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Generation and Characteristics of Plutonium and Americium Contaminated Soils Underlying Waste Sites at Hanford

September 2019

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U.S. DEPARTMENT OF ENERGY

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Summary

In 2012, a Hanford site-wide review on plutonium and americium geochemistry (Cantrell and Felmy 2012) identified remaining research challenges associated with defining scientifically defensible end-states and supporting remediation decisions. Three research challenges were identified in this review:

> "1. Determine the transformations of Hanford Site sediments in response to changes in waste/groundwater composition. Significant mineralogical transformations can take place when wastes contact Hanford sediments. These transformations can significantly impact the solubility and acidic adsorption of plutonium and americium and possibly result in the generation of pseudo colloids that could facilitate plutonium/americium migration.
>
> 2. Assess the impact of changes in waste/groundwater chemistry on the potential for plutonium/americium solubilization or colloid formation. Changes in waste or groundwater chemistry can greatly impact the chemical form or speciation of plutonium and americium. Knowledge of plutonium and americium speciation will be crucial in terms of evaluating the potential for solubilization, adsorption or remobilization of adsorbed complexes, colloid formation, and colloid interactions with sedimentary minerals.
>
> 3. Establish the role of organic complexants and/or non-aqueous solvents in the transport of plutonium/americium in the deep subsurface. Plutonium has been found to be associated with TBP and the presence of non-aqueous solvents, at least in certain Z-9 sediments. It will be important to establish the role of non-aqueous solvent in past movement of plutonium and its potential role in future mobility."

Since the time of this review, a remedy has been identified for the plutonium-contaminated waste sites. The remedy involves the removal of upper soil and debris to a specified depth, followed by disposal either onsite at Hanford's Environmental Remediation and Disposal Facility or at the Waste Isolation Pilot Plant (WIPP), the only deep geologic long-lived radioactive waste repository in the United States (DOE/RL-2015-23, Rev.0)

The present report further defines the plutonium and americium bearing waste, its release history and its process origins and compositions for three ground disposal sites – 216-Z-1A, 216-Z-9, and 216-Z-12 to support Lawrence Livermore National Laboratory's (LLNL) Science Focus Area on *Subsurface Biogeochemistry of Actinides.* The work at LLNL is focused on identifying plutonium mobility in clean sediments, including potential interactions with co-contaminants disposed beneath the 216-Z-9 trench. Hence, this report provides sediment characteristics at these waste sites in the 200 West Area of the Hanford Site and describes contaminated 216-Z-9 sediment retrieval undertaken in the 1970s. The process feed origins and the different Plutonium Finishing Plant processes that generated the waste are described in detail. Based on these data, the compositions of the resulting wastes have been reconstructed, including the plutonium and americium inventory, and information on co-contaminant disposal gathered. These co-contaminants can constitute chemical markers and may play roles in plutonium and americium disposition, speciation, and migration. Further detail on the compositions of the native and waste-affected sediments is provided, thus identifying the alteration of the bulk substrates that host the plutonium and americium. In investigating these topics, additional information from prior studies of waste disposition is considered, yielding key insights into plutonium and americium solubilities as well as behaviors during leaching.

The present investigations found the chemistry of the waste to be extremely complex. The wastes contain varying concentrations of aluminum, magnesium, manganese, calcium, iron, chromium, lead, nickel, mercury, cadmium, gallium, sodium, nitrate, fluoride, sulfate, hydroxide, chloride, organic extractants, and lard oil, as well as the plutonium and americium. Key waste signatures, including waste chemistry and plutonium-bearing particle morphology, are described. These signatures, in combination with examination of contaminated sediments from beneath the waste sites, will allow mechanisms responsible for plutonium and americium migration to be elucidated.

Plutonium is present in vadose zone sediments from near surface discharges as discreet particles (PuO_2) and as a second, more mobile particle type associated with silicate mineral hydrolysis, possibly forming a silica gel, as well as highly sorbed complexes and very low aqueous concentrations. Aqueous and adsorbed plutonium and americium complexes present in low concentrations in the waste as a result of the aqueous/organic waste chemistry (organic complexes from lard oil, tributyl phosphate, and their breakdown products), may have precipitated upon dilution in the subsurface. Plutonium concentrations in contaminated sediments are proportional to particle surface and decrease overall with depth. Results from previous studies on plutonium- and americium-contaminated sediments show that americium is more mobile than plutonium for acidic wastes, but not for pH-neutral to alkaline wastes. Data presented here for sediments under 216-Z-1A, 216-Z-9, and 216-Z-12 show considerable plutonium and americium transport under initial disposal conditions with deep penetration (~35 m) into the vadose zone in some cases. In sediments where americium is more mobile, it may pose a greater threat to groundwater than plutonium. Thus, as is the case for plutonium, controls on its solubility must be determined.

This report provides the technical basis for interpreting data obtained from field samples and will allow waste chemistry impacts on plutonium/americium re-mobilization mechanisms to be assessed. This report helps address the three previously identified research challenges – sediment transformations, solution chemistry impacts, and the role of organic complexants and solvents – in plutonium and americium contaminated Hanford sediments. Ultimately, these and potential future studies will lead to a defensible description of plutonium and americium mobility in relation to waste site conditions that can be interpreted to balance the risks posed by their migration and envisioned remediation activities.

Acknowledgments

This document was prepared by the Deep Vadose Zone - Applied Field Research Initiative at Pacific Northwest National Laboratory. Funding for this work was provided by the U.S. Department of Energy Richland Operations Office. The authors acknowledge key discussions with Robert Kasper and John Swanson, whose work in the 1970s and 1980s is foundational to the content of this report. The authors greatly appreciate the technical reviews provided by Jason Capron, Paul Seeley, Vicky Freedman and Jim Szecsody, and technical editing provided by Matt Wilburn.

Acronyms and Abbreviations

AK	Acceptable Knowledge
ANN	aluminum nitrate nonahydrate
ARIES	Advanced Recovery and Integrated Extraction System
ASME	American Society of Mechanical Engineers
CFR	Code of Federal Regulations
DBBP	dibutylbutyl phosphonate
DBP	dibutyl phosphate
DMO	direct metal oxidation
LASL	Los Alamos Scientific Laboratory
LLNL	Lawrence Livermore National Laboratory
LOI	loss on ignition
MCL	maximum contaminant level
NQAP	Nuclear Quality Assurance Program
PFP	Plutonium Finishing Plant
PNNL	Pacific Northwest National Laboratory
PRF	Plutonium Reclamation Facility
SS&C	sand, slag, and crucible
TBP	tributyl phosphate
VCP	vitrified clay pipe
WIPP	Waste Isolation Pilot Plant
XRD	X-ray diffraction
XRF	X-ray fluorescence

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1.0 Introduction

Plutonium is of great concern to human health as it is radiotoxic, primarily emitting alpha radiation that is easily absorbed by tissue, causing cancer, and it is long-lived in the environment, with the most common isotope, plutonium-239, having a half-life of 24,110 years (Cantrell and Felmy 2012). Virtually all plutonium in the environment is anthropogenic, released from research facilities, waste disposal, nuclear fuel reprocessing facilities, nuclear weapons production facilities, and nuclear accidents. Plutonium mobility in the subsurface environment is controlled by complex hydrological (dispersion, advection, dilution) and geochemical (redox, precipitation/dissolution, adsorption/desorption, complexation, colloid formation) processes, as well as by radioactive decay to primarily uranium, neptunium, and americium isotopes. However, due to its potentially greater environmental mobility and radiotoxicity, the americium-241 daughter produced from beta decay of plutonium-241 represents an important risk driver at many plutonium-contaminated sites.

At the Hanford Site, in southeastern Washington state, billions of gallons of process wastewater containing plutonium mixed with other contaminants were released into the subsurface during the generation of plutonium for the Manhattan Project. Although most unrecoverable plutonium-containing wastes went to storage tanks, some liquid process wastes containing plutonium-238, -239, -240, -241 and americium-241 were disposed to environmental sediments in trenches, cribs, and ponds within the Plutonium Finishing Plant (PFP) closure zone, and in an injection well (216-B-5). Some of the major plutonium-bearing waste ground disposal structures associated with PFP operations were the 216-Z-9 trench, 216-Z-12 crib, and 216-Z-1A tile field, and the generation and characteristics of wastes disposed to these sites are described in this report.

In 2012, a Hanford site-wide review on plutonium and americium geochemistry (Cantrell and Felmy 2012) identified remaining research challenges associated with defining scientifically defensible end-states and supporting remediation decisions. Since this review, a remedy has been identified at the plutonium-contaminated waste sites. The remedy involves the removal of upper soil and debris to a specified depth, followed by disposal either onsite at Hanford’s Environmental Remediation and Disposal Facility or at the Waste Isolation Pilot Plant (WIPP), the only deep geologic long-lived radioactive waste repository in the United States (DOE/RL-2015-23, Rev. 0).

Based on unresolved research needs stated in Cantrell and Felmy (2012), and to answer concerns that were raised by the Hanford Advisory Board River and Plateau Committee in 2017 in response to the remedial action work plan prepared by the U.S. Department of Energy (DOE/RL-2015-23, Rev. 0,), PNNL has engaged with Lawrence Livermore National Laboratory (LLNL) to continue investigating plutonium mobility at Hanford. LLNL has an Office of Science Biological and Environmental Research (BER) funded Science Focus Area on ‘Subsurface Biogeochemistry of Actinides’ and is focused on identifying plutonium mobility in clean sediments, including potential interactions with co-contaminants disposed beneath the 216-Z-9 trench. The goal is to identify (i) mechanisms responsible for migration of shallow contaminant plutonium into the deep subsurface at disposal sites in the Hanford 200 West Area and; (ii) the potential for existing plutonium and americium in the deep vadose zone to be remobilized to groundwater.

To support LLNL’s characterization effort and remedy decisions at the 200-PW-1 Operable Unit, the historical process chemistry and waste releases were reconstructed. This information serves three purposes: (i) provide a record of the plutonium and americium inventory; (ii) identify key waste signatures, including the chemical form and morphology of plutonium-bearing particles, that may be present in the subsurface; and (iii) generate simulant wastes to assess the impact of waste chemistry on plutonium and americium re-mobilization mechanisms. Information on the generation and compositions of the wastes disposed to the Hanford Site’s 216-Z-9 trench from the RECUPLEX Process, similar wastes disposed to the 216-Z-1A tile field from the Plutonium Reclamation Facility (PRF), and dilute waste disposed to 216-Z-12 crib are presented. The removal of a significant amount of the disposed plutonium by excavating the top 30 cm of soil at the bottom of 216-Z-9 trench in the mid-1970s is reviewed to inform the current retrieval, treatment, and disposal plan. Results from previous studies on plutonium- and americium-contaminated sediments are described, including identification of relevant sediment transformations caused by changes in waste/groundwater composition, that can affect the solubility and adsorption of plutonium and americium. The possible influence of co-disposed organics on the transport of plutonium and americium is also discussed.

It is the intent of this report to identify the potential mechanisms for plutonium and americium mobility based on release history, waste chemistry, and sediment characteristics at the Hanford Site. An understanding of these mechanisms, and information on plutonium and americium mobility, may offer the potential consideration of other remediation approaches, when combined with additional sampling to evaluate further movement as function of co-contaminant chemistry.

2.0 Plutonium Processing at the Hanford Site

The first shipment of plutonium, in the form of a concentrated plutonium nitrate paste, was sent from the Hanford Site's 231-Z building in Washington State to the Los Alamos Scientific Laboratory (LASL) for finishing into atomic explosives on February 2, 1945. Shipments continued at an accelerating pace through the summer of 1945 with efforts to fuel atomic weapons via plutonium. The United States' mission for routine Pu weapons parts production was shifted from LASL to Hanford on July 5, 1949, with the commissioning of Hanford's PFP in the 234-5Z building, although limited shipments of the paste to LASL continued to support their development of nuclear explosive devices (Gerber 1997).

These Pu finishing operations included the conversion of the Pu nitrate pastes to solids of Pu oxalate, oxide, fluoride, metal, and ultimately to parts for nuclear weapons. The PFP (Figure 1), currently undergoing demolition, is a complex consisting of the original 234-5Z building and associated added structures, most notably for the present purposes, the 236-Z PRF and the 242-Z Americium Recovery Building, in Hanford's 200 West Area. During the 1945-1949 period, prior to the operation of the 234-5Z building, off-specification Pu nitrate product was recycled to the lanthanum fluoride precipitation stages (buildings 224-T and 224-B) in the Hanford Site's Bismuth Phosphate T and B (reprocessing) plants and then to the 231-Z building, using a Pu peroxide precipitation process, or directly to 231-Z for purification (Sections 2 and 8 of Gerber 1997).

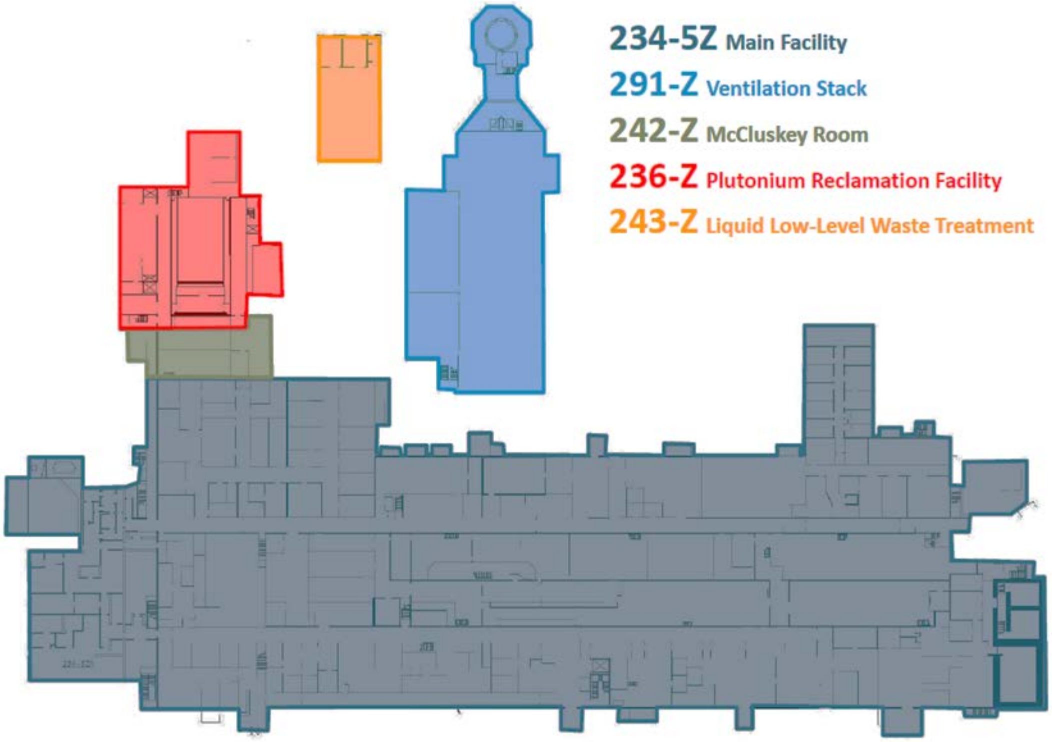

Figure 1. Plutonium Finishing Plant Buildings (Teynor 2015; note that the McCluskey Room is the location of the Americium Recovery Building)

With the advent of Pu finishing operations at Hanford in 1949, recovery of Pu from the various PFP finishing scrap streams (oxalate, oxide, fluoride, metal, and associated scraps including filtrates, metal foundry, and machining residues) became imperative. While the initial recovery of Pu-bearing scrap generated at PFP began by dissolution in nitric acid, HNO_3, the remaining Pu purification steps were using the same methods as the 231-Z and T and B Bismuth Phosphate plants, augmented in 1952 with start of the REDOX (reprocessing) Plant. The recovered Pu was added to the Pu separated at the B, T, and REDOX reprocessing plants and sent to 231-Z and/or PFP for further purification and processing (Section 8 of Gerber 1997).

The necessity of a dedicated Pu scrap recovery facility was apparent from the beginning of PFP operations in 1949. Accordingly, the already practiced Pu-bearing scrap dissolution steps were augmented by two ensuing in-house Pu purification processes – RECUPLEX (1955-1962) and the PRF (236-Z building; 1964-1994). The PRF wastes were processed for americium, Am, and trace Pu recovery at 242-Z from 1964, just after start of PRF operations, until August 30, 1976, when an explosion in an ion exchange column permanently shut down the 242-Z operations (Section 11.3 of Gerber 1997). Both the RECUPLEX and PRF processes were based on solvent extraction of tetravalent Pu [Pu(IV)] from HNO_3 solution into tributyl phosphate (TBP) extractant diluted in carbon tetrachloride (CCl_4), while the Pu and Am recoveries in 242-Z and in waste polishing operations within RECUPLEX were based on dibutylbutyl phosphonate (DBBP) solvent extraction and subsequent purification and concentration of the Am product through ion exchange. The placement of RECUPLEX and the PRF within the Pu process cycle at the PFP is shown within the dashed rectangle in Figure 2 with the 242-Z Waste Treatment Facility shown to its right. The operations of RECUPLEX and the PRF with 242-Z are described in the following two sections of this report.

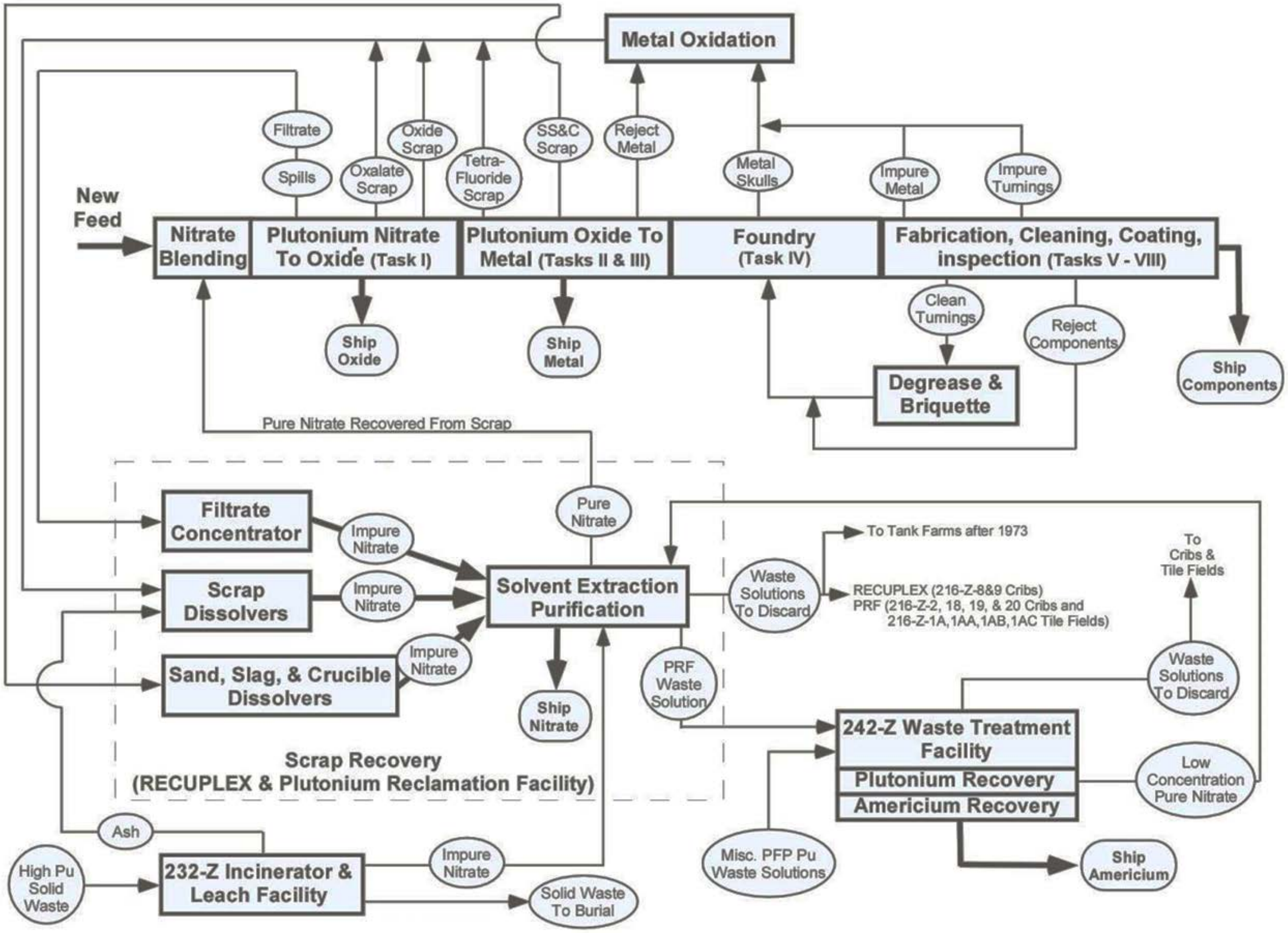

Figure 2. Plutonium Processing Cycle at the PFP (Hoyt and Teal 2004)

2.1 The RECUPLEX Process

Although the RECUPLEX acronym has been attributed to **REC**overy of **U**ranium and **PL**utonium by **EX**traction (page 9-1 of Gerber 1997), uranium was not recovered in this process. According to Judson (page 8; 1956a), the RECUPLEX facility had two purposes:

> *(1) Recovery of plutonium from metallurgical wastes in a manner that will permit its direct recycle to the wet chemistry operations of the main line; and (2) Coupling to wet chemistry operations (both at HAPO*[1] *and offsite) of the product solutions from Bismuth Phosphate Plants and off-standard product solutions from Redox and Purex Plants.*

The Bismuth Phosphate plants (the T, 1944-1956, and B, 1945-1954, Plants), the REDOX Plant (S Plant, 1952-1967), and the PUREX Plant (A Plant, 1956-1972; 1983-1990) all reprocessed irradiated fuels at the Hanford Site.

Ultimately, coupling of the reprocessing plants' Pu product output to RECUPLEX was not implemented, leaving only scrap recovery in the RECUPLEX mission. The acronym plausibly would derive from the original goal of Pu **REC**overy from scrap and **C**o**UPL**ing of impure and dilute reprocessing plant Pu products as purification feed by solvent **EX**traction for conversion to Pu metal (pages 4-5 of Blasewitz 1951). A decisive reference describing the source of the name RECUPLEX has not been located.

RECUPLEX, first operated as a prototype, beginning July 11, 1955, was fully integrated within the PFP in 1957 by installing larger and more durable equipment with improved shielding and instrumentation, and continued operation through April 7, 1962. On that date, due to inadvertent solution routing during non-standard operations, a nuclear criticality occurred. The facility was shut down immediately and then cleaned out and dismantled (Section 9 of Gerber 1997).

The RECUPLEX process flowsheet, Figure 3, outlines the main features of its operation (Judson 1958). The wastes disposed to the 216-Z-9 crib solely arose from operation of RECUPLEX.

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[1] HAPO is Hanford Atomic Products Operation.

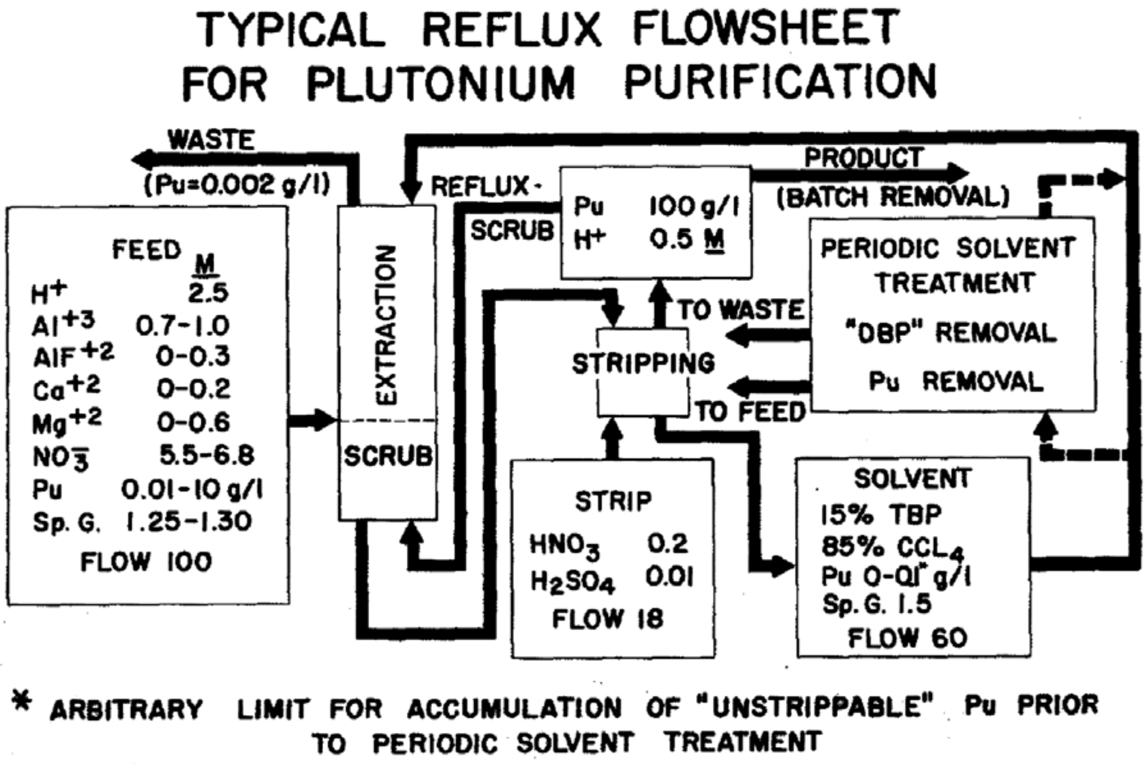

Figure 3. RECUPLEX Block Flow Diagram (Figure 1 of Judson 1958)

RECUPLEX was a solvent extraction process using ~15% TBP diluted in CCl_4 to effectively separate Pu(IV) from ~2.5 M HNO_3 solution containing nitrate salts of other metals, primarily aluminum, calcium, and magnesium. The 15% TBP organic solvent constituted in CCl_4 had greater density (~1.5 g/cm^3) than the aqueous feed solution (1.25-1.30 g/cm^3), a density differential of 0.20-0.25 g/cm^3, so that the dense organic phase fell through the rising aqueous phase in the liquid-pulsed, perforated-plate extraction column. Later plant studies showed that when aqueous and organic solution densities differed by <0.15 g/cm^3 for clean extraction columns or <0.17 g/cm^3 for silica-coated columns, undetectable emulsions occurred, entraining impurities in the stripping column and, thus, impurities in the product (Bruns 1959a). Part of the reason for the lower density differential was the TBP concentration increase from 15% to 23% (density ~1.46 g/cm^3) in later RECUPLEX operation (Bruns 1959a) and potentially evaporative loss in processing of the volatile dense CCl_4.

The feed solutions had variable compositions and widely varied Pu concentrations (0.01 to 10 g Pu/liter) because of the diverse scrap sources being processed, including supernatant solutions from Pu(IV) oxalate precipitation; scrap from reduction of plutonium tetrafluoride, PuF_4, to Pu metal; scrap from other operations (e.g., Pu metal casting and machining); and spills. The characteristics of these scraps are presented in Section 2.3.2 in this report.

Scrap dissolution generally occurred using hot 6-13 M HNO_3, accelerated by intentional or incidental addition of fluoride ion as fluoride salts. The strong complexation of Pu by fluoride to form PuF^{3+} was responsible for significant enhancement of dissolution rates. For example, sand, slag, and crucible (SS&C) scrap from Pu metal reduction contained calcium fluoride (CaF_2) by-product as the fluoride source whereas fluoride, as sodium fluoride, NaF, was provided to help dissolve recycled metal or PuO_2, plutonium dioxide. Once the Pu was dissolved, the excess “free” (non-complexed) highly corrosive fluoride was complexed itself by addition of aluminum ion as aluminum nitrate, $Al(NO_3)_3$ to form AlF^{2+}

ions. The aluminum ion provided high ionic strength to act as a salting agent to help drive the Pu(IV) into the organic phase during solvent extraction.

RECUPLEX process control would have been difficult given its low but varied Pu feed concentrations and high feed composition variability. To improve process control, much of the extracted Pu was returned to the solvent extraction column, leveling the otherwise widely ranging Pu feed concentrations. This "reflux" operation also improved decontamination from impurities (Judson 1958) and increased the Pu concentrations in the product Pu nitrate solutions. The purified Pu was stripped (back-extracted) from the loaded organic phase using 0.2 M HNO_3 containing 0.01 M sulfuric acid (H_2SO_4) to yield a ~100 g Pu/liter solution in 0.5 M HNO_3 suitable for processing to PuO_2 or Pu metal through the Pu(IV)-oxalate precipitation process.

As shown in Figure 3, the organic solvent itself underwent intermittent purification to remove the radiolytic and hydrolytic TBP decomposition product DBP, dibutyl phosphate. The wastes from the solvent extraction step, containing ~0.002 g Pu/liter and the impurities accompanying the feed solutions and the organic purification waste containing DBP went to the 216-Z-9 crib after being treated with concentrated sodium hydroxide, NaOH, solution to attain pH 2.5. Dilute RECUPLEX cell drainage went to the 216-Z-8 crib (Gerber 1997).

Process upsets occasionally would occur, causing high Pu levels in the RECUPLEX waste (raffinate). To recover this Pu, batch contacts of the raffinate with 50 vol% DBBP in CCl_4 diluent were conducted, as needed, during the last 2 years of RECUPLEX operation (page L-11 of Smith 1973). The used DBBP-bearing extractant was disposed directly to the 216-Z-9 crib in 100-liter batches (Section B.2.1.1 of DOE 1991). The DBBP was not retained to avoid its inadvertent mixing with the TBP-CCl_4.

2.2 The Plutonium Reclamation Facility and the 242-Z Waste Treatment Facility

The criticality that occurred at RECUPLEX on April 7, 1962, accelerated the plans already underway to construct its replacement, the PRF. Construction began in June 1962 with the plant completed in December 1963 and hot processing beginning on May 6, 1964 (Section 12 of Gerber 1997). The design objectives of the new facility (Finch 1959) were to:

> *(1) provide capacity to handle forecasted loads,*
>
> *(2) reduce personnel exposure to radiation under current and future plutonium processing conditions,*
>
> *(3) allow process work to be done in nuclearly-safe equipment (minimizing required administrative controls),*
>
> *(4) reduce loss of plutonium to the ground, and*
>
> *(5) allow future campaigned segregation of plutonium of different exposure levels.*

The PRF mission and flowsheet were like that of RECUPLEX; i.e., Pu scrap recovery using TBP solvent extraction in CCl_4 diluent; but using an improved design. The design features and process experience for the first 3 years of PRF operation, 1964-1967, were summarized by Bruns (1967) and inform much of this section of the report. Like RECUPLEX, the PRF also used reflux operations, returning a portion of the purified Pu nitrate solution product to the solvent extraction column to increase and level widely ranging Pu feed concentrations to improve decontamination and increase the Pu nitrate product concentration, reducing demand on the product concentrators. For improved personnel radiological safety, the PRF was constructed in a concrete-shielded canyon facility using narrow, $\lesssim$5-inch (15-cm) diameter "pencil tanks" and process vessels for nuclear criticality safety (Bruns 1967; Section 4.1 of Delegard and Casella 2016 and references therein).

