, liver, kidneys delivering a large dose equivalent there due to the large quality factor of alpha radiation. Smaller doses are also delivered to the bone marrow, gastro-intestinal tract and other body tissues.

Subcutaneous intakes of 0.05-0.18  $\mu Ci/gm$  of body weight in dogs caused the development of acute radiation sickness with implied prodromal syndrome and died within 10 days to 4 weeks after injection. Lethal subacute radiation sickness was induced by an intake of 0.02-0.03  $\mu Ci/gm$  of body weight. Chronic radiation sickness was caused by a very low intake of 0.0025  $\mu Ci/gm$  of body weight, leading to death between 6-12 months after administration.

In rats, injected doses of 0.0392  $\mu Ci/gm$  of body weight caused death within 30 days.

Even-though humans and dogs are physiologically different, one can hypothesize that for a typical 50 kgs human, acute radiation thickness would be caused by:

$$(0.05 - 0.18) \frac{\mu Ci}{gm} \times 50kg \times 10^3 \frac{gm}{kg} = (2.5 - 9)mCi$$

or:

$$(2.5 - 9)mCi \times 0.223 \frac{\mu gm}{mCi} = (0.5575 - 2.007)\mu gm$$

of  $Po^{210}$ .

## ISOTOPIC POWER PRODUCTION

If the energy release per disintegration is  $E$  in MeV, the specific power of an isotope is given by:

$$P' = \frac{E\lambda N_0}{g} \text{ [MeV/(gm.sec)]} \quad (26)$$

Since:

$$N_0 = \frac{gA_v}{M} \text{ [nuclei]} \quad (27)$$

where:  $A_v$  is Avogadro's number =  $0.6 \times 10^{24}$  [nuclei/mole],

$M$  is the atomic weight in amus.

One can write for the specific power of the isotope:

$$P' = \frac{E\lambda A_v}{M} \text{ [MeV/(sec.gm)]} \quad (28)$$

where the weight of the isotope (g) cancels out.

We can express the specific power in watts per gram using the conversion factor:

$$1 \text{ [MeV/sec]} = 1.6 \times 10^{-13} \text{ [Watts]}$$

as:

$$P' = 1.6 \times 10^{-13} \frac{E\lambda A_v}{M} \text{ [Watts(th)/gm]} \quad (29)$$

For  $\text{Po}^{210}$ :

$$\begin{aligned} P' &= 1.6 \times 10^{-13} \frac{E\lambda A_v}{M} \\ &= 1.6 \times 10^{-13} \frac{5.30433 \times 0.6931 \times 0.6 \times 10^{24}}{138.376 \times 24 \times 60 \times 60} \\ &= 140.573 \frac{\text{Watts(th)}}{\text{gm}} \end{aligned}$$

Thus just one gram of  $\text{Po}^{210}$  generates 140.573 Watts(th) of heat energy and makes it a candidate to be used as a light weight but short term heat and thermoelectric power for space applications.

It is comparable to the specific activity of  ${}_{96}\text{Curium}^{242}$  which is also an alpha emitter and undergoes spontaneous fission with decay energy of 6.216 MeV and a half-life of 162.8 days and a specific power of:

$$\begin{aligned} P' &= 1.6 \times 10^{-13} \frac{E\lambda A_v}{M} \\ &= 1.6 \times 10^{-13} \frac{6.216 \times 0.6931 \times 0.6 \times 10^{24}}{162.8 \times 24 \times 60 \times 60} \\ &= 121.505 \frac{\text{Watts(th)}}{\text{gm}} \end{aligned}$$

These are thermal Watts of power generated as heat. If conversion of thermal energy to electricity is attempted, then the specific electrical power output in electrical Watts per gram becomes:



$$\begin{aligned}
P_e &= \eta_{th} P' \\
&= 1.6 \times 10^{-13} \frac{\eta_{th} E \lambda A_v}{M} \text{ [Watts(e)/gm]}
\end{aligned}
\tag{30}$$

where:  $\eta_{th}$  is the overall conversion efficiency.

