PLUTONIUM PROCESSING AT LOS ALAMOS

Los Alamos
NATIONAL LABORATORY
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About the cover

The cover photo shows an annular ring of purified plutonium weighing several kilograms, prepared using modern plutonium processing. Inset at the bottom of the ring is an historical sample of a half microgram of plutonium deposited on a strip of platinum by Glenn Seaborg and Emilio Segré and on display at the Smithsonian Institution.

Plutonium Processing at Los Alamos

Introduction

The element plutonium occupies a unique place in the history of science, technology, and international relations. After the initial discovery of only a few atoms, it is now generated by transmutation of uranium in nuclear reactors on a large scale and has been separated in ton quantities in large industrial facilities. The intense interest in plutonium has always centered on the nexus between nuclear weapons and domestic nuclear power—drawing energy from an atomic nucleus that can be tapped for a multiplication factor of millions in energy output relative to chemical energy sources.

Historically, plutonium was first produced in production reactors; extracted, concentrated, and converted to either an oxide or fluoride; and then reduced to metal. The resulting metal was used for fabrication of various parts and components. The fabrication process itself generates major quantities of waste and scrap plutonium that must then be recovered and recycled.

In modern times, the feed material for preparing and refining metallic plutonium and its important compounds now includes recovered and recycled residues and scrap material. This in turn drives the current technology selection for processing, preparing, and refining. In addition, the technology selection must take nuclear material safeguards, accountability, criticality safety, radiation exposure, and environmental protection into consideration.

David L. Clark and Gordon Jarvinen of the Seaborg Institute and Cynthia Kowalczyk, Jim Rubin, and Mary Ann Stroud of Plutonium Manufacturing and Technology Division contributed to this issue.

Virtually all plutonium operations at Los Alamos occur within the Plutonium Facility at TA-55, shown in this aerial photograph. It is the nation's most modern plutonium facility and opened in 1978.

In 2008, more than 2200 metric tons of plutonium exists throughout the world in the form of spent nuclear fuel, nuclear weapons components, various nuclear inventories, legacy materials, and wastes. Regardless of your views on how this situation came to be, it is clear that these large plutonium inventories must be prudently managed for many centuries. We will have to stabilize and store excess plutonium, secure it against theft and diversion, and research modern reactor concepts to reduce plutonium inventories. To succeed, we will have to improve our understanding of plutonium by continuing to work at the frontiers of science, and continuing to attract and retain the best and the brightest talent of the next generation.

Under NNSA's proposed preferred alternative, Los Alamos will maintain its role as the center of excellence for nuclear weapons design and engineering, and plutonium research, development, and manufacturing. As the nuclear weapons program becomes smaller as part of the NNSA weapons complex transformation, Los Alamos' Stockpile Manufacturing and Support (SMS) Directorate must maintain the breadth of capabilities that support stockpile stewardship and nuclear deterrence while also producing innovative discoveries that will lead to new missions in plutonium science and engineering. Plutonium processing will be a key component of the Los Alamos mission for the foreseeable future.

Virtually all plutonium operations at Los Alamos occur within the Plutonium Facility at Technical Area 55. It is the nation's most modern plutonium facility, consisting of a 75,000-square-foot building that is built to withstand 200-mile-per-hour tornadic winds and any credible seismic event. TA-55, as the facility is commonly called, opened in 1978.

The work at TA-55 supports a wide range of national programs, such as stockpile stewardship, nuclear materials stabilization, materials disposition, nuclear forensics, nuclear counter-terrorism, and nuclear energy. Each of these programs revolves around plutonium. In stockpile stewardship, for example, pure plutonium metal is used to manufacture nuclear-weapon pits or to conduct experiments related to maintenance of the nation's nuclear stockpile. The materials disposition program recovers plutonium from decommissioned weapons and processes it for eventual disposal or for burning as mixed oxide (MOX) fuel.

Almost all the plutonium at TA-55 has been recycled, having been recovered from previous TA-55 operations or from operations at other sites. But plutonium continually undergoes radioactive decay, and trace amounts of uranium, neptunium, and americium impurities accumulate in aged metal. These impurities must be removed before the material can be reused. In addition, the plutonium used for an experiment may have been alloyed, become oxidized, or been formed into a chemical compound; it too must be purified before reuse.

Thus, a significant portion of the work done at TA-55 involves chemical processing to produce pure plutonium metal or compounds such as the oxide (PuO_2). Anion exchange, solvent extraction, and pyrochemical processing are the three production-scale techniques that are used extensively. Nitric and hydrochloric acid processing produces purified plutonium dioxide, which is

then further processed by pyrochemical operations to produce very pure plutonium metal.

Nitric acid processing has been used over the last 30 years to process literally tons of plutonium. Hydrochloric acid processing has been used for the last 15 years, allowing for processing of a wider variety of plutonium materials. Pyrochemical processing was used extensively at the Rocky Flats Plant in Colorado and is still used to purify plutonium at TA-55. While all three processes are efficient and robust, they produce a prodigious stream of low-level and transuranic (TRU) waste. There are various repositories around the country for low-level waste, including one at Los Alamos. The Waste Isolation Pilot Plant (WIPP) in New Mexico is the nation's repository for defense-related TRU waste. Several R&D successes at Los Alamos, however, have dramatically reduced the waste volume that results from these processes.

The work at TA-55 supports a wide range of national programs, such as stockpile stewardship, nuclear materials stabilization, materials disposition, nuclear forensics, nuclear counterterrorism, nuclear energy, and power-source technology for interplanetary exploration. Each of these programs revolves around plutonium. This photo shows workers monitoring a nitrate processing operation inside a glovebox.

