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^{238}Pu PROCESSING AT THE SAVANNAH RIVER PLANT

by

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INTRODUCTION

The Savannah River site was established in 1950 by the U.S. Atomic Energy Commission to produce special nuclear materials for the nation's defense program. The plant's products have also included a number of nonmilitary isotopes. ^{238}Pu has been produced in kilogram quantities beginning in 1960. It was the first radioisotope to be used as a power source for space applications when the Transit 4A satellite was launched in 1961. Since then, ^{238}Pu has been used as a reliable energy source for many other satellites and other power sources (Table 1).

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SUMMARY

^{238}Pu is produced by irradiating ^{237}Np. The ^{237}Np is produced as a byproduct when natural or enriched uranium is irradiated with neutrons. The ^{237}Np is separated by solvent extraction and ion exchange. It is converted to NpO_2 and fabricated into targets for irradiation (Figure 1).

The irradiated targets are "cooled" and dissolved in strong nitric acid. The ^{238}Pu and ^{237}Np are separated from fission products and other cationic impurities and from each other by three cycles of anion exchange (Figure 2).

The ^{237}Np is recycled to produce more targets for irradiation. The pure ^{238}Pu solution is precipitated as Pu oxalate and calcined to PuO_2. After several powder-conditioning steps, the PuO_2 is hot pressed into fuel forms. Each form is encased in iridium for loading into a specially designed power unit for space application.

DISCUSSION

Production and Properties of ^{238}Pu

The main product from irradiation of ^{238}U in nuclear reactors is ^{239}Pu produced by the reaction:

$$^{238}U(n,\gamma)\ ^{239}U \xrightarrow{\beta^-} {}^{239}Np \xrightarrow{\beta^-} {}^{239}Pu$$

A byproduct, ^{237}Np, is produced in much lower yield by the reactions:

$$^{238}U(n,2n)\ ^{237}U \xrightarrow{\beta^-} {}^{237}Np$$

$$^{235}U(n,\gamma)\ ^{236}U(n,\gamma)\ ^{237}U \xrightarrow{\beta^-} {}^{237}Np$$

The byproduct ^{237}Np is separated from ^{239}Pu and fission products in the large radiochemical separation plant by solvent extraction and ion exchange processes (Figure 3).[1,2] The Np is converted to NpO_2 and fabricated for irradiation to produce ^{238}Pu.

$$^{237}Np(n,\gamma)\ ^{238}Np \xrightarrow{B^-} {}^{238}Pu$$

Because the neutron capture cross section of ^{238}Pu is about three times that of ^{237}Np, the irradiation of ^{237}Np to produce ^{238}Pu is limited to relatively short exposures to minimize production of higher Pu isotopes. With recovery and recycle of the unconverted ^{237}Np, relatively efficient overall conversion to ^{238}Pu is realized. Fission products are generated in irradiated ^{237}Np targets predominantly by fission of ^{238}Np and ^{239}Pu.

The radiation properties of ^{238}Pu have been described in detail by Stoddard and Albenesius.[3] The alpha and gamma spectra for ^{238}Pu are shown in Figure 4. Alpha radiation is the major source of energy released by ^{238}Pu (0.55 watt per gram) and is the major cause of radiation damage to processing materials such as organic solvents and ion exchange resins. Typical Savannah River ^{238}Pu, with an isotopic composition of 81% ^{238}Pu, 15% ^{239}Pu, 2.9% ^{240}Pu, 0.8% ^{241}Pu, 0.1% ^{242}Pu, and 1.2 ppm ^{236}Pu has an alpha activity of 5.1×10^{11} dis/(sec-g), equivalent to 13.8 Ci/g.

Gamma radiation from ^{238}Pu is predominantly of low energy, an important reason for its suitability for use in isotopic power generators. The gamma radiation results from several sources:

- Alpha decay of Pu isotopes and their daughters
- Spontaneous fission of ^{238}Pu
- Fission products, from spontaneous fission and those not removed in chemical processing
- *Interaction of alpha particles with oxygen.*

Of these sources, the most predominant are soft gammas (43.6, 99.6, and 152 keV) accompanying ^{238}Pu alpha decay. Higher energy gammas occurring in lower abundance are predominantly from the daughters of ^{236}Pu, and from products of spontaneous fission of ^{238}Pu.

Neutrons from ^{238}Pu arise principally from (α,n) reactions with low atomic number elements. The neutron radiation from pure ^{238}Pu metal is small [$\sim 2 \times 10^3$ n/(sec-g ^{238}Pu)], resulting from spontaneous fission of ^{238}Pu. In dilute nitrate solution or in the form of PuO_2, typical product emits $\sim 2 \times 10^4$ n/(sec-g ^{238}Pu); more than 90% of the neutron emission results from the (α,n) reaction with ^{18}O.

Chemical Processing Irradiated ^{237}Np to Recover ^{238}Pu

The irradiated NpO_2-Al targets are cooled at least 100 days to allow decay of short-lived fission products, particularly ^{131}I. They are then dissolved in 10M HNO_3 containing mercuric nitrate and potassium fluoride catalysts. The targets dissolve slowly with little volatilization of ^{131}I. When dissolution is complete, the Np is in the (VI) valence state and the plutonium is in the (IV) and (VI) valence states in the nitric acid-aluminum nitrate solution.

