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Okan H. Zabunoglu

*Iowa State University*

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**Reprocessing of long-cooled nuclear fuel: Process description  
and plant design**

**Zabunoglu, Okan H., Ph.D.**

**Iowa State University, 1988**

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**Reprocessing of long-cooled nuclear fuel:**

**Process description and plant design**

**by**

**Okan H. Zabunoglu**

**A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of the  
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**Major: Nuclear Engineering**

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Signature was redacted for privacy.

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## 1. INTRODUCTION

This study, concerned with reprocessing of long-cooled LWR (Light Water Reactor) fuels, is a part of a larger study the purpose of which is to investigate the whole back-end of the NFC (Nuclear Fuel Cycle). A generalized and simplified flow chart of the back-end of the NFC with reprocessing of short-cooled fuel is shown in Figure 1.

The minimum required spent LWR fuel cooling time before reprocessing is around 150 days and almost all reprocessing plants in the world have been designed to handle 150-day cooled fuels. Until at least the year 2020, however, the cooling period for LWR fuels in the U.S.A. will probably be 10 years or longer because commercial application of reprocessing in the U.S.A. was suspended by government decisions in 1976 and the SF (Spent Fuel) discharged from reactors has been accumulated in reactor pools. Table 1 exhibits the rate of SF production and accumulation in the U.S.A. since 1960 and also includes future projections.

Reprocessing of SF serves the purpose of recovering the unburned U (Uranium) and produced and unburned Pu (Plutonium) in SF. Reprocessing plants have always been designed to obtain a highly pure Pu product together with a U product which is decontaminated enough to allow direct-contact handling subsequently. However, if the Pu product of the reprocessing is going to be burned in nuclear reactors, there appears to be no need for producing highly pure Pu in reprocessing,

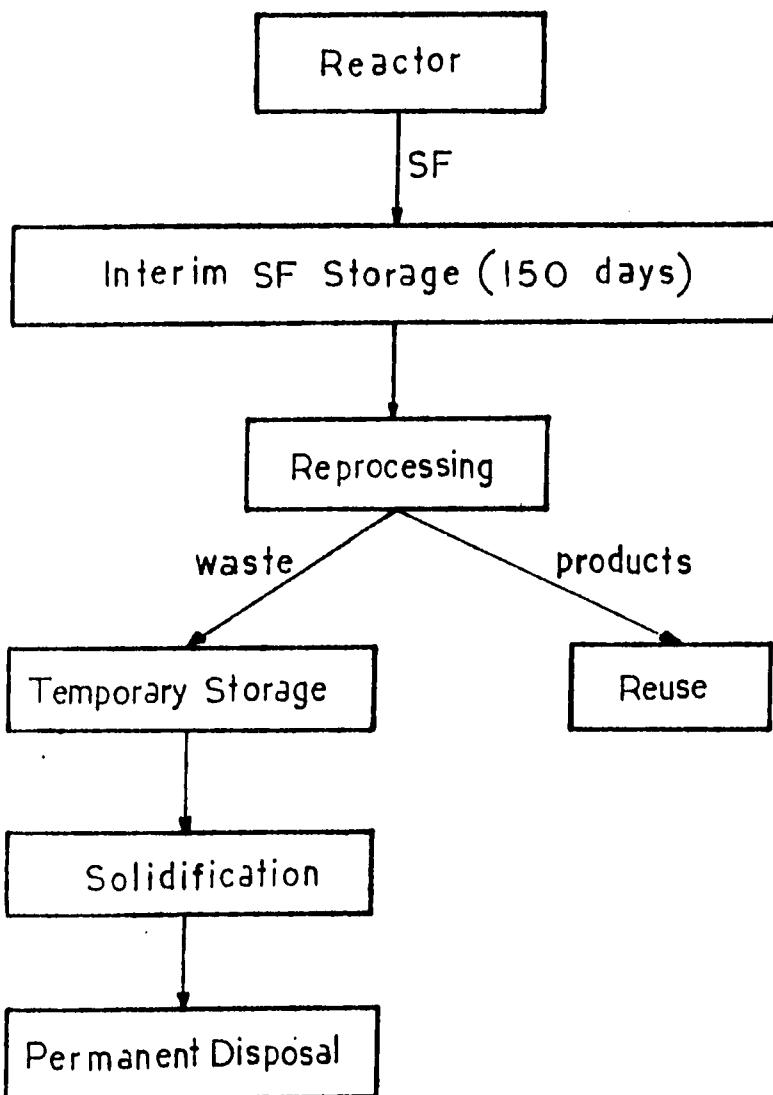


FIGURE 1. A Generalized and Simplified Flow Chart of the Back-End of the NFC with Reprocessing of Short-Cooled Fuel

TABLE 1. SF Production and Accumulation in the U.S.A.<sup>a</sup>

Year	Installed Capacity (MWe)	SF Production(MT) Annual	Cumulative
1970	6107	140	—
1974	29550	692	150
1975	36742	951	1101
1980	52516	1255	7081
1987	87100	1787	17573
2000	90000	1896	42184

<sup>a</sup> Source: Reference [1].

which, during MOX (Mixed Oxide) fuel fabrication, would have to be mixed with U anyway.

This consideration leads to a concept referred to as "coprocessing", in which complete separation of U and Pu is not practiced but the aim is to produce a U+Pu mixed product and a U product.

This study investigates the simplifications over the standard Purex reprocessing method resulting from (1) the long-cooling periods (10 years or so), and (2) the adoption of the coprocessing concept, and proposes a simplified and more economic design for Purex reprocessing.

Besides reprocessing, another major step in the back-end of the NFC is waste disposal. Whether reprocessing is applied or not, waste disposal is a big problem awaiting solution and will be briefly discussed below. Application of reprocessing changes the form of waste to be disposed of from SF to HLFPW (High Level Fission Product Waste). In the U.S.A., according to the NWPA (Nuclear Waste Policy Act) of 1982, the Department of Energy takes responsibility for managing the SF now accumulating at reactor sites by 1998. The DOE's plan is as follows. The SF delivered by the utilities in 1998 and thereafter will be stored for 5 years (first batch from 1998 to 2003) and prepared for final disposal in an MRS (Monitored Retrievable Storage) facility, and then transferred to a repository to be buried [2]. Although, in this plan, the assumed form of waste for disposal is SF, Section 222 of the NWPA of 1982 requires the investigation and development of alternative means for waste disposal, one of which is obviously disposal of HLFPW generated in reprocessing [2].

A study concerned with the disposal of SF and HLFPW was made at ISU (Iowa State University) in parallel with this study [3]. The waste disposal study assumed a total capacity of 72,000 MTHM (Metric Ton Heavy Metal) and an operational time of 30 years for the first repository. During the first 5 years, waste will be received at the repository at a rate of 1310 MTHM per year, during the next 25 years waste receiving rate will be 2620 MTHM per year. The first repository will start operation in 2003 and receive at least 15-year old waste.

In the case of reprocessing short-cooled (150-day) SF, the HLFPW generated needs to be stored in liquid form for around 5 years before solidification because of its high heat liberation rate [4]. When the long-cooled SF is reprocessed, which is the subject of this study, the HLFPW can be solidified right after being generated. This allows the design of the waste solidification process as an integral part of the reprocessing plant and results in a different flow chart from that in Figure 1 for the back-end of the NFC. Figure 2 exhibits a generalized and simplified flow chart of the back-end of the NFC with reprocessing of long-cooled fuel. In such a case, if scheduled receipt of the SF and shipment of the wastes and products are assumed to be implementable, a reprocessing plant can be designed with almost no storage capacity for SF, liquid and solidified HLFPW, U and Pu products, and solid ILW (Intermediate Level Waste).

