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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

METHODS FOR REMOVING TRANSURANIC ELEMENTS FROM WASTE SOLUTIONS

by

S. A. Slater, D. B. Chamberlain, C. Conner,
J. Sedlet, B. Srinivasan, and G. F. Vandegrift

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ABSTRACT

This report outlines a treatment scheme for separating and concentrating the transuranic (TRU) elements present in aqueous waste solutions stored at Argonne National Laboratory (ANL). The treatment method selected is carrier precipitation. Potential carriers will be evaluated in future laboratory work, beginning with ferric hydroxide and magnetite. The process will result in a supernatant with alpha activity low enough that it can be treated in the existing evaporator/concentrator at ANL. The separated TRU waste will be packaged for shipment to the Waste Isolation Pilot Plant.

1. Introduction

Waste solutions containing transuranic (TRU) elements are being stored in facilities operated by the Waste Management (WM) organization within the Environment and Waste Management Division at Argonne National Laboratory (ANL). These facilities are located in Building 306 at the ANL-East site.

Treatment of the liquid TRU wastes stored in Building 306 would alleviate two problems associated with their storage: the high radionuclide inventory in the building and the scarcity of storage space for the wastes. Building 306 has reached 82% of its allowable stored radionuclide limit. If it exceeds this limit, it must be reclassified as a Class 2 Nuclear Facility. Such reclassification would cost millions of dollars, so ways are being sought to reduce the building's radionuclide inventory. Transuranic elements are a large fraction of the Building 306 inventory. This report evaluates treatment methods to process these wastes to reduce their volume and prepare the concentrate in a form suitable for storage at the Waste Isolation Pilot Plant (WIPP).

The objective of this project was to develop a treatment scheme to separate and concentrate TRU elements from aqueous solutions and reduce the alpha activity in the supernatant to a level low enough that it can be treated in the existing WM equipment. The process outlined here focuses on TRU waste. By definition, TRU waste is waste that is contaminated with alpha-emitting transuranic radionuclides (uranium-233 and radionuclides with atomic numbers of 93 and above) with a half-life greater than 20 years and in concentrations greater than 100 nCi/g [ANL].

This report evaluates a range of treatment methods, including several chemical techniques (precipitation, carrier precipitation, solvent extraction, ion exchange, and extraction chromatography) and one physical technique (evaporation/distillation). Carrier precipitation was chosen for further development because it is simple and robust and it can be performed in a glovebox. A flow diagram is presented detailing the proposed carrier precipitation process (Section 4), and guidelines are discussed for determining whether the supernatant from this process can be treated at ANL while remaining within activity lists (Appendix A). In the next stage of the project, carrier precipitation by ferric hydroxide and magnetite will be investigated.

2. Characterization of TRU Waste to Be Processed

Table 1 gives a random selection of the TRU waste that is stored by WM. The alpha activity of the waste was calculated based on the radionuclides and quantities recorded on waste requisitions by

Table 1. Sampling of TRU Waste Requisitions Received by Waste Management

Generator ^a (Requisition Number)	Radionuclide	Quantity, g	Total Alpha Activity, nCi/g	Reported Chemical Component	Reported Chemical Quantity	Solution Volume (pH)	
NBL (RL 01328)	Pu-239	9.72E+00	1.04E+05	Nitric Acid	50%	6 L (1)	
	Pu-240	6.30E-01		Hydrochloric Acid Potassium Carbonate	20%		
	Pu-241	3.77E-02			50 g		
	U-235	9.81E+00					
	U-238	7.38E-01					
CMT (RL 01805)	Am-241	6.44E-02	1.11E+05	EDTA	0.005M	2 L (4)	
				Pyridine	0.01%		
CMT (RL 01819)	Pu-239	1.13E+01	7.17E+05	Nitric Acid	5M	1 L (<1)	
	Pu-240	7.00E-01		Hydrochloric Acid	5M		
CMT (RL 01824)	Pu-239	1.80E-01	1.12E+04	Nitric Acid	1M	1 L (<1)	
	Pu-240	1.10E-02		Zinc Nitrate	50 g		
CMT (RL 01833)	Pu-239	2.29E+00	3.79E+05	Potassium Chloride	30 g	500 mL (<1)	
	Pu-240	4.60E-01		Lithium Chloride	25 g		
	Depleted U-238	8.96E+01		Nitric Acid	1M		
				Hydrochloric Acid	1M		
CMT (RW 21224)	Pu-239	1.80E-02	1.21E+02	Hydrochloric Acid	0.3M	22.7 L (<1)	
	Am-241	5.40E-04		Cadmium	0.780 g		
	Np-237	4.10E-03		Zirconium	0.110 g		
	Eu-154	7.05E-09		Potassium	0.310 g		
	Cs-137	7.85E-07		Lithium	0.120 g		
	Depleted U-238	4.40E-01					
CMT (RW 22665)	Pu-239	1.45E+00	2.69E+04	Nitric Acid	10 %	3.75 L (<1)	
	Pu-240	9.00E-02		Hydrochloric Acid	10 %		
	Am-241	3.1E-03					
	Np-237	4.30E-02					
	Cs-137	3.55E-05					
	U-238	8.7E+01					

^aNBL = New Brunswick Laboratory; CMT = Chemical Technology Division, Argonne National Laboratory.

the waste generators. Information from the waste requisitions was the starting point in determining the process to be used to remove the TRU elements from waste solutions. The presence of organic complexing agents, such as EDTA (ethylenediamine-tetraacetic acid), will make the separation more difficult. Also, hazardous components in the supernatant will require treatment as a mixed waste. Most of the wastes were generated by a few researchers and are stored in small containers; compatible wastes will be combined for more efficient bulk processing.

Because of the variety of waste compositions and the possible inaccuracy of the waste requisitions, it will be necessary to assay each batch of waste solution for its total alpha activity before and after processing. The TRU content of the solid after processing will be calculated by using a mass balance. To package the TRU wastes appropriately for transportation, the alpha activity per drum of waste must be known. In some cases, knowledge of the chemical composition may also be required. The TRU waste must meet the acceptance criteria for the WIPP (discussed in Appendix B).

3. Techniques for Processing TRU Waste

In designing a process to treat TRU waste, several factors must be considered. The process must be simple, yet robust, and operable in a glovebox. High decontamination factors (DFs)* are also required for the TRU treatment process. Table 2 shows characteristic TRU isotopes and the grams per liter of each isotope corresponding to activities of 0.1 and 100 nCi/mL. For example, for waste requisition RL 01328 (Table 1), a DF of approximately 10^6 would be required to reduce the alpha activity of the waste to 0.1 nCi/mL. That activity concentration, 0.1 nCi/mL, is the limit on alpha activity in the supernatant being sent to the existing evaporator/concentrator system (Appendix A). This limit could be met by supernatants with activity levels in the range of 10 to 50 nCi/mL (Appendix A), depending on the amount of suspended solids in the supernatant.

Table 2. Concentrations of Some TRU Nuclides Corresponding to Activity Concentrations of 0.1 and 100 nCi/mL

Nuclide	Specific Activity, Ci/g	Concentration in grams/liter ^a for 0.1 nCi/mL	Concentration in grams/liter ^a for 100 nCi/mL
Am-241	3.43E+00	2.92E-08	2.92E-05
Am-243	1.99E-01	5.03E-07	5.03E-04
Cf-249	3.99E+00	2.51E-08	2.51E-05
Cm-244	8.09E+01	1.24E-09	1.24E-06
Np-237	7.05E-04	1.42E-04	1.42E-01
Pu-238	1.71E+01	5.85E-09	5.85E-06
Pu-239	6.62E-02	1.51E-06	1.51E-03
Pu-240	2.28E-01	4.39E-07	4.39E-04
Pu-242	3.82E-03	2.62E-05	2.62E-02
U-233 ^b	9.68E-03	1.03E-05	1.03E-02

^aReported concentrations assume only one isotope in solution. If several isotopes are present, the allowable concentration of each will be lower.

^bUranium-233 is not a transuranic element, but by definition it is considered TRU waste.

$$*DF = \frac{\text{alpha activity concentration in the feed}}{\text{alpha activity concentration in the effluent}}$$

The following techniques for processing TRU waste were considered: precipitation, carrier precipitation, solvent extraction, ion exchange and other chromatographic techniques, and evaporation/distillation. These methods are briefly described in the following sections. Details on the chemical separation techniques are given in Appendix C and the physical separation technique is given in Appendix D.

3.1 Precipitation

Precipitation has been used extensively within the nuclear weapons complex to recover and purify plutonium [KATZ]. For example, precipitation by oxalate and peroxide is a well established technique [KATZ]. Precipitation is a simple, robust process that has much in common with the processes used in the WM mixed-waste treatment facility [VANDEGRIFT]. However, because of the low TRU concentrations required after processing to meet the 0.1 nCi/mL limit on alpha activity in the supernatant (see Table 2), precipitation is likely to be insufficient. The solubilities of slightly soluble TRU compounds are likely to still be too high. Precipitation is discussed further in Appendix C, Section 1.

3.2 Carrier Precipitation

Carrier precipitation (also known as coprecipitation) maintains the simplicity of the precipitation process, but another reagent is added to the process to "carry" the precipitation of a minor constituent in solution. Both the major and the minor precipitated components must be insoluble salts of the precipitating agents. Because the concentration of a minor component (in this case the TRU element) in the supernatant is not governed by its solubility but by its partitioning between the precipitant and the solution, the concentration of the species in solution can be orders of magnitude lower than its solubility. Carriers used in carrier precipitation include bismuth phosphate; insoluble fluorides, hydroxides, and oxalates; magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$ or Fe_3O_4); potassium carbonate; lanthanum sulfate; and zirconium phosphate. Ferric hydroxide and magnetite are the two types of carriers that will be considered here for the carrier precipitation process. Carrier precipitation is discussed in Appendix C, Section 1.

3.3 Solvent Extraction

The TRU elements are soluble in many water-immiscible organic liquids, and this property makes possible a variety of solvent extraction separation procedures. Commonly used extraction solvents are tributyl phosphate (TBP), octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide (CMPO), and methyl isobutyl ketone (hexone). Of the available solvents, the most efficient extractant currently available for all the TRU elements is the TRUEX solvent, which was developed at ANL. The Separation Sciences and Technology (SST) Section of the Chemical Technology (CMT) Division at ANL has considerable expertise in the processing of TRU waste solutions generated by the New Brunswick Laboratory (NBL) and CMT [STEINDLER, BATTLES-1992, BATTLES-1993]. Although treatment of these TRU waste solutions has been successful, the process used, continuous countercurrent solvent extraction, is not appropriate for small feed volumes. Startup and shutdown procedures generate large volumes of waste relative to the feed, if actual run times are only a matter of hours and not weeks.

A variation on solvent extraction techniques that is being developed by CMT/SST is the magnetically assisted chemical separation (MACS) process. In the MACS process, the chemical properties of coated polymer/ferromagnetic beads are used to selectively separate contaminants onto the beads. The beads are then recovered from solution by using a magnet. The MACS process can be

used to separate TRU elements from solution; however, it has a low capacity for these elements. For TRU treatment, the MACS process may be used as a polishing step. Solvent extraction techniques are discussed further in Appendix C, Section 2.

3.4 Chromatographic Methods

The following three sections summarize chromatographic column methods that were considered for the TRU treatment process.

3.4.1 Ion Exchange Resins

Separation by means of ion exchangers has some superficial similarities to carrier precipitation. The ions to be separated exchange with ions bound on the resin; thus, the resin can be compared to a precipitate in that the ions are removed from solution as a solid phase.

Chelating agents can also be chemically attached to the polystyrene-divinylbenzene copolymer that is used to prepare cation and anion exchange resins. A polyfunctional resin, Diphonix, is commercially available from Eichrom Industries [HORWITZ-1993A]. A laboratory unit that employs this resin for waste water purification is completing feasibility tests in the Chemistry Division at ANL. However, the capacity of these resins is not high, and large columns would be necessary for solutions with TRU concentrations in the grams per liter range. This method could serve as a polishing step for the filtrate from the TRU treatment process.