## OTHER USES

Polonium is used to eliminate static electricity in equipment that is caused by processes such as the rolling of paper, wire or sheet metal in addition to beta emitters. It is also used in brushes for removing dust from photographic films.

$^{210}\text{Po}$  occurs naturally in a low concentration in the Earth's crust with an abundance of 1 part in  $10^{15}$ . As a decay product of the gaseous radon  $^{222}\text{Rn}$  gas, from uranium contained in soil and phosphate fertilizer,  $^{210}\text{Po}$  attaches itself in solid form to the leaves of the tobacco plants and together with  $^{210}\text{Pb}$  is deposited in the lung alveoli of smokers affecting them through their energetic radiation:



This adds a radio toxicity component to the benzo-a-pyrene chemical component of cigarettes smoke.

The Russian Chechnya dissident and Russian secret service defector Alexander Litvinenko, who fled to the UK and established a freelance private investigator business, is suspected to have been poisoned in central London in 2006. A public inquiry found that his killers were two former KGB agents, possibly at the employ of the Federal Security Service of the Russian Federation (FSB), who slipped radioactive  $^{210}\text{Po}$  into his tea or sushi food at the Millennium Hotel. A team of British scientists identified its unusual alpha radiation. Authorities charged the two assassins with murder in absentia. Russia refused to extradite them and they have denied any involvement in the killing. Alexander Litvinenko died three weeks later of suspected poisoning by radioactive  $^{210}\text{Po}$ , believed to have been dropped into a tea cup. Palestinian leader Yasser Arafat, is suspected to have been assassinated with  $^{210}\text{Po}$  added into his toothpaste.

$^{210}\text{Po}$  decays rapidly and leaves no trace through negative beta decay with a half-life of 5.01 days. It is an alpha emitter without gamma radiation which makes it undetectable with gamma-ray detection equipment positioned at ports of entry.

## RADIUM

Radium is a radioactive element in the second group of the periodic system and is one of the alkaline earth metals. It was so named because of the intense radioactivity that it displays. Its discovery followed Henry Becquerel's observation around 1896 that some

salts of uranium gave out radiation similar to x-rays discovered by Roentgen a few days earlier. Pierre and Marie Curie obtained the element from pitchblende, an ore of uranium.

Radium and its disintegration products exist in mineral springs and in seawater, and occur in both igneous and sedimentary rocks. Accordingly the use of bottled mineral water should be carefully scrutinized for its source and the possibility of including radium. Otherwise, its mineral source health claim might be in fact a health hazard.

It is present in minute quantities at about  $1 \times 10^{-7}$  gm in 1 gm of pitchblende, and only as  $5 \times 10^{-12}$  gm in each gm of rocks.

The metal is brilliantly white, turning black by forming a nitride when exposed to air. It readily attacks quartz or glass, and rapidly decomposes water to yield a hydroxide. It possesses the highest atomic weight of the alkaline earth metals, including calcium, strontium and barium.

A past application of radium was for therapeutic purposes, its main action being a selective destruction of tumor cells.

Radium has been used in the past in the manufacture of luminous paint for the dials of industrial and aeronautical apparatus and machinery. Embodying radium in phosphorescent zinc sulfide produces the paint. This yields a weak light capable of being seen in the dark. The amount needed is minuscule at about 0.1 mg per gram of zinc sulfide. Luminosity declines as a function of time, and radon gas can emanate from it, which is tending to limit their use. The sulfate of radium is blended with gold powder, which is then heated and rolled into thin sheets and strips. These are used for special purposes in electronics and for the activation of luminous paints. Light emitting diodes have replaced this application.

A famous radiation accident occurred in the case of the luminous watch dial painters, which used to sharpen the edge of their paintbrushes by licking them on their tongues. These workers accidentally ingested amounts of radioactivity to increase their cancer rate above the general population level. This suggests care in the handling of antique watches acquired for show in homes and in the antique road shows.

