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PRECONCEPTUAL DESIGN FOR SEPARATION OF PLUTONIUM AND GALLIUM BY ION EXCHANGE

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by Ion Exchange

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DISCLAIMER

The following effort is intended to represent a potential design for ion exchange separation of plutonium from gallium, but not necessarily the only design or most efficient design. Furthermore, the design presented in this study is preconceptual and therefore purposely neglects many details. The material balances are based strictly on stoichiometric amounts rather than actual operating experience in order to avoid classification as Unclassified Controlled Nuclear Information. This approximation neglects the thermodynamics and kinetics which can significantly impact the amount of reagents required. Consequently, the material resource requirements and waste amounts presented in this report should be considered ideal minimums.

PreConceptual Design for Separation of Plutonium and Gallium by Ion Exchange

1.0 ABSTRACT

The disposition of plutonium from decommissioned nuclear weapons, by incorporation into commercial UO_2-based nuclear reactor fuel, is a viable means to reduce the potential for theft of excess plutonium. This fuel, which would be a combination of plutonium oxide and uranium oxide, is referred to as a mixed oxide (MOX). Following power generation in commercial reactors with this fuel, the remaining plutonium would become mixed with highly radioactive fission products in a spent fuel assembly. The radioactivity, complex chemical composition, and large size of this spent fuel assembly, would make theft difficult with elaborate chemical processing required for plutonium recovery.

In fabricating the MOX fuel, it is important to maintain current commercial fuel purity specifications. While impurities from the weapons plutonium may or may not have a detrimental affect on the fuel fabrication or fuel/cladding performance, certifying the effect as insignificant could be more costly than purification. Two primary concerns have been raised with regard to the gallium impurity: (1) gallium vaporization during fuel sintering may adversely affect the MOX fuel fabrication process, and (2) gallium vaporization during reactor operation may adversely affect the fuel cladding performance. Consequently, processes for the separation of plutonium from gallium are currently being developed and/or designed. In particular, two separation processes are being considered: (1) a developmental, potentially lower cost and lower waste, thermal vaporization process following PuO_2 powder preparation, and (2) an off-the-shelf, potentially higher cost and higher waste, aqueous-based ion exchange (IX) process. While it is planned to use the thermal vaporization process should its development prove successful, IX has been recommended as a backup process. This report presents a preconceptual design with material balances for separation of plutonium from gallium by IX.

2.0 BACKGROUND

Tens of metric tons of plutonium from decommissioned weapons may be dispositioned as MOX fuel. Weapons-based plutonium can have a significant quantity of gallium (up to 1-wt %), which is introduced during nuclear material fabrication. The possibility exists that gallium can have a deleterious affect on the MOX fuel fabrication process, or the fuel cladding performance during reactor operation. Therefore, the prudent approach is to develop and/or design processes which can separate the plutonium from gallium prior to fuel fabrication. While thermal vaporization has been selected as the primary process for removal of gallium from plutonium in the oxide form, aqueous based processing is being maintained as an off-the-shelf contingency. In fact, aqueous based processing by IX was the plutonium purification reference process in the Data Report for the MOX Fuel Fabrication Programmatic Environmental Impact Statement (PEIS) (Reference 1, Section 4.2). Since preparation of the PEIS Data Report, it has been determined vaporization may separate gallium from plutonium with less waste, less risk of criticality, and ultimately less cost (this process is referred to as Thermally Initiated Gallium Removal or TIGR). However, since the TIGR process is currently under development such that its effectiveness has not yet been completely demonstrated, consideration of aqueous based IX processing for gallium separation from plutonium is being maintained as a contingency.

In-light of this rationale, a preconceptual flowsheet has been prepared for off-the-shelf IX separation. All equipment required for this IX-based flowsheet is currently available from commercial vendors, and the necessary unit operations (i.e. dissolution, separation, and product preparation) have been previously demonstrated at U.S. Department of Energy (DOE) facilities (Reference 2).

3.0 PROCESS DESCRIPTION

The principal unit operations required for separation of plutonium and gallium by ion exchange (IX) are shown in Figure 1. By the use of nitric acid and water recycle, the waste products are limited to TRU waste, mixed waste, and emissions. The TRU waste is essentially due to the americium present in the weapons-based plutonium, the mixed waste consists of the plutonium contaminated organic ion exchange resin, and the emissions are due to NO_x, CO_2 and water vapor.

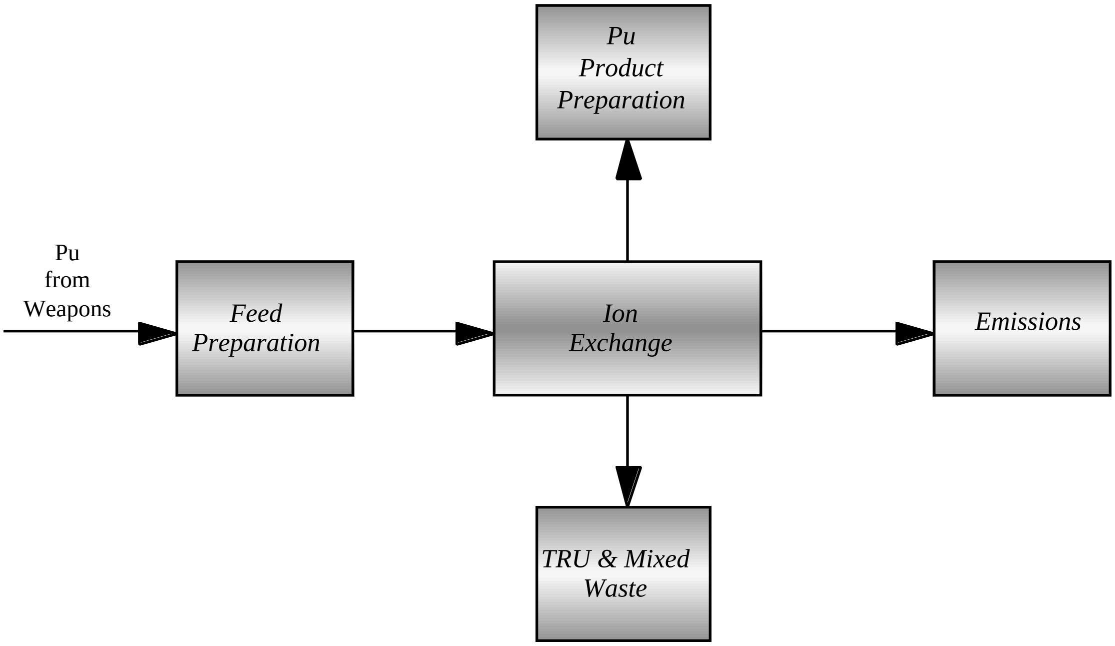

Figure 1. Process Block Diagram

Figure 2 shows the feed conditions for the detailed IX flow sheet to be used as the basis for this preconceptual design. The basis for selecting the feed conditions is described in the following text. The basis for determining the overall material balances, including waste which results from the various feed streams, is detailed in the following Material Balances section.

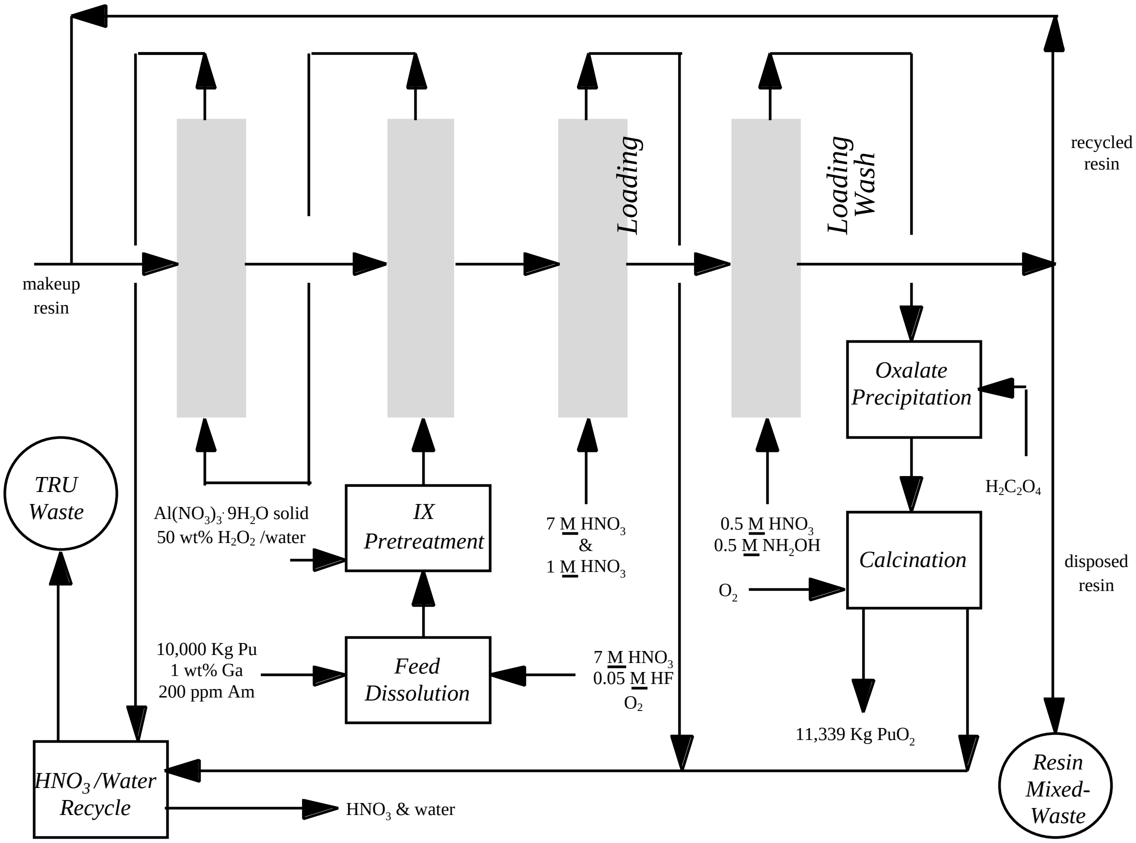

Figure 2. Overall Process Flowsheet with Feed Characteristics

3.1 Oxidation of Metal

The ARIES/HYDOX process (Reference 3) has been selected as the means for converting Pu-metallic weapon pits to plutonium oxide. This processes has been selected based upon the need to disposition relatively-complex plutonium metal configurations. In producing plutonium oxide, the ARIES process essentially involves changing metallic plutonium to a plutonium hydride powder, converting the hydride to a nitride, and then converting the plutonium nitride to plutonium oxide. The intermediate nitride step avoids the direct oxidation of hydride, which eliminates the presence of hydrogen with oxygen in potentially explosive combinations. If the baseline thermal vaporization process is used to remove gallium, the gallium is essentially vaporized from the PuO_2 following partial reduction of Ga_2O_3 to Ga_2O by hydrogen at a very low pressure (this avoids explosion concerns). The gallium depleted plutonium oxide is then ready for MOX fuel fabrication.