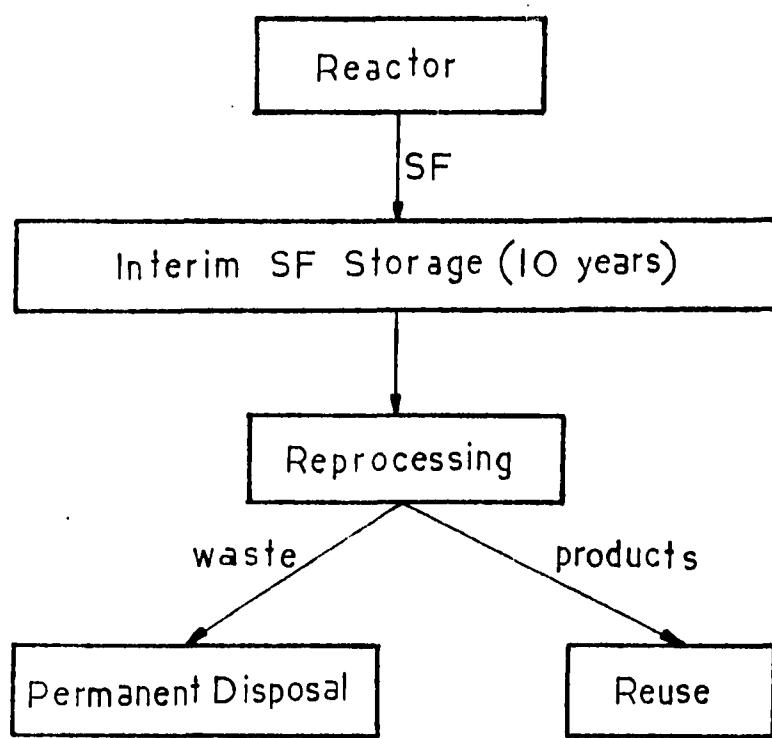


FIGURE 2. A Generalized and Simplified Flow Chart of the Back-End of the NFC with Reprocessing of Long-Cooled Fuel

## 2. IMPORTANT FACTORS AFFECTING REPROCESSING

### 2.1. Composition and Activity of SF

Composition and activity of SF mainly depend on the lengths of irradiation and cooling periods, composition of fresh fuel, and the neutron spectrum to which the fuel is exposed. Tables 2 and 3, condensed from the data given in Reference [5], exhibit the composition and activity constituents of typical UO<sub>2</sub> SF at the end of 150-day and 10-year cooling periods.

The most important points to be noticed in the data given in Tables 1 and 2 are:

- The decrease in overall FP (Fission Product) activity in a 10-year cooling time; the FP activity of 10-year cooled fuel is nearly 13 times less than that of 150-day cooled fuel.
- The change in the roles of contributors to overall FP activity; while Zr (Zirconium), Nb (Niobium), and Ru (Ruthenium) are the most important contributors to overall FP activity in 150-day cooled fuel, Cs (Cesium), Sr (Strontium), Ba (Barium), and Y (Yttrium) become the greatest constituents of FP activity after 10 years of cooling.
- The  $\beta$  activity of U-237, which dominates the  $\beta$  activity of the U product of reprocessing, and its decline with time.
- The  $\beta$  activity of Pu-241, which dominates the  $\beta$  activity of the Pu product of reprocessing.

TABLE 2. Actinides in Spent LWR Fuel<sup>a</sup>

Isotope	Half-life	Amount(kg/y)	Activity(Ci/y) <sup>b</sup>
U-234	2.47E5 Y	3.14	19.4 (a)
U-235	7.10E8 Y	2.15E2	0.461 (a)
U-236	2.39E7 Y	1.14	7.22 (a)
U-237	6.75 d	9.15E-7	74.7 (β)
U-238	4.51E9 Y	2.57E4	8.56 (a)
U Total		2.60E4	35.6 (a) 74.7 (β)
Pu-236	2.85 Y	2.51E-4	1.34E2 (a)
Pu-238	8.60E1 Y	5.99	1.01E5 (a)
Pu-239	2.44E4 Y	1.44E2	8.82E3 (a)
Pu-240	6.58E3 Y	5.91E1	1.30E4 (a)
Pu-241	1.32E1 Y	2.77E1	2.81E6 (β)
Pu-242	3.79E5 Y	9.65	3.76E1 (a)
Pu Total		2.46E2	1.23E5 (a) 2.81E6 (β)
Other Actinides			
Total		2.53E1	5.19E5 (a) 5.94E2 (β)
All Actinides			
Total		2.63E4	6.42E5 (a) 2.81E6 (β)

<sup>a</sup> Source: Reference [5] (page 369).<sup>b</sup> Uranium-fueled 1000-MWe PWR, 3-year fuel life, 150 days after discharge.

TABLE 3. FP Activity in Spent LWR Fuel<sup>a</sup>

FP	Activity (Ci/y) <sup>b</sup>		
	At discharge	150-day cooling	10-year cooling
Sr	1.38E8	4.76E6	1.65E6
Y	2.08E8	6.48E6	1.65E6
Zr	9.62E7	7.54E6	5.15E1
Nb	2.30E8	1.44E7	2.30E1
Ru	7.57E7	1.36E7	1.50E4
Rh	1.17E8	1.36E7	1.50E4
I	2.66E8	6.04E1	1.02
Cs	1.56E8	8.75E6	2.56E6
Ba	1.51E8	2.73E6	2.18E6
Pm	3.16E7	2.74E6	2.11E5
Eu	6.56E6	3.67E5	1.27E5
Other FPs	2.28E9	3.90E7	2.52E5
<b>TOTAL</b>	<b>3.76E9</b>	<b>1.14E8</b>	<b>8.66E6</b>

<sup>a</sup> Source: Reference [5] (pages 354-356).<sup>b</sup> Uranium-fueled 1000-MWe PWR, 3-year fuel life.

## 2.2. Required Cooling Time Prior to Reprocessing

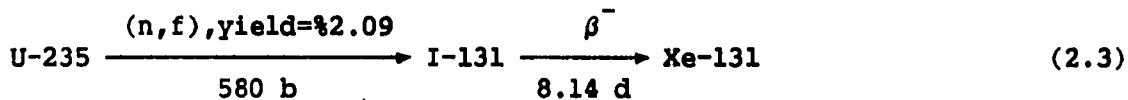
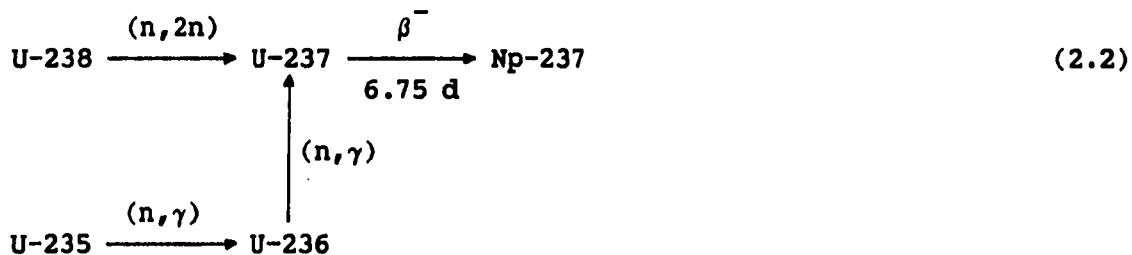
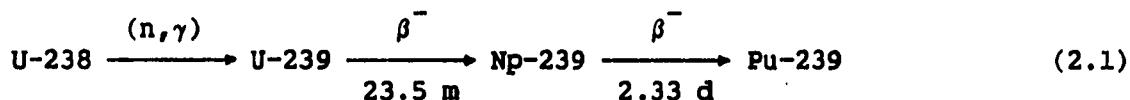
General reasons for and/or benefits from cooling SF before reprocessing are:

1. Decay of U-237, thus reducing the  $\beta$  activity that will remain in the decontaminated U product after reprocessing,
2. Decay of I (Iodine)-131, thus getting rid of considerable amounts of a toxic and active gaseous isotope before reprocessing,

3. Decay of Np (Neptunium)-239, thus preventing potential losses of valuable Pu-239,

4. Decay of overall FP activity, thus reducing the overall activity level of SF significantly.

The nuclear reactions under consideration for estimating the required cooling period prior to reprocessing are given below.



Because of the relatively short life of Np-239 and comparatively smaller importance of I-131, the decisive isotope over the length of the cooling period is U-237. Since U-237 is highly  $\beta$  active and will remain in the decontaminated U product, it will be responsible for almost all of the  $\beta$  activity in the U product. Consequently, it is a prime requirement that the U-237 activity, during the cooling period, decrease to a level that allows the direct-contact handling of the U

product of reprocessing. Note that the U product from reprocessing needs to be enriched before being fed into a reactor, and enrichment is a difficult and complicated process even when direct contact handling is permitted.