## **SODIUM**

Sodium is a metallic element in the first group in the periodic table of the elements, and is an alkali metal. Its symbol Na comes from the word "Natrun," the name of its mineral in Arabic, mined in ancient times from the Wadi Al Natroun, or the Natroun Valley in the Western Desert of Egypt. It was used in the drying and preservation of mummies in Pharaonic times. Its English name (sodium) comes from soda. It is plentiful and extensively dispersed in nature. It is most common in sea water as common salt, and is also in rock salt as NaCl or sodium chloride. It occurs in Chile saltpetre:  $\text{NaNO}_3$  used with charcoal and sulfur in the manufacture of black powder, and borax:  $\text{Na}_2\text{B}_4\text{O}_7 \cdot \text{H}_2\text{O}$ .

It is manufactured by the electrolysis of a fused mixture of sodium chloride and calcium chloride. The metal is silver white, tarnishing as soon as it is exposed to the atmosphere. It is thus stored in paraffin or in kerosene. It is very soft and can be cut with a knife. It violently interacts with water to form caustic soda and hydrogen, which can be collected and ignited.

It comes fourth after silver, copper and gold as a conductor of heat and electricity. It is the most electropositive of the metals with the exception of cesium, rubidium and potassium.

It is the favored coolant for liquid metal fast breeder reactors. There it acts as an efficient coolant with a large thermal inertia. Not being a good moderator, the neutron spectrum remains in the fast region where breeding of the fissile isotope  $\text{Pu}^{239}$  from the fissionable isotope  $\text{Uranium}^{238}$  can be achieved. This breeding process can produce more fissile nuclei than those originally fissioned to obtain the neutrons. At a breeding ratio of larger than unity, a negative fuel cost in the production of nuclear power is in fact achieved. This led to a suggestion that with fast breeder reactors, nuclear energy could become “too cheap to meter.” Of course, this ignores the capital cost and the operation and maintenance components and conveyance in the price of electricity.



Figure 32. The Experimental Breeder Reactor I, EBR-I, in the Idaho desert turned into a museum.



Figure 33. The Experimental Breeder Reactor I, EBR-I, lighted up a string of light bulbs with the first produced nuclear electricity on December 20, 1951.



Figure 34. The Experimental Breeder Reactor II, EBR-II, at Idaho used a sodium coolant.

The first nuclear electricity was produced on December 20, 1951 in the Experimental Breeder Reactor I or EBR-I at Idaho (Figs. 33, 34). It was turned into a museum after an accident, and was superseded by the Experimental Breeder reactor II (Fig. 28), which successfully produced electricity for more than 25 years.

Alloyed with potassium, sodium yields a eutectic NaK alloy that is liquid at room temperature with the composition of 77 percent potassium and 23 percent sodium.

Being such a good heat transfer medium, it is used in the hollow shanks of aircraft and tank engines as a cooling medium. The sodium occupies 60 percent of the valve shank

interior drawing heat twice as much as steel. The valve can thus operate under maximum load without the head failing at the high temperatures involved.

Because it is highly reactive with air, it must be isolated from it with a blanket of nitrogen gas to avoid oxidation. It is also reactive with water, so that double walled heat exchangers are used to transfer heat from sodium to water.

The  $\text{Na}^{24}$  isotope is a strong gamma emitter with a short half-life of 15.02 hours. It emits gammas with energies of 1.369 and 2.754 MeV. It has found a use in the radiographic examination of ancient monuments.

## STRONTIUM

Strontium is an alkaline earth metal found in nature as its sulfate: celestine. It is also found as strontianite its carbonate:  $\text{SrCO}_3$ . It occurs in numerous mineral springs and in the ash of many fossil power plants, from which it can be extracted.

The oxalate and other salts are used to produce the red color in tracer bullets and fireworks.