Three cycles of anion exchange separate the Np and Pu from fission products, other cations, and from each other (Figure 2).[3] In preparation for the first anion exchange cycle, the solution is adjusted to ~8M nitrate, and ferrous sulfamate is added to produce Np(IV) and Pu(III). The solution is heated to ~55°C to oxidize excess Fe(II) to Fe(III) and Pu(III) to Pu(IV) without oxidation of Np(IV). The Np(IV) and Pu(IV) form hexanitrato anions, $M(NO_3)_6^{2-}$, which are strongly sorbed on the strong base macroporous anion exchange resin. Typical loading is ~40 g of actinide per liter of resin. Most aluminum, iron, and fission products are easily removed by washing with $8M\ HNO_3$-0.005M KF. The Np(IV) and Pu(IV) are coeluted with dilute nitric acid.

In the second anion exchange cycle, the feed is adjusted to $8M\ HNO_3$, ferrous sulfamate and heat are added to produce the hexanitrato anionic complexes, and the complexes are then cosorbed on the resin. The plutonium is eluted selectively as Pu(III) with $5.5M\ HNO_3$ containing ferrous sulfamate and hydrazine reductants. The $Np(NO_3)_6^{2-}$ remains sorbed on the resin. A wash with $8M\ HNO_3$-0.005M KF provides further decontamination from fission products and iron. The Np(IV) is eluted with dilute nitric and is transferred from the heavily shielded area of the plant to lightly shielded glove boxes for conversion to NpO_2 for preparation of targets for irradiation.

In the third cycle, the feed is adjusted to $8M\ HNO_3$ and the $Pu(NO_3)_6^{2-}$ is sorbed. A strong acid wash removes fission products and iron, and Pu(IV) is eluted with dilute nitric acid. The purified Pu solution is transferred to shielded glove boxes for conversion to PuO_2 for preparation of fuel forms. The overall decontamination factor for Np and Pu from fission products for the three anion exchange cycles is $\sim 10^6$.

The separation of Np and Pu in the second cycle is affected by a number of parameters, including the resin cross-linking, the concentration of nitric acid, the Fe(III)/Fe(II) ratio in the plutonium elutriant solution, the resin particle size, the Np/Pu ratio sorbed on the resin, the temperature, and the type of resin.[4] The effects of elutriant acid concentration and type of resin are shown in Figure 5. Gel-type resin, Dowex® 1-X3, works well while Dowex® 1-X4 or higher cross-linking does not give adequate separation. The strong base macroporous resins (Dowex® MSA-1) give somewhat better separation than the gel resins. For a given resin, 40-60 mesh particle size gives better separation than 20-50 mesh.

The useful life of anion exchange resin for processing ^{238}Pu is quite short. The resin is visibly darkened after a single cycle lasting 8 hours although there is little loss in capacity. Operating experience has demonstrated a useful resin life for ^{238}Pu processing of ~1500 (g of ^{238}Pu)(hr of exposure)/L of resin.

This process has been used successfully and safely for more than 20 years to process many kilograms of ^{238}Pu at the Savannah River Plant.

^{237}Np Target Preparation

Two methods for production of neptunium targets have been used at Savannah River. Initially, a powder metallurgy process was used to fabricate dense target slugs of NpO_2 dispersed in aluminum metal powder.[5] The powder blend was compacted at ambient temperature to about 90% of theoretical density and the compacts were jacketed by sintering in an aluminum can at 550 to 625°C at ~20 tons per square inch. Metallurgical bonding of the core and cladding occurred primarily by grain growth across the interface.

At present, the target form is a long tube with the NpO_2-Al mix sheathed with aluminum. As with the slug, NpO_2 and aluminum powder are blended and the mixture is compacted at ambient temperature. These small compacts are assembled into a core within a partially pre-welded billet (Figure 6). After insertion of all compacts, the rear plug and ring are welded in place. The billet is outgassed at elevated temperature under vacuum to ensure bonding between the core and aluminum sheath during extrusion. When outgassing is complete, the billet is cooled and the evacuation tube is sealed.

In preparation for extrusion, the billet is placed in the electrically heated extrusion press and preheated. The extrusion press ram is brought forward, forcing the billet over a mandrel and through a die to produce a tube with the alloy core uniformly positioned within the aluminum sheath. After cleaning, the tube is cold-drawn to a final diameter and wall thickness (Figure 6).

Fabrication of $^{238}PuO_2$ Fuel Forms

All of the ^{238}Pu has been produced in SRP reactors and converted to $^{238}PuO_2$ in SRP separations plants since 1959. Prior to 1978, the fuel forms were produced at Los Alamos National Laboratory (LANL) and at Mound Laboratory. The Plutonium Fuel Form facility (PuFF) at Savannah River was started up in 1978 producing iridium-encapsulated 100-watt $^{238}PuO_2$ spheres for Multihundred Watt (MHW) Radioisotope Thermoelectric Generators (RTG's). This program was completed in 1980. The PuFF facility is now producing iridium-encapsulated 62.5-watt $^{238}PuO_2$ right circular cylinders for General Purpose Heat Sources (GPHS). The GPHS fuel fabrication process as developed at LANL and refined for production by Savannah River Laboratory (SRL) is shown in Figure 7. The process yields fuel forms that are dimensionally stable for extended periods at temperatures to 1400°C, and that have microstructures capable of accommodating decay helium and temperature gradients without cracking.

