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PRESENT STATUS AND FUTURE DIRECTION OF PLUTONIUM PROCESS CHEMISTRY

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ABSTRACT

Large-scale plutonium recovery/processing facilities are currently operated at the U. S. Department of Energy Hanford, Los Alamos National Laboratory, Rocky Flats, and Savannah River sites. This paper presents an overview of plutonium process chemistry used at these sites, with particular emphasis on solution chemistry involved in recovery, purification, and waste treatment operations. By extrapolating from the present system of processes, this paper also attempts to chart the future direction of plutonium process development and operation. Areas where a better understanding of basic plutonium chemistry will contribute to development of improved processing are called out.

INTRODUCTION

Plutonium processing operations originated at Los Alamos and Hanford as part of the Manhattan Project in 1943. Hanford Operations separated plutonium from irradiated reactor fuel, whereas Los Alamos purified plutonium, as well as recovered the plutonium from scrap and residues. In the 1950's, similar processing facilities were constructed at Savannah River and Rocky Flats.

A limited overview of the process chemistry used at these sites will be presented. This paper will also attempt to bridge, at least partially, the gap between ongoing fundamental plutonium research and development, and applied technology needs. We believe it is important to bridge this gap, since a continuous flow of knowledge about plutonium chemistry from academic and government laboratories to the Plant is necessary and beneficial in motivating and stimulating fundamental research and development studies. The research and development areas called out in this paper are representative, we feel, of those where fundamental research and development can make a timely and substantial contribution. Our hope is that at least some of our suggestions will be pursued.

PLUTONIUM PROCESSING AT LOS ALAMOS

Plutonium processing at Los Alamos falls into three categories:

- 1) preparation and purification of plutonium metal,
- 2) purification and preparation of plutonium oxide, and
- 3) recovery and purification of plutonium from scrap generated in the above two programs, as well as that scrap generated in the research programs at Los Alamos and other laboratories throughout the country.

Each of these programs has areas that need investigation and evaluation so as to eliminate processing problems, while yielding less residue and a purer product.

Preparation and Purification of Plutonium Metal

At Los Alamos, plutonium metal is prepared by two methods--direct reduction of the oxide by calcium (DOR)^{1,2}, and reduction of PuF₄ by calcium in our metal preparation line (MPL)³ (see Figure 1).

In the DOR process, the plutonium content of the reduction slag is so low that the slag can be sent to retrievable storage without further processing. The metal button that is produced is no purer than the oxide feed and/or the calcium chloride salt. Los Alamos purifies the button by electrorefining^{4,5}, yielding a metal ring that is > 99.96 percent plutonium. Research and development is yet to be done on preparing pure CaCl₂ or recycling the CaO₂-CaCl₂ slag left after DOR. The CaO₂ could be chlorinated in an inert atmosphere (no CO₂, O₂, or H₂O), and thus have a salt free of carbonate. Los Alamos believes the presence of carbonate leads to metal with a high carbon content, which makes the metal have undesirable properties.

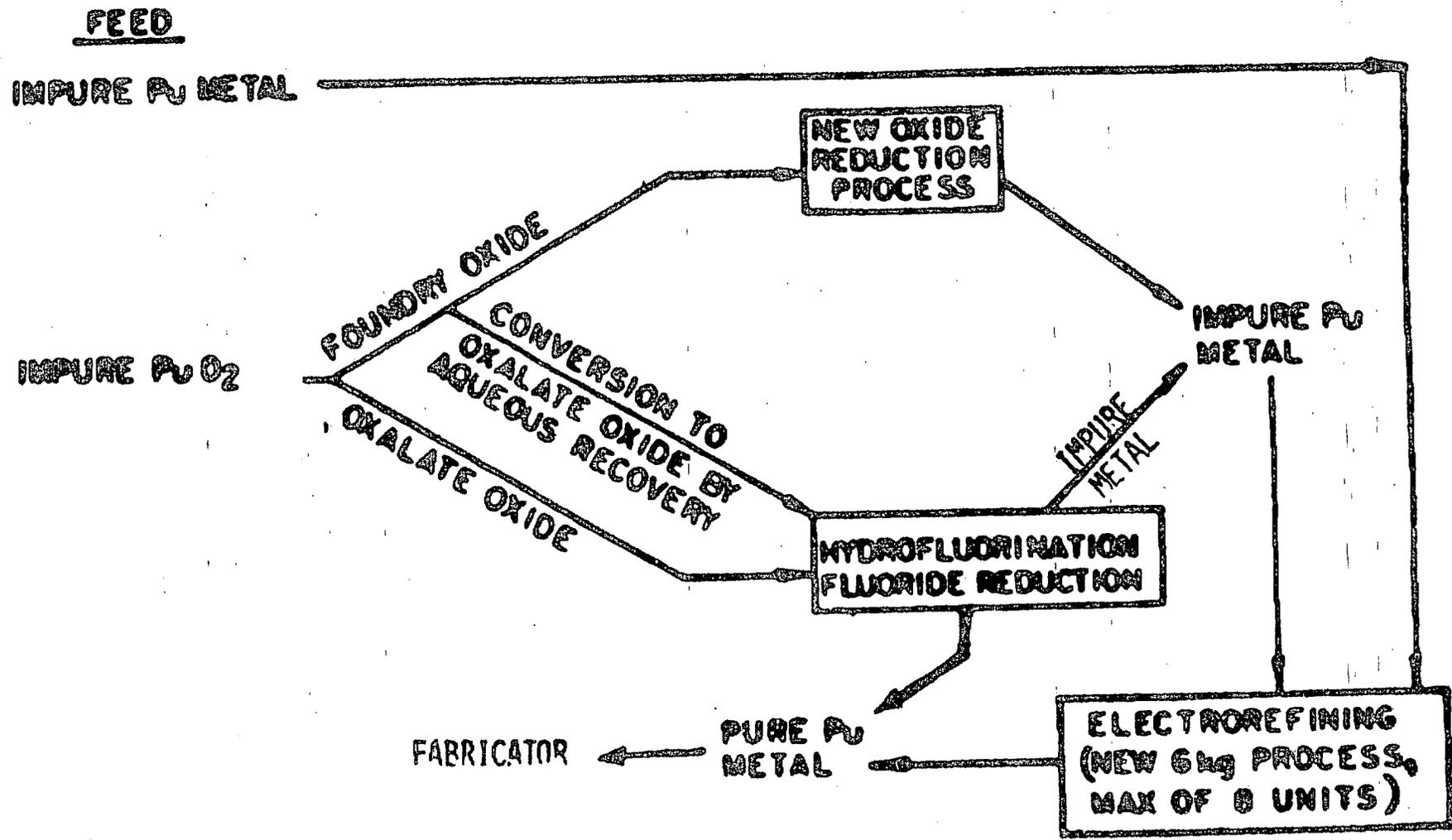


FIGURE 1. METAL PREPARATION AND PURIFICATION

The MPL at Los Alamos can accept either plutonium nitrate solution or plutonium oxide as feed. If the feed is the nitrate solution, then the process steps are: precipitation of plutonium peroxide, hydrofluorination of the peroxide to PuF_4 , and reduction of the PuF_4 to metal. If the feed is oxide, then it is hydrofluorinated to produce PuF_4 , which is then reduced to Pu metal with Ca metal. This metal usually meets the specifications set by the metal fabrication personnel. This process is well-defined--most parameters are known. Some work should be done, however, in measuring the decontamination factor for certain elements when they are in the same solution with cations and anions that are nonroutine, such as high Al, Ca, Am, SO_4 , $\text{H}_2\text{C}_2\text{O}_4$, etc.

Purification and Preparation of Oxide

Los Alamos processes certain residues to an oxide suitable for the MPL, meaning that the PuO_2 feed can be easily hydrofluorinated.

If the oxide has been prepared by calcination of the oxalate, then that oxide can be easily converted to PuF_4 , whereas other oxides have poor fluorination characteristics.