3.4.2 Inorganic Ion Exchangers

Inorganic ion exchangers are rarely used, but they might have application for TRU treatment if the exchangers were packaged for disposal. These resins are generally not elutable and, unlike organic resins, cannot be concentrated by incineration.

3.4.3 Extraction Chromatographic Method

Extraction chromatography is a process in which solvents capable of extracting TRU elements are sorbed on inert supports and then used to extract the TRU elements from solution and retain them in solid form. Several extractants have been used in this way, but the material of greatest interest in this case consists of the TRU·EX solvent absorbed on a polystyrene-divinylbenzene polymer. This resin is commercially available as TRU·SPEC [HORWITZ-1993B]. The low capacity of these materials makes them impractical for removing TRU elements from waste solutions with TRU concentrations in the grams per liter range. They may be considered for use as a polishing step. Ion exchange and extraction chromatography are discussed further in Appendix C, Section 3.

3.5 Evaporation/Distillation

Evaporation/distillation could be used to remove enough water and acid that the concentrated waste could be neutralized and packaged for disposal. High decontamination factors (10^7 - 10^9) are possible with commercially available stills; thus, the distillate could be neutralized and fed to the evaporator system. The major advantage of evaporation/distillation is the ability to work on any aqueous waste stream with minimal chemical additions. Acidic, basic, and complexant-containing waste can be evaporated without any significant changes in procedure; however, the still would likely

be fabricated of glass to accommodate the large feed variability and could be subject to accidental breakage. Evaporation/distillation is discussed further in Appendix D.

4. Recommendations

We recommend that a carrier precipitation process be used to treat the wastes stored in Building 306. This recommendation is based on this method's potential for success and the ease and cost of its implementation and operation. Carrier precipitation is considered the simplest, most robust, and least costly chemical procedure. The technology is relatively simple: the TRU elements are recovered in a solid phase, and a single solution remains to be treated by evaporation/concentration. The evaporation/distillation process is a close second. It is the simplest procedure overall, but environmental, safety, and health (ES&H) concerns would make its implementation difficult. These ES&H concerns are discussed in Appendix E.

Among the potential carriers for carrier precipitation methods, ferric hydroxide has the greatest prospect of early success and will be studied first. In addition, magnetite will be evaluated. Boyd and Klochen [BOYD, KLOCHEN] were able to obtain high decontamination factors (approximately 10^4) with magnetite in one precipitation step. Our planned approach for laboratory studies is given in Appendix F.

A reverse strike precipitation can be used if the first (direct strike) precipitation does not remove the TRU elements sufficiently. This second precipitation would be more effective if the solution were acidified first or if a homogeneous precipitation were used. A homogeneous precipitation will usually produce a precipitate that is more compact and more easily filtered. Diphonix, TRU•SPEC columns, and MACS particles may also be evaluated for polishing.

A treatment flow diagram is given in Fig. 1. This figure shows the path of waste through the TRU treatment process and the fate of the various process streams. This diagram assumes that the waste treatment method used is carrier precipitation. It is also assumed that the TRU concentrations in the waste are high enough that the solid precipitate would be TRU waste (i.e., >100 nCi/g).

After the first precipitation step, the resulting slurry is filtered to separate the solids from the liquid. The total solids content and the total alpha activity of the filtrate are then measured as outlined in Appendix A. If the activity of the filtrate is >100 nCi/g (decision junction A in Fig. 1), then the filtrate must be sent to the second precipitation step. (A column polishing step could also be used at this point.) If the activity of the filtrate is <100 nCi/g, then a calculation is needed (Appendix A) to determine whether the solids, if processed in the evaporator/concentrator system, will be TRU or nonTRU waste (decision junction B). This decision depends on the TRU concentration remaining in solution and the amount of dissolved solids present. If TRU waste will be produced, then the filtrate must be sent to the second precipitation step and not processed in the evaporator/concentrator system.

If TRU waste will not be generated during waste concentration, a decision needs to be made on whether to process the filtrate in the evaporator or concentrator (decision junction C). This decision depends on the solids content. For high solids contents, the waste should be concentrated in the concentrator. For low solids contents, the waste can first be processed in the evaporator.

If the activity of the filtrate from the first precipitation step is >100 nCi/g (decision junction A), a second precipitation is needed. After filtration, the total solids and alpha content of the filtrate is determined. Decision junction A is then used again to determine what to do with this waste. The activity of filtrate at this point in the process should be <100 nCi/g. On the basis of the feed and

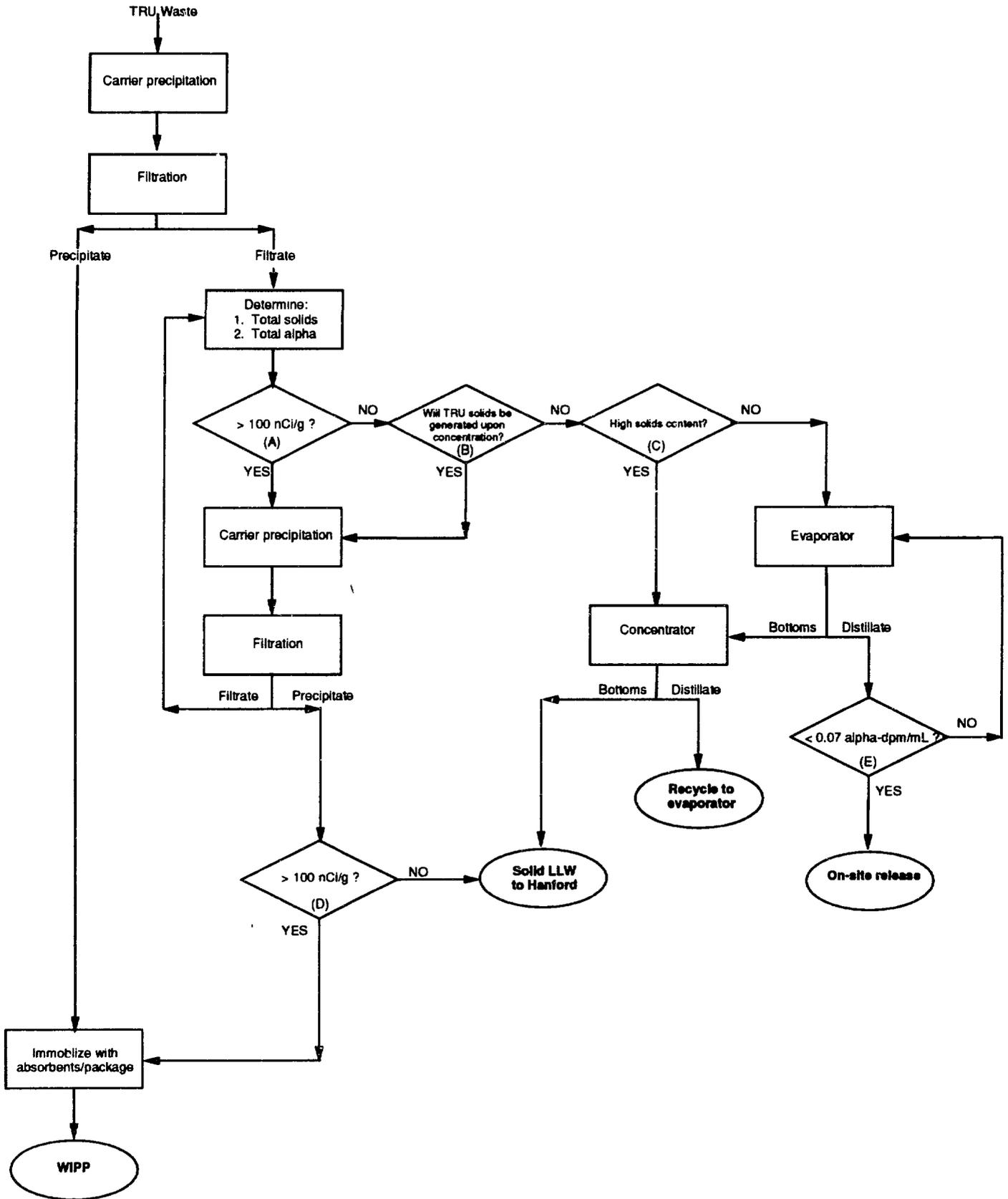


Fig. 1. Flow Diagram for TRU Waste Treatment Process (LLW = low-level radioactive waste).

and filtrate analysis or a separate solids sample analysis, the solids from the second precipitation step will either be TRU or nonTRU. If the precipitate is TRU, the solids will be sent to WIPP; if nonTRU, the waste will be sent to Hanford as low-level waste (decision junction D). The waste acceptance criteria and upper limits for WIPP are outlined in Appendix B.

The fifth decision junction (E) is based on limits in U.S. Department of Energy Order 5400.5 and limits the activity in the evaporator distillate that can be discharged to Sawmill Creek.

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APPENDIX A

LIMITS ON ALPHA ACTIVITY IN THE EVAPORATOR/CONCENTRATOR SYSTEM

1. Introduction

As part of our technical support to Waste Management, we developed criteria that set limits on the quantity of TRU material that can be fed to the evaporating system in Building 306. These limits were established for two reasons: (1) to determine whether the minor amounts of alpha activity already being processed are acceptable and (2) to determine the maximum amount of alpha activity that can be processed in the evaporator. This limit can then be used to determine how much additional alpha activity can be added to the evaporator feed. The maximum permissible alpha activity that can be processed is determined such that none of the following four criteria are exceeded:

- Maximum derived air concentration (DAC) for the Building 306 high bay
- Generation of TRU waste in the concentrator bottoms (>100 nCi/g)
- Alpha in the distillate >0.07 dpm/mL
- Quantities of material that could cause criticality.

These four limits are discussed below, and step-by-step guidelines are provided for adding alpha-contaminated waste to the evaporator feed tank.

2. Maximum Derived Air Concentration for Building 306 High Bay

The following DAC calculation was done to determine the maximum amount of alpha activity allowable in the Building 306 high bay. The DAC calculation is outlined in the *ANL Environment, Safety & Health Manual* [ANL-A]. The formula (Eq. 1) takes a number of factors into account, such as the various levels of containment and the dispersability of the material:

$$q = \frac{0.02 C_{DAC} \cdot 2000 \cdot V \cdot \lambda_v}{f_a \cdot f_r} \quad (1)$$

where	q	=	total activity of dispersible material allowed (μCi)
	0.02	=	2% of C_{DAC} is the policy value for dispersible radioactive material
	C_{DAC}	=	the DAC value for the specified nuclide [ANL-B] ($\mu\text{Ci}/\text{m}^3$)
	2000	=	number of hours in a work year
	V	=	room volume (m^3 ; 4400 m^3 for Building 306 high bay)
	λ_v	=	effective air changes per hour (h^{-1} ; 0.6 h^{-1} for Building 306 high bay)
	f_a	=	maximum fraction of airborne material (for hooded enclosures, 10^{-2} to 10^{-3} ; for gloveboxes, 10^{-6} to 10^{-8})
	f_r	=	fraction of material that could become airborne inside containment over 2000 hours (for liquids, 10^{-2} to 10^{-3} ; for powders, 10^{-1} to 10^{-2}).

For the following calculation, conservative estimates were used. A value of 10^{-2} was assumed for f_a . The concentrator bottoms dump into a vented drum; this configuration is similar to a fume

hood ($f_a = 10^{-2}$ to 10^{-3}). A value of 10^{-2} was also assumed for f_r . The concentrator bottoms have a toothpaste-like consistency and are, therefore, somewhere between a solid and liquid (f_r for liquids is 10^{-2} to 10^{-3} ; for solids, 10^{-1} to 10^{-2}). The high bay has a room volume of 4400 m^3 with an air flow rate of $440 \text{ m}^3/\text{min}$; thus, the theoretical air change in the high bay is 6 h^{-1} . However, after applying a 0.1 mixing factor (the value suggested in [ANL-B]) the effective number of air changes is 0.6 h^{-1} . The maximum allowable amounts of activity (q) were calculated for four isotopes (Table 3).