3.2 Dissolution of Oxide

In general, the dissolution of plutonium metal with moderate acids such as nitric acid (HNO_3), is much more difficult than dissolution of plutonium oxide. While plutonium metal can be satisfactorily dissolved with strong acids such as HCl, the stronger acids tend to excessively corrode separations processing equipment (Reference 4, Chapter 4 - Section 4 and Chapter 6 - Section 8). For this reason, plus the fact that plutonium oxide preparation from metallic plutonium pits is being developed as part of the ARIES/HYDOX process, plutonium/gallium oxide rather than metal is the feed form of choice for aqueous-based processing.

In keeping with a PreConceptual Design based upon off-the-shelf technology, it is desired to use either nitric acid alone, or nitric acid with a small amount of HF, for dissolution of the plutonium/gallium oxide feed. If nitric acid alone is used, while the waste is less the design must be based on the French Electrolytic Dissolution process (Reference 5), which is currently the only industrial based process for plutonium oxide dissolution with only nitric acid. In order to be conservative with waste estimates, plutonium oxide dissolution with a small amount of HF added to the nitric acid will be the basis for this design. Typical conditions for dissolution are those which result in 7 $\underline{M}$ HNO_3 and 0.05 $\underline{M}$ HF as feed for the IX operation (Reference 1).

3.3 Ion Exchange (IX)

The technical basis for ion exchange separation of plutonium from gallium has been described in Reference 6. Anion rather than cation exchange has been selected as the basis for this Preconceptual Design due to currently existing plutonium anion exchange operations (see Reference 1).

The IX process is essentially divided into three steps: (1) loading of plutonium nitrate on the anion exchange resin while gallium and americium remain in the original feed solution, (2) washing of the resin following completion of the loading step to remove interstitial liquid which contains gallium and americium (which results from decay of ^{241}Pu), and finally (3) elution of the resin to remove the plutonium and regenerate the resin for repeat loading.

During the loading step, the plutonium nitrate solution resulting from the dissolution of plutonium oxide by nitric acid with a small amount of HF, tends to form plutonium nitrate anion complexes at nitrate concentrations greater than 5 to 6 $\underline{M}$ (Reference 7, Section 13-3.2.d). If the resulting dissolved plutonium nitrate conditions are carefully controlled, the Pu^{IV+} oxidation state will predominate, and is highly exchangeable with an anion exchange resin as a nitrated anion complex. In contrast, the gallium and americium ions are essentially nonexchangeable with the anion exchange resin for these conditions (Reference 6, Chapter 8 - Figure 8). Consequently, plutonium will preferentially exchanged under carefully controlled conditions.

As described in Reference 6, the Pu^{IV+} species in nitric acid is more extractable on anion exchange resins than the other plutonium oxidation states (such as Pu^{III+} and Pu^{VI+}). Consequently, following dissolution a pretreatment step is required to prevent fluoride loading of the resin , and another pretreatment step is required to maintain predominance of the Pu^{IV+} oxidation state. The formation of Pu^{III+} can be minimized by maintaining the free nitrate (NO_3^-) concentration at 7 $\underline{M}$; but for Pu^{IV+} to predominate, hydrogen peroxide (H_2O_2) must be added to prevent formation of Pu^{VI+} (Reference 7, Section 13-1.4). Addition of

HF to enhance PuO_2 dissolution in nitric acid (HNO_3) will tend to form PuF_4 complexes which can compete and interfere with the exchange of the plutonium nitrate anion complexes (Reference 7, Section 13-3.2). Consequently, aluminum nitrate can be added so that the F^- anion will complex with the Al^{3+} cation and minimize the formation of PuF_3. It is important to note that complete formation of the most exchangeable form of plutonium (i.e. $[Pu^{IV+}(NO_3^-)_6]^{=}$) is not necessary because as the most exchangeable species is exchanged from solution to resin, the species in solution will maintain an equilibrium mix which implies continued formation of the most extractable species.

A wash step follows the plutonium loading in order to remove interstitial liquid bearing gallium and amercium, prior to the elution step. This interstitial liquid is actually the plutonium feed solution which remains in the column once loading is discontinued. Two wash steps are used in order to prepare the column for elution with hyrdoxylamine (H_2NOH). The first wash is 7 $\underline{M}$ HNO_3 which is concentrated in NO_3^- in order to prevent Pu oxidation state change on the resin, or plutonium nitrate anion decomplexation, which in either case will cause the plutonium to leave the resin. This wash solution is routed to the waste since it has significant quantities of gallium and americium. The second wash is 1 $\underline{M}$ HNO_3 which prepares the resin for elution with hydroxylamine, since hydroxylamine can react and form gases with more concentrated HNO_3 (such as 7 $\underline{M}$). Since the second wash is more dilute in NO_3^-, some plutonium may leave the resin, but since it should have little gallium or americium present, this wash can be routed to the plutonium product collection.

And finally, the elution and resin regeneration can be combined in a single step. The elution (plutonium removal from resin) is achieved by two mechanisms. The first is passing dilute nitric acid through the column which decomplexes the plutonium nitrate anion in accordance with Equations 1-3.

$$Pu^{IV+} + 6(NO_3^-) = Pu(NO_3)_6^{=} \qquad \text{Equation 1}$$

$$K_{eq} = \frac{[Pu(NO_3)_6^{=}]}{[Pu^{IV+}][NO_3^-]^6} \qquad \text{Equation 2}$$

$$[Pu(NO_3)_6^{=}] = K_{eq}[Pu^{IV+}][NO_3^-]^6 \qquad \text{Equation 3}$$

Equation 1 is simply the stociometric chemical reaction for the formation of the doubly charged plutonium nitrate anion complex. Equation 2 represents the idealized equilibrium expression where square brackets define concentrations. And finally, Equation 2 is rearranged to yield Equation 3 which indicates the affect of the free nitrate anion (NO_3^-) concentration on the formation of the plutonium nitrate anion complex. From Equation 3 it is apparent that reducing the free nitrate anion concentration (or nitric acid concentration as shown by Equation 4) will also reduce the plutonium nitrate anion complex.

$$HNO_3 = H^+ + NO_3^-$$

$$K_{eq} = \frac{[H^+][NO_3^-]}{[HNO_3]}$$

and since $[H^+] = [NO_3^-]$

$$[NO_3^-] = K_{eq}[HNO_3]^{1/2} \qquad \text{Equation 4}$$

If the plutonium does not exist as a nitrated anion, it will not remain on the IX resin. Similar behavior occurs for the single charged plutonium nitrate anion complex [$Pu(NO_3)_5^-$], and triple charged or greater anion complexes which exist at only very small concentrations, if at all. The second mechanism used to affect removal of plutonium from the IX resin is the use of hydroxylamine (H_2NOH), which can be used in conjunction with the dilute nitric acid. Hyrdoxylamine acts as a reducing agent for the Pu^{IV+} nitrated anion complex. The Pu^{IV+} is reduced from the +4 oxidation state to the plus three (Pu^{III+}), which does not readily form nitrated anion complexes (Reference 7, Section 12-7). By doing this, the plutonium decomplexes from the nitrate on the IX resin and then enters solution. Typical conditions for the elution are 0.5 $\underline{M}$ HNO_3 and 0.5 $\underline{M}$ H_2NOH (Reference 1). The free nitrate in solution also serves to recharge (or replace) the anion sites which were consumed by the plutonium nitrate anion complexes. These recharged sites are then available to repeat the plutonium loading step.

It is important to charge the fresh (never before used) resin with nitrate anions the initial time prior to loading.

3.4 Plutonium Product Preparation

Precipitation of Pu^{III+} oxalate may be accomplished from solutions containing as little as 1 g-Pu/L and not more than 4 $\underline{M}$ HNO_3 (Reference 7, Section 15-1.4). Oxalic acid may be added as a solid or liquid, at a rate not particularly important. After approximately a thirty minute digestion period, the precipitate is washed with water and dried.

Calcination of plutonium oxalate precipitate versus direct calcination of plutonium nitrate has the advantage of forming less dense plutonium oxide particles (Reference 7, Section 15.1-6). The less dense particles can be more suitable for follow on operations such as MOX fuel pellet formation by sintering.

3.5 Recycle Operations

There are numerous places in the proposed Flowsheet shown in Figure 2 for which recycle operations could significantly reduce waste streams. Since this is a preconceptual design, the details of recycle will not be produced here; but rather, it is assumed classical evaporation and distillation unit operations will be used to separate nitric acid and water for recycle from the salts.

3.6 Waste Generation

As noted in Section 3.5, much of the nitric acid and all of the water water will be recycled, while the salts will be separated as waste. Additionally, following the specified number of regenerations, the IX resin will become waste as well. HF was selected for dissolution of PuO_2 rather than electrolytic dissolution developed by the French; however, the use of electrolytic dissolution would eliminate the need for $Al(NO_3)_3$.

4.0 MATERIAL BALANCES

4.1 Dissolution of Oxide

The following conditions were assumed for dissolution of the plutonium oxide in nitric acid (HNO_3) and hydrofluoric acid (HF).

(1) 10-MT Pu metal feed
(2) PuO_2 formation per the Pit Disassembly and Conversion Facility (PDCF)
(3) Conditions following feed dissolution shall be approximately 150 g-Pu/L at approximately 7 M free nitrate (NO_3^-), i.e. not complexed with plutonium. The plutonium concentration has been selected as one-half of 300 g-Pu/L which is the approximate maximum concentration without formation of plutonium polymer in nitric acid solution (Reference 8, Pg 59). The ion exchange column diameter will be selected for sub-critical operation. The free nitrate anion concentration following dissolution, and entering the ion exchange column, is based upon achieving maximum resin loading for a strong-base anion-exchange resin (Reference 9, Chapter 8, Figure 8).
(4) The plutonium-nitrate anion complex following dissolution will consist of essentially 100% double charged anion, $Pu(NO_3)_6^=$ (Reference 10). While some $Pu(NO_3)_5^-$ will exist as well, the equilibrium determination is difficult at best, such that assuming 100% $Pu(NO_3)_6^=$ will conservatively estimate nitrate consumption and hence nitrate waste. Additionally, as $Pu(NO_3)_6^=$ is preferentially exchanged over $Pu(NO_3)_5^-$, the single-charged anion will convert to the double-charge anion in solution in order to maintain equilibrium.
(5) 0.05 M HF will be added to the HNO_3 to enhance PuO_2 dissolution (Reference 7, Section 16-1.2.b.1). Feedstock for HNO3 and HF, shall be ~15 M HNO_3, and 52 wt% water for HF. These are typical concentrated acids which can be readily purchase from most chemical suppliers (Reference 11). The use of concentrated acids minimizes water waste.