^{238}Pu oxalate is precipitated by the reverse strike method (plutonium nitrate solution added into oxalic acid solution) to yield 4 to 6 μm crystals (Figure 8). The plutonium oxalate is converted to PuO_2 by heating at 735°C for two hours. The oxide is reacted with ^{16}O to yield a product with a much lower neutron emission rate from the (α,n) reaction. The PuO_2 is ball milled to <1 μm particle size and then the fine powder is cold pressed into compacts. The compacts are broken and screened to <125 μm and are divided for heat treatment at 1100 and 1600°C. The granules from heat treatment are blended and hot pressed into fuel forms

(Figure 9).[7] The fuel forms are heat treated, vacuum outgassed, and encapsulated in iridium shells.

A simplified process has been developed whereby large agglomerates of small crystals (40 to 100 μm) are precipitated rather than formed mechanically as in the GPHS process (Figure 8). After conversion to PuO_2 and heat treatment of the powder, the large particles are directly hot pressed to yield the fuel form.[8] The direct fabrication process has been demonstrated to yield a full-scale integral GPHS fuel pellet with desired microstructure. This process for producing $^{238}PuO_2$ fuel forms is safer, simpler, and more cost-effective, but will require impact verification tests before implementation as a production process.

Production of High-Purity ^{238}Pu (Low ^{236}Pu)

Production of ^{238}Pu by irradiating ^{237}Np yields a plutonium product containing 1 to 2 ppm ^{236}Pu. The decay chain of ^{236}Pu yields daughter products which emit high energy gammas which limit the use of ^{238}Pu for heart pacemakers or medical uses. ^{238}Pu with a much lower ^{236}Pu content is produced by irradiation of ^{241}Am to yield partial conversion to ^{242}Cm, which in turn yields ^{238}Pu by alpha decay. This process was used at SRP to produce about 50 g of ^{238}Pu with ~5 ppb ^{236}Pu. The irradiated ^{241}Am targets were dissolved and the mixed Pu isotopes were separated by anion exchange. The remaining ^{242}Cm was stored for five months and the high-purity ^{238}Pu formed by alpha decay was separated by anion exchange. ^{238}Pu oxalate was precipitated and calcined to $^{238}PuO_2$. The final product was ~99% ^{238}Pu with ~5 ppb ^{236}Pu.

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TABLE 1

Summary of Radioisotope Thermoelectric Generators Successfully Launched by the United States (1961-1982)

Power Source	Spacecraft	Mission Type	Launch Date	Status
SNAP-3B7	TRANSIT 4A	Navigational	6/29/61	Satellite shut down but operational
SNAP-3B8	TRANSIT 4B	Navigational	11/15/61	Satellite ceased transmitting
SNAP-9A	TRANSIT 5BN-1	Navigational	9/28/63	Satellite ceased transmitting
SNAP-9A	TRANSIT 5BN-2	Navigational	12/5/63	Navigational capacity ceased, but SNAP-9A telemetry operational
SNAP-19B	NIMBUS III	Meteorological	4/14/69	Monitoring ceased
SNAP-27	APOLLO 12	Lunar	11/14/69	Station shut down
SNAP-27	APOLLO 14	Lunar	1/31/71	Station shut down
SNAP-27	APOLLO 15	Lunar	7/26/71	Station shut down
SNAP-19	PIONEER 10	Planetary	3/2/72	Still operating
SNAP-27	APOLLO 16	Lunar	4/16/72	Station shut down
TRANSIT-RTG	TRIAD	Navigational	9/2/72	Still operating
SNAP-27	APOLLO 17	Lunar	12/7/72	Station shut down
SNAP-19	PIONEER 11	Planetary	4/5/73	Still operating
SNAP-19	VIKING 1	Mars Lunar	8/20/75	Lander shut down
SNAP-19	VIKING 2	Mars Lander	9/9/75	Lander shut down
MHW-RTG	LES-8	Communications	3/14/76	Still operating
MHW-RTG	LES-9	Communications	3/14/76	Still operating
MHW-RTG	VOYAGER 2	Planetary	8/20/77	Still operating
MHW-RTG	VOYAGER 1	Planetary	9/5/77	Still operating