The  $\beta$  activity of natural U in equilibrium with its short-lived decay products, 0.68  $\mu\text{Ci/g}$ , is commonly considered as the specification of allowable  $\beta$  activity remaining in the decontaminated U product [5].

The time period in which the activity of 6.75-day U-237 in SF decays to this specified permissible level is around 150 days, which is usually referred to as "minimum required cooling time" for spent LWR fuel, and has so far been one of the most important factors to be taken into account in the design of a reprocessing plant.

Because commercial reprocessing has not been applied in the U.S.A. in the past 15 years, there is a large backlog of SF waiting in reactor pools, 17575 MT to be quantitative [1] (see Table 1). Even if reprocessing is initiated today in the U.S.A., the SF to be reprocessed is going to be at least cooled for 10 years. If standard reprocessing designs are applied, much less active fuel is going to be processed in plants designed for much more active fuel, which is an economic penalty.

It is one of the objectives of this study to examine simplifications over the standard Purex reprocessing design stemming from the lower activity in SF.

### 2.3. Required Decontamination

The decontamination factor, denoted as DF and defined as the activity in SF before reprocessing divided by that remaining in products after reprocessing, is one of the most important specifications that a reprocessing plant must be designed to ensure. DFs required are strictly dependent on the subsequent use of the recovered materials.

#### 2.3.1. Required DF for the U Product

Since the U product of reprocessing needs enrichment and, in enrichment, some operations are by direct-contact, the final  $\beta$  activity in the U product should not significantly exceed 0.68  $\mu\text{Ci/g}$  and the total  $\alpha$  activity in the U product should be close to that of U itself. By definition, the DF required is a function of initial activity in SF. As a result, the difference between the activities of 150-day and 10-year cooled fuels (a factor of 13) reflects directly in the required DF of the U product from FPs, as shown in Table 4.

#### 2.3.2. Required DF for the Pu Product

Commonly accepted specifications call for a Pu product containing less than 0.1 w/o (weight percent) U and no more than 200 ppm (parts per million) FPs [5,6]. These demanding specifications may be attributed to the intent of having weapon-grade Pu available as the output of reprocessing plants. Almost all reprocessing plants in the world have been designed to meet these demanding specifications for the Pu product [5].

TABLE 4. Required DFs for U and Pu Products of Reprocessing

For U product	150-day cooling	10-year cooling
DF <sub>U-FP</sub>	7.0E6	5.0E5
DF <sub>U-a</sub>	2.0E4	2.0E4
For Pu product	Common Specifications	Adopted Specifications in This Study
DF <sub>Pu-FP</sub>	1.0E6-1.0E7	500-1500
U in Pu	< 0.1 w/o	94-95 w/o

If the main goal is to have as clean and as safe a power production as possible, having Pu in a pure form somewhere in the cycle implies not only increased reprocessing plant requirements but also increased diversion risks, meaning a "faux pas" from the safeguardability standpoint.

The fact that, in a civilian technology adopting the maximum energy utilization of Pu, the normal route of the Pu product of reprocessing is into the MOX fabrication plants, where Pu is mixed with certain amounts of U and fabricated into MOX fuel elements to be burned in typical LWRs, leads to the following arguments.

- There is no need to produce an almost U-free Pu stream in reprocessing. About 5-6 w/o Pu in U would be acceptable for

thermal reactor fuels, which would correspond to slightly enriched  $\text{UO}_2$  fuels, and about 25 w/o Pu in U for FBR (Fast Breeder Reactor) fuels [7,8].

- High decontamination of Pu from FPs is not required, either, because the  $\beta$  activity of the Pu itself in SF (specifically of Pu-241) is high enough to be dominant in any case (see Tables 2 and 3).

The first argument gives rise to a coprocessing concept, which, after the codecontamination of U and Pu from FPs, employs a partial-partitioning process to produce a U stream and a U+Pu mixed stream. The U+Pu mixed product does not call for additional decontamination because of the high activity of Pu itself, and does not need to be enriched because of its specified Pu content, 5-6 w/o Pu in U, which, when fabricated into MOX fuel, will correspond to the slightly enriched  $\text{UO}_2$  fuel. The standard and proposed specifications for decontamination of the Pu product of reprocessing are presented in Table 4.

In 1983 Exxon Nuclear Company developed a conceptual design of an integrated reprocessing-fabrication plant, named SAFAR (Safeguarded Reprocessing and Fabrication), employing a coprocessing flow sheet [9]. They used the previously designed, but not built, Exxon reprocessing plant [10,11,12], which applied the standard Purex method for short-cooled SF, as a reference, and expanded it for fabrication of LMFBR (Liquid Metal Fast Breeder Reactor) fuels. The emphasis of the SAFAR design was on the safeguardability issue. Several modifications to the

previously designed Exxon plant were proposed to enhance the safeguardability features. Adoption of the coprocessing concept was one of these modifications since it results in a flow sheet that never separates Pu from U completely; thus making it more difficult and time-consuming for a potential diverter to convert Pu to the desirable pure form. The main emphasis of this study, however, is on the fact that the SF to be reprocessed is already long-cooled and resulting radiation levels to be dealt with during the reprocessing operations are much lower compared to those in the standard cases. The coprocessing flow sheet will be adopted because it reduces the decontamination requirements for the Pu product of the reprocessing by changing its final form, eliminates several process steps, and also improves the safeguardability features. It should be noted that the adoption of the coprocessing concept is not related to the fact that the SF being dealt with is long-cooled. It is found equally favorable to apply a coprocessing flow sheet in case of reprocessing short-cooled SF, as in the SAFAR project [9].

### 3. SOLVENT EXTRACTION METHOD

#### 3.1. Description

Solvent extraction is a proven method for nuclear fuel reprocessing and is the only one that has been applied on the industrial scale so far. A general flow sheet of the solvent extraction reprocessing method is depicted in Figure 3.

Cooled SF elements are first sheared into small lengths to let the fuel be exposed to HNO<sub>3</sub> for subsequent dissolution. Sheared fuel elements are contacted with HNO<sub>3</sub> in a leacher tank. Fuel, containing U, Pu, other actinides, and FPs, is quantitatively dissolved in HNO<sub>3</sub> while cladding materials and fuel hardware remain essentially undissolved. The leacher solution is clarified to remove suspended solids and then fed into an adjustment tank, where concentrations and valence states of elements of interest are adjusted by addition of HNO<sub>3</sub>, H<sub>2</sub>O, and suitable redox agents, usually N<sub>2</sub>O<sub>4</sub> or NaNO<sub>2</sub>. Solid-free and concentration-and-valence-adjusted fuel solution is ready for solvent extraction at this point.

Cladding hulls from the leaching step and solid particles from the clarification step are packaged as waste after being washed with dilute HNO<sub>3</sub> and H<sub>2</sub>O. Washings go into the fuel solution.

The off-gases from the leaching step, which contain major fractions of FP gases and nitrogen oxides (NO<sub>x</sub>), are first passed through a NO<sub>x</sub> absorption step, and then sent to the off-gas treatment