Historical perspective

Lawrence Berkeley National Laboratory

Below, from left to right: Early production-scale plutonium purification processes in Building D were conducted in wooden gloveboxes. A sparge tube is inserted into the furnace. The crucible is broken off to reveal the plutonium button and salt residue. (Note the much larger area of glass used in the older gloveboxes.) The electrochemical cell used in today's electrorefining process hasn't changed much from what was used in the early 1960s.

Plutonium was discovered in 1940 by Glenn Seaborg and colleagues at the University of California, Berkeley. A small sample of the isotope plutonium-239, created in 1941, was stored for many years in a cigar box. A message on the cover of the box read: "Very Valuable Sample. Do not disturb in any way." Seaborg and Emilio Segré presented the cigar box and sample to the Smithsonian Institution in 1966.

Los Alamos has been at the forefront of plutonium research since 1943 and the early days of the Manhattan Project. Plutonium operations moved in 1945 from the original technical area to TA-21 (DP Site), where they remained until 1978 when the Plutonium Facility (PF-4) at TA-55 became operational. PF-4 was designed to be the nation's premier actinide research and development facility. Today it is the only remaining facility in the DOE complex with the capability to separate and purify all isotopes and chemical forms of plutonium, as well as other actinides.

The red arrow points to the plutonium processing building, known as Building D, in the original war-time tech area. Ashley Pond, seen in the upper right of the photo, is still the centerpiece of downtown Los Alamos.

Plutonium operations moved to DP Site in 1945.

Dixon Wolf

The Radiological Laboratory, Utility, Office Building (RLUOB), which is currently under construction at Los Alamos, is the first phase of the Chemistry and Metallurgy Research Replacement (CMRR) Project. This element of the CMRR Project supports the relocation and consolidation of mission-critical analytical chemistry, materials characterization, and actinide research and development capabilities, which will ensure continuous national-security mission support beyond 2010.

The photo above shows air-dried plutonium(III) oxalate from aqueous nitrate operations. The oxalate is converted into pure plutonium dioxide (below) by calcining at 600 degrees Celsius. While plutonium dioxide is normally olive green, samples can be various colors. It is generally believed that the color is a function of chemical purity, stoichiometry, particle size, and method of preparation, although the color resulting from a given preparation method is not always reproducible.

NITRIC ACID PROCESSING

Nitric acid is used both as a dissolution agent and a processing medium. Impure scrap plutonium or plutonium-contaminated items, such as glass, graphite casting molds, magnesium oxide crucibles, and incinerator ash, can be dissolved in or leached with nitric acid, while impure plutonium dioxide can be dissolved in the acid. (Dissolving plutonium metal in nitric acid produces an unstable residue that is pyrophoric and susceptible to shock-induced explosions. Thus for processing, if the plutonium is not already an oxide, it is converted to one by burning the metal in air.)

During processing, the plutonium containing nitric acid solution is passed through a column packed with thousands of beads of an anion-exchange resin. The resin is an organic polymer that contains cationic (positively charged) sites incorporated into the solid polymer with the charge balanced by mobile anions (negatively charged) such as nitrate. These mobile anions can be displaced by other anionic species in solution that bind to the fixed cationic sites on the resin depending on their relative affinity for the cationic site.

Plutonium in the tetravalent oxidation state is one of only a handful of elements that can form stable anionic complexes in nitric acid; it binds to the cationic sites on the resin as the plutonium hexanitrato complex, $Pu(NO_3)_6^{2-}$. This Pu(IV) complex has the highest sorption coefficient of any metal ion to certain cationic resins and has a peak value for sorption at nitric acid concentrations of about 7 molar (M). Pu(IV) is preferentially sorbed under these conditions, while most other elements simply flow through the column and are washed from the system using additional amounts of nitric acid, leaving the plutonium bound to the column.

Once the resin has been "loaded and washed," the plutonium is recovered by sending an eluting solution (0.35-0.5 M nitric acid) through the column. The Pu(IV) has little affinity for the resin in the dilute nitric acid, so it desorbs and flows with the solution into holding tanks. The Pu(IV) in the dilute nitric acid solution is then reduced to Pu(III) by the addition of a solution of hydroxyl-amine. After the plutonium has been converted to the trivalent state, a small molar excess of oxalic acid is added to precipitate Pu(III) oxalate decahydrate, $Pu_2(C_2O_4)_3 \cdot 10H_2O$. The solid oxalate is collected by filtration, dried, and converted to pure plutonium dioxide by calcining at 600 degrees Celsius (°C). The PuO_2 is then converted to metal or used directly for production of mixed oxide (MOX) nuclear fuels.

As with all plutonium processes, anion-exchange produces waste contaminated with low levels of plutonium. The resin does not remove all the plutonium from solution, and thus the nitric acid solutions always contain small amounts of plutonium after they have passed through the anion-exchange process. The contaminated effluents from the column and the holding tanks are therefore sent to an evaporator. The evaporator bottoms, which contain most of the

residual plutonium, other actinides, and impurity elements are stabilized in cement and disposed of as TRU waste at the WIPP facility.

The condensed water and nitric acid vapor from the evaporator is sent to a second evaporator that recovers most of the nitric acid for recycle in plant operations. The condensate from the nitric acid recovery system is a very dilute nitric acid stream that has very low levels of alpha activity. This liquid is piped to holding tanks in the Radioactive Liquid Waste Treatment Facility at TA-50, where it is further treated with a series of processes including flocculation/precipitation, ultrafiltration, and reverse osmosis to produce water with very low levels of alpha activity that meets permit requirements, and then discharged to the environment following New Mexico Environment Department (NMED) regulations.