(6) Dissolution chemistry for Ga_2O_3, Am_2O_3, and other minor constituents can be ignored due to their low concentrations.

Figure 3 highlights the materials balances for the Dissolution and pretreatment steps shown in Figure 2. The bold italics of Figure 3 are the given values from the previous steps (1)-(5), which are used to establish the complete material balances. The material balance calculations are shown in the text following Figure 3.

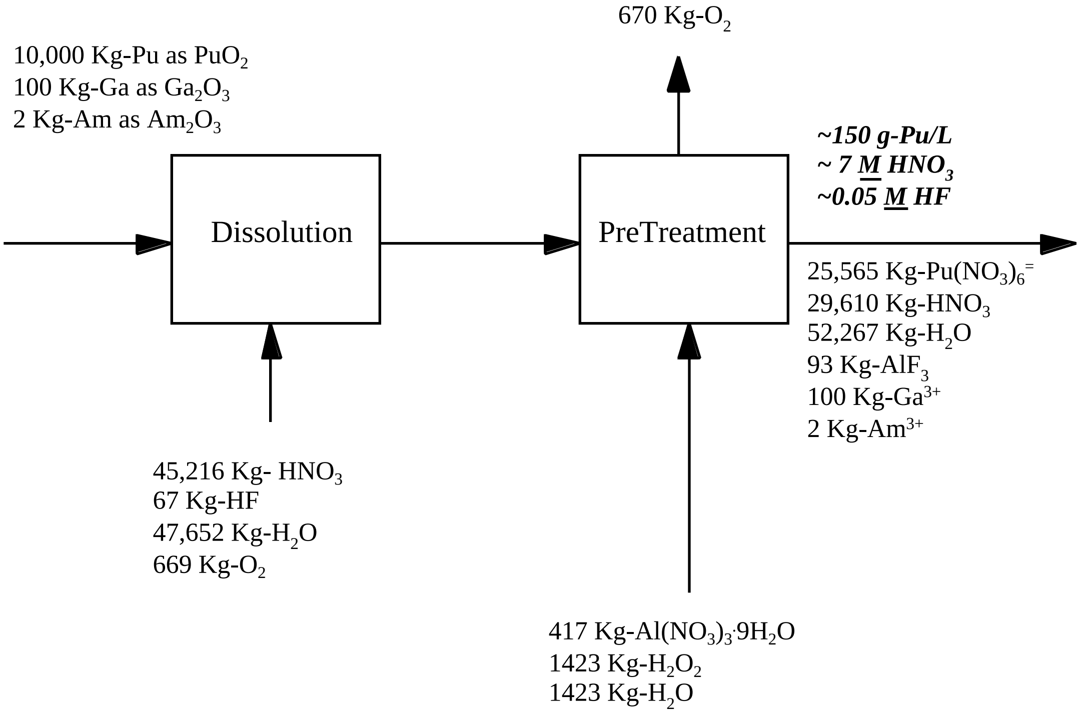

Figure 3. Material Balances for Oxide Dissolution and IX Pretreatment

Dissolution Reaction:

$PuO_2 + 6HNO_3 \text{ -> } Pu(NO_3)_6^{=} + 2H_2O + 2H^+$

The dissolution can be made fumeless, as the Europeans do (Reference 4, Chapter 10, Section 4.4), by the addition of oxygen.

$PuO_2 + 6HNO_3 + 1/2(O_2) \text{ -> } Pu(NO_3)_6^{=} + 3H_2O$

Approximate (assume ^{239}Pu) moles of plutonium per 10,000 Kg:

$$(10\ \text{MT-Pu})\frac{(1000\ \text{Kg})}{\text{MT}}\ \frac{(1\ \text{gmole- Pu})}{(0.239\ \text{Kg -Pu})} = 41{,}841\ \text{gmole-Pu}$$

Amount of nitrate complexed with plutonium during dissolution for $Pu(NO_3)_6^{=}$:

$$(41{,}841\ \text{gmole-Pu})\frac{(6\ \text{gmole-}NO_3^-)}{(1\ \text{gmole-Pu}\ )} = 2.5105\times10^5\ \text{gmole-}NO_3^-$$

Nitric acid required for complexation:

$$(2.5105\text{x}10^5 \text{ gmole-NO}_3^-)\frac{(0.063 \text{ Kg-HNO}_3)}{(1 \text{ gmole-NO}_3^-)} = 15{,}816 \text{ Kg-HNO}_3$$

Total volume of feed solution required for IX based on 150 g-Pu/L:

$$\frac{(10{,}000 \text{ Kg- Pu})}{(0.150 \text{ Kg-Pu/L})} = 66{,}667 \text{ L}$$

Amount of free nitrate/nitric acid required for 7 M NO_3^- following dissolution:

$$(7 \text{ gmole-NO}_3^-\text{/L})(66{,}667 \text{ L}) = 4.6667\text{x}10^5 \text{ gmole-NO}_3^-$$

$$(4.6667\text{x}10^5 \text{ gmole-NO}_3^-)\frac{(0.063 \text{ Kg-HNO}_3)}{(1 \text{ gmole-NO}_3^-)} = 29{,}400 \text{ Kg-HNO}_3$$

Total nitric acid required for dissolution/IX:

$$(15{,}816 + 29{,}400) \text{ Kg} = 45{,}216 \text{ Kg-HNO}_3$$

Water present with concentrated nitric acid used as feed stock (15 M at ρ =1.4, Reference 11):

$$\frac{(0.30 \text{ H}_2\text{O})}{(0.70 \text{ HNO}_3)} (45{,}216 \text{ Kg-HNO}_3) = 19{,}378 \text{ Kg-H}_2\text{O}$$

Amount of water present in the 7 M nitric acid following dissolution can be approximated as 64 wt% (Reference 12, pg D-238):

$$\frac{(0.64 \text{ H}_2\text{O})}{(0.36 \text{ HNO}_3)} (29{,}400 \text{ Kg-HNO}_3) = 52{,}267 \text{ Kg-H}_2\text{O}$$

Amount of oxygen required for fumeless dissolution:

$$(41{,}841 \text{ gmole-Pu})\frac{(0.5 \text{ gmole-O}_2)}{(1 \text{ gmole-Pu})} = 20{,}920 \text{ gmole-O}_2$$

$$(20{,}920 \text{ gmole-O}_2)\frac{(0.032 \text{ Kg-O}_2)}{(1 \text{ gmole-O}_2)} = 669 \text{ Kg-O}_2$$

Water produced per fumeless dissolution:

$$(41{,}841 \text{ gmole-Pu})\frac{3 \text{ gmole-H}_2\text{O}}{1 \text{ gmole- Pu}}\frac{0.018 \text{ Kg-H}_2\text{O}}{1 \text{ gmole-H}_2\text{O}} = 2259 \text{ Kg-H}_2\text{O}$$

Hydrofluoric acid required at 0.05 M:

(0.05 gmole-HF/L)(66,667 L) = 3333 gmole-HF

$$(3333 \text{ gmole-HF})\frac{0.020 \text{ Kg-HF}}{1 \text{ gmole-HF}} = 67 \text{ Kg-HF}$$

Water present with concentrated hydrofluoric acid (HF) used as feed stock (48 wt% HF, Reference 11):

$$\frac{(0.52\ H_2O)}{(0.48\ HF)}\ (67 \text{ Kg-HF}) = 73 \text{ Kg-}H_2O$$

Table 1 summarizes conditions for the Dissolution step of Figure 4.

Component	Mass (Kg)	Input(i) or Output(o)	Unit Operation
PuO_2	11,339	feed (i)	PDCF[b]
$Pu(NO_3)_x^{(4-x)}$	Y[a]	dissolved PuO_2 (o)	pretreatment
HNO_3	15,816	complexed Pu feed (i)	
	29,400	7 M feed (i)	
HF	67	0.05 M feed (i)	
H_2O	19,378	HNO_3 feed (i)	
	73	HF feed (i)	
	28,201	feed (i)	
	47,652		
	2259	fumeless dissolution (o)	pretreatment
	49,911		
O_2	669	feed (i)	

[a] Y=[(239+62x)/239](10,000 Kg)

[b] PDCF=Pit Dissassembly & Conversion Facility

Table 1. Dissolution Summary

4.2 IX Feed Pretreatment

The following conditions were assumed for pretreatment of the plutonium nitrate anion prior to ion exchange.

(1) Aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$] will be added as a solid (Reference 2, pg. 10) to complex the free fluoride anion (F^-) following feed dissolution, so that the fluoride does not form the less exchangeable species PuF_4. $Al(NO_3)_3 \cdot 9H_2O$ will be added at a stoichiometric amount such that the Al^{3+} cation consumes all the available fluoride.

(2) While the ~7 M nitric acid resulting from dissolution should promote the formation of the desired, more exchangeable Pu^{IV+} oxidation state over Pu^{III+}, the addition of hydrogen peroxide (H_2O_2) is necessary to inhibit the formation of the less exchangeable Pu^{VI+}. Hydrogen peroxide as a reductant for Pu^{VI+} has the advantage of not contributing to solid waste. A stoichiometric amount of H_2O_2 should be adequate for Pu^{VI+} reduction, for conditions of moderate HNO_3 concentration and non-dilute plutonium concentration (Reference 7, Section 13-1.4.b). Complete elimination of Pu^{III+} and Pu^{VI+} are not necessary as they will convert to Pu^{IV+} in order to maintain equilibrium in the liquid, as the Pu^{IV+} exchanges onto the resin. This will slow the kinetics of exchange as the conversion must first occur. This can be dealt with by increasing the IX column residence time. H_2O_2 will be added as a 50 wt% water solution (Reference 11).

