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CONCEPTUAL DESIGN FOR SEPARATION OF PLUTONIUM AND GALLIUM BY SOLVENT EXTRACTION

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1.0 INTRODUCTION

A potential use for plutonium from decommissioned nuclear weapons is incorporation into commercial UO_2-based nuclear reactor fuel for power generation. This fuel, which would be a combination of plutonium oxide with uranium oxide, is referred to as a mixed oxide (MOX). In fabricating this fuel, it is important to maintain current commercial fuel purity specifications. While introducing impurities from the weapons plutonium may or may not have a detrimental affect on fuel performance, certifying the effect as insignificant could be more costly than purification.

Weapons plutonium can have a significant amount of gallium present which will force the MOX fuel out of purity specification limits, and could have a negative affect on fuel performance. Consequently, numerous methods of purifying the plutonium prior to MOX fabrication have been proposed. A solvent extraction process based on aqueous nitric acid and organic tri-butyl phosphate (TBP) has been suggested as a fully developed method for separating gallium from the plutonium. This document summarizes a Conceptual Design proposed for separating plutonium from gallium by nitric acid/TBP based solvent extraction. In addition, this process will also separate a significant amount of americium from the plutonium. This conceptual design is based on existing separations data and off-the-shelf equipment.

An important aspect of this Conceptual Design is the deliberate lack of a scrub section, which makes spent nuclear fuel reprocessing impractical with the existing equipment. In addition, the inclusion of a partitioning section will permit the recycle of MOX scrap, without the scrub section required for spent fuel reprocessing.

2.0 PROCESS FLOWSHEET

The principal unit operations required for separation of plutonium and gallium by most solvent extraction processes are shown in Figure 1. The Feed Preparation and Solvent Extraction operations are the most important for this study. The Pu-Product operation will involve classical oxalate precipitation of liquid Pu-nitrate followed by calcination. The Ga-Waste operation will involve volume reduction and immobilization for permanent disposal. It is expected a waste disposal facility will exist at the site chosen for the plutonium/gallium separation. Because a significant amount of americium from plutonium decay will be disposed of with the gallium, the gallium waste will likely become a transuranic (TRU) waste requiring disposal in the Waste Isolation Pilot Plant (WIPP), or disposal in an underground repository such as Yucca Mountain.

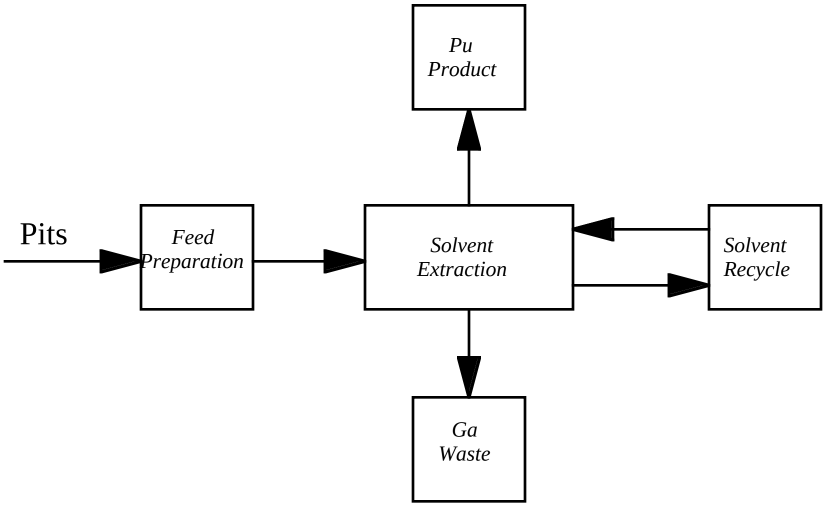

Figure 1. Solvent Extraction Block Diagram

The detailed process flowsheet which serves as the Conceptual Design for the plutonium and gallium separation is shown in Figure 2. If a partition step is added to Figure 2, between the extraction and strip banks, then MOX scrap recycle is possible. As noted in the Introduction Section, without a scrub step, nuclear fuel reprocessing with this design is not practical. Figure 2 will be used as the basis for determining material balances and cost estimates for follow-on activities to this work.