Table 3. Maximum Amount of Alpha Activity in Concentrator Bottoms Collection Drum (existing system)

Isotope	C_{DAC}^a , $\mu\text{Ci}/\text{m}^3$	Maximum Activity, μCi
Pu-239	2.5E-6	2620
Am-241	2.5E-6	2620
U-235	1.7E-5	17,800
U-238	1.7E-5	17,800

^a[ANL-C].

Assuming the worst case—that all of the alpha activity in the concentrator bottoms is due to Pu-239 or Am-241—then the activity limit for the current system is $2620 \mu\text{Ci}$. For a safety margin, we suggest a limit of $1300 \mu\text{Ci}$.

Once the new drum discharge system (with a sealed drum cover) is installed, these limits will increase. The f_a for this system will be 10^{-6} , because this sealed discharge system has a configuration similar to a glovebox (for a glovebox, f_a is 10^{-6} to 10^{-8}). The f_r will remain at 10^{-2} . Using these values to compute the maximum allowable activity gives the quantities shown in Table 4.

Table 4. Maximum Amount of Alpha Activity in Concentrator Bottoms Collection Drum (new system)

Isotope	Maximum Activity, μCi
Pu-239	2.6E+7
Am-241	2.6E+7
U-235	1.8E+8
U-238	1.8E+8

These values are sufficiently large that TRU waste would be generated long before they are exceeded.

The evaporator feed tanks (EFTs) are all sealed systems. Therefore, they have an $f_a > 10^{-6}$. Because of this, the DAC limit for the room containing the EFTs would be large, and handling the slightly elevated levels of alpha in the EFTs will not be a problem.

3. Determination of the Potential for TRU Waste Generation

The limit for TRU waste is 100 nCi/g, but for a margin of safety, we suggest a limit of 50 nCi/g. To determine whether TRU waste will be generated, the total alpha and total solids in a sample must be measured. Once the total alpha and total solids are measured, the alpha activity in a sample is divided by the total solids in the sample. For example, a sample from a 1500-gal (5700-L) EFT containing 100 nCi/L of alpha activity was found to have 10 g/L total solids. The total alpha present in the 5700 L is

$$\text{Total alpha } (\mu\text{Ci}) = \frac{100 \text{ nCi/L} \cdot 5700 \text{ L}}{1000 \text{ nCi}/\mu\text{Ci}} = 570 \mu\text{Ci} \quad (2)$$

Because 570 μCi is less than the DAC processing limit of 1300 μCi described above, this waste could be processed. However, it is still necessary to determine if TRU waste would be generated.

If the waste were evaporated to dryness, the total solids generated would be

$$10 \text{ g/L} \cdot 5700 \text{ L} = 57,000 \text{ g solids} \quad (3)$$

Because these solids contain 570 μCi of alpha activity (Eq. 2), the TRU content would be

$$\frac{\text{Total alpha}}{\text{Total solids}} = \frac{570 \mu\text{Ci}}{57,000 \text{ g}} (1000 \text{ nCi}/\mu\text{Ci}) = 10 \text{ nCi/g} \quad (4)$$

This waste is below the 50 nCi/g limit specified above, so the resulting concentrated waste will not be TRU. Therefore, the waste may be processed in the evaporator/concentrator unit, provided that it meets the alpha activity and suspended solids content criteria. However, if either limit is exceeded, additional calculations are required to determine concentration factors and amounts of feed that can be processed in one run.

The result calculated in Eq. 4 can be calculated another way by using the concentration of alpha activity and the concentration of solids to obtain the same result:

$$\frac{\text{Concentration of alpha activity}}{\text{Concentration of solids}} = \frac{100 \text{ nCi/L}}{10 \text{ g/L}} = 10 \text{ nCi/g} \quad (5)$$

4. Alpha Discharge Limits for the Distillate

To meet the sewer discharge limits, the distillate must contain <0.07 dpm(alpha)/mL (3.2×10^{-5} nCi/mL). For the current evaporator system, estimates of the decontamination factor (DF)* are not available. However, the system currently processes waste containing 0.005 to 0.02 nCi/mL of alpha activity, and the distillate meets the 0.07 dpm(alpha)/mL discharge limit. Because estimates for the DFs in the system are not available, we suggest that an initial upper limit on alpha activity in the

* $DF = \frac{\text{alpha activity concentration in the feed}}{\text{alpha activity concentration in the distillate}}$

feed be set at 0.1 nCi/mL. It may be necessary to decrease this level if the distillate fails to meet the discharge limits. Because the distillate is collected in a suspect waste tank (SWT), distillate failing to meet the alpha discharge limit may be re-evaporated to reduce the activity levels to below discharge limits.

For the new evaporator system, the DF is estimated to be 10^5 .* On the basis of this value and the alpha discharge limit of 0.07 dpm/mL, the evaporator bottoms can contain up to 3.2 nCi/mL of activity. Assuming a concentration factor of 7.5 is obtained in the evaporator (i.e., 1500 gal of feed is evaporated to 200 gal before going to the concentrator), the feed can contain 0.43 nCi/mL of activity and still meet the alpha discharge limits for the distillate.

5. Criticality

Because of the small quantities of fissile material involved (<500 mg Pu-239), criticality is not an issue. In addition, administrative controls are in place that do not allow critical quantities of transuranic isotopes in the building.

6. Wastes to Be Processed Directly in the Concentrator

Once the new concentrator system is installed, wastes can be fed directly to the concentrator. Wastes containing solids or large quantities of dissolved solids would be good candidates for direct concentrator processing. However, the same limits still cannot be exceeded: generation of TRU waste in the concentrator bottoms (>100 nCi/g), the maximum derived air concentration (DAC) for the Building 306 high bay, and quantities of material that could cause criticality. The analysis in Section A.1 showed the maximum allowable alpha activity in the high bay to be 1300 μ Ci (which includes safety factor of two). Gross alpha analysis of a sample of the waste will indicate whether it exceeds this limit.

To determine if TRU waste will be generated, the total solids in a sample must be measured by evaporating the sample and weighing the residue. Once the total solids have been determined, the alpha activity is divided by the total solids to determine if TRU waste would be generated. For example, a sample from a 20 L carboy containing 10 μ Ci/L alpha activity was found to contain 500 g/L total solids. The concentration of alpha activity is divided by the concentration of solids:

$$\frac{10 \mu\text{Ci/L} \cdot 1000 \text{ nCi}/\mu\text{Ci}}{500 \text{ g/L}} = 20 \text{ nCi/g} \quad (6)$$

Because 20 nCi/g is below the suggested limit of 50 nCi/g, TRU waste will not be generated if this waste is processed.

* A DF of 10^5 is conservative for the LICON units being installed. Decontamination factors greater than 10^6 have been observed in similar units.

7. Guidelines for Adding Alpha-Containing Waste to the Evaporator Feed Tank

The following are some step-by-step guidelines for adding alpha-contaminated waste to the evaporator system.

- a. Sample the EFT that is almost full and obtain gross alpha (nCi/mL) and total solids (g/mL). Alpha activity levels in the EFT typically range from 0.005 to 0.02 nCi/mL.
- b. Use Eq. 7 to determine the maximum amount of alpha activity allowed in the EFT without generating TRU waste in the concentrator bottoms:

$$MA = 50 \text{ nCi/g} \cdot TS \quad (7)$$

where MA = maximum alpha activity in the EFT (nCi/mL)

TS = total solids (determined in Step 1)

- c. Combine several likely candidate wastes and measure the gross alpha (nCi/mL). Wastes with activity >100 nCi/g cannot be used.
- d. Determine if the activity level calculated in Step 2 exceeds the guideline for generating distillate that is >0.07 dpm(alpha)/mL. The maximum alpha activity concentration for an EFT in the current system is 0.1 nCi/mL (may need to be decreased if distillate fails to meet the alpha discharge limits). The maximum alpha activity concentration in an EFT in the new system is 0.43 nCi/mL.
- e. If the activity calculated in Step 2 is less than the limit set in Step 4, go to Step 7.
- f. If the activity calculated in Step 2 is greater than the limit set in Step 4, set the maximum amount of alpha activity allowed in the EFT to 0.43 nCi/mL.
- g. Determine if the amount of alpha activity calculated in Step 2 (Eq. 7) or Step 6 exceeds the DAC limit (1300 μ Ci for the existing system; 1.3×10^7 μ Ci* for the new system). Be sure to reduce the DAC limit by the amount of activity already contained in a partially full drum. For example, if the concentrator bottoms are to be discharged into a drum already containing 300 μ Ci of activity, the EFT could only contain 1000 μ Ci of activity instead of 1300 μ Ci.

Multiply the maximum alpha activity calculated in Step 2 (Eq. 7) or Step 6 by the volume of the EFT:

$$TA = \frac{AC \cdot V}{1000 \text{ nCi}/\mu\text{Ci}} \quad (8)$$

where TA = total alpha in EFT (μ Ci)

AC = alpha concentration in the EFT from Step 1 (nCi/mL)

V = volume of EFT (mL)

* Includes factor of two for safety.

- h. If the total alpha activity in the EFT is less than the DAC limit, then alpha-containing waste can be added to the EFT. If the DAC limit is exceeded, go to Step 9. To calculate the volume of the alpha-containing waste to add, use Eq. 9:

$$WV = \frac{V (MA - AC)}{(WA - MA)} \quad (9)$$

where WV = volume of alpha-contaminated waste to add to the EFT (mL)
 V = volume of the EFT (mL)
 MA = alpha concentration calculated in Step 2 (Eq. 8) or Step 6 (nCi/mL)
 AC = alpha concentration in the EFT from Step 1 (nCi/mL)
 WA = concentration of alpha activity in the waste to be added from Step 3 (nCi/mL)

After calculating, go to Step 10.

- i. If the total alpha activity calculated in Step 7 exceeds the DAC, then determine the quantity of waste to add by using Eq. 10.

$$WV = \frac{DAC - (AC \cdot V)}{WA} \quad (10)$$

where WV = volume of alpha-contaminated waste to add to the EFT (mL)
 DAC = DAC limit used in Step 7 (μ Ci)
 AC = alpha concentration in the EFT from Step 1 (nCi/mL)
 V = volume of the EFT (mL)
 WA = concentration of alpha activity in the waste to be added from Step 3 (nCi/mL)

- j. Add the correct volume of waste, as calculated in Step 8 or Step 9, to the EFT.

REFERENCES FOR APPENDIX A

ANL-A

Argonne National Laboratory, Environment, Safety and Health Division, *Environment, Safety & Health Manual*, Vol. II, Chapter 5-18, pp. 1-7, April 1991.

ANL-B

Argonne National Laboratory, Environment, Safety and Health Division, *Environment, Safety & Health Manual*, Vol. II, Chapter 5-18, p. 2, April 1991.

ANL-C

Argonne National Laboratory, Environment, Safety and Health Division, *Environment, Safety & Health Manual*, Vol. II, Appendix A, April 1991.

APPENDIX B

WASTE ACCEPTANCE CRITERIA FOR EMPLACEMENT OF TRU WASTES
IN THE WASTE ISOLATION PILOT PLANT1. Introduction

The requirements that must be fulfilled to place radioactive waste in the Waste Isolation Pilot Plant (WIPP) in Carlsbad, New Mexico, are given in the Waste Isolation Pilot Plant Waste Acceptance Criteria (WIPP WAC) document [WIPP]. A brief summary of the waste form and waste package requirements, abstracted from that document, is given in Section 5 of this appendix. Other requirements pertaining to transportation, preparation of shipping manifests, preparation of data packages, etc., must also be fulfilled; see [WIPP] for details on these requirements.

The WIPP facilities will become operational no earlier than 1998. Therefore, any updates to the WIPP WAC in the interim period (1994-1998) must be taken into account, and this document must be revised accordingly.

2. Summary of Criteria

The important points governing the preparation of wastes suitable for emplacement in WIPP have been extracted from [WIPP]. Some points were clarified through telephone conversations with WIPP Project Integration Office (WPIO) personnel [ELLIOT]. Written clarification should be obtained from WPIO personnel before committing to a particular method of waste package preparation, and no waste should be packaged before certification is obtained. A summary of the information given in the WIPP Waste Acceptance Criteria document follows.