In another process, Los Alamos prepares oxide that meets the purity and particle specifications of NE-E 13-1T (see Figure 2). In this process, the decontamination factors for each of the precipitations need to be determined for the process conditions employed. Leary, et al.⁶ reported many decontamination factors for certain peroxide precipitations, but not for these specific conditions and impurities. Less data exist for decontamination factors obtained by oxalate precipitations that are made with our conditions. Fuel fabricators have specified that the oxide feed to their plant must contain less than 15 ppm fluoride, based on Pu content. This indicates a need to know the behavior of the fluoride ion during peroxide and oxalate precipitation of plutonium from a variety of conditions. The behavior of many cations during these precipitations also need to be studied.

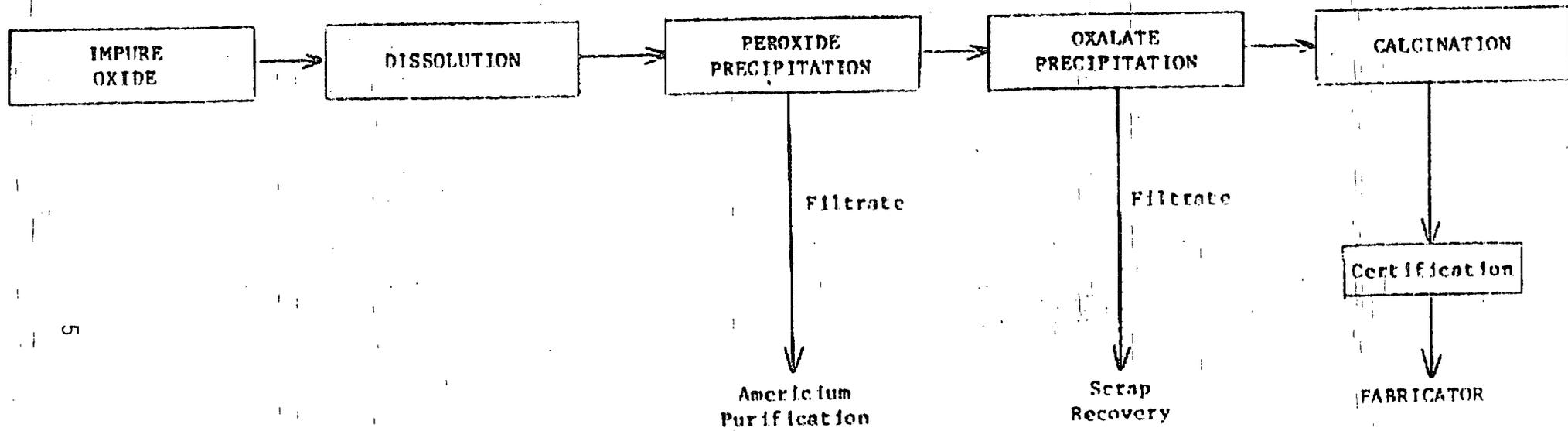


Figure 2. PuO₂ Purification and Preparation

Plutonium Scrap Processing

Los Alamos has been processing unirradiated plutonium scrap since 1944.⁷ Scrap processing is presently being done at the new plutonium facility, using the flowsheet shown in Figure 3. Feed to this system comes from the varied research programs at Los Alamos and from other sites through the auspices of the Central Scrap Management Office (CSMO) at Savannah River. Los Alamos is processing a wide variety of residues, including Pu-Be neutron sources, polystyrene-PuO₂-UO₂ blocks, incinerator ash, Pu-U alloys and oxides, Pu-Zr alloys and oxides, Pu-Np alloys and oxides, Pu-Th alloys and oxides, etc.

Processes have been developed for these scrap items (see Figure 3), but we need to know more about: Pu-Np separations; Pu-Th separations; oxalate precipitations for both plus 3 and plus 4 valences; valence stabilization; dissolution methods for high-fired impure oxides; in-line alpha monitors to measure extremely low concentrations of Pu + Am in 7M HNO₃ solutions; and solubility of various mixtures of PuO₂ and UO₂ under a variety of conditions. These processes may be either aqueous or pyrochemical methods.

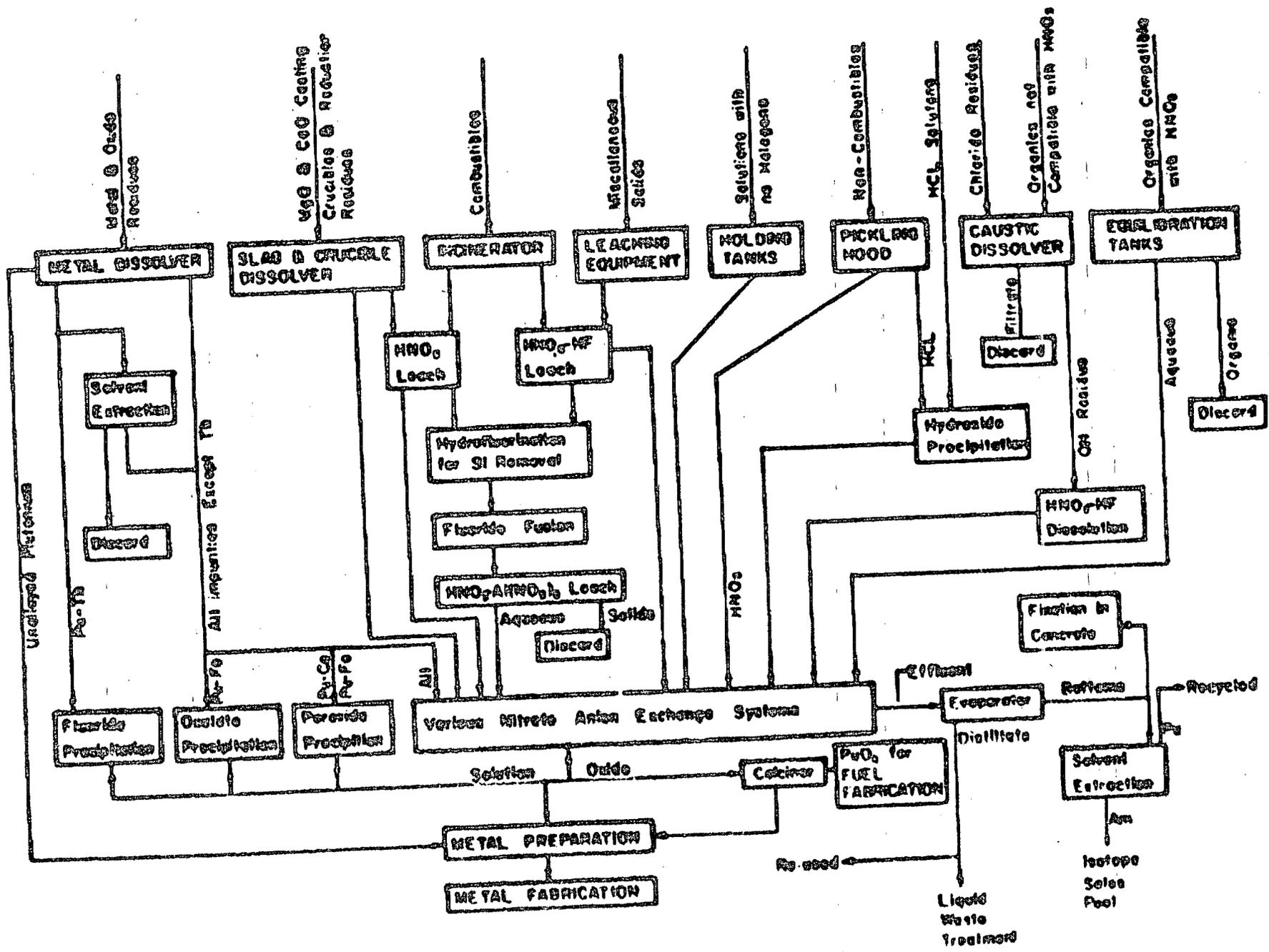


Figure 3. Flow of Material in Scrap Recovery

PLUTONIUM PROCESSING AT ROCKY FLATS

Chemical processing activities involve the recovery of plutonium from Rocky Flats Plant scrap, waste materials and residues, and effluent streams. The final product of this recovery and purification effort is high-purity plutonium metal for use in foundry operations.