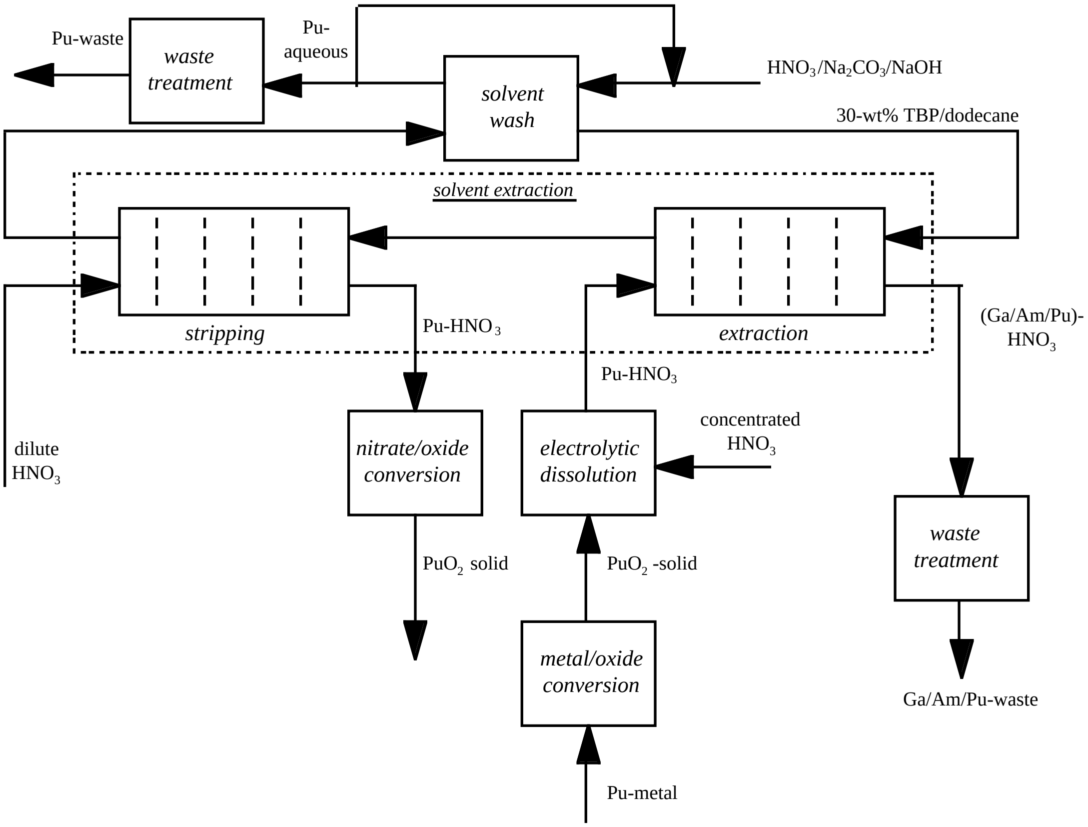

Figure 2. Solvent Extraction Process Flowsheet

3.0 PROCESS SPECIFICS

3.1 Oxidation of Metal

In keeping with a fully developed solvent extraction process such as Purex, dissolution of PuO_2 is favored over direct dissolution of Pu metal. Dissolution of Pu-metal requires the addition of very strong acids such as HF, which not only can affect extraction behavior but also can be corrosive to the equipment. The formation of Pu-oxide from Pu-metal has been practiced often in the past. One approach is to form a hydride powder from the bulk metal, and then essentially execute a controlled burn of the hydride. A process similar to this, and known as HYDOX (Reference 2), is being developed as part of the MOX program.

3.2 Dissolution of Oxide

In keeping with a Conceptual Design based upon existing data, it is desired to use nitric acid alone for dissolution of the plutonium feed. Plutonium metal in most any form is not readily dissolved in nitric acid alone. Plutonium oxide up to 25 wt % in solid solution with uranium oxide, as is the case in spent fuel, is readily dissolved in nitric acid alone. However, plutonium oxide as itself is not readily dissolved in nitric acid alone. Based upon these facts, electrolytic dissolution of plutonium oxide has been selected for preparation of the solvent extraction feed.

Electrolytic dissolution of actinide-oxides with essentially nitric acid alone, has been used by the French since 1990 on an industrial scale (Reference 3). Essentially nitric acid alone refers to the catalytic-type use of silver to facilitate the reduction of Pu^{VI+} to Pu^{IV+}. Figure 3 shows the mechanisms involved in electrolytic dissolution, and outlined in Equations 1-4 (Reference 4). It is worth noting that (1) the silver does not become part of the dissolved plutonium species and hence it's catalytic-type behavior and (2) while $Pu^{IV+}(NO_3)_4$ is more extractable than $(Pu^{VI+})O_2(NO_3)_2$, and will exist at a significant concentration following dissolution, the Pu^{VI+} species will be used as the basis for this study in order to be conservative.

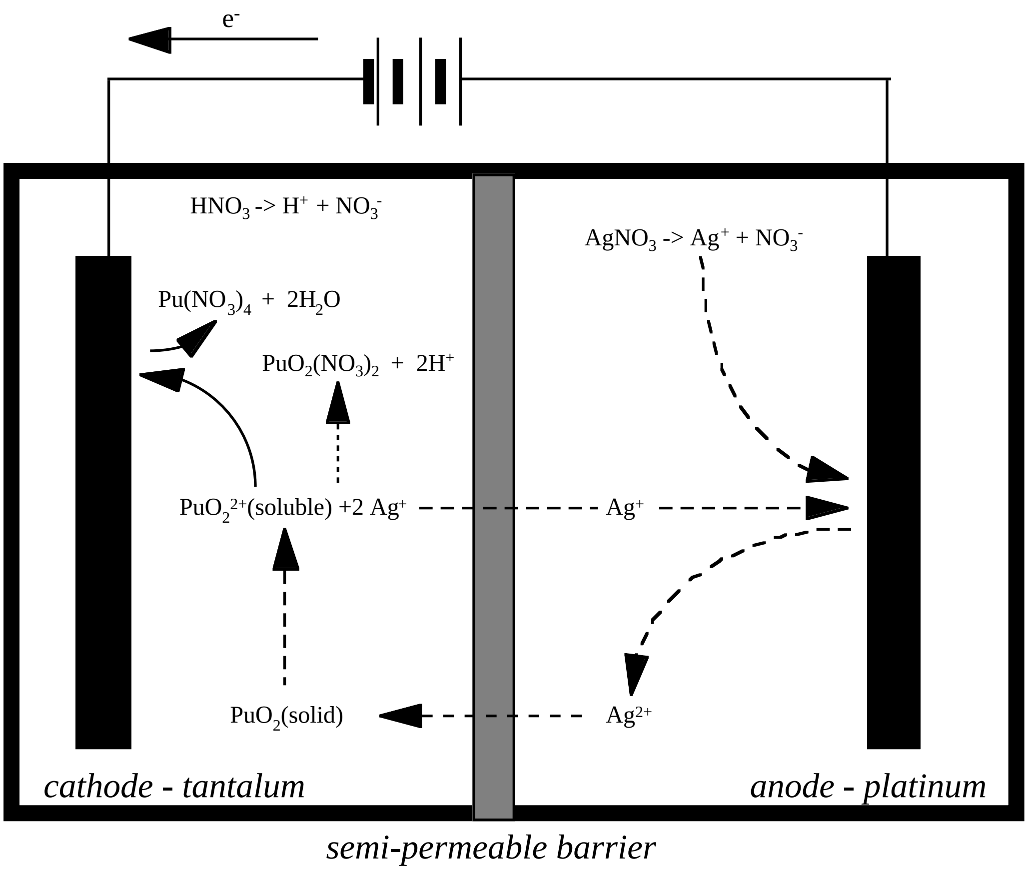

Figure 3. Electrolytic Dissolution of PuO_2

Addition of Ag^+ ion:

$$AgNO_3 \longrightarrow Ag^+ + NO_3^- \qquad \text{Equation 1}$$

Electrolytic oxidation of Ag^+:

$$Ag^+ \longrightarrow Ag^{2+} + e^- \qquad \text{Equation 2}$$

Oxidation of solid PuO_2 to soluble PuO_2^{2+} by reduction of Ag^{2+}:

$$PuO_{2,solid} + 2Ag^{2+} \longrightarrow PuO_2{}^{2+}{}_{soluble} + 2Ag^+ \qquad \text{Equation 3}$$