The isotope strontium<sup>90</sup> is a fission product with a half-life of 29 years emitting beta particles and no gammas. In the periodic table, it lies directly below calcium. From the fallout from the nuclear testing in the atmosphere, or from reactor accidents, this isotope if ingested mimics calcium and is a bone seeker. Once ingested, it remains for a lifetime, and constitutes in this situation a health hazard.

Because it does not emit gamma rays and is a pure beta emitter it is a suitable choice for nuclear batteries and a source of electrons for Micro Electro Mechanical Devices (MEMS).

## LEAD

Lead is an economical and very effective as a shield against gamma rays. It has a high attenuation coefficient for gamma rays of low and high energy. In the region of 3 MeV energy there is a dip in the gamma ray attenuation coefficient offering a window for the escape of radiation at that energy. As a result, a buildup of radiation at that energy occurs in thick lead shields and must be dealt with.

Lead is not a very effective neutron absorber. In fact it is less effective than iron. The fast neutrons mean free path of neutrons in lead in the energy range of 2-5 MeV is 11-14 cms.

If neutrons irradiate pure lead, no significant activation occurs. This makes the access of lead parts in a reactor a simple process. Combining lead and water is used as an effective shield combination. In fact, a lead-water combination can be much lighter than equivalent steel-water combination or even concrete.

Commercial lead contains some impurities such as silver, copper, antimony, iron, and zinc. These must be taken into account when considering the activation of lead shields.

Table 10. Properties of Lead

Property	Value	Units
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Density	11.34	g / cm <sup>3</sup>
Melting point	327.4	°C
Coefficient of linear expansion	229.3 x 10 <sup>-6</sup>	°C <sup>-1</sup>
Thermal conductivity	8.5 x 10 <sup>-2</sup>	cal / (°C.cm.sec)
Young's modulus	0.2 x 10 <sup>5</sup>	kg / cm <sup>2</sup>
Shear modulus	0.7 x 10 <sup>5</sup>	kg / cm <sup>2</sup>
Tensile strength, 20 °C	122	kg / cm <sup>2</sup>

Lead is not a good structural material and does not possess good mechanical properties as shown in Table 10. Its properties deteriorate rapidly with increased temperature. Creep also affects vertical lead sheets and it is necessary to mount them in lead frames, which are then fastened to the support structure. Gaps must not be left between lead and the support structures. Lead must be cast to fill these gaps, which would lead to radiation streaming. Before casting lead, the surfaces of the faceplates should be mechanically cleaned or ground, washed with 50 percent hydrochloric acid and then covered with tin.

Other than using monolithic blocks of lead, lead shot or balls of different sizes can be used in shields as a filling. Densities of balls higher than 8.5 t/m<sup>3</sup> can be achieved by using a mixture of 56.2 percent of lead as balls of 22 mm in diameter, 28.3 percent as balls of 5.6 mm in diameter, and 15.5 percent as small diameter shot. After vibration, a binding agent such as paraffin can be melted in.

Contrary to a view held for some time, there is no need to avoid contact between lead and steel in aqueous solutions, since the corrosion rate is negligible, even in solutions containing boric acid as a neutron absorber.

Attempts were made at developing shielding materials consisting of crushed boron in molten lead. This would offer both a gamma and neutron-shielding alternative.

Lead and lead-bismuth alloys are suggested as a cooling medium for fast reactors designs. It was suggested by Ragheb as a cooling medium for inertial confinement fusion designs.

## AMERICIUM

Over time, the small amount of plutonium<sup>241</sup> present in weapons-grade plutonium decays, resulting in a buildup of americium<sup>241</sup>. This is called americium ingrowth. Americium absorbs neutrons during the fission process, making it undesirable for use in nuclear weapon pits. In addition, it presents a gamma radiation hazard which increases over time.

Americium ingrowth is regularly removed from plutonium weapons. It is used for various commercial uses such as smoke detectors. In 1980, americium recovery ceased and the material has been discarded as a waste since 1986.