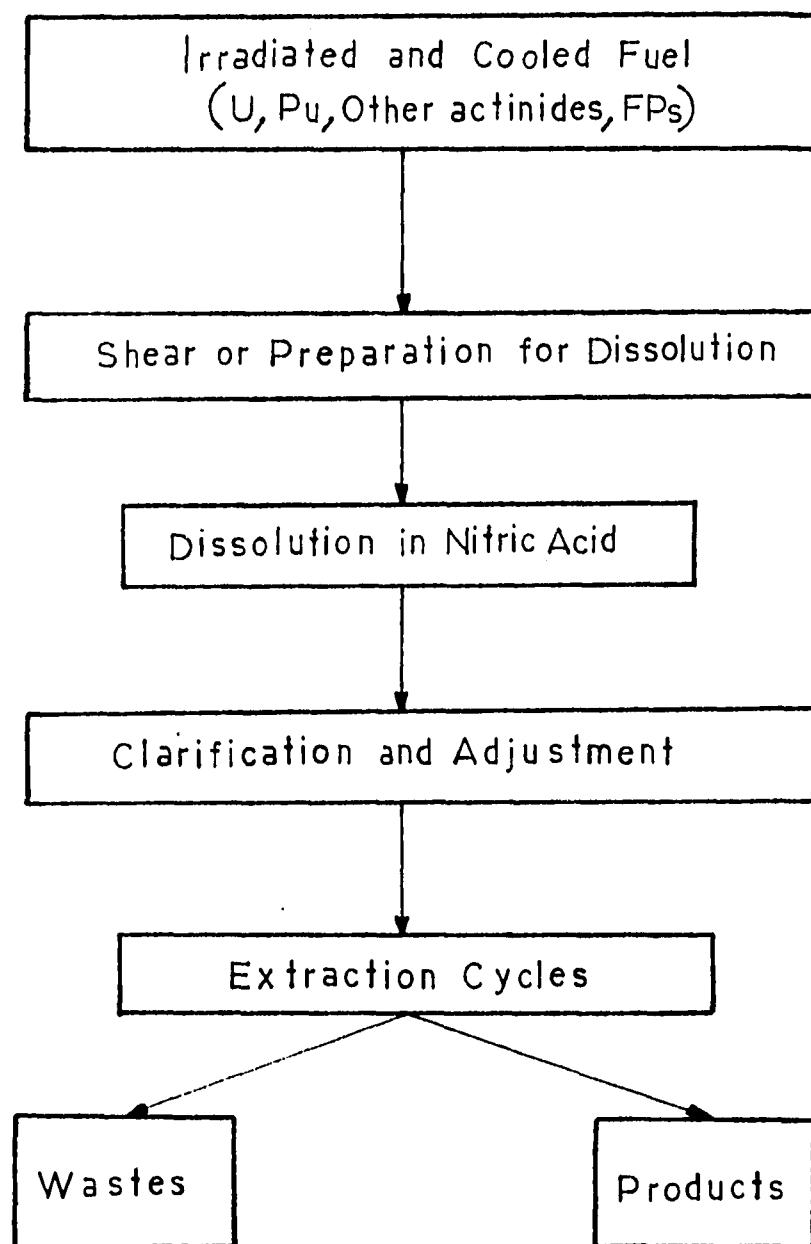


FIGURE 3. A Simplified Flow Chart of Solvent Extraction Method

where iodine and krypton removal are accomplished. The off-gases from the shearing step go directly to the off-gas treatment; they contain no NO<sub>x</sub> gases.

The adjusted fuel solution enters the solvent extraction process. In the first cycle, codecontamination, U and Pu are separated from almost all of the FPs. Then, in the standard process, U and Pu are partitioned, and each product stream is purified until the necessary decontamination factors are obtained. The final decontaminated products of the solvent extraction process are aqueous nitrate solutions, the contents of which comply with the specifications mentioned in Section 2.3. (Table 4). The process proposed in this dissertation will be discussed later.

### 3.2. Basics of Solvent Extraction

When an aqueous solution containing a single solute, A, is contacted with an organic solvent for a time long enough to allow equilibrium to be reached, solute A is partitioned between the aqueous and organic phases. The factor by which a solute is distributed between the aqueous and organic phases is called the "distribution coefficient (D)" of that solute for that solvent, and is given by the expression

$$D_A = \frac{y_{A,E}}{x_{A,R}} \quad (3.1)$$

where  $y_{A,E}$  is the concentration of A in the (organic) extractant and  $x_{A,R}$  is the concentration of A in the (aqueous) raffinate.

A contactor is a vessel in which the two phases are contacted. The original solution, usually aqueous, entering the contactor is referred to as "feed". The organic and aqueous streams leaving the contactor are called "extract" and "raffinate" phases, respectively. For most aqueous-organic phase pairs in solvent extraction applications, the aqueous phase is the heavier one, so it usually enters the contactor near the top and flows down through the organic phase.

Single-stage equilibrium of solvent extraction is shown in Figure 4. If feed solution contains two solutes, A and B, one of which, A, has a large D and the other, B, has a relatively small D for a specific solvent, upon contact with the solvent most of A is going to transfer into the solvent phase while most of B remains in the aqueous solution; this accomplishes the separation of the two solutes.

If solute A is a desirable one, one to be recovered or decontaminated, and B is considered undesirable or a contaminant, after defining the recovery of a solute, i, as  $r_i = E y_{i,E} / F x_{i,F}$  (see Figure 4 for the description of nomenclature), the definition of the decontamination factor of A from B follows by the expression

$$DF_{A-B} = r_A / r_B.$$

The fact that the extract phase leaving the contactor after a single contact with the feed solution is still capable of extracting

**FIGURE 4. Single-Stage Equilibrium of Solvent Extraction**

---

F=Relative volumetric flow rate of the feed stream (lt/hr)

E=Relative volumetric flow rate of the solvent stream (lt/hr)

$x_{A,F}$ =Molarity of solute A in the feed stream (moles/lt)

$x_{B,F}$ =Molarity of solute B in the feed stream (moles/lt)

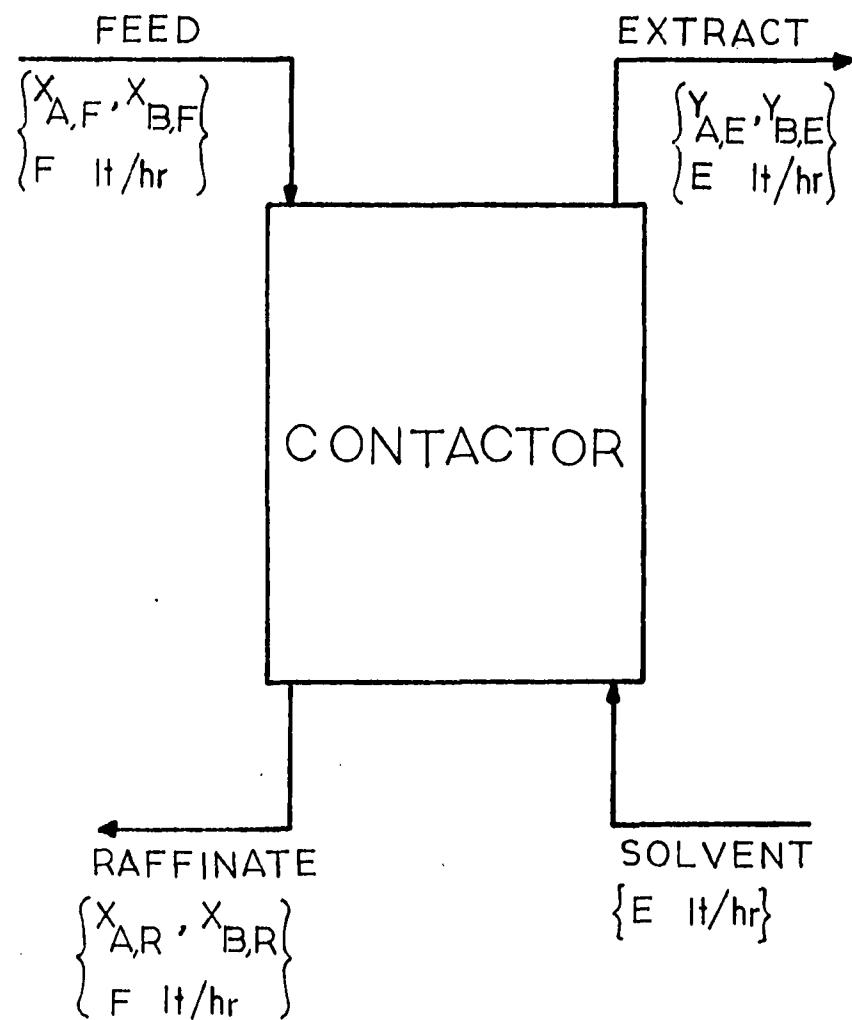
$x_{A,R}$ =Molarity of solute A in the raffinate stream (moles/lt)

$x_{B,R}$ =Molarity of solute B in the raffinate stream (moles/lt)

$y_{A,E}$ =Molarity of solute A in the extract stream (moles/lt)

$y_{B,E}$ =Molarity of solute B in the extract stream (moles/lt)

---



more of extractable solutes leads to the contactor arrangement called "cascade", resulting in more efficient use of solvent.

An extraction cascade is shown in Figure 5. Either many single-stage contactors such as mixer settlers, or a tall column contactor can be used to construct an extraction cascade. A column contactor is assumed to have many single-stage contactors, each of which is referred to as "theoretical stage" and defined as a section of the column contactor in which a single stage equilibrium is reached.