Fluoride/aluminum complexation reaction:

$$3HF + Al(NO_3)_3 \cdot 9H_2O \text{ -> } AlF_3 + 3H^+ + 3NO_3^- + 9H_2O$$

Aluminum required for fluoride:

$$(3333\ \text{gmole-F}^-)\frac{(1\ \text{gmole-Al}^{3+})}{(3\ \text{gmole- F}^-)} = 1111\ \text{gmole-Al}^{3+}$$

$$(1111\ \text{gmole-Al}^{3+})\frac{[1\ \text{gmole -Al(NO}_3)_3.9\text{H}_2\text{O}]}{(1\ \text{gmole- Al}^{3+})}\ \frac{(0.375\ \text{Kg-Al(NO}_3)_3.9\text{H}_2\text{O})}{[1\ \text{gmole-Al(NO}_3)_3.9\text{H}_2\text{O}]} =$$

$$417\ \text{Kg-Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}$$

$$(1111\ \text{gmole-Al}^{3+})\frac{(1\ \text{gmole- AlF}_3)}{(1\ \text{gmole-Al}^{3+})}\ \frac{(0.084\ \text{Kg-AlF}_3)}{(1\ \text{gmole-AlF}_3)} = 93\ \text{Kg-AlF}_3$$

Water produced from decomposition of aluminum nitrate nanohydrate:

$$[1111\ \text{gmole-Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}]\frac{9\ \text{gmole -H}_2\text{O}}{1\ \text{gmole- Al(NO}_3)_3.9\text{H}_2\text{O}}\ \frac{0.018\ \text{Kg-H}_2\text{O}}{1\ \text{gmole-H}_2\text{O}} = 180\ \text{Kg-H}_2\text{O}$$

Nitric acid produced by decomposition of aluminum nitrate nanohydrate and H^+ from HF dissociation:

$$[1111\ \text{gmole-Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}]\frac{3\ \text{gmole-HNO}_3}{1\ \text{gmole- Al(NO}_3)_3.9\text{H}_2\text{O}}\ \frac{0.063\ \text{Kg-HNO}_3}{1\ \text{gmole-HNO}_3} =$$

$$210\ \text{Kg-HNO}_3$$

Reaction for hydrogen peroxide reduction of Pu^{VI+}:

$$Pu^{IV+} = Pu^{VI+} + 2e^-$$

$$Pu^{VI+} + 2e^- + H_2O_2 \text{ -> } Pu^{IV+} + H_2O + 1/2(O_2)$$

Hydrogen peroxide required:

$$\frac{(10{,}000\ \text{Kg-Pu})}{(0.239\ \text{Kg-Pu/gmole-Pu})}\ \frac{(1\ \text{gmole-}H_2O_2)}{(1\ \text{gmole- Pu})}\ \frac{(0.034\ \text{Kg-}H_2O_2)}{(1\ \text{gmole-}H_2O_2)} = 1423\ \text{Kg-}H_2O_2$$

Oxygen produced from reduction reaction:

$$\frac{(1423\ \text{Kg-}H_2O_2)}{(0.034\ \text{Kg-}H_2O_2\text{/gmole-}H_2O_2)}\ \frac{(0.5\ \text{gmole -}O_2)}{(1\ \text{gmole }H_2O_2)}\ \frac{(0.032\ \text{Kg-}O_2)}{(1\ \text{gmole-}O_2)} = 670\ \text{Kg-}O_2$$

Water produced from reduction reaction:

$$\frac{(1423\ \text{Kg-}H_2O_2)}{(0.034\ \text{Kg-}H_2O_2\text{/gmole-}H_2O_2)}\ \frac{(1\ \text{gmole- }H_2O)}{(1\ \text{gmole }H_2O_2)}\ \frac{(0.018\ \text{Kg-}H_2O)}{(1\ \text{gmole-}H_2O)} = 753\ \text{Kg-}H_2O$$

Water produced from 50 wt% hydrogen peroxide solution:

$$(1423\ \text{Kg-}H_2O_2)\ \frac{(1\ \text{Kg-}H_2O)}{(1\ \text{Kg-}H_2O_2)} = 1423\ \text{Kg-}H_2O$$

Table 2 summarizes conditions for the Pretreatment step of Figure 3.

Component	Mass (Kg)	Input(i) or Output(o)	Unit Operation
$Pu(NO_3)_x^{(4-x)}$	Y[a]	Pu feed (i)	dissolution
$Pu(NO_3)_6^{=}$	25,565	pretreated IX feed (o)	loading
$Al(NO_3)_3{\cdot}9H_2O$	417	feed (i)	
H_2O_2	1423	feed (i)	
HNO_3	210	$Al(NO_3)_3{\cdot}9H_2O$ rxn (o)	loading
	29,400	dissolution feed (i)	dissolution
	29,610		
F^-	64	HF dissociation (i)	dissolution
H_2O	1423	H_2O_2 feed (i)	
	49,911	dissolution feed (i)	dissolution
	753	H_2O_2 rxn (o)	loading
	180	$Al(NO_3)_3{\cdot}9H_2O$ rxn (o)	loading
	52,267		
O_2	670	H_2O_2 rxn (o)	disposal
AlF_3	93	$Al(NO_3)_3{\cdot}9H_2O$ rxn (o)	loading
Ga^{3+}	100	Pu feed (i)	dissolution
	100	pretreated IX feed (o)	loading
Am^{3+}	2	Pu feed (i)	dissolution
	2	pretreated IX feed (o)	loading

[a]Y=[(239+62x)/239](10,000 Kg)

Table 2. Pretreatment Summary

4.3 IX Resin Loading

Figure 4 highlights the materials balances for the IX Loading step shown in Figure 2. The material balance calculations are shown in the text following Figure 4.

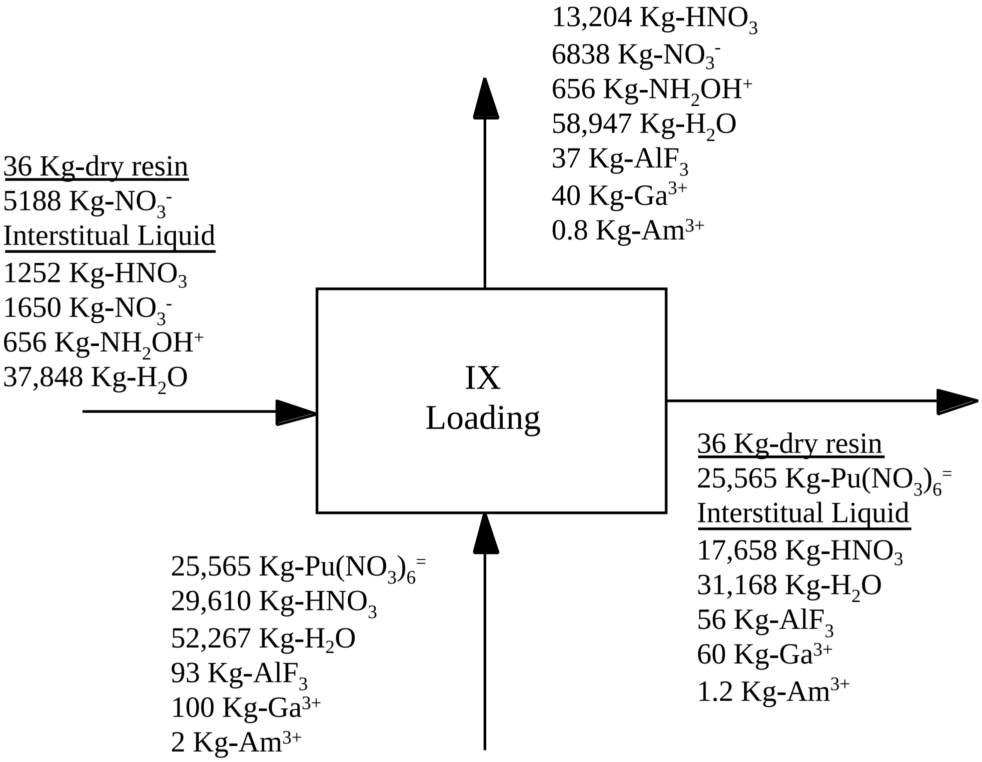

Figure 4. Material Balances for IX Loading

Plutonium loaded on IX resin:

10,000 Kg-Pu

The minimum resin required assuming equilibrium loading, and based upon a typical strong-base anion resin such as Reillex^{TM} HPQ (Reference 13), is determined as follows:

$$(10{,}000\ \text{Kg-Pu})\frac{(1\ \text{gmole- Pu})}{(0.239\ \text{Kg -Pu})}\ \frac{[2\ \text{meq/gmole -Pu}(NO_3)_6^=]}{(4.1\ \text{meq/Kg-dry resin})}\ \frac{[1\ \text{gmole -Pu}(NO_3)_6^=]}{(1\ \text{gmole- Pu})} =$$

20,410 Kg-dry resin

This is not the total amount of resin consumed, because the ability to regenerate and recycle greatly reduces the resin consumption as shown in the following.

However, the author's discussions with personnel who have experience operating similar processes indicate the resin loading should not exceed ~65 g-Pu/L-resin. This is based on the following criticallity concern. While the IX column can be easily designed as subcritical for most aqueous solutions of plutonium, the presence of an organic resin replaces aqueous hydrogen atoms with carbon. These carbon atoms may not moderate differently than hydrogen, but carbon does not capture neutrons as does hydrogen.

The resin interstitial liquid can be determined as follows. The maximum packing factor for identical size spheres is defined as face-centered cubic, and corresponds to 74 vol% (Reference 14, Chapter 4, Section 3). This implies the liquid volume between IX resin particles consumes a minimum of 26% of the total combined volume. Based on Table 16-3 of Reference 15, the moisture content for a typical strong-base anion exchange resin in use is ~ 50 wt%, and the wet density is ~ 45 lb/ft^3 (721.5 Kg/m^3).

The total column volume required for exchange, independent of regeneration, is:

$$\frac{20{,}410\text{ Kg-dry resin}}{(1\text{ Kg-dry resin}/2\text{ Kg-wet resin})}\;\frac{1}{(0.7215\text{ Kg-wet resin/L})}\;\text{x}\;\frac{1}{(0.74)} = 76{,}455\text{ L}$$

$$\frac{(10\text{ MT -Pu})}{(76{,}455\text{ L -column})}\;\frac{(10^6\text{ g})}{(1\text{ MT})} = 130\text{ g-Pu/L-column}$$

Since the criticallity limit is 65 g-Pu/L-resin, and it is assumed the entire column is loaded with resin, the resin will be loaded to only 50% capacity. This will not increase resin or reagent consumption, but it will double the number of operating cycles. This is based on resin regeneration, and the recycle of nitric acid and water.