The PRF solvent extraction flowsheet is depicted in Figure 4. In contrast with RECUPLEX and its use of 15 vol% TBP in CCl_4, the PRF flowsheet used 20 vol% TBP in CCl_4 to extract Pu(IV) from HNO_3 solution. The higher TBP concentration allowed higher Pu loadings into the organic phase while the ~24-foot (~7.2-meter) long, 99 pulse-plate extraction column (ARHCO 1976) provided significantly enhanced contact and phase disengagement capability compared with RECUPLEX.

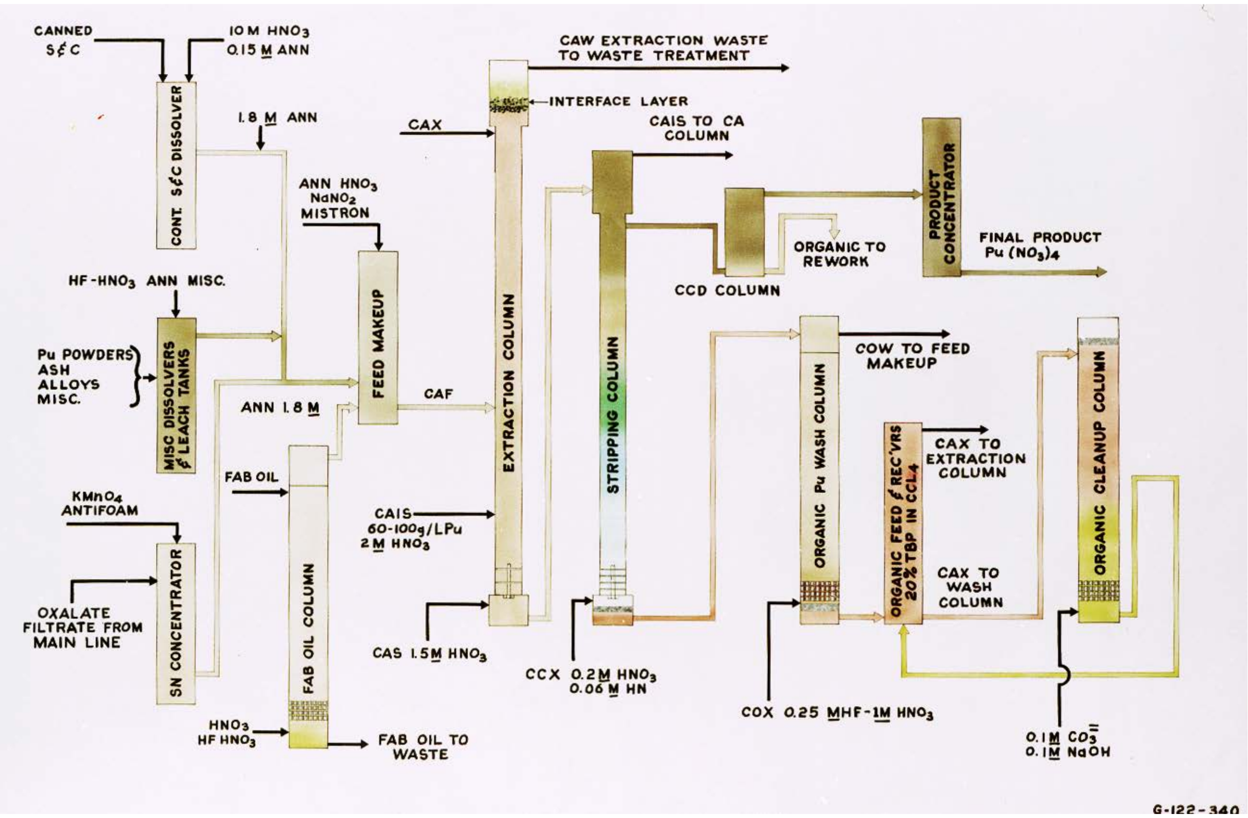

Figure 4. PRF Flowsheet (from Figure 2 of Bruns 1967 from Hanford drawing 38336-3CN)

The three primary Pu scrap feeds to the PRF were similar to those for RECUPLEX; "Canned S&C" (canned slag and crucible solids), the "Pu Powders, Ash, Alloys, etc." (various other solid scrap), and "Oxalate Filtrate from the Main Line." They are shown in the left side of Figure 4. Another scrap type, "Fab Oil," is found just to the right of the oxalate filtrate. Each of these scrap types was treated to achieve full solids dissolution in HNO_3, and in the case of the oxalate filtrate, to destroy oxalic acid using $KMnO_4$ (potassium permanganate).

The various impure Pu nitrate solution feeds then were collected in the "Feed Makeup" tank, where ANN [aluminum nitrate nonahydrate; $Al(NO_3)_3{\cdot}9H_2O$] was added to increase salting strength; HNO_3 added to reach the desired ~2 M concentration; $NaNO_2$ (sodium nitrite) added to adjust the Pu valence to the (IV) state; and Mistron®, a fine powder talc, added to aid in aqueous/organic disengagement.[1] The adjusted aqueous feed solution, called CAF, entered near the middle of the "Extraction Column" shown in the left center of Figure 4. The 20 vol% TBP in CCl_4 extractant entered near the top of the extraction column and

---

[1] The function of Mistron® is discussed in more detail later in this report.

flowed downward because of its greater density through the rising aqueous solution. Perforated pulse plates arrayed along the length of the extraction column enhanced the aqueous/organic contact. The Pu concentration in the extraction column was augmented by the introduction of the “reflux” stream, containing 60 to 100 g Pu/liter solution in 2 M HNO_3, below the CAF introduction point. Near the bottom of the extraction column, the CAS stream (1.5 M HNO_3) was introduced to scrub the Pu-loaded organic of any remaining non-extractable impurities. The aqueous phase was disengaged from the organic phase at the top of the extraction column (see “Interface Layer”) with the more buoyant aqueous phase containing the non-Pu metal salts (e.g., aluminum, magnesium, calcium, iron, potassium, and sodium nitrate plus in-grown americium), leaving the extraction column as the CAW stream. As in RECUPLEX, this stream went for further treatment, described subsequently, using DBBP extraction of residual Pu before discarding the treated waste to the 216-Z-1A crib.

Meanwhile, the Pu-loaded solvent proceeded to the top of the “Stripping Column” (shown near the center of Figure 4), where it then flowed downward through another pulse-plate arrangement to encounter the upwardly flowing aqueous CCX stream containing 0.2 M HNO_3 and 0.06 M hydroxylammonium nitrate (denoted HN in Figure 4). The HN chemically reduced the Pu to the non-extractable Pu(III) oxidation state, causing it to enter the upwardly rising aqueous phase, exiting the stripping column at the top as CAIS, to butt the Pu concentration in the extraction column, and as purified Pu, near the top of the stripping column to enter the “CCD Column.” There, the Pu-rich aqueous stream was washed with fresh CCl_4 to remove vestiges of the TBP/CCl_4 solvent, which were then recycled. The fully purified Pu aqueous stream then went to the “Product Concentrator,” which used stream stripping to polish the solution of organic traces, destroy the residual HN, heat-oxidize the Pu to the (IV) state, and build the Pu(IV) nitrate, $Pu(NO_3)_4$, solution product concentration to ~200 g Pu/liter.

The TBP-CCl_4 extractant exited the stripping column to be treated in three steps:

1. By washing with CO_X (0.25 M HF, hydrofluoric acid, in 1 M HNO_3) in the “Organic Pu Wash Column” to remove Pu traces with the Pu-bearing COW stream going to aqueous feed makeup;

2. By adjustment to the target 20 vol% TBP concentration for return as CAX, the extractant used in the Extraction Column, in the “Organic Feed & Rec’vers 20% TBP in CCl_4” column; and/or

3. By treatment with 0.1 M carbonate (CO_3^{2-}) in 0.1 M NaOH to remove DBP with the aqueous phase going to the waste stream (not shown in Figure 4) and the purified solvent being returned to the “Organic Feed & Rec’ver 20% TBP in CCl_4” column.

Further description of the PRF solvent extraction process is provided elsewhere (Bruns 1967; Ludowise 1980).

As depicted in Figure 5, most of the wide variety of scrap feeds to the PRF are like those processed by RECUPLEX from PFP sources. However, the PRF also received scrap from other Hanford laboratory sources and “Misc. Pu Solids” and “Misc. Pu Liquids” from offsite sources. The offsite sources generally were from the U.S. weapons complex – the Rocky Flats Plant, the Savannah River Site, the Lawrence Livermore National Laboratory, and the Los Alamos Scientific (later National) Laboratory – but also included Pu-bearing materials from the United Kingdom obtained under barter programs (Gerber 1997). The major scrap feeds are described in more detail in the next section of this report.

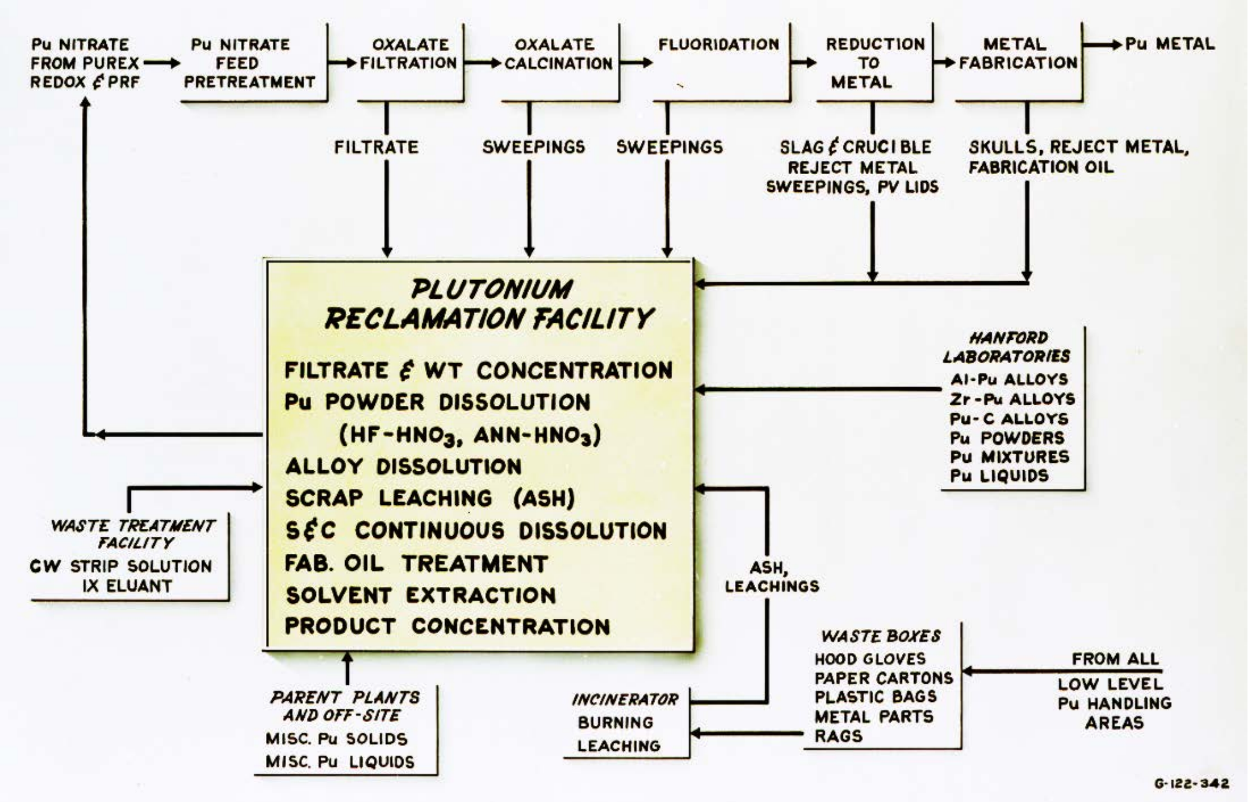

Figure 5. Plutonium Scrap Recovery Sources for the PRF (from Figure 1 of Bruns 1967 from Hanford drawing 38336-4CN)

From August 1964 until April 1969, nearly the same interval as the May 1964 until April 1969 period for the PRF waste disposal to the 216-Z-1A tile field, the PRF CAW was treated at the Americium Recovery Building, 242-Z (page 14 of Owens 1981). As indicated near the center of Figure 6, Am (and trace Pu) was extracted from the PRF CAW by a 30 vol% solution of DBBP in CCl_4 with the wastes disposed to the Z-1A tile field.

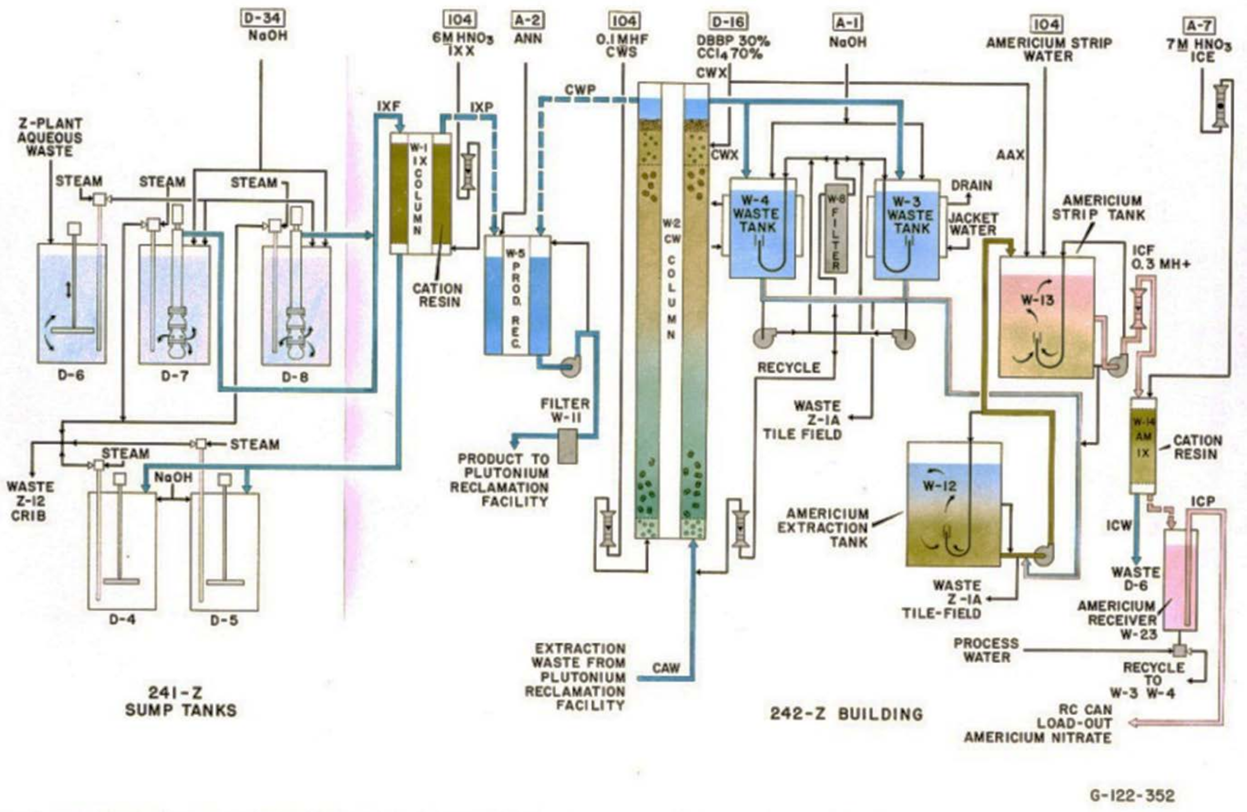

Figure 6. Waste Treatment and Americium Recovery Flowsheet for the 242-Z Building

2.3 Scrap Materials Processed in RECUPLEX and the PRF

The major scrap feeds to RECUPLEX and PRF included:

- Filtrates and spills from the plutonium nitrate aqueous conversion process to precipitate Pu(IV) oxalate – $Pu^{4+} + 2\ H_2C_2O_4 + 6\ H_2O \rightarrow Pu(C_2O_4)_2{\cdot}6H_2O_{\ (solid)} + 4\ H^+$. As shown in Figure 4, this scrap was treated with $KMnO_4$ and heated to destroy the excess oxalic acid and dissolve any Pu(IV) oxalate that escaped filtration. An antifoam agent was used to break the bubbles formed by carbon dioxide evolution.
- SS&C scrap from the residues of bomb reduction of PuF_4 to Pu metal according to the reaction with calcium metal – $PuF_4 + 2\ Ca \rightarrow Pu + 2\ CaF_2$. At Hanford, the PuF_4 reaction with Ca was “boosted” by the exothermic reaction of Ca with elemental iodine: $Ca + I_2 \rightarrow CaI_2$. The bomb reductions occurred in magnesium oxide, MgO, crucibles banked by MgO sand within metal pressure vessels. The SS&C thus contained excess Ca metal, CaF_2, CaI_2, MgO crucible fragments and sand, and plutonium in the form of PuO_2, unconverted PuF_4, and non-coalesced metal. This scrap was crushed and collected in non-tinned steel cans or plastic jars and dissolved using 10 M HNO_3 and 0.15 M ANN (Figure 4).
- Scrap plutonium solids, generally present as PuO_2, but also including off-specification PuF_4 or PuF_4 from failed bomb reduction runs, off-specification Pu(IV) oxalate, and Pu metal. The PuO_2 itself included off-specification oxide from Pu(IV) oxalate calcination, off-specification Pu metal product that has been burned to produce PuO_2, burnt metal from casting skulls (Pu metal remaining in the pouring crucible used when PFP produced Pu metal shapes for weapons), burnt metal turnings/chips from shaping Pu metal for weapons parts, residues from other Hanford facilities and offsite sources, and PuO_2 from incinerator ash. Because the 232-Z incinerator and leach facility only operated for

3 months (from 8 January 1962 until the RECUPLEX criticality on 7 April 1962; page 10-5 of Gerber 1997), incinerator ash was a negligible RECUPLEX feed but was a consequential feed to PRF.

- Fabrication oil. As seen in Figure 4, the fab oil was treated with HNO_3 and HF to dissolve the Pu metal fines suspended in these machining fluids.

2.3.1 Pu(IV) Oxalate Filtrates

RECUPLEX operated solely within the time the PFP converted Pu solutions to solids using the Pu(IV) oxalate precipitation process.[1] The initial RECUPLEX operations would have received Pu(IV) oxalate filtrates from batch operations, but from 1957 until the shutdown in 1962 accepted filtrates from continuous Pu(IV) oxalate processing.

The filtrate from the batch operation were treated by an "oxalate kill" designed to oxidize excess oxalate by treatment with $KMnO_4$ as catalyst and oxidation by hot nitric acid. According to Harmon et al. (Figure 11.7; 1961), filtrate after the oxalate kill was 0.32 g Pu(IV)/liter (1.34×10^{-3} M), 2.0 g K^+/liter (5.1×10^{-2} M), and 2.8 g Mn^{2+}/liter (5.1×10^{-2} M) in 2.0 M HNO_3. Filtrate concentration after concentration by boiling yielded 1.4 g Pu(IV)/liter (5.8×10^{-3} M), 7.3 g K^+/liter (~0.18 M), and 10 g Mn^{2+}/liter (0.18 M) in 5 M HNO_3 (Figure 1 in Maffei 1957). Filtrates after the oxalate kill from the continuous Pu(IV) oxalate precipitation process used at the time of later RECUPLEX and PRF operations had similar concentrations of 0.4 g Pu/liter (1.7×10^{-3} M) and 0.03 M each K^+ and Mn^{2+} in 2 M HNO_3 (Rodgers 1986).

One would expect these evaporatively concentrated filtrates to contain iron, chromium, and nickel (Fe, Cr, and Ni, respectively) from stainless steel process vessel corrosion. Concentrated and aged filtrate solutions characterized after years-long storage (Table 1) indeed show these corrosion products. Metals frequently found in other Pu scrap materials (Al, Ca, Mg, and Na) suggest these nominal Pu(IV) oxalate filtrate solutions were contaminated. Manganese dioxide (MnO_2) also was present as a solid residue.

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[1] Plutonium precipitation at the PFP used Pu(III) oxalate from July 1949 until start of Pu(IV) oxalate processing on 21 March 1952. Plutonium(IV) oxalate precipitation was used from 1952 onward.

Table 1. Concentrated and Aged Pu(IV) Oxalate Filtrate Solution Compositions

Analyte	Concentration		
	Barney 1996 (μg/mL)	Jones 2001 (μg/mL)	Average (M)
Fe	15700	15200	0.277
Na	12800	12960	0.560
Al	3500	4608	0.150
Mn	NR[(a)]	2800	0.0255
Cr	750	2464	0.0309
K	6500	2440	0.114
Ni	510	2016	0.0215
P	NR	1976	0.0319
Ca	600	912	0.0189
Mg	480	295	0.0159
Zn	NR	816	0.0125
Pu	31400	24000	0.116
Am	61	NR	0.00025
U	180	NR	0.00076
H^+	3.37 M	7.0 M	5.2
NO_3^-	210000	NR	3.39
Cl^-	26600	NR	0.750
F^-	1100	NR	0.0579

(a) NR – not reported

2.3.2 SS&C Scrap Processing

Calciothermic[1] reductions of PuF_4 to produce Pu metal took place within MgO crucibles banked with MgO sand within metallic pressure vessels heated in induction furnaces. The slag arising from these processes contained CaF_2, CaI_2, calcium oxide (CaO) from calcium metal reaction with PuO_2, non-coalesced Pu metal, unreacted PuF_4, PuO_2, and excess calcium metal. The MgO sand and crucible materials constituted the balance of the SS&C scrap. If reductions were successful, the dense Pu metal product sank through the slag, coalesced at the bottom of the crucible, and solidified as a pure metal regulus (called "button") with mass ranging from ~500 g in earlier processing to ~2000 g beginning in 1957. Slag adhering to the button was removed mechanically and the buttons generally were exposed to strong HNO_3 to dissolve and remove traces of SS&C.

The SS&C scrap from bomb reduction of PuF_4 to form a 490-g (2.05-mole) Pu metal button included 970 g (24.1 moles) of MgO (from a 500-g crucible and 470 g of packing sand), 1228 g (moles) of CaF_2, 92 g (0.31 moles) of CaI_2, 45 g (1.1 moles) of excess calcium metal, and 10 g (0.04 moles) of unconverted Pu (Figure 11.14 of Harmon et al. 1961). A Hanford process flowsheet to produce a 1980-g (8.28-mole) Pu metal button shows 1480 g (36.7 moles) of MgO (from a 880-g crucible and 600 g of packing sand), 1228 g (15.7 moles) of CaF_2, 109 g (0.37 moles) of CaI_2, 60 g (1.1 moles) of CaO, 192 g (4.8 moles) of excess calcium metal, and 35 g (0.15 moles) of unconverted Pu (Hanford 1965 but originally dating from 1957 when the ~2-kg buttons first were made). This latter composition thus is more representative of the SS&C scrap processed by RECUPLEX and matches that processed at the PRF.

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[1] Calciothermic means the exothermic reaction of a compound, in this case PuF_4, with calcium metal.

A 1985 material balance for the bomb reduction process, expected to be very similar to the process used during the time of RECUPLEX operations, is shown in Table 2 (Rodgers 1986).

Table 2. Hanford 1985 Bomb Reduction Material Balance for ≈2000-g Plutonium Button Basis (taken from Appendix A, Exhibit 1B, of Rodgers 1986)

Input			Product				Acceptable Knowledge[a]
Material		Mass (g)	Material		Mass (g)	Mass (%)	Mass (%)
Charge and Reagents	PuF_4	2702	Button	Pu	2030	100	–
	Ca	973	Sand, Slag & Crucible	MgO	1480	46.7	46.5
	I	47		CaF_2	1338	42.2	42.0
Crucible and Sand	MgO crucible	880		CaI_2	54	1.7	1.7
	MgO sand	600		Ca	280	8.8	8.8
				Pu	20	0.6	0.4[b]

(a) From assessment of PFP residual SS&C scrap for disposal (Edwards 2006).

(b) Also contains 0.1 mass% PuF_4, 0.1 mass% PuO_2, and 0.4 mass% SiO_2. Arsenic (<2 ppm), cadmium (<0.1 ppm), chromium (<32 ppm), and lead (<7 ppm) also are listed as toxic metals at their maximum levels based on essential material specifications and observed Pu metal product quality history. Other metals are known to be present but not listed (Edwards 2006).

As shown in Table 2, the Transuranic Waste Certification Program based on "Acceptable Knowledge" or AK for SS&C scrap packaging for disposal during PFP de-inventory provided a composition (Edwards 2006) very similar to that given by Rodgers (1986). However, under AK, the chemical disposition of the Pu is defined beyond elemental (uncoalesced) Pu metal and includes PuF_4 and PuO_2. It is noted that finely dispersed uncoalesced Pu metal would be very susceptible to air oxidation. Silica, SiO_2, is also identified, because it is a constituent in the MgO crucibles and sand at 0.5 wt% maximum according to 1987 Essential Materials specifications (RHO 1987a,b). This Essential Materials specification likely was used to provide the AK estimate. However, in 1958, the Essential Materials specifications for MgO crucibles, maximum 1.5 wt% SiO_2, and MgO sand, maximum 0.15 wt% SiO_2, (Chemical Processing Department 1958) would lead to perhaps 0.6 wt% SiO_2 in the RECUPLEX-processed SS&C.

As also shown in Table 2, the nominal Pu conversion efficiency was about 99%. However, the Pu complement in SS&C scrap occasionally would be much greater, should the charge fail to fully react during bomb reduction, or the Pu metal fail to fully coalesce in forming a button. Such SS&C scrap would be very rich in Pu and prime material for recycle. Studying SS&C scrap from Hanford and other United States plutonium processing sites provides information on the routes to form Pu phases present in waste streams, i.e., failure to react to form Pu metal or failure of the Pu metal to coalesce.

Scientists at Argonne National Laboratory examined Hanford SS&C scrap using transmission electron microscopy and energy dispersive spectroscopy to find CaF_2 and sub-stoichiometric plutonium oxide; i.e., PuO_{2-x} (Behrens et al. 1995). At Los Alamos National Laboratory, X-ray diffraction (XRD) analyses of crushed and sieved SS&C (likely from Los Alamos) showed that the <90-μm fraction was mostly CaF_2. In the same studies, scanning electron microscopy, electron backscatter, and X-ray emission spectroscopy analyses of various SS&C samples showed that the most likely Pu form was as oxide appearing as Pu-rich inclusions in the MgO or CaO/CaF_2 rather than as discrete Pu oxide as noted in the higher magnification Argonne studies (Avens et al. 1989, 1990). Phases identified in SS&C scrap items from Rocky Flats by Savannah River Site scientists were remarkably uniform, with CaF_2, CaO, calcium hydroxide [$Ca(OH)_2$], MgO, and PuO_2 common to all samples, although in different proportions. Calcium carbonate ($CaCO_3$)

also was present in many items (Gray and Korinko 1999). The presence of CaO, $Ca(OH)_2$, and $CaCO_3$ would seem to be from the reaction of calcium metal with moist air.

Significantly, PuF_4 was not observed by XRD in any of the described analyses, even those identified as having “high” Pu concentrations, but CaF_2 invariably was observed. Although failure to coalesce is judged unlikely by a process expert,[1] the combined presence of CaF_2 and high Pu concentrations point to failure of the metal to coalesce, remaining instead widely dispersed within the slag where it would be subject to ready air-oxidation, particularly in the presence of moisture. The broad XRD peaks reported by Gray and Korinko (1999) indicate 10 to 12 nm crystallite size for PuO_2. These small crystallites show that the PuO_2 likely arose by room temperature atmospheric oxidation of Pu metal produced after firing of the reduction charge and not from PuO_2 residues within the reduction charge feed that would have been subjected to the 1500-2000°C bomb reduction temperatures and thus grown to >100-nm crystallites (see Table 3).

Table 3. Mean PuO_2 Crystallite Size as Functions of Starting Compound and Oxidation Temperature

Calcination Temp. (°C)	Crystallite Size[(a)] (nm) for PuO_2 Prepared from:				Calcination Temp. (°C)	Size (nm)
	Nitrate	Peroxide	Oxalate[(b)]	Hydroxide		Metal[(c)]
240	11.5	3.8	4.1	5.6	100	10.5
400	13.0	5.2	5.7	6.1	300	12.2
600	11.8	27.7	13.7	10.0	500	16.7
800	100	48.0	27.5	29.1	700	26.9
1000	100	100	100	55.0	900	44.2

(a) Moseley and Wing 1965.
(b) Similar crystallite sizes for PuO_2 prepared by calcination of Pu(IV) oxalate at 270, 300, 480, 510, 550, and 600°C were 3, 11, 11, 17, 25, and 28 nm, respectively (Pallmer 1956).
(c) Metal air-oxidized at room temperature then calcined at 100, 300, 500, 700, and 900°C (Molen and White 1967).

According to Christensen and Rayburn (1983), reduction misfires result from inadequate heating to melt the slag, not failure of the reaction to occur, and may leave all or part of the Pu metal as powder or finely dispersed metal beads throughout the slag. They attributed the insufficient heating to too great of a fraction of PuO_2 (rather than the intended PuF_4) in the reduction charge. But failure to coalesce also could be from too low temperature before ignition of the charge, after which external induction heating is terminated.

To prepare the solvent extraction solution feed, the SS&C was dissolved in concentrated HNO_3 containing $Al(NO_3)_3$ to complex the fluoride at a 0.33 Al/F mole ratio (Figure 7). This ratio provided enough free fluoride to dissolve the Pu present in the SS&C but maintain sufficiently low fluoride to prevent PuF_4 precipitation. The iodine used in bomb reduction at Hanford would have caused downstream scrap processing problems. Therefore, the iodide was removed in the scrap dissolution step by HNO_3 oxidation to iodate ion (IO_3^-) followed by reduction to elemental iodine by addition of oxalic acid, $H_2C_2O_4$, and steam stripping of the iodine by venting in the dissolver off-gases (Figure 7; see also Procedure 103 in Hanford 1955). Once the iodine was removed, more HNO_3 was added to complete Pu dissolution under vapor reflux conditions. Finally, more $Al(NO_3)_3$ was added to attain a 3.3 Al/F mole ratio. This masking of fluoride by aluminum ion caused the dispersed previously fluoride-stabilized silica

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[1] FAX. 4 August 1999. EA Conrad, KH Nuclear Operations, Rocky Flats, Golden, Colorado, to AM Murray, Westinghouse Savannah River Laboratory, Aiken, South Carolina.

to coagulate, making it more readily filterable. The filtered silica solids were discarded separately but, as will be seen, some also stayed with the solutions going to solvent extraction. Later PRF operations used centrifugation to clarify solutions. The SS&C scrap filtrate solution (and thus RECUPLEX process feed) composition, containing 0.5 g Pu/liter and dissolved Mg^{2+}, Ca^{2+}, Al^{3+}, and AlF^{2+} in 2.5 M HNO_3, is shown in the lower right corner of the flowsheet in Figure 7. The PRF SS&C scrap filtrate would have had a similar composition.