- a. Wastes must be in solid form.
- b. If the waste is in the form of powder or ash or similar particulate material, which could become airborne easily, then the waste must be immobilized. If it can be shown that the waste form will not become easily airborne, then immobilization may not be necessary, and an alternative means of fixing the waste can be adopted, such as packaging the material in secondary containers.
- c. ANL waste treatment methods are expected to yield sludge (solids combined with some amount of liquid). Solid absorbents (e.g., bentonite, vermiculite) may be used to absorb the liquids.
- d. Residual liquid must not exceed 1% of the volume of each internal container.
- e. Fifty-five-gallon drums may be used for packing the immobilized wastes or absorbed wastes. The absorbed waste must be packed in a secondary container (steel cans or plastic bags) to prevent the material from becoming airborne.
- f. The specific activity of the waste must be >100 nCi/g. The mass of the primary and secondary containers, liners etc., are excluded from the mass in specific activity calculations. However, the mass of immobilization agents or absorbent materials is included in the specific activity calculations. This requirement could be a problem for some wastes if WIPP requires immobilization by means of grout or glass.

Immobilizing a sludge whose activity is >100 nCi/g could result in a waste form whose activity is <100 nCi/g. A waste package prepared in such a manner is not acceptable either to WIPP (because the specific activity is <100 nCi/g) or to Hanford (because it has been diluted in the grouted form). The rules and regulations governing the shipment of waste to the Hanford site are given in the Hanford Solid Waste Acceptance Criteria manual [WILLIS].

- g. Explosives and compressed gases are not permitted in the waste containers.
- h. TRU wastes which contain hazardous wastes are permitted, but additional restrictions apply. These wastes must meet the requirements in the WIPP Resource Conservation and Recovery Act (RCRA) Part A and Part B applications.
- i. The mass of a single TRU nuclide that can be placed in a drum is governed by the limits established by the total activity and the wattage. The more restrictive of the two applies. Table 5 gives the most restrictive limit for each nuclide in both grams per drum and curies per drum. For all nuclides except U-233, the more restrictive criterion is the wattage limitation; for U-233, the more restrictive criterion is the total activity limitation.
- j. The surface dose rate of the containers must not be >200 mrem/h or 10 mrem/h at 2 meters.
- k. Removable surface contamination must not be >50 pCi/100 cm² for alpha activity, and not >450 pCi/100 cm² for beta/gamma activity.

Table 5. Nuclide Limits per 55-gal Drum

Nuclide	Nuclide Limit, g/drum	Nuclide Limit, Ci/drum
U-233	2.00E+02	1.95E+00
Np-237	8.60E+03	6.13E+00
Pu-236	9.61E-03	5.16E+00
Pu-238	3.14E-01	5.43E+00
Pu-239	9.22E+01	5.80E+00
Pu-240	2.51E+01	5.77E+00
Pu-241	5.43E+01	5.65E+03
Pu-242	1.54E+03	6.10E+00
Am-241	1.55E+00	5.38E+00
Am-243	2.77E+01	5.59E+00
Cm-242	1.46E-03	4.89E+00
Cm-244	6.28E-02	5.14E+00
Cf-252	4.43E-03	2.41E+00

1. After processing, wastes will be packaged as follows; however, further communications are necessary to fill in the details, as discussed in Section 5 of this appendix, and no waste should be packaged without certification.
 - The processed waste will be placed in 55-gal drums lined with 90-mil-thick high-density polyethylene. The drum lid will contain a carbon composite filter and the rigid liner will be punctured [TRUCON].
 - Vermiculite (#2 grade) will be used to immobilize the waste, and twice as much absorbent as needed will be used [TRUCON]. In [TRUCON], it is suggested that 43 gal of vermiculite and 12 gal of waste sludge be used per 55-gal drum.
- m. Shipping of the waste drums to WIPP is governed by additional regulations, which are given in the WIPP WAC but are not discussed in this document.

3. Further Communication with WIPP Project Integration Office Personnel

The treatment method proposed in this report will give rise to a sludge, an intimate mixture of solids and liquids (in this case mostly water) that must be converted to a solid. A method for converting sludge to solid is not described in the WIPP WAC. However, from telephone conversations with WPIO personnel, we have learned that sorbents may be added to the sludge, and the sorbed mixture can be packed into 55-gal drums, provided additional bagging or internal containment is used. Adding absorbents to sludge will remove the water, but at the same time it will create a solid particulate waste containing the TRU nuclides. The particle size in this solid cannot be estimated without additional work, and, therefore, no assurance can be given that particles $<10\ \mu\text{m}$ in size represent $<1\ \text{wt}\%$ of the waste or that particles $<200\ \mu\text{m}$ in size represent $<15\ \text{wt}\%$ (two WIPP requirements for particulate wastes). Written certification of the following should be obtained from the WPIO: Is the use of absorbents and internal containment acceptable to immobilize the waste sludge? How should the internal containment be done? Is there any need to analyze particle size? If grouting is necessary to immobilize the TRU wastes, what happens if waste is generated that is not acceptable to WIPP or Hanford?

The criticality ("Pu-239 FGE") or activity (Pu-Ci) limits are given for several TRU nuclides in [WIPP] or in [NU PAC]. However, if wastes containing different TRU nuclides are to be placed in the same drum, it must be assured that the total of the nuclides does not exceed these limits. A calculation procedure for giving such an assurance is suggested in this appendix. The procedure was discussed with WPIO personnel, but, again, written approval must be obtained from the WPIO for using the method suggested here or for replacing it with other computation methods.

4. WIPP WAC Criteria

The waste acceptance criteria for contact-handled transuranic wastes (CH-TRU) and remote-handled transuranic wastes (RH-TRU) are given in the WIPP WAC document. This report deals only with CH-TRU wastes, because that is the only form of waste that will be produced in the proposed process. ANL must obtain prior certification to prepare and place wastes at the WIPP. This section summarizes the requirements for obtaining certification and for preparing the waste form and waste packaging. Several of these criteria can be successfully met only if the elemental and isotopic compositions of the solid wastes are known. The CMT Division will be able to carry out the required analyses.

4.1. Quality Assurance

To obtain certification to prepare and place waste at the WIPP, ANL must have a project plan and a quality assurance plan reviewed and approved by the following offices:

- U.S. Department of Energy Headquarters Office of Environmental Restoration and Waste Management (DOE/EM).
- U.S. Department of Energy WIPP Project Integration Office and Waste Acceptance Criteria Certification Committee (DOE/WPIO) and (WACCC).
- U.S. Department of Energy WIPP Project Site Office (DOE/WPSO).

4.2. Waste Form Requirements

Several requirements dealing with properties of the wastes, such as the physical form, particle size, and residual liquids, must be satisfied so that the solid TRU wastes are acceptable for placement in the WIPP. The requirements are given below, as abstracted from [WIPP]. The treatment of ANL wastes is expected to result in a sludge, but [WIPP] does not give specific guidance on converting the sludge to a form suitable for placement in the WIPP. Nonetheless, we have made recommendations in Section 4.2(i) below for obtaining a solid waste from the sludge. These recommendations are based on our interpretation of the requirements given in Section 4.2(b), in addition to what we were able to learn from telephone conversations with WPIO personnel [ELLIOT].

- a. Wastes must be in solid form.
- b. Powders, ashes, and particulate materials must be immobilized if >1% by weight of the waste consists of particulate material <10 μm in diameter, or if >15% by weight consists of particulate material <200 μm in diameter. In our discussions with personnel at WPIO [ELLIOT], we learned that different immobilization options are available depending on the waste matrix. For example, inorganics can be immobilized by using Portland cement, and organics can be immobilized in a hot plastic melt such as polyethylene.
- c. Residual liquids are restricted to approximately 1% by volume of each internal container. A 55-gal drum may contain several internal containers. Note that ANL is planning to use 55-gal drums for packaging (see Section 4.3(a)). Residual liquids are defined as the liquid remaining in well-drained internal containers, condensation of moisture, and liquid separation resulting from sludge or resin settling [WIPP].
- d. Pyrophoric materials other than radionuclides must be rendered safe by mixing them with chemically stable materials (e.g., concrete, glass), or they must be processed to remove their hazardous properties. Not more than 1% by weight of the waste in each container may be pyrophoric forms of radionuclides, and these must be generally dispersed in the waste.
- e. No explosives are permitted.
- f. No compressed gases are permitted.

- g. TRU wastes which contain hazardous elements will be accepted into the WIPP only if the hazardous elements exist as co-contaminants with the TRU waste. It must be determined whether the waste is regulated by RCRA. If so, it must meet the requirements in the WIPP-RCRA Part A and Part B applications. Characteristic corrosive, reactive, and ignitable materials are not acceptable at WIPP. Wastes containing such materials must be treated to remove the hazardous characteristic. Since ANL wastes are in aqueous acid solutions, neutralization is needed to satisfy the corrosivity characteristic; the pH of the neutralized waste must be between 2 and 12.5 to satisfy the RCRA limit.
- h. The specific activity of the TRU waste must be >100 nCi/g or $>2.2 \times 10^5$ dpm(alpha)/g. The weight of the added external shielding, waste containers, and rigid liners is not taken into account in this calculation. However, the mass of material mixed with the waste either to immobilize it or to absorb the liquids will be included in all specific activity calculations.
- i. The treatment of ANL wastes is likely to result in the formation of sludge, that is, solids mixed with water with a pH between 2 and 12.5. The water in the wastes may be absorbed by using suitable absorbents, such as bentonite or vermiculite [ELLIOT]. Note that [WIPP] does not provide a list of suitable absorbents. Other references and/or WPIO personnel must be consulted when selecting the most suitable absorbents for ANL sludge. The removal of liquid from the sludge will result in the production of a solid waste. If the abundance and particle size of the resulting solid fall within the criteria given in Section 4.2(b), the solid may require immobilization. However, from telephone conversations with WPIO personnel [ELLIOT], we learned that sludges containing absorbent materials may be prepared for placement in the WIPP by bagging the absorbed wastes or sealing them in smaller internal containers before placing the wastes in a 55-gal drum (see Section 4.3(a)). WPIO personnel can answer specific questions regarding proper preparation of sludges resulting from treatment processes.

4.3. Waste Package Requirements

The WIPP waste package requirements cover the following: acceptable types of waste containers, mass limits for radionuclides to prevent nuclear criticality, activity limits, wattage limits in containers, surface contamination limits, and surface dose rate limits. Among these, the criticality limit and the wattage limit restrict the mass and activity of TRU nuclides that can be placed in waste containers/packages. For a single TRU nuclide in a drum, the lower of the two, criticality or wattage, defines the limit for the drum. For a mixture of TRU nuclides in a drum, the sum effect of all nuclides in the drum must pose neither a criticality hazard nor a health hazard. The contamination limits and dose rate limits assure minimum exposure to workers involved in handling and transporting the containers.

- a. ANL is planning to use 55-gal drums for waste packaging. The 55-gal drums will have a 90-mil-thick rigid liner made of high-density polyethylene (HDPE), which will be punctured [TRUCON]. The drum lid will contain a carbon composite filter [TRUCON]. The waste package limit is 1000 lb per 55-gal drum. There are additional requirements for a TRUPACT-II (Transuranic Package Transporter II) and the total shipment gross vehicle

weight (GVW). The TRUPACT-II is a waste package containing fourteen 55-gal drums in two packs of seven.

For immobilization purposes, a 55-gal (208-L) drum cannot be filled to capacity with materials such as Portland cement (density 3.16 g/mL) since the weight of the cement alone (657 kg) will exceed the 1000-lb (455-kg) drum limit. Low-density absorbent materials (e.g., bentonite, vermiculite) can occupy the whole volume of the drum without exceeding the 1000-lb limit. But in this case, additional internal containers (steel cans or plastic bags) should be used to contain the absorbent materials and prevent them from becoming airborne. The weight of the internal containers must be included in the total weight.

- b. The maximum quantity of any single TRU nuclide that can be placed in a waste container (package) is determined by either the criticality limit or the wattage limit; the lower of the two must always be used. Several TRU nuclides can be placed in the same drum, provided the criticality and wattage limits are not exceeded for the mixture. The criticality limits are discussed here, and the wattage limits are discussed in Section 4.3(d).