### 3.3. Purex Solvent Extraction Method

The Purex method employs TBP (Tri Butyl Phosphate) in a hydrocarbon diluent as the solvent. TBP has been very satisfactory for reprocessing nuclear fuels so far, and both technically and economically there seems no reason for careful consideration of other solvents.

#### 3.3.1. Physical Properties of TBP

TBP has almost all the properties of an ideal solvent except for high viscosity and a density close to that of H<sub>2</sub>O. To improve these properties, TBP is diluted with a hydrocarbon such as kerosene or n-dodecane, thus achieving better mixing and separation of the phases in contractors. Important physical properties of TBP and 30 v/o TBP in n-dodecane are exhibited in Table 5.

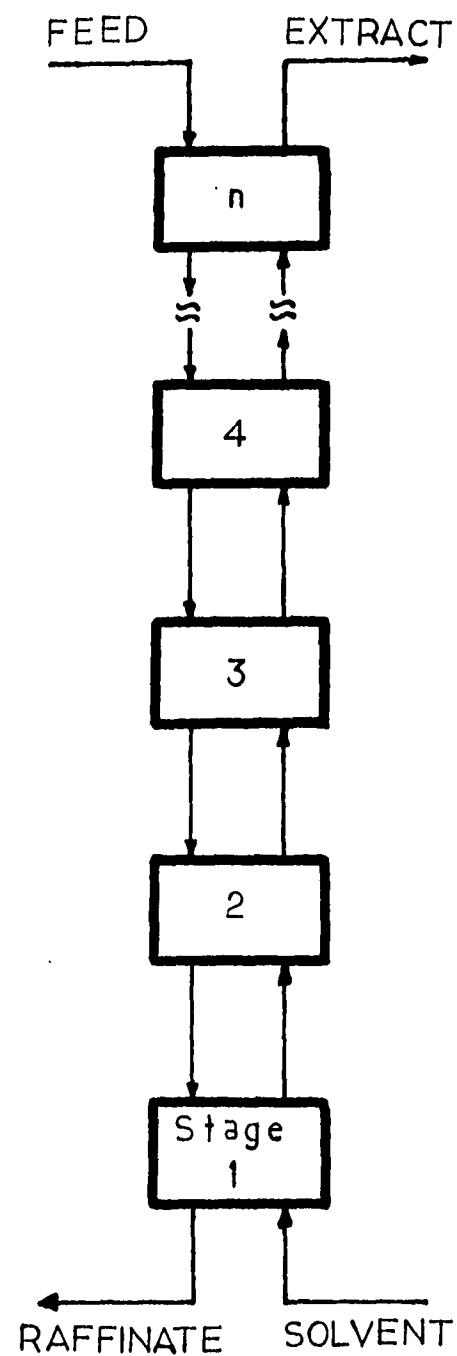


FIGURE 5. An Extraction Cascade

TABLE 5. Physical Properties of TBP and 30 v/o TBP in n-Dodecane<sup>a</sup>

TBP	
Molecular weight	266
Color	Water white
Odor	Mildly sweet
Viscosity at 25 °C	0.0332 poise
85 °C	0.0080 poise
Boiling point at 760 Torr	289 °C
15 Torr	173 °C
1 Torr	121 °C
Density at 25 °C	0.9724 g/ml
Solubility in water at 25 °C	0.39 g/liter
Solubility of water in TBP	64 g/liter
n-dodecane      30 v/o TBP in n-dodecane	
Molecular weight	170.34
Density at 25 °C	0.749 g/ml      0.814 g/ml
Viscosity at 25 °C	0.014 poise      0.0173 poise
Normal boiling point	216 °C

<sup>a</sup> Source: Reference [5] (pages 173 and 510).

Although TBP is quite stable against radiolysis, it still degrades under intense radiation fields, yielding the degradation products, DBP (Di Butyl Phosphate) and MBP (Mono Butyl Phosphate), the main product being DBP [5,13]. DBP forms strong complexes with Zr, U(VI), and Pu(IV).

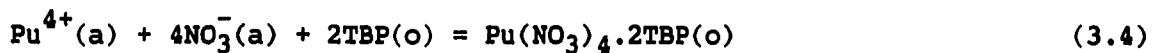
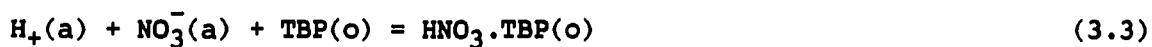
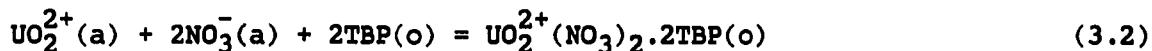
Complexing with Zr decreases the DFs from Zr and also gives rise to formation of cruds, which are insoluble, slimy materials that may

cause irregular extraction behavior, especially in the primary extraction cycle, where the highest activity levels are experienced [14,15]. It has been reported that in the German pilot plant at Karlsruhe the first cycle mixer-settler was plugged due to crud formation and the operation had to be shut down [15]. Because mixer-settlers employ longer-contact times and have a larger dead volume, they are more susceptible to crud formation compared to column contactors. When processing highly active solutions, use of pulse columns, which have a shorter contact time than do mixer settlers, or centrifugal contactors, which are relatively complicated and expensive but employ very short contact times, has been favored [5,9].

Complexes of DBP with U and Pu show very high distribution coefficients and cannot be stripped out of the solvent phase during stripping. This may result in losses of U and Pu unless the solvent phase is thoroughly washed and wash solutions are recycled.

### 3.3.2. Extraction Mechanism with TBP

The extent to which a solute is extracted into the solvent phase depends on its ability to form complexes with the solvent. Complex formation of U, Pu, and HNO<sub>3</sub> with TBP are as follows.



where a and o denote aqueous and organic phases, respectively. The right hand side complexes prefer the organic phase. Most of the FPs cannot form similar complexes with TBP and remain in the aqueous phase, thus making it possible to codecontaminate U and Pu from FPs products.

The equilibrium constant for reaction (3.2) can be written as, assuming activity coefficients of unity,

$$K_U = \frac{[UO_2^{2+}(NO_3)_2 \cdot 2TBP(o)]}{[UO_2^{2+}(a)][NO_3^-(a)]^2[TBP(o)]^2} \quad (3.5)$$

where brackets represent concentrations.

Recalling the definition of the distribution coefficient, the distribution coefficient of U can be expressed as

$$D_U = K_U [NO_3^-(a)]^2 [TBP(o)]^2 \quad (3.6)$$

where  $[TBP(o)]$  is the free TBP concentration in the organic phase.

According to Eq. (3-6), as nitrate concentration of the aqueous phase and free TBP concentration of the organic phase increase,  $D_U$  increases by the second power. However, as nitrate concentration of the aqueous phase increases, the free TBP concentration of the organic phase decreases because of the extraction of  $HNO_3$  into TBP (Reaction (3.3)). Above some  $HNO_3$  concentration, the extraction of  $HNO_3$  into TBP becomes significant and  $D_U$  starts decreasing with increasing  $HNO_3$  concentration. This trend can be better observed in Figure 6.