The liquid interstitial volume can be determined as follows:

$$0.26[2(76{,}455\text{ L})] = 39{,}756\text{ L-liquid volume}$$

The total resin consumption can now be determined as follows. Based upon the author's conversation with those who have processed plutonium with similar anion exchange resins, it is estimated based upon utilizing resin regeneration, that one column volume of resin (6 in. I.D. by 6 ft length) can process 2.5 MT plutonium.

$$(10\text{ MT-Pu}/2.5\text{ MT-Pu}) = 4\text{ column volumes of resin consumed}$$

$$V=\pi r^2 l = \pi(3\text{ in})^2\left(\frac{0.0254\text{ m}}{1\text{ in}}\right)^2\frac{(6\text{ ft})}{(1\text{ ft}/12\text{ in})}\left(\frac{0.0254\text{ m}}{1\text{ in}}\right)$$

$$= \pi(3\text{ in})^2(72\text{ in})\left(\frac{0.0254\text{ m}}{1\text{ in}}\right)^3 = 0.033343\text{ m}^3$$

$$\text{Resin mass} = (\text{resin fraction})\rho V$$

$$= 0.74(0.7215\ \text{Kg-wet resin/L})\frac{(1\ \text{Kg- dry resin})}{(2\ \text{Kg-wet resin})}(0.033343\ \text{m}^3)\frac{(1000\ \text{L})}{(1\ \text{m}^3)}$$

$$= 8.9011\ \text{Kg-dry resin}$$

(8.9011 Kg-dry resin/column volume)(4 column volumes) = 35.604 Kg-dry resin

The composition of interstitial liquid in equilibrium with the resin following loading can then be determined as follows.

(39,756 L/66,667 L)(29,610 Kg-HNO_3) = 17,658 Kg-HNO_3
(39,756 L/66,667 L)(52,267 Kg-H_2O) = 31,168 Kg-H_2O
(39,756 L/66,667 L)(93 Kg-AlF_3) = 56 Kg-AlF_3
(39,756 L/66,667 L)(100 Kg-Ga^{3+}) = 60 Kg-Ga^{3+}
(39,756 L/66,667 L)(2 Kg-Am^{3+}) = 1.2 Kg-Am^{3+}

In order to complete the material balances shown in Figure 4, it is necessary to estimate the composition of interstitial liquid and of the resin prior to loading, i.e. following regeneration. The composition of interstitial liquid in equilibrium with the regenerated resin entering the loading cycle, and forced out of the resin upon loading, is determined in the Section on Elution/Regeneration later in this text. The results are summarized in the following.

Recharged resin:
5188 Kg-NO_3^- on resin and replaced by plutonium during loading

Interstitial liquid from Elution/Regeneration:
39,756 L liquid
1650 Kg-NO_3^- in liquid
1252 Kg-HNO_3 in liquid
656 Kg-NH_2OH in liquid
37,848 Kg-H_2O in liquid

The composition of the effluent from which the plutonium has been removed is simply (1) the interstitial liquid in the recharged resin, and (2) the resin nitrate displaced by the plutonium nitrate anion, and (3) the pretreated dissolved feed minus the plutonium and minus that left in the interstitial resin space upon completion of loading.

The summary of Loading conditions is shown in Table 3.

Component	Mass (Kg)	Input(i) or Output(o)	Unit Operation
$Pu(NO_3)_6^{=}$	25,565	feed(i)	pretreatment
$Pu(NO_3)_6^{=}$	25,565	resin(o)	wash
NH_2OH^+	626	interstitial liquid(i)	regeneration
	626	waste(o)	recycle
HNO_3	13,204	waste(o)	recycle
	29,610	feed(i)	pretreatment
	17,658	interstitial liquid(o)	wash
	1252	interstitial liquid(i)	regeneration
NO_3^-	1650	interstitial liquid(i)	regeneration
	6838	waste(o)	recycle
	5188	resin(i)	regeneration
	5188	resin(o)	wash
H_2O	58,947	waste(o)	recycle
	52,267	feed(i)	pretreatment
	31,168	interstitial liquid(o)	wash
	37,848	interstitial liquid(i)	regeneration
AlF_3	37	waste(o)	disposal
	56	interstitial liquid(o)	wash
	93	feed(i)	pretreatment
Ga^{3+}	40	waste(o)	recycle
	60	interstitial liquid(o)	wash
	100	feed(i)	recycle
Am^{3+}	0.8	disposal(o)	recycle
	1.2	interstitial liquid(d)	wash
	2	feed(i)	recycle
resin	36	feed(i)	

Table 3. IX Loading Summary

4.4 IX Pre-Elution Wash

Figure 5 highlights the materials balances for the IX Wash step shown in Figure 2. The material balance calculations are described in the text following Figure 5.

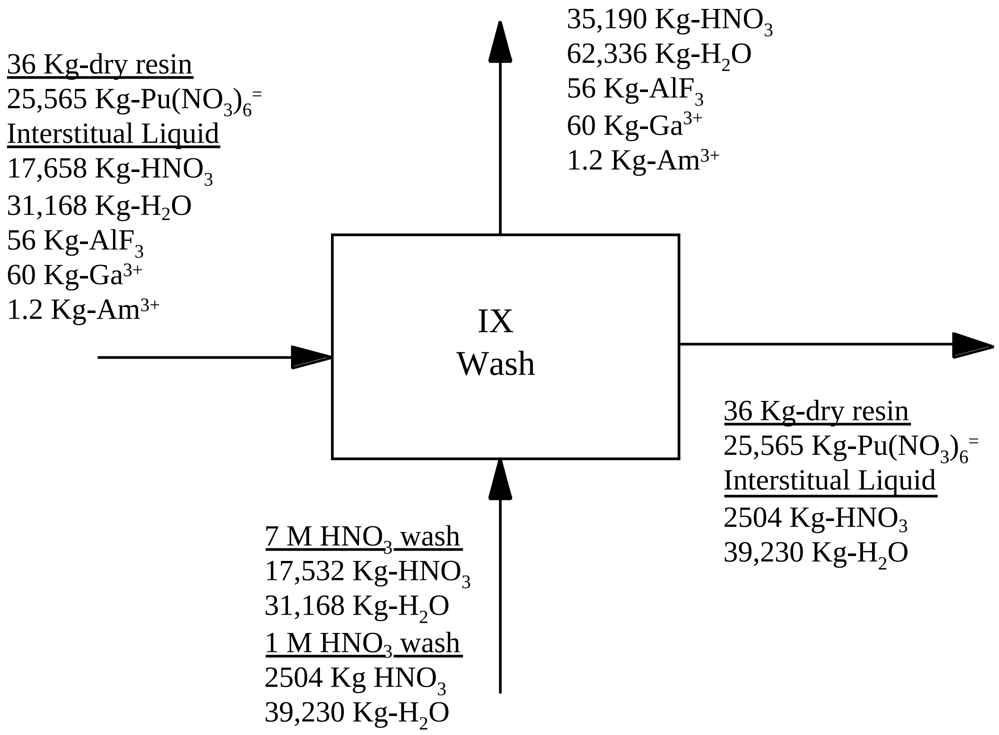

Figure 5. Material Balances for IX Wash

Conditions for the IX wash are (1) one interstitial column volume (39,756 L) of 7 $\underline{M}$ HNO_3 to rinse the interstitial volume remaining from the Loading step, and (2)) one interstitial column volume (39,756 L) of 1 $\underline{M}$ HNO_3 to rinse the 7 $\underline{M}$ HNO_3 prior to addition of the hydroxyl amine during elution. Hydroxyl amine will react vigorously with concentrated nitric acid.

One-interstitial column volume (39,756 L) at 7 $\underline{M}$ HNO_3:

$$\frac{7 \text{ gmole-HNO}_3\text{ /L}}{(1 \text{ gmole-HNO}_3/0.063 \text{ Kg-HNO}_3)}(39{,}756 \text{ L}) = 17{,}532 \text{ Kg-HNO}_3$$

The amount of water with 7 $\underline{M}$ HNO_3 (64 wt% H_2O) is:

$$(0.64/0.36)(17{,}532 \text{ Kg-HNO}_3) = 31{,}168 \text{ Kg-H}_2\text{O}$$

One-interstitial column volume (39,756 L) at 1 $\underline{M}$ HNO_3:

$$\frac{1 \text{ gmole-HNO}_3\text{ /L}}{(1 \text{ gmole-HNO}_3/0.063 \text{ Kg-HNO}_3)}(39{,}756 \text{ L}) = 2504 \text{ Kg-HNO}_3$$

The amount of water with 1 M HNO$_3$ (94 wt% H_2O - Reference 12, pg D-238) is:

(0.94/0.06)(2504 Kg-HNO_3) = 39,230 Kg-H_2O

The final 1 M HNO3 wash remains as interstitial liquid for the Elution/Regeneration step. See Table 4 for a summary of the Wash step.

Component	Mass (Kg)	Input(i) or Output(o)	Unit Operation
$Pu(NO_3)_6^{=}$	25,565	resin(i)	loading
$Pu(NO_3)_6^{=}$	25,565	resin(o)	elution
HNO_3	17,532[a]	7 M feed(i)	
	2504	1 M feed(i)	
	2504	interstitial liquid(o)	elution
	17,658[a]	interstitial liquid(i)	loading
	35,190	waste(o)	recycle
H_2O	31,168	7 M feed(i)	
	39,230	1 M feed(i)	
	39,230	interstitial liquid(o)	elution
	31,168	interstitial liquid(i)	loading
	62,336	waste(o)	recycle
AlF_3	56	waste(o)	recycle
	56	interstitial liquid(i)	loading
Ga^{3+}	60	waste(o)	recycle
	60	interstitial liquid(i)	loading
Am^{3+}	1.2	waste(o)	recycle
	1.2	interstitial liquid(i)	loading

[a] these values should be identical, but differ due to round-off error

Table 4. IX Wash Summary

4.5 IX Elution/Regeneration

Figure 6 highlights the materials balances for the IX Elution/Regeneration step shown in Figure 2. The material balance calculations are described in the text following Figure 6.