Pu^{VI+} nitrate complexation:

$$PuO_2^{2+} + 2HNO_3 \longrightarrow PuO_2(NO_3)_2 + 2H^+ \qquad \text{Equation 4}$$

Pu^{IV+} reduction to Pu^{IV+}, followed by nitrate complexation:

$$PuO_2^{2+} + 2e^- + 4H^+ + 4NO_3^- \longrightarrow Pu(NO_3)_4 + 2H_2O \qquad \text{Equation 5}$$

where $PuO_2^{2+} = [Pu^{VI+}(O^{2-})_2]^{2+}$

$Pu(NO_3)_4 = [Pu^{IV+}(NO_3^-)_4]$

The reduction of Pu^{VI+} to Pu^{IV+} can be further promoted by the addition of hydrogen peroxide (H_2O_2).

3.3 Solvent Extraction

There are three primary steps required in the preparation of a solvent extraction conceptual process design.

(1) Determine the extraction and stripping distribution coefficients for Pu and Ga.
(2) Determine the Pu recovery and Ga decontamination for a given process configuration.
(3) Select the extraction equipment.

3.3.1 *Distribution coefficients*

Equations 6 through 8 represent in a general sense the complexation reactions required to form the organic soluble plutonium or gallium complexant.

$$[Pu^{IV+}] + 4[NO_3^-] + 2[TBP] \longrightarrow [Pu(NO_3)_4 \cdot 2TBP] \qquad \text{Equation 6}$$

$$[(Pu^{VI+})O_2] + 2[NO_3^-] + 2[TBP] \longrightarrow [PuO_2(NO_3)_2 \cdot 2TBP] \qquad \text{Equation 7}$$

$$[Ga^{3+}] + 3[NO_3^-] + 2[TBP] \longrightarrow [Ga(NO_3)_3 \cdot 2TBP] \qquad \text{Equation 8}$$

Equation 9 is the equilibrium expression derived from Equation 8, which expresses the dependency of gallium complex formation on TBP concentration. Equation 9 will be used later in this text to estimate the gallium distribution coefficient for conditions of this study.

$$K = [Ga(NO_3)_3 \cdot 2TBP]/\{[Ga^{3+}][NO_3^-]^3[TBP]^2\} \qquad \text{Equation 9}$$

3.3.2 *Pu recovery and Ga decontamination*

If both aqueous and organic feed conditions are known as shown in Figure 4, an exact solution for the number of stages, versus plutonium extraction and gallium decontamination, is possible given constant distribution coefficients. Based on these assumptions, Equation 10 defines the recovery of plutonium and Equation 11 defines the decontamination of gallium (Reference 1- Chapter 4, Section 6.2).

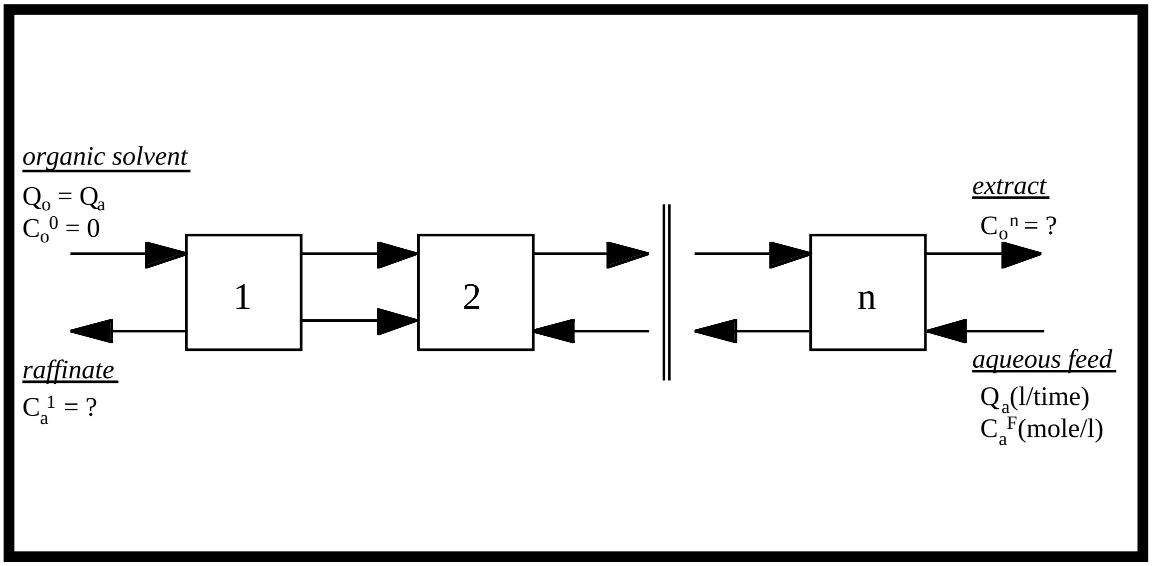

Figure 4. Counter-current Multi-stage Solvent Extraction

$$\rho = \beta[(\beta^{n}-1)/(\beta^{n+1}-1)] + \beta^{n+1}[(\beta-1)/(\beta^{n+1}-1)][C_o^0/(DC_a^F)] \qquad \text{Equation 10}$$

where $\beta = D(Q_o/Q_a)$

$$f_{Pu/Ga} = (\beta_{Pu}/\beta_{Ga})[(\beta_{Pu}^{n}-1)/(\beta_{Ga}^{n}-1)][(\beta_{Pu}^{n+1}-1)/(\beta_{Ga}^{n+1}-1)] \qquad \text{Equation 11}$$

Distribution coefficients for this study are based on the work of Reference 5 and Reference 6 (Tables 13.49 & 13.51). Reference 5 was used as the basis gallium extraction (or decontamination). Reference 6 was used as the basis for the plutonium extraction and strip. Figure 5 shows the distribution coefficient data of Reference 5.