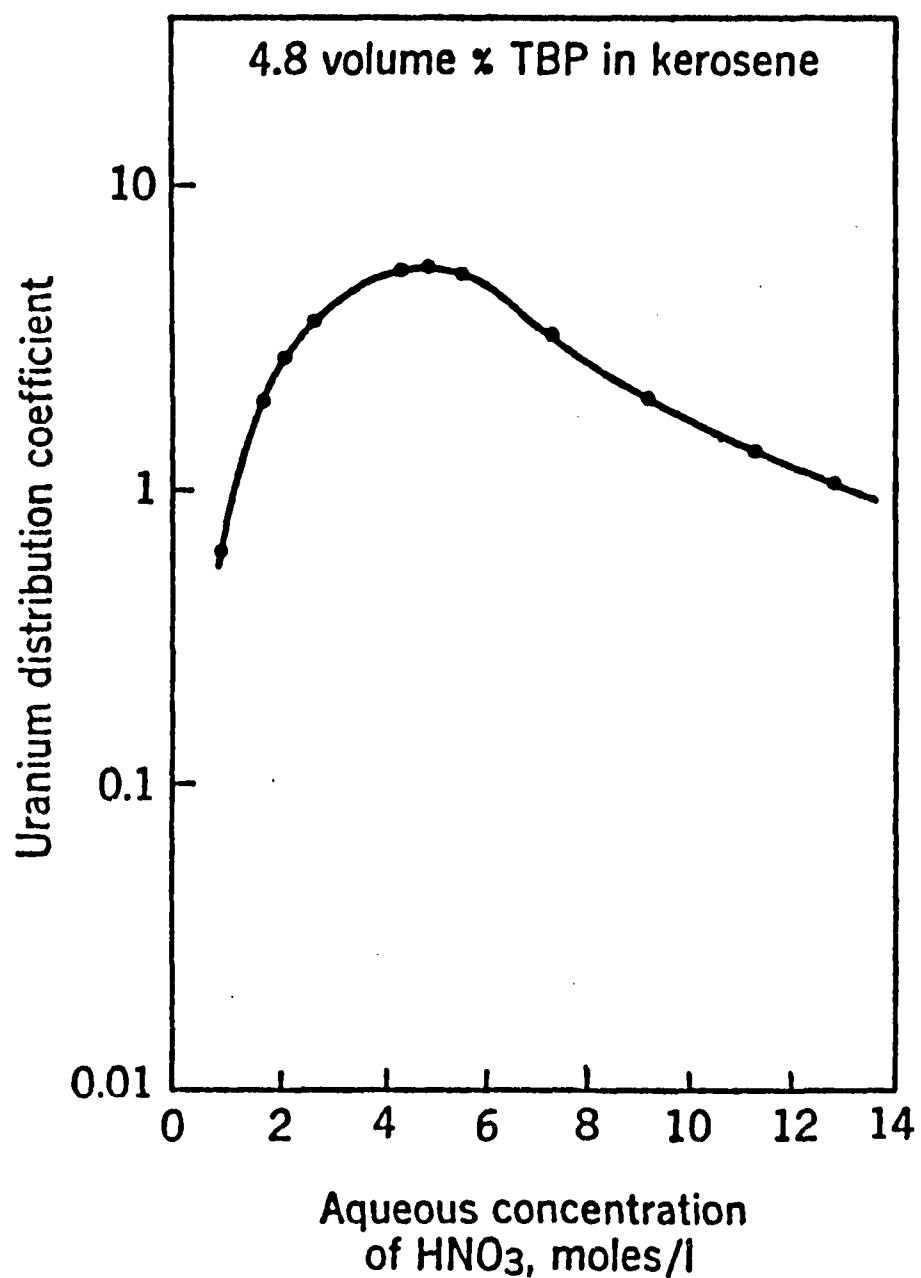


FIGURE 6.  $D_U$  as a Function of  $\text{HNO}_3$  Molarity in Aqueous Phase [5]

The distribution coefficients of solutes of interest in Purex reprocessing are given as a function of  $\text{HNO}_3$  concentration in aqueous phase in Figure 7. Separations in the Purex method are based on the differences in the distribution coefficients of U, Pu(IV), Pu(III), and FPs, as can be seen in Figure 7.

### 3.3.3. Basic Processes in Purex Solvent Extraction

3.3.3.a. Extraction When an aqueous solution containing U, Pu, and FPs is contacted with TBP in a diluent, almost all of the U and Pu migrate into the solvent phase while almost all the FPs remain in the aqueous solution because of the differences in the distribution coefficients. This process is called "extraction", and achieves the primary separation of the desired and the undesired.

3.3.3.b. Scrubbing If the organic stream leaving the extraction process, loaded with U, Pu, and small amounts of FPs, is contacted with a  $\text{HNO}_3$  solution, most of the FPs and small amounts of U and Pu in the solvent phase will be washed back into the aqueous phase. This process is referred to as "scrubbing", and serves to improve the decontamination of U and Pu from FPs.

3.3.3.c. Stripping If the solvent phase, loaded with extractable components, is brought into contact with a dilute  $\text{HNO}_3$  solution, the extracted components in the solvent phase will prefer the aqueous phase and leave the solvent phase because of their small distribution coefficients at low  $\text{HNO}_3$  concentrations, as shown in Figure 7. This process, called "stripping", makes it possible to

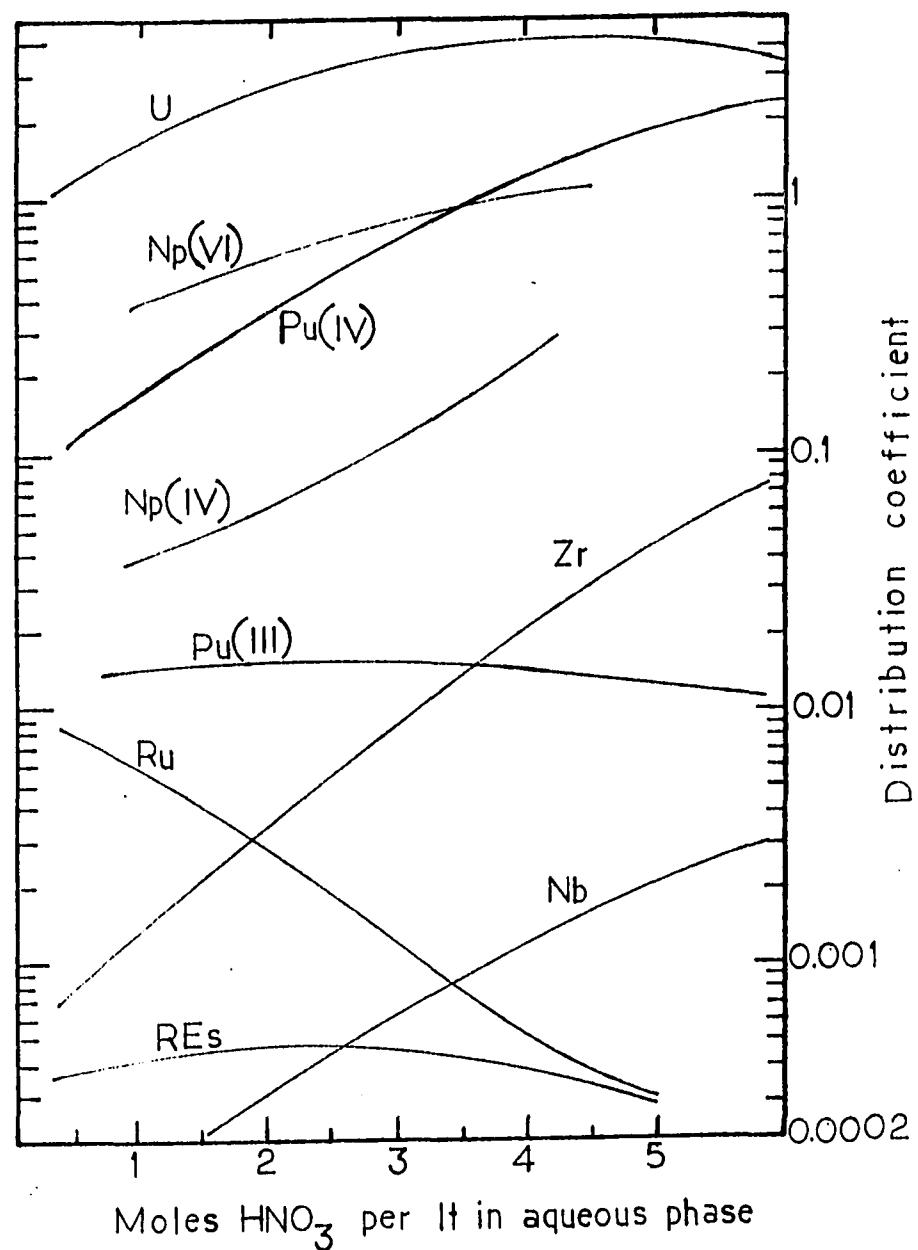


FIGURE 7. Distribution Coefficients of U, Pu, and FPs as a Function of  $\text{HNO}_3$  Molarity in Aqueous Phase [5,16]

obtain the extractable (desirable) products in an aqueous solution, which is the suitable form for subsequent processes.

#### 3.3.4. Basic Cycles of Purex Method

3.3.4.a. Codecontamination Cycle (Primary Extraction) The codecontamination cycle usually consists of an extraction and a scrubbing process, and accomplishes the major portion of decontamination of U and Pu from FPs. Extraction and scrubbing processes can be performed in the lower and upper parts of the same column contactor, a compound contactor, with the feed solution entering the column near the midpoint.