Over decades, Los Alamos has improved the nitric acid processing operations to reduce the hazardous components in the waste streams. For example, because some plutonium remains sorbed to the anion-exchange resin, ultimately the used resin must also be disposed of as a TRU waste to the WIPP. In the late 1980s, Los Alamos collaborated with Reilly Industries, Inc., to develop Reillex^{TM} HPQ resin. Compared with earlier anion-exchange resins, HPQ has improved sorption properties for plutonium. It is also less prone to radiolytic or

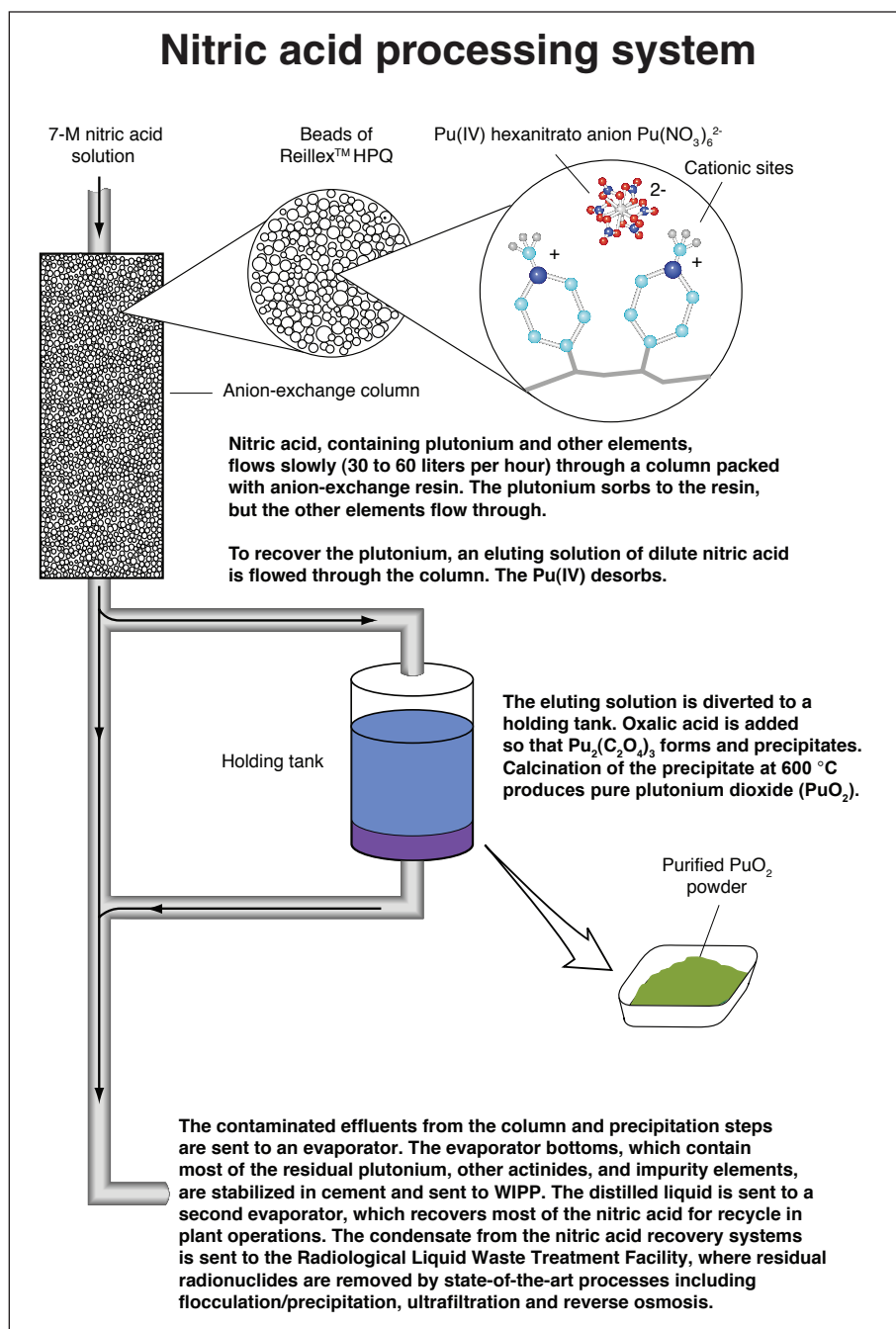**Nitric acid process**
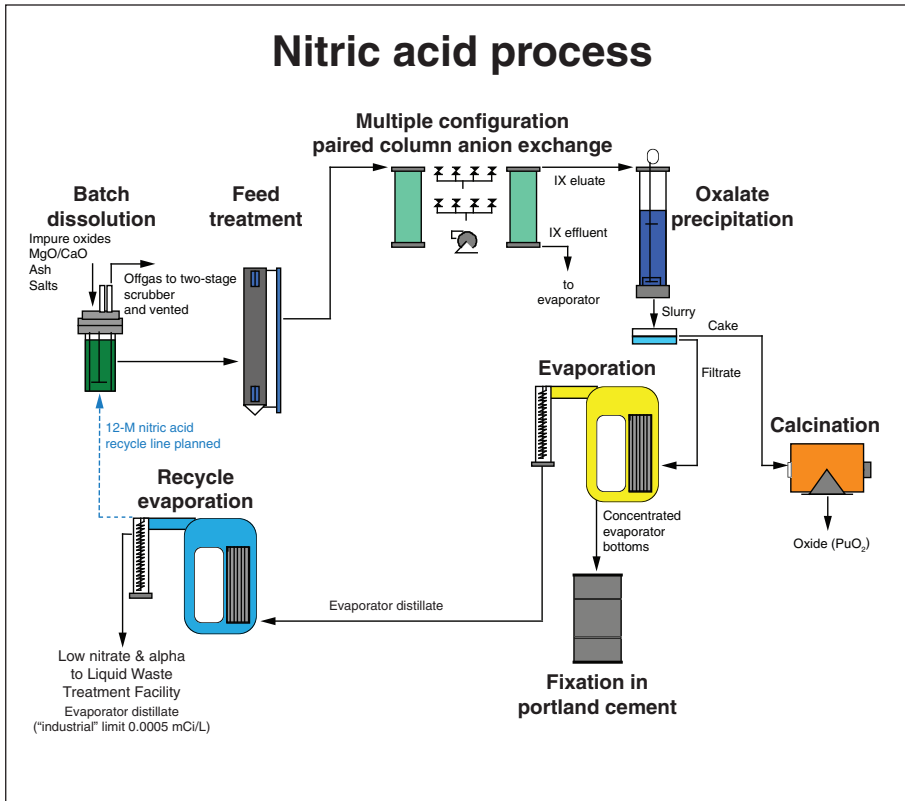
Jarvinen receives Seaborg award