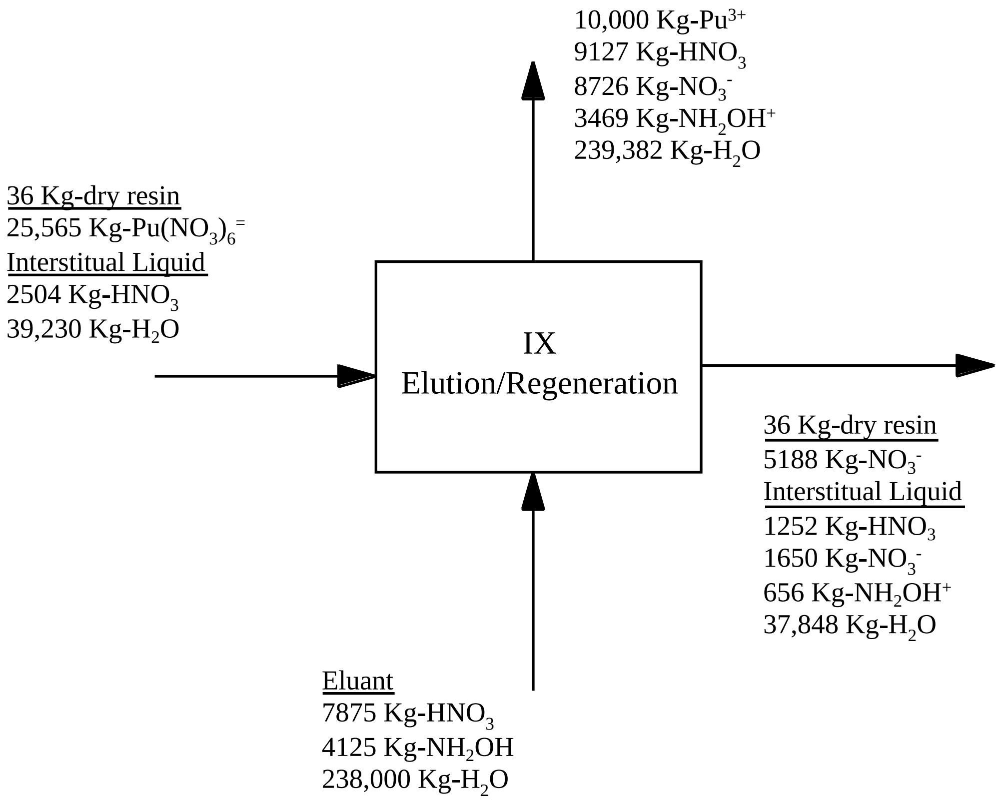

Figure 6. Material Balances for IX Elution/Regeneration

Elution/Regeneration conditions are specified by Reference 2 as 0.5 $\underline{M}$ NH_2OH, and 0.5 $\underline{M}$ HNO_3.

The Pu^{3+} will elute at approximately 40 g-Pu/L, so that the following amount of NH_2OH and HNO_3 will be required.

$$\frac{10{,}000\text{ Kg- Pu}}{0.040\text{ Kg-Pu/L}} = 2.5\text{x}10^5\text{ L}$$

$$\frac{0.5\text{ gmole-}NH_2OH/L}{(1\text{ gmole-}NH_2OH/0.033\text{ Kg -}NH_2OH)}(2.5\text{x}10^5\text{ L}) = 4125\text{ Kg-}NH_2OH$$

$$\frac{0.5\text{ gmole-}HNO_3/L}{(1\text{ gmole-}HNO_3/0.063\text{ Kg-}HNO_3)}(2.5\text{x}10^5\text{ L}) = 7875\text{ Kg-}HNO_3$$

Water present in 0.5 $\underline{M}$ HNO_3 and 0.5 $\underline{M}$ NH_2OH:

Since pure water is approximately (1-Kg/L)/(0.018-Kg/gmole) = 55.6 $\underline{M}$,

$$\rho_{H2O} \sim \rho_{0.5\ \underline{M}\ (NH2OH,H2O)}$$

Therefore, the amount of water present in a mixture of 0.5 <u>M</u> NH_2OH and 0.5 <u>M</u> HNO_3 will be approximately:

(250,000 - 4125 - 7875)Kg = 238,000 Kg-H_2O

Following reduction of the Pu^{IV+} to Pu^{3+}, hydroxylamine will be assumed to exist in an oxidized form according to:

$Pu^{IV+} + NH_2OH \rightarrow Pu^{3+} + NH_2OH^+$

Nitrate anion released during hydroxylamine reduction:

$$[41{,}841 \text{ gmole-Pu(NO}_3)_6^{=}]\frac{(6 \text{ gmole-NO}_3^{-})}{[(1 \text{ gmole -Pu(NO}_3)_6^{=}]}\frac{(0.062 \text{ Kg-NO}_3^{-})}{(1 \text{ gmole- NO}_3^{-})} = 15{,}564 \text{ Kg-NO}_3^{-}$$

Nitrate anion consumed by resin upon release of $Pu(NO_3)_6^{=}$:

$$[41{,}841 \text{ gmole-Pu(NO}_3)_6^{=}]\frac{(2 \text{ gmole-NO}_3^{-})}{[(1 \text{ gmole -Pu(NO}_3)_6^{=}]}\frac{(0.062 \text{ Kg-NO}_3^{-})}{(1 \text{ gmole- NO}_3^{-})} = 5188 \text{ Kg-NO}_3^{-}$$

Interstitial liquid following Elution/Regeneration:
39,756 L liquid
(39,756 L/2.5x10^5 L)(7875 Kg-HNO_3) = 1252 Kg-HNO_3
(39,756 L/2.5x10^5 L)(15,564-5188) Kg-NO_3^- = 1650 Kg-NO_3^-
(39,756 L/2.5x10^5 L)(4125 Kg-NH_2OH^+) = 656 Kg-NH_2OH^+
(39,756 L/2.5x10^5 L)(238,000 Kg-H_2O) = 37,848 Kg-H_2O

See Table 5 for a summary of the Elution/Regeneration step.

Component	Mass (Kg)	Input(i) or Output(o)	Unit Operation
$Pu(NO_3)_6^{=}$	25,565	resin(i)	wash
Pu^{3+}	10,000	eluate(o)	precipitation
HNO_3	7875	feed(i)	
	9127	eluate(o)	precipitation
	1252	interstitial liquid(o)	loading
	2504	interstitial liquid(i)	wash
HN_2OH	4125	feed(i)	
HN_2OH^+	3469	eluate(o)	precipitation
	656	interstitial liquid(o)	loading
H_2O	238,000	feed(i)	
	239,382	eluate(o)	precipitation
	37,848	interstitial liquid(o)	loading
	39,230	interstitial liquid(i)	wash
resin	36	waste(o)	disposal

Table 5. IX Elution/Regeneration Summary

4.5 Plutonium Oxalate Precipitation/Calcination

A number of precipitation processes are available; however, oxalate is one of a few which produces essentially no solid waste (Reference 4, Chapter 9, Figure 9.8).

$$2Pu^{3+} + 3H_2C_2O_4 + 9H_2O \rightarrow Pu_2(C_2O_4)_3{\cdot}9H_2O + 6H^+$$

Figure 7 highlights the materials balances for the Precipitation/Calcination steps shown in Figure 2. The material balance calculations are shown in the text following Figure 7.

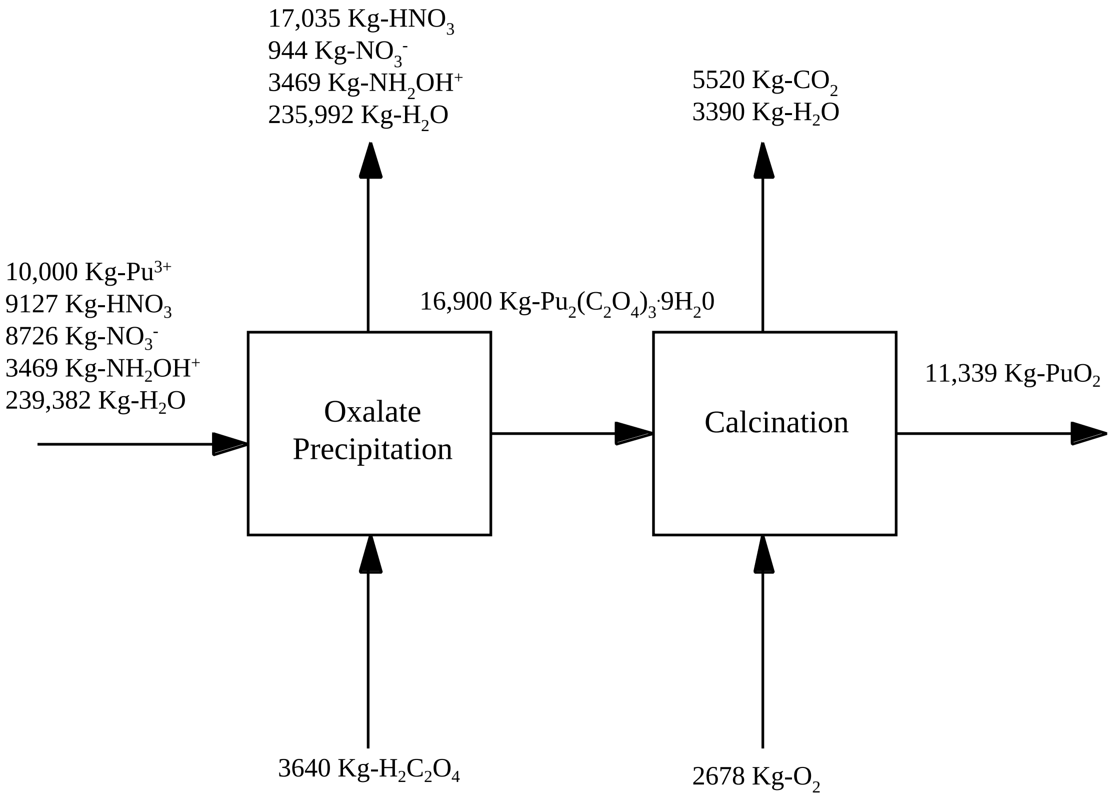

Figure 7. Material Balances for Precipitation/Calcination

Oxalate required:

$$\frac{(10{,}000\text{ Kg-Pu})}{(0.239\text{ Kg-Pu/gmole-Pu})}\frac{\left(3\text{ gmole }H_2C_2O_2\right)}{\left(2\text{ gmole Pu}\right)}\frac{\left(0.058\text{ Kg }H_2C_2O_2\right)}{\left(1\text{ gmole }H_2C_2O_2\right)} = 3640\text{ Kg-}H_2C_2O_4$$

Water consumed by plutonium oxalate formation:

$$\frac{(10{,}000\text{ Kg-Pu})}{(0.239\text{ Kg-Pu/gmole-Pu})}\frac{(9\text{ gmole }H_2O)}{(2\text{ gmole Pu})}\frac{(0.018\text{ Kg }H_2O)}{(1\text{ gmole }H_2O)} = 3390\text{ Kg }H_2O$$