## IRON AS STAINLESS STEEL

Stainless steel is a spin-off from nuclear applications requiring stringent corrosion resistance. It was initially used in gaseous diffusion enrichment to resist corrosion through

its nickel content from UF<sub>6</sub>, and later in centrifuge enrichment and liquid metal reactors vessels and piping.

Lately, the 316L stainless steel alloys with extremely low concentrations of manganese, referred to as ultralow-manganese alloys, which contain less than 0.05 percent Mn, are superior in corrosion resistance to low-manganese alloys, which contain less than 0.5 percent Mn, and standard 316L alloys which contain less than 2 percent Mn.

The generation and redeposition of manganese weld fumes are thought to be responsible for pitting corrosion in as-welded 316L stainless steel during exposure to gaseous atmospheres containing halogens such as fluorine, chlorine, bromine and minute amounts of water vapor.

Table 11. Stainless steel alloy composition.

Element %	Standard S31603 316L	Ultralow Mn alloy Bar stock	Ultralow Mn alloy Tubing
Cr	16-18	17.27	16.9
Ni	10-14	13.12	14.26
Mo	2-3	2.6	2.43
Mn	2 max	0.01	0.01
S	0.03 max	0.0015	0.001
Si	1 max	0.01	0.05
C	0.03 max	0.016	0.006
Fe	balance	balance	balance

## TANTALUM

Tantalum is a rare metal found in Australia (56 percent), Africa (19 percent), Brazil (16 percent), China (5 percent) and Canada (4 percent). This high performance metal has a high melting point, high strength, high ductility, high reliability, high resistance to corrosion and high thermal conductivity making it a highly efficient, highly reliable and environmentally versatile component for use in a wide variety of applications.

The largest application for tantalum (68 percent) is in the electronics capacitor industry in such products as cell phones, DVD players, personal computers, digital cameras, gaming platforms, LCD monitors, wireless devices, telephone switch boards and computer networks because of its unequalled capacity to store and release electrical charges.

Other electronics applications (11 percent) are in PC memory chips, igniter chips for car air bags and other automotive electronics. In addition, tantalum is used in the manufacture of super alloys (8 percent) for jet engines, turbines, space vehicles, nuclear reactors, power plants and chemical equipment due to its extreme hardness; in the manufacture of carbides (5 percent) for cutting tools, drill bits, excavator and bulldozer teeth and the forming of dies; in sputtering targets (2 percent) for use as optical coatings, memory chips and silicon wafers for use in micro compressors; in military and recreational ammunition (1 percent) and in the manufacture of a variety of other products (3 percent) such as rayon fibers, heat shields, ink jet printers, x-ray film, hip and knee replacement

systems because of its non-corrosive nature, and in the manufacture of surgical instruments and appliances.

## **MOLYBDENUM**

Molybdenum or just moly has several interesting characteristics that make its usage integral to several forms of energy production.

It has the sixth highest melting point of any element. It is highly corrosive resistant and does not expand, contract, harden, or soften under extreme temperature changes. Of all the commercially used metals, molybdenum has the lowest heating expansion.

Molybdenum is added to steel and cast iron to make metal alloys and superalloys that are much greater in strength. It can be found in anything from airplanes and cars to construction beams and filaments.

Molybdenum can be found in almost every modern drill. It greatly increases the strength of the drill and can limit technical mishaps, reducing costs. Molybdenum is needed in every aspect from drilling exploratory holes in an oil and natural gas field to drilling the production and injection wells that go into getting a geothermal power plant up and running.

It is used in long wall coal mining operation and can be found in the shearers used to extract the coal and the conveyers used to transport it. In an open-pit, truck-and-shovel operation, molybdenum is again used in both the extraction and transportation processes.