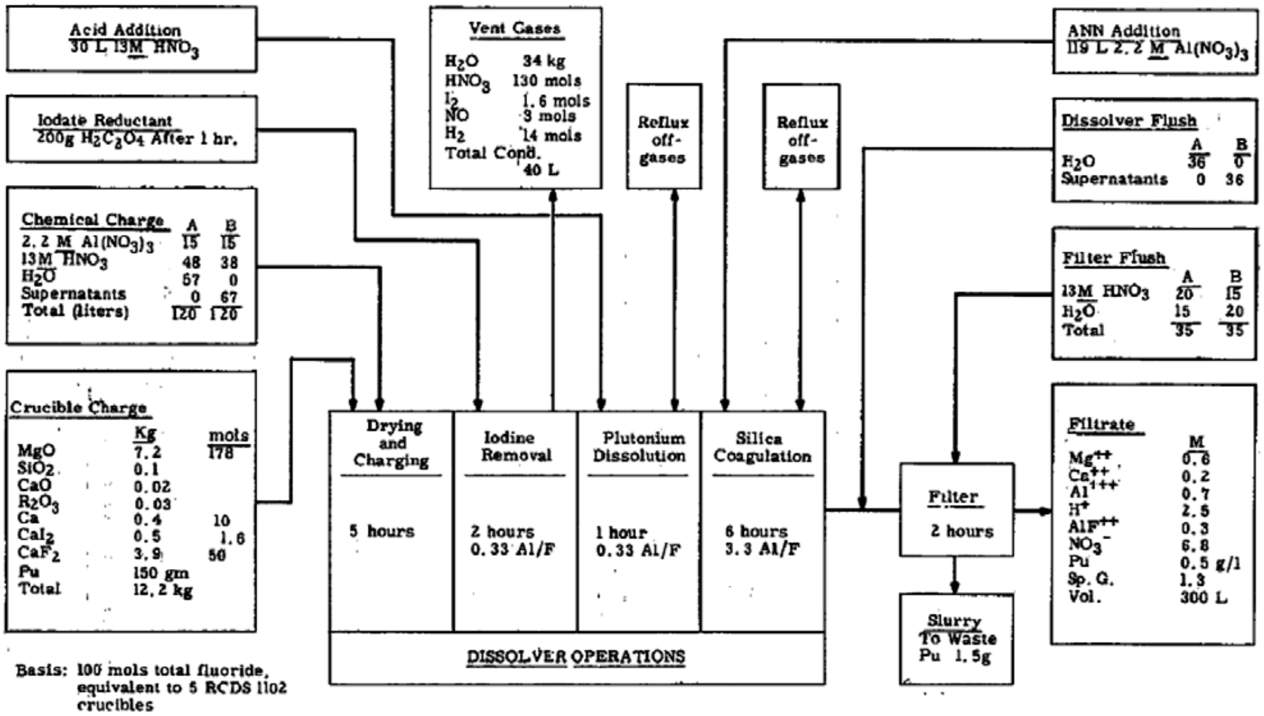

Figure 7. SS&C Dissolution Flowsheet in RECUPLEX (Figure 5 of Judson et al. 1956a)

Scrap from unfired charges or charges that misfired or failed to coalesce Pu metal in bomb reduction were processed according to the flowsheet shown in Figure 8. This scrap would contain much if not all of the original Pu depending on whether any Pu metal button formed. It also would contain iodine in some form and thus require the iodine volatilization step and would contain fluoride as PuF_4 or CaF_2. Reject and spilled PuF_4 also would have been processed through RECUPLEX (Figure 3) and PRF (Figure 4). The PuF_4 was dissolved by itself or with accompanying SS&C scrap in hot concentrated HNO_3. Such fluoride-rich feeds require $Al(NO_3)_3$ to complex the fluoride and yet allow enough fluoride to promote dissolution.

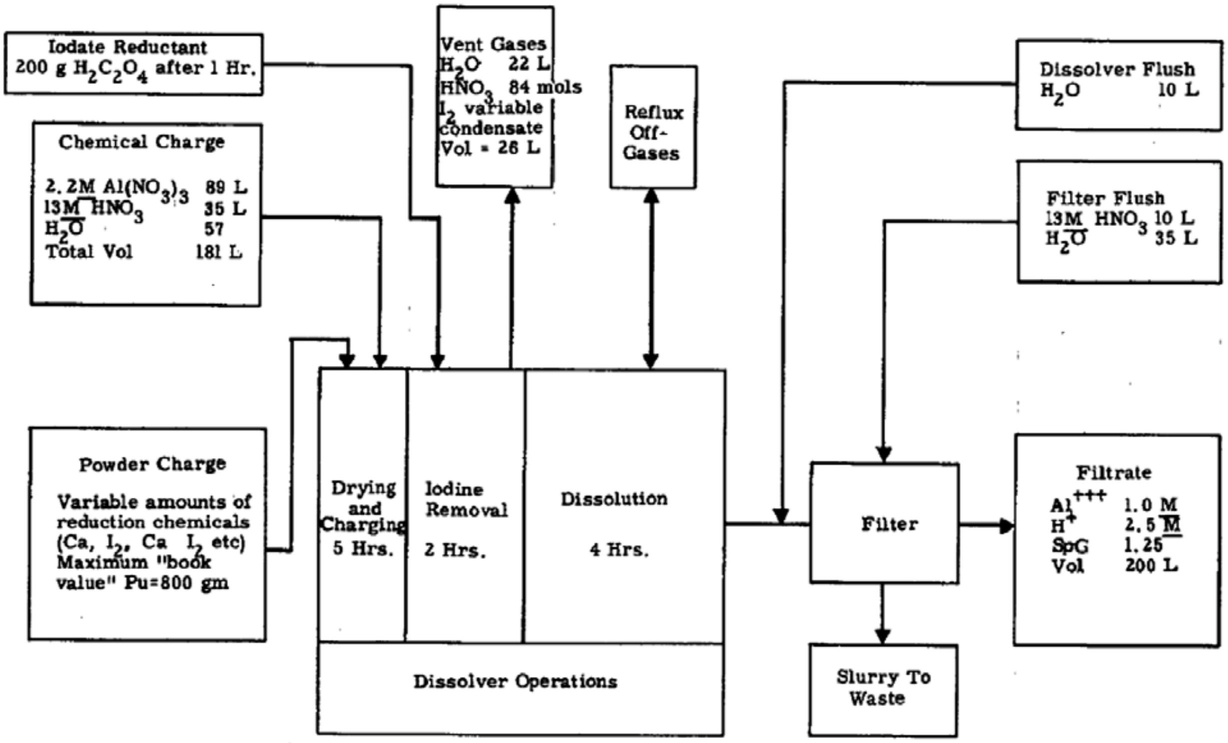

Figure 8. Scrap Dissolution for Reduction Misfire Charges (Figure 7 of Judson et al. 1956a)

The flowsheet to process scrap PuO_2, including from inadequate hydrofluorination, is shown in Figure 9. Such scrap required fluoride, added as sodium fluoride (NaF), to effect Pu dissolution. Once the Pu scrap was dissolved, the excess fluoride was complexed by aluminum ion addition as $Al(NO_3)_3$.

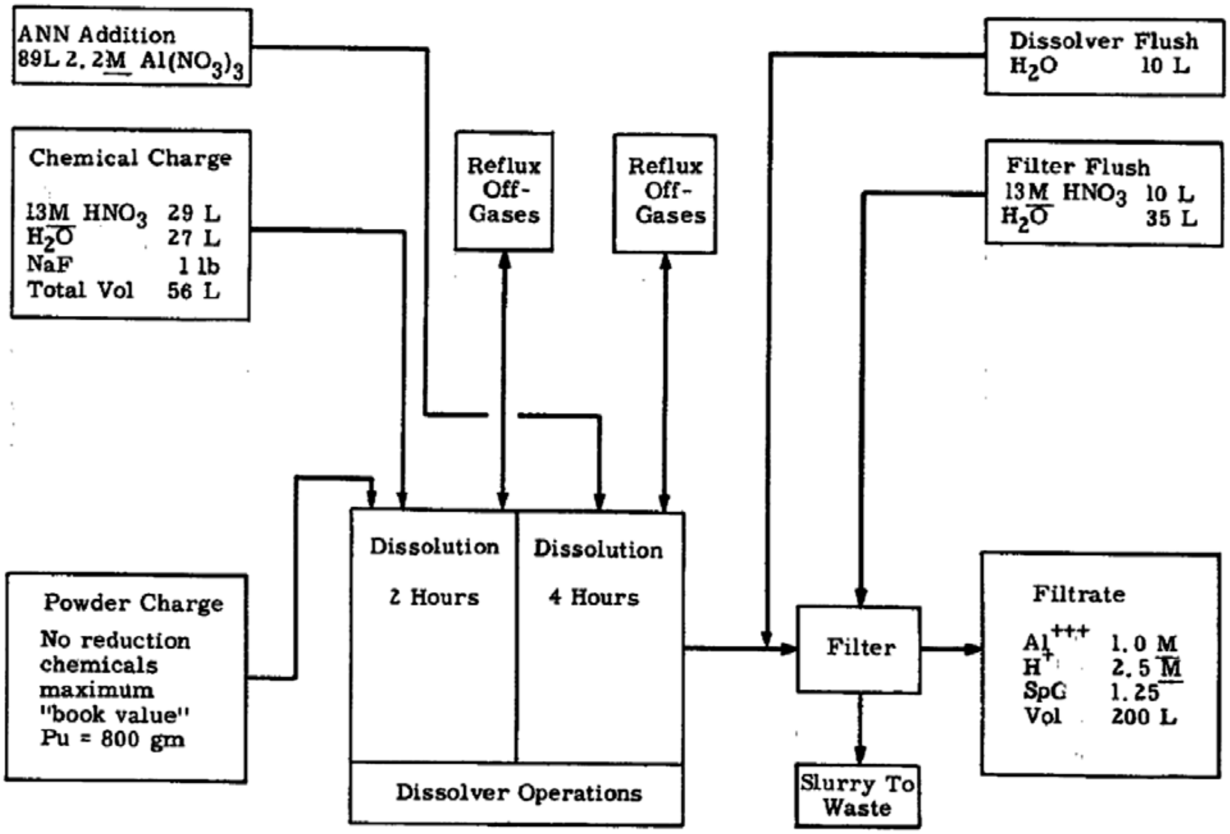

Figure 9. Pu Oxide Scrap Dissolution Flowsheet (Figure 8 of Judson et al. 1956a)

2.3.3 Oxidized Reject Metal, Turnings, and Casting Skulls

According to Figure 2, impure and reject Pu metal, after first being burnt to the oxide, went to RECUPLEX or PRF, respectively, for purification and recycle. However, until May 1961, the Pu metal casting skulls were dissolved in a concentrated HNO_3 solution containing fluoride before being fed to RECUPLEX; after that date, the skulls were first burned to PuO_2 before dissolution (page 9-7 of Gerber 1997). The skull dissolution flowsheet, accommodating both metal and oxide, is shown in Figure 10.

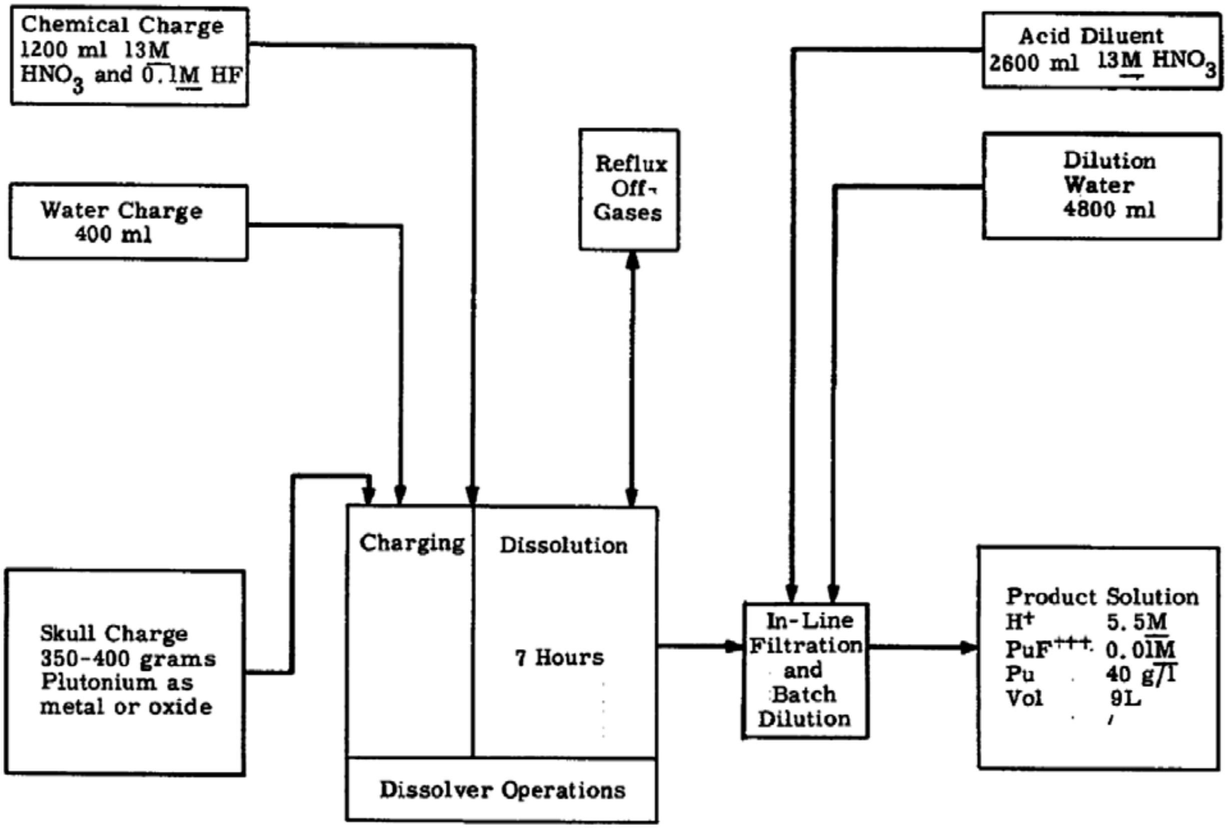

Figure 10. Skull and Oxide Dissolution Flowsheet (Figure 9 of Judson et al. 1956a)

2.3.4 Burning of Plutonium Metal

The first step in recycle of massive Pu metal was burning the metal to PuO_2 (Figure 2). The metal was ignited either by flame (gas torch) or by Calrod-type electrical resistance loops and continued burning until complete or near-complete oxidation. Buttons burn like charcoal, glowing to a bright orange color (see Figure 3 of Haschke et al. 2000) with 930-1000°C internal temperature for bulk 570- to 1770-g pieces (Mishima 1966). The burning buttons were stirred to improve air access and accelerate oxidation.

Felt (1967) investigated the burning characteristics of 1- to 3-kg Pu metal buttons and smaller 0.2- to 1-kg Pu metal pieces (both α-phase), ~0.7-kg δ-phase metal pieces,[1] casting skulls (δ-phase), and turnings, also δ-phase. Felt (1967) described Pu metal button burning as follows:

> *Metal ignition usually required 60 to 70 sec[onds] of torch contact to establish a satisfactory burn. Spread of the burn throughout the metal took 12 to 15 min[utes], and reached a peak temperature of about 825° C. Following the peak temperature, a decrease of 200° C occurred in the next 30 min[utes], leveling to 600° C; with a gradual decrease of 20° C per hour until completely oxidized. The burning metal was a bright cherry-red color with a gradually-increasing surface oxide coating. There was no flaming or flashing from the burning mass. After reaching the peak temperature, the metal was 150° C above its melting point. Containment and extinguishment became a*

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[1] Alloying of α-phase pure Pu metal with gallium stabilized the more readily machinable δ-phase used to fabricate weapons parts.

> *problem of handling molten plutonium metal encased by an oxide-molten metal shell. Any disturbance of the shell would cause the metal to spew.*

Combustion of massive Pu metal pieces is not self-sustaining at later stages because of a relative lack of fuel to sustain high temperatures, smothering by-product PuO_2, oxygen depletion, or nitrogen blanketing. Therefore, the product could be incompletely burnt. The burnt metal would be cooled and collected into slip lid or food pack cans for later processing. With extended storage, sealed food pack cans holding such burnt metal often collapsed inwardly (see also Table 3 of Eller et al. 2004), with the collapse attributed to unburnt metal reacting with atmospheric oxygen or nitrogen within the can to form PuO_2 or plutonium nitride, PuN, respectively. Only by nitrogen consumption is differential pressure (i.e., > 0.2 atmospheres) sufficient to collapse a food pack can. To prevent such collapse during extended storage, complete Pu metal oxidation later was ensured by supplemental furnace heating in air of the initial burnt metal to make so-called “twice-burned” PuO_2. At the time of the intense Pu processing during RECUPLEX and PRF operations, such reburning likely would not have been done because time of storage would be short. This means that some Pu metal was fed with the dominant PuO_2 to the scrap dissolvers.

The Pu oxide formed by burning Pu metal also sinters to form large particles or flakes. In one PFP study, the product of burning a gallium-bearing “Dow metal” button (likely from Rocky Flats)[1] at 600° to 650°C was so coarse that 29 wt% did not pass a 600-µm screen (Campbell and Panesko 1971). According to this report, “Most of this coarse oxide consisted of small layers curled at the edges; with a few bigger, brittle layers which were retrievable with tweezers.” The particulate products of massive Pu metal burnt above 600°C have a bimodal size distribution with mass-based maxima centered at about 30 µm and 600 µm (Haschke 1992). Oxidation of δ-phase Pu metal in ARIES (Advanced Recovery and Integrated Extraction System; at Los Alamos) furnaces within a tumbling basket as well as in a static muffle furnace at ~500°C with completion at ~1000°C yields a trimodal particle size distribution centered at ~2, 15, and 50 µm (Wayne et al. 2018). These particle sizes are much larger than the ~1-2 µm found for Pu metal allowed to oxidize in room temperature air (Wayne et al. 2018). Further details on the nature of burnt metal, including its appearance suggestive of “petrified wood” (Figure 11), are provided in Appendix C and Sections 5.3.2 and 5.3.3 of Delegard and Jones (2015) and references cited therein.[2]

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[1] Rocky Flats was operated at that time by the Dow Chemical Company.

[2] See also Figures 4(A), 4(B), and 4(C) of Wayne et al. 2018 to observe the “petrified wood” appearance of burnt Pu metal.

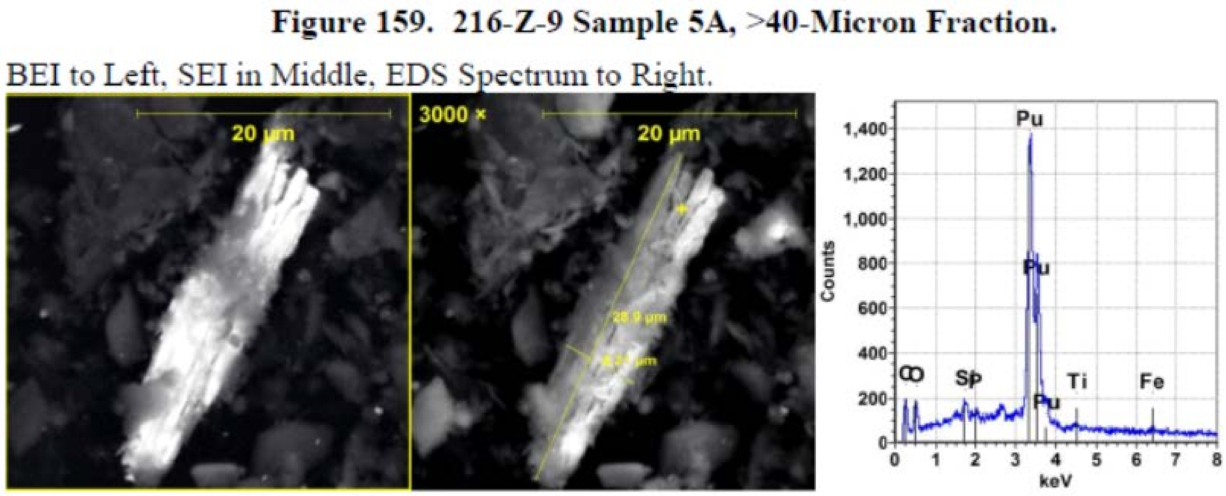

Figure 11. Plutonium-Rich “Petrified Wood” Plutonium Particle from the Z-9 Crib (McCoskey and Cooke 2013)

Gallium used to stabilize the δ-Pu metal phase has been found at 5000 to 9000 parts per million (0.5 to 0.9 wt%), or 1.7 to 3.0 atom%, from weapons parts oxidized by ARIES direct metal oxidation (DMO) at Los Alamos (Wayne 2014). The oxidation occurs in a 75% O_2 / 25% He mixtures held between 475 and 575°C with enough O_2 to satisfy PuO_2 stoichiometry. The oxide “chips” and powder are then calcined for an additional 130-135 minutes at 950-1040°C in the 75:25 O_2:He mixture. Gallium disposition after DMO is not known but likely is as gallium sesquioxide, Ga_2O_3. Gallium present in burnt recycle δ-Pu metal being processed by RECUPLEX and PRF would be dissolved by HNO_3/HF, and, being inextractable, would be discharged with other impurities (e.g., Al, Fe) in the respective solvent extraction raffinates.

2.3.5 Disposal of Fabrication Oil

δ-Pu metal alloyed with gallium was fabricated into nuclear weapons parts at the PFP by ordinary machining methods using lathes and cutting tools. The cutting lubricant/coolant for machining was 50 vol% lard oil diluted in CCl_4. This lubricant/coolant was called fabrication oil or fab oil (Appendix A of Last and Rohay 1993). The lard oil is pig fat; i.e., triglycerides (esters of organic acid groups on glycerin backbone) of variable composition. The organic acid groups include saturated (primarily palmitate and stearate) and unsaturated (primarily oleate and linoleate) groups (Herb 1960). The machined metallic Pu parts were rinsed with CCl_4 to remove the fab oil, thus diluting the lard oil complement to about 25 vol%. The fab oil and rinse were filtered to remove the Pu turnings and chips. As shown in Figure 4, the fab oil was treated with HNO_3 containing HF in the “Fab Oil Column” with the aqueous phase containing the dissolved Pu going for recycle.

In RECUPLEX, the clarified and acid-treated fab oil and rinse were discarded to the Z-9 crib. Fabrication of weapons parts at PFP ceased in mid-December 1965. The PRF, which began operations on 6 May 1964 (page 12-6 of Gerber 1997), reportedly received a “minor amount” of triolein (page 14 of Price et al. 1979).[1] The 216-Z-1A crib received the PRF wastes, including the treated fab oil, from start of PRF operations until April 1969 with minor amounts of the PRF wastes also going to the adjacent 216-Z-1 and -2 cribs (page 14 of Owens 1981).

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[1] The description of the compound as triolein, $(C_{17}H_{33}CO_2)_3C_3H_5$, is likely a misstatement. Triolein is a symmetric triglyceride based on three monosaturated oleate groups on a glycerol backbone and thus differs from lard.

Because the fab oil was discarded with the acidic aqueous waste and was treated with HNO_3/HF to dissolve the contained Pu metal and oxide, triglyceride hydrolysis to the constituent saturated and unsaturated organic acids and glycerol is likely. Further oxidation reactions also are likely, especially in the presence of nitrate and iron. The composition and distribution of the lard oil breakdown products is unknown but plausibly would include hydroxy carboxylic acid or other organic species that could complex Pu and Am.

2.3.6 Disposal of RECUPLEX and PRF Solvent Extraction Raffinates, and 242-Z Raffinates

The raffinates from RECUPLEX solvent extraction were disposed to the Z-9 crib by way of three waste tanks (L-2, L-3, and L-8) within the PFP. Samples were taken of each 1000-liter waste batch to ensure that the Pu concentration was below 0.013 g Pu/liter (Teal 2007). The solutions were treated with 50% (~19 M) NaOH solution to a point just short of precipitating solids (page 25 of Hanford 1955; pH ~2.5, pages 71-73 of Judson et al. 1956b), meaning the solutions still contained a high complement of acid capacity given the ~0.84 M aluminum present in the waste from the combined feed and strip solutions. During operations, a waste tank was drained about every 8 hours.

PRF operations commenced on 6 May 1964 with Z-1A receiving its wastes, May 1964 to April 1969 (page 14 of Owens 1981). From August 1964, the PRF solvent extraction raffinate, the CAW, was processed to remove Pu traces and Am through the 242-Z waste treatment facility (Owens 1981; Chapter 11 of Gerber 1997). Neutralization of acid from the CAW took place to prepare the feed for Am and Pu removal at 242-Z. In the end, the combined PRF aqueous waste composition was like that of the RECUPLEX wastes. A “minor amount” of triolein; i.e., fab oil; reflecting the cessation of weapons parts fabrication at PFP in mid-December 1965 and working off the RECUPLEX fab oil backlog (pages 3-6, 12-6, and 15-1 of Gerber 1997) also took place at PRF. The organic wastes from the PRF and 242-Z processing included CCl_4 diluent and the TBP and DBBP solvent extractants.

2.3.7 Formation of Solvent Extraction Crud

Crud consists of solvent-based organic materials and/or inorganic materials that exist as either solids or gummy precipitates from the aqueous and organic layers in solvent extraction processes. Crud generally aggregates at the aqueous-organic interface but also can collect on equipment surfaces.

Ritcey (1980) gave the following definition of crud in a review:

> *Crud is defined as the material resulting from the agitation of an organic phase, an aqueous phase, and fine solid particles, that form a stable mixture. Crud usually collects at the interface between the organic and aqueous phases. Other names that have been used for the phenomena are grungies, mung, gunk, sludge, etc.*

The International Union of Pure and Applied Chemistry, IUPAC, defines solvent extraction crud as (Rice et al. 1993):

> *A deposit or emulsion at the interface between two partially settled phases. Notes:*
>
> i. *The phenomenon of crud formation arises from many causes and this definition does not imply any single one.*
>
> ii. *Other terms – some unprintable – have been used but crud is the generally accepted term.*

RECUPLEX experienced difficulties with crud. An early crud observation and characterization (Brunstad 1958) showed that silica and TBP breakdown products were involved with

> *. . . extraction column emulsification to be related to the presence of tributyl phosphate disintegration products and hydrocarbon oil in a feed tank. Dispersed silica contributed to the emulsification. Silica dispersion is related to high fluoride concentration and an insufficient aluminum to fluoride ratio.*

The crud also contained aluminum, phosphorus, calcium, and magnesium, all of which would be expected in dissolved SS&C scrap being extracted by TBP. The presence of hydrocarbon oil is surprising as the RECUPLEX diluent is CCl_4 and suggests that the TBP or perhaps the CCl_4 was contaminated. In the same study, a separate sample of interface crud was washed with water, causing formation of a white slow-settling solid in the aqueous phase and a gray organic, which, with further washing with CCl_4, formed “gelatinous translucent beads.” The white solids and the gelatinous beads contained silica as a major constituent and minor amounts of aluminum, phosphorus, calcium, and magnesium. DBBP also was investigated and tested at RECUPLEX as a solvent (page 11-1 of Gerber 1997) and could have contributed to crud.

Emulsification in the RECUPLEX solvent-extraction process was exacerbated by processing of more concentrated feeds containing correspondingly higher loads of scrap impurities including silica. Silica gels form by the action of acid on certain mineral types (Terry 1983). While some silicate minerals are impervious to acid attack, other silicate minerals break down completely in acid, with the metallic cations and the silica dissolving completely. The silica then exceeds its solubility, polymerizes, and precipitates as gel. Some other silicate minerals lose their cations and leave a siliceous residue. The solubility of silica as functions of temperature and HNO_3 concentration is shown in Figure 12.

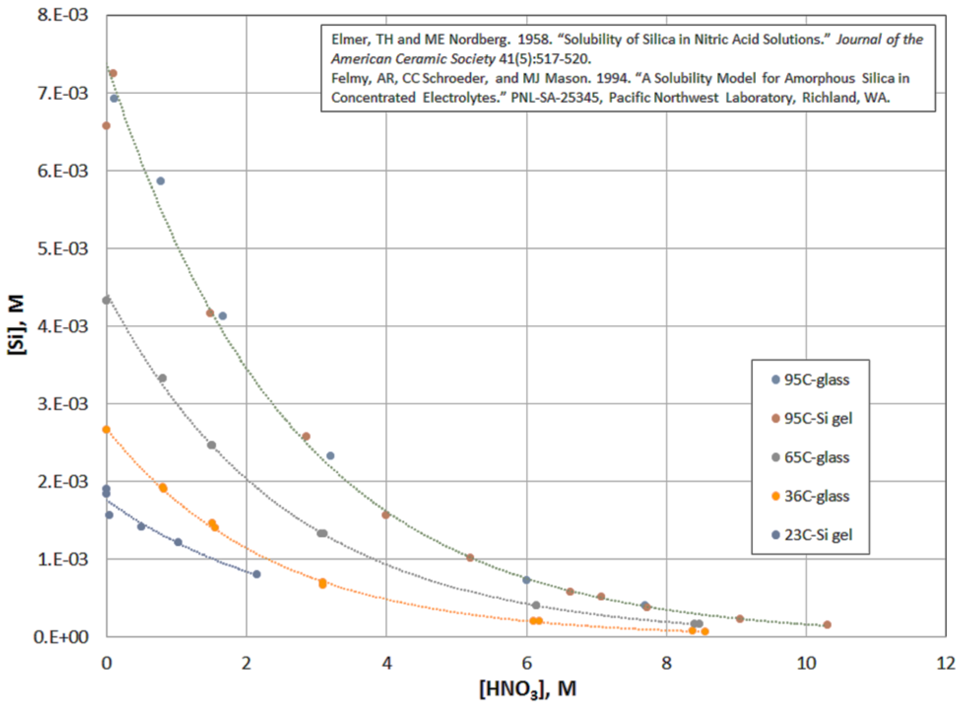

Elmer, TH and ME Nordberg. 1958. “Solubility of Silica in Nitric Acid Solutions.” *Journal of the American Ceramic Society* 41(5):517-520.
Felmy, AR, CC Schroeder, and MJ Mason. 1994. “A Solubility Model for Amorphous Silica in Concentrated Electrolytes.” PNL-SA-25345, Pacific Northwest Laboratory, Richland, WA.