The original plutonium recovery and purification processes were adopted from Los Alamos processes by the Austin Company in 1950 (the original engineering construction contractor for Rocky Flats). The processes at Rocky Flats are still similar today, in many respects, to the Los Alamos process. The details of the processes at Rocky Flats are given in the next paper.

Figure 4 shows a flowsheet for plutonium processing at Rocky Flats. Impure plutonium metal is sent through a molten salt extraction (MSE) process to remove americium. The purified plutonium metal is sent to the foundry. Plutonium metal that does not meet foundry requirements is processed further, either through an aqueous or electrorefining process. The waste chloride salt from MSE is dissolved; then the actinides are precipitated with carbonate and redissolved in 7M HNO₃; and finally, the plutonium is recovered by an anion exchange process.

Impure plutonium oxide residues are dissolved in 12M HNO₃-0.1M HF under refluxing conditions, and then the plutonium is recovered and purified by anion exchange. Plutonium is leached from other residues, such as metal and glass, and is also purified by anion exchange. The purified plutonium eluate from the anion exchange process is precipitated with hydrogen peroxide. The plutonium peroxide is calcined to the oxide, and the plutonium oxide is fluorinated. The plutonium tetrafluoride is finally reduced to the metal with calcium.

Acid waste streams are sent through a nitric acid recovery process, and then to a secondary plutonium recovery anion exchange process. The acid waste streams are then sent to waste treatment.

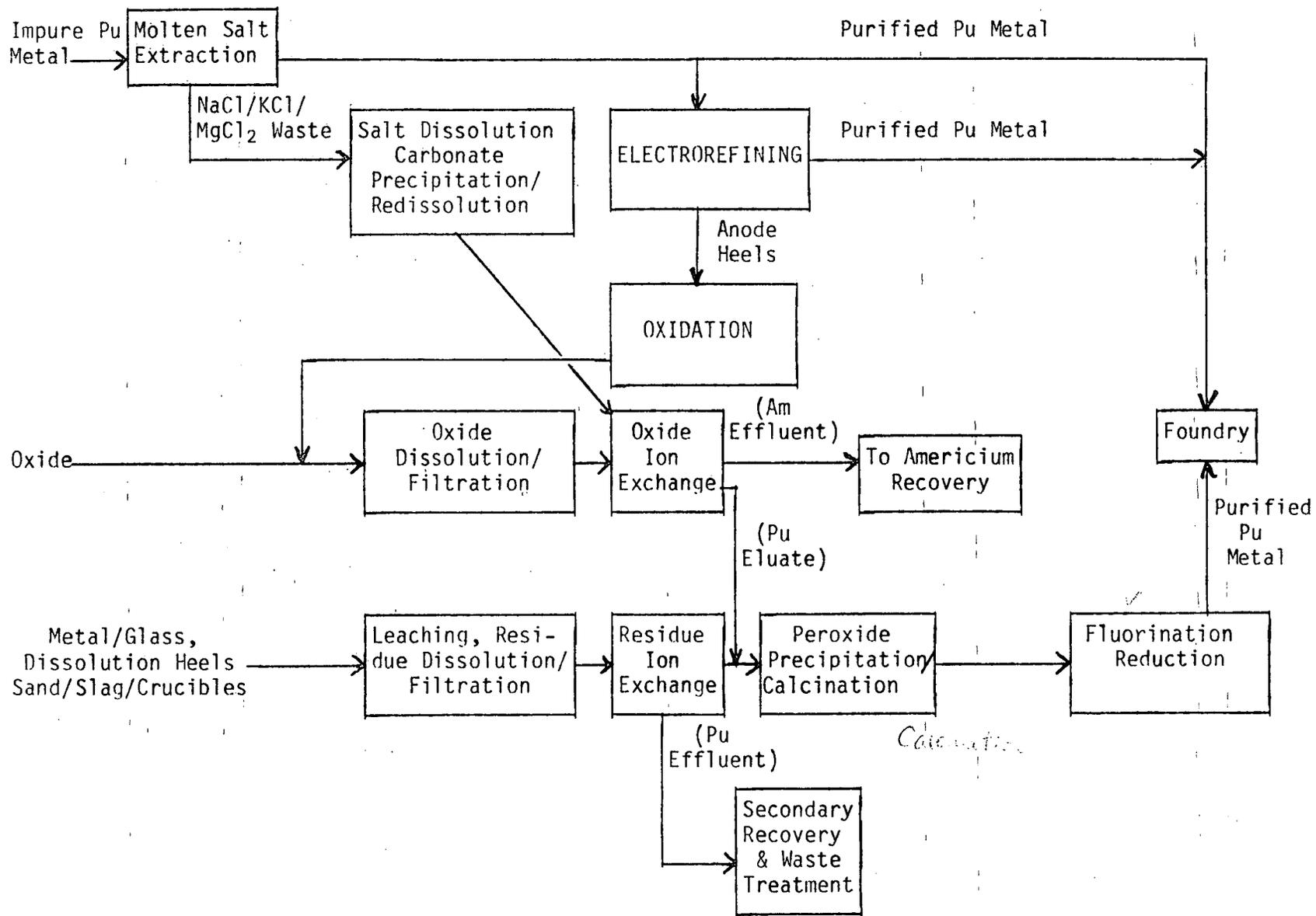


Figure 4. Plutonium Recovery Processes at Rocky Flats

The process chemistry research needs of Rocky Flats are similar to Los Alamos. Since there are several differences in the processes, a few additional plutonium research areas will be noted. The precipitation of plutonium (III) and americium (III) carbonates from dissolved MSE residues yields actinide (III) carbonates or hydroxyl carbonates.⁸ The physicochemical properties of these compounds are needed, as well as an understanding of the soluble complexes formed in carbonate solution at high pH.

More studies are needed on elucidating the dissolution mechanism of plutonium dioxide in $\text{HNO}_3\text{-HF}$, and on other methods of dissolution. Electrolytic methods should be investigated, as well as other dissolution media, such as H_2SO_4 , H_3PO_4 , HCl , molten salts, etc.⁹ Since MSE residues are processed by aqueous methods, this and other advantages warrant further study of a complete HCl processing plant.

The chemistry of plutonium liquid-to-solid conversion processes, especially peroxide and oxalate precipitation, should be studied. Research and development of direct thermal denitration methods should be pursued.

Direct oxide reduction (DOR) is presently being tested on production equipment. Eventually, it is hoped to eliminate the fluorination and bomb reduction processes and replace them with DOR. Again, the problems associated with LANL DOR process problems apply here.

Higher capacity, better-performing, and more radiation-resistant separation materials are needed, such as new ion exchange resins.¹⁰ Solvent extractants, similar to dihexyl-N,N-diethylcarbamoylmethylphosphonate,¹¹ are needed to selectively recover actinides from acidic wastes. The application of membranes and other new techniques should be explored.

The chemistry of waste treatment processes and the development of new processes are fertile areas of research work. The speciation of

plutonium in basic and laundry wastes is needed. For example, if soluble plutonium complexes in basic wastes can be destroyed, perhaps ultrafiltration could replace the flocculent-carrier precipitation process. The chemistry of plutonium (VII) and of ferrites--a candidates waste treatment process--needs to be explored.¹²

The chemistry of pyrochemical separation processes is another fertile area of research; e.g., new molten salt systems, scrub alloys, etc.; and the behavior of divalent plutonium in these systems. Studies of liquid plutonium metal processes should also be explored, such as filtration methods to remove impurities. Since Rocky Flats uses plutonium as metal, methods to convert plutonium compounds to metal and purify the metal directly are high-priority research projects.