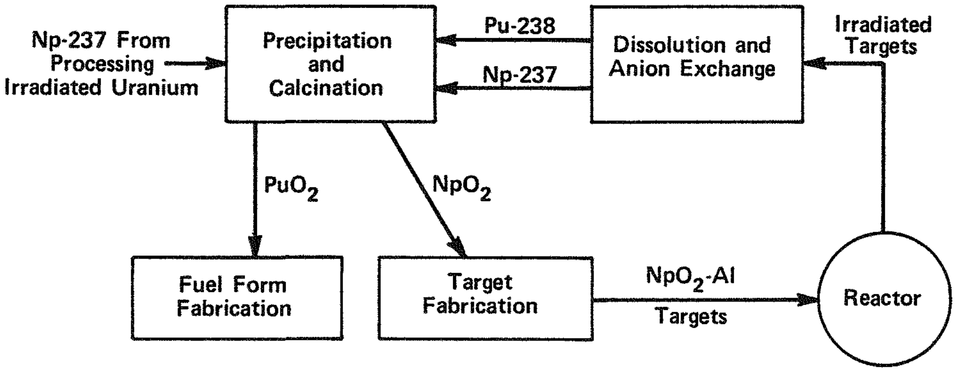


FIGURE 1. Overview of ^{238}Pu Production at Savannah River

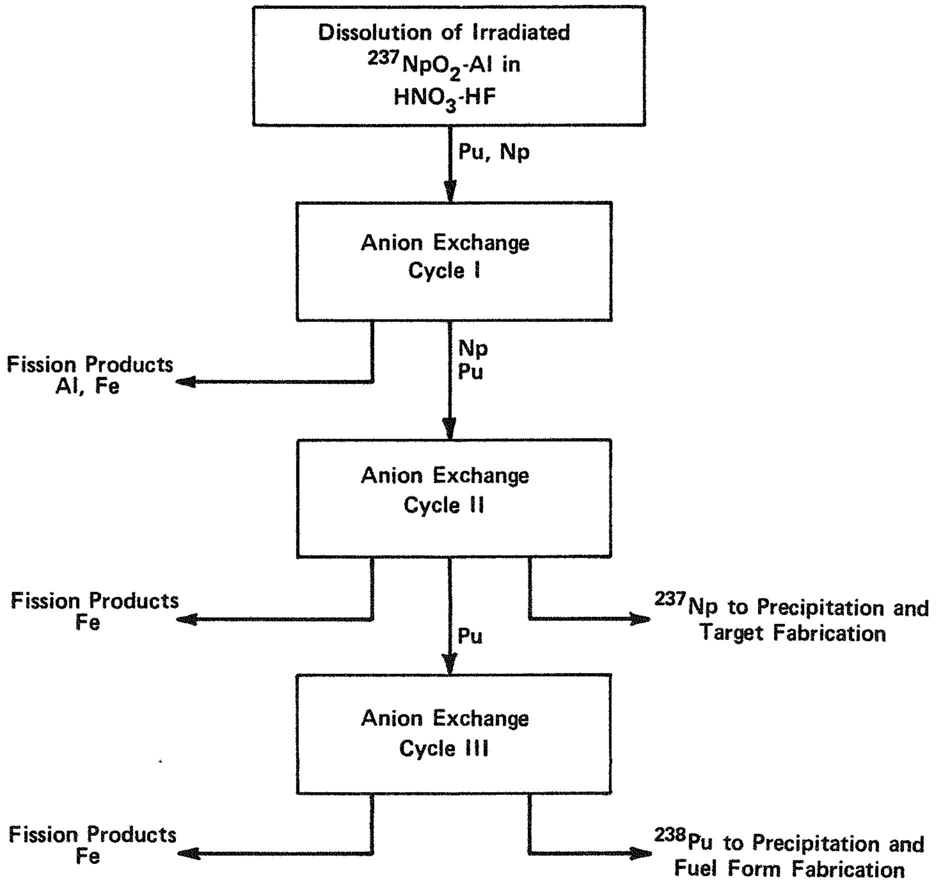


FIGURE 2. Processing Irradiated ^{237}Np to Recover ^{238}Pu at Savannah River

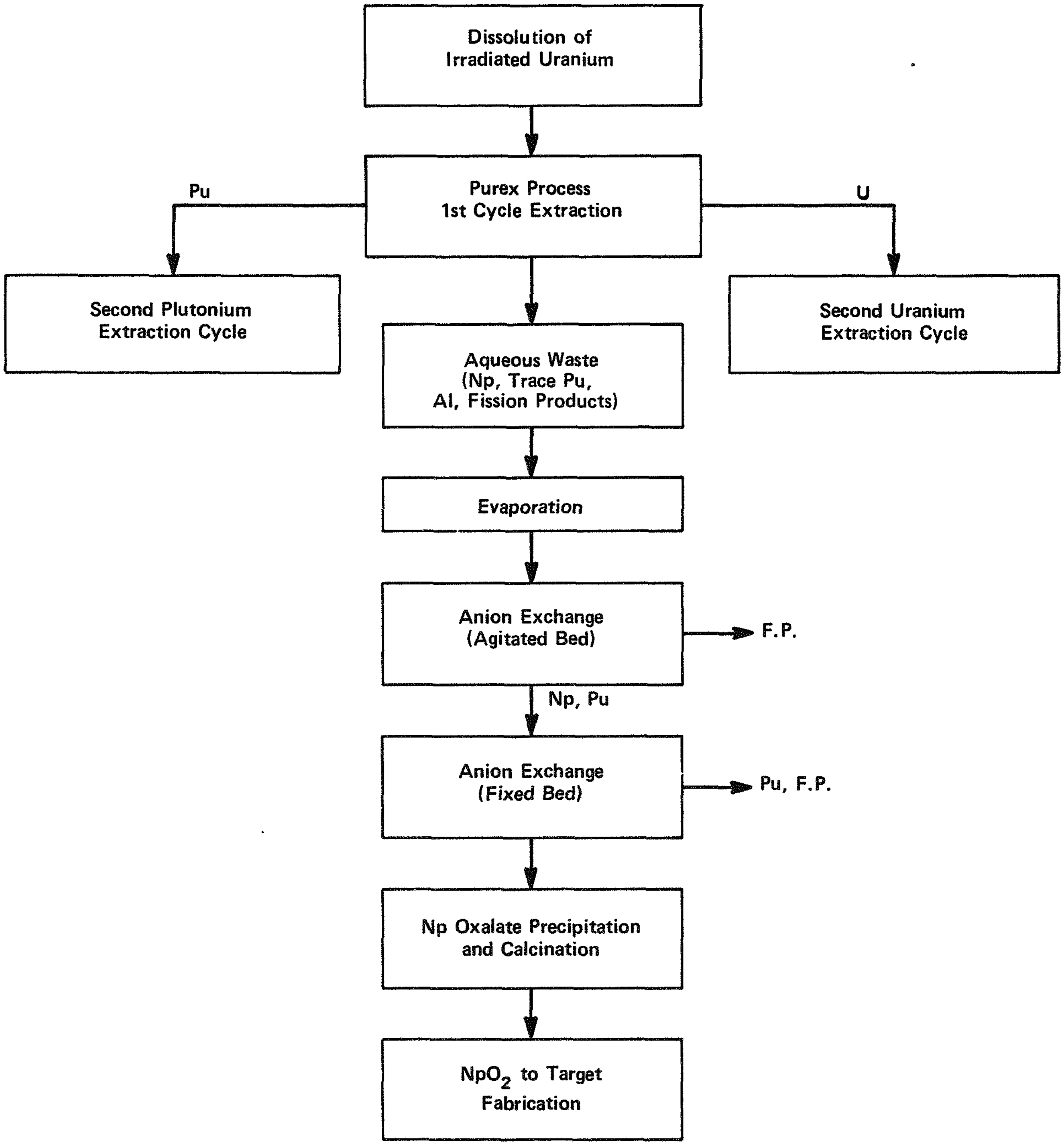