Figure 12. Solubility of Silica in Nitric Acid (Elmer and Nordberg 1958; Felmy et al. 1994)

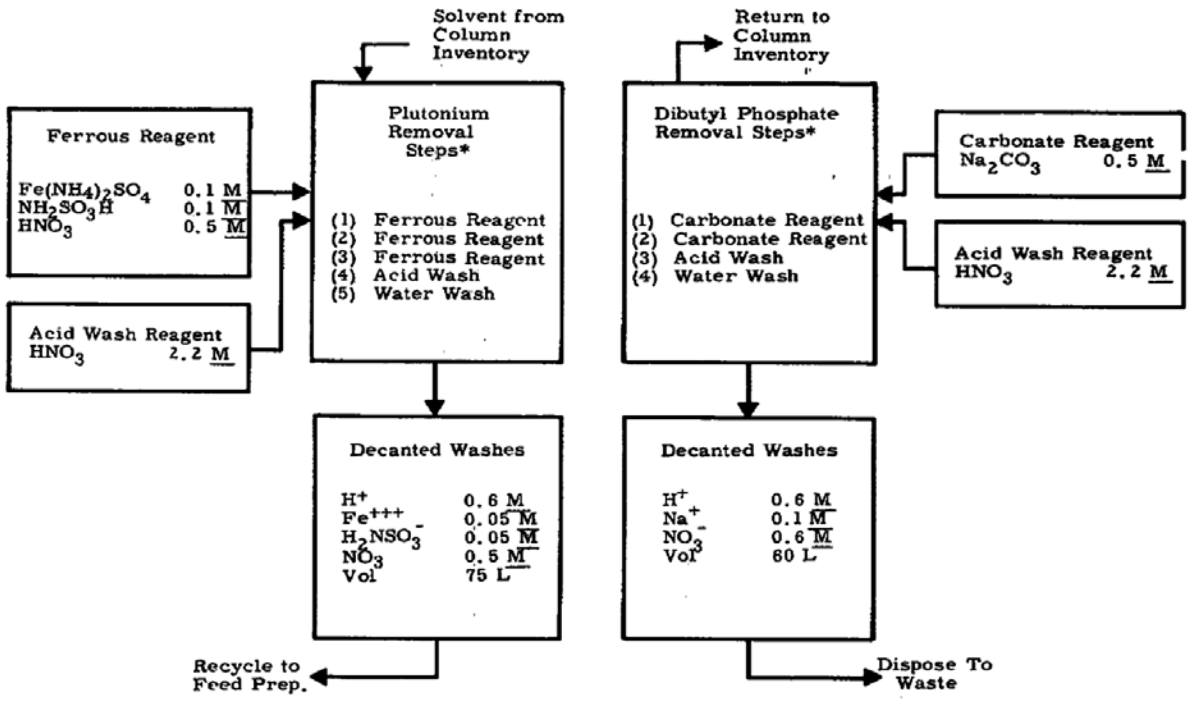
Suspended scrap impurities in the RECUPLEX Process could be coagulated by addition of 50 to 100 parts per million, by weight, of a fine powder talc, $MgSiO_3$, trade named Mistron® (Bruns 1959b). The action of Mistron is described in a more recent PRF flowsheet document (PFP Process Engineering Group 1988, Section 3.2.10):

> *The surface(s) of the Mistron particles have organophilic and hydrophilic properties. These characteristics allow the Mistron particles to be suspended in the aqueous phase and have an organic controlling surface. The Mistron reduces the potential for the formation of emulsions and column flooding by* neutralizing *electric charges of particles suspended at the aqueous-organic interface. This reduces repulsion between aqueous bubbles making coalescence easier (Bruns 1959b). The aqueous-organic phase disengaging time and Mistron concentration are related. Generally, higher concentrations of Mistron are required to provide adequate disengaging times for conditions of high salt, mass transfer and organic coated solids (crud)….*

The Mistron® localized the solids at the organic/aqueous interface by coagulation and thus helped phase disengagement. The coagulated solids then were removed periodically by moving the interface up the column where the solids could be decanted, assayed for contained Pu, processed for Pu recovery if necessary, or, if low in Pu concentration, discarded to the Z-9 crib. Mistron® also was used in the PRF. Further description of interfacial cruds, the roles of DBP, silica, other finely flocculent solids, and entrainment of Pu-bearing particles from incompletely dissolved scrap is provided in an overview of crud within Hanford TBP-based extraction processes (Delegard and Casella 2016).

2.3.8 Solvent Treatment and Disposal

The TBP solvent in CCl_4 was found to accumulate "unstrippable" Pu through the buildup of DBP and its strong complexation with Pu(IV). The DBP forms by radiolytic and acid-catalyzed hydrolytic decomposition of TBP. Solvent treatment occurred in two steps, as shown in Figure 13. The first step was removal of Pu from the DBP complex by its chemical reduction to Pu(III) using a solution of 0.1 M ferrous ammonium sulfate [$Fe(NH_4)_2(SO_4)_2$] and 0.1 M sulfamic acid (H_3NSO_3) in 0.5 M HNO_3 followed by a 2.2 M HNO_3 wash to rinse out the iron. The combined Pu-bearing solution was returned for solvent extraction processing and recovery of Pu values. The second step was treatment of the solvent with 0.5 M sodium carbonate (Na_2CO_3) solution, removing the water-soluble DBP, and then treating the solvent with 2.2 M HNO_3 to restore the acid-loaded form suitable for solvent extraction service. The TBP-CCl_4 extractant also was adjusted to maintain the proper 15 vol% TBP concentration.



*Basis: 200 L solvent; each wash to be 15 L in volume; contact time 10 minutes.

Figure 13. Solvent Treatment for Plutonium and DBP Removal (Figure 28 of Judson et al. 1956b)

3.0 Estimate of Materials Discarded to Waste Sites in the 200 West Area

3.1 Estimate of Materials Discarded to 216-Z-9

In April 1973, about 11 years after the closure of RECUPLEX, a key engineer knowledgeable in RECUPLEX operations estimated the quantities of material discharged to the Z-9 crib (Bruns 1973). This estimate, refined as will be discussed, is shown in Table 4, assuming that the masses were in English (not metric) tons. The crib received 4.09×10^6 liters of waste solution over its July 1955 – June 1962 life (Table 13 and page 53 of Owens 1981), of which 163 metric tons (1.09×10^5 liters at 1.5 g/cm^3 solution density) are CCl_4-based organic solution as extractant and machining fluids, leaving 3.98×10^6 liters of aqueous waste. The carbonaceous material listed with the solids in Table 4 would include the solvent-softened plastics and glovebox gloves (based on Appendix L of Smith 1973). The total 900-kg estimated inventory of cadmium, Cd, in the crib evidently was used for criticality safety during process operations. Another ~11 kg of Cd was added as ~1100 liters of 10 g Cd/liter solution in August 1973 to provide supplemental neutron absorption criticality safety margin (Smith 1973). The 50% NaOH used to adjust the waste to pH 2.5 was overlooked in Bruns' 1973 summary but is included here as described in footnote "d" to Table 4. The cation:anion balance, not including the chloride arising from in-ground CCl_4 decomposition, is 1.02:1 based on the data shown in Table 4.

Table 4. RECUPLEX Inputs to the Z-9 Crib (Bruns 1973)

		Constituent Inventory		
Constituent	Compounds	Metric Tons	10^6 moles	Average Aq. Conc. (M)(a)
Al	$Al(NO_3)_3$, $Al(OH)_3$, $AlF(OH)_2$; small amounts of Al_2O_3, $Al_2(SO_4)_3$, $AlCl_3$	91	3.36	0.84
Mg	$Mg(NO_3)_2$, $Mg(OH)_2$; possibly some $MgSO_4$, $MgCO_3$, $MgCl_2$	32	1.31	0.33
Ca	$Ca(NO_3)_2$, $Ca(OH)_2$, CaF_2; small amounts of $CaSO_4$, $CaCO_3$	27	0.68	0.17
Fe	$Fe(NO_3)_3$, $Fe(OH)_3$, FeF_3; small amounts of $Fe_2(CO_3)_3$, $Fe_2(SO_4)_3$	23	0.41	0.10
Cr, Pb, Ni	As nitrates and hydroxides	1.8	0.030	0.0076
Hg(b)	$Hg(NO_3)_2$, $Hg(OH)_2$	0.09	0.00045	0.00011
Cd	$Cd(NO_3)_2$, $Cd(OH)_2$	0.82	0.0073	0.0018
Ga (c)	$Ga(NO_3)_3$	0.00013	0.0000018	0.00000046
Na (d)	$NaNO_3$	206	8.96	2.25
Pu	PuO_2, $Pu(SO_4)_2$, $Pu(OH)_4$, $Pu(OH)_x$, PuF_4, $PuCl_4$, $Pu(CO_3)_2$, $Pu(NO_3)_4$	0.09	0.00038	0.00010
Am	Am_2O_3, $Am(NO_3)_3$, $Am(OH)_3$	0.0023	0.0000094	0.0000024
NO_3	Metal nitrates	1361	21.9	5.51
F	AlF^{2+}	27	1.43	0.36
SO_4	$CaSO_4$, $Al_2(SO_4)_3$, $Pu(SO_4)_2$	1.8	0.019	0.0047
OH(d)	$Al(NO_3)_2OH$	6.1	0.398	0.10
Cl	From CCl_4 deteriorating to HCl, CO, CO_2	91	2.56	0.64
Solids	SiO_2, Al_2O_3, $Fe_2(DBP)_3$, $CaSO_4$, $Al_2(CO_3)_3$, $MgSiO_3$, carbonaceous material, other metallic DBP – e.g., Cr	5.4		
Organic extractants	15-25% TBP in CCl_4, DBBP, trace MBP *(apparently as liquids; DBP is present with solids)*	109		
Mach. Oils	50% lard oil in CCl_4	54		
Total		1954		

(a) Average concentration assuming 3.98×10^6 liters total aqueous waste solution volume.

(b) Not included in Bruns (1973). Mercuric nitrate was used to catalyze Pu-Al alloy scrap dissolution in HNO_3 (page 11-2 of Teal 2007).

(c) Not included in Bruns (1973). The actual quantity of gallium from δ-Pu metal scrap – e.g., casting skulls, reject alloy, and turnings/chips – is unknown but estimated to be present in 20% of the total Pu recycled (Figure 2). Gallium is estimated to be 0.7 wt% of δ-Pu. Thus, the total Ga in Z-9 is (100 kg Pu × 0.2 × 0.007 =) 0.14 kg.

(d) Not included in Bruns (1973). Plant operations used 50% NaOH solution to adjust RECUPLEX raffinates to pH 2.5 prior to discharge and sporadically Na_2CO_3 to remove DBP from solvent (Figure 3). The sodium estimate is based on 3.98×10^6 liters of combined solvent extraction raffinate and back-extraction solution containing 2.15 M HNO_3 (Figure 2) without hydrolyzing the 0.84 M $Al(NO_3)_3$ (pH ~1.55) in the waste. Reaching pH 2.5 for 0.84 M $Al(NO_3)_3$ would require an additional ~0.1 M NaOH above that needed to neutralize HNO3 [Figure IV-14(b) of REDOX 1951] such that (2.15 + 0.10 =) 2.25 M acid was neutralized requiring ($3.98\times10^6 \times 2.25$ =) 8.95×10^6 moles of NaOH or ~206 tons of sodium. The Na_2CO_3 quantity used in solvent treatment and discarded to the crib was much smaller, impossible to estimate, and thus was ignored.

The organic compound quantities disposed to the 216-Z-9 crib are shown in Table 5. The ~450 metric tons total mass of the TBP and DBBP extractants and the lard oil, all in CCl_4 diluent, is nearly three-times greater than the 163 tons estimated by Bruns (1973). As shown in a Table 5 note, even greater estimates were made in 1991 by process engineer and operator recollections of total CCl_4 discards.

Table 5. RECUPLEX Organic Compound Inputs to the Z-9 Crib (Rohay et al. 1994 and references therein)

Compound	Density (kg/L)	Molecular weight (g/mol)	Volume (L)	Mass (metric tons)	10^3 moles
CCl_4	1.59	153.82	233,000 [a]	370	2408
TBP	0.973	266.32	27,900	27.1	102
DBBP	0.946	250.31	46,500	44.0	176
Lard oil	0.92	859.74 [b]	9,300	8.56	10

(a) Total CCl_4 estimates range from 83,000 liters (based on Owens 1981, which was derived from Bruns 1973) to 300,000 liters (based on 1991 interviews of RECUPLEX managers, engineers, and technicians); page B-12 of DOE (1991). The 233,000-liter CCl_4 estimate from Rohay et al. (1994) is based on quantities of TBP, DBBP, and lard oil and the complementary quantities of CCl_4 associated with the 15 volume% TBP, 50 vol% DBBP, and 25 vol% lard oil streams.

(b) Lard oil molecular weight estimate based on constituent fatty acid analyses given by Herb et al. (1959).

3.2 Estimate of Materials Discarded to 216-Z-1A

The nominal aqueous waste composition received at 216-Z-1A from the PRF May 1964 until April 1969 was 0.15 M HNO_3, 0.2 M $Al(NO_3)_3$, 0.3 M $AlF(NO_3)_2$, 0.3 M $Mg(NO_3)_2$, 0.2 M $Ca(NO_3)_2$, and 0.95 M $NaNO_3$; the organic waste contained TBP, DBBP, and CCl_4 (pages 14-19 of Owens 1981). Relatively dilute and pH neutral lab and process wastes with ~35 g Pu were received at Z-1A from June 1952 until March 1959 but are negligible compared with the PRF wastes. The Z-1A wastes from the PRF thus had higher HNO_3 concentration but lower Al, Na, and total ionic strength, including total acid capacity (equivalent concentration to reach neutral pH), than the disposed RECUPLEX wastes (composition shown in Table 4). However, an early PRF flowsheet indicates that, like for RECUPLEX, 50 wt% NaOH solution was used to adjust the waste solution to pH 2.5 prior to its discharge to the crib (Figure 4 of Bruns 1963). Given that the PRF feeds and process chemicals contained little sodium, the relatively high (0.95 M) $NaNO_3$ concentration suggests that at least partial neutralization of HNO_3 by NaOH occurred, and this is supported by the NaOH adjustment made in Am removal and Pu polishing processing in 242-Z. The supplemental NaOH required to adjust the remaining 0.15 M HNO_3-bearing waste also containing 0.2 M $Al(NO_3)_3$ to pH 2.5 would be about 0.01 M NaOH above that needed to neutralize the HNO_3 [based on Figure IV-14(b) of REDOX 1951] or ~0.16 M NaOH total. This would increase the final $NaNO_3$ concentration by the same amount. The resulting nominal aqueous waste composition thus would be 0.2 M $Al(NO_3)_3$, 0.3 M $AlF(NO_3)_2$, 0.3 M $Mg(NO_3)_2$, 0.2 M $Ca(NO_3)_2$, and 1.11 M $NaNO_3$ assuming negligible (<1%) solution volume increase incurred by use of 50 wt% (~19 M) NaOH for pH adjustment.

The aqueous solution volume discharged to the 216-Z-1A crib from PRF operations beginning May 1964 until the crib was retired in April 1969 was 5.2 million liters. These discards contained 57.4 kg of Pu (page 14 and Table 3 of Owens 1981). A further 1 million liters of pH-neutral solution was received in the adjacent Z-1 crib from non-PRF PFP operations between June 1949 and March 1959 (page 14 and Table 2 of Owens 1981), but this solution is assumed to have drained to the water table in the intervening 62 months before PRF startup in May 1964. The aqueous inputs to the 216-Z-1A crib from PRF operations are shown in Table 6 based on the data of Owens (1981) and the above discussion.

Table 6. PRF Aqueous Inputs to the Z-1A Crib from the PRF (Owens 1981)

Constituent	Compounds[(a)]	Constituent Inventory[(b)] Metric tons	Constituent Inventory[(b)] 10^6 moles	Avg. Aq. Conc., M
Al	$Al(NO_3)_3$	28.1	1.04	0.2
	$AlF(NO_3)_2$	42.1	1.56	0.3
Mg	$Mg(NO_3)_2$	37.9	1.56	0.3
Ca	$Ca(NO_3)_2$	41.7	1.04	0.2
Fe	$Fe(NO_3)_3$	87.1	1.56	0.3
Na[(c)]	$NaNO_3$	132.7	5.77	1.11
F	AlF^{2+}	29.6	1.56	0.3
NO_3	Metal nitrates	1164	18.77	3.6
Pu	PuO_2, $Pu(NO_3)_4$	0.0574	0.000240	4.6E-05
Am[(d)]	Am_2O_3, $Am(NO_3)_3$, $Am(OH)_3$	0.0014	0.0000058	1.1E-06
Total		1563		

(a) Other constituents and their compounds were present at lower concentrations (similar to 216-Z-9 receipts; see Table 4: e.g., Ga, Cr, Ni, Pb, sulfate, chloride, and DBP) but were not reported by Owens (1981).

(b) Inventory based on 5.20×10^6 liters total aqueous waste solution volume (Owens 1981).

(c) Not all $NaNO_3$ included in Owens (1981). Plant operations used 50% NaOH solution to adjust PRF raffinates to pH 2.5 prior to discharge (Figure 4 of Bruns 1963) and 0.1 M Na_2CO_3 in 0.1 M NaOH was used to remove DBP from solvent (Figure 2 of Bruns 1967). Owens (1981) estimated 0.95 M $NaNO_3$ and 0.15 M HNO_3. Based on 5.20×10^6 liters of aqueous waste discharge (Owens 1981) and 0.2 M $Al(NO_3)_3$, the 0.15 M HNO_3 in the waste would require 0.15 M NaOH plus an additional ~0.01 M NaOH above that needed to neutralize HNO_3 to reach pH 2.5 [Figure IV-14(b) of REDOX 1951] such that (0.95 + 0.16 =) 1.11 M $NaNO_3$ was present in the final waste. The quantity of Na_2CO_3 and NaOH used in solvent treatment and discarded to the crib was much smaller, not reported, and thus was ignored.

(d) The Am quantity was estimated based on the Am/Pu ratio shown in Table 4 for Z-9 and the reported inventory of Pu in Z-1A. Subsequent decay of an unknown amount of ^{241}Pu would increase the Am quantity present in the Z-1A crib.

As was the case for RECUPLEX and its discharges to the Z-9 crib, the PRF also discharged organic compounds to the Z-1A crib. The same four organic compounds – CCl_4, TBP, DBBP, and lard oil – were discharged. The quantities and volumes were estimated as seen in Table 7 (based on Table A-4 of Rohay et al. 1994).

Table 7. PRF Organic Compound Inputs to the Z-1A Crib (Rohay et al. 1994 and references therein)

Compound	Density (kg/L)	Molecular Weight (g/mol)	Volume (L)	Mass (metric tons)	kmoles
CCl_4	1.59	153.82	171,000	272	1768
TBP	0.973	266.32	23,900	23.3	87
DBBP	0.946	250.31	27,500	26.0	104
Lard oil	0.92	859.74 [a]	11,000	10.1	12

(a) Lard oil molecular weight estimate based on constituent fatty acid analyses given by Herb et al. (1959).

3.3 Dilute Waste Collection in the 241-Z-361 Tank and Its Discharge to the 216-Z-12 Crib

Another major plutonium-bearing waste ground disposal structure associated with PFP operations was the 216-Z-12 crib. This crib received a composited mix of so-called “low-salt” wastes from several PFP sources. These wastes were collected in the ~4900-ft^3 (~139,000-liter) liquid volume 241-Z-361 settling tank (Jones 1998). The 241-Z-361 tank discharge went to Z-12 from March 1959 until May 1973, a period of high Pu processing throughput at the PFP. The 241-Z-361 tank, in turn, was fed by five cylindrical stainless-steel stirred tanks: D-3, D-4, D-5, D-6, D-7, and D-8 (pages 16-19 of Kasper 1982).

The waste sources, and their associated descriptions, volumes, and Pu contents, are shown in Table 8 (based on Table 1 of Jones 1998). The volume is dominated (~81%) by the vacuum-jet eductor water used to scrub excess HF gas from the hydrofluorination of PuO_2 used to produce PuF_4; this stream contained ~11% of the total Pu. The Pu associated with the hydrofluorinator waste would be in the form of PuF_4 with perhaps 5% of the plutonium present as unconverted PuO_2. The Pu burden in the 241-Z-361 waste is dominated (~69%) by the alkaline scrubber solution used to treat the off-gases from the scrap incinerator (building 232-Z; see Figure 2). Though high in plutonium quantity with the Pu present as PuO_2, the incinerator scrubber stream constituted only ~0.26% of the total waste volume sent to 241-Z-361. The Pu present in the remaining waste feeds to 241-Z-361 (~20% of the total Pu in ~13% of the volume) largely would have been in acidic aqueous solution.

Table 8. Low-Salt Aqueous Process Streams 1969 Discharge Rates from PFP Going to 241-Z-361 (Jones 1998)

Stream	Source	Volume (liters/year)	Pu (g/year)	Chemical Constituents
Uncontaminated lab wastes	Cooling equipment in lab	4.81×10^5	0	None
Contaminated lab wastes	Lab sink drains	6.59×10^5	100	Misc. lab chemicals
Waste treatment aq. wastes	Ion exchange	3.26×10^5	60	Al, Ca, Mg nitrate
Incinerator scrubber	Caustic scrubber solution	2.3×10^4	600	NaOH
PRF condensate	PRF product concentrators	2.04×10^5	12	Dilute HNO_3
Hydrofluorinator off-gas jet	Water from vacuum jet	7.214×10^6	100	Dilute HF
	Total	8.907×10^6	872	

The constituents in the wastes sent to 241-Z-361 during 1969 operations were estimated as shown in Table 9 (based on Table 2 of Jones 1998, assuming 8.907×10^6 liters total volume as shown in Table 8 and including acid, H^+, to achieve cation:anion charge balance).

Table 9. Process Chemical Discharge as Low-Salt Waste to 241-Z-361 in 1969 (Jones 1998)

Constituent	Mass (kg)	Concentration (M)[(a)]
H^+		3.18×10^{-2} [(b)]
Al^{3+}	96	3.99×10^{-4}
Ca^{2+}	320	8.96×10^{-4}
Mg^{2+}	128	5.91×10^{-4}
Mn^{2+}	13	2.66×10^{-5}
Na^+	7394	3.61×10^{-2}
F^-	6100	3.60×10^{-2}
NO_3^-	19904	3.60×10^{-2}
Pu	0.87	4.09×10^{-7}

(a) Assuming 8.907×10^6 liters total solution volume; Table 1, based on the similar Pu quantities.
(b) Concentration to achieve charge balance.

If the waste were treated with soda ash (sodium/potassium carbonate) to reach pH 10 (page 18 of Kasper 1982) or with NaOH solution to achieve pH 8 (page 18 and 21 of Kasper 1982) or 10-12 (page 17 of Jones 1998), the Na^+ concentration would increase by the equivalent initial acid concentration to give ~0.068 M total sodium in the treated solution for discharge to the Z-12 crib. At this pH, most of the aluminum would precipitate and the discharged solution composition would be ~0.036 M NaF, 0.032 M $NaNO_3$, 0.0009 M $Ca(NO_3)_2$, 0.00059 M $Mg(NO_3)_2$, and 0.000027 M $Mn(NO_3)_2$. It is likely that the manganese would be oxidized to form very low solubility MnO_2 and precipitate in the 241-Z-361 tank. These dissolved salt concentrations would be broadly representative of the concentrations discharged over the lifetime of Z-12 operations. Based on many of the same data, similar, although not identical, concentrations were derived in Kasper's study (Table 5 of Kasper 1982).

The various plant wastes entered the rectangular 241-Z-361 tank (~7.8 meters long, 4.5 meters wide, and ~5.1 to 5.4 meters deep, with sloped bottom) at one end through a baffled inlet to decrease turbulence and overflowed through the opposite, deeper, and baffled outlet end, about 7.8 meters away. The working liquid depth of the tank averaged ~4.4 meters, about 0.9 meters below the tank ceiling to provide the original 138.8 m^3 working volume.

Ignoring any solids buildup in the tank bottom, the nominal waste residence time in the tank at the throughput rates shown in Table 8 would have been about 137 hours. The solids depth in 1977, after its last discharge to Z-12, was about 2.3 meters (inferred from 90-inch segment length in a sludge sample; page 8 of Jones 1998). The sludge depth in 1999 was 2.00 meters at the shallow end and 2.30 meters at the deepest end of tank 241-Z-361 and the sludge volume ~67 m^3 (Section 3.3.3.2 of Hampton and Miller 2001). Therefore, at the end of service, the working depth of the tank was only ~2.1 meters and the residence time approximately halved to ~65 hours, allowing more easily suspended particles, including those of Pu, to wash to the Z-12 crib. However, during the early times of Z-12 operation with the most earnest Pu processing throughput, 1959-1961, annual discharge rates were up to five-times greater (Appendix A of Jones 1998), making residence times about 1 day for a heel-free tank and proportionately lower depending on the heel quantity present.

Overall, about 273 million liters of solution and 25.1 kg Pu were discharged to 241-Z-361 during the March 1959 to May 1973 Z-12 crib operational lifetime (Appendix D of Jones 1998). Similar numbers, 281 million liters and 25.1 kg Pu, were provided in Appendix A of Kasper (1982). The total discharged through the 241-Z-361 settling tank over its mid-1949 through May 1973 lifetime was almost 480 million liters of solution and 30.8 kg Pu (Appendix D of Jones 1998). The average plutonium concentration discharged to 241-Z-361 during the period where overflow went to the Z-12 crib thus was 3.84×10^{-7} M, only marginally lower than the 4.09×10^{-7} M Pu in the waste fed to the 241-Z-361 settling tank in 1969 as shown in Table 9. The average plutonium concentration over the 1949-1973 241-Z-361 settling tank operational lifetime was lower, 2.68×10^{-7} M. Although Kasper (1982) assumed that all of the Pu measured in 241-Z-361 between 1959 and 1973 ended up in the 216-Z-12 crib, a more realistic assumption is that most of the solids in the waste, including the plutonium because of pH adjustment, were retained in the 241-Z-361 settling tank as a sludge (Lipke, 1997). However, lofting of finely suspended solids to the cribs must have occurred to an unknown extent.

Samplings and analyses of the 241-Z-361 tank contents were performed five times from 1975 to 1977; i.e., after retirement of the tank (page 7 of Jones 1998). Layering of the sludge was manifest in appearance and in differing plutonium concentrations. A single sludge sample had 0.91 g Pu/liter (Lundgren as reported on page 7 of Jones 1998), 0.06 to 1.37 g Pu/liter and averaging 0.33 ± 0.25 g Pu/liter were found for 37 broadly taken samples (Dodd, recalculated, Table 9 of Jones 1998), and 0.09 to 0.32 g Pu/liter, averaging 0.18 ± 0.09 g Pu/liter for 12 samples from various depths of a single sampling riser (Bouse, Table 10 of Jones 1998).

A 241-Z-361 tank characterization campaign occurred 1999-2000 (Hampton and Miller 2001). Top-to-bottom core samples, named 263 and 264, from risers E and F, respectively, were taken and composite layers prepared based on the extruded core strata colors, textures, and alpha activities. Riser E (core 263) is located near the center of the tank while riser F (core 264) is to the left of the flow centerline and about ¼ of the distance from the input point. Core 263 showed 19 strata from which eight composites were prepared (samples 263-1 through -8); core 264 showed 11 strata from which five composite layers prepared (samples 264-1 through -5).

The pH values for the composite samples from both cores were similar, ranging from 7.91 to 9.18 (Table 3-57 of Hampton and Miller, 2001). The plutonium concentration data from Tables 3-30, 3-32, and 3-35; the sludge thickness data from Table 3-11; and the sludge density data from Table 3-58; all from Hampton and Miller (2001); were combined to estimate the Pu concentrations in these composite layers and the overall Pu quantities as estimated from the two core samples taken from tank 241-Z-361. Values for the Pu contents in a void in the second core were estimated based on the similar concentrations and densities found in the bracketing composites. Plutonium concentrations ranged from 0.10 to 0.84 g/liter and averaged 0.42 ± 0.22 g Pu/liter (at 1 standard deviation). The plutonium concentration profiles as functions of depth for the two cores are shown in Figure 14. Except for the uppermost layers, these concentration profiles are similar. The total Pu content in the 241-Z-361 tank based on the complete core collected from near the center of the tank (core 263) was 31.9 kg (Jones 2008) compared with 30.8 kg discharged through this settling tank per process records (Appendix D of Jones 1998). Therefore, by these metrics, all or nearly all of the plutonium entering the 241-Z-361 settling tank was held in that tank. Based on total throughput and longer service time of the Z-12 crib, higher throughput rates when the Z-12 crib was operating, and the shallower settling depths as the 241-Z-361 tank became more laden with settled solids, it is likely that overflow plutonium existed and would have reported to the Z-12 crib.

A conservative estimate of the Pu quantity discharged to the Z-12 crib can be made based on soil measurements reported in Kasper (1982). The Pu was sharply distributed along the centerline of the trench, with concentrations falling off steeply laterally and decreasing by >10-fold within 1 meter of depth (Kasper, 1982). To a first approximation, the average concentration along the centerline and to 1 meter of depth was ~1×10^{-6} Ci ^{239,240}Pu/g. The area contaminated to this level was no more than 8 meters wide and 50 meters long meaning the contaminated volume was $<1\times8\times50 = 400$ m^3 or 4×10^5 liters. The density of dry sand/gravel mixtures is 1650 g/liter and the specific activity of weapons Pu is ~0.07 Ci/g Pu. Therefore, the Pu inventory in Z-12 is given by equation (1); i.e., <9.4 kg:

4×10^{5} liters × 1×10^{-6} Ci ^{239,240}Pu/g sediment × 1650 g sediment/liter × g Pu/0.07 Ci ^{239,240}Pu = 9.4 kg Pu (1)

The total quantity of plutonium discharged through the 241-Z sump tanks and the amount found in the 241-Z-361 settling tank agree closely, supporting the premise that the settling tank functioned reasonably well in removing solids from the low-salt waste stream (Pu Oxide Team, 2017). Demonstrably, however, up to 9.4 kg of plutonium overflowed the settling tank from March 1959 until May 1973 and reported to the Z-12 crib as found by sampling and characterization (Kasper 1982). This quantity constitutes as much as ⅓ of the 30.8 kg of plutonium input to the 241-Z-361 waste settling tank in this period and suggests that residence/settling times were inadequate to remove the plutonium. This also suggests that the plutonium that did report to the Z-12 crib would be in solution or finer, less readily settling, particles.

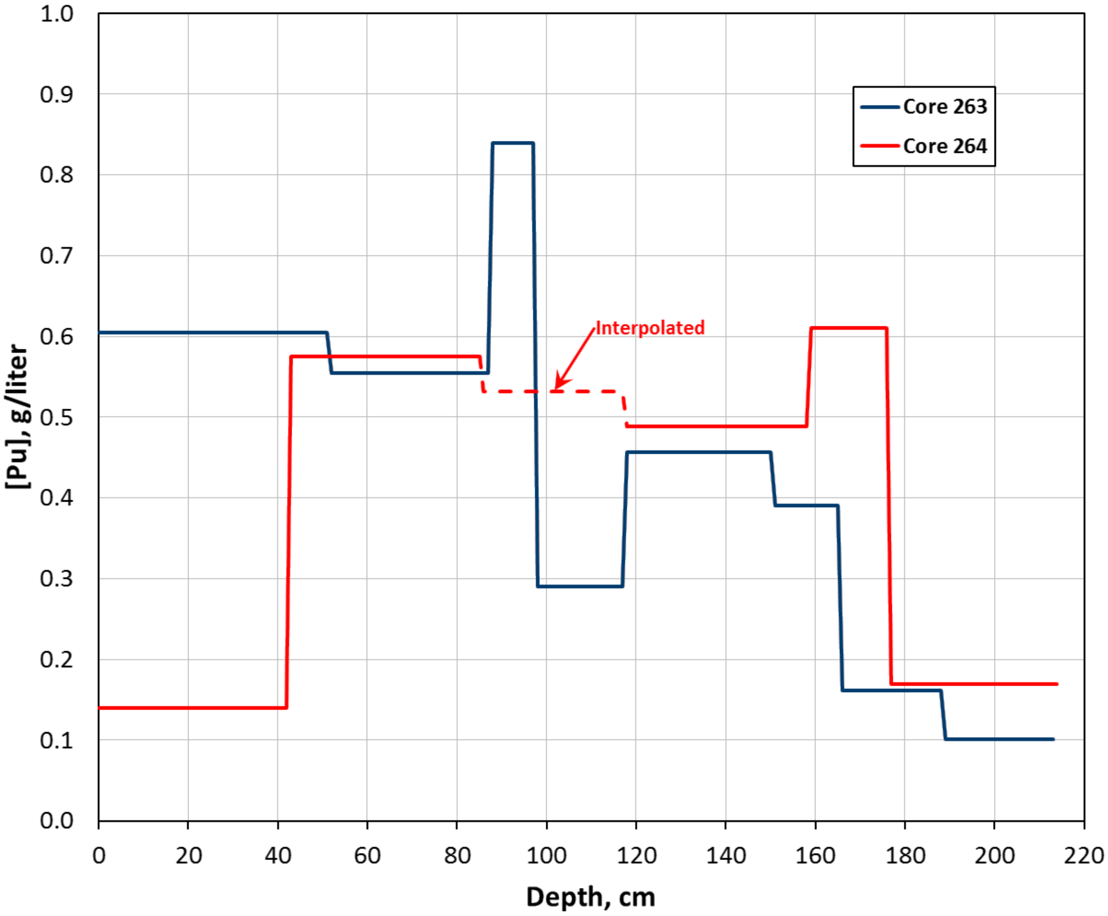


Figure 14. Plutonium Concentration Profiles in Tank 241-Z-361 from Cores 263 and 264

The state of the plutonium discharged to the 241-Z-361 settling tank and further, as a fine suspension to the Z-12 crib, would vary according to its source. The Pu scrubbed from the incinerator was PuO_2, about 69% of the total Pu, and would have been unchanged by its treatment in the 241-Z-361 tank and downstream conditions. The dissolved Pu in the acidic process solutions, about 20% of the total Pu and present at ~6×10^{-7} M (calculated from Table 8), would have hydrolyzed upon pH adjustment and become colloidal $PuO_2\cdot xH_2O$, potentially coprecipitated with polyvalent cations such as iron or manganese. The PuF_4 discharged in the ~0.06 M HF from the hydrofluorinator eductor jetting (page 3 of Jones 1998) would have hydrated to form solid $PuF_4\cdot2.5H_2O$ and dissolved as its solubility in water is ~4×10^{-4} M (Griffo et al. 1964), much greater than its ~6×10^{-8} M concentration in the eductor water even with 0.06 M

HF present. Upon the waste being made alkaline and upon interaction with sediments, this, too, would hydrolyze to form colloidal $PuO_2 \cdot xH_2O$. Metals and radionuclides associated with inorganic colloids have been investigated in terms of transport. While Cs-137 very strongly adsorbs to sediments, inorganic colloidal Cs may be advected a greater distance (Flury et al., 2002), as could Cr (Zhou et al., 2019). Further modeling of Cs colloidal formation and transport, however, indicates over the long transport times in the vadose zone, colloids would aggregate (Czigany et al., 2005). Thus, generation of intrinsic colloids, e.g., $PuO_2 \cdot xH_2O$, that could facilitate plutonium migration, must be considered. Treatment with soda ash would favor conversion of the Pu to soluble anionic Pu(IV) carbonate complexes. The potential for the Pu to interact with carbonate present in the sediments to form soluble Pu(IV) carbonato species also must be considered.