The product of the codecontamination cycle, the extract phase, is a TBP-in-diluent solution containing almost all of the U and Pu, small amounts of other actinides, and very small amounts of the FPs that were present in the feed solution.

The raffinate phase from the codecontamination cycle carries practically all of the FPs in the feed solution and, being classified as high-level waste (HLW), goes into HLW tanks.

Sometimes and particularly if there is holdup between the codecontamination stage and subsequent stages, a stripping step is also included in the codecontamination cycle to obtain an aqueous product solution. This reduces radiolysis of the solvent by shortening the contact time of the solvent with radioactivity, and may be favored for short-cooled fuels, for which solvent radiolysis can be a serious problem. A simple sketch of the codecontamination cycle is included in Figure 8.

3.3.4.b. Complete Partitioning Cycle In the complete partitioning cycle, the extract phase from the codecontamination cycle is contacted with a  $\text{HNO}_3$  solution containing a reductant. When reduced to the trivalent state, Pu favors the aqueous phase (see Pu(III) distribution coefficient in Figure 7), and leaves the solvent phase. Proper choice of a reductant ensures that U will not be reduced from the hexavalent state (the most extractable state) and will remain in the solvent phase. A TBP solution is also fed into the partitioning contactor from the bottom to re-extract the U that may be washed into the aqueous phase during this stripping with the  $\text{HNO}_3$  solution containing a reductant. As a result, almost all the Pu fed into the process leaves the cycle in the aqueous phase while U leaves the cycle in the organic phase; thus a complete separation of U and Pu is accomplished. A simple sketch of the complete partitioning cycle is included in Figure 8.

Reducers that can be used in the complete partitioning cycle include a) hydroxylamine, b) ferrous sulfamate, c) tetravalent U, and d) electrolytic reduction. Ferrous sulfamate has the disadvantage of adding metallic impurities to the process solutions. Tetravalent U and electrolytic reduction require more complicated and expensive equipment [17]. Hydroxylamine seems to be the most favorable reductant although it yields relatively slow reduction rates [17,18].

In general, whatever reductant is used, the partitioning contactor is very difficult to control because of the competing oxidation-

reduction reactions. Major upsets and deviations from theoretical expectations are more likely to occur in the complete partitioning cycle than in the other cycles. The most problematic reaction is re-oxidation of trivalent Pu, which is controllable only with difficulty and may give rise to poor separation and unpredictable concentrations of Pu in the product streams [19,20].

3.3.4.c. Purification A purification cycle consists of a series of extraction, scrubbing, and stripping functions and achieves additional decontamination of the U and Pu product streams. Some tail-end treatments such as silica-gel or ion exchange are often included in the purification cycles.

#### 3.3.5. A Flow Sheet of the Standard Purex Method

The standard Purex process consists of a codecontamination cycle, a complete partitioning cycle, a U stripping cycle, and one or two purification cycles for each product stream (U and Pu). The number of purification cycles is decided by the decontamination factors required. For 150-day cooled typical LWR fuels usually two purification cycles are needed to obtain the necessary decontamination factors for each product: U and Pu. A flow sheet of the standard Purex method is presented in Figure 8.

**FIGURE 8. A Flow Sheet of the Standard Purex method**

---

A=codecontamination cycle

A1=scrubbing

A2=extraction

B=complete partitioning cycle

B1=Pu stripping with reduction of Pu

B2=re-extraction of U

C=U stripping

---

1=aqueous feed solution

2=scrub solution ( $\text{HNO}_3$  of intermediate concentration)

3=aqueous waste solution (to HLW treatment)

4=organic solvent (30 v/o TBP in a diluent)

5=organic product from the codecontamination cycle

6= $\text{HNO}_3$  solution containing a reductant

7=organic solvent (30 v/o TBP in a diluent)

8=aqueous Pu product (to purification cycles)

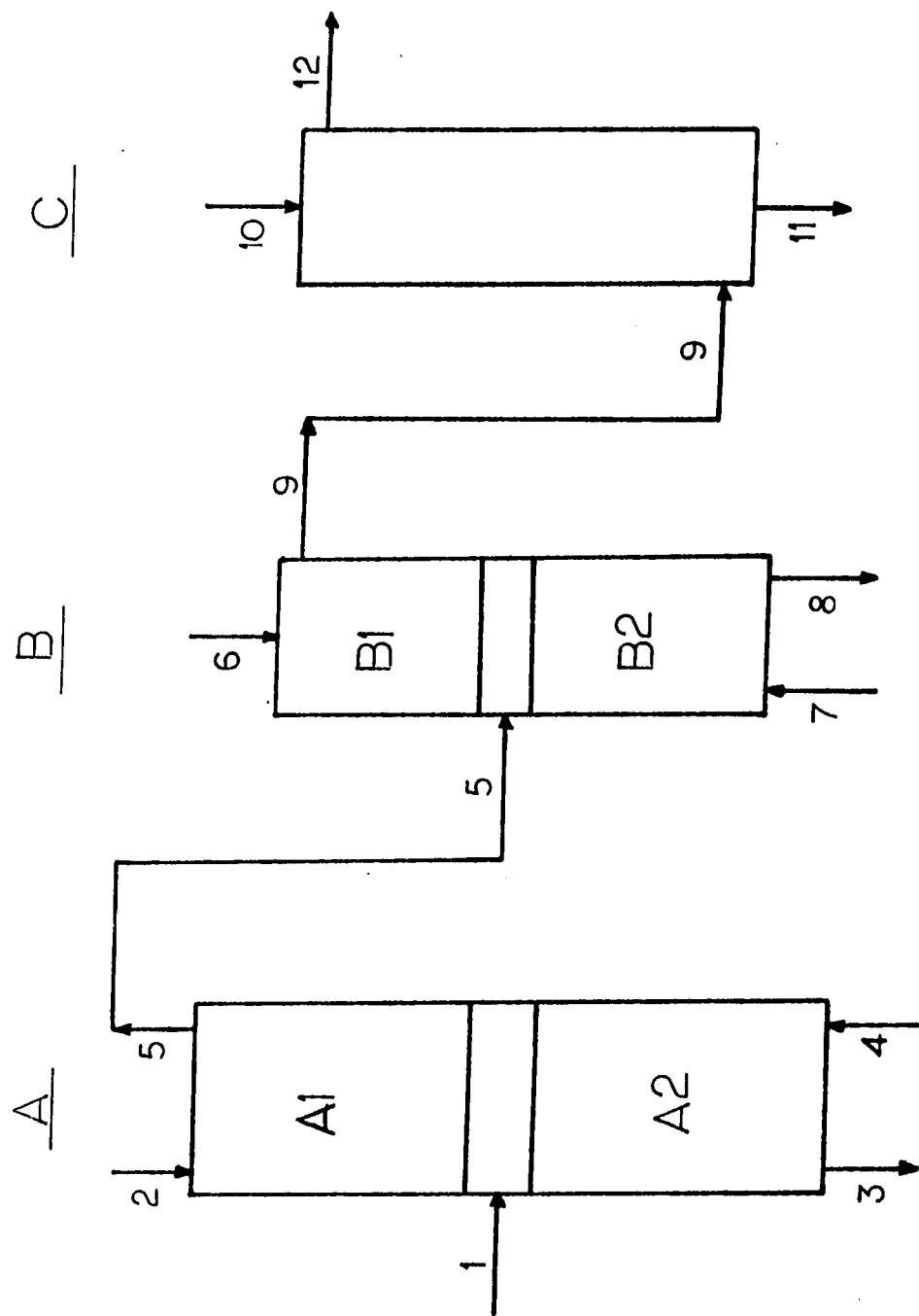
9=organic U product

10=strip solution (dilute  $\text{HNO}_3$ )

11=aqueous U product (to purification cycles)

12=used organic solvent (to used solvent treatment)

---



### 3.4. Proposed Purex Method

#### 3.4.1. Cycles in the Proposed Flow Sheet

3.4.1.a. Codecontamination Cycle The codecontamination cycle is exactly the same as that in the standard Purex method, as explained in Section 3.3.4.a. However, the long cooling before processing permits longer contact in simpler extraction equipment (i.e., pulse columns instead of centrifugal contactors), and thus both yields of product and decontamination factors should be improved.