Gordon Jarvinen is the 2008 winner of the Glenn T. Seaborg Actinide Separations Award. Jarvinen was honored for his innovative research on processes that can be used to recycle plutonium and other actinides in the service of national interests.

His scientific accomplishments include research into water-soluble polymers and separation of plutonium-238 for NASA interplanetary space missions; the separation of trivalent actinides from lanthanides for advanced nuclear fuel cycles using liquid-liquid extraction; the fundamental coordination chemistry involved in extraction processes; and novel membrane separations that mimic ion-channels in biological systems.

Jarvinen is the fourth Los Alamos scientist to receive the award since it was created in 1984. The recipient is chosen by a panel of experts from seven national laboratories and is truly recognition from peers within the actinide separations community. Seaborg, the award's namesake and first recipient, was the codiscoverer of nine actinide elements.

Jarvinen is currently associate director of the Los Alamos branch of the Glenn T. Seaborg Institute and is a scientific advisor to *Actinide Research Quarterly.*

chemical degradation in the harsh conditions of solutions of nitric acid containing high concentrations of alpha-emitting plutonium isotopes. The enhanced stability of Reillex HPQ allows the resin to be used for approximately 50 plutonium recovery cycles before being replaced.

Nitric acid processing system

7-M nitric acid solution

Beads of Reillex™ HPQ

Pu(IV) hexanitrato anion Pu(NO$_3$)$_6$$^{2-}$

Cationic sites

Anion-exchange column

Nitric acid, containing plutonium and other elements, flows slowly (30 to 60 liters per hour) through a column packed with anion-exchange resin. The plutonium sorbs to the resin, but the other elements flow through.

To recover the plutonium, an eluting solution of dilute nitric acid is flowed through the column. The Pu(IV) desorbs.

Holding tank

The eluting solution is diverted to a holding tank. Oxalic acid is added so that Pu$_2$(C$_2$O$_4$)$_3$ forms and precipitates. Calcination of the precipitate at 600 °C produces pure plutonium dioxide (PuO$_2$).

Purified PuO$_2$ powder

The contaminated effluents from the column and precipitation steps are sent to an evaporator. The evaporator bottoms, which contain most of the residual plutonium, other actinides, and impurity elements, are stabilized in cement and sent to WIPP. The distilled liquid is sent to a second evaporator, which recovers most of the nitric acid for recycle in plant operations. The condensate from the nitric acid recovery systems is sent to the Radiological Liquid Waste Treatment Facility, where residual radionuclides are removed by state-of-the-art processes including flocculation/precipitation, ultrafiltration and reverse osmosis.

Dry operations

The purified plutonium dioxide produced by the aqueous chloride or aqueous nitrate process operations needs to be thermally treated before use in the pyrochemical processing operations. To ensure that all residual moisture and remaining trace amounts of volatile components are eliminated, the oxide is subjected to a high-temperature (850 degrees Celsius) calcination. As needed, this calcination process may be followed by sieving and mechanical blending to ensure homogeneity and flowability of the final oxide product. The combination of calcination, sieving, and blending is commonly referred to as dry operations. The term dry operations is also used to include the manipulation of dry solids from other processes such as direct metal oxidation or hydride/dehydride used in pit disassembly and conversion (see *ARQ* 1st/2nd Quarters 2008).

This sequence of photos shows an initial plutonium(IV) oxalate (far left) that was prepared from nitric acid processing as a feed for mixed oxide (MOX) fuel. The oxalate is calcined in a furnace (left) to produce purified plutonium dioxide (right). The resulting plutonium dioxide can be blended using a special apparatus (far right) with other batches for a homogeneous product.