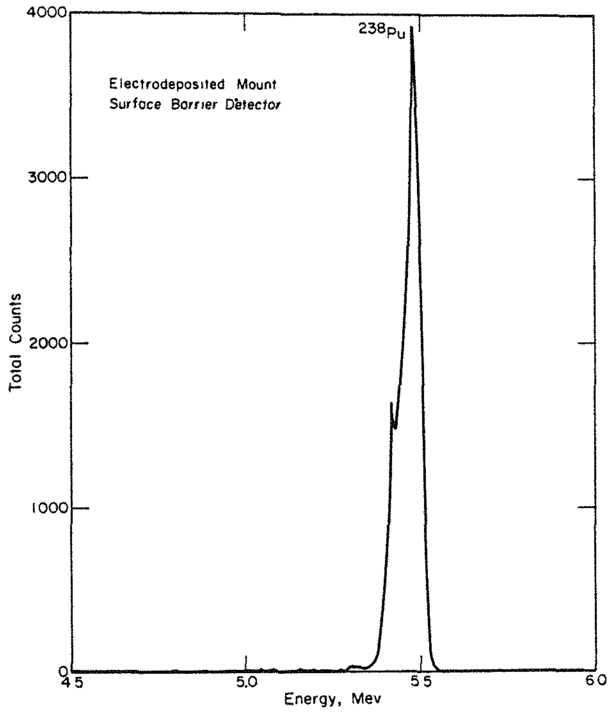
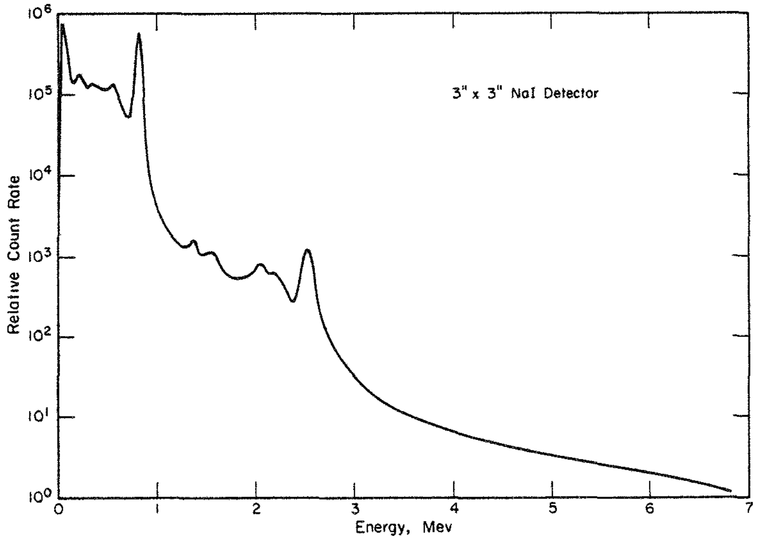


FIGURE 3. Recovery of ^{237}Np from Irradiated Uranium at Savannah River



ALPHA SPECTRUM OF ^{238}Pu PRODUCT



TOTAL GAMMA SPECTRUM OF ^{238}Pu PRODUCT
(Approximately 30 days after processing)