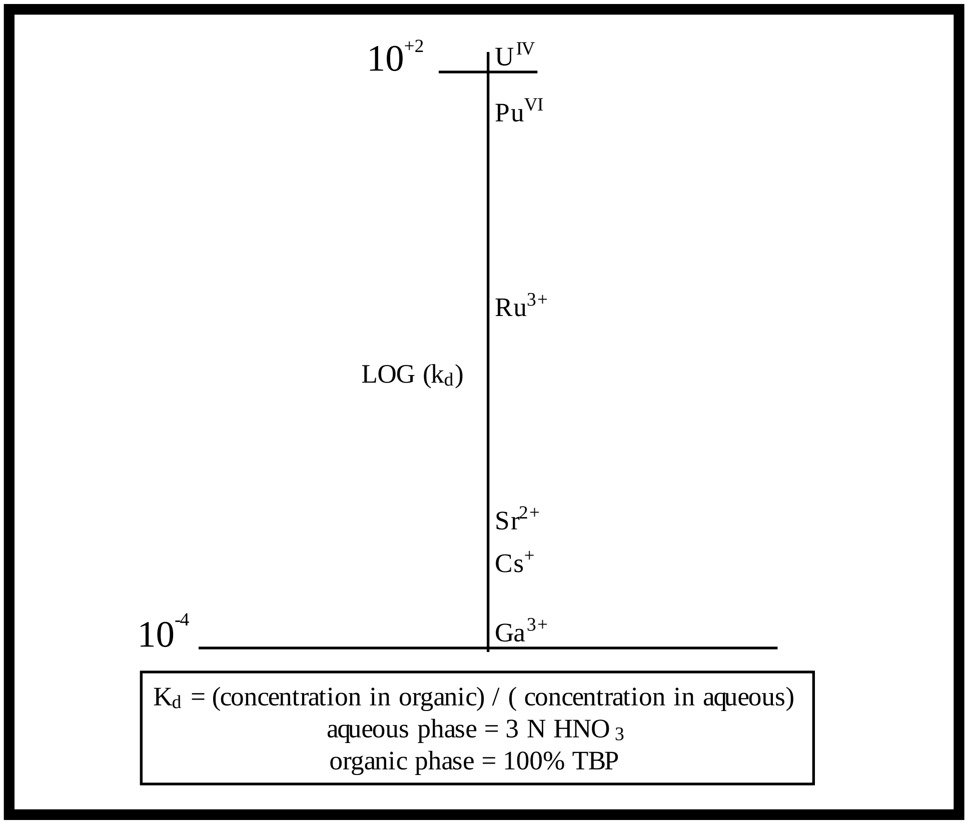

Figure 5. Distribution Coefficients for Nitric Acid/TBP from Reference 5

Common fission products along with plutonium and gallium, are shown in Figure 5 to qualitatively indicate the ease of separating gallium from plutonium. It is species such as ruthenium which dictate the need for a scrub section during processing with nitric acid and tri-butyl phosphate. Scrubbing is used to further separate fission products which partially extract with the uranium and plutonium during nuclear fuel reprocessing. For the conditions of this study, a scrub section is not required due to the large difference between the plutonium and gallium distribution coefficients. Hence, the proposed Conceptual Design for this study is not capable of reprocessing spent nuclear fuels.

In order to solve Equations 10 and 11 for the extraction section of Figure 2, feed conditions have been defined as those shown in Figure 6.