From top to bottom: Plutonium dioxide is the feed material for the MCDOR process. After the reaction is complete, the melt settles and cools, forming a plutonium button at the bottom of the crucible and a calcium chloride salt cake above it. The crucible is broken away and the plutonium button is mechanically separated from the salt cake. In the lower photo the plutonium button is pictured on top of the salt cake.
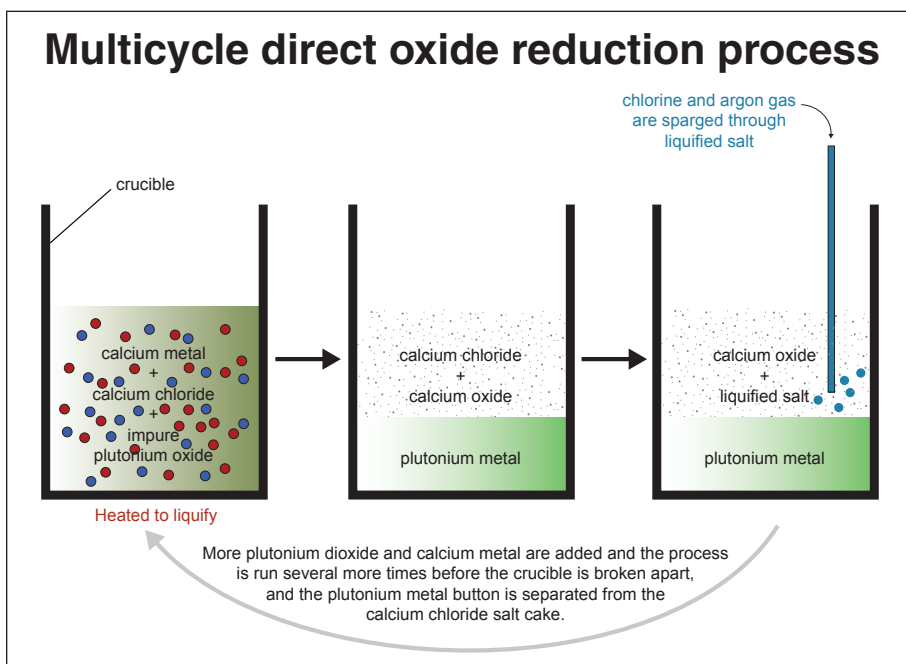
PYROCHEMICAL SALT PROCESSING

Pyrochemical processes involving molten calcium, potassium, and sodium chlorides are used at TA-55 to prepare and purify plutonium metal. Two advantages of these methods are the compactness of their equipment and their rapid reaction kinetics.

Multicycle direct oxide reduction

The plutonium dioxide from nitric acid or hydrochloric acid processing is converted to plutonium metal in a pyrochemical process called multicycle direct oxide reduction (MCDOR). In the MCDOR process, plutonium dioxide (PuO_2) is reduced with calcium metal to produce plutonium metal and calcium oxide (CaO). The reaction takes place in a molten calcium chloride solvent ($CaCl_2$), which dissolves the resulting CaO and allows the plutonium metal to coalesce in the bottom of the magnesium oxide (MgO) crucible to form a metal button.

The reaction occurs at about 820 °C with a temperature spike to 875 °C, and takes about 15 minutes. After completion of the reaction, the melt is allowed to settle and cool while the plutonium forms a metal button at the bottom of the crucible, and the calcium chloride forms a salt cake that solidifies above the metal.

The calcium oxide is then converted back to calcium chloride *in situ* by bubbling chlorine gas through the molten salt. Once the salt is regenerated, more

Multicycle direct oxide reduction process

chlorine and argon gas are sparged through liquified salt

crucible

calcium metal
+
calcium chloride
+
impure
plutonium oxide

Heated to liquify

calcium chloride
+
calcium oxide

plutonium metal

calcium oxide
+
liquified salt

plutonium metal

More plutonium dioxide and calcium metal are added and the process is run several more times before the crucible is broken apart, and the plutonium metal button is separated from the calcium chloride salt cake.
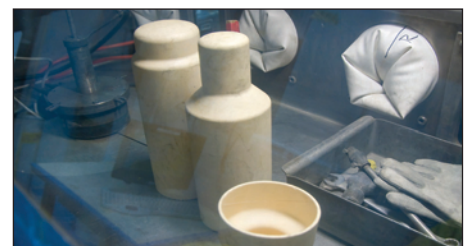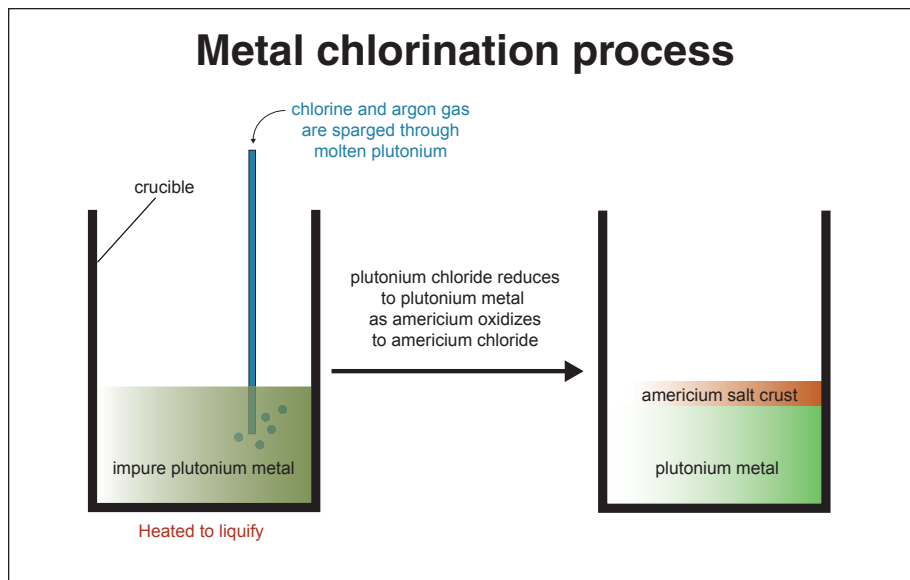
plutonium dioxide and calcium metal can be added to the crucible to produce more plutonium metal. The MCDOR process can be run several times before the plutonium metal button is recovered and the salt and crucible discarded as TRU waste.
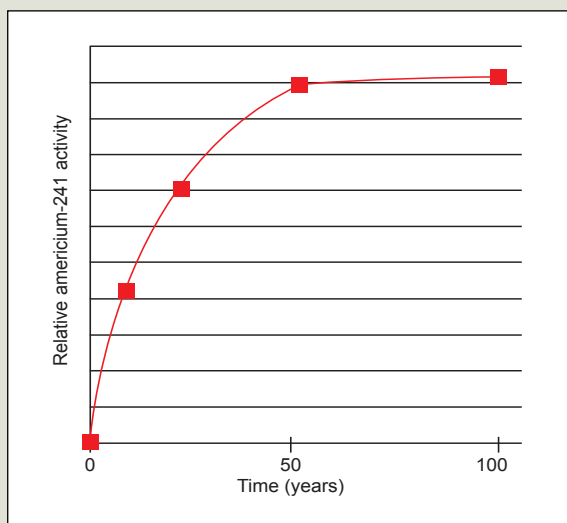
Metal chlorination