3.4 Plutonium Discharge to Groundwater via the 216-B-5 Injection Well

The 241-B-361 settling tank overflow was the source of an alkaline (or neutral) contaminated waste stream from the bismuth phosphate process (B-plant), which was injected into the groundwater aquifer via the 216-B-5 reverse injection well. Between 1945 and 1947, an estimated 23 million liters of plutonium-bearing waste (37 Ci Pu) was disposed with 150 g Pu-239 and 0.3 g Pu-241 (Jacques and Kent, 1991). Most of the plutonium remains in the sediments near the original disposal location. 216-B-5 plutonium-bearing wastes come from a different plant (B-plant) and process (bismuth phosphate) than the 234-5 waste disposals. The disposed Pu quantity is also much lower and was injected directly into the groundwater, not released to subsurface soils and sediments above the vadose zone. The 216-B-5 injection well will not be considered further in this report as this report is focused on the 234-5 disposal sites.

4.0 Construction and Recovery Operations at Waste Sites in the 200 West Area

4.1 216-Z-9 Crib Construction and Mining

Construction of the 216-Z-9 crib (an enclosed trench) was completed in 1955 to receive aqueous and organic waste solutions from RECUPLEX. The crib's flat, rectangular, 9.14×18.29-meter floor with the natural sand and gravel sediments slope upward from their margins to a 23-cm-thick, rectangular (27×36.5 meter), concrete slab cover. The cover is supported 6.1 meters above the crib bottom at the periphery by the soil surface and by six columns. The original crib dimensions, before the mining operations, are shown in Figure 15. The RECUPLEX wastes entered the crib by a primary and spare 3.8-cm stainless steel inlet pipe about 5.2 meters above the crib floor (page 1 of Ludowise 1978; see also Section 3 of Teal 2007) at the north end of the crib. Further information on the construction and properties of 216-Z-9 is found on pages 52-61 of Owens (1981).

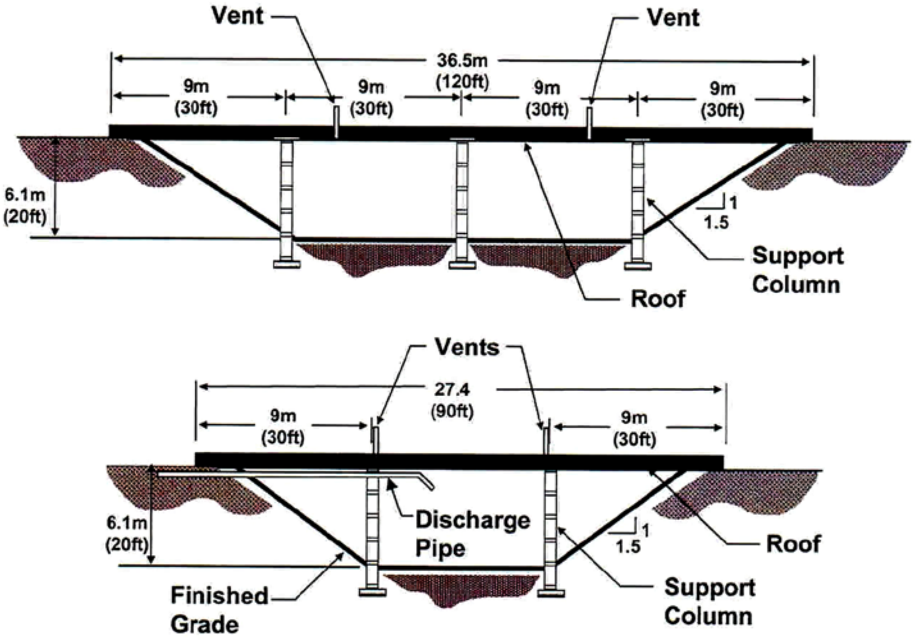


Figure 15. As-Constructed 216-Z-9 Crib during Time of Service (Figure 2-3 of Winkel 2018)

Early in RECUPLEX operations, concern arose that the large quantities of Pu disposed to the Z-9 crib could lead to a nuclear criticality; later the prospect of recovering valuable Pu from crib sediments also becoming attractive (Section 15.2 of Gerber 1997). Therefore, retrieval of the top 12-inches (~30 cm) of the Z-9 sediments was undertaken. Support buildings were constructed prior to this peculiarly unique mining operation (Figure 16). The structures were suspended from steel I-beam supports with the loads borne by the crib roof support columns and on the soil grade to eliminate load on the cover slab. Access ports were opened through the cover slab. Two ~107-cm-diameter circular ports were prepared for the soil excavation equipment, two 51-cm-diameter risers opened for camera equipment, a ~2.9×3.3-m rectangular opening made for the operations cubicle, a ~0.8×1.6-m rectangular opening made for the soil removal pathway, a ~0.9×3.5-m rectangular opening for the stairwell into the crib, a 20-cm diameter circular riser cut for access to the base of the soil conveyor, and a 33-cm diameter circular riser prepared for ventilation. These and other details on the mining structures and slab penetrations are found in Hopkins et al. (2008).

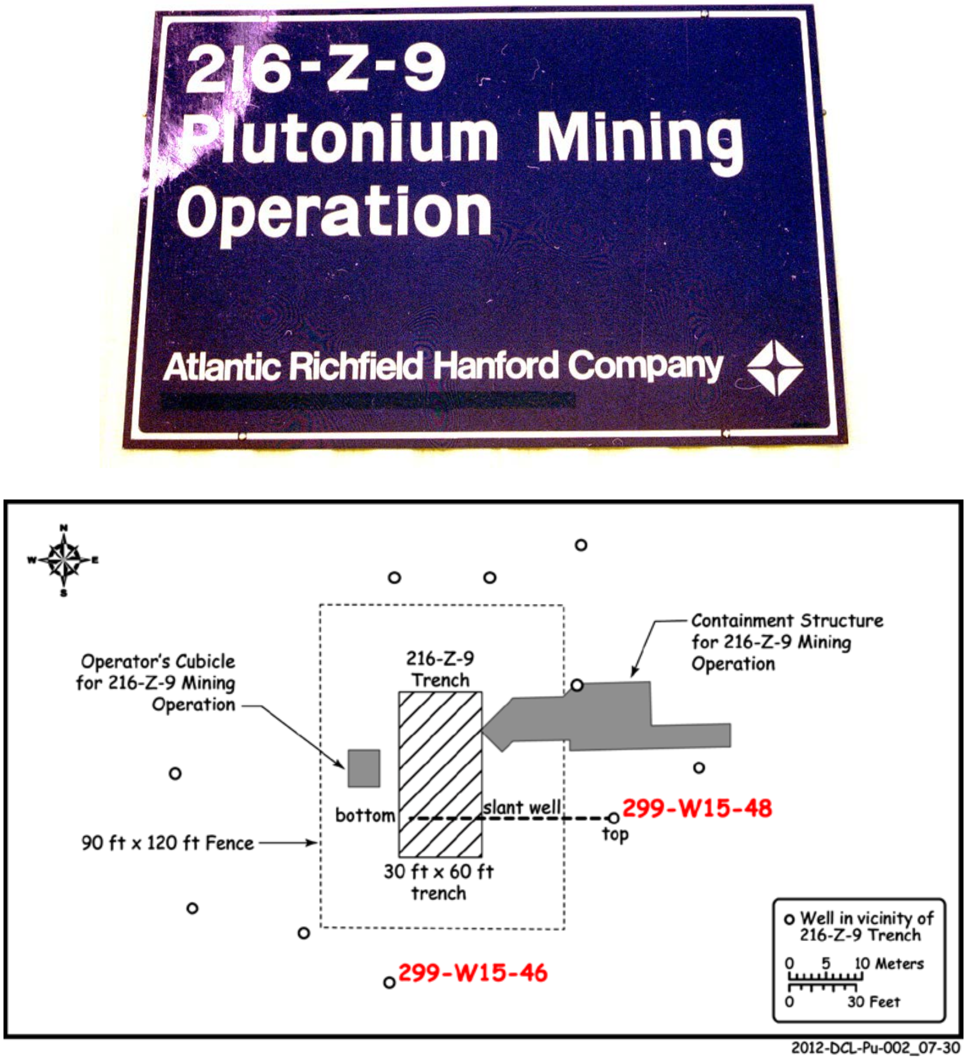


Figure 16. Support Buildings for 216-Z-9 Plutonium Mining. Top: Sign on support building (image 72698-29CN from Hanford Site photo archive). Bottom: Support building (216-Z-9A) and operations cubicle layout (Figure 3.4 of Cantrell and Felmy 2012)

The mining equipment, cover slab support columns, the sloped crib sediment walls, and the cubicle in the upper right from which the mining operations were conducted are shown in Figure 17. The sediment container conveyor (yellow apparatus to the left and in front of the support column), the stairway (left and just behind the left column), and the sediment clamshell digger on its boom (at the bottom of the stairway) likewise are shown in this view. The underside of the crib-covering slab had been armored in ceramic tiles when the crib was constructed to impede attack from acid fumes of the disposed waste.

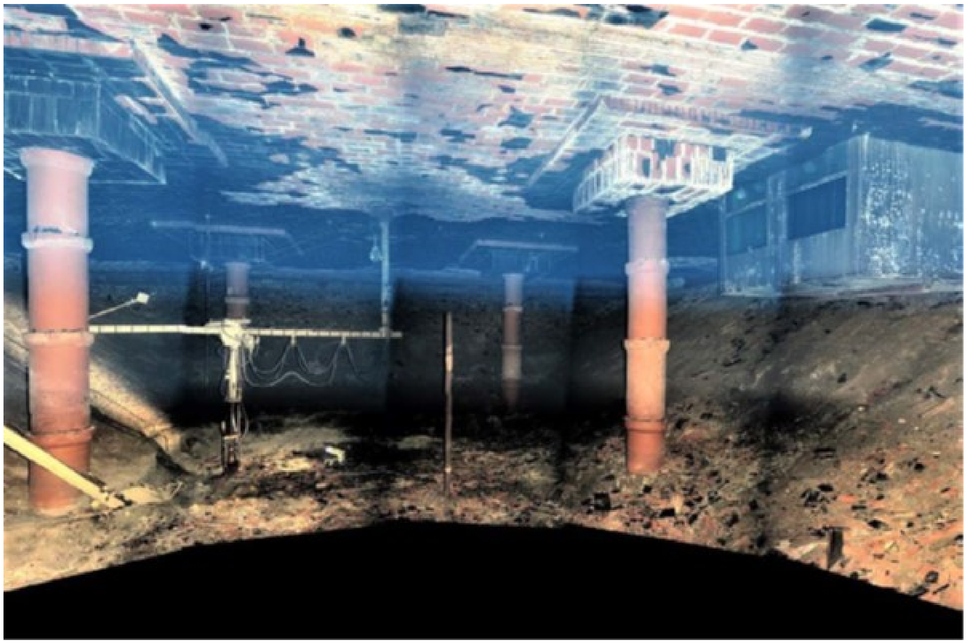


Figure 17. View to the North Interior of the Z-9 Crib When Mining Was Underway (Figure 2-4 of Winkel 2018; note operations cubicle in ceiling to the right)

Figure 18 better shows the mining equipment, including the 11-liter-capacity clamshell digger on the boom to the left, the stairway at the center, and the conveyor (lower right to upper center) for removing the soil-filled containers. This view to the west-southwest was taken from the left operations cubicle window. The inside of the remote mining operations cubicle and the viewing windows into the crib are shown in Figure 19.

Figure 18. Interior View of Z-9 Crib and Crib Soil Removal Equipment Prior to Mining Operations (taken through operations cubicle window; image 72698-32CN from Hanford Site photo archive)

Figure 19. View of Z-9 Crib Mining Operations Cubicle and Windows into Z-9 (image 72698-30CN from Hanford Site photo archive)

The estimate of ~100 kg of Pu disposed to Z-9 shown in Table 4 proved to be fairly accurate based on subsequent retrieval and analysis of the top 30-cm of soil from the bottom of the 30×60-foot (9.14×18.29-meter) crib, or ~49-m^3 volume, from which 58 kg of Pu was packaged into 5222 10-liter canisters, giving ~51-m^2 retrieved sediment volume (page 16 of Ludowise 1978). The disposed aqueous waste volume was ~3800 m^3, about 76-times the volume of crib soil retrieved. The crib soil mining took place in August 1976, halted 4 months to resolve technical issues, and then ran continuously from 11 January 1977 until completion on 14 July 1978. The retrieved 58 kg of Pu was 54% higher than the 38 kg estimated to be in the top 30 cm by prior non-destructive methods, with the total crib inventory estimated to range from 28 to 69 kg. If the 54% correction factor is applied to the higher estimate of Pu in the crib (69 kg), then (1.54×69=) 106 kg of Pu was present initially leaving (106-58=) 48 kg of Pu still in the crib (studies summarized in pages 5-10 of Ludowise 1978).

The moisture, organic, and cadmium concentrations were measured daily as the soil was retrieved. Moisture ranged from 0.2 to 24.4 wt% (5 wt% average) and organic constituents ranged from 0.2 to 46.4 wt% (7.1 wt % average). Strangely, the cadmium concentration was stated to range from 0.2 to <0.8 wt% (page 16 of Ludowise 1978).

Ultimately, Pu leaching and recovery from the retrieved Z-9 sediments was judged not worthwhile with 86.8% of the sediment was deemed waste and the balance recoverable or potentially recoverable (pages

15-9 and 15-11 of Gerber 1997). The retrieved and canned crib sediments still are present on the Hanford Site awaiting disposal to the WIPP. The following text from an e-mail from Daniel A. Arrenholz to Calvin H. Delegard, 28 August 2018, describes their current condition:

> *Processing of the Z-9 cans for WIPP purposes occurred during the 2009 – 2011 timeframe. This processing consisted of unloading the cans from the drums, puncturing the cans to breach all layers of confinement, and inserting a toggle bolt to ensure the breach could be seen during subsequent* radiography *as part of the WIPP waste certification process. The outer cans were approximately 10L and the inner cans were approximately 9L (the configuration was a bag of soil, 9L can, another bag, all placed into the 10L can, the lid of which was circumferentially taped closed). During this repackaging, the contents of each drum was split into two daughter drums (4 cans each and one also received the plywood spacer). None of this waste has been shipped to WIPP yet.*

4.2 216-Z-1A Tile Field Construction

The 216-Z-1A crib design was like a septic tile-field, a central line of vitrified clay pipe (VCP) with herringbone distributor VCPs branching off horizontally at 45-degree angles (Figure 20). The Z-1A crib was constructed in 1949 and used from June 1949 until March 1959 to receive dilute overflow liquid waste from the adjacent 216-Z-l, 216-Z-2, and 216-Z-3 cribs (Owens 1981). Disposal of PRF wastes to the Z-1A tile field commenced May 1964 and continued until May 1966 with discharge into the 216-Z-1AA section using a 2-inch stainless steel pipe threaded through the trunk line 8-inch VCP. In May 1966, the discharge point was moved 100 feet further down the main trunk to the 216-Z-1AB section, receiving wastes from June 1966 until October 1967. In October 1967, the discharge point was moved a further 75 feet down the trunk to discharge to the 216-A-1AC section. Wastes were delivered there from October 1967 until April 1969 when the facility was retired (page 14 of Owens 1981). The Z-1A tile field also received wastes from the Americium Recovery Building from August 1964 until April 1969, nearly the same interval as the May 1964 until April 1969 period for the PRF wastes.

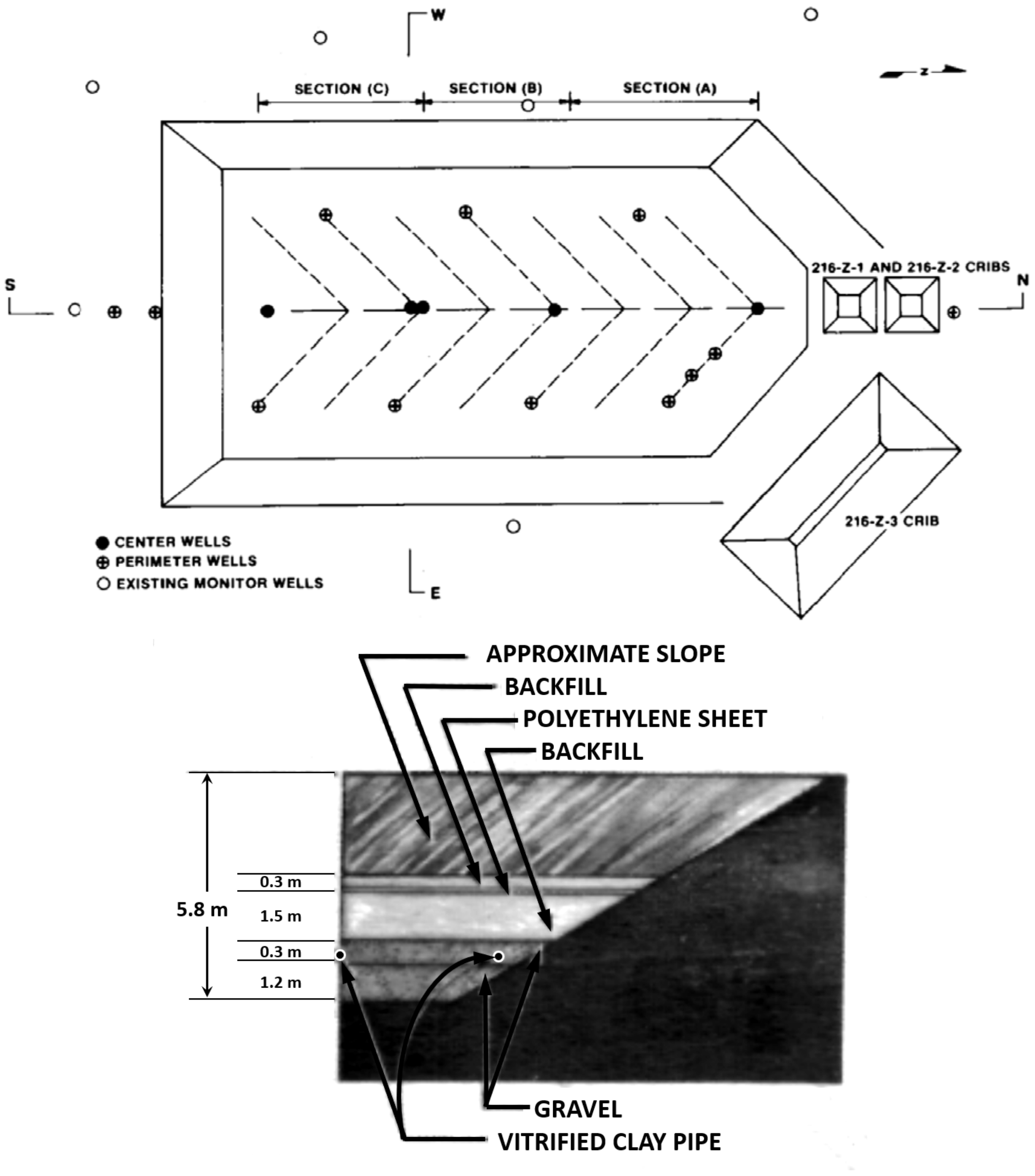


Figure 20. Plan View (above) of 216-Z-1, Z-2, Z-3, and Z-1A Cribs and Section View (below) of 216-Z-1A (Kasper et al. 1979, Kasper 1982)

4.3 216-Z-12 Crib Construction

Construction of 216-Z-12 began with a rectangular excavation having a 25×110 m surface dimension, with a depth of 6.1 m to the bottom of the crib (Kasper 1982). The excavation had inward sloping sides, resulting in a 6.1 by 91.4 m floor dimension (Figure 21). Three wells to measure liquid levels in the crib were emplaced on concrete pads on the crib bottom. Clean, washed, and graded gravel (0.9 m thick) was laid on the bottom of the crib. A single central distribution pipe was laid directly on top of the gravel layer with no slope. Gravel (40 cm) was laid over the pipe and a polyethylene sheet was laid on top of the gravel. The excavation was backfilled to grade.

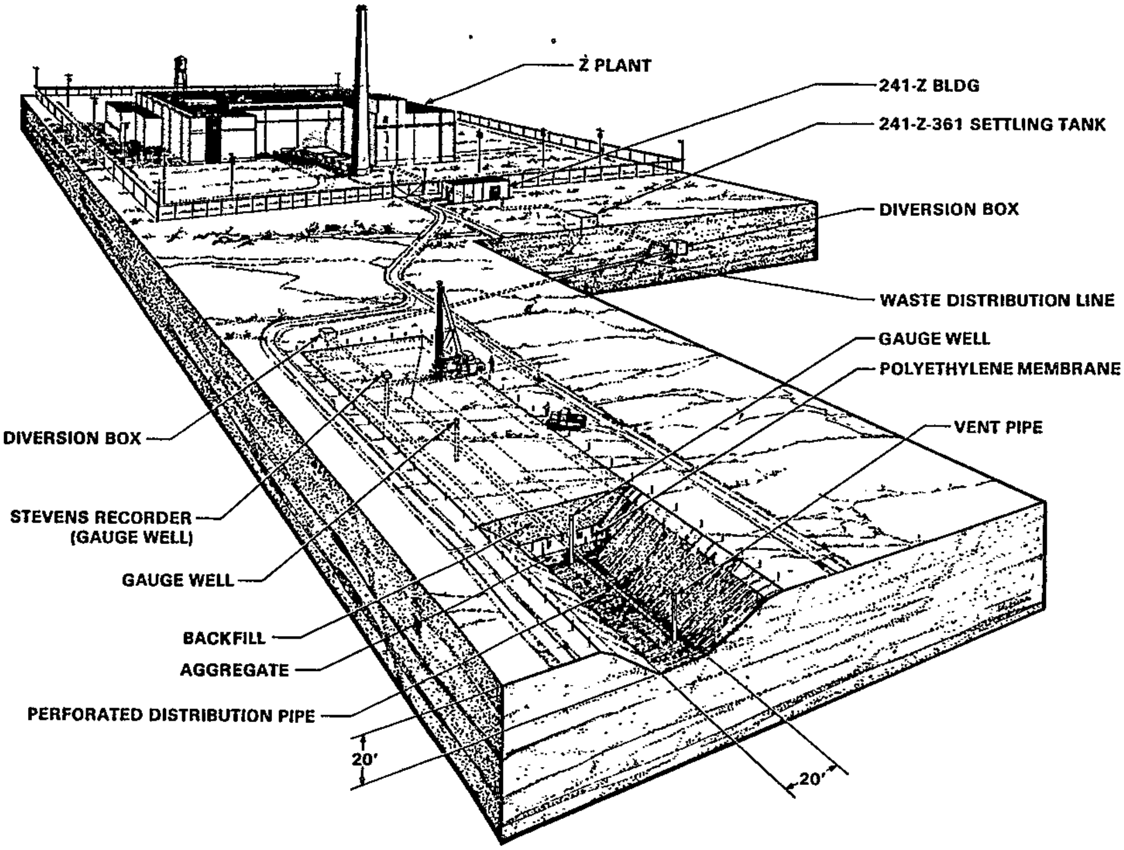


Figure 21. The 216-Z-12 Crib (Figure 6 in Kasper 1982)

5.0 216-Z-9 Trench, 216-Z-1A Tile Field, and 216-Z-12 Crib Sediment Stratigraphy

The stratigraphy and granulometry of the sand/gravel and rock underlying the 216-Z-9 trench, 216-Z-1A tile field, and 216-Z-12 crib are shown in Figure 21 as interpolated from logs of wells located around these sites. The bedrock Elephant Mountain member is found ~529 feet below grade and is part of the Miocene age Columbia River Basalt Group. Three thick layers of coarse- to fine-grained sediments overlie the basalt. Going upward, they are Neogene (~23 to 2.6 million years, Ma, ago) fluvial deposits of the Ringold formation; colluvial (gravity-slumped), alluvial (water-deposited), eolian (wind-deposited), and pedogenic (soil-forming) deposits of the Cold Creek unit (indicated as the Plio-Pleistocene unit in the top of Figure 22); and Pleistocene cataclysmic ice-age flood deposits called the Hanford formation (Xie et al. 2003). The water table is about 203 feet (~62 meters) below grade but varies slightly, of course, with surface elevation variability in the region. Further details on the Ringold and Hanford formations are provided by Xie et al. (2003):

> *The Ringold formation 1) contains an abundance of lighter colored, rounded granite and quartzite cobbles; 2) often has a bimodal grain size distribution; and 3) is often weathered to a reddish, orange color from iron oxide staining associated with its diagenesis and partial cementation.*
>
> *The coarse-grained Hanford formation sediments occasionally have an open framework of dark, subangular to subrounded basaltic gravels with a poorly sorted matrix of silt and sand, lacking any significant weathering alteration as a result of its rapid burial during cataclysmic floods and its younger age.*

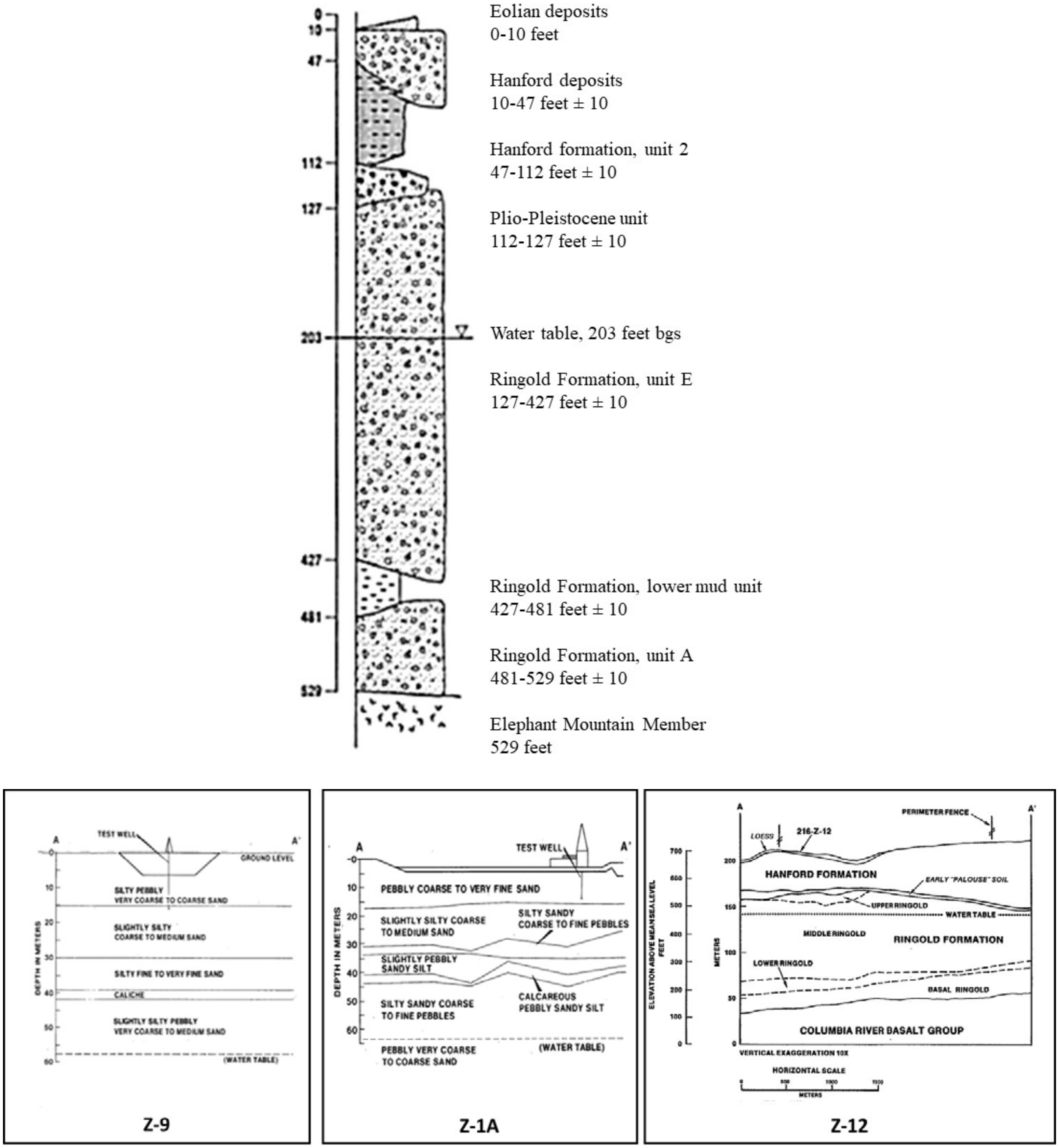


Figure 22. Stratigraphy and Granulometry of Sediments beneath the 216-Z-9, 216-Z-1A, and 216-Z-12. Top: stratigraphy (Figure 2 of Parker and Singleton 1995; see also page C-6 of Lindsey 1996). Bottom: granulometry (from Figures 1, Z-9, and 2, Z-1A, of Price and Ames 1975 and Figure 12, Z-12, of Kasper 1982; descriptions seemingly related to US Geological Survey terms[1])

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[1] USGS Open-File Report 2006-1195; https://pubs.usgs.gov/of/2006/1195/htmldocs/images/chart.pdf

Various dating methods indicate the Ringold Formation to be no older than 8.5 Ma and no younger than 3.4 Ma (i.e., late Miocene to middle Pliocene) and was deposited in numerous layers by the early Columbia River system (page 8 of Lindsey 1996).