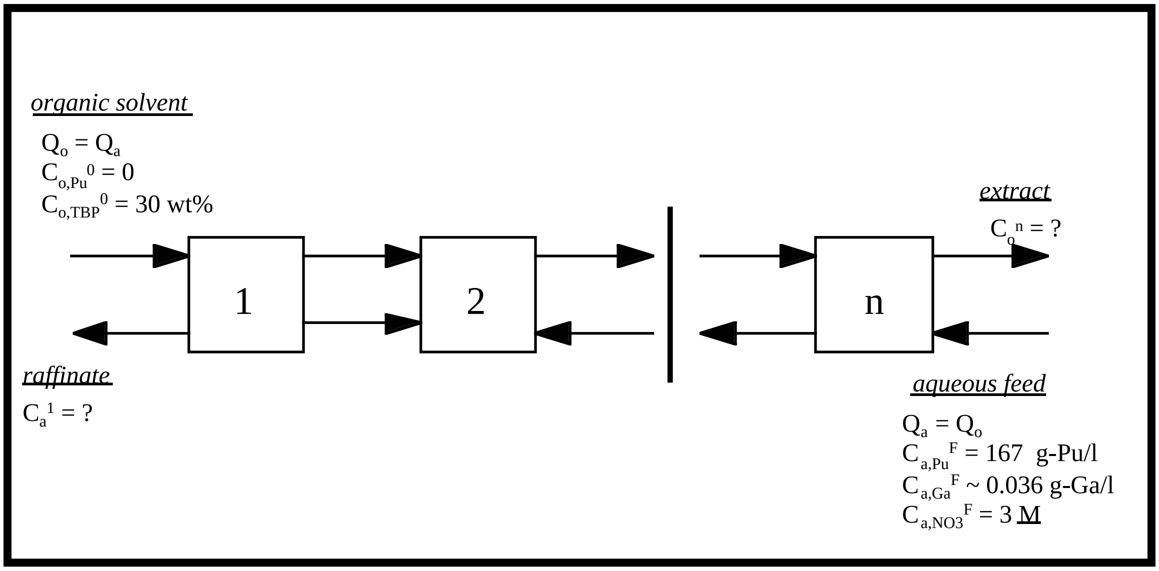

Figure 6. Extraction Conditions

Equal aqueous and organic flowrates often produce optimum hydraulics in the contacting equipment, and consequently provide a good starting point for a conceptual design. Hydraulics affect the interfacial area and consequent mass transfer required for equilibrium stages. It is assumed all equipment is designed for subcritical conditions independent of plutonium concentration. The plutonium concentration exiting the electrolytic dissolover is approximately 167 g-Pu/L (Reference 3). Classical nitric acid and TBP feed concentrations for this process are 3 M HNO_3 and 30-volume(v/o) % TBP. The maximum gallium concentration in the feed is defined as 1 wt %.

The gallium distribution coefficient for 30 v/o % TBP, based on the values of 100% TBP shown in Figure 5, was determined by rearranging Equation 9 to yield Equation 12.

$$C_{Ga(NO3)3.2TBP} = K_{Ga}(C_{Ga3+})(C_{NO3-})^3(C_{TBP})^2 \qquad \text{Equation 12}$$

rearranging yields:

$$D(30\text{ wt.\% TBP}) = (0.30)^2 D_{100\%\text{-TBP}}$$

$$D_{Ga}(3\underline{M}\text{ HNO}_3\text{, 30 \% TBP}) = (0.30)^2(10^{-4}) \sim 10^{-5}$$

where normality (N) and molarity ($\underline{M}$) are equal fro nitric acid.

As reported in Reference 6;

$$D_{Pu(IV+)}(3\underline{M}\text{ HNO}_3\text{, 30 \% TBP}) = 16$$
$$D_{Pu(VI+)}(3\underline{M}\text{ HNO}_3\text{, 30 \% TBP}) \sim 3.5$$

$$D_{Pu(IV+)}(0.1\underline{M}\text{ HNO}_3\text{, 30 \% TBP}) = 0.023$$
$$D_{Pu(VI+)}(0.1\underline{M}\text{ HNO}_3\text{, 30 \% TBP}) \sim 0.05$$

Figure 7 shows the results of estimating Pu extraction and Ga decontamination for 3 $\underline{M}$ HNO_3 and 30 v/o% TBP, based on Equations 10 and 11. The y-axis of Figure 7 represents the logarithm of g-Pu in gallium waste per MT-Pu feed, and ppm-Ga in the Pu product. The gallium waste exits the extraction section, and the plutonium product exists the strip section (see Figure 2). Pu^{VI+} rather than Pu^{IV+} has been used as the basis for extraction and strip behavior in order to be conservative.

Example extraction section calculations follow:

$$\rho = \beta[(\beta^n-1)/(\beta^{n+1}-1)] + \beta^{n+1}[(\beta-1)/(\beta^{n+1}-1)][C_o^0/(DC_a^F)]$$

The Pu recovery for 10-extraction stages is:

$$\rho_{Pu} = 3.5\{[(3.5)^{10}-1]/[(3.5)^{11}-1]\} \sim 0.9999974$$

where $\beta_{Pu} = D(Q_o/Q_a) = 3.5(1) = 3.5$

$C_{o,Pu}{}^0 = 0$

the Pu loss per MT-Pu feed is;

$$(1-0.9999974)(1\text{-MT})(1000\text{ Kg/MT})(1000\text{ g/Kg}) \sim 3\text{ g-Pu}$$

The Ga passed to the Pu loaded solvent product for 1-extraction stage is:

$$\rho_{Ga} = 10^{-5}\{(10^{-5}-1)/[(10^{-5})^2-1]\} \sim 0.00001$$

where $\beta_{Ga} = D(Q_o/Q_a) = 10^{-5}(1) = 10^{-5}$

the Ga in Pu product per MT of Pu feed at 1-wt % Ga feed is;

$$(10^{-5})[0.01(1\text{-MT})(1000\ \text{Kg/MT})(1000\ \text{g/Kg})] = 0.1\ \text{g-Ga}.$$