The amount of Pu-239 placed in a 55-gal drum must be no greater than 200 g (equivalent to 12.6 Ci), to prevent nuclear criticality. (Note that wattage limitations will reduce the amount of Pu-239 even more for most of the nuclides.) For other nuclides, the masses that can be safely placed in the drum are calculated with reference to Pu-239 and expressed in terms of Pu-239 fissile gram equivalents ("Pu-239 FGE"). The information in Appendix 1.3.7 of [NU PAC] was used in the calculations reported here. The criticality limits for several TRU nuclides (with the limit for Pu-239 at 200 g) are given in column 3 of Table 6. The mass limit in grams has been converted to activity in curies (column 4) by using the value for specific activity (Ci/g) shown for each nuclide. The specific activity values are referenced in [NU PAC]. Because Pu-236, Cm-242, and Cf-252 are not fissile, no limits are given for them. Nuclear activity limits are given in columns 5 and 6 of Table 6 and are discussed in Section 4.3(c). Uranium-233 is included in the table even though it is not a transuranic nuclide because at concentrations greater than 100 nCi/g its hazards are similar to those posed by transuranic nuclides. The limits given in Table 6 are for a single nuclide in a 55-gal drum. In a TRUPACT-II, the "Pu-239 FGE" must be less than 325 g for the entire payload. If a mixture of TRU nuclides is to be placed in the same drum, then Eq. 11 may be used to demonstrate that the 200-g "Pu-239 FGE" limit in a 55-gal drum has not been exceeded:

$$\sum_{i=1}^n \frac{M_i}{\text{"Pu-239 FGE"}} < 1.0 \quad (11)$$

where M_i is the mass of nuclide i in the drum and "Pu-239 FGE" is the mass of nuclide i as given in column 3 of Table 6. In Eq. 11, activity can be substituted for mass throughout, since mass and curie limits are directly proportional. Note that Eq. 11 is not stated explicitly either in [NU PAC] or in

[WIPP]. Telephone conversations with WPIO personnel suggest that Eq. 11 may be used to assure that the criticality limit for a mixture of TRU nuclides will not exceed the "Pu-239 FGE" limit of 200 g/55-gal drum.

- c. The waste packages must not exceed 1000 Ci of Pu-239 equivalent activity (PE-Ci). The PE-Ci values (both mass and curie limits) for several TRU nuclides are given in columns 5 and 6 of Table 6. Both limits are given for the sake of comparison with the corresponding limits in columns 3 and 4. More information on calculating PE-Ci is provided in Appendix A in [WIPP]. If a mixture of TRU nuclides is present in the drum, then an equation similar

Table 6. Specific Activities, Criticality Limits, and Activity Limits for TRU Nuclides in a 55-gal Drum^a

Nuclide	Specific Activity, Ci/g	Criticality Limit, Pu-239 FGE ^b		Activity Limit, PE-Ci ^c	
		g	Ci	g	Ci
U-233	9.76E-03	2.00E+02	1.95E+00	4.10E+05	4.00E+03
Np-237	7.13E-04	1.33E+04	9.51E+00	1.4E+06	1.00E+03
Pu-236	5.37E+02	not fissile		5.77E+00	3.10E+03
Pu-238	1.73E+01	1.77E+03	3.06E+04	63.6E+00	1.10E+03
Pu-239	6.29E-02	2.00E+02	1.26E+01	1.59E+04	1.00E+03
Pu-240	2.30E-01	8.89E+03	2.04E+03	4.35E+03	1.00E+03
Pu-241	1.04E+02	8.89E+01	9.24E+03	5.00E+02	5.20E+04
Pu-242	3.97E-03	2.67E+04	1.06E+02	2.77E+05	1.10E+03
Am-241	3.47E+00	1.07E+04	3.71E+04	2.88E+02	1.00E+03
Am-243	2.02E-01	1.55E+04	3.13E+03	4.95E+03	1.00E+03
Cm-242	3.35E+03	not fissile		8.66E+00	2.90E+04
Cm-244	8.18E+01	2.22E+03	1.82E+05	2.32E+01	1.90E+03
Cf-252	5.44E+02	not fissile		6.4E+00	3.50E+03

^aSpecific activities from [NU PAC], criticality limits calculated from data in [NU PAC], and activity limits reproduced from [WIPP].

^bFGE = fissile gram equivalent

^cPE-Ci = Pu-239 equivalent activity

to Eq. 11 can be used to show that the 1000 PE-Ci limit is not exceeded for the drum. In this case, the actual activities in curies of nuclides in the drum form the numerator of the equation; the corresponding PE-Ci limits in curies from column 6 of Table 6 form the denominator of the equation. The criticality and wattage limits generally restrict the activity in the 55-gal drums to significantly less than 1000 PE-Ci.

- d. The limit for TRU nuclides is based on criticality and wattage limits. The wattage limit for a 55-gal drum with one layer of plastic confinement around the waste matrix, excluding the HDPE drum liner, is 0.1797 watt/drum. This limit is based on information in [TRUCON], which is based on shipping requirements; these requirements are more stringent than the WIPP criteria. Table 7 gives the wattage limits allowed for a 55-gal drum for each nuclide. These values were calculated by using the specific activity and decay heat of each nuclide. The values for the decay heat and the specific activity are

referenced in [NU PAC]. CH-TRU packages in which the average thermal power density (or decay heat) exceeds 3.5 watt/m³ must have the thermal power recorded on the data package. However, this limit should never be reached, given the wattage limitation of 0.1797 watt/drum (0.90 watt/m³).

- e. The surface dose rate of the waste containers must be no greater than 200 milliroentgen equivalent man per hour (mrem/hr) or 10 mrem/hr at a distance of 2 m. Neutron contributions of greater than 20 nrem/hr must be documented separately. External dose rates on the loaded TRUPACT-II must not exceed 200 mrem/hr at the surface, or 10 mrem/hr at 2 m.

Table 7. Specific Activities, Decay Heats, and Wattage Limits for TRU Nuclides in a 55-gal Drum^a

Nuclide	Specific Activity, Ci/g	Decay Heat, W/g	Wattage Limits	
			g/drum	Ci/drum
U-233	9.76E-03	2.84E-04	6.33E+02	6.18E+00
Np-237	7.13E-04	2.09E-05	8.60E+03	6.13E+00
Pu-236	5.37E+02	1.87E+01	9.61E-03	5.16E+00
Pu-238	1.73E+01	5.73E-01	3.14E-01	5.43E+00
Pu-239	6.29E-02	1.95E-03	9.22E+01	5.80E+00
Pu-240	2.30E-01	7.16E-03	2.51E+01	5.77E+00
Pu-241	1.04E+02	3.31E-03	5.43E+01	5.65E+03
Pu-242	3.97E-03	1.17E-04	1.54E+03	6.10E+00
Am-241	3.47E+00	1.16E-01	1.55E+00	5.38E+00
Am-243	2.02E-01	6.49E-03	2.77E+01	5.59E+00
Cm-242	3.35E+03	1.23E+02	1.46E-03	4.89E+00
Cm-244	8.18E+01	2.86E+00	6.28E-02	5.14E+00
Cf-252	5.44E+02	4.06E+01	4.43E-03	2.41E+00

^aSpecific activity from [NU PAC], decay heat from [NU PAC], and wattage limits calculated from data in [NU PAC] and [TRUCON].

- f. The removable surface contamination of the waste package must be no greater than 50 pCi/100 cm² for alpha-emitting radionuclides and 450 pCi/100 cm² for beta/gamma-emitting radionuclides.
- g. Gases may be generated by radiolysis, microbiological degradation, etc. Gas-generating wastes have additional packaging requirements. See [WIPP] for details.

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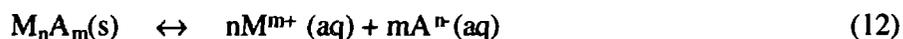
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APPENDIX C

TECHNICAL BASIS FOR CHEMICAL SEPARATION TECHNIQUES

1. Precipitation and Carrier Precipitation

A compound will precipitate from solution when the concentrations of the individual constituents exceed the compound's solubility product constant, K_{sp} . The chemical equation (Eq. 12) representing the dissolution of a compound containing one cation and one anion is



where M is the cation and A is the anion.

The equilibrium constant for this reaction is given in Eq. 13:

$$K = \{M^{m+}\}^n \{A^{n-}\}^m \quad (13)$$

where the brackets indicate the activity of the ions; the activity of the solid is unity. In this report, this constant is termed the solubility product. For the very insoluble compounds with which we will be dealing, the concentrations are very low and are thus nearly equivalent to the activities. Equation 13 then becomes

$$K = [M^{m+}]^n [A^{n-}]^m \quad (14)$$

where the square brackets indicate concentration in moles per liter.

From this equation we can calculate one of the terms, e.g., the concentration of the cation, if the other two terms are known. Also, if all three terms are known, we can predict whether a particular combination of ion concentrations will result in the formation of a precipitate. If the right-hand side of the equation exceeds the solubility product, the compound will precipitate.

For plutonium, the solubility products are 2.5×10^{-23} for the trivalent hydroxide and 5.0×10^{-64} for the tetravalent hydroxide [MORSS]. The solubility products for all the tri- and tetravalent TRU hydroxides are similar. To illustrate these calculations, we can use waste requisition data from Table 1. Requisition RW 22665 has a Pu-240 concentration of $1.4 \times 10^{-4} \text{M}$. If this solution is made 1M in hydroxyl ions and the plutonium is reduced to the trivalent state, the concentration product is $[1.4 \times 10^{-4}] [1]^4$. At this point, $\text{Pu}(\text{OH})_3$ should precipitate, and the plutonium concentration remaining in solution, now a saturated solution of $\text{Pu}(\text{OH})_3$, should be $[2.5 \times 10^{-23}] / [1]^4$ or $2.5 \times 10^{-23} \text{M}$, equivalent to $4 \times 10^{-13} \text{ nCi/L}$. This filtrate is well below the TRU concentration limit of 100 nCi/g , which is equivalent to 10^5 nCi/L (if the solution density is unity) or $6.7 \times 10^{-6} \text{M}$ Pu-239. Even with a plutonium solution at the lower limit of the TRU concentration, the solubility product will be exceeded even at low hydroxyl ion concentrations and the hydroxide should precipitate, leaving a saturated solution of Pu(III) at a concentration of $2.5 \times 10^{-23} \text{M}$, as given earlier. The solubility product of the tetravalent hydroxide is considerably lower than that of the trivalent hydroxide, so after the Pu(IV) is precipitated, the plutonium concentration in the filtrate would be substantially less.

On this basis, one precipitation of the hydroxides should be sufficient to precipitate all the TRU elements (including U-233) and to reduce their content in the filtrate to levels low enough for direct discharge to sanitary effluents.

The problem with these calculations is that the solubility products were calculated from the free energies of formation of the constituents, but, since those are thermodynamic values, they represent equilibrium conditions, which are not achieved immediately after precipitation. Days may be required to achieve equilibrium, and it is well known that as these gelatinous precipitates age, their crystallinity increases and they become less soluble. In addition, the precipitate may not consist only of the hydrous oxide or hydroxide if other ions are present, and, in the case of the tetravalent actinides, colloidal-size particles can form as the solution is neutralized. These colloids may not be absorbed and carried down when a hydroxide is precipitated. This problem with colloids may be the cause of some of the low decontamination factors (DFs) recorded in the literature [MARTELLA, IAEA]. Since the trivalent hydroxides are not subject to the polymerization problems of the tetravalent hydroxides (discussed at the end of this section), it is preferable to reduce the latter to the trivalent state before precipitation.

The solubility products of the freshly precipitated TRU hydroxides should be measured and reported. They would represent realistic and attainable values for use in this TRU treatment project. It should be possible to make such measurements, rather than rely on thermodynamic calculations, because of the high sensitivity obtainable by radioactivity measurements.