The Cold Creek, or Plio-Pleistocene, unit represents, first, reworkings of the upper portion of the Ringold formation in the interval between 3.4 Ma and the advent of the first of the cataclysmic Ice Age floods.[1] The Cold Creek unit consists of pedogenic (soil-formed) calcium carbonate, silt, basalt gravel, and reworked Ringold deposits including Columbia River deposits. For much of this period and the earlier Ringold formation times, large shallow inland lakes were present, explaining the carbonate (caliche) beds found in the Ringold and Cold Creek units. The Cold Creek rock itself is mixed, gray to white, quartz-based and uncemented sandy pebble to cobble gravel (Lindsey 1996).

The Hanford formation, the topmost of which was laid down by multiple (as many as 40) Missoula floods at the end of the last Ice Age (15,000 to 13,000 years ago), contains uncemented silt, sand, and mixed nearby (Washington) basalt gravel and upstream granite and metamorphic glacial scrapings and erosional detritus from northern Washington and Idaho.

The mineralogy of the sand and gravel samples found in the Ringold and Hanford formations underlying the Hanford 200 West Area (within which lies 216-Z-9) has been summarized (Xie et al. 2003). These summary analyses are based on electron microscope (Table 10) and petrographic (Table 11) analyses and the normalized elemental oxide distributions (based on aluminum, silicon, iron, calcium, potassium, titanium, and manganese) using X-ray fluorescence (XRF) measurements (Table 12).

Table 10. Average Mineralogy of Hanford and Ringold Formations Under 200-W by Electron Microscope (Table B.1 of Xie et al. 2003)

Mineral	Hanford (17 samples)	Ringold (18 samples)
Quartz	38.4 ± 12.8	37.0 ± 12.4
Microcline	15.3 ± 4.4	18.7 ± 8.0
Plagioclase	22.2 ± 7.2	15.5 ± 6.8
Pyroxenes	5.0 ± 7.8	1.1 ± 2.5
Calcite	1.9 ± 1.7	7.9 ± 9.1
Magnetite	4.5 ± 4.1	5.7 ± 4.6
Amphiboles	5.5 ± 5.7	5.6 ± 6.4
Albite	1.0 ± 2.3	0.9 ± 2.5
Ilmenite	1.3 ± 1.5	3.7 ± 3.0
Epidote	1.8 ± 3.8	1.5 ± 2.1
Sphene	0.2 ± 0.4	0.0 ± 0.0
Apatite	0.5 ± 0.9	0.7 ± 1.2
Mica	2.5 ± 3.7	1.7 ± 5.2

---

[1] Cataclysmic glacial dam-break floods predating the most recent (15,000-13,000 years ago) Ice Age floods are postulated and may have impacted the Cold Creek formation stratigraphy.

Table 11. Average Mineralogy of Hanford and Ringold Formations Under 200-W by Petrography (Table B.2 of Xie et al. 2003)

Mineral	Hanford (6 samples)	Ringold (16 samples)
Quartz	20.7 ± 6.3	36.8 ± 10.0
Plagioclase feldspar	19.3 ± 9.2	14.2 ± 5.6
Mafic	29.9 ± 20.7	14.2 ± 9.2
Sedimentary aggregate	1.9 ± 0.8	7.2 ± 6.4
Feldspar	3.9 ± 2.1	4.1 ± 1.8
Pyroxene	2.0 ± 0.8	0.9 ± 1.0
Hornblende	1.1 ± 0.6	0.5 ± 0.3
Biotite	3.1 ± 2.0	1.2 ± 0.7
Muscovite	0.4 ± 0.5	0.3 ± 0.3
Opaques	1.6 ± 0.9	0.8 ± 0.6
Garnet	0.2 ± 0.4	0.2 ± 0.3
Epidote	0.0 ± 0.1	0.1 ± 0.2
Granitic	6.8 ± 3.6	11.4 ± 4.1
Metamorphic	0.8 ± 0.6	2.0 ± 1.4
Carbonate	0.9 ± 0.9	0.3 ± 0.5
Other	7.4 ± 1.5	5.7 ± 2.9

Table 12. Average Oxide Composition of Hanford and Ringold Formations Under 200-W by XRF (Table B.3 of Xie et al. 2003)

Oxide	Hanford (27 samples)	Ringold (41 samples)
Al_2O_3	15.1 ± 2.7	11.9 ± 1.9
SiO_2	72.1 ± 1.3	78.7 ± 1.1
FeO	4.5 ± 2.4	3.8 ± 0.7
CaO	4.9 ± 1.0	3.1 ± 0.2
K_2O	2.2 ± 0.1	1.9 ± 0.1
TiO_2	1.1 ± 0.3	0.65 ± 0.02
MnO_2	0.11 ± 0.02	0.069 ± 0.003

The primary difference between the upper Hanford and lower Ringold sediment layers is the greater mafic complement in the Hanford sediment (Table 11), reflecting the presence of erosional basalt scoured by the Ice Age Missoula floods. Correspondingly, the Hanford sediment also contains more aluminum, iron, and calcium and less silicon than the Ringold sediment (Table 12) and more plagioclase and pyroxene (Table 10). To the present authors, the higher complement in the Hanford sediments of less-weathered basalt, and its contained glassy matrix and ferrous iron (Fe^{2+}), and basalt's higher vulnerability for alteration by the acidic RECUPLEX and PRF wastes may cause chemically reducing conditions to be established in acidic waste-wetted soils.

6.0 Characterization of Pu and Am in Subsurface Sediments

Prior to discussing plutonium contaminated sediments, it is useful to present thermodynamic equilibrium speciation and solubility calculations of relevance to the Hanford subsurface, in order to understand the conditions under which plutonium is expected to be mobile. The Eh-pH diagram in Figure 23 is for plutonium at a concentration of 10^{-10} M in pure water. Under these conditions, the stability field for the hydrated amorphous PuO_2 solid covers an extensive range, dominating most of the Eh range above pH 6. Although consideration of this simple case is useful for context, the actual speciation of plutonium in the Hanford subsurface is expected to be vastly different due to: (i) the presence of ligands such as HCO_3^- and HPO_4^{2-} in Hanford Site groundwater creating stability fields for additional solid phases e.g. $PuPO_4$; and (ii) the influence of complexation as a result of the organic co-contaminants present in the complex waste streams.

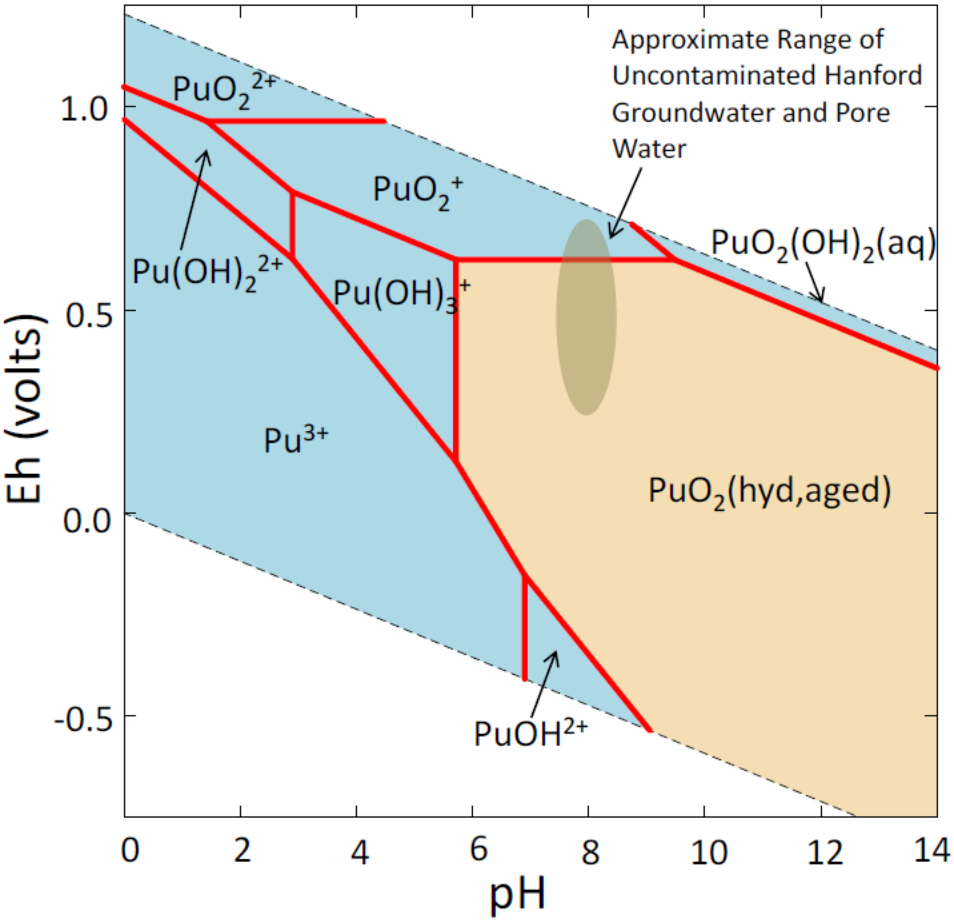

Figure 23. Eh pH Diagram for Plutonium at a Concentration of 10^{-10} M (1,500 pCi/L, the maximum contaminant level, MCL) in Pure Water (298.15 K, 0.1 MPa) (Figure 4.2 in Cantrell and Felmy, 2012)

Contaminated soils from two core samples from the 216-Z-9 crib were examined by autoradiography, electron microscopy, and electron microprobe to establish the disposition of Pu within the sediments and the impacts the acidic disposed wastes had on the native minerals (Ames 1974; Price and Ames 1976). The earlier report described examination of the top 60 cm; the latter described samples taken to 9-m depth. The Pu and Am concentration distributions as functions of depth run in approximately parallel fashion as shown in Figure 24. However, by 9-m depth, the Am has shown greater mobility. For 216-Z-1A sediment core samples, the greater mobility of Am is clearly shown by the increasing Am/Pu concentration ratio with depth. Later more comprehensive analyses of Am and Pu concentrations with depth in Z-1A (Appendix B of Price et al. 1979) confirm the greater mobility of Am as shown in Figure 25 for two wells at the crib centerline. The Am/Pu activity ratio of 0.1-0.2 shown at the shallower depths for these two wells would be expected for ~6- to 14-years after reactor discharge for weapons-grade plutonium (Figure 26; ~6.7 wt% ^{240}Pu; based on Hedengren and Goldberg 1987). The greater Am/Pu ratios at greater depths indicate more rapid movement of Am through the soil column.

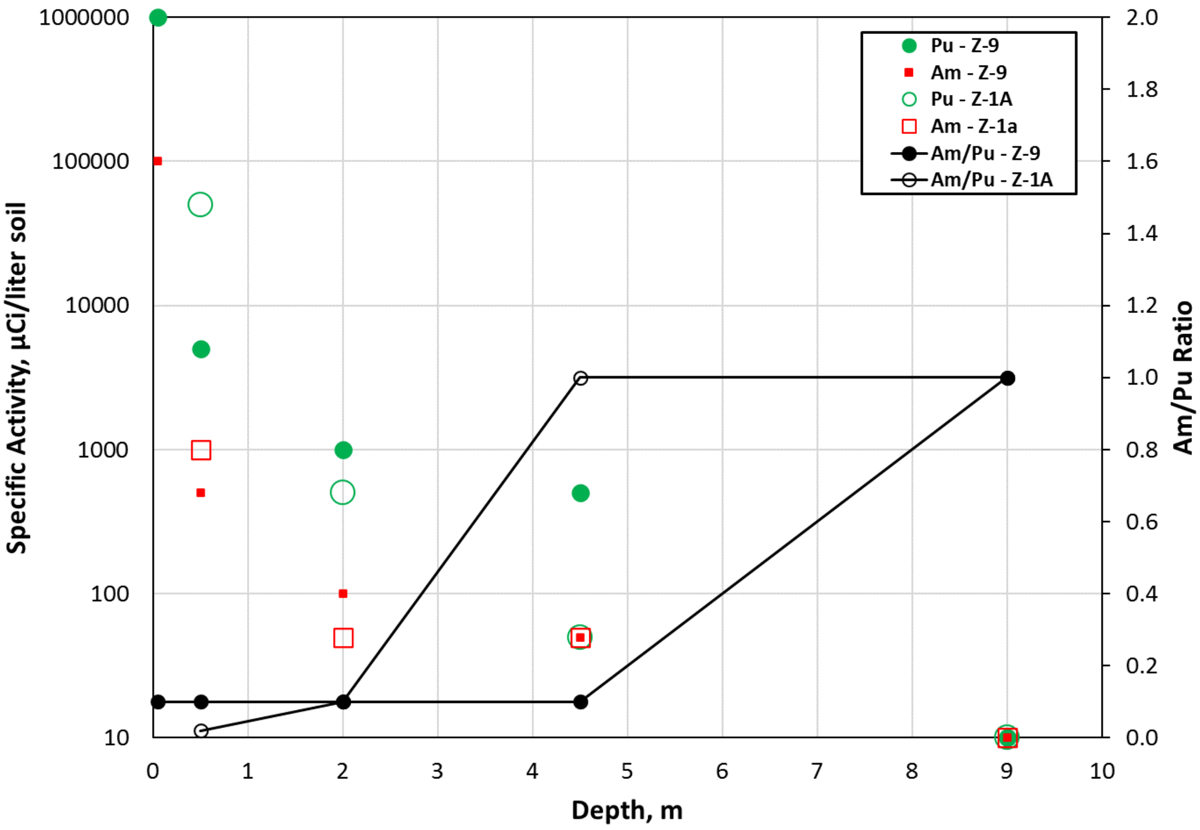

Figure 24. Plutonium and Americium Concentrations and Americium/Plutonium Concentration Ratios in 216-Z-9 and 216-Z-1A as Functions of Depth (data from Table I of Price and Ames 1975)

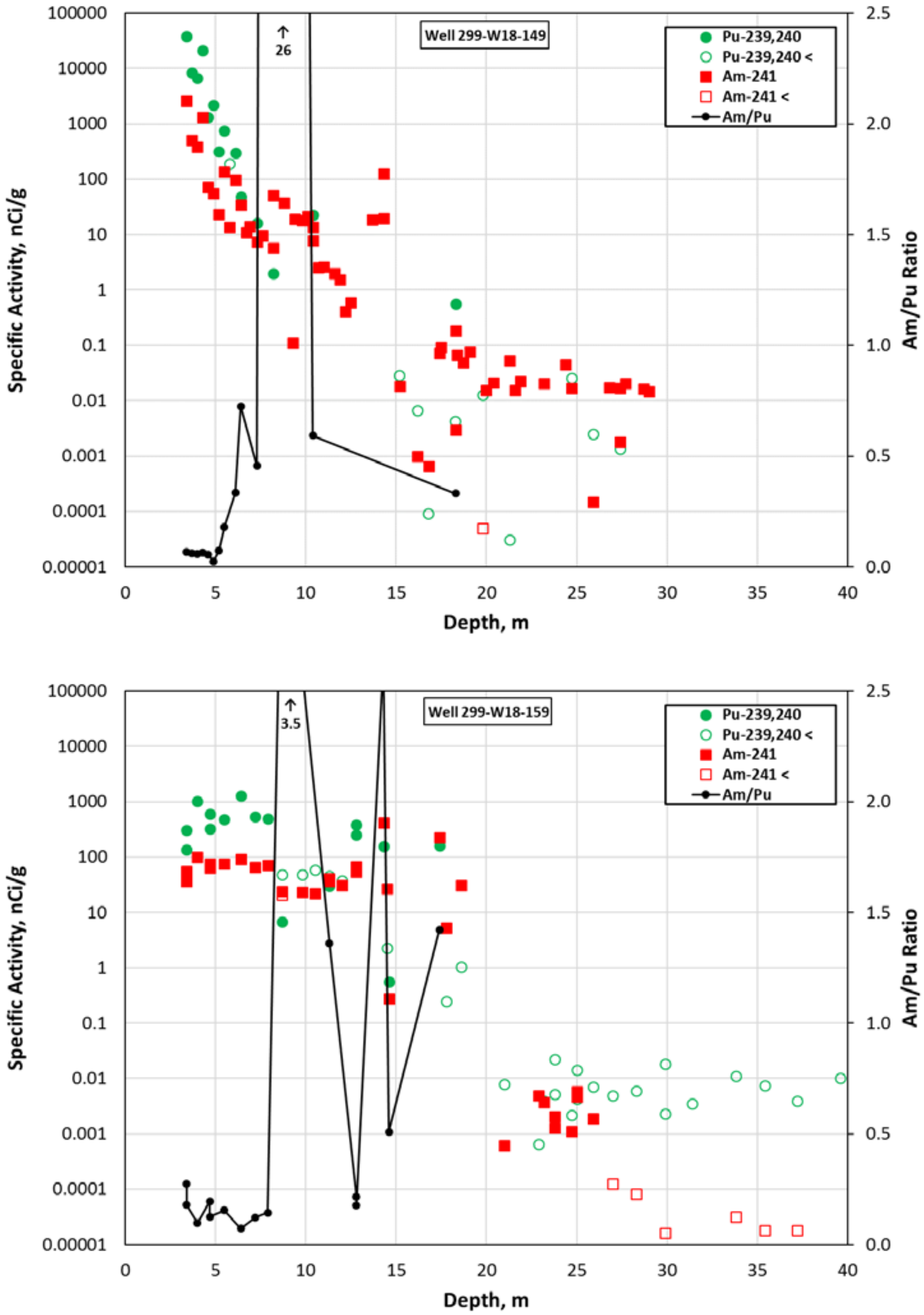

Figure 25. Plutonium and Americium Concentrations and Americium/Plutonium Concentration Ratios in Two Centerline Wells in 216-Z-1A as Functions of Depth (data from Appendix B of Price et al. 1979)

The Am and Pu concentrations in sediment samples from a centerline well from the 216-Z-12 crib are shown in Figure 277. As was observed for Z-9 and Z-1A samples, the Pu and Am concentration distributions also run in parallel. However, in contrast with the increasing mobility of Am in the high-salt and acidic wastes disposed to the Z-9 and Z-1A structures, the Am from the low-salt and moderate pH wastes disposed to the Z-12 crib does not show increasing mobility compared with Pu as depth increases and the ^{241}Am/^{239,240}Pu alpha activity ratio averages ~0.2. Four of the 40 Am/Pu ratios are somewhat greater than the ~0.2 average but the concentration data also have appreciable analytical uncertainty. As shown in **Error! Reference source not found.**6, ^{241}Am/^{239,240}Pu alpha activity ratio of 0.2 would be expected for weapons-grade plutonium (~6.7 wt% ^{240}Pu) about 14 years after Hanford reactor discharge.

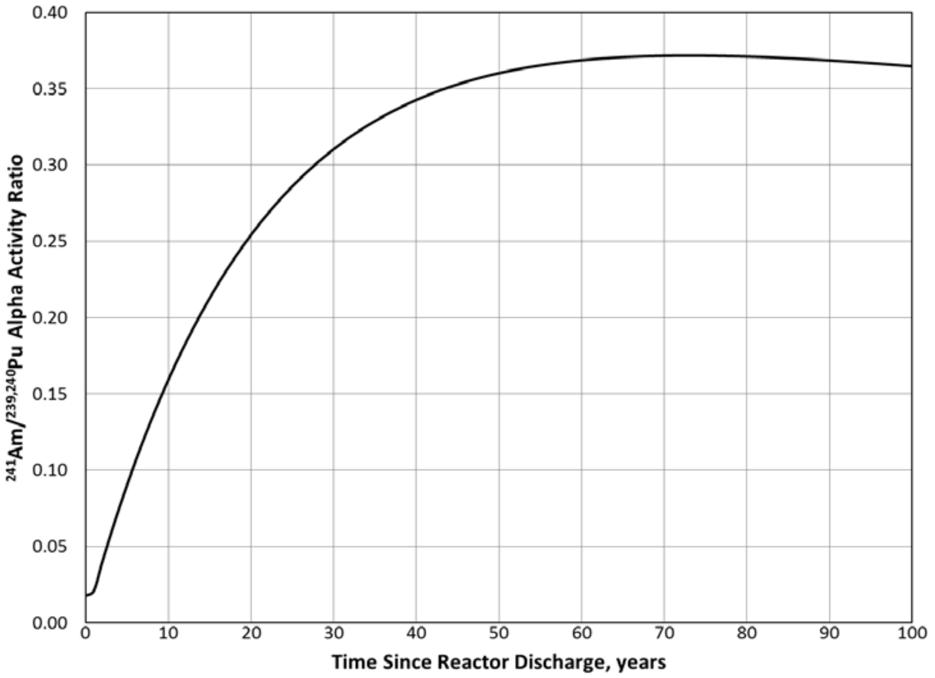

Figure 26. Americium-241/Pu-239,240 Alpha Activity Ratio for Weapons-Grade Plutonium as a Function of Time from Reactor Discharge

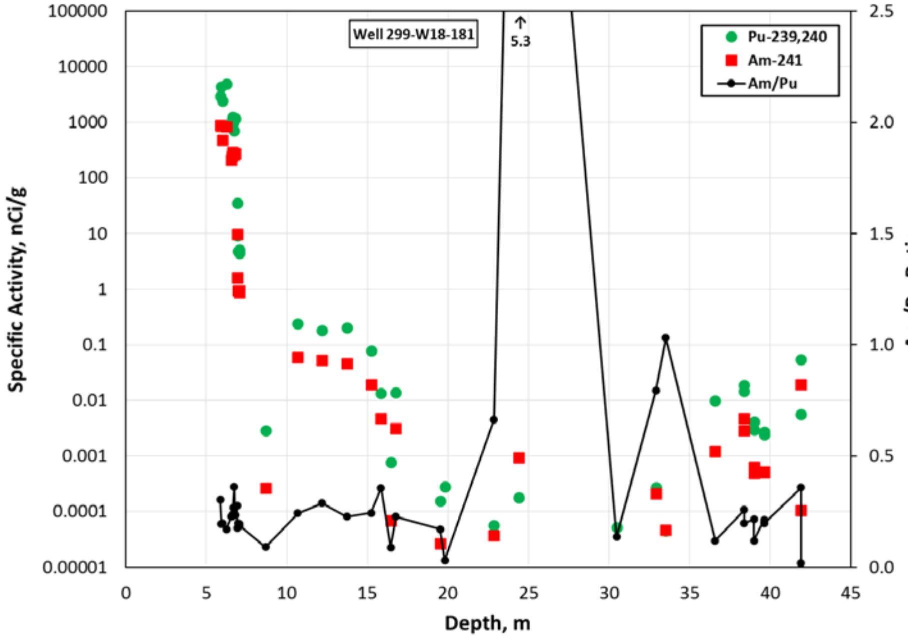

Figure 27. Plutonium and Americium Concentrations and Americium/Plutonium Concentration Ratios in Centerline Well in 216-Z-12 as Functions of Depth (data from Appendix C of Kasper 1982)

As noted by Kasper (1982):

> *Plutonium and americium distribution were similar and the ratio of americium to plutonium activity beneath most of the crib was approximately 0.2. These results suggested that the americium activity observed beneath the 216-Z-12 Crib was derived primarily from the in situ decay of* ^{241}*Pu discharged in the waste.*

The same relative mobilities of Pu and Am in the sediments of the Z-1A, Z-9, and Z-12 waste disposal facilities also have observed by Felmy et al. (2017). It is further noted that in the acidic wastes disposed to Z-1A and Z-9, both Am and Pu largely existed in solution though with an appreciable complement of solid phase Pu and included Am. However, the Am and Pu in the pH-neutral wastes disposed to Z-12 from incinerator and hydrofluorinator scrubber solutions almost exclusively were present in solid phases. The dissolved Am^{3+} in the acidic Z-1A and Z-9 wastes would be much more mobile than the readily hydrolyzed dissolved Pu^{4+} thus explaining americium's greater migration downgradient in these structures.

The highest Pu concentration in Z-9, 1 Ci ^{239}Pu/liter of sediment, is found in the top inch (~2.5 cm) of depth in the crib (Figure 28) and corresponds to approximately 28 g total Pu/liter. Curiously, the highest concentrations are in the southern half of the crib, away from the PRF waste input line which is at the north end. For Z-1A, the highest Pu concentration is 0.0382 Ci ^{239,240}Pu/kg of sediment (page 68 of Price et al. 1979) or about 0.06 Ci (~1 g) Pu/liter assuming a crib soil bulk density of 1.5 kg/liter.

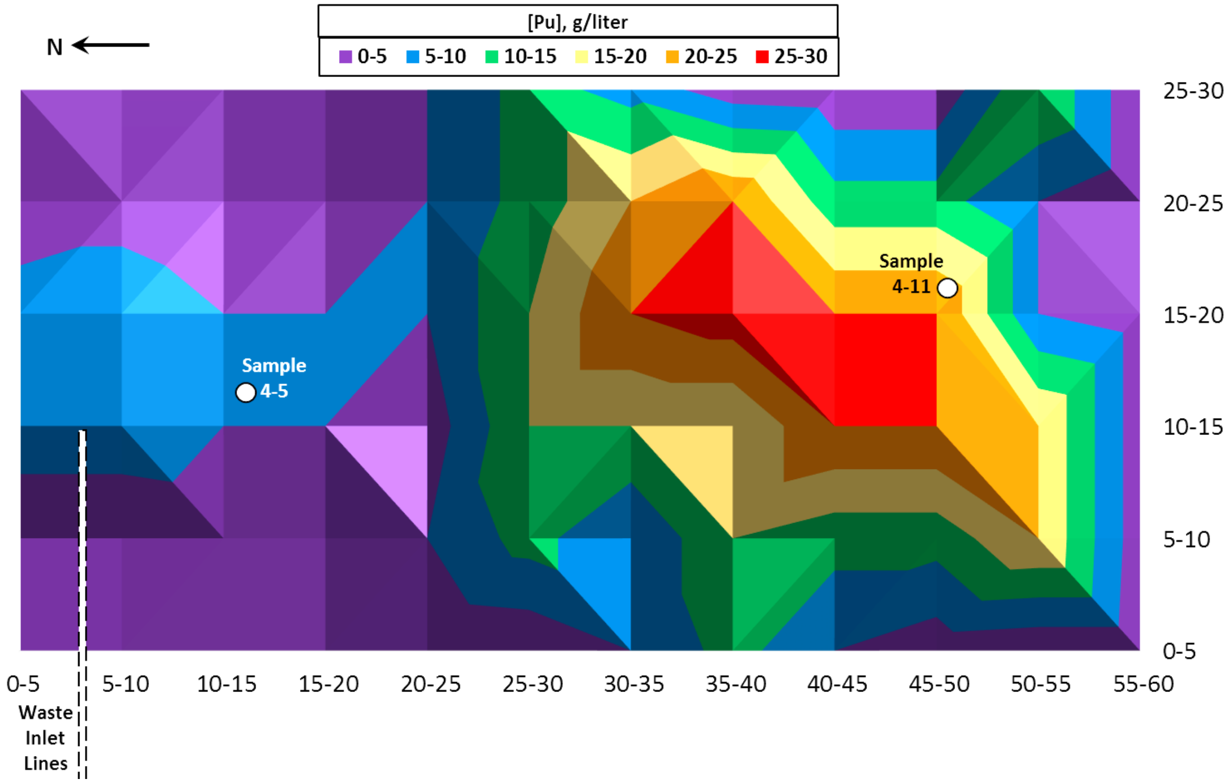

Figure 28. Plutonium Concentration Profile in Top Inch of Z-9 (based on pages N-17 and B-4 of Smith 1973)

The earlier characterization of the top 60-cm from two different cores of Z-9 (named 4-11 and 4-5; see Figure 28 for the sampling locations) showed two types of Pu according to autoradiographic and microprobe examination (Ames 1974). Discrete Pu-bearing particles, generally found to be PuO_2 by XRD and up to 10 µm diameter, were near the top of the 4-11 core but were found along the entire 60-cm length of the 4-5 core. A "sludge" deposited from the waste at the top of the 4-11 core was credited with acting as a filter to remove the particulate Pu. The sludge from another surficial Z-9 location was analyzed, first by loss on ignition (LOI) to 750-800°C and then by digestion and analysis of the residues. The LOI treatment would have removed water, converted hydroxyl functions to oxide, and volatilized or burned away organic compounds like CCl_4 and lard oil. The analyses, Table 13, before and after accounting for LOI, are compared with average Hanford formation sediment composition (taken from Table 12). The normalized sludge composition (after LOI), compared with that of Hanford formation sediments, is relatively depleted in Si and Al and enriched in Fe, Mg, Ca, Na, and slightly in K. The SiO_2:Al_2O_3 mass ratio is 5.7 in the sludge and 4.8 in the Hanford sediment, showing some relative enrichment of Al (likely) or depletion of Si (unlikely) in the waste-affected sediments.

Table 13. Composition of Sludge from Top Layer of Z-9 (sludge composition from page K-5 of Smith 1973; Hanford sediment composition from Table B.3 of Xie et al. 2003)

Mineral Oxide	Sludge		Hanford Formation
	wt%	Normalized	
SiO_2	41.6	54.0	72.1
Al_2O_3	7.3	9.5	15.1
FeO	12.1	15.7	4.5
MgO	5.7	7.4	
CaO	6.8	8.8	4.9
Na_2O	1.0	1.3	
K_2O	2.1	2.7	2.2
TiO_2	0.5	0.6	1.1
LOI	20.8		
Sum	97.9	100.0	99.9

The sludge also was treated with room temperature water for a 1-minute shake (no reaction with everything settling) and 75°C water for 2 hours, showing no oil layer, perhaps not surprising as TBP density is near that of water. Similar treatment conditions but with CCl_4 showed no visible reaction with 50% of the material floating at room temperature and a residual white scum after the CCl_4 evaporated at 75°C (the scum perhaps being lard oil, TBP, and DBBP). Parallel treatments with 12 M HNO_3 containing 0.3 M HF disintegrated the sludge at room temperature, forming an emulsion with some floating material, while 75°C heating in acid generated gas disintegrated the soil and formed an emulsion, but gave no floating material. These observations are consistent with the existence of organic material mixed in the soil (Appendix K of Smith 1973).

The second Pu type was present at much lower concentrations but was found over the length of both 60-cm cores. This more mobile Pu coincided with silicate mineral hydrolysis occurring by acidic waste attack. Chemical analyses of the acid-affected sediments by electron microprobe showed loss of alkali (e.g., K) and alkaline (e.g., Mg, Ca) earth elements and loss of metamorphic minerals as compared with parallel uncontaminated sediments (Ames 1974).

More extensive characterization of 216-Z-9 and of related 216-Z-1A crib sediments was reported in the subsequent account (Price and Ames 1975). The 216-Z-1A crib investigations explored the leaching of

Al, K, Mg, Ca, and Fe from waste-affected basalt and feldspar inclusions within the basalt groundmass. As noted earlier in this report, the Z-1A crib received wastes from PRF like the RECUPLEX wastes discharged to Z-9.

As seen in the present Table 14 and Table 15, and by Figure 6 of Price and Ames (1975), mineral alteration occurred for both mineral types but was much greater for the groundmass (finely-grained) basalt (Table 14) than for the feldspar (Table 15). For the feldspar analyses, it was found that although alkali and alkaline earth cations disappeared from the feldspar structure, the anorthite and orthoclase share increased relative to albite (i.e., leaching was greater for sodium).