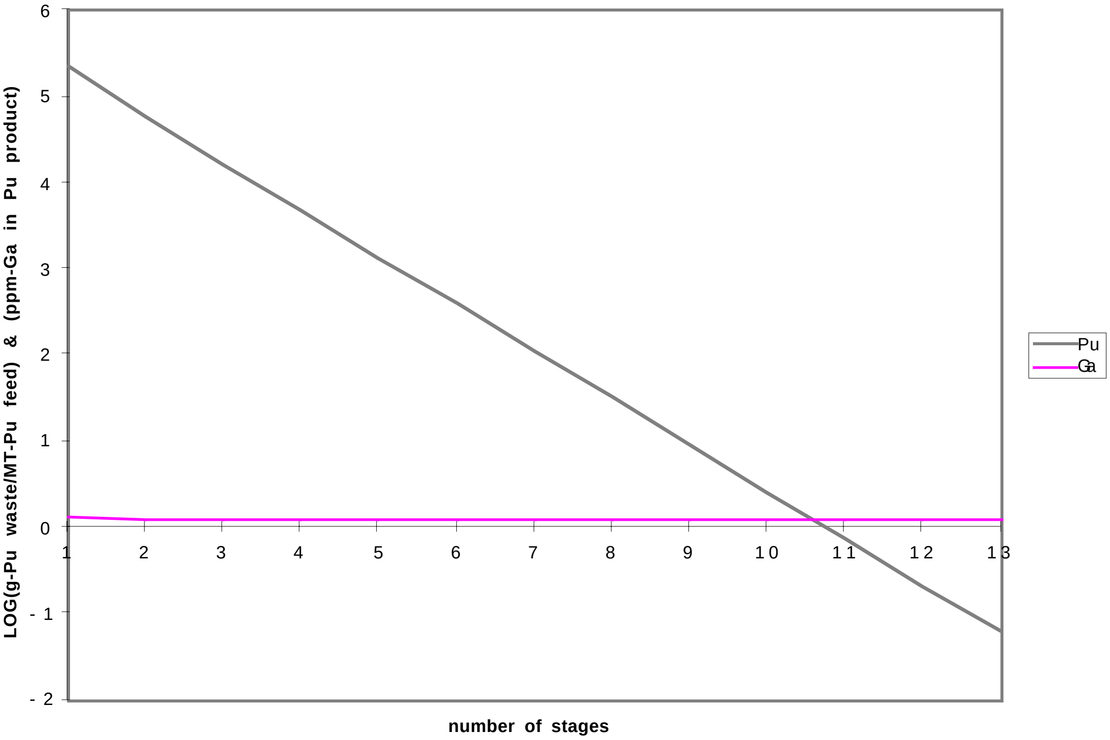

Figure 7. Stages Required for Extraction of Pu and Decontamination of Ga

In order to solve Equations 10 and 11 for the stripping section of Figure 2, feed conditions have been defined as those shown in Figure 8. As in the Extraction section, equal aqueous and organic flowrates often produce optimum hydraulics in the contactors. Assuming nearly complete Pu recovery in the extraction section, and equal flowrate and phase ratios in the extraction and strip sections, the plutonium concentration in the solvent feed to the strip section is identical to the aqueous feed to the extraction section, i.e. 167 g-Pu/L. The aqueous nitric acid feed for the stripping section is 0.1 M. While the Pu distribution coefficient decreases with decreasing nitric acid concentration, which is desirable for stripping, some nitric acid is required in the strip section for adequate phase separation during settling. It is assumed any Ga which extracts with the Pu in the extraction section, will strip with the Pu in the strip section and exit with the aqueous Pu product.

Distribution coefficients for stripping are the inverse of that for extraction. Therefore, the Pu^{VI+} distribution coefficient for stripping in 0.1 $\underline{M}$ nitric acid and 30 vol % TBP is:

$$D(Pu^{VI+}) = 1/0.05 = 20$$

Based upon the strip section feed conditions shown in Figure 8, the Pu distribution coefficient for stripping, and Equation 10 of this text, Figure 9 has been generated according to the example calculations which follow.

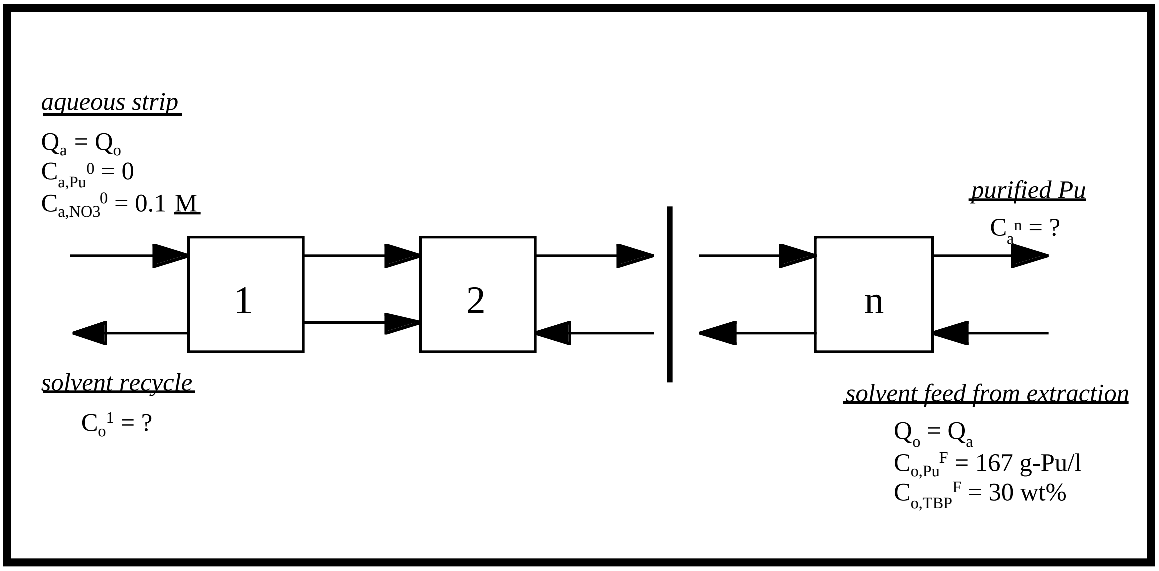

Figure 8. Stripping Conditions

Example Strip section calculations follow:

$$\rho = \beta[(\beta^n-1)/(\beta^{n+1} -1)] + \beta^{n+1}[(\beta-1)/(\beta^{n+1} -1)][C_o^0/(DC_a^F)]$$

The Pu recovery for 4 strip stages is:

$$\rho_{Pu} = 20(20^4-1)/(20^5-1) \sim 0.9999941$$

based upon reverse extraction

$$\beta_{Pu} = D(Q_o/Q_a) = (1)(20) = 20$$

$$C_{o,Pu}^0 = 0$$

the Pu loss per MT-Pu feed is;

$$(1-0.9999941)(1\text{-MT})(1000\ Kg/MT)(1000\ g/Kg) \sim 6\ g\text{-Pu}$$

The y-axis of Figure 9 represents the logarithm of g-Pu waste in recycled solvent per MT Pu feed. It is assumed the plutonium remaining in the solvent will be aqueous-based waste following the solvent wash.