If the TRU elements do not precipitate in basic solution for whatever reason, it should be possible to remove them from solution by precipitating a suitable insoluble compound that will carry the TRU elements down with it. If the concentration of a trace ion in solution is so low that the addition of a precipitating agent (in this case, a compound such as sodium hydroxide that yields hydroxide ions in solution) will not cause the solubility product to be exceeded, a nonisotopic carrier ion (such as iron) that forms an insoluble compound with the precipitating agent can be used to form a precipitate that can carry the trace ion with it [WAHL]. This process is known as coprecipitation or carrier precipitation. The latter term is used in this report. The fraction of trace ion carried is independent of its concentration over a very wide concentration range because the composition of the precipitate is essentially unchanged by the presence of a trace amount of another ion. As a first approximation, the fraction of the trace ion carried can be assumed to be the same as the fraction of carrier compound precipitated.

It has long been known that a compound precipitated from solution will occlude or absorb to some extent other substances present in the solution in trace quantities. In a few cases, the amount occluded or absorbed is sufficient to measurably increase the weight of the precipitate. In a gravimetric chemical analysis this introduces an error, and analytical chemists have devised methods to minimize the amount of foreign substance carried. In the present case, however, we wish to achieve the opposite effect; that is, we wish to maximize the amount of transuranic element carried. This requires a study of the variables that affect the amount carried.

There are several mechanisms by which a trace ion will be carried. For example, if a trace cation forms an insoluble compound with the anion of the carrier precipitate and has the same crystal structure as the precipitate, then the cation can find a location in the precipitated crystal in which to lodge. This isomorphous replacement results in the most effective carrying. Carrying can also occur by absorption even if the two compounds involved do not form isomorphous crystals, or if the ionic sizes are very dissimilar. Absorption can occur if the trace ion and the carrier precipitate have opposite charges and if the surface area of the precipitate is large. In this case, prolonged digestion can increase the fraction carried.

Carrying can also occur by internal absorption rather than surface absorption. In this process the trace ion is incorporated on the surface of a growing crystal and is covered by additional layers of the crystal. Another carrying mechanism is mixed crystal formation. In this anomalous case, carrying occurs when the trace ion is somehow incorporated into the lattice of the carrier compound, even though the two compounds have different crystal structures.

In all carrying situations, the precipitate may be enriched or deficient in the trace ion relative to the solution. It is, of course, desirable for the precipitate to be enriched, so that complete carrying can be obtained without necessarily precipitating all of the carrier. Whether enrichment occurs can only be determined with certainty by experiment. But if the trace compound is less soluble than the carrier compound, enrichment is likely. For example, in the case of barium and radium, the nitrate and chloride salts of radium are less soluble than those of barium. This enabled Hahn and Strassman to show by fractional crystallization that the 12-day beta activity produced when uranium is irradiated with neutrons is due to a barium isotope and not a radium isotope as originally thought [GLASSTONE].

Because the rate of diffusion of a trace ion in solution into the interior of a crystal is very low, the method of precipitation greatly affects the fraction carried. Once the precipitate forms, additional carrying is low, but not zero. It is best if the carrier anion is added slowly with stirring so precipitation occurs throughout the solution (direct strike). If the compound containing the cation is added after the carrier anion is mixed into the solution (reverse strike), then complete precipitation of the cation occurs only in a small volume near the top of the solution, and most carrying will have to be done on a "preformed precipitate." Subsequent digestion, especially at an elevated temperature, can increase the carrying process because of dissolution and recrystallization at the surface of the precipitated particles.

Many variables can affect the degree of carrying. Among these are the concentrations of the carrier cation, the rate and order of addition of the carrier and precipitating agent, the digestion time of the precipitate, the temperature of precipitation and of the solution/precipitate during digestion, the chemical composition of the solution, the oxidation state of the TRU element, and the mechanism of the coprecipitation process. Optimum conditions must be determined experimentally.

Carrier precipitation was the first method used to separate plutonium from neutron-irradiated uranium [WICK]. Plutonium and the other TRU elements form a number of insoluble compounds in acidic and basic solutions, and these compounds can become the basis of a separation method. The effectiveness of insoluble compounds as carriers depends on the completeness of carrying, since the goal is to reduce the concentration of TRU elements in the filtrate to <0.1 nCi/mL (Appendix A). The concentration in moles per liter corresponding to this activity is given in Table 8 for a number of TRU nuclides. As the table shows, only very low concentrations can be permitted to remain in solution. Thus, the precipitate must be very insoluble ($K_{sp} \sim 10^{-12}$) if the trace ion is to be removed from the solution to the same extent as the carrier, or the trace ion must preferentially concentrate in the precipitate. The various compounds that can be used to carry the TRU elements include ferric hydroxide (alone or with ferrous hydroxide to form magnetite, Fe_3O_4); calcium, bismuth, and zirconium phosphate; calcium and lanthanum fluoride; calcium and lanthanum oxalate; potassium carbonate; and sulfate. The carriers are discussed by group below.

Hydroxides. Ferric hydroxide, the prime candidate for a carrier separation method, has a solubility product of 2.64×10^{-39} [WEAST]. If ferric hydroxide is precipitated from 1 M OH^- solution, the resulting iron concentration is $[Fe^{+3}] = 2.64 \times 10^{-39}/[1]^3 = 2.64 \times 10^{-39} \text{ M}$, or less than one ion per 10^{16} liters. The concentration of a TRU ion remaining in solution should be approximately the same as that of the carrier ion. A plutonium concentration of $2.64 \times 10^{-39} \text{ M}$ easily meets the nonTRU criterion

Table 8. TRU Nuclide Concentrations Corresponding to 0.1 nCi/mL

Nuclide	Half-Life, years	Specific Activity, Ci/g	Concentration, <u>M</u>
Am-241	4.58E+02	3.43E+00	1.21E-10
Am-243	7.95E+03	1.99E-01	2.07E-09
Cf-249	3.61E+02	3.99E+00	1.01E-10
Cm-244	1.76E+01	8.09E+01	5.07E-12
Np-237	2.14E+06	7.05E-04	5.98E-07
Pu-238	8.64E+01	1.71E+01	2.46E-11
Pu-239	2.44E+04	6.62E-02	6.32E-09
Pu-240	6.58E+03	2.28E-01	1.83E-09
Pu-241	1.32E+01	1.03E+02	4.03E-12
Pu-242	3.79E+05	3.82E-03	1.08E-07
U-233	1.62E+05	9.68E-03	4.43E-08

(i.e., $<6.32 \times 10^{-6} \text{M}$ Pu-239). Other insoluble hydroxides should also function as well, although the iron hydroxides have been the most studied and used. Both iron(II) and iron(III) hydroxides can be expected to carry all the TRU elements in all their oxidation states, as well as U-233, because uranium forms insoluble diuranates, $(\text{NH}_4)_2\text{U}_2\text{O}_7$ and $\text{Na}_2\text{U}_2\text{O}_7$, in solutions of hydroxyl ions. Carbonate ion must be excluded from uranium solutions because uranium forms a strong, soluble carbonate complex in basic solution.

Different investigators have reported different DFs for a single ferric hydroxide precipitation, from 300 to 19,000 for plutonium and americium [IAEA, MARTELLA, AKATSU]. The Martella report states that some plutonium was lost when the hydroxide was washed with water. This is not surprising and is common for hydroxide precipitates. Such precipitates should be washed with a basic solution containing a salt, such as ammonium chloride, to prevent dissolution and peptization of the precipitate. Akatsu reported DFs ranging from 290 to 19,000 for a hydroxide precipitation created by adding calcium or sodium hydroxide to a 7M nitric acid solution containing other acids and several metal ions, including iron. Akatsu made a second ferric hydroxide precipitation by adding ferric ion to the supernatant from the first precipitation, which gave overall DFs ranging from 1600 to 55,000 and reduced the alpha activity from $\sim 10^7$ nCi/L to 195 nCi/L. The iron concentration for the second precipitation was quite low, about 0.01 mg/mL (0.0002M); better decontamination could be expected if the iron concentration were increased by a factor of 10, if the supernatant were acidified, and if a direct strike were used.

A mixture of ferrous and ferric oxide, magnetite, has been reported to be more effective than ferric hydroxide alone and gives a more compact precipitate, improving filtration [HARDING]. Magnetite is the highly magnetic oxide of iron ore. Compared to ferric hydroxide, magnetite precipitation can reduce the generation of solid by-product waste by up to 80%. Magnetite generated *in situ* and preformed magnetite were found to be equally effective. In tests on several samples from one waste solution, carrier precipitation with magnetite reduced the plutonium concentration from 6620 nCi/L to 0.7 nCi/L in one step [BOYD, KLOCHEN]. Two disadvantages of magnetite are that it is strongly influenced by interfering ions and that it is not effective with waste that has a high ionic content [BOYD]. Concentrations of calcium and magnesium at 1 g/L interfere with carrying by magnetite precipitated *in situ*, while preformed magnetite can tolerate 5 g/L of these elements. Phosphate, fluoride, and silicate are among the anions that interfere. Again, less interference occurs with preformed magnetite. The

magnetite can be removed by using a magnet, thus avoiding the need for filtration or centrifuging [BOYD].

Magnesium carbonate has also been studied as a carrier for the actinides [GONCHAROVA]. Complete carrying was reported, but no filtrate concentrations were given.

A recent development has been the use of potassium ferrate (K_2FeO_4), a highly oxidized iron compound containing iron(IV) [MWIP]. It is readily reduced in basic solution to ferric hydroxide, and it acts as a carrier and flocculating agent. The manufacturer claims it is superior to precipitated ferric hydroxide and other flocculating agents in that it removes colloidal particles better and produces a more compact and easily filterable precipitate. The compound is difficult to make and is expensive. However, it may be possible to obtain the compactness and filtration advantages of potassium ferrate [GORDON] by the homogeneous precipitation of ferric hydroxide.

Oxalates. Because the TRU elements form insoluble oxalates in slightly acidic (and in basic) solution, they may be precipitated by oxalic acid or an oxalate salt if present in sufficient concentration; or, if present at low concentrations, they can be carried out of solution when another insoluble oxalate, such as calcium or lanthanum oxalate, is precipitated. Precipitation of plutonium oxalate has been used extensively to purify plutonium [WEIGEL-1986A, RYDBERG-1955A, BURNEY-1984]. Oxalate precipitation has also been used to separate americium and curium from waste solutions [GRAY].

Because of these uses, the solubility of the plutonium oxalates have been carefully studied. The solubility of the trivalent oxalate is given by $[\text{Pu}(\text{mg/L})] = 3.24[\text{H}^+]^3[\text{H}_2\text{C}_2\text{O}_4]^{-3/2}$ [WEIGEL-1986A]. A solution consisting of 0.1M H^+ and 1.0M $\text{H}_2\text{C}_2\text{O}_4$ would contain 214 nCi/L of plutonium. If the acid concentration were lowered to 0.02M and the oxalate concentration were increased to 1.0M , the solubility would drop to 1.7 nCi/L, which is less than the target concentration of 0.1 nCi/mL. The solubility of the tetravalent oxalate is too large to reduce the filtrate to the required concentration, apparently as a result of the formation of the trioxalate complex [MARTELLA].

Bismuth, thorium and iron(II) oxalates will also carry the tri- and tetravalent TRU elements out of solution [GREB, WEIGEL-1986A, COLEMAN, BURNEY-1974].

For calcium oxalate carrier precipitation, DFs ranging from 50 to >1000 have been reported for plutonium and from 1700 to 5000 for americium [IAEA]. The same publication reports a DF of 1.4 for neptunium. This value seems unreasonably low, but it may be due to complex formation. Carrying of plutonium and neptunium with an oxalate should be conducted with the elements in their trivalent state because of complex formation. An interesting study of the carrying of plutonium by lanthanum oxalate is presented in [GREB]. These workers have shown that 98-99% of the plutonium can be carried out of solution by precipitating only 20-30% of the lanthanum. In that study, carrying occurred by anomalous mixed crystal formation.