The plutonium metal produced by MCDOR is not very pure, however, because calcium chloride always contains trace amounts of impurities that are readily absorbed by the plutonium. The method of purification depends to some extent on the nature of the impurities present. If the plutonium feed has been in storage for many years, it will have a high content of americium-241 that will need to be removed in a process known as metal chlorination (MC), formerly referred to as molten salt extraction (MSE). Americium-241 spontaneously grows into plutonium as a result of plutonium-241 beta decay. If the americium content is low, the metal can be purified by electrorefining (ER).

For americium removal by metal chlorination, the plutonium is heated above the melting point in a magnesium oxide (MgO) crucible and reacted with chlorine gas. This produces plutonium trichloride ($PuCl_3$), *in situ*, which then reacts with the americium in the metal to produce americium trichloride ($AmCl_3$). The americium trichloride and some plutonium trichloride form an easily removed salt crust on top of the purified plutonium metal.

Metal chlorination process

crucible

chlorine and argon gas
are sparged through
molten plutonium

plutonium chloride reduces
to plutonium metal
as americium oxidizes
to americium chloride

impure plutonium metal

Heated to liquify

americium salt crust

plutonium metal

From top to bottom: Plutonium feed material is placed in a crucible inside a safety can. Plutonium trichloride is produced after the plutonium is heated and reacted with chlorine gas. The resulting americium chloride salt crust is usually a greenish color. A newly designed crucible means the plutonium ingot doesn't have to go through metal coalescence because it's already the correct shape and size.

AMERICIUM-241 INGROWTH

Not all impure plutonium metal produced by multicycle direct oxide reduction needs to undergo metal chlorination. However, if the plutonium has sat in storage for many years, it will have undergone radioactive decay of plutonium-241. This isotope has a half-life of 14.35 years and decays by beta decay into americium-241. The americium-241 has a 433-year half-life and yields alpha particles and gamma rays when it decays. The gamma rays add significant worker exposure from aged plutonium and removal of americium reduces dose to personnel during subsequent processing. Americium also represents an unwanted impurity in weapons-grade plutonium.

COALESCENCE/INGOT CASTING

After the americium is extracted from the impure metal, the plutonium metal must be cast into a cylindrical geometry that is compatible with the electrorefining cell. Pieces of plutonium from the metal chlorination process, along with pieces and turnings not requiring americium removal, are cast in a heated, stirred magnesia crucible, sometimes containing calcium chloride salt and a small amount of calcium metal. The resulting ingots are the correct size for use in the electrorefining cell.

Scraps of plutonium metal are melted into a single piece in the coalescence process. Impure plutonium metal is also cast into ingots (shown above) in preparation for electrorefining—the final step in the purification process.

Electrorefining

Electrorefining (ER) is the process used to convert impure plutonium metal—in the form of ingots cast from feed material processed by multicycle direct oxide reduction (MCDOR) or metal chlorination (MC)—into refined plutonium metal pure enough for use in national security programs.

In the ER process, liquid plutonium oxidizes from the anode ingot into a molten-salt electrolyte. The resulting Pu(III) ion is transported through the salt to the cathode, where it is reduced back to metal. The process is carried out at 740 °C in a molten salt consisting of an equimolar mixture of sodium chloride–potassium chloride (NaCl/KCl) containing a small amount of plutonium chloride ($PuCl_3$) as a seeding agent to charge the electrolyte with Pu(III) before a current is passed and ensures the initial reduction of plutonium at the cathode.

The process is performed in a double-cupped, vitrified magnesia crucible. The inner cup contains the impure metal ingot that serves as the anode material. The electrolyte salt casting (or plug) is placed on top of the ingot. The crucible is placed inside a tantalum safety can and placed inside the furnace and heated. A tungsten rod is suspended in the impure metal pool to serve as the anode rod, and electrically insulated from the salt by a magnesia sleeve. A cylindrically shaped sheet of tungsten is suspended in the annular space between the two cups and serves as the cathode.