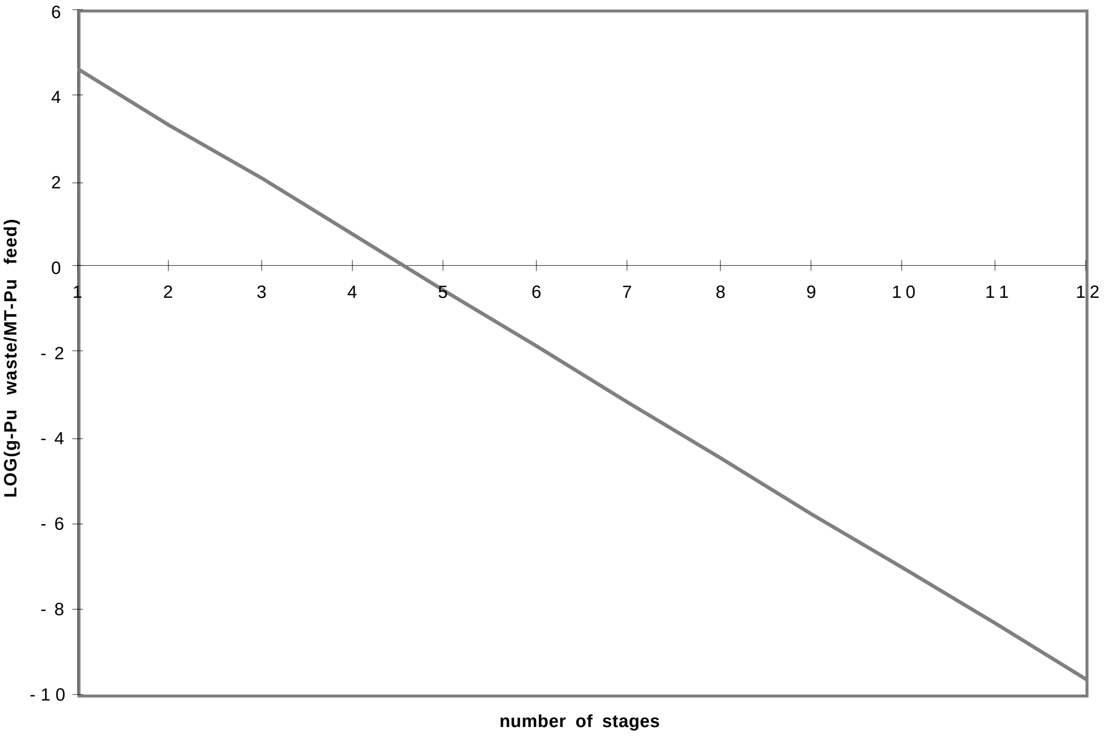

Figure 9. Stages Required for Strip of Pu from Solvent

3.3.3 *Solvent extraction equipment*

Centrifugal contactors have been selected as the contacting equipment for the solvent extraction. This is due to their (1) small compact size, (2) criticality conscious design, (3) demonstrated high reliability, and (4) rapid achievement of steady-state operation. The centrifugal contactor size most appropriate for the process flows of this study is the 5.5-cm-diameter shown in Figure 10. The 5.5-cm-diameter centrifugal contactor design is highly evolved with respect to (1) fabrication, (2) hydraulic performance, and (3) mass-transfer performance (Reference 7). The 5.5-cm-diameter centrifugal contactors shown in Figure 10 are in a cascade configuration of 8-strip stages, 2-scrub stages, and 4-extract stages from left-to-right. The back row of stages in Figure 10 are difficult to see as they are diagonally off-set; however, their electrical connections are visible. The 5.5-cm-diameter maximum throughput is 0.1-MT of heavy metal per day or 3-L/min total, whichever is limiting. The 5.5-cm-diameter centrifugal contactor geometry guarantees subcritical operation independent of plutonium inventory (or concentration).