FIGURE 4. Alpha and Gamma Spectra of ^{238}Pu Product

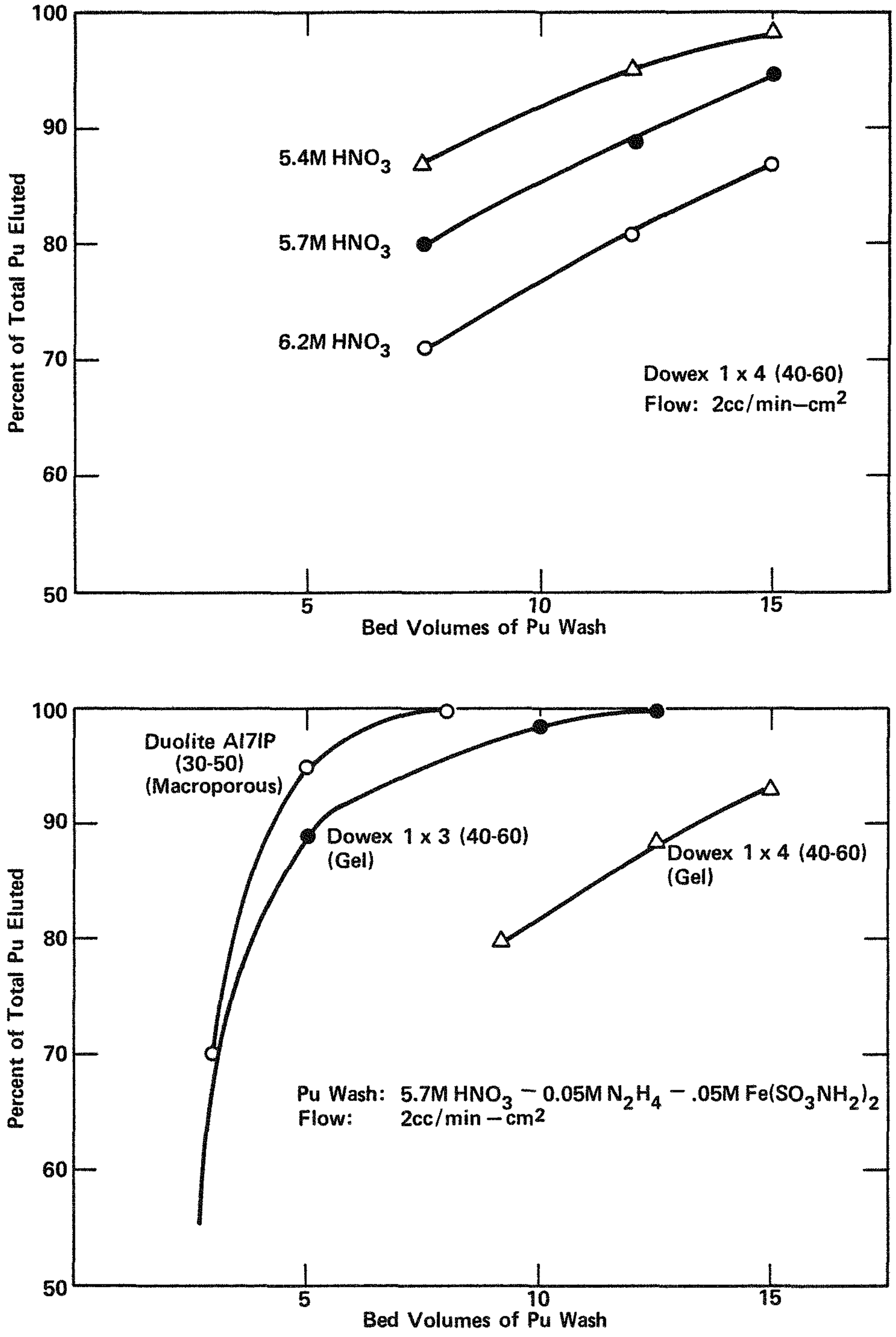


FIGURE 5. Effect of Acid Concentration and Type of Anion Exchange Resin on Separation of ^{237}Np and ^{238}Pu