Nitric acid produced by H+ released by oxalate reaction and existing nitrate:

$$(41{,}841\text{ gmole-Pu})\frac{(3\text{ gmole }H_2C_2O_2)}{(2\text{ gmole Pu})}\frac{(2\text{ gmole- }H^+)}{(1\text{ gmole-}H_2C_2O_2)}\frac{(1\text{ gmole- }NO_3^-)}{(1\text{ gmole- }H^+)}\text{ x}$$

$$\frac{(0.063\text{ Kg-}NO_3^-)}{(1\text{ gmole -}NO_3^-)} = 7782\text{ Kg-}NO_3^-$$

$$(7782\text{ Kg-}NO_3)\frac{(0.063\text{ Kg-}HNO_3)}{(0.062\text{ Kg-}NO_3^-)} = 7908\text{ Kg-}HNO_3$$

Plutonium oxalate formed:

$$\frac{(10{,}000\text{ Kg-Pu})}{(0.239\text{ Kg-Pu/gmole-Pu})}\frac{[0.5\text{ gmole }Pu_2(C_2O_2)_3.9H_2O]}{(1\text{ gmole Pu})}\frac{[0.808\text{ Kg }Pu_2(C_2O_2)_3.9H_2O]}{[1\text{ gmole }Pu_2(C_2O_2)_3.9H_2O]}$$

$$= 16{,}900\text{ Kg }Pu_2(C_2O_4)_3{\cdot}9H_2O$$

Plutonium oxalate calcination to oxide:

$Pu_2(C_2O_4)_3{\cdot}9H_2O + 2O_2 \rightarrow 2PuO_2 + 6CO_2 + 9H_2O$

Oxygen consumed by calcination:

$$\frac{(10{,}000\text{ Kg-Pu})}{(0.239\text{ Kg-Pu/gmole-Pu})}\frac{(2\text{ gmole }O_2)}{(1\text{ gmole Pu})}\frac{(0.032\text{ Kg }O_2)}{(1\text{ gmole }O_2)} = 2678\text{ Kg-}O_2$$

Plutonium oxide product produced:

$$(10{,}000\text{ Kg-Pu})\frac{(0.271\text{ Kg }PuO_2)}{(0.239\text{ Kg Pu})} = 11{,}339\text{ Kg-}PuO_2$$

Carbon dioxide produced:

$$\frac{(10{,}000\text{ Kg-Pu})}{(0.239\text{ Kg-Pu/gmole-Pu})}\frac{(6\text{ gmole }CO_2)}{(2\text{ gmole Pu})}\frac{(0.044\text{ Kg }CO_2)}{(1\text{ gmole }CO_2)} = 5520\text{ Kg }CO_2$$

Water produced:

$$\frac{(10{,}000\text{ Kg-Pu})}{(0.239\text{ Kg-Pu/gmole-Pu})}\frac{(9\text{ gmole }H_2O)}{(2\text{ gmole Pu})}\frac{(0.018\text{ Kg }H_2O)}{(1\text{ gmole }H_2O)} = 3390\text{ Kg }H_2O$$

See Table 6 for a summary of the Precipitation/Calcination steps.

Component	Mass (Kg)	Input(i) or Output(o)	Unit Operation
Pu^{3+}	10,000	eluate(i)	elution
PuO_2	11,339	final product(o)	product
HNO_3	9127	eluate(i)	elution
	17,035	waste(o)	recycle
NO_3^-	8726	eluate(i)	elution
	944	waste(o)	recycle
HN_2OH^+	3469	eluate(i)	elution
	3469	waste(o)	disposal
H_2O	239,382	eluate(i)	elution
	235,992	waste(o)	recycle
	3390	waste(o)	recycle
$H_2C_2O_4$	3640	feed(i)	
O_2	2678	feed(i)	
CO_2	5520	waste(o)	disposal

Table 6. Precipitation/Calcination Summary

4.6 Recycle and Disposal

The recycle concepts will be defined only in general terms for this PreConceptual Design. Figure 8 shows the recycle and disposal concepts, along with the associated materials as calculated in the following text.

It is assumed that free nitrate can act as a reducing agent, and oxidized hydroxyl amine can act as an oxidizing agent, such that at the appropriate temperature they can react and form NO_x.

$$2NO_3^- + 2NH_2OH^+ \rightarrow NO_2 + NO + 3H_2O$$

$$\frac{\left(4125 \text{ Kg-}NH_2OH^+\right)}{\left(0.033 \text{ Kg/gmole}\right)} = 125{,}000 \text{ gmole-}NH_2OH^+$$

$$\frac{\left(7782 \text{ Kg-}NO_3^-\right)}{\left(0.062 \text{ Kg/gmole}\right)} = 125{,}516 \text{ gmole-}NO_3^-$$

It is assumed for these calculations that the amount of NH_2OH^+ and NO_3^- available are identical within round-off error. The nitric acid consumption is due to (1) preloading of the resin with nitrate anion and (2) reaction with oxidized hydroxyl amine, and consequent production of NO_x and water.

$$\frac{\left(1\ \text{meq/gmole-NO}_3^-\right)}{\left(4.1\ \text{meq/Kg-dry resin}\right)}\left(36\ \text{Kg- dry resin}\right) = 148\ \text{gmole-NO}_3^-$$

$$[(125{,}000+148)\text{gmole-NO}_3^-](0.063\ \text{Kg-HNO}_3\text{/gmole}) = 7750\ \text{Kg-HNO}_3\ \text{consumed}$$

$$(125{,}000\ \text{gmole})\frac{\left(1\ \text{gmole NO}_2\right)}{\left(2\ \text{gmole- NH}_2\text{OH}^+\right)}(0.046\ \text{Kg-NO}_2\text{/gmole}) = 2875\ \text{Kg-NO}_2\ \text{produced}$$

$$(125{,}000\ \text{gmole})\frac{\left(1\ \text{gmole NO}\right)}{\left(2\ \text{gmole- NH}_2\text{OH}^+\right)}(0.030\ \text{Kg-NO}_2\text{/gmole}) = 1875\ \text{Kg-NO produced}$$

$$(125{,}000\ \text{gmole})\frac{\left(3\ \text{gmole H}_2\text{O}\right)}{\left(2\ \text{gmole- NH}_2\text{OH}^+\right)}(0.018\ \text{Kg-H}_2\text{O/gmole}) = 3375\ \text{Kg-H}_2\text{O produced}$$

Based upon the difference in vapor pressures, the separation and recycle of nitric acid and water is straight-forward.

The TRU waste can be reduced to essentially salts as follows.

$$\frac{\left(100\ \text{Kg-Ga}^{3+}\right)}{\left(0.070\ \text{Kg/gmole}\right)}\frac{\left(3\ \text{gmole- NO}_3^-\right)}{\left(1\ \text{gmole-Ga}^{3+}\right)} = 4286\ \text{gmole-NO}_3^-$$

$$\frac{\left(100\ \text{Kg-Ga}^{3+}\right)}{\left(0.070\ \text{Kg/gmole}\right)}\frac{\left[1\ \text{gmole-Ga}\left(\text{NO}_3\right)_3\right]}{\left(1\ \text{gmole-Ga}^{3+}\right)}\frac{\left[0.256\ \text{Kg- Ga}\left(\text{NO}_3\right)_3\right]}{\left[1\ \text{gmole-Ga}\left(\text{NO}_3\right)_3\right]} = 366\ \text{Kg-Ga(NO}_3)_3$$

$$\frac{\left(2\ \text{Kg-Am}^{3+}\right)}{\left(0.243\ \text{Kg/gmole}\right)}\frac{\left(3\ \text{gmole- NO}_3^-\right)}{\left(1\ \text{gmole-Ga}^{3+}\right)} = 25\ \text{gmole-NO}_3^-$$

$$\frac{\left(2\ \text{Kg-Am}^{3+}\right)}{\left(0.243\ \text{Kg/gmole}\right)}\frac{\left[1\ \text{gmole-Am}\left(\text{NO}_3\right)_3\right]}{\left(1\ \text{gmole-Am}^{3+}\right)}\frac{\left[0.429\ \text{Kg- Am}\left(\text{NO}_3\right)_3\right]}{\left[1\ \text{gmole-Am}\left(\text{NO}_3\right)_3\right]} = 4\ \text{Kg-Am(NO}_3)_3$$

Since the nitrate resources for Ga^{3+} and Am^{3+} were not included in those of the Dissolution section due to their small requirements, the consumption is neglected in this section as well.

The water requirements and effluent are equal to the water present in the feed reagents, which includes HNO_3, HF, $Al(NO_3)_3.9H_2O$, and NH_2OH. Assuming the following concentrations for feed reagents:

HNO_3 @ 15 <u>M</u> = 30 wt% H_2O	3321 Kg
HF @ 52 wt% H_2O	73 Kg
$Al(NO_3)_3.9H_2O$ @ 43 wt% H_2O	180 Kg
NH_2OH @ 76 wt% H_2O	17,187 Kg
Total	22,181 Kg