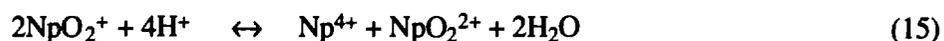
Phosphates. Bismuth phosphate will precipitate from slightly acid solution and carry with it all tri- and tetravalent actinides, so it will remove all actinide elements except uranium [WEIGEL-1986B]. Its ability to precipitate from acid solution may be an advantage since many stable elements form insoluble phosphates only in basic solution. Bismuth phosphate carrying was the first method used to separate plutonium from neutron-irradiated uranium. For the most effective carrying, the phosphate must be precipitated hot ($\sim 80^\circ\text{C}$) and digested, with stirring, for about 1 h. Zirconium phosphate is a very insoluble compound and coprecipitates tetravalent TRU elements [RYDBERG-1955B, MAGNUSSON],

usually forming a gelatinous precipitate. Its ability to carry trivalent actinides can be investigated. Other phosphates may also carry well in basic solution.

Other insoluble compounds of the TRU elements that have been used for separation or purification are the fluorides, sulfates, and carbonates. They will be discussed briefly in order to be comprehensive, but they do not appear to offer any advantages over the hydroxides, oxalates, or phosphates. The fluorides of the TRU elements are insoluble in acid solution in their lower oxidation states. They can be precipitated, if present in sufficient concentration, or carried on calcium and lanthanum fluoride, if present in trace concentrations [WEIGEL-1986A, COLEMAN, CLEVELAND, SCHLYTER, LUERKENS]. The double sulfates of potassium and lanthanum will carry trivalent TRU elements [WEIGEL-1986A, COLEMAN]. Potassium carbonate has been used to precipitate plutonium from near-neutral solutions [MARTELLA]. Plutonium will precipitate and carry only in the tetravalent oxidation state. The use of calcium carbonate as a carrier for tetravalent plutonium has also been studied [GINZBURG]. The highest percentage carried was reported to be 97%, but the study was examining the mechanism of carrying, not the completeness of carrying.

Before leaving the discussion of precipitation, it is important to consider the oxidation states (valences) and species that occur in solutions of the TRU elements. All of the TRU elements have a trivalent oxidation state in aqueous solution. For americium, curium, and the higher atomic number elements, this is the most stable oxidation state. In this state, the ions are well behaved and act in a reproducible manner. Hydrolysis does not occur in solutions containing 0.1M hydrogen ion or greater. Although americium exhibits the IV, V, and VI oxidation states in solution, these oxidation states are difficult to produce and maintain, and they will not be encountered in waste solutions. Uranium, neptunium, and plutonium also exhibit the III oxidation state. However, for uranium and neptunium, this state can be produced only by strong reducing agents such as zinc metal or electrolysis, and chemical separations from waste solutions that use this state are impractical. The III state of plutonium can be reliably obtained by using reducing agents such as ascorbic acid, ferrous ion, sulfite ion, or sulfur dioxide. The most stable oxidation states for uranium, neptunium, and plutonium are the VI, V, and IV states, respectively. The hexavalent state of uranium (UO_2^{2+}) is well behaved and undergoes predictable chemical reactions. (In the other direction, for the actinide series, the most stable states for protactinium, thorium, and actinium are V, IV and III, respectively.)

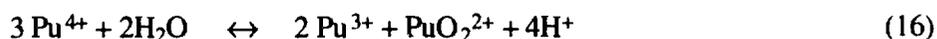
Complications occur in dealing with neptunium and plutonium because they can exist in aqueous solutions in all the oxidation states from III through VIII. The octavalent state can be obtained only in alkaline solution by treatment with very strong oxidizing agents and will not be encountered in waste solutions. The other oxidation states, IV through VI for neptunium and III through VI for plutonium, can exist together in acidic solution. Each state can exist in appreciable concentration because the electrode potentials of these oxidation states allow the intermediate states to disproportionate into both higher and lower states. The disproportionation of the V state into the IV and VI states is illustrated by the reaction for neptunium [FAHEY]:



This equation shows that the reaction requires four hydrogen ions for two neptunyl ions, so the disproportionation reaction is favored in high acid solutions. Thus, the equilibrium ratio* for the reaction is only 4×10^{-7} in 1M HClO_4 but 200 in 8.7M HClO_4 . The degree of disproportionation increases with

*Equilibrium ratio = $\frac{[\text{Np(IV)}][\text{Np(VI)}]}{[\text{Np(V)}]^2}$.

increasing neptunium concentration because two neptunium atoms must interact for the reaction to occur. The disproportionation of the IV state into the III and VI states is illustrated by plutonium:



In this case, the reaction is favored in low acid solutions and at high plutonium concentrations because three plutonium ions are involved. The complete reaction may occur in two steps.

In view of the multiplicity of oxidation states that can exist together in aqueous solutions, it is important to use oxidizing or reducing agents to convert these elements to known and singular oxidation states before initiating precipitation steps. This precaution will ensure reproducible results.

A further complication occurs in the IV state; Pu(IV) is known to hydrolyze in very dilute acid solution to form colloidal-size particles. In this state, termed "plutonium polymer," the plutonium may not undergo the chemical reactions expected of the Pu^{4+} ion. It is reported that it is very difficult to convert the polymer to the ionic IV state. A possible method for doing so is to break the Pu-O bonds in the polymer with hydrofluoric acid and to reduce the plutonium to Pu(III). It may be possible to remove the polymer from solution by procedures known to destroy or absorb colloids. Flocculating agents such as ferric or aluminum hydroxide or absorbing agents such as bentonite clay may remove plutonium polymer from solutions, and polyelectrolytes may neutralize the charge on the colloid and allow it to settle out in larger particles. It is likely that Np(IV) undergoes the same polymerization, but this has not been recorded.

Another factor that may prevent these elements from undergoing the expected precipitation (or other separation) reactions is the presence of chelating agents such as EDTA (ethylenediamine-tetraacetic acid) and DTPA (diethylenetriamine-pentaacetic acid). These compounds complex TRU elements much more strongly in basic solution than in acidic solution, and the complexed species will not precipitate with hydroxide addition. To avoid this problem, it may be necessary to carry out precipitation in acid solution, or to add a relatively large amount of a transition metal cation, such as copper (II), that also forms a strong complex with chelating agents, to displace the TRU element from these complexes.

Additional information on the chemical properties of the TRU elements may be obtained from [WEIGEL-1986A, WEIGEL-1986B, COLEMAN, BURNEY-1984, CLEVELAND, and CHOPPIN].

The applicability and usefulness of published DFs to this work requires comment. It is expected that the residual TRU concentration in the filtrate after precipitation would be independent of the initial concentration, because we are dealing with very slightly soluble compounds. If this is the case, the DF is not the proper way to evaluate a precipitation process. The amount of TRU elements remaining in the filtrate can also be a function of the other compounds in the waste solution, so results obtained for one waste may not be applicable to other solution compositions.

Because of the complex chemical behavior of several of the TRU elements and because of the presence of high concentrations of many stable constituents in the waste solutions, laboratory experiments to evaluate projected chemical separations will be required. These are discussed in Appendix F.

2. Solvent Extraction

The TRU elements are soluble in many water-immiscible organic liquids, and this property makes possible a variety of procedures for separation by solvent extraction. Solvent extraction is most applicable

in nitrate or chloride systems. Sulfate, phosphate, fluoride, and oxalate anions usually hinder extraction because they form complexes, or precipitate, or both. The TRU elements are predominately tri- or tetravalent in acid solution; uranium is predominately hexavalent. The ions in the tetra- and hexavalent oxidation states are more readily extractable than those in the trivalent state, so adequate separation by this method will be more difficult to achieve for the elements above neptunium. Commonly used extractants are TBP, CMPO, and hexone. Of the available extraction processes, the TRUEX process [VANDEGRIFT], in which the solvent is CMPO and TBP dissolved in a high-molecular-weight hydrocarbon, is the most efficient and would be the first choice. It will extract all the TRU elements.

An effective solvent extraction process can be designed and operated. However, solvent extraction is not efficient for treating low volumes of feed that varies in composition. The ANL-CMT Separation Science and Technology (SST) Section used the TRUEX process to treat more than 100 L of waste from NBL, but short runs due to low feed volumes (<50 L) cause a two- to three-fold increase in volume of the nonTRU product due to start up and shutdown procedures.

A variation on solvent extraction techniques that is being developed by the SST Section is the magnetically assisted chemical separation (MACS) process. In the MACS process, ferromagnetic embedded polymer beads are further coated with (1) either a selective ion exchange material or a solvent containing an organic complexant for cesium and strontium or (2) solvents for selective separation of TRU elements. (The beads themselves are formed from iron or another magnetic material and coated with either an organic polymer [i.e., polystyrene-divinylbenzene copolymer] or an ion exchange resin.) By their chemical nature, these coatings selectively separate the contaminants onto the beads, and the beads can be recovered from the solution by using a magnet. The MACS process can be used to separate TRU elements from solution; however, with high-level waste, the process has a low capacity for the TRU elements.

3. Ion-Exchange Chromatography

Separation on ion exchangers has some superficial similarities to carrier precipitation. The ions to be separated exchange with ions ionically bonded to the resin; thus, the resin can be compared to a precipitate in that the ions are removed from solution as a solid phase. The removal mechanisms are quite different, however. Both cation and anion exchangers will remove Pu(IV), Np(IV), and U(VI) from solution, but the trivalent elements (Am, Cm), which do not form strong anionic complexes, can be removed from solution only by cation exchange resins.

A potential process involves absorption of the TRU elements from dilute acid solution on a cation resin and disposal of the resin itself. This could be done by a batch process without resorting to a column. The TRU elements need not be removed from the resin if this waste form is satisfactory. If not, it would be feasible to remove the TRU elements from the resin with strong acid and evaporate the product solution to dryness. A preliminary separation step, perhaps using precipitation (e.g., carrying on calcium phosphate), may be necessary if the major components of the waste interfere with complete absorption of the TRU elements. The distribution coefficient (amount per gram of resin/amount per milliliter of solution) is on the order of 1000 for trivalent TRU elements removed from a cation resin by <1M HCl; this coefficient is about 6000 for Pu(IV), and presumably for Np(IV), removed from anion resins by 12M HCl [WEIGEL-1986A, COLEMAN, BURNEY-1974].

Chelating agents can also be chemically attached to the polystyrene-divinylbenzene copolymer that is used to prepare the usual cation and anion exchange resins. One of these, a polyfunctional resin containing gem-diphosphonic and sulfonic acid functional groups, gives a distribution coefficient for the

tri- and tetravalent TRU elements of 10^5 at 1 M HNO_3 . This resin is available commercially as Diphonia from Eichrom Industries [HORWITZ]. A laboratory unit in which this resin is used for waste water purification is operating in the Chemistry Division at ANL, and this unit could be used to polish the filtrate if prior treatments leave more than 0.1 nCi/mL of TRU elements behind.

Inorganic ion exchangers, such as the hydrous oxides and zirconium phosphate, give distribution coefficients as large or larger than the cation organic ion-exchange resins discussed above. They are rarely used but might have application for TRU treatment if the exchangers were packaged for disposal (they are not subject to oxidation and decomposition as are the organic resins).

In a process termed extraction chromatography, solvents capable of extracting TRU elements are absorbed on inert supports, where they extract the TRU elements and retain them in solid form. Several extractants have been used in this way, but the combination of greatest interest here consists of the TRUEX solvent absorbed on a polystyrene-divinylbenzene copolymer. This is commercially available as TRU•SPEC from Eichrom Industries.

An ion exchange process that would meet the goal of removing TRU elements from solution to $<0.1\text{ nCi/mL}$ can be developed, but it would be more expensive and more complex than precipitation.

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APPENDIX D

TECHNICAL BASIS FOR PHYSICAL SEPARATION TECHNIQUE

Evaporation can be used to remove sufficient quantities of water and/or acid from a TRU waste solution that the concentrated waste can be packed directly for disposal (after neutralization to a nonhazardous pH range). A flow diagram of the evaporation treatment process is shown in Fig. 2. After evaporation to ~4.0 g/L Pu-239 FGE (fissile gram equivalent) and neutralization, the waste may be absorbed and packaged.