Table 14. Original and Crib Z-1A Waste-Altered Basalt Groundmass Compositions (Table II of Price and Ames 1975)

	SiO_2	Al_2O_3	K_2O	MgO	CaO	FeO	TiO_2	P_2O_5	Total
Area					Original Groundmass				
1G	62.1	13.5	2.4	2.5	7.6	10.5	1.9	0.3	100.8
2G	62.1	13.7	1.7	3.0	7.4	11.4	1.8	0.3	101.4
3G	62.5	13.3	2.5	2.4	7.4	11.5	2.0	0.5	102.1
Area					Altered Groundmass				
4G	62.5	0.4	0.06	–	0.1	2.1	1.3	0.3	69.5
5G	57.3	4.4	0.4	1.6	0.1	8.8	2.2	0.7	75.5
6G	56.3	1.8	0.1	–	0.1	7.4	1.8	0.2	67.7

Table 15. Original and Crib Z-1A Waste-Altered Feldspar Compositions (Table III of Price and Ames 1975)

Sample	Ab:An:Or[a]	Si	Al	Ca	K	Na	Fe	Sum(Ca,K,Na,Fe)
				Original Feldspar				
1F	40.4 : 57.8 : 1.8	10.351	5.490	2.138	0.067	1.493	0.146	3.844
2F	40.2 : 58.0 : 1.8	10.425	5.385	2.139	0.066	1.481	0.160	3.846
				Altered Feldspar				
3F	35.6 : 61.2 : 3.2	10.397	5.442	2.230	0.115	1.298	0.106	3.749[b]
4F	38.8 : 58.6 : 2.6	10.537	5.260	2.109	0.092	1.401	0.181	3.783[b]

(a) Ab = albite, $NaAlSi_3O_8$; An = anorthite, $CaAl_2Si_2O_8$; Or = orthoclase, $KAlSi_3O_8$.
(b) Analyses show losses of alkali and alkaline earth cations from the feldspar structure.

Radiochemical analyses and leaching tests were performed for the 4-5 and 4-11 fractions of the Z-9 crib sediment samples (Swanson 1973). These studies sought to characterize the Pu species present in the sediment by examining the Pu behavior upon exposing sediments to different leaching media. Plutonium concentrations in the Z-9 sediments decrease as a function of depth as shown in Figure 24 and Figure 29, just as was shown in Figure 23 and Figure 24for Z-1A sediments. For sample 4-11, the greatest Pu concentration is ~9 mg Pu/g at 1-inch depth and plateaus to ~0.1 g Pu/g at ~15 to 21-inch depth. Sample 4-5 ranges from ~1 mg Pu/g at ~1-inch depth to ~0.08 mg Pu/g at ~22-inch depth. Assuming the bulk density of these sandy sediments is 1.6 g/cm^3, the Pu concentrations range from about 14 g/liter for the shallowest 4-11 sample to 0.13-0.16 g/liter for the 21 to 22-inch deep 4-11 and 4-5 samples. These values are comparable to those observed at corresponding depths shown in Figure 22.

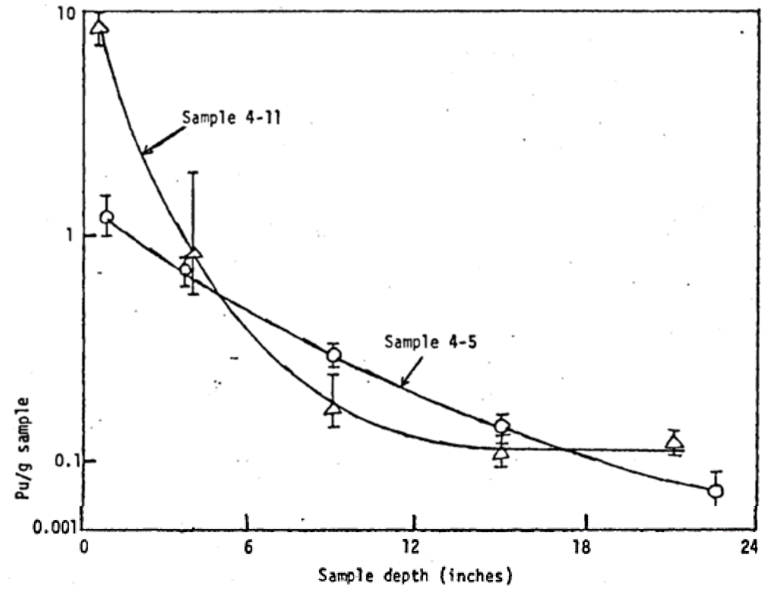

Figure 29. Plutonium Concentrations for Samples 4-5 and 4-11 of 216-Z-9 as Functions of Depth (Figure 5 of Swanson 1973)

Plutonium concentrations found in particle size fractions sieved from sample 4-11 sediment collected at 2 to 6-inch, 6 to 12-inch, and 18 to 24-inch depths are shown in Table 16. Also provided are the sediment mass fractions found at each size range (granulometry) and the Am/Pu mass ratio. It is seen that relatively more “fines” with particle size < 0.0625 mm are found in the uppermost (2-6-inch depth) fraction. This may be because of fine solids collected from the RECUPLEX waste discharge or chemical breakdown of the native minerals by acidic waste attack but either explanation is speculative. The Am/Pu mass ratios seem to be little affected by depth or particle size meaning the Am and Pu, at least at these shallow depths, behave similarly. Whether this similar behavior is by Am and Pu coinciding in the same particle types (e.g., ^{241}Am in-grown from ^{241}Pu decay within PuO_2) or by Am and Pu having similar chemical interactions with the sediment is unknown. The latter explanation, however, seems less likely. The integrated Pu concentrations (1.09, 0.18, and 0.12 mg Pu/g sediment) decrease steeply in the samples at the three depth ranges (2-6, 6-12-inches, and 18-24 inches) but correspond with the concentrations shown in Figure 29.

Table 16. Plutonium Distributions in Sample 4-11 as Functions of Depth and Particle Size (Table IV of Swanson 1973)

Particle Size Range (mm)	>2	1-2	0.5-1	0.25-0.5	0.125-0.25	0.0625-0.125	<0.0625	Sum or Average
Mid-size (mm)	4	1.5	0.75	0.375	0.1875	0.09375	0.03125	
Specific Surface Area (cm^2/g) [a]	5.56	14.8	29.6	59.3	119	237	711	
Depth (inches)				Sediment Mass%				
2-6	42	20	19	5.4	4.3	4.9	4.6	100.2
6-12	43	26	19	5.2	2.3	2.1	1.9	99.5
18-24	40	26	22	6.4	2.2	1.4	1.7	99.7
Depth (inches)				[Pu] (mg/g sediment)				
2-6	0.13	0.22	0.60	1.8	3.0	3.2	10.7	1.09
6-12	0.093	0.093	0.14	0.29	0.36	0.86	2.48	0.18
18-24	0.082	0.10	0.10	0.18	0.28	0.39	1.13	0.12
Depth (inches)				Surface [Pu] (mg/cm^2 sediment)				
2-6	0.0468	0.0297	0.0405	0.0608	0.0506	0.0270	0.0301	0.0408 ± 0.0126
6-12	0.0335	0.0126	0.0095	0.0098	0.0061	0.0073	0.0070	0.0122 ± 0.0096
18-24	0.0295	0.0135	0.0068	0.0061	0.0047	0.0033	0.0032	0.0096 ± 0.0095
Depth (inches)				Weight% Pu in Size Fraction				
2-6	5.1	4.1	10	9.0	12	14	45	99.2
6-12	22	14	15	8.4	4.6	10	26	100.0
18-24	26	21	18	9.4	4.9	4.4	16	99.7
Depth (inches)				Am/Pu Mass Ratio				
2-6	0.0025	0.0023	0.0021	0.0022	0.0021	0.0023	0.0021	0.0022 ± 0.0001
6-12	0.0023	0.0021	0.0021	0.0018	0.0019	0.0020	0.0020	0.0020 ± 0.0002
18-24	0.0022	0.0020	0.0017	0.0013	0.0017	0.0016	0.0014	0.0017 ± 0.0003

(a) Specific surface area of the sediment particles assuming spherical particles, average particle diameter is at the mid-size of the range, the >2-mm particle average diameter is 2× the lower limit, and the <0.0625 particle average is 1/2 of the upper limit.

For all three sample 4-11 sediment depths, the Pu concentrations increase steeply with decrease in particle size. For example, as shown in Table 16, the largest (>2-mm) particles for the 2 to 6-inch depth contain 0.13 mg Pu/g while the finest particles (<0.0625 mm) at the same depth contain 10.7 mg Pu/g sediment, an ~80-fold greater concentration. The relative Pu concentration ranges by particle size are lower at greater depths but still substantial: a factor of (2.48/0.093 =) ~27 for the 6 to 12-inch deep horizon and (1.13/0.082 =) ~14 for the 18 to 24-inch horizon.

Because the Pu concentration increases with decreasing particle size, it could be thought that the Pu concentration is proportional to the constituent particles' surface area. The calculated areal Pu concentrations, in units of mg Pu per cm^2 of particle surface area, are provided in Table 16 based on the data provided by Swanson (1973). For the 2 to 6-inch depth, the values are reasonably consistent, ranging about a factor of two for the seven particle size bins and averaging 0.041 ± 0.013 mg Pu/cm^2. The values are not so consistent for the other two depths, however, and trend to greater areal concentration as the particle size increases. However, as would be expected, the areal concentrations for a given particle size decrease with depth.

The concentrations of water for the 4-5 and 4-11 sediments samples were measured as functions of depth using weight loss on drying at room temperature and by ethanol (EtOH) leaching for water with analysis by infrared absorption (Table V of Swanson 1973). The TBP concentrations also were measured, using CCl_4 extraction and infrared absorption. The results, summarized in Table 17, show that the two water analysis methods give similar results and that the concentrations of both water and TBP decrease with depth. Sample 4-11 has greater TBP and water concentration than sample 4-5 in their respective top layers, but the water concentrations are comparable below about 1.5 to 2 inches. Note that the retrieved sediments taken during mining of the top 12 inches of the crib showed 5 wt% water, on average, a value somewhat lower than observed for the 4-11 and 4-5 samples but well within the 0.2 to 24.4 wt% H_2O range observed for the retrieved sediments taken from the top 12 inches (page 16 of Ludowise 1978).

Table 17. Water and TBP Concentrations in Sediments (Table V of Swanson 1973)

		Wt% H_2O		
Sample	Depth (inches)	Drying at 23°C	EtOH Extraction	wt% TBP
4-11	0-1	31	32, 33	1.4, 1.3
4-11	1-2	12, 13		1.0
4-11	2-6	9, 11		0.65, 0.61, 0.75
4-11	6-12	4.9	5.4	0.57
4-11	12-18	4.4		0.45
4-11	18-24	4.1		0.49
4-5	0-1.5		8.4	<0.1
4-5	1.5-6	9.4		
4-5	6-12	6.0		
4-5	12-18	5.6		
4-5	18-21	4.6		

Plutonium leaching from the sediments by CCl_4 and ethanol was measured as well. The results, Table 18, for the 18 to 24-inch horizon of sample 4-11 show ethanol to leach more Pu than does CCl_4. Interestingly, while the percentage of Pu mobilized by leaching increases with depth, the Pu concentration with respect to the sediment mass remains approximately constant. As seen in Table 18, the TBP concentration is more than 10-times greater for the 4-11 sample than the 4-5 sample. Accordingly, the Pu removed by the ethanol leach is about 10-times greater for the 4-11 than the 4-5 sample. Overall, however, the Pu mobilized by either CCl_4 or ethanol is a small fraction of the total.

Table 18. Plutonium Leaching by CCl_4 and Ethanol (Table 1 of Swanson 1973)

		%Pu Removed		Pu Removed (mg/g sample, using EtOH)
Sample	Depth (inches)	CCl_4	EtOH	
4-11	0-1		0.1	0.01
4-11	2-6	0.1		
4-11	6-12		5	0.006
4-11	12-18		9	0.009
4-11	18-24	3	7	0.01
4-5	0-1.5	0.01		
4-5	6-12		0.3	0.001

Plutonium leaching by various concentrations of HNO_3 also was tested (Swanson 1973). Little Pu removal occurred with dilute HNO_3 (concentration and amount unstated). Most leach testing was done using 5 M HNO_3 at ~23°C room temperature. Leaching of the 4-5 and 4-11 samples taken from various depth horizons using multiple contacts with the 5 M HNO_3 leachant is shown in Figure 30 as functions of leaching contact and contact time. Other experiments showed that an apparent equilibrium Pu concentration was reached within a day. Thus, Pu removed by leaching would only increase by refreshing the leachant. Because of this, it was postulated that the Pu removed from the sediment was limited by the solubility of an unspecified Pu species.

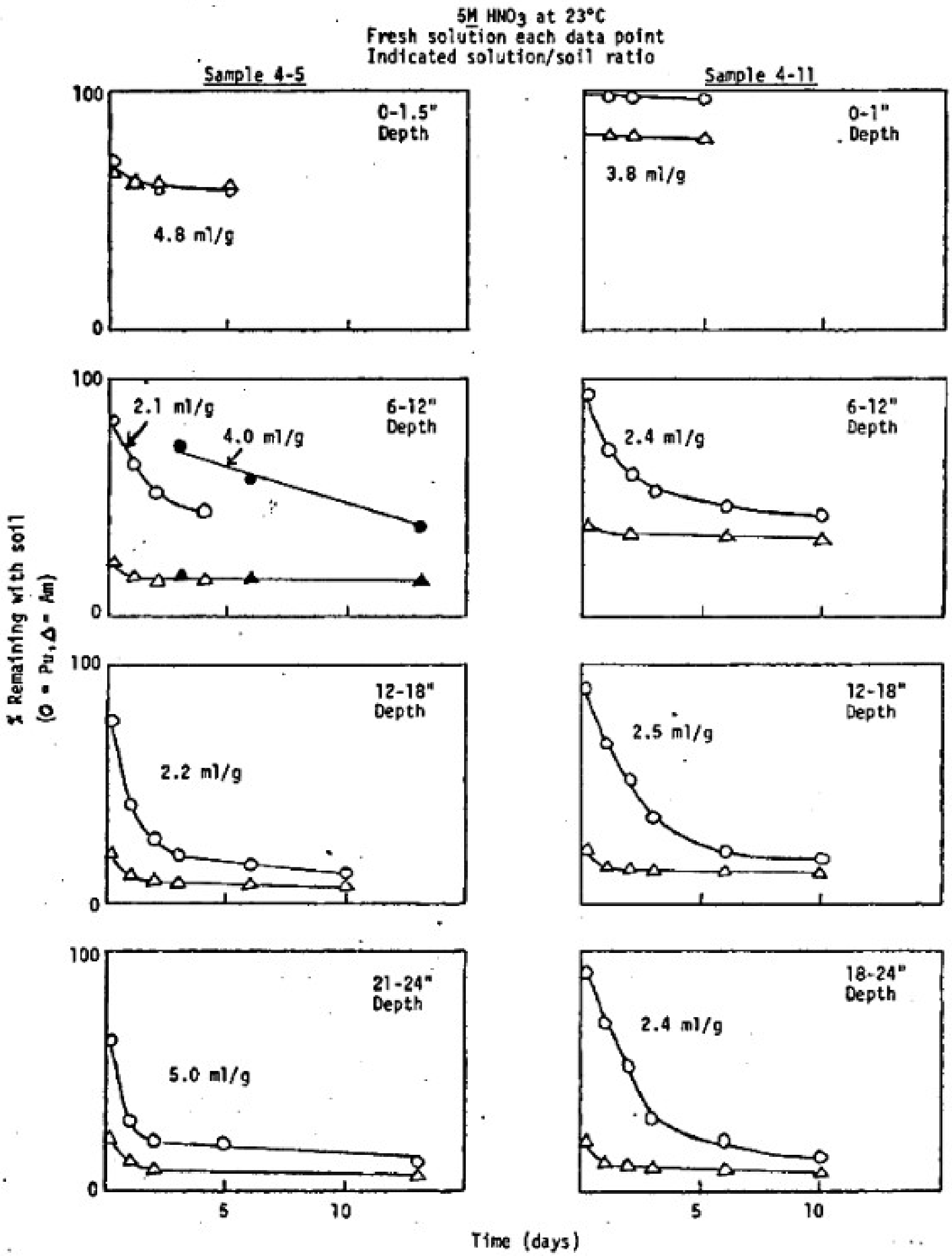

Figure 30. Z-9 Sediment Leaching Behavior Using 5 M HNO_3 (Figure 1 of Swanson 1973)

To test this hypothesis, the Pu solution concentrations in each of these leaching contacts were back-calculated based on the Pu concentrations in the starting sediments as shown in Figure 29, the solution/soil ratios stated in Figure 29, and the fractions of Pu removed for each leach contact also shown in Figure 30. If the Pu concentrations were solubility-limited, constant Pu concentrations would be expected for succeeding leach contacts. The results for the 4-5 and 4-11 sediment samples at their various depths within Z-9 are shown in Figure 31.

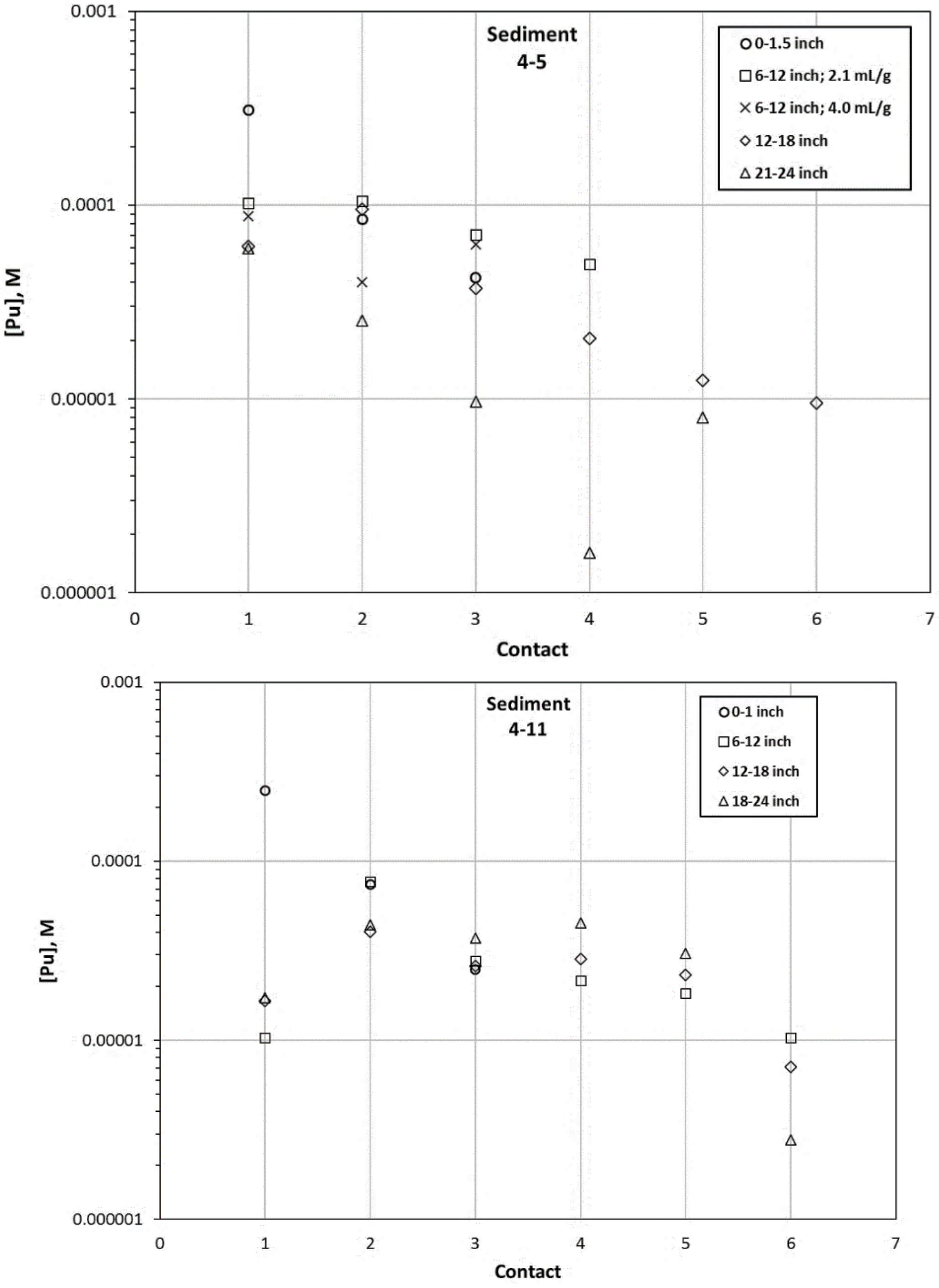

Figure 31. Pu Solution Concentrations in Multiple Leach Contacts with 4-5 and 4-11 Z-9 Sediment (based on data from Swanson 1973)

A Pu concentration plateau or pause at about 3-5×10^{-5} M is, in fact, observed for both sample cores but is more pronounced for the 4-11 core. Clearly, this concentration lies far below the solubility of Pu(IV) nitrate in 5 M HNO_3. The solubility-defining solid phase is not identified by Swanson (1973).

Sediment pretreatments to effect improved Pu leaching from the 12 to 18-inch horizon of the 4-11 core sample also were studied (Table II of the Swanson 1973 and associated text). Pretreatments included contacts with 2.5 M potassium hydroxide (KOH), ethanol, 30% TBP in normal paraffin hydrocarbon (NPH; like kerosene), and sequential treatment with ethanol and then KOH solution. All of these, some with supplementary heating, were followed by contact with 5 M HNO_3. A four-day contact with 2.5 M KOH, including 3 hours at 100°C, decanting of the alkaline solution, and then leaching with 5 M HNO_3 removed 60% of the Pu from the sediment sample, a much better result than observed in the absence of the KOH pretreatment, in which only 7% of the Pu was removed. If the KOH solution was not separated before the 5 M HNO_3 was added, only 6% of the Pu was removed. Therefore, the KOH was effective in removing an agent that was responsible for Pu remaining with the solid phase.

Pretreatment of the 21 to 24-inch horizon of the 4-5 sediment using 2.5 M potassium bicarbonate or carbonate ($KHCO_3$ and K_2CO_3, respectively) removed 65% of the Pu (multiple contacts) and 25% of the Pu (nearly all in the first of multiple contacts), respectively (Swanson 1973). These (bi)carbonate treatments would help solubilize Pu as carbonate complexes. Subsequent treatment with 5 M HNO_3 rapidly removed most of the remainder of the Pu.

Another type of experiment contacted the 12 to 18-inch horizon of the 4-11 sediment with 5 M HNO_3 and an immiscible upper layer of 30% TBP-in-NPH (pages 11-12 of Swanson 1973). This combined one-step process of leaching and solvent extraction removed 80% of the Pu from the sediment with nearly all the dissolved Pu reporting to the organic phase.

The concentrations of Pu leached from 216-Z-9 sediment samples 4-11A and 4-5A with 0.0015 M $CaCl_2$ (a simple simulated groundwater) were measured (Rai et al. 1980). Although further details on the sediment samples, such as their sampling depths and mass-specific Pu concentrations, were not reported, it is likely that the 4-11A sample was from 0 to 15.1 cm depth and 4-5A was from the 0 to 15.2 cm depth of the Z-9 crib based on information provided on the parent samples in Table 10 of Ames (1974).

The soil samples first were water-washed to remove soluble salts before being contacted with 0.0015 M $CaCl_2$ and allowed to equilibrate. Similar parallel tests were run for both sediment types but spiked with 5 mg of "crystalline" PuO_2 having well-defined XRD pattern. Quadruplicate tests for each sample source, even after rinsing, were acidic. The pHs of the 4-11A sediment tests ranged from ~4.4 to 5.2; those of the 4-5A tests ranged from ~4.2 to 4.8. Significantly, Pu concentrations in tests both with and without PuO_2 spike were similar (~1.6×10^{-8} to 1.6×10^{-7} M) and in the range observed for tests run with PuO_2 only. From these observations, Rai et al. (1980) inferred that the 4-11A and 4-5A samples contained PuO_2. This inference was supported by the observed presence of PuO_2 in 4-11A as shown by XRD (Ames 1974). Rai et al. (1980) also noted that although the 4-11A and 4-5A samples arose from wastes high in organic material content, the organic materials notably did not enhance Pu solution concentrations above those observed in the presence of PuO_2 alone. Rai et al. (1980) reported that JM Cleveland at the Rocky Flats Plant near Golden, Colorado, similarly observed no influence of organic materials on Pu concentrations in soils contaminated with (Pu) lathe cooling oils.[1]

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[1] Similar leach tests in 0.0015 M $CaCl_2$ with sediment sample Z12-1D, from the 216-Z-12 crib, also were conducted by Rai et al. (1980). This sediment sample was otherwise undescribed so no information on its Pu concentration, well source, or depth was provided; efforts to find this information from other resources were unsuccessful. In duplicate tests, the Pu concentrations found after contact were ~3×10^{-11} M and the pH ~7.2, slightly lower than

Aggressive conditions for Pu leaching from Z-9 sediments also were investigated with the goal of Pu recovery (Panesko 1972). Interestingly, the solution:soil ratio was not a strong determinant on the extent of Pu recovery. The recommended leaching conditions were 12 M HNO_3 containing 0.3 M HF at 100°C. Under these conditions, two such contacts recovered up to 96% of the Pu (for two of the tested sediments) and left a residue containing 0.02 g Pu per liter (i.e., ~0.001 wt%). Lower HNO_3 or HF concentrations or lower temperature gave lower Pu recoveries. At these high HNO_3 concentrations, dissolved silica was <0.25 g/liter (<0.01 M), in agreement with expected silica solubility shown in Figure 12.

The effectiveness of the alkaline pretreatments (i.e., KOH, $KHCO_3$, and K_2CO_3) of Z-9 crib sediments before HNO_3 leaching; the retention of Pu for sediments treated with KOH but acidified without separation; and the effectiveness of 5 M HNO_3 leaching with simultaneous solvent extraction by TBP in NPH in the experiments by Swanson (1973) are consistent with the potential association of Pu with silica gels. If Pu is truly associated with silica gels, alkaline conditions, particularly with KOH, would help solubilize the silica, effectively metathesize the combined Pu-silicate, and form finely particulate Pu(IV) hydrated oxide, $PuO_2{\cdot}xH_2O$, while dissolving silica as potassium silicate. The $PuO_2{\cdot}xH_2O$ metathesis product then would be amenable to dissolution in HNO_3. In the acidic leaching test with associated TBP/NPH solution, the exchangeable Pu (from silica or other solid substrate) could also be displaced by HNO_3 and then removed from the aqueous solution by solvent extraction into the TBP-NPH organic phase.

Process characterization shows that silica gels arise from HNO_3 dissolution of silicate-bearing scrap for feed to RECUPLEX, both as a separable solid phase (after coagulation) and as a significant contributor to interfacial crud. Silica gel residues also would be expected based on the observed interaction of acidic PRF wastes (which have compositions like RECUPLEX wastes) with Hanford basalt and feldspar sediment minerals (Price and Ames 1975; see Table 14 and Table 15 in the present document). Therefore, the interaction of Pu with silica gels in the acidic crib sediments should be considered. Some early work on the exchange of Pu and other elements with silica gel in acid conditions may provide useful insights (Ahrland et al. 1960).

Two parallel saturated column leaching tests of Z-1A sediment contaminated by acidic PRF waste discharge were conducted to determine the extent of Am and Pu mobilization under groundwater intrusion and massive surface flooding conditions (Delegard et al. 1981). The sediment, a slightly silty fine sand, was taken from about the 9-m depth of the Z-1A crib, contained 107 nCi ^{239}Pu/g and 100 nCi ^{241}Am/g, and had pH 3.9 when contacted with water. The surface flood was simulated using 0.01 M $CaCl_2$ solution (30 mM ionic strength; pH 6.2) and the Hanford-affected groundwater was simulated using ~1.0 mM Na^+, 0.17 mM K^+, 0.5 mM Mg^{2+}, 0.5 mM Ca^{2+}, 1.1 mM H_4SiO_4, 0.7 mM NO_3^-, 0.4 mM SO_4^{2-}, and 1.3 mM HCO_3^- (4.5 mM ionic strength; pH 8.1). The leach solutions were introduced to the bottoms of identical 2.5-cm-diameter and 22-cm-long glass columns, each packed with 180 g of sediment with the leach solutions pumped upward to ensure saturation at ~2.6 cm/hour flow rate. The effluent solutions were collected and analyzed for pH, Am, Pu, and chemical solute concentrations. Small-scale batch contacts of Z-1A sediment aliquots also were performed at roughly equal sediment:solution mass ratios using distilled and deionized (DI) water; 0.01, 0.1 and 1 M $CaCl_2$; 0.01, 0.1 and 0.3 M $Al(NO_3)_3$; and 0.01, 0.1, and 1 M NaF.

The Pu and Am for the column tests initially eluted in similar patterns but with the Pu molar concentration about two orders of magnitude lower than those of Am. The lower Pu concentrations and plutonium’s lower specific activity meant the Pu concentrations soon went below alpha spectrometry detection. The Am elution concentrations as functions of pH are shown in Figure 32. Also shown in

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expected for native Hanford sediments. With PuO_2 spike, the Pu concentrations rose 300-fold to ~$9{\times}10^{-9}$ M at pH ~6.6 corresponding with those for PuO_2 alone.

Figure 32 are Am concentrations observed by Rai et al. (1981) in batch leaching tests of acidic Z-9 sediment samples and in survey of other studies of Am interaction with geologic media. Rai et al. (1981) observed the Am concentrations to decrease linearly 10-fold with unit pH increase and attributed this to solubility control by an unspecified solid phase.