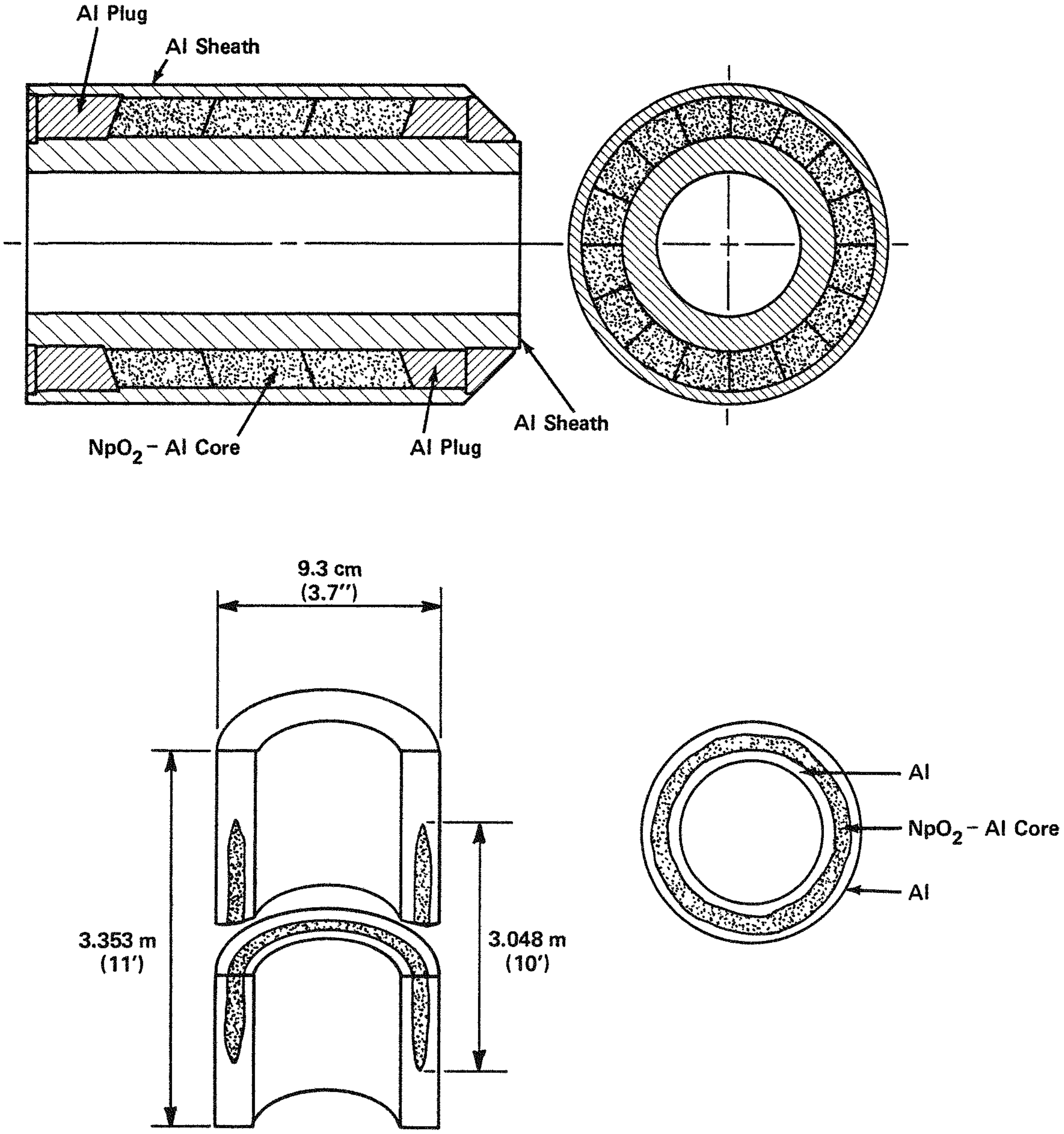


FIGURE 6. Neptunium Oxide Target Billet Assembly and Target Tube

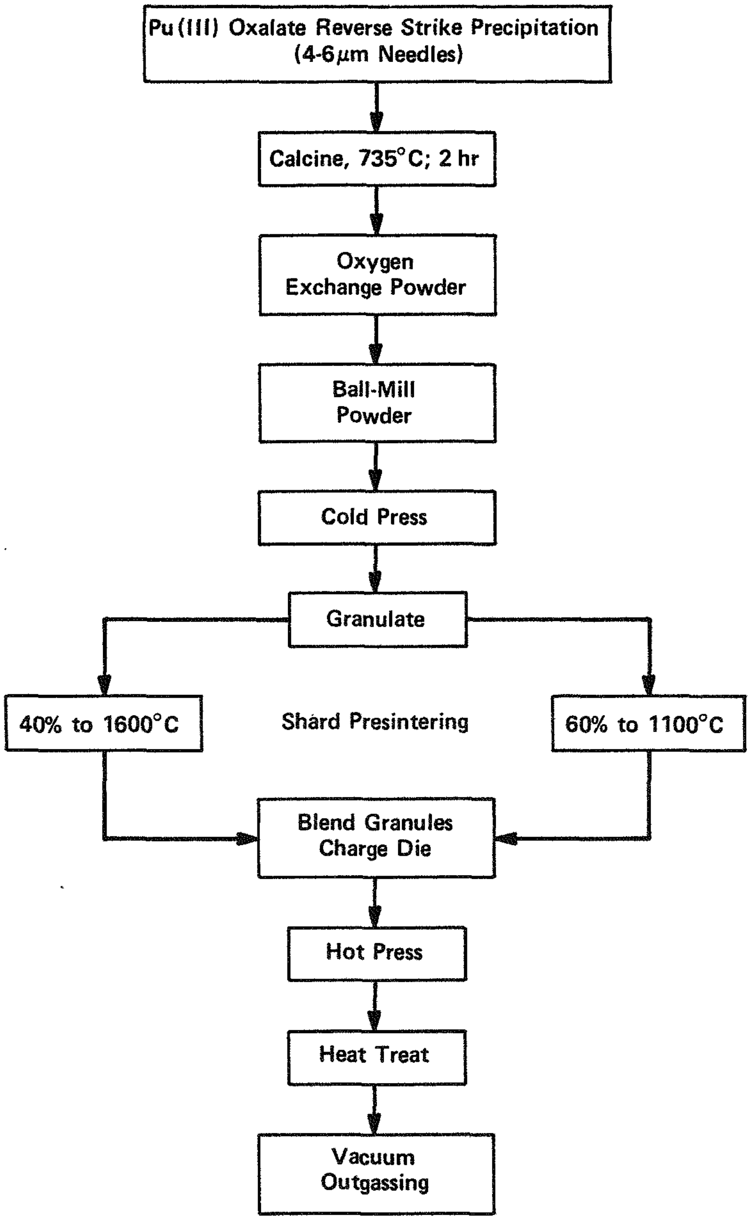
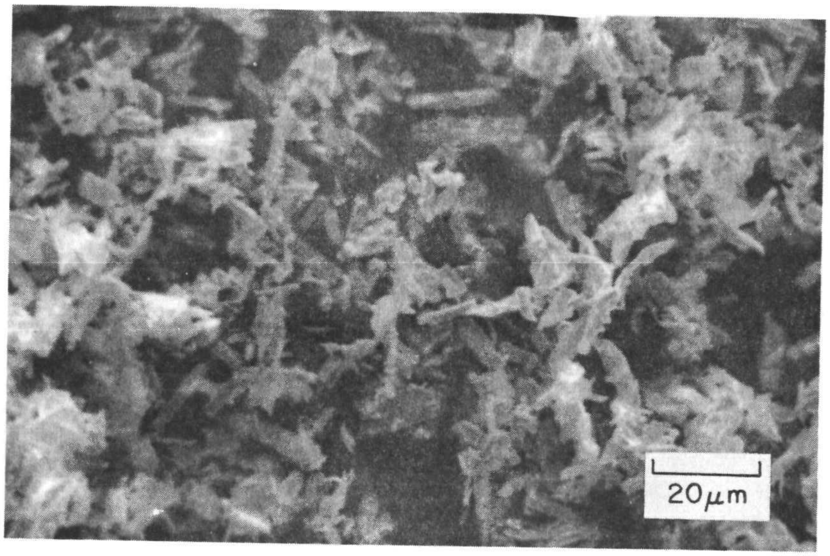
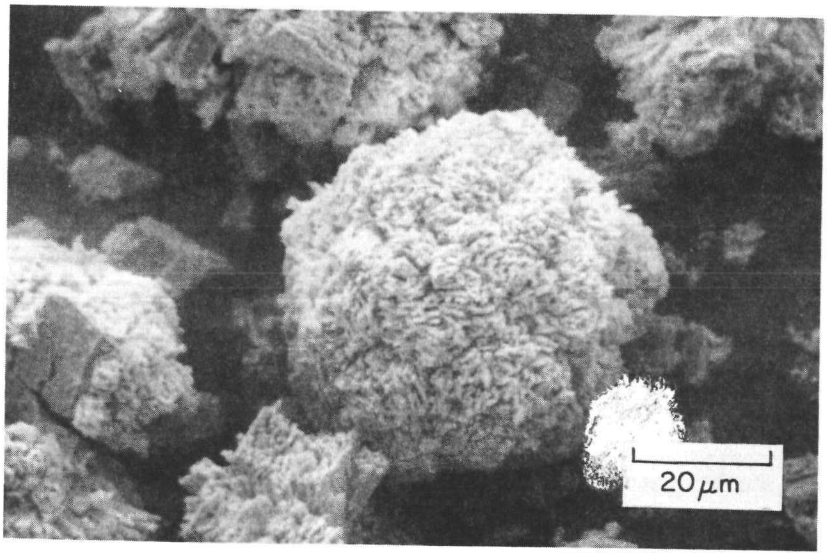