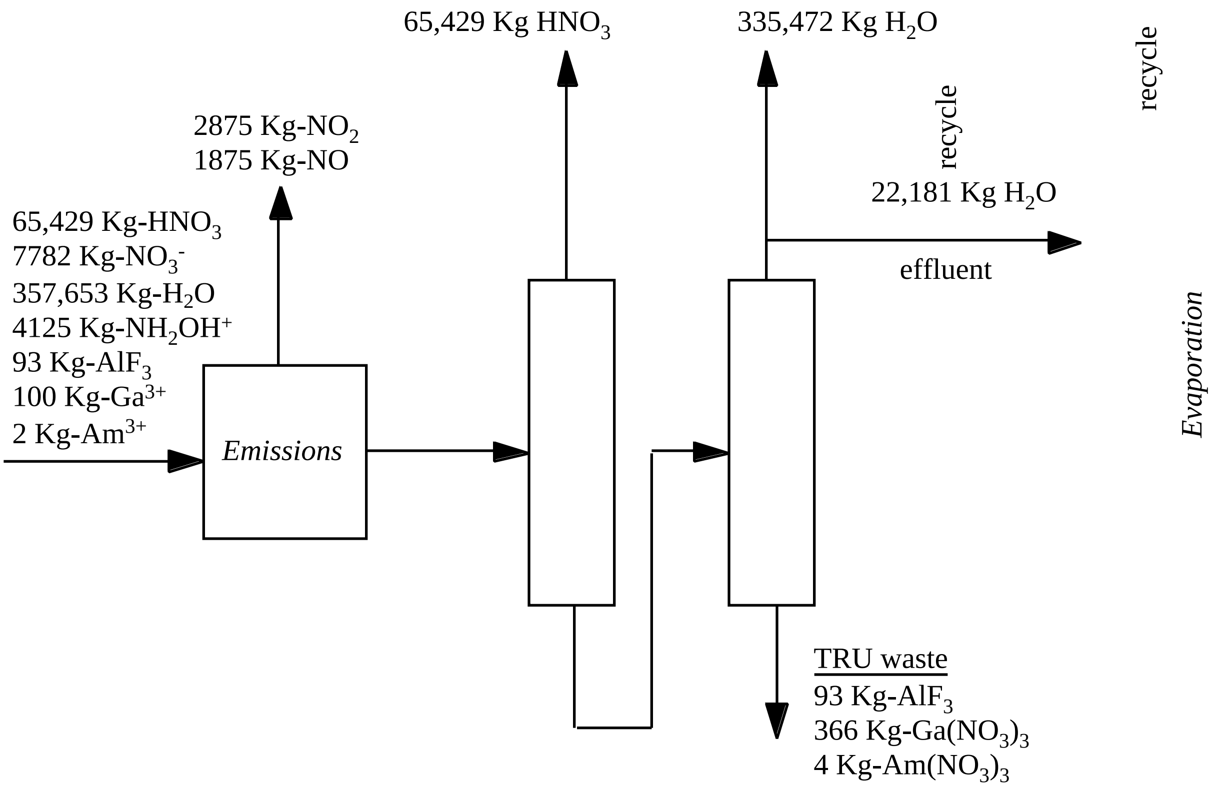

Figure 8. Recycle and Disposal Unit Operations

5.0 SUMMARY

Figure 9 shows the material balances which were developed based on the previous assumptions and calculations.

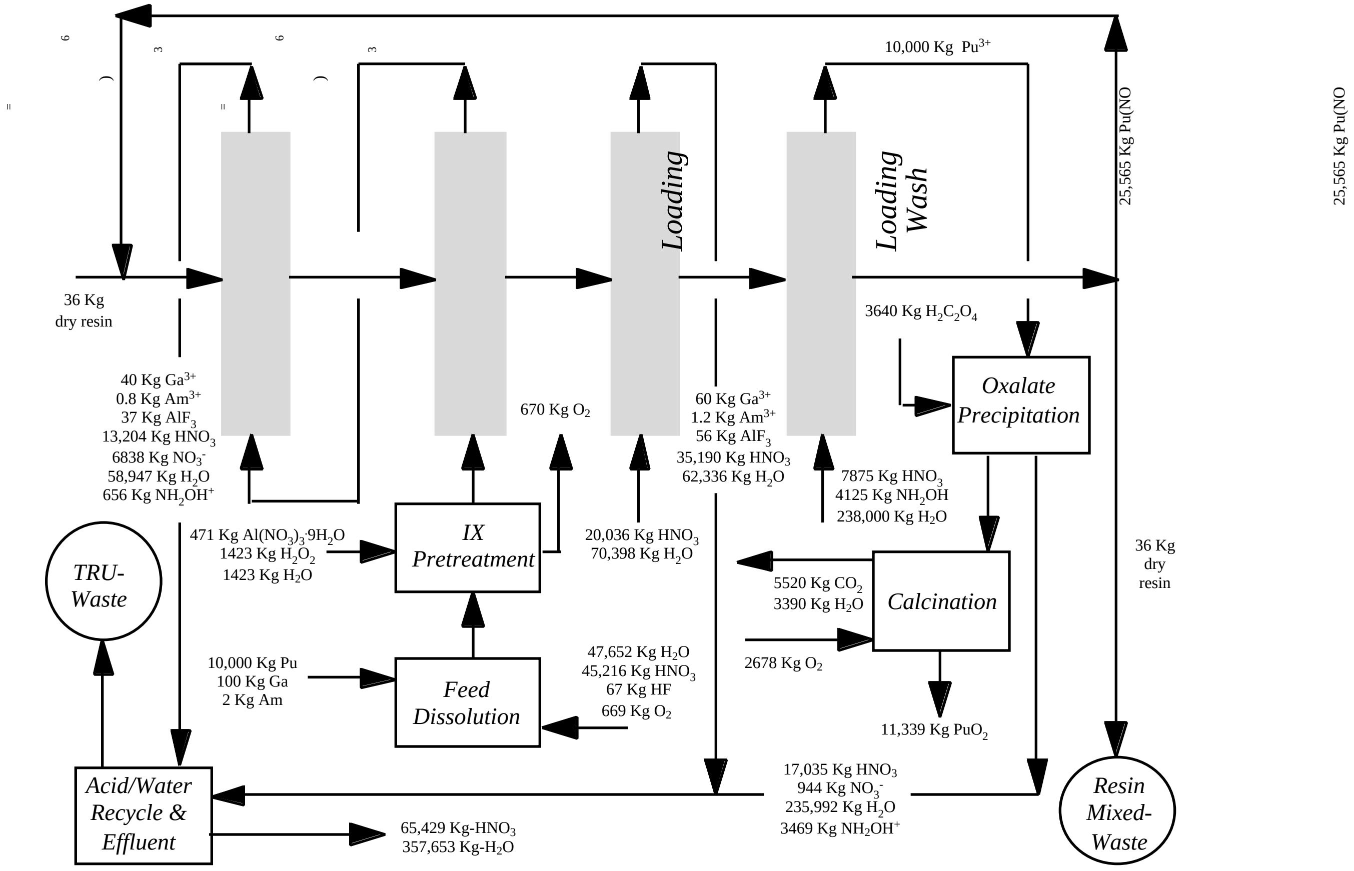

Figure 9. Overall Material Balances

Figure 10 is a reproduction of Figure 2 with a complete set of material balances added.

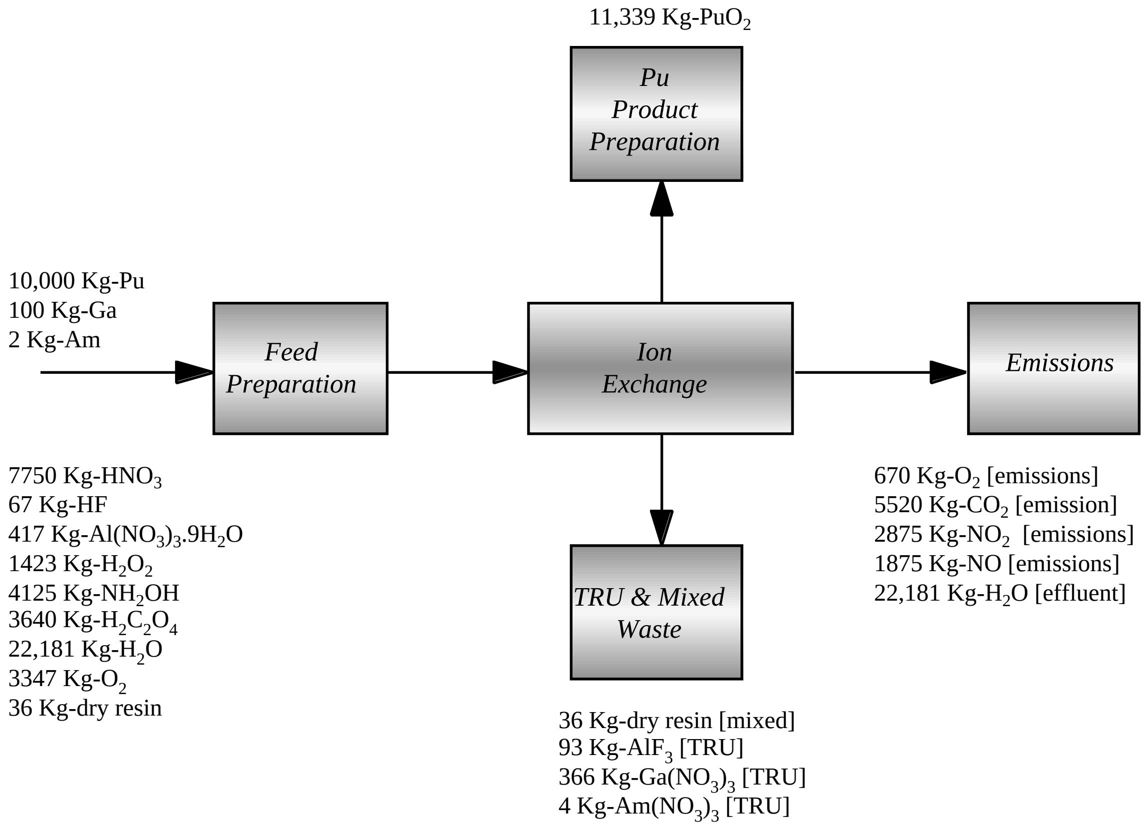

Figure 10. Feed, Product, and Waste Quantity Summary

This study was concerned with the amount of reagents used and waste generated, not the throughputs (rates) and consequent equipment size. Throughputs and equipment sizing will be left to future more detailed design efforts. However, at this point limited information is availbale based upon subcritical equipment configurations.

Based upon the results from the Loading Section of this report:

(33.34 L/column-loading)(65 g-Pu/L) = 2.167 Kg-Pu/column-loading

$$\frac{10{,}000 \text{ Kg-Pu}}{2.167 \text{ Kg-Pu/column -loading}} = 4614 \text{ column-loadings}$$

Based upon the author's discussions with those who have operated plutonium IX processes, the superficial liquid velocity through the column (2.75 cm/min) can be used to estimate the number of processing lines required.

$$\frac{(6\ \text{ft/column})(12\ \text{in/ft})(2.54\ \text{cm/in})}{(2.75\ \text{cm/min})} = 67\ \text{min/column}$$

Assuming operations for 5 days/week and 6 hrs/day (1 hr startup and 1 hr shutdown), and four column passes per column-loaded (i.e. 1-loading, 2-wash, & 1-elution/regeneration):

(4 column-passes/column-loading)(67 min/column-pass) = 268 min/column-loading

$$\frac{(6\ \text{hr/day})\left[5(52)\ \text{days/yr}\right]}{\dfrac{(268\ \text{min/column- loading})}{(60\ \text{min/yr})}} = 349\ \text{column-loadings/yr possible with one process line}$$

Therefore one line can process:

$$\frac{(349\ \text{column- loadings/yr})}{(4614\ \text{column -loadings/10 MT-Pu})} = 0.75\ \text{MT-Pu/yr for one process line}$$

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