The corrosion resistance, combined with temperature insensitivity, makes molybdenum very important in the production of oil and natural gas pipelines. The Alaskan Pipeline consists of a half inch metal alloy that could handle a pressure up to 25,000 psi and temperatures of negative 70 degrees Fahrenheit. Up to 7 percent molybdenum was used in the 800 miles of the Alaskan pipeline delivering the USA with approximately 775,000 barrels of oil per day.

Molybdenum is also used as a hydro processing catalyst in petroleum production. It is used to remove sulfur and nitrogen in making light, sweet crude. Canadian oil sands and the tar oil from Venezuela are examples of oil that contain high levels of external elements that need to be purged in order to create light, sweet crude oil.

Molybdenum can be found in every modern turbine used in a power plant. All power plants, except wind and water, directly use heat to turn a turbine. In the highly abusive environment of a turbine, strength, corrosion resistance, and heat insensitivity make molybdenum the perfect industrial metal for power plant turbines. It greatly increases the life span, reducing the cost of the power plant.

In a geothermal power plant, molybdenum can be found in the back-pressure turbine or the condenser and pumps that re-inject the fluids back into the Earth.

In wind energy, molybdenum is used in the actual structure of the windmill and can be found in everything from the bearings to the generator.

In hydroelectricity, molybdenum can be used in the turbines and generators.

Molybdenum's contributions to the world of nuclear energy are by far the most significant. Newly developed high performance stainless steel (HPSS) contains up to 7.5 percent molybdenum. This alloy can more than triple the life of aging fleet condenser tubes. Brass, copper, and nickel made up the alloys previously used in fleet condenser tubes. Although these alloys were efficient in conducting heat, their life span was only



eight years. HPSS conductors were brought into play about 30 years ago. As of right now, the longest HPSS conductor has remained in service for over 26 years and is still going strong.

Older copper alloy fleet condenser tubes had corrosion issues. This affected the power plant in a couple of ways. It allowed for the buildup of corrosive materials, reducing the efficiency of the power plant. Also, the corrosion rendered weak spots in the fleet condenser tube, which could then result in holes. This was just not acceptable, because chemicals like sodium and chloride could leak and damage other vital parts of the reactor. Corrosion resistance leading to less buildup of undesirable substances increased the capacity of reactors by up to 20 percent.

The International Molybdenum Association (IMOA) says that an average nuclear power reactor contains about 520,000 feet of stainless steel alloy. Some larger reactors contain over 1 million feet of stainless steel alloy. With the metal alloy containing up to 8 percent molybdenum.

## **ALUMINUM**

Aluminum is a soft, non-magnetic metal that is the 3rd most abundant element in the Earth's crust after oxygen and silicon. Its primary ore is bauxite with a yearly production of 53.4 million metric tonnes. It is readily recycled and has been used as nuclear fuel cladding because of its low neutron absorption cross-section. It is used in transport, packaging, construction and household goods.

Aluminum is one of the most reactive metals in the periodic table, when it burns, it causes a very intense fire. This disadvantage is outweighed by its strength, flexibility and exceptional low density. Aluminum oxide forms a skin on the pure metal the moment it is exposed to air, and helps it resist corrosion. This oxide is so hard that it is used to make sandpaper and other abrasive materials.

Sapphire gemstone crystals, formed from aluminum oxide, are second only to diamonds in their hardness. Industrial sapphires were made of the size of a large bucket, suitable for use in bullet-proof glass, airplane windows and scratch-resistant smartphone displays. Naturally-occurring sapphires can take 50,000 years to form. They can be manufactured within a week in ovens made of molybdenum. A sapphire hard drive is reported to have been developed that can store information for up to a million years.

Aluminum was isolated in 1825, and remained so scarce that it was valued higher than silver for decades since it is too reactive to occur in its pure form in nature. Its primary ore is bauxite, a reddish-brown ore named after the French town "Les Baux," where it was first discovered. Bauxite is melted in a mineral called cryolite, and then an electric current is passed through it, separating the oxygen atoms from the aluminum metal. It takes 4 metric tonnes of bauxite to produce 1 metric tonne of aluminum.

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