3.4.1.b. Partial Partitioning Cycle The partial partitioning cycle makes use of the differences in the distribution coefficients of U(VI) and Pu(IV), shown in Figure 9, to produce a U+Pu aqueous solution instead of the practically pure Pu aqueous solution in the complete partitioning. The partial partitioning cycle may replace the complete partitioning cycle in the standard Purex method. Employing the partial partitioning cycle, it is possible to obtain an aqueous U solution containing a specified percentage of Pu (5-6 w/o Pu in case of LWR fuels, 20-25 w/o in case of FBR fuels) and an organic U stream without needing the addition of a reductant to the system. A simple sketch of the partial partitioning cycle is included in Figure 10.

The objectives of the partial partitioning cycle are (1) to strip as much Pu as possible into the aqueous phase, and (2) to obtain the specified U/Pu ratio in the aqueous product, without adding a reductant into the system. This requires scrubbing with dilute (nearly 0.1 M)  $\text{HNO}_3$  solutions, operating near room temperature, and careful adjustment

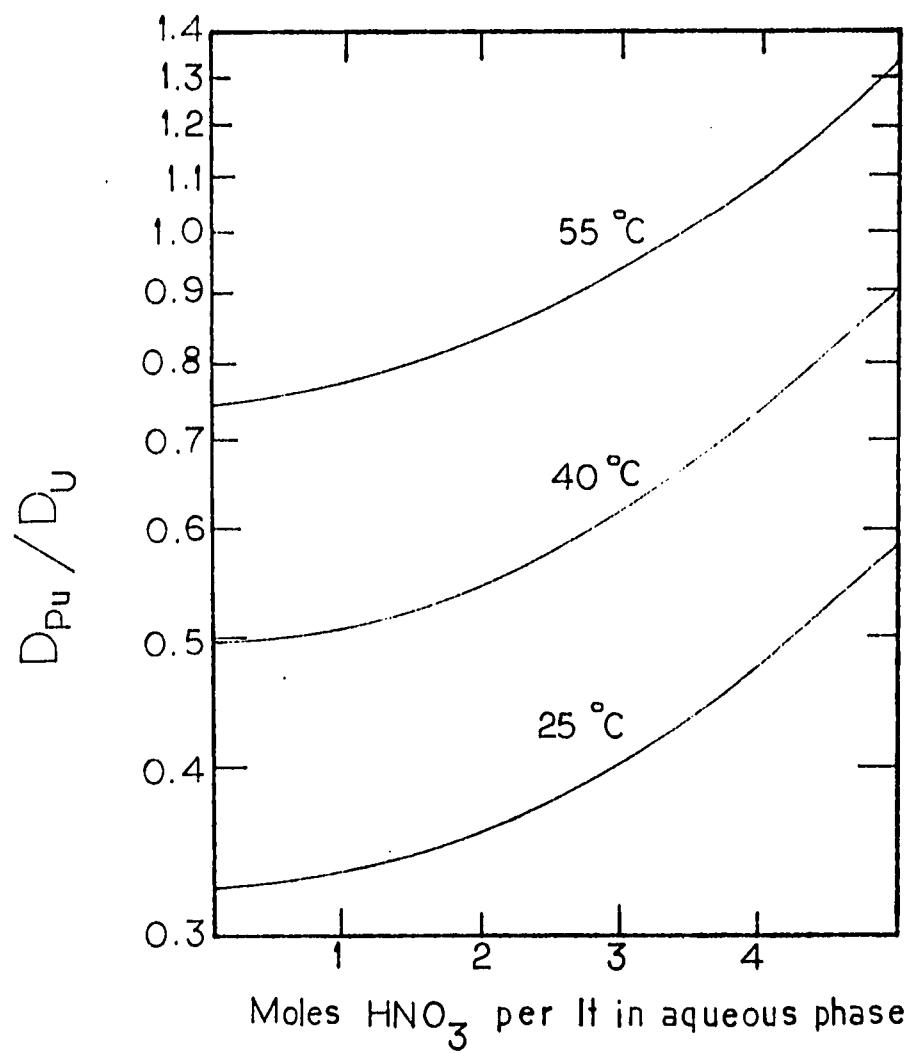


FIGURE 9.  $D(\text{Pu(IV)})/D(\text{U})$  as Function of  $\text{HNO}_3$  Molarity in Aqueous Phase [5]

and control of flow rates. As can be observed in Figure 9, the greatest difference between the distribution coefficients of U and Pu(IV) occurs at low HNO<sub>3</sub> concentrations and near room temperature. All the complications arising from the task of reducing Pu(IV) to Pu(III) in the complete partitioning cycle are avoided in the partial partitioning cycle.

The partial partitioning of U and Pu is commonly called "coprocessing" because it leads to an aqueous product solution containing both U and Pu. As mentioned in Section 2.3.2., this product solution does not require additional decontamination because Pu in it is high-enough beta active and can be transferred to a MOX fabrication plant after being solidified.

3.4.1.c. Finish Partitioning Cycle      The organic product stream leaving the top of the partial partitioning contactor contains U and small amounts of Pu. Because of the high activity of Pu, the decontamination of U from Pu activity obtained up to this stage is not acceptable. This requires another cycle where the decontamination of U from Pu is completed by use of a reducing agent. In this additional cycle, which will be called "finish partitioning" in this study, the organic product of the partial partitioning cycle is brought into contact with a HNO<sub>3</sub> solution of intermediate concentration (2.0 to 2.5 M) containing a reductant, preferably hydroxylamine because it does not add any metallic impurities to the system. Pu is reduced to Pu(III) and washed into the aqueous phase together with very small amounts of

U. A simple sketch of the finish partitioning cycle is included in Figure 10.

The finish partitioning cycle functions like a complete partitioning cycle but differs from it in the following ways:

1. The amount of Pu fed into the finish partitioning cycle is much less than that fed into the complete partitioning cycle (to be quantitative, the Pu concentration in the feed is 3 to 7 w/o of that in the complete partitioning cycle). This leads to a significant decrease in the difficulties arising from Pu reduction during the operation of the complete partitioning contactor. Even if similar difficulties are encountered in the finish partitioning contactor, their relative importance will be considerably reduced because of the much smaller amount of Pu involved.
2. It is not necessary to feed a solvent phase into the finish partitioning cycle for re-extracting the U that is washed back into the aqueous phase during the scrubbing. Because the aqueous product of the finish partitioning is going to be mixed with the aqueous U+Pu product stream of the partial partitioning cycle, small amounts of U in the aqueous stream from the finish partitioning cycle are easily tolerable.

3.4.1.d. U Stripping Cycle      The U stripping cycle is exactly the same as the stripping process described in Section 3.3.3.c.: it washes the U product in the solvent phase into the aqueous phase.

### 3.4.2. The Proposed Purex Flow Sheet

The proposed flow sheet consists of a codecontamination, a partial partitioning, a finish partitioning cycle, and a U stripping cycle and is sketched in Figure 10.

It should be noted that the partial partitioning cycle achieves a better decontamination from FPs for the U product than does the complete partitioning cycle in the standard Purex process because the scrubbing solution is a dilute  $\text{HNO}_3$  solution in partial partitioning, whereas in complete partitioning the scrubbing solution is a  $\text{HNO}_3$  solution of intermediate concentration. As can be seen in Figure 7, except for Ru all the FPs display lower distribution coefficients at lower  $\text{HNO}_3$  concentrations.

The finish partitioning cycle also achieves some decontamination for the U product because it involves scrubbing with a  $\text{HNO}_3$  solution. Thus, the finish partitioning cycle is not really an extra cycle in the whole process, as it acts as a purification cycle for the U product. Indeed, our calculations indicate that after finish partitioning the U product is adequately decontaminated for general-purpose use if SF being processed is around 10-year cooled, which will be discussed in the next chapter.

FIGURE 10. The Proposed Purex Flow Sheet

---

A=codecontamination cycle

A1=scrubbing

A2=extraction

B=partial partitioning cycle

B1=Pu stripping without reduction of Pu

B2=re-extraction of U

C=finish partitioning cycle

D=U stripping

---

1=aqueous feed solution

2=scrub solution ( $\text{HNO}_3$  of intermediate concentration)

3=aqueous waste (to HLW treatment)

4=organic solvent (30 v/o TBP in a diluent)

5=organic product from the codecontamination cycle

6=dilute  $\text{HNO}_3$  solution

7=aqueous U+Pu product

8=organic solvent (30 v/o TBP in a diluent)