Stirring and passing a dc current between the anode and cathode accomplish the process. Plutonium oxidizes at the anode and reduces back to metal at the cathode. The liquid metal drips off the cathode and into the annular space. After cooling to room temperature, the cell is broken apart and the plutonium recovered as an annular metal casting, or "ER ring."
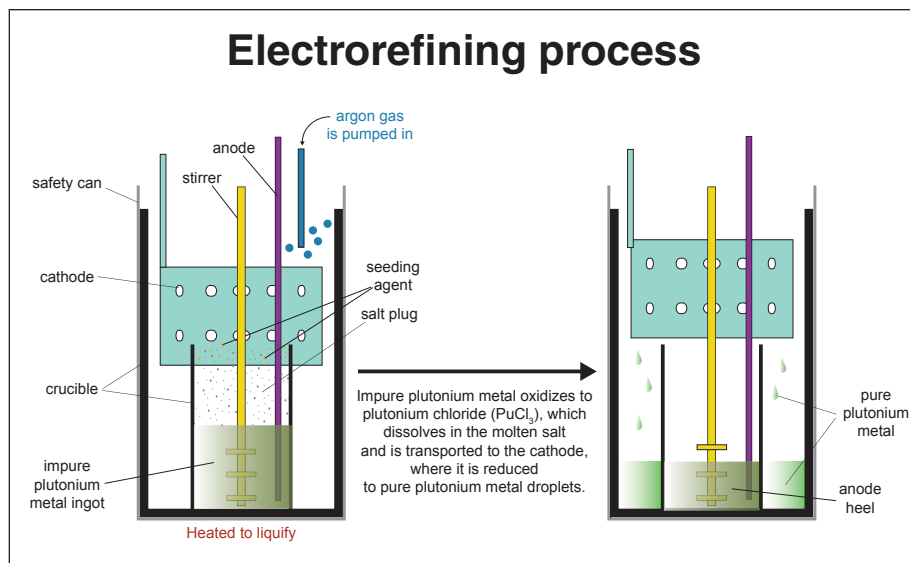
This plutonium ingot, produced by coalescence, will be the feed material for the electrorefining process.
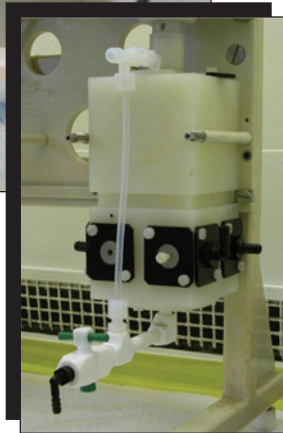

The final product: a ring of high-purity plutonium metal. The ring will be broken into pieces with a sample breaking press, and a small sample of one piece will be analyzed for purity. The remainder of the pieces will be stored until needed in a special container under inert atmosphere to keep the plutonium from oxidizing.

Electrorefining process

argon gas is pumped in

anode

stirrer

safety can

cathode

seeding agent

salt plug

crucible

impure plutonium metal ingot

Heated to liquify

Impure plutonium metal oxidizes to plutonium chloride ($PuCl_3$), which dissolves in the molten salt and is transported to the cathode, where it is reduced to pure plutonium metal droplets.

pure plutonium metal

anode heel

AQUEOUS CHLORIDE PROCESSING

Pyrochemical processing generates plutonium- and americium-bearing residues as a byproduct of high-purity plutonium metal production. The bulk of these residues are chloride salts containing significant amounts of retained plutonium, which is recovered through aqueous hydrochloric acid processing. Plutonium oxide recovered from these processed chloride residues provides approximately half of the high-quality oxide needed by the multicycle direct oxide reduction (MCDOR) process.

Los Alamos has been processing aqueous chloride solutions since the 1980s. In March 1993, the Experimental Chloride Extraction Line (EXCEL) became operational at TA-55. Since then, full-scale plutonium recovery has been employed using hydrochloric acid (HCl) to dissolve and leach various feed materials such as metal turnings, impure metals, pyrochemical residues, and returns of analytical solutions. Aqueous chloride processes are used to purify, stabilize, and produce plutonium suitable for long-term storage or future weapons applications.

The aqueous chloride recovery process begins with dissolution or leaching of a solid feed in 6-8 molar (M) HCl. Acid is added slowly to prevent an uncontrollable exothermic reaction.

Dissolution is performed while sparging the solution with argon gas into a vacuum trap and acid scrubber. The argon flow prevents the buildup of explosive mixtures of hydrogen and air that may result from the reaction of metal with water and acid. Overall dissolution efficiency is on the order of 98 percent.

Solvent extraction is the primary process used to separate the plutonium from the impurities in chloride operations. The aqueous plutonium solution is then vigorously mixed with an organic solution containing tributyl phosphate (TBP) in a centrifugal contactor.

The TBP extracts the plutonium into the organic phase. The organic solution is "cleaned" by "scrubbing" it with a basic aqueous solution. The organic layer is then contacted with a new, lower-concentration aqueous chloride solution and agitated, which causes the TBP to release (or strip) the plutonium into the new, aqueous chloride solution.

After purification by solvent extraction, the purified plutonium is recovered by precipitation as an oxalate cake. In oxalate precipitation, the plutonium is first reduced to plutonium(III), followed by precipitation with oxalic acid ($H_2C_2O_4$) to produce plutonium(III) oxalate decahydrate

Aqueous chloride processing uses liquid-liquid solvent extraction to separate plutonium from impurities using annular centrifugal contactors like the one shown at right. These are arranged inside a glovebox that is specially coated on the inside to resist corrosion (above). Centrifugal contactors have many desirable properties for plutonium processing such as low hold-up volume, short residence time, low solvent degradation, small space requirements, and short start-up time.

$[Pu_2(C_2O_4)_3 \cdot 10H_2O]$. The oxalate cake is placed in a furnace can and calcined to produce high-purity plutonium(IV) dioxide (PuO_2).

To treat the HCl raffinate solutions from the solvent extraction of plutonium and the filtrate from the oxalate precipitation, the waste streams are made caustic by the addition of concentrated potassium hydroxide, that is, excess hydroxide is used to neutralize all the acid until the pH of the solution is 8 or higher. Under these conditions, the actinides precipitate to a large extent and can be removed by filtration. The resulting precipitate, commonly called a hydroxide cake, is filtered, air dried, and then calcined.