FIGURE 7. The ^{238}Pu GPHS Fabrication Process



PuO_2 (Reverse Strike Precipitation)



PuO_2 (Direct Strike Precipitation)

FIGURE 8. Particle Size and Morphology of $^{238}PuO_2$

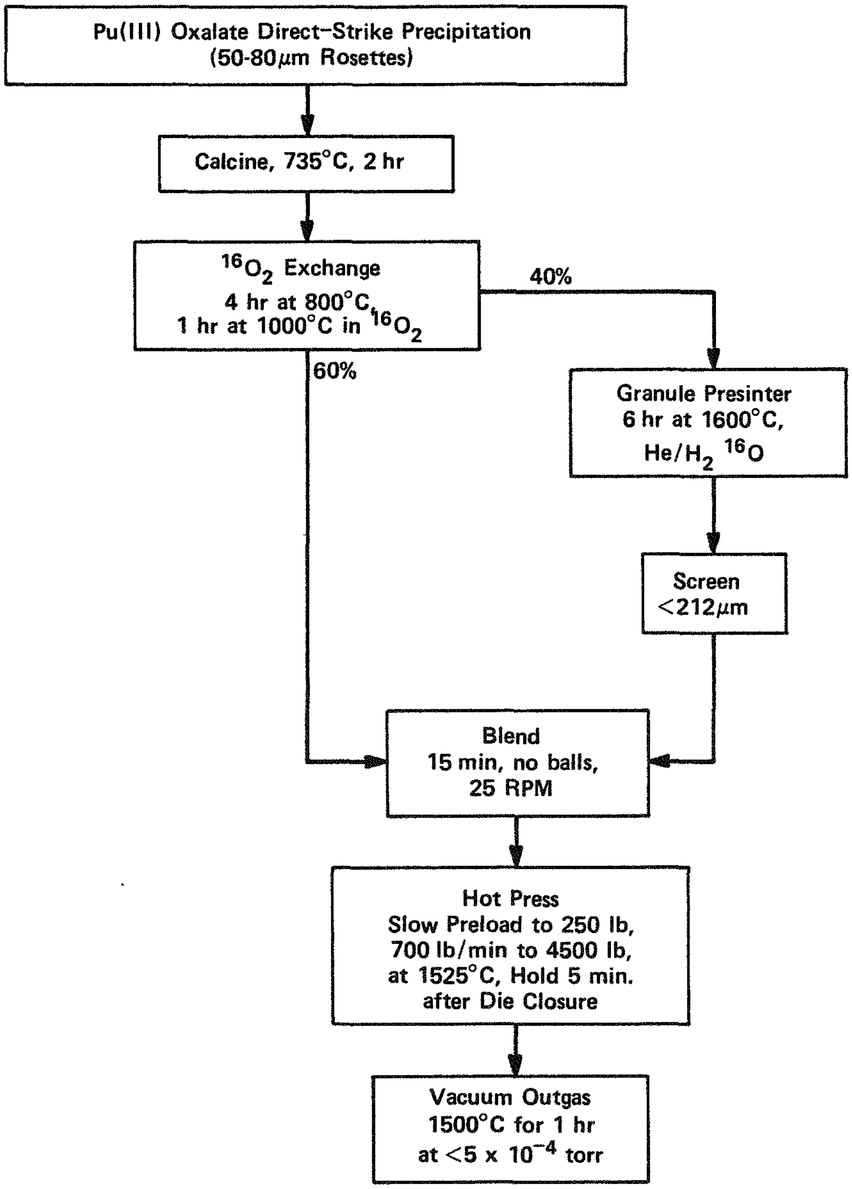


FIGURE 9. The ^{238}Pu Direct Fabrication Process