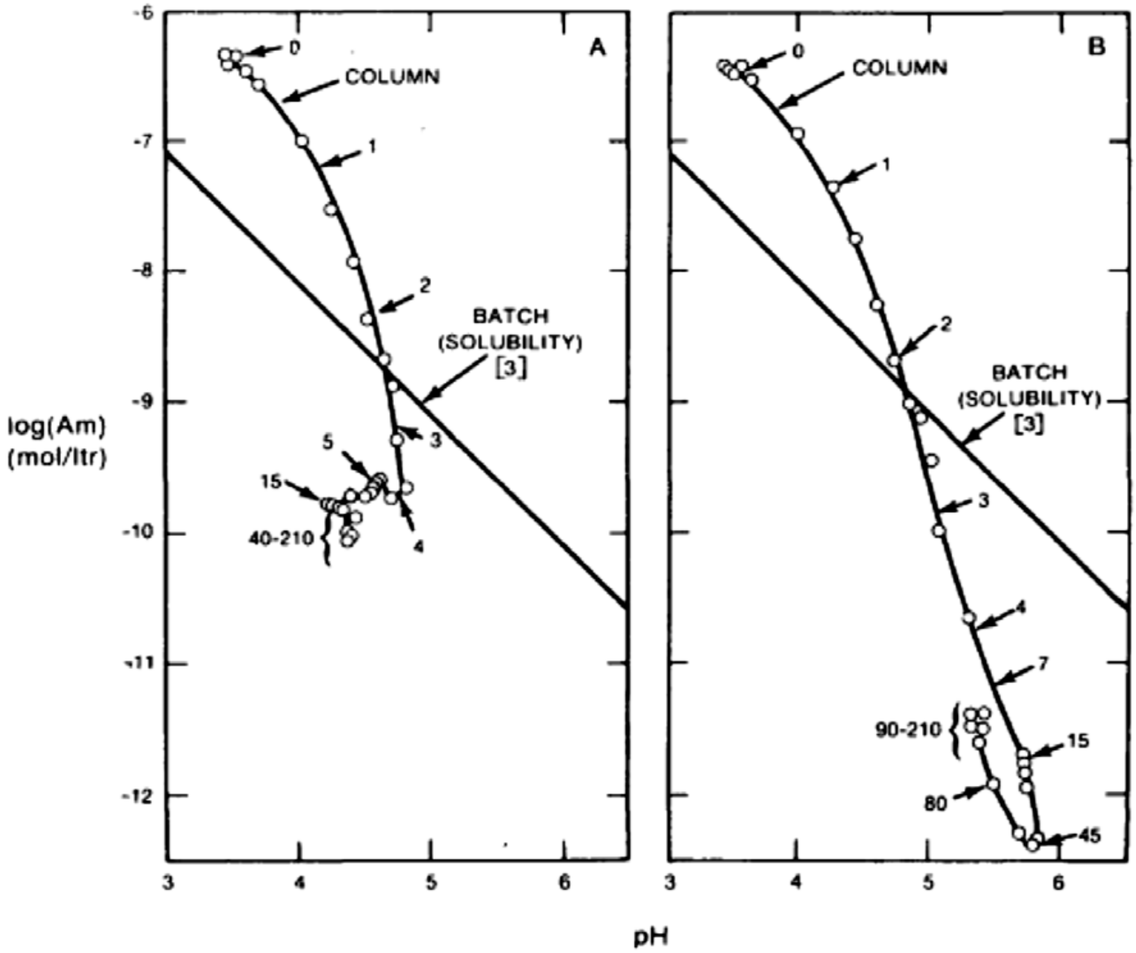

Figure 32. Saturated Column Americium Leaching from 216-Z-1A Sediments Using A: 0.01 M $CaCl_2$ and B: Simulated Groundwater. Numbers show throughput column pore volumes. (Figure 1 of Delegard et al. 1981)

As shown in Figure 32, the Am concentrations in the first two pore volumes exceeded the concentrations expected based on batch tests (Delegard et al. 1981). The Am bolus was paralleled by marked cation elution, not shown here, and at pH ~3.5, somewhat lower than in simple batch tests with water (pH ~3.9). Over 80% of the Am ultimately leached was removed in the first of the 210 leachant pore volumes passed through each column. The pH generally increased with added leachant, but the waste-affected sediment even after 210 column volumes remained buffered well below that normally found in native Hanford sediments (pH ~8). The Am concentrations decreased with continued throughput leachant volume. After 210 pore volumes, however, only ~30% of the Am and less than 1% of the Pu were removed from the sediment by each solution. The chloride, fluoride, and nitrate elution were slightly retarded in the column tests, indicating that the sediment behaved as a weak anion exchanger.

The Am concentrations as functions of pH in the batch tests using water and solutions of $CaCl_2$, $Al(NO_3)_3$, and NaF (Delegard et al. 1981) followed closely the line observed by Rai et al. (1981) in their related tests and survey of related Am interactions with geologic media.

7.0 Summary

This report summarizes the different process chemistries that generated the waste disposed to plutonium-bearing waste ground disposal structures in the 200 West Area at the Hanford Site. The compositions of the wastes have been reconstructed, including the plutonium and americium inventory, and information on co-contaminant disposal. The chemistry of the waste is extremely complex, containing varying amounts of aluminum, magnesium, manganese, calcium, iron, chromium, lead, nickel, mercury, cadmium, gallium, sodium, nitrate, fluoride, sulfate, hydroxide, chloride, organic extractants, and lard oil, as well as the plutonium and americium. The waste chemistry, and information on the chemical form and morphology of plutonium-bearing particles, are key waste signatures allowing mechanisms responsible for migration to be elucidated through examination of contaminated sediments from beneath the waste sites.

Results from previous studies on plutonium- and americium-contaminated sediments show that americium is more mobile than plutonium for acidic wastes but not so for pH-neutral to alkaline wastes. Plutonium is present in sediments both as discreet particles (PuO_2) and as a second, more mobile particle type associated with silicate mineral hydrolysis, possibly forming a silica gel. Plutonium concentrations in sediments decrease with depth. The ratio of americium to plutonium is similar down to a depth of 36 cm, suggesting that americium and plutonium coincide in the same particle types (e.g., ^{241}Am in-grown from ^{241}Pu decay within PuO_2). Plutonium concentration increases with decreasing particle size, therefore is proportional to constituent particle surface area. The amount of plutonium in sediments that is mobilized by solvents such as carbon tetrachloride and ethanol is only a small fraction of the total plutonium. Concentrated nitric acid leaches some, but not all the plutonium in the sediment, and is limited by the solubility of an unidentified plutonium phase. Pretreatment of sediments with potassium hydroxide removes the agent that is retaining the plutonium in the solid phase and enhances the effect of leaching with concentrated nitric acid. Treatment of sediments with bicarbonate solubilizes the plutonium as a carbonate complex. Organic (TBP) extraction of acidified sediments removed 80% of the plutonium.

In column leach studies simulating massive water intrusion into acidic Z-1A sediments, americium was found to be more mobile than plutonium. Americium concentrations in batch contact tests of acidic Z-9 and Z-1A sediments were found to decrease a factor of 10 with each unit pH increase. Further work is required to identify solubility-determining americium-bearing solid phases.

These results inform characterization efforts that assess the impact of changes in waste chemistry on sediment transformation and plutonium/americium re-mobilization mechanisms. Additional microscopic and spectroscopic measurements will be conducted on contaminated sediments from beneath 200 West Area waste sites to identify plutonium and americium phases at the micrometer-scale. Sediment analysis based on sequential extraction procedures will be conducted to provide data on mobile and immobile plutonium and americium present in sediments. Ultimately, this will lead to a defensible description of plutonium and americium mobility in relation to waste site conditions that can be interpreted in terms of migration and remediation risks.

8.0 Quality Assurance

This work was performed in accordance with the Pacific Northwest National Laboratory (PNNL) Nuclear Quality Assurance Program (NQAP). The NQAP complies with the United States Department of Energy Order 414.1D, *Quality Assurance*, and 10 CFR 830 Subpart A, *Quality Assurance Requirements*. The NQAP uses NQA-1-2012, *Quality Assurance Requirements for Nuclear Facility Application* as its consensus standard and NQA-1-2012 Subpart 4.2.1 as the basis for its graded approach to quality.

This work represents a review of the literature. The information associated with this report should not be used as design input or operating parameters without additional qualification.

9.0 References

10 CFR 830, Subpart A. 2011. "Quality Assurance Requirements." Code of Federal Regulations, U.S. Department of Energy, Washington, D.C.

Ahrland S, I Grenthe, and B Noren. 1960. “The Ion Exchange Properties of Silica Gel I. The Sorption of Na^+, Ca^{2+}, Ba^{2+}, UO_2^{2+}, Gd^{3+}, Zr(IV) + Nb, U(IV) and Pu(IV).” *Acta Chemica Scandinavica* 14:1059-1076. http://actachemscand.org/pdf/acta_vol_14_p1059-1076.pdf

Ames LL. 1974. *Characterization of Actinide Bearing Soils: Top Sixty Centimeters of 216-Z-9 Enclosed Trench*. BNWL-1812, Battelle Pacific Northwest Laboratories, Richland, Washington. https://www.osti.gov/biblio/4313915-characterization-actinide-bearing-soils-top-sixty-centimeters-enclosed-trench

ARHCO. 1976. *WE-1 Pulse Column Cartridge Assembly & Details*. Report No. H-2-27743, Atlantic Richfield Hanford Company, Richland, Washington.

ASME NQA-1-2012. "Quality Assurance Requirements for Nuclear Facility Applications." The American Society of Mechanical Engineers, New York, New York.

Avens LR, JT McFarlan, and UF Gallegos. 1989. *Magnetic Separation as a Plutonium Residue Enrichment Process*. LA-UR-89-3410. Los Alamos National Laboratory, Los Alamos, New Mexico. https://www.osti.gov/biblio/5453395-magnetic-separation-plutonium-residue-enrichment-process

Avens LR, UF Gallegos, and JT McFarlan. 1990 “Magnetic Separation as a Plutonium Residue Enrichment Process.” *Separation Science and Technology* 25(13-15):1967-1979. https://doi.org/10.1080/01496399008050437

Barney GS. 1996. “Results of Testing EIChrom Resins for Pretreatment of Stored Plutonium Solutions Prior to Solidification,” in Letter Report 15F00-96-032, CS Sutter to EC Vogt, “Summary Reports of the Solution Stabilization Testing Performed in Support of 94-1 Program Activities,” Westinghouse Hanford Company, Richland, Washington.

Behrens RG, EC Buck, NL Dietz, JK Bates, E Van Deventer, and DJ Chaiko. 1995. *Characterization of Plutonium-Bearing Wastes by Chemical Analysis and Analytical Electron Microscopy*. ANL-95/35. Argonne National Laboratory, Argonne, Illinois. https://www.osti.gov/biblio/170576-characterization-plutonium-bearing-wastes-chemical-analysis-analytical-electron-microscopy

Blasewitz AG. 1951. *Recuplex Feasibility Report*. HW-22596, Hanford Atomic Products Operation, Richland, Washington. https://reading-room.labworks.org/Files/GetDocument.aspx?id=D197304657

Bruns LE. 1959a. *Recuplex Product Impurity Study*. HW-60844, Hanford Atomic Products Operation, Richland, Washington. https://reading-room.labworks.org/Files/GetDocument.aspx?id=D8343014

Bruns LE. 1959b. *Mistron as a Deemulsification Agent in the RECUPLEX Solvent Extraction System*. HW-58770, Hanford Atomic Products Operation, Richland, Washington. https://reading-room.labworks.org/Files/GetDocument.aspx?id=D8383829

Bruns LE. 1963. *Start-up Flowsheets for the Plutonium Reclamation Facility (CAC-880), Edition I*. HW-79586, Hanford Atomic Products Operation, Richland, Washington. https://reading-room.labworks.org/Files/GetDocument.aspx?id=D8574888

Bruns LE. 1967. “Geometrically Favorable Plutonium Scrap Recovery Plant.” *Chemical Engineering Progress Symposium Series* No. 80, 63:156-162.

Bruns LE. 1973. “RECUPLEX Input to Z-9 Crib.” Letter report to RE Isaacson, Atlantic Richfield Hanford Company, Richland, Washington.

Brunstad A. 1958. *Emulsification and Precipitation in the RECUPLEX Columns*. HW-55674, Hanford Atomic Products Operation, Richland, Washington. https://reading-room.labworks.org/Files/GetDocument.aspx?id=D6053931

Campbell MH and JV Panesko. 1971. Internal letter to LM Knights (Manager), “Tentative Indications from the Burning of a Portion of One Dow Button and Dissolution of Oxide.” Atlantic Richfield Hanford Company, Richland, Washington.

Cantrell KJ and AR Felmy. 2012. *Plutonium and Americium Geochemistry at Hanford: A Site-Wide Review*. PNNL-21651, Pacific Northwest National Laboratory, Richland, Washington. https://www.pnnl.gov/main/publications/external/technical_reports/pnnl-21651.pdf

Chemical Processing Department. 1958. *Essential Materials Manual*. HW-54125. Hanford Atomic Products Operation, Richland, Washington. https://reading-room.labworks.org/Files/GetDocument.aspx?id=D8413478

Christensen DC and JA Rayburn. 1983. *Pyrochemical Recovery of Plutonium Fluoride Reduction Slag*. LA-9655-MS. Los Alamos National Laboratory, Los Alamos, New Mexico. https://www.osti.gov/biblio/6058055-pyrochemical-recovery-plutonium-fluoride-reduction-slag

Charboneau SL, A Hopkins, CS Sutter, and JA Teal. 2007. *Decommissioning the 216-Z-9 Crib Plutonium Mining Facility at the Plutonium Finishing Plant: Issues Characterization*. HNF-304575-FP, Rev.0. Fluor Hanford Co., Richland, Washington

Czigany S, M Flury, and JB Harsh. 2005. *Colloid stability in vadose zone Hanford sediments*. Environmental Science and Technology. 39(6), 1506-1512.

Delegard CH, SA Gallagher, and RB Kasper. 1981. “Saturated Column Leach Studies: Hanford 216-Z-1A Sediment.” Presented at “International Symposium on the Migration in the Terrestrial Environment of Long-Lived Radionuclides,” 27-31 July 1981 and in the proceedings of that meeting, “Environmental Migration of Long-Lived Radionuclides,” International Atomic Energy Agency, Proceedings Series STI/PUB/597, 1982; also as RHO-SA-210, 1981, Rockwell Hanford Operations, Richland, Washington.

Delegard CH and SA Jones. 2015. *Chemical Disposition of Plutonium in Hanford Site Tank Wastes*. PNNL-23468; WTP-RPT-234, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington. https://www.pnnl.gov/rpp-wtp/documents/WTP-RPT-234_rv1.pdf

Delegard CH and AJ Casella. 2016. *Literature Review: Crud Formation at the Liquid/Liquid Interface during TBP-based Solvent-Extraction Processes*. PNNL-25888, Pacific Northwest National Laboratory, Richland, Washington. https://www.osti.gov/servlets/purl/1430463

DOE Order 414.1D. 2011. "Quality Assurance." U.S. Department of Energy, Washington, D.C. Approved 4/25/2011.

DOE. 1991. *Expedited Response Action Proposal (EE/CA & EA) for 200 West Area Carbon Tetrachloride Plume*. DOE/RL-91-32, Draft B. U.S. Department of Energy, Richland, Washington. http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D196078303

DOE. 2016. *Remedial Design/Remedial Action Work Plan for the 200-CW-5, 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*. DOE/RL-2015-23. U.S. Department of Energy, Richland Operations Office, Richland, Washington.

Edwards JA. 2006. *Acceptable Knowledge Document for Sand, Slag, and Crucible Waste at Plutonium Finishing Plant Waste Stream SS&C01*. HNF-30023, Rev. 1, Fluor Hanford, Richland, Washington.

Eller PG, RW Szempruch, and JW McClard. 2004. *Summary of Plutonium and Oxide Storage Package Failures*. LA-UR-04-1453, Los Alamos National Laboratory, Los Alamos, New Mexico. http://lib-www.lanl.gov/cgi-bin/getfile?01054987.pdf

Elmer TH, and ME Nordberg. 1958. "Solubility of Silica in Nitric Acid Solutions." *Journal of the American Ceramic Society* 41(5):517-20. http://dx.doi.org/10.1111/j.1151-2916.1958.tb12907.x

Felmy AR, CC Schroeder, and MJ Mason. 1994. "A Solubility Model for Amorphous Silica in Concentrated Electrolytes." Presented at *Symposium of Scientific Issues Related to Safety and Treatment of Hanford Tank Wastes,* Washington, DC, August, 1994. Pacific Northwest Laboratory, Richland, Washington. http://www.osti.gov/scitech/servlets/purl/10110157-3hjADX/webviewable/

Felmy, A, S Clark, and M Triplett. 2017. Plutonium and Americium Geochemistry at Hanford. PNNL-SA-123148. Presented to the Hanford Advisory Board, River and Plateau Committee, January 17, 2017, Richland, WA, Pacific Northwest National Laboratory, Richland, WA. https://www.hanford.gov/files.cfm/PNNLfinal.pdf

Felt RE. 1967. *Burning and Extinguishing Characteristics of Plutonium Metal Fires*. ISO-756, Isochem, Incorporated, Richland, Washington.

Finch LW. 1959. *Preliminary Project Proposal Plutonium Reclamation Facility – Z Plant (Project CAC-880)*. HW-61777, Hanford Atomic Products Operation, Richland, Washington. https://reading-room.labworks.org/Files/GetDocument.aspx?id=D4272247

Flury M, JB Mathison, and JB Harsh. 2002. *In situ mobilization of colloids and transport of cesium in Hanford sediments*. Environmental Science and Technology. 36(24), 5335-5341.

Gerber MS. 1997. *History and Stabilization of the Plutonium Finishing Plant (PFP) Complex, Hanford Site*. HNF-EP-0924, Fluor Daniel Hanford, Incorporated, Richland, Washington. http://www.osti.gov/scitech/biblio/325360

Gray JH and PS Korinko. 1999. *Measurement of Moisture Content in Sand, Slag, and Crucible Materials*. WSRC-TR-99-00275, Westinghouse Savannah River Laboratory, Aiken, South Carolina. https://www.osti.gov/biblio/12335-measurement-moisture-content-sand-slag-crucible-materials

Griffo JS, WB Brown, and FD Lonadier. 1964. *Solubility of Plutonium Compounds*. MLM-1191, Mound Laboratory, Miamisburg, Ohio. http://www.osti.gov/scitech/biblio/4659828

Hampton BK and MS Miller. 2001. *241-Z-361 Tank Characterization Report*. HNF-8735 Rev 0 and HNF-8735 Rev 0A, Rev Fluor Hanford, Richland, WA.

Hanford. 1955. RECUPLEX *Operating Manual*. HW-35030, Plant Processes Sub-section, Separations Technology Section, Engineering Department, Hanford Atomic Products Operation, Richland, Washington. https://reading-room.labworks.org/Files/GetDocument.aspx?id=D1636575

Hanford. 1965. *Process Flow Diagram Material Balance*. H-2-19247, Sheet 1 of 2, Hanford Atomic Products Operation, Richland, Washington.

Harmon, KM, BF Judson, WL Lyon, RA Pugh, and RC Smith. 1961. "Plutonium Reconversions." In *Fuel Reprocessing*, SM Stoller and RB Richards, editors, Volume II in *Reactor Handbook*. Interscience Publishers, Incorporated, New York, New York.

Haschke JM. 1992. *Evaluation of Source-Term Data for Plutonium Aerosolization*. LA-12315-MS, Los Alamos National Laboratory, Los Alamos, New Mexico. http://lib-www.lanl.gov/cgi-bin/getfile?00193529.pdf

Haschke JM, TH Allen, and LA Morales. 2000. "Surface and Corrosion Chemistry of Plutonium." *Los Alamos Science* 26(2):252-273, NG Cooper, editor, Los Alamos National Laboratory, Los Alamos, New Mexico. https://permalink.lanl.gov/object/tr?what=info:lanl-repo/lareport/LA-UR-98-2297

Hedengren DC and HJ Goldberg. 1987. *ORIGEN2 Predictions of N Reactor Fuel Actinide Composition*. RHO-SD-CP-TI-105, Rockwell Hanford Operations, Richland, Washington.

Herb SF, P Madigman, and RW Riemenschneider. 1960. "Analysis of Fats and Oils by Gas-Liquid Chromatography and by Ultraviolet Spectrophotometry." *Journal of the American Oil Chemists Society* 37:127-129. https://link.springer.com/article/10.1007/BF02644928

Hopkins A, C Sutter, DB Klos, JA Teal, L Oates, FW Bond, E Mattlin, and S Clarke. 2008. *Structural Characterization of the 216-Z-9 Crib Prior to Decontamination and Demolition Using Robot Crawler and High Resolution Photography*. Paper 8117, WM 2008 Conference, Phoenix, Arizona. http://www.wmsym.org/archives/2008/pdfs/8117.pdf. See also SL Charboneau, AM Hopkins, CS Sutter, and JA Teal. 2007. *Decommissioning The 216-Z-9 Crib Plutonium Mining Facility At The Plutonium Finishing Plant: Issues Characterization*. HNF-34075·FP, Rev 0, Fluor, Richland, Washington. https://www.osti.gov/servlets/purl/908812

Hoyt RC and JA Teal. 2004. *Plutonium Finishing Plant Operations Overview (1949-2004): Contamination Events and Plutonium Isotope Distributions of Legacy Holdup Material in Process Systems*. HNF-22064, Rev. 0 (OUO), Fluor Hanford Company, Richland, Washington.

Jacques DI and SK Kent. 1991. *200-PB-5 Operable unit technical baseline report*. WHC-MR-0270. Prepared for the U.S. Department of Energy by Westinghouse Hanford Co., Richland, Washington.

Jones SA. 1998. *Tank 241-Z-361 Process and Characterization History*. HNF-1989, Rev. 1, B&W Hanford Company, Richland, Washington.

Jones SA. 2001. Letter Report 1AC00-01-004, to JR Ewalt, "Test Plan for Oxalic Acid Addition to Magnesium Hydroxide Precipitation Solution Stabilization Process." Fluor Daniel Hanford, Incorporated, Richland, Washington.

Jones TE. 2008. *Inventory Estimates for Sludge Currently in Tank 241-Z-361*. SGW-35955, Rev 0, Fluor, Richland, WA.

Judson BF, KM Harmon, LE Bruns, BA Chandler, FF Cole, HW Crocker, RB Guenther, WL Lyon, and RW McKee. 1956a. *Semi-Works Operation of the RECUPLEX Facility – Volume 1*. HW-44776 VOL1, Hanford Atomic Products Operation, Richland, Washington. https://reading-room.labworks.org/Files/GetDocument.aspx?id=D199117620

Judson BF, KM Harmon, LE Bruns, BA Chandler, FF Cole, HW Crocker, RB Guenther, WL Lyon, and RW McKee. 1956b. *Semi-Works Operation of the RECUPLEX Facility – Volume 2*. HW-44776 VOL2, Hanford Atomic Products Operation, Richland, Washington. https://reading-room.labworks.org/Files/GetDocument.aspx?id=D199117622

Judson BF. 1958. "Plutonium Recovery by a Reflux Solvent-Extraction System." Chapter 7-1 of *Progress in Nuclear Energy Series III – Process Chemistry*, Volume 2, FR Bruce, JM Fletcher and HH Hyman, editors, Pergamon Press, New York, New York. See also HW-49441 A, http://reading-room.labworks.org/Files/GetDocument.aspx?id=D8277166

Kasper RB, SM Price, MK Additon, RM Smith, GV Last, and GL Wagenaar. 1979. *Transuranic Distribution beneath a Retired Underground Disposal Facility, Hanford Site*. RHO-SA-131, Rockwell Hanford Operations, Richland, Washington.

Kasper RB. 1982. *216-Z-12 - Transuranic Crib Characterization: Operational History and Distribution of Plutonium and Americium*. RHO-ST-44.

Last GV and VJ Rohay. 1993. *Refined Conceptual Model for the Volatile Organic Compounds – Arid Integrated Demonstration and 200 West Area Carbon Tetrachloride Expedited Response Action*. PNL-8597, Pacific Northwest Laboratory, Richland, Washington. https://www.osti.gov/servlets/purl/10151709

Lindsey KM. 1996. *The Miocene to Pliocene Ringold Formation and Associated Deposits of the Ancestral Columbia River System, South-central Washington and North-central Oregon*. Open File Report 96-8, Washington State Department of Natural Resources, Olympia, Washington. http://file.dnr.wa.gov/publications/ger_ofr96-8_ringold_formation.pdf

Lipke EJ. 1997. *Engineering Study of the Criticality Issues Associated with Tank 241-Z-361*. HNF-2012, Duke Engineering and Services, Richland, WA.

Ludowise JD. 1978. *Report On Plutonium Mining Activities At 216-Z-9 Enclosed Trench*. RHO-ST-21, Rockwell Hanford Operations, Richland, Washington. https://pdw.hanford.gov/arpir/pdf.cfm?accession=0076183H

Ludowise JD. 1980. *Plutonium Reclamation Facility Engineering Training Manual*. RHO-MA-246. Rockwell Hanford Operations, Richland, Washington.

Maffei HP. 1957. *Continuous Task I – II*. HW-51006, Hanford Atomic Products Operation, Richland, Washington. https://reading-room.labworks.org/Files/GetDocument.aspx?id=D8526278

McCoskey JK and GA Cooke. 2013. *Characterization of Plutonium-Bearing Waste in the High-Level Waste Storage Tanks 241-SY-102, 241-TX-118, and 241-AZ-101 and the Plutonium Finishing Plant Z-9 Crib, Rev. 1*. LAB-RPT-12-00006, Washington River Protection Solutions, LLC, Richland, Washington.

Mishima J. 1966. *Plutonium Release Studies II. Release from Ignited Bulk Metallic Pieces*. BNWL-357, Battelle Northwest Division, Richland, Washington. http://www.osti.gov/scitech/biblio/4453507

Molen GF and RD White. 1967. *Properties of Plutonium Oxide, Part II*. RFP-927, The Dow Chemical Company, Golden Colorado. http://www.osti.gov/scitech/biblio/4339665. Note that Part I is the report by Moseley and Wing (1965).

Moseley JD and RO Wing. 1965. *Properties of Plutonium Dioxide*. RFP-503, The Dow Chemical Company, Golden, Colorado. http://www.osti.gov/scitech/biblio/4613823.

NQAP-2012, "Nuclear Quality Assurance Program (NQAP) Manual." Pacific Northwest National Laboratory, Richland, Washington.

Owens KW. 1981. *Existing Data on The 216-Z Liquid Waste Sites*. RHO-LD-114. Rockwell Hanford Operations, Richland, Washington. https://www.osti.gov/servlets/purl/5703558

Pallmer PG. 1956. *Crystallite Sizes of PuO_2 Powder*. HW-44585, Hanford Atomic Products Operation, Richland, Washington. http://www.osti.gov/scitech/biblio/4162958.

Panesko JV. 1972. *Plutonium Recovery from Soil*. ARH-2570. Atlantic Richfield Hanford, Company, Richland, Washington.

Parker DL and KM Singleton. 1995. *Description of Work {DOW) for Two DNAPL Investigation Wells at the 216-Z-9 Trench*. BHI-00183, Rev. 00, Bechtel Hanford, Incorporated, Richland, Washington

PFP Process Engineering Group. 1988. *PRF Solvent Extraction Depletion Flowsheet – High Uranium / High Fluoride Feed.* Section 3.2.10, PFD-Z-180-00001, Westinghouse Hanford Company, Richland, Washington.

Price SM and LL Ames. 1976. “Characterization of Actinide-Bearing Sediments Underlying Liquid Waste Disposal Facilities at Hanford”. Paper IAEA-SM-199/87, pages 191-211, *Transuranium Nuclides in the Environment*, STI/PUB/410, International Atomic Energy Agency, Vienna, Austria. Also published as ARH-SA-232.
https://inis.iaea.org/collection/NCLCollectionStore/_Public/07/238/7238004.pdf?r=1&r=1

Price SM, RB Kasper, MK Additon, RM Smith, and GV Last. 1979. *Distribution of Plutonium and Americium beneath the 216-Z-1A Crib: A Status Report*. RHO-ST-17, Rockwell Hanford Operations, Richland, Washington.

Pu Oxide Team (W. L. Isom, T. J. Venetz, J. G. Reynolds, D. L. Herting, D. E. Place, T. L. Sams, C.H. Delegard, S.A. Jones, R.C. Hoyt, T.E. Jones, J.A. Teal, D.E. Bowers, D.C. Lini, R. A. Watrous). 2017. *Review of Plutonium Oxide Receipts into Hanford Tank Farms*. RPP-RPT-50941, Rev. 1. Prepared by Washington River Protection Solutions for the U.S. Department of Energy Office of River Protection, Richland, Washington.

Rai, D, RJ Serne, and DA Moore. 1980. “Solubility of Plutonium Compounds and Their Behavior in Soils”. *Soil Science Society of America Journal* 44(3):490-495.
https://doi.org/10.2136/sssaj1980.03615995004400030010x

Rai D, RG Strickert, DA Moore, and RJ Serne. 1981. “Influence of an Americium Solid Phase on Americium Concentrations in Solutions.” *Geochimica et Cosmochimica Acta* 45:2257-2265.
https://doi.org/10.1016/0016-7037(81)90075-2

REDOX. 1951. *REDOX Technical Manual*. HW-18700, Hanford Works, Richland, Washington. https://reading-room.labworks.org/Files/GetDocument.aspx?id=DA02344322

RHO. 1987a. “Magnesium Oxide - Essential Materials Specifications.” EMS-Z-132-00312. Rockwell Hanford Operations, Richland, Washington.

RHO. 1987b. “Magnesium Oxide Crucibles - Essential Materials Specifications.” EMS-Z-132-00373. Rockwell Hanford Operations, Richland, Washington.

Rice NM, HMNH Irving, and MA Leonard. 1993. “Nomenclature for Liquid-Liquid Distribution (Solvent Extraction) (IUPAC Recommendations 1993).” *Pure & Applied Chemistry* 65(11):2373-96. http://dx.doi.org/10.1351/pac199365112373

Ritcey GM. 1980. “Crud in Solvent Extraction Processing – a Review of Causes and Treatment.” *Hydrometallurgy* 5(2):97-107. http://dx.doi.org/10.1016/0304-386X(80)90031-6

Rodgers LH. 1986. *1985 Remote Mechanical C (RMC) Line Campaign Report*. RHO-RE-EV-85, Rockwell Hanford Operations, Richland, Washington. https://reading-room.labworks.org/Files/GetDocument.aspx?id=D8397993

Rohay VJ, KJ Swett, and GV Last. 1994. *1994 Conceptual Model of the Carbon Tetrachloride Contamination in the 200 West Area at the Hanford Site*. WHC-SD-EN-TI-248, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Smith AE. 1973. *Nuclear Reactivity Evaluations of 216-Z-9 Enclosed Trench*. ARH-2915, Atlantic Richfield Hanford Company, Richland, Washington. https://inis.iaea.org/collection/NCLCollectionStore/_Public/05/120/5120615.pdf

Swanson JL. 1973. *Nature of Actinide Species Retained by Sediments at Hanford: Interim Progress Report*. BNWL-B-296, Battelle Pacific Northwest Laboratories, Richland, Washington. https://www.osti.gov/biblio/4374249-nature-actinide-species-retained-sediments-hanford-interim-progress-report

Teal JA. 2007. *Characterization Information for the 216-Z-9 Crib at the Plutonium Finishing Plant*. HNF-31792, Fluor, Richland, Washington.

Terry B. 1983. “The Acid Decomposition of Silicate Minerals Part I. Reactivities and Modes of Dissolution of Silicates.” *Hydrometallurgy* 10(2):135-50. http://dx.doi.org/10.1016/0304-386X(83)90002-6

Teynor T. 2015. *Plutonium Finishing Plant Progress Update – Hanford Advisory Board*. Presentation, 15 slides. U.S. Department of Energy, Richland Operations Office, Richland, Washington. http://www.hanford.gov/files.cfm/Attachment_7_RL_HAB_PFP_R2_vid.pdf

Wayne DM. 2014. *Thermal and Physical Properties of Plutonium Dioxide Produced from the Oxidation of Metal: a Data Summary*. LA-UR-14-20201, Los Alamos National Laboratory, Los Alamos, New Mexico. https://www.osti.gov/biblio/1114456-thermal-physical-properties-plutonium-dioxide-produced-from-oxidation-metal-data-summary

Wayne DM, LG Peppers, DS Schwartz, and PC DeBurgomaster. 2018. "Surface Area and Particle Size Distribution of Plutonium Oxides Derived from the Direct Oxidation of Pu Metal." *Journal of Nuclear Materials* 511:242-263. https://doi.org/10.1016/j.jnucmat.2018.08.056

Winkel JR. 2018. *CSER 18-003: Criticality Safety Evaluation Report for the 216-Z-9 Crib*. CHPRC-03737, Rev. 0, CH2M Hill Plateau Remediation Company, Richland, Washington.

Xie Y, GV Last, CJ Murray, and R Mackley. 2003. *Mineralogical and Bulk-Rock Geochemical Signatures of Ringold and Hanford Formation Sediments*. PNNL-14202, Pacific Northwest National Laboratory, Richland, Washington.
https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-14202.pdf

Zhou B, Y Wu, J Chan, S Wang, Z Qiao, and S Hu. 2019. *Wetting-drying cycles enhance the release and transport of autochthonous colloidal particles in Chinese loess*. Human and Ecological Risk Assessment: An International Journal, 25:1-2, 335-353. https://doi.org/10.1080/10807039.2019.1571402

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