At this point, the caustic liquid waste has a very low activity of about 2.5 millicuries per liter and it is sent to the Radiological Liquid Waste Treatment Facility for further treatment through a series of processes similar to those noted earlier for the nitric acid solution processing. However, when the Chloride Line Extraction and Actinide Recovery (CLEAR) gloveboxes are activated in the future (see sidebar on Page 16), activity levels in the waste stream could possibly be further reduced to acid or industrial waste discharge limits and could simplify waste operations.

Hydrochloric acid process
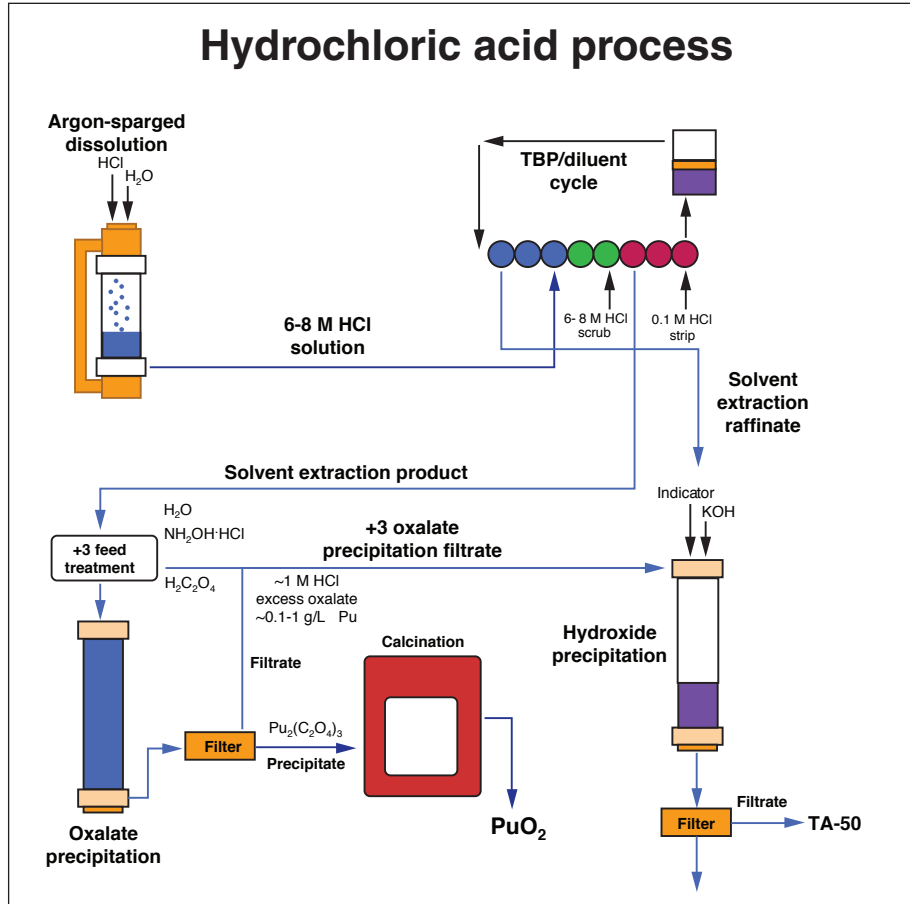
Further reading

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"Cleanup of Hydrochloric Acid Waste Streams from Actinide Processes Using Extraction Chromatography," L.D. Schulte, J.R. FitzPatrick, R.R. Salazar, B.S. Schake, and B.T. Martinez, *Separations Science & Technology,* Vol. 30, 1995.

"Plutonium," Chapter 7, D.L. Clark, S.S. Hecker, G.D. Jarvinen, and M.P. Neu, *The Chemistry of the Actinides and Transactinides,* 3rd Edition, Springer, 2006.

"Preliminary Evaluation of Alternative Flow Sheets and Technology Improvements for Aqueous Processing in the Modern Pit Facility," M.A. Stroud and L.D. Schulte, Los Alamos National Laboratory report, LA-14204, 2005.

The future is CLEAR

In the near future, TA-55 will begin to use the Chloride Line Extraction and Actinide Recovery (CLEAR) gloveboxes. When originally designed, the CLEAR glovebox line was built primarily to reduce activity levels in the waste stream by extracting the actinides (plutonium, americium, and uranium) out of the waste stream. Recently, with the increase in demand for americium (Am) from the oil/gas logging and smoke-detector industries, americium is a viable marketing element for interaction with private industry. Extraction chromatography is used to separate plutonium and/or americium from other elements in solution but may be used to remove any actinide from the dissolved solution. Depending on the chromatography resin, the plutonium can be in the +3 or +4 oxidation state.

CLEAR employs extraction chromatography to combine the selectivity of liquid-liquid extraction with the ease of operation of column chromatography. A mixture of liquid extractants (illustrated in the diagram below right) is used in the CLEAR process to recover plutonium and/or americium from solution.

CLEAR process

Raffinate from solvent extraction

Extraction chromatography Pu(IV)/Pu(VI) from Am(III)

13% + 27% TBP (tributyl phosphate)

Extraction chromatography Am(III) from impurities

1. H_2O, $NH_2OH \cdot HCl$
2. $H_2C_2O_4$

30% + 10% DAAP (di-amyl, amyl phosphonate)

Americium oxalate

KOH, indicator

Hydroxide

Precipitate

To TA-50

Precipitate

Hydroxide solids	$Am_2(C_2O_4)_3 \cdot x\ H_2O$
Calcination	Calcination
Hydroxide cake	AmO_2