PLUTONIUM PROCESSING AT HANFORD

Recovery-Separation Technology

Irradiated Fuel

A historically important and continuing mission at the Hanford site is to chemically process irradiated reactor fuel to recover and purify weapons-grade plutonium. Over the last 40 years, or so, several processes and plants--Bismuth Phosphate, REDOX, and PUREX--have been operated to accomplish this mission. Presently, only the Hanford PUREX Plant is operational. The Hanford PUREX Plant, which has not been operated since the fall of 1972, is scheduled to start up in the early 1980's to process stored and currently produced Hanford N-Reactor fuel. Of non plutonium-production reactors built at the Hanford site, only the N-Reactor is still operating.

Figure 5 illustrates, albeit in very brief fashion, the essentials of the technology to be employed in producing pure PuO_2 from irradiated N-Reactor fuel. Following receipt of the fuel in the PUREX Plant, Zircaloy-2 cladding is chemically removed by dissolution with boiling $\text{NH}_4\text{F-NH}_4\text{NO}_3$ solution (Zirflex process). Small amounts of UF_4 resulting from attack of uranium metal core by the Zirflex process reagent are metathesized to $\text{Na}_2\text{U}_2\text{O}_7$ and then dissolved along with unattacked uranium metal in HNO_3 . Standard and well-known PUREX process technology is practiced to recover, separate, and purify plutonium. New equipment has been installed in the Hanford PUREX Plant to convert, via plutonium oxalate, the purified $\text{Pu}(\text{NO}_3)_4$ product solution from the third plutonium cycle to PuO_2 for shipment offsite. Following customary Hanford site practice, the denitrated ($\sim 0.5\text{-}1.0\text{M}$ HNO_3) PUREX process high-level waste (HLW) containing small amounts of plutonium and varying amounts of other actinides (Am, Np, and U) will be adjusted to $> \text{pH } 9$ by addition of NaOH , and stored in newly constructed underground double-shell tanks.

Hydrated iron oxide (so-called "sludge") precipitates when NaOH is added to HLW and carries down almost all the plutonium and most of the

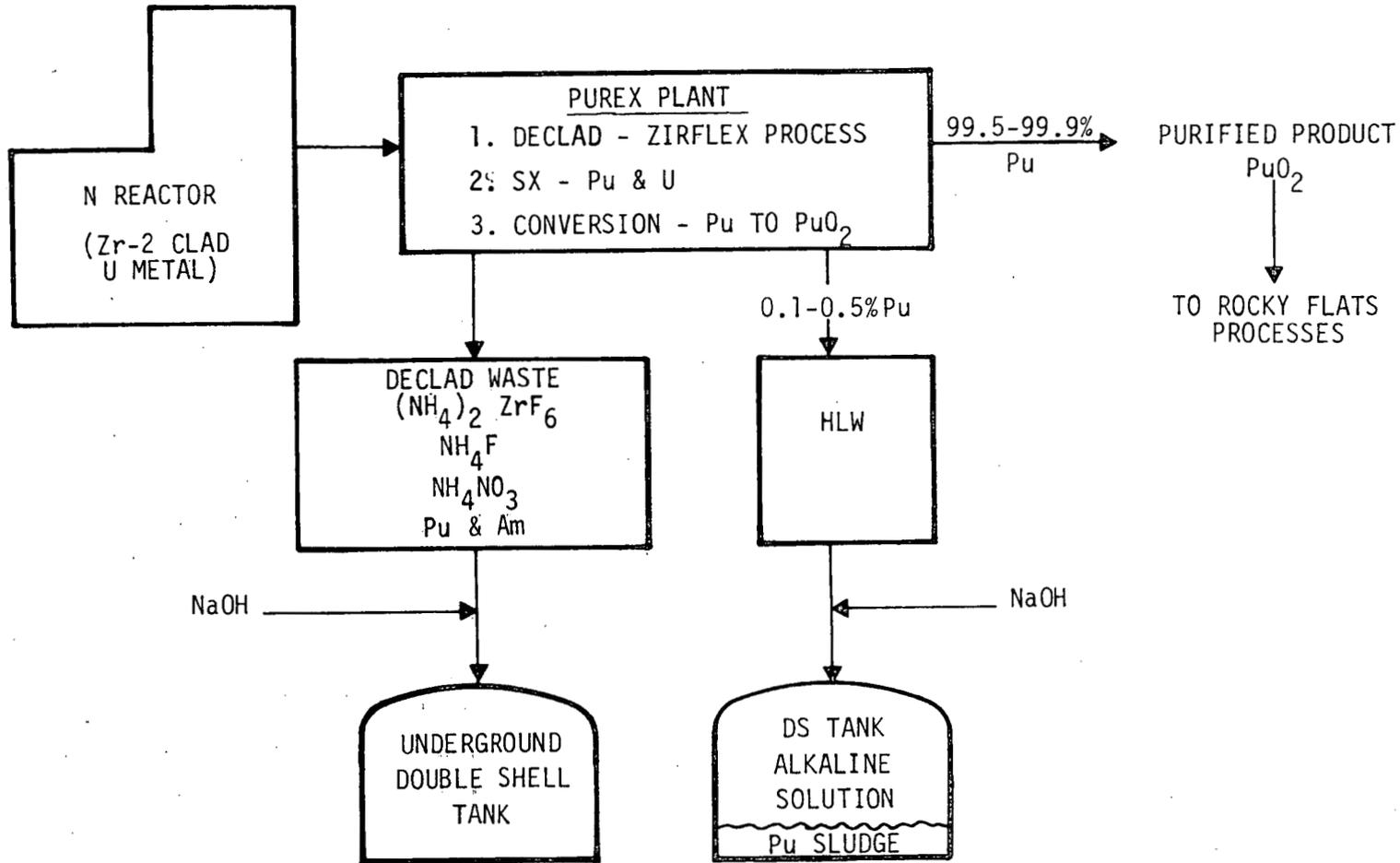


Figure 5. Hanford Site: Irradiated Fuel Processing

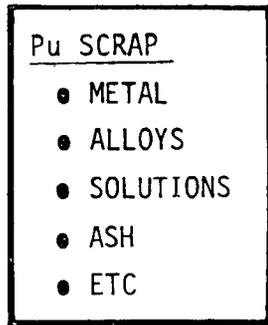
other actinides in the HLW. From past production operations at Hanford, approximately 100 old single-shell tanks contain varying amounts of sludge and plutonium. In-situ analysis (by neutron activation methods) of these old sludges to determine their plutonium content is seriously hampered by lack of fundamental information regarding the chemical nature and environment, and the size of the precipitated plutonium. Research to provide the needed data base is, as called out subsequently, needed and desirable.

Current plans for restart of Hanford PUREX Plant call for storage of neutralized ($\text{pH} > 9$) spent decladding solution in double-shell tanks. Depending upon operating procedures, from two to four such tanks (each costing about \$10,000,000) will be needed to store spent decladment. (The spent decladment will not, according to present planning, be mixed with alkaline HLW.) There is an economic incentive to find inexpensive and safe alternative treatment/storage schemes for handling the spent cladding solution. Key to such schemes is, as discussed subsequently, concentration of plutonium and americium, their chemical species in the decladding solution, and a simple method for removing them efficiently.

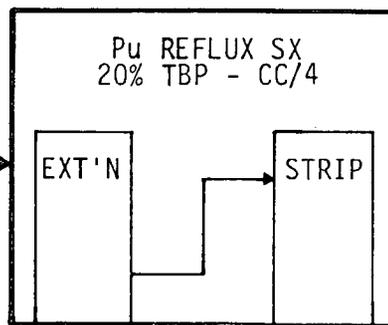
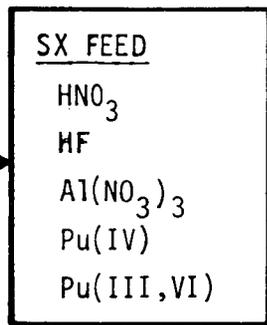
Plutonium Scrap Processing

In addition to recovering plutonium from irradiated reactor fuel, a Plutonium Reclamation Facility (PRF)^{13,14} is operated at the Hanford site to recover, separate, and purify kilogram amounts of plutonium from a wide range of unirradiated scrap materials. As illustrated in Figure 6, a 20 percent TBP- CCl_4 solution is used to extract Pu(IV) from HNO_3 -HF- $\text{Al}(\text{NO}_3)_3$ solutions of dissolved scrap. The final product solution from the strip column contains, typically, 50 gL^{-1} plutonium. One of the more troublesome chemical problems encountered from time to time in PRF operations is engendered by disproportionation of Pu(IV) to Pu(III) and Pu(VI). Six-valent plutonium is less well extracted by TBP than is Pu(IV), while Pu(III) is not extracted by TBP. Because of the wide variability in the composition of the aqueous feed to the PRF extraction column, unrecognized Pu(IV) disproportionation can cause

Figure 6. Hanford Site: Plutonium Scrap Processing



DISSOLVE
 HNO_3 - HF



ACID WASTE

NaOH

DS TANK

Pu PRODUCT SOL'N

PuO_2

TO ROCKY FLATS

undesirably high plutonium losses until necessary empirical flowsheet changes are made. This experience emphasizes a need for research to (a) develop a useful tool (e.g., nomograph, etc.) to predict quickly and reliably the extent of Pu(IV) disproportionation in solvent extraction process feed solutions, and (b) if possible, development of a reliable on-line instrument to measure concentrations of plutonium in (III), (IV), and (VI) oxidation states in feed and raffinate solutions.

Plutonium Technology Needs: R&D Opportunities

Spent Zirflex Process Decladding

Needs. The basic perceived need is to devise and develop a simple process for selective and efficient removal of plutonium (and ^{241}Am) from spent Zirflex process decladding solution. To satisfy this need, it may be necessary--or prove beneficial--to determine, by appropriate physiochemical methods, the nature of the plutonium (and americium) species in the decladding solution. Availability of a satisfactory transuranium removal scheme may be one of the key factors in devising an alternative to storage in expensive double-shell tanks for spent Zirflex process solution at the Hanford site.

Background Information--Possible Approaches. Swanson,¹⁵ Smith,¹⁶ Phillips,¹⁷ and others have described many aspects of the Zirflex process but, unfortunately, not the form or charge of plutonium and other actinides in spent decladding solution. Presumably, soluble amounts of these elements are present as fluoride complexes--but this remains to be proven.

We are not aware of any previous studies of the removal of plutonium or americium from $(\text{NH}_4)_2\text{ZrF}_6\text{-NH}_4\text{F-NH}_4\text{NO}_3$ solutions. For ready plant-scale application, precipitation, sorption on inorganic materials, or batch solvent extraction processes may all be satisfactory. An inexpensive inorganic material with great selectivity and capacity for sorbing actinides, and with suitable hydraulic properties, would be especially attractive.

Disproportionation of Pu(IV)

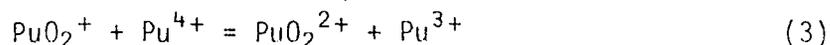
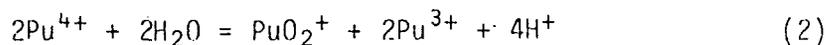
Needs. There are several needs associated with the occurrence, detection, and mitigation of the disproportionation of Pu(IV) in applied plutonium recovery/purification procedures. First, there is a great need for much more detailed information concerning the effect of typical process conditions [e.g., temperature, concentration of plutonium, hydrogen ion, nitrate ion, nitrite ion, fluoride ion, other metal ions (e.g., Al³⁺, Fe³⁺, etc.), etc.] on the occurrence and extent of the reaction:



Ideally, this information should be made available in the form of easy-to-use nomographs or empirical equations which can be quickly and rapidly solved on a programmable desk calculator. Next, as yet undeveloped instrumentation which can be used on an in-line basis to analyze process streams for the concentrations of plutonium in different oxidation states is also needed.

Nitrite ion is often used in plutonium solvent extraction systems to oxidize Pu(III) to Pu(IV) and to reduce Pu(VI) to Pu(IV). But HONO, produced in HNO₃ media, is extractable into TBP-diluent systems and can interfere with subsequent reductive stripping of plutonium. There is thus a need to find a reagent comparable to nitrite ion in its reactions with Pu(III) and Pu(VI), but which does not extract into TBP solutions.

Background Information--Possible Approaches. Disproportionation reactions of Pu(IV) (Eqs. 1 and 2) and Pu(V) (Eq. 3) have been known and studied since Manhattan Project days.^{18,19}



The importance of Pu(VI) and Pu(III) as products of the disproportionation of both Pu(IV) and Pu(V) is called out by Eqs. (1) and (3).

Eqs. (1) and (2) also indicate the great dependence of the disproportionation reactions on acidity. For example, at room temperature, measurable disproportionation of Pu(IV) occurs at HNO₃ concentrations below 1.5M, while at 98°C, disproportionation of Pu(IV) occurs at HNO₃ concentrations less than 8M.

Previous studies of the plutonium disproportionation reaction have generally, and understandably, emphasized an academic approach with simple acid solutions to elucidate fundamental plutonium chemistry. These past investigations should provide a firm springboard for the more general and advanced research and development we are recommending. The approach developed and advocated by Silver²⁰⁻²³ for calculating the concentrations of plutonium in various oxidation states in aqueous media may prove to be a very valuable tool, particularly when it is supplemented by comprehensive data for disproportionation in solutions typical of those encountered in industrial-scale processes.

Spectrophotometric methods for determining concentration of Pu(III, IV, VI, and "polymer") in nitrate media have been reported.²⁴ Adaptation of such procedures to routine rapid in-line analysis of feed and raffinate solutions may be possible.

We are not able to suggest a suitable reagent to replace HONO for counteracting disproportionation of Pu(IV) in nitrate media. We can only emphasize the benefits to large-scale plutonium separation (via TBP extraction) of finding such a reagent.

Plutonium in "Sludge"-Chemical Species and Particle Size

Needs. The exact chemical species of plutonium present in sludge in Hanford single-shell tanks is not known; likely candidates include either hydrated oxide or polymer, or both. Similarly, the size of the precipitated plutonium particles is not known. These data are needed in connection with the desire to use economically advantageous in-situ passive neutron activation techniques to measure the plutonium content of the Hanford sludge. One preferred technique makes use of the

reaction $^{63}\text{Cu} (\alpha, n) ^{64}\text{Cu}$ to estimate plutonium content. Sensitivity and calibration of this technique is quite dependent upon the chemical environment of the alpha-emitting plutonium atoms. Specifically, such factors as the number and type of neighboring atoms (e.g., O, Na, Al, etc.) and the diameter (size) of the plutonium species impact the neutron flux, which can activate ^{63}Cu to ^{64}Cu . Experimentation to characterize the nature and properties of the plutonium species produced when Hanford PUREX HLW is made alkaline thus needs to be performed. Such experimentation should include effects of aging of sludges at elevated temperatures over long (i.e., years) times.

Background Information--Possible Approaches. That freshly precipitated hydrated iron oxide effectively scavenges plutonium (and various other radionuclides) from aqueous waste solution has long been known. Plant-scale use is made of this chemical fact at the Department of Energy (DOE) Rocky Flats and Los Alamos sites in site waste management schemes.^{25,26} Sludges produced at the Rocky Flats and Los Alamos sites are believed to be closely akin to those produced and stored in Hanford single-shell tanks. We are not aware of any recent studies to characterize the nature of the plutonium solid forms in any plant-produced sludges. Recent advances in the availability of sensitive microcharacterization equipment (e.g., SEM, STEM, etc.) should enable suitable determination of the nature and properties of plutonium and other actinides in sludge. Techniques applied by Milligan and coworkers in characterizing the nature of the amorphous hydrous gel which precipitates when ammonia or alkali is added to a solution of Am(III), provide a reference point for characterization of sludge.^{27,28}

PLUTONIUM PROCESSING AT SAVANNAH RIVER

The primary mission of the Savannah River Plant (SRP) is to produce special nuclear materials--primarily plutonium-239 and tritium--for use in the nation's defense program. In addition, the plant's products include important nonmilitary isotopes: plutonium-238 is utilized in the nation's space program as an energy source; americium-241 is utilized in oil well logging and smoke detectors; and californium-252 is used in industrial, medical, and research activities. The plant has also produced a wide variety of other important nonmilitary isotopes: cobalt-60, which is used in the diagnosis and treatment of cancer; plutonium of various isotopic compositions for use in various research activities, such as breeder research reactors; and heavy water (D_2O), which is used as a moderator/coolant in nuclear reactors.

The facilities at Savannah River (Figure 7) consist of five heavy-water-moderated and cooled production reactors, two chemical separations areas as a heavy water extraction plant, several test reactors, reactor fuel and target processing facilities, the Savannah River Laboratory, and many other facilities necessary to support the operations. During the 1960's, two of the production reactors were shut down and placed in standby condition; one of these is scheduled to start up again in the fall of 1983. Two test reactors and the heavy water extraction plant have also been shut down.

Figure 8 illustrates, in very brief fashion, the essentials of the flow of materials from the reactors through the separations area. Depleted uranium targets are processed through the F-Area canyon by well-known PUREX process technology. Enriched uranium fuel elements are processed through the H-Area canyon by a modification of the PUREX process. Irradiated neptunium targets are processed through the H-Area canyon by an ion exchange process.

Following receipt of the irradiated depleted uranium targets in the F-Area Separations Area, aluminum cladding is chemically removed by dis-

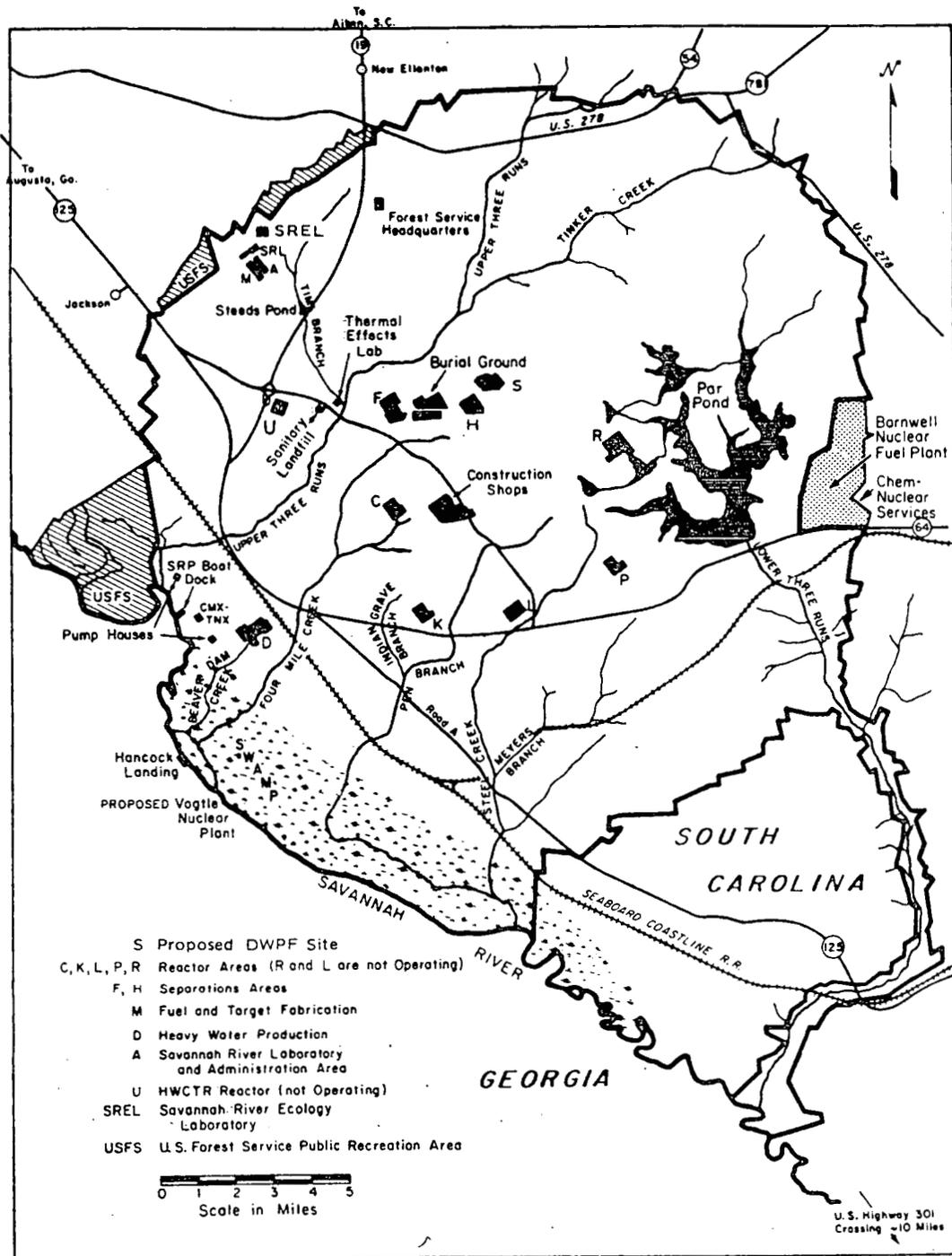


FIGURE 7. The Savannah River Plant Site

SEPARATIONS PROCESSES

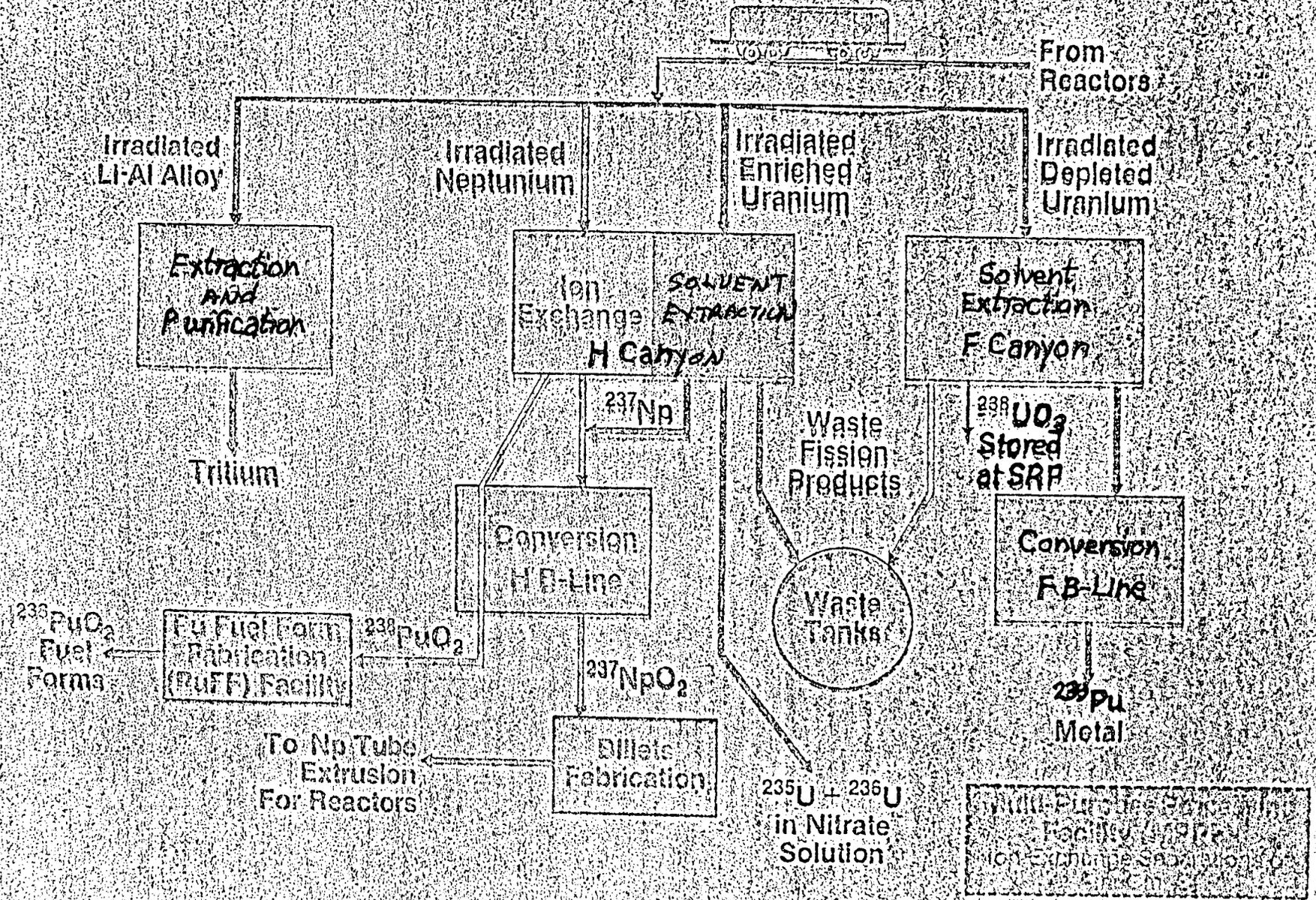


Figure 8. Separation Process at Savannah River Plant

solution with a NaNO_3 - NaOH solution and sent to waste storage. The bare uranium targets are then dissolved in boiling 10M HNO_3 . Standard and well-known PUREX process technology is used to separate and purify both the plutonium and the uranium. The uranium solutions are evaporated by successive evaporation steps, first to $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and then denitrated to UO_3 . The plutonium solutions are then concentrated by cation exchange and precipitated as PuF_3 . The precipitate is roasted in an oxygen atmosphere to a mixture of ~73 mole % PuF_4 and 27 mole % PuO_2 before undergoing a calciothermic reduction to plutonium metal for shipment offsite. Waste solutions from these processes which contain residual plutonium and small amounts of neptunium are processed through one of two anion exchange systems to recover both the plutonium and neptunium. The waste streams are then evaporated, acid stripped, and adjusted to $\text{pH} > 13$ by addition of NaOH before storage in underground double-shell tanks.

Following receipt of the burned enriched uranium fuel in the H-Area canyon, this aluminum-clad Al-U alloy is dissolved in HNO_3 catalyzed with $\text{Hg}(\text{NO}_3)_2$. The dissolver solution is frequently blended with dissolved offsite fuels, such as university research reactors and HFIR cores from Oak Ridge, before the purified uranium and neptunium are separated and purified by a modification of the PUREX process. The purified $\text{UO}_2(\text{NO}_3)_2$ solution is shipped offsite for conversion to uranium metal. This uranium metal is reprepared into fuel tubes from the SRP reactors. Since this uranium is repeatedly recycled through the reactors, the ^{236}U content has grown over the years. The purified neptunium, produced in the fuel tubes by the irradiation of the ^{236}U , is concentrated by anion exchange, precipitated as an oxalate, and calcined to the oxide. This NpO_2 is then fabricated into Al-clad NpO_2 -Al cement targets and returned to the reactors to produce plutonium-238.

Following receipt of the irradiated neptunium targets in the H-Canyon, these targets are dissolved in HNO_3 catalyzed with $\text{Hg}(\text{NO}_3)_2$. The ^{237}Np and ^{238}Pu are then purified and partitioned from each other by two cycles of anion exchange. Both products are further purified by

anion exchange, precipitated as oxalate, and calcined to oxide. The purified NpO_2 is fabricated into heat sources for use in the nation's space program.

The waste streams from the H-Area processes are evaporated, acid-stripped, and adjusted to $\text{pH} > 13$ by addition of NaOH before storage in underground double-shell tanks.

In addition to fuel and targets from SRP reactors, SRP also reprocesses a wide variety of fuels from offsite research reactors and a wide range of unirradiated plutonium scrap materials. Following customary Savannah River practice, initial processing of each offsite material is designed to transform the actinides to a solution that is compatible with one of the solvent extraction cycles in either of the separations areas. A major advantage of this practice is that the uranium and plutonium isotopics can be blended over a wide range. Since the actinide can be introduced to the mainline process at several different points, a greater range of contaminants can be handled by routine operations. This simplifies many of the initial purification steps over the steps that would be necessary if only one entry point was available.

Savannah River Plutonium Technology Needs: Research and Development Opportunities

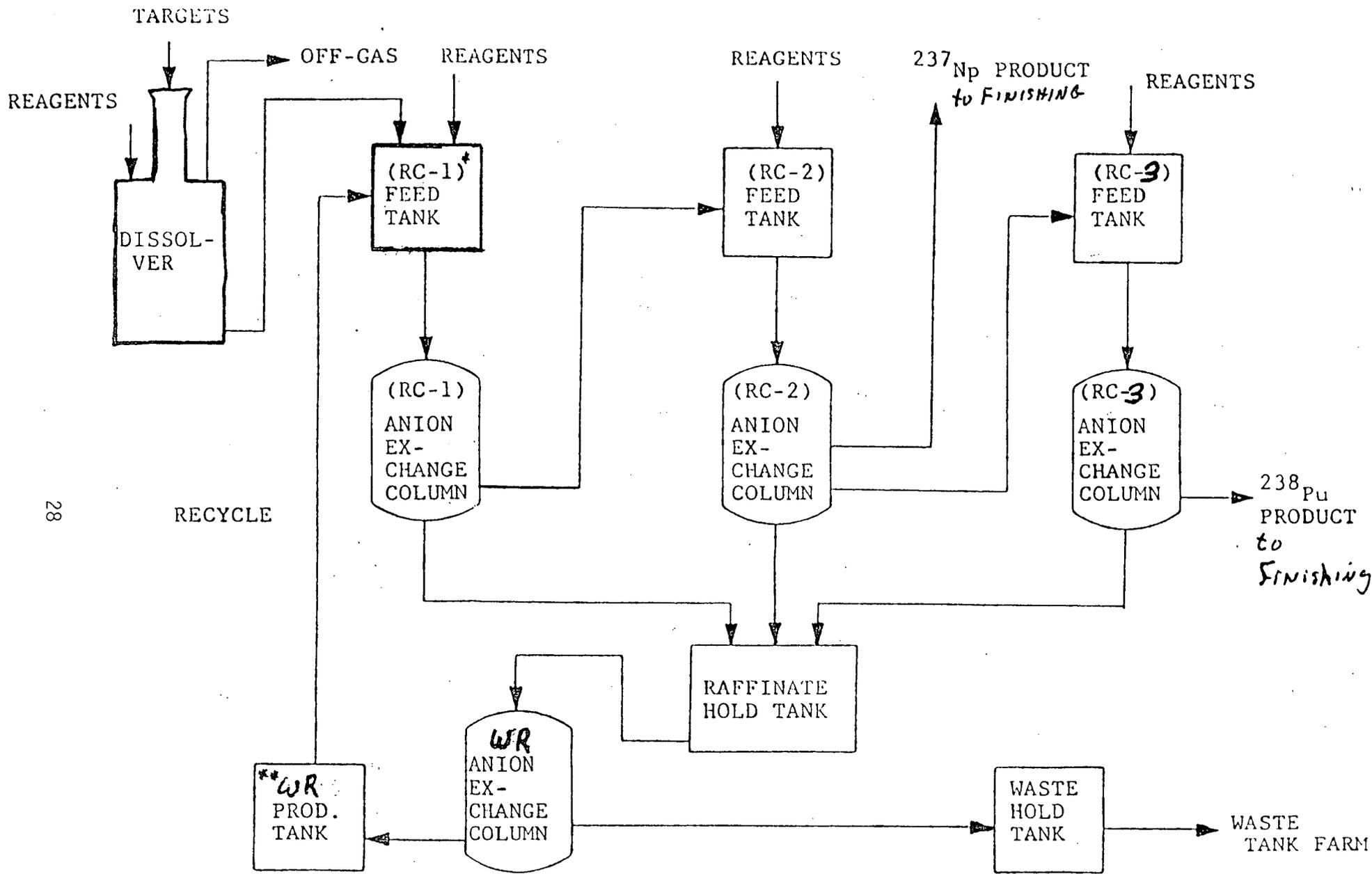
Refractory Oxides

Savannah River processing of both irradiated and unirradiated plutonium oxide materials is increasing. Much of this oxide material was calcined at 650°C or less; however, some of this oxide was calcined at temperatures up to 1700°C . Whereas the material calcined at the lower temperatures is fairly easy to dissolve in HNO_3 - HF solutions, material calcined at the higher temperatures becomes an intractable refractory oxide. Better methods, which can be scaled to a production mode, are needed to convert these refractory oxides to a form amenable to reprocessing. Some advances have been made in aqueous dissolution, using an electrolytic assist to fluoride dissolution. But further

chemical and engineering data are needed to convert this into a viable production process. Several laboratories have also studied a fluoride volatility process which shows promise. Some of the problems encountered in the volatility process could, perhaps, be overcome by the use of atomic fluorine instead of molecular fluorine.

Plutonium-238 Production

The flowsheet for the reprocessing of neptunium targets to recover ^{238}Pu is shown in Figure 9. The major problems with this flowsheet is the incomplete partitioning of ^{237}Np and ^{238}Pu on the anion exchange columns. This cross-contamination is the result of either incomplete valence adjustments or an unwanted valence readjustment during the partitioning step. A better understanding of oxidation-reduction reaction kinetics and valence states equilibria as a function of the concentrations of valence adjustment chemicals, total plutonium, plutonium-238, neptunium, and temperature is needed.



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* RC = Resin Column
 ** WR = Waste Recovery

Figure 9. ^{238}Pu Separations Process at Savannah River Plant

REFERENCES

1. Mullins, L. J. and Foxx, C. L., "Direct Reduction of $^{238}\text{PuO}_2$ to Metal," Los Alamos National Laboratory Report LA-9073, January 1982.
2. Mullins, L. J., Christensen, D. C., and Babcock, B. R., "Fused Salt Processing of Impure Plutonium Dioxide to High-Purity Metal," Los Alamos National Laboratory Report LA-9154-MS, January 1982.
3. Baker, R. D., "Preparation of Plutonium Metal by the Bomb Method," Los Alamos Scientific Laboratory Report LA-473, 1946.
4. Mullins, L. J., Leary, J. A., Morgan, A. N., and Maraman, W. J., *I&EC Proc. Des. Dev.*, 2 (1963).
5. Mullins, L. J. and Morgan, A. N., "A Review of Operating Experience at Los Alamos Plutonium Electrorefining Facility, 1963-1977," Los Alamos National Laboratory Report LA-8943, December 1981.
6. Leary, J. A., Morgan, A. N., and Maraman, W. J., *Second Eng. Chem.*, 51, 27 (1959).
7. Christensen, E. L. and Maraman, W. J., "Plutonium Processing at the Los Alamos Scientific Laboratory," Los Alamos Scientific Laboratory Report LA-3542, April 1969.
8. Hagan, P. G., Navratil, J. D., and Cichorz, R. S., *J. Inorg. Nucl. Chem.*, 43, 1054 (1981).
9. Bray, L. A. and Ryan, J. L., in Actinide Recovery From Waste and Low-Grade Sources, J. D. Navratil and W. W. Schulz (eds.), Harwood Academic Publishers, New York, 1982, p. 129.
10. Navratil, J. D. and Martella, L. L., *Nucl. Technol.*, 46, 105 (1979).
11. Schulz, W. W. and Navratil, J. D., in Recent Developments in Separation Science, Vol. VII, N. N. Li (ed.), CRC Press, Boca Raton, Florida, 1982, p. 31.
12. Boyd, T. E. and Kochen, R. L., "Ferrite Treatment of Actinide Waste Solutions: A Preliminary Study," U.S. DOE Rept. RFP-3299, Rockwell International, Golden, Colorado, July 30, 1982.
13. Bruns, L. E., in Preparation of Nuclear Fuels, Nuclear Engineering, Part XVIII, Chemical Engineering Progress Symposium Series No. 80, Vol. 63, pp. 156-182. American Institute of Chemical Engineers, New York, 1967.

14. Bruns, L. E., in Proceedings of the International Solvent Extraction Conference, The Hague, April 19-23, 1971, Vol. 1, p. 186, Society of Chemical Industry, London, 1971.
15. Swanson, J. L., The Selective Dissolution of Zirconium or Zircaloy Cladding by the Zirflex Process, Report A/Conf. 15/2429, June 1958, Second United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, 1958.
16. Smith, P. W., The Zirflex Processes Terminal Development Report, U.S. AEC Report HW-65979, General Electric Co., Richland, WA, 1960.
17. Phillips, J. F., Dissolution of Oxide-Coated Zirconium and Zirconium Alloys, U.S. AEC Report BNWL-600, Pacific Northwest Laboratory, Richland, WA, 1968.
18. Cotton, F. A., and Wilkinson, G., Advanced Inorganic Chemistry - A Comprehensive Text, 2nd Ed., Interscience, New York, 1968, pp. 1180.
19. Katz, J. J., and Seaborg, G. T., The Chemistry of the Actinide Elements, Methuen, London, 1957, pp. 420.
20. Silver, G. L., Effect of Hydrolysis on the Disproportionation of Tetravalent and Pentavalent Plutonium Ions, U.S. AEC Report MLM-1743, Mound Laboratory, Miamisburg, OH, 1970.
21. Silver, G. L., The Three Actinide Equilibrium Problem, U.S. AEC Report MLM-2007, Mound Laboratory, Miamisburg, OH, 1973.
22. Silver, G. L., Minor Problems in Aqueous Plutonium Chemistry, U.S. AEC Report MLM-2075, Mound Laboratory, Miamisburg, OH, 1973.
23. Silver, G. L., Plutonium Disproportionation Reactions: Some Unresolved Problems, U.S. AEC Report MLM-1807, Mound Laboratory, Miamisburg, OH, 1971.
24. Colvin, C. A., Quantitative Determination of Plutonium Oxidation States in Variable Nitric Acid Solutions for Control Laboratories-- Spectrophotometric, U.S. AEC Report RL-SA-33, General Electric Co., Richland, WA, 1965.
25. Emelity, L. A., Christensen, C. W., and Kline, W. H., in Practices in the Treatment of Low- and Intermediate-Level Radioactive Wastes, IAEA, Vienna, 1966, pp. 187.
26. Ryan, E. S., Vance, J. N., and Maas, M. E., in Practices in the Treatment of Low- and Intermediate-Level Radioactive Wastes, IAEA, Vienna, 1966, pp. 517.
27. Milligan, W. O., Beasley, M. L., Lloyd, M. H., and Haire, R. G., Acta Crystallog., Sect. B., 24, 978, 1968.

28. Milligan, W. O., Crystal Structure and Morphology of Hydrous Oxides and Hydroxides in the Lanthanide and Actinide Series, Final Report June 1, 1969-May 31, 1972. U.S. AEC Report ORO-3955-3, Oak Ridge Operation Office, Oak Ridge, TN, 1972.