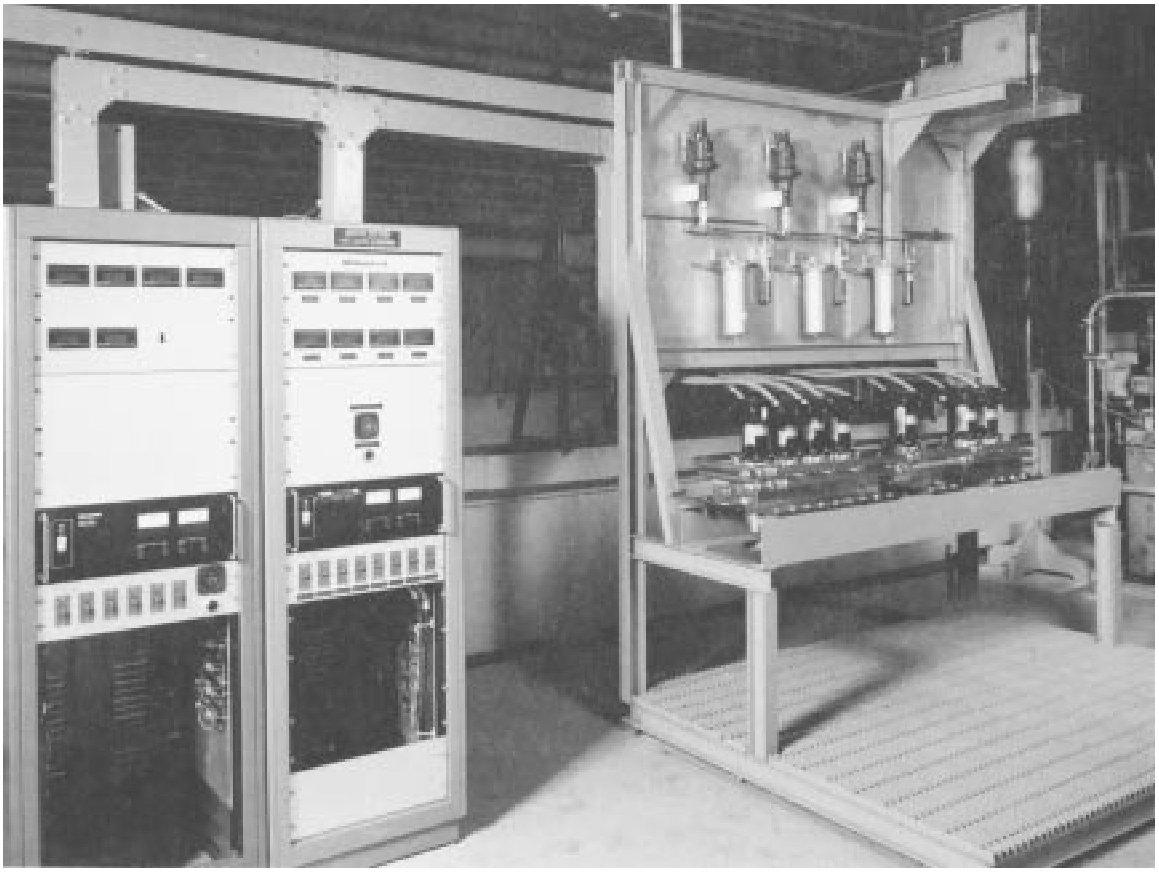

Figure 10. 5.5-cm-Diameter Centrifugal Contactors

3.4 Solvent Wash

There are two primary purposes for the inclusion of a solvent wash operation. The first is minimization of plutonium which returns with the recycled solvent to the extraction section. The second is removal of hydrolyzed TBP. The affect of plutonium in the recycled solvent is increased plutonium losses in the gallium waste from the extraction section. The affect of TBP hydrolysis is the formation and accumulation of dibutyl and monobutyl phosphoric acid in the solvent. These acidic species in the solvent can form plutonium complexes which will not strip from the solvent; and hence, accumulate in the solvent upon recycle.

A reasonable solvent wash design is based upon a caustic aqueous wash to remove dibutyl and monbutyl phosphoric acid, followed by very dilute nitric acid wash to further strip the Pu and rebalance the solvent pH. The caustic wash can consist of Na_2CO_3 and/or NaOH. Centrifugal contactors are an excellent choice for solvent wash equipment

3.5 Plutonium Product

Plutonium nitrate conversion to PuO_2 can be achieved by several means (Reference 1 - Chapter 9, Section 4.7). The most simple, which requires a very pure stream of plutonium nitrate, is direct thermal decomposition more commonly known as calcination. Another conversion process for less pure plutonium is precipitation as either a peroxide or oxalate, followed by calcination. While the direct thermal decomposition (calcination) is more simple, the precipitation followed by calcination has been used more frequently on an industrial scale.

3.6 Gallium Waste

The gallium waste stream will consist primarily of gallium nitrate and americium nitrate, with a very small amount of plutonium nitrate. Other elements may present in the original Pit material at concentrations assumed to be less than gallium; and consequently, may also be present in the waste stream. For this conceptual design it is assumed the waste activity is due primarily to americium which is the decay product of plutonium, and a Hazardous waste is not created.

Since americium predominantly exists as a plus-three cation in 3 M nitric acid, it is assumed to be inextractable as gallium. Therefore, as a first approximation for this Conceptual Design, the waste activity will be based on all of the americium present in the original Pit material, which is approximately 200 ppm maximum. The plutonium activity will be neglected at this time since the amount will depend on the cascade configuration, which can be selected later based on overall cost considerations.

Example activity calculations:

$$\begin{aligned}\lambda_{\text{Pu-239}} &= \ln(2)/t_{1/2} \\ &= \ln(2)/[24{,}400 \text{ yr}(365\text{day/yr})(24\text{hr/day})(3600\text{s/hr})] \\ &= 9.01\times10^{-13} \text{ (disintegrations/atom)/s or (dps)}\end{aligned}$$

λ = activity
$t_{1/2}$ = half-life

$$\begin{aligned}N_{Pu} &= (6.023\times10^{23} \text{ atom/mole})/(239\text{g/mole}) \\ &= 2.52\times10^{21} \text{ atom/g}\end{aligned}$$

$$\begin{aligned}(\lambda_{Pu}\, N_{pu}) &= (9.01\times10^{-13} \text{ dps})(2.52\times10^{21} \text{ atom/g}) \\ &= 2.27\times10^{9} \text{ dps/g}\end{aligned}$$

$$\begin{aligned}\text{10 nano-Ci Pu} &= [10 \text{ nano-Ci}(37 \text{ dps/nano-Ci})]/(2.27\times10^{9} \text{ dps/g}) \\ &= 1.63\times10^{-7} \text{ g-Pu}\end{aligned}$$

λ_{Am-241} = ln(2)/$t_{1/2}$
= ln(2)/[458 yr(365day/yr)(24hr/day)(3600s/hr)]
= 4.8×10^{-11} (disintegrations/atom)/s or (dps)

N_{Am} = (6.023×10^{23} atom/mole)/(241g/mole)
= 2.50×10^{21} atom/g

(λ_{Am} N_{Am}) = (4.8×10^{-11} dps)(2.5×10^{21} atom/g)
= 1.2×10^{11} dps/g

Since the mole weights of Pu-239 and Am-241 are approximately equal:

(Am-activity/Pu-activity) ~ (1.2×10^{11} dps/2.27×10^{9} dps) = 53

With regard to calculating final waste volumes, it has been assumed the americium concentration is 200 ppm in the feed, or 200 g-Am/MT-Pu feed.

100 nano-Ci Am= [100 nano-Ci(37 dps/nano-Ci)]/(1.2×10^{11} dps/g)
= 3.08×10^{-8} g-Am

200 g-Am(10 nano-Ci Am/3.08×10^{-9} g-Am) = 6.4×10^{11} nano-Ci Am

Since Class-C LLW can not exceed 100 nano-Ci/gram-waste for TRUs, if less than 6400 MT of total waste is generated, the waste may be classified as TRU waste based on Am alone.

(6.4×10^{11} nano-Ci Am)/(100 nano-Ci/gram-waste) = 6.4×10^{9} g-waste (6400 MT)

The activity for plutonium is provided in the previous text for similar waste calculations once the cascade configuration, and consequent plutonium losses, are determined.

4.0 References

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