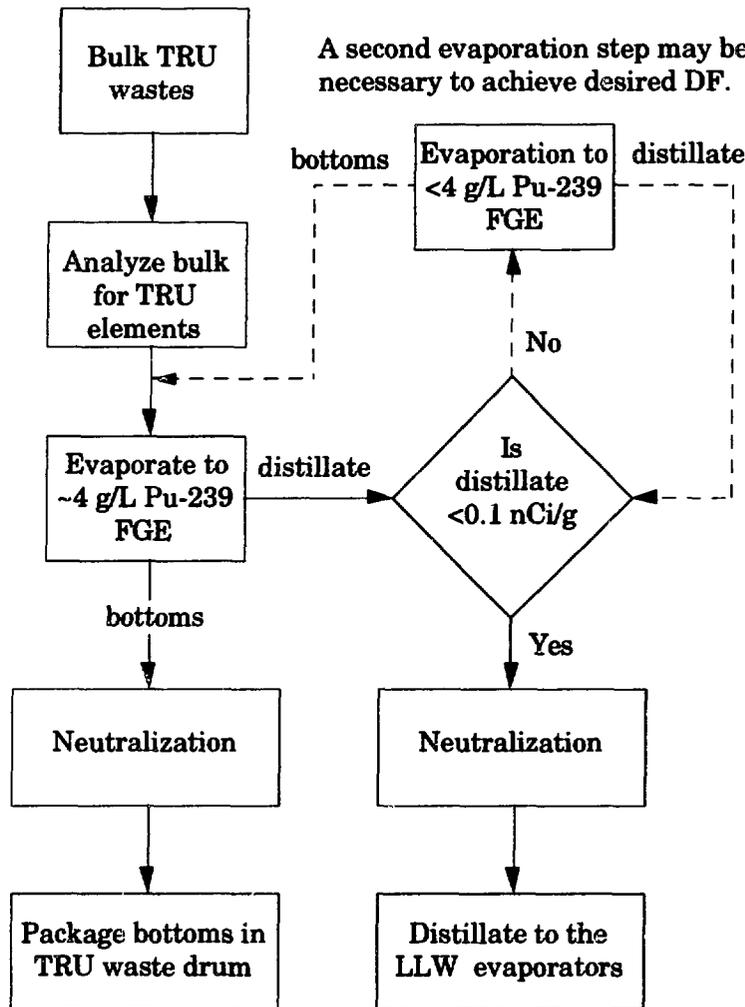


Fig. 2. Flow Diagram of Evaporation Treatment Process.

The limit of 4 g/L Pu-239 FGE maximizes the amount of TRU waste in each drum and thus reduces the number of drums requiring disposal. The calculation (Eq. 17) is based on the mass limit for WIPP packages of 92.2 g Pu-239 FGE per drum and on two assumptions: (1) that neutralizing the bottoms will increase the volume by a factor of 2 and (2) that a 55-gal waste package will contain 45 L (12 gal) of liquid and 163 L (43 gal) of absorbent. Thus,

$$\text{Pu Conc. (g/L)} = \left[\frac{92.2 \text{ g Pu-239 FGE}}{\text{Drum}} \right] \left[\frac{\text{Drum}}{45 \text{ L liquid}} \right] [2 \text{ (neutralization volume increase)}] = 4 \text{ g/L} \quad (17)$$

Further evaporation is not beneficial because of the limits on the quantities of TRU isotopes in each drum. After subsequent testing and neutralization, the distillate may be filtered and further processed in the low-level waste (LLW) evaporators or discharged directly, depending on its activity level.

The major advantage of evaporation is that any aqueous waste stream can be processed with a minimum of chemical additions. Acidic, basic, and complexant-containing waste can be evaporated without any significant changes in procedure. The oxidation states of the TRU elements do not need to be adjusted. Other treatment methods may require chemical analysis to determine the exact chemical composition of the waste, and, on the basis of that analysis, special chemical additions may be required to bring about the appropriate chemical environment. With evaporation, if a sufficiently large DF can be obtained, the distillate may be discharged directly after neutralization. If the waste is neutral or basic, even neutralization may not be necessary.

The major disadvantages of evaporation are that a very high decontamination factor (DF) is required to produce low-activity distillate, criticality-safety by geometry may be a problem, neutralization of the bottoms and distillate is likely to be required, glass stills are subject to heat stress and cracking, and difficulty in obtaining the required approval for operation is expected. To produce distillate with activity <0.1 nCi/mL, it is likely that a $DF > 10^7$ may be required. However, it may be possible to attain DFs of this magnitude in a still-type evaporator. A typical still type evaporator is shown in Fig. 3 [POPE]. A still is a batch or semibatch evaporator that attains good liquid/vapor separation (thus attaining high DFs) by a long separation region and reflux of distillate to the separation region. The reflux washes the separation region with pure liquid to further enhance separation.

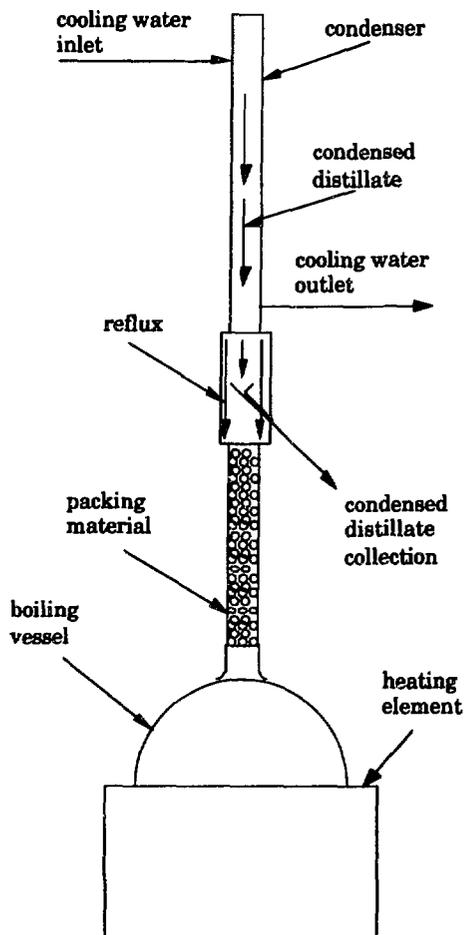


Fig. 3.

Typical Still-Type Evaporator [POPE].

To obtain the required processing rates, the boiling vessel might not be criticality-safe by geometry. Potentially, all other process options face the same problem as well. Even though no special chemical treatment is needed for evaporation, simple neutralization of the evaporator bottoms and distillate will be required if the pH is <2 or >12.5. However, no messy solid/liquid separation will be required, because once the neutralization is complete, the entire batch may be absorbed and packaged.

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APPENDIX E

DISCUSSION OF ENVIRONMENT, SAFETY, AND HEALTH CONCERNS

1. Overview

The policy of ANL is that its activities will be conducted so that worker and public safety is given the highest priority. The Laboratory will comply with all applicable federal and state laws, regulations, and orders to protect the health and safety of workers and the public and to minimize accidental damage to property.

The governing document on health and safety issues is the *Environment, Safety and Health Manual (ANL-East)* issued by the Environment, Safety, and Health (ESH) Division [ANL]. This manual should be consulted when any questions or problems arise involving these issues. In addition, the names and phone numbers of the following individuals and sections shall be prominently posted in the workplace:

- Divisional Safety Officer,
- Divisional Environmental Compliance Officer,
- Area Health Physics Technicians and Health Physicist,
- Industrial Hygiene Section of the ES&H Division,
- Health Physics Section Manager, and
- Emergency Safety Officer in ESH Division.

2. Training

The Project Supervisor shall maintain a written, auditable record of the training received by the worker. The Divisional Safety Officer shall verify that the training is adequate and satisfactory before work begins. No actual hands-on work shall be performed until all employees involved are adequately trained and understand any and all potential hazards.

3. Specific Areas of Concern

Respiratory Protection. Because this process is expected to operate in a glovebox environment, additional respiratory protection is not expected to be required except during nonroutine events. However, the proper level of respiratory protection can be specified by Industrial Hygiene.

Skin Protection. Skin protection shall be provided when working with waste solutions and chemicals. Industrial Hygiene can provide information on the appropriate gloves.

Protective Clothing. Protective clothing provided by ANL shall be used for all work.

Hazardous Chemicals. Hazardous chemicals (both chemical and radioactive) will be present in the waste solution and may be generated during the treatment process. Some examples include sodium hydroxide, which is very caustic and needs to be handled with care, and acid solutions, which can potentially irritate the skin.

All hazardous and nonhazardous components need to be treated with the safety measures specified by the material safety data sheets (see next entry) and/or the Divisional Safety Officer. Spill control measures shall be in place before work begins.

Material Safety Data Sheets (MSDSs). This information shall be available in the work areas for all chemicals (reagents) used. Such sheets are available from vendors of the reagents. Also, Industrial Hygiene maintains a large data base of MSDSs.

Dosimetry. All personnel involved in the treatment process shall wear all the necessary dosimeters. The necessary dosimeters shall be determined by the area Health Physicist.

Criticality. If WM has a current Criticality Hazard Control Statement (CHCS), it should be examined by the Divisional Safety Officer to determine if any changes are needed for this project. If a CHCS does not exist, the Divisional Safety Officer and Project Manager shall determine if one is necessary. Criticality safety in treating TRU wastes will be of great importance. To avoid criticality, two options will be considered: (1) administrative control of the quantity of fissile material in the system, and (2) designing the system to be criticality-safe by geometry. Administrative controls limit the quantities of fissile material to an amount that cannot go critical in any shape or form. The criticality-safe by geometry approach limits the dimensions to less than 6 in. in diameter. Therefore, potentially critical amounts of fissile material cannot go critical because of the geometry. A combination of the two will probably be required to ensure that criticality will not be a problem.

Waste Disposal. Any and all waste generated (radioactive and nonradioactive) shall be properly documented and disposed of according to the existing regulations.

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APPENDIX F

PROJECTED LABORATORY TESTS OF PRECIPITATION PROCESSES

In view of the complex chemical properties of some of the TRU elements, discussed briefly in Appendix C, Section 1, the laboratory experiments described below must be conducted before a final process is produced. The first carrier tested will be ferric hydroxide; the second will be magnetite. It is expected that one or both of these carriers will be satisfactory. The oxidation states and the concentration ranges of the TRU nuclides that require testing and evaluation are shown in Table 9. Other variables that require study and that are the same for all nuclides and oxidation states are

- Carrier concentration: 0.1 to 10 mg/mL.
- Precipitation temperature: room temperature, 50°C, 80°C.
- Digestion time: 5 to 60 min.
- Precipitating agents: sodium and calcium hydroxides.
- Order of addition: direct and reverse strikes.
- Volumes tested: 5 to 500 mL (not all volume and concentration combination will be tested).
- Other constituents: mineral acids, alkali and alkaline earth metals, aluminum nitrate, zirconium nitrate, oxalic acid, EDTA, DTPA, and other constituents as necessary.
- Initial acidity: 0.1 to 10M.

Tests will first be performed with 10 mL solution volumes and with low TRU concentrations because these tests can be performed rapidly and the amounts of alpha emitters will be low enough to run the tests in standard hoods. Test volumes and concentrations will be increased rapidly if no problems are encountered. Final testing is planned on simulated and actual waste solutions. For the polishing step, the inorganic ion exchangers, Diphonix columns, and/or the MACS process may be studied.

As is the case with all planned experimental work, modifications in the plan can be expected based on the results obtained.

Table 9. Laboratory Tests for Evaluating Precipitation Processes

TRU Nuclide	Oxidation States	Initial Concentration		
		nCi/mL	mg/mL	mM/mL
Am-241	+3	1E+0 to 1E+3	3.0E-7 to 3.0E-4	1.2E-9 to 1.2E-6
Pu-239	+3, +4	1E+0 to 1E+4	2.0E-5 to 2.0E-1	6.3E-11 to 6.3E-5
Np-237	+5	1E+1 to 1E+4	1.4E-3 to 1.4E-10	1E-8 to 1E-5
U-233	+6	1E+0 to 1E+2	1.0E-4 to 1.0E-2	4.4E-10 to 4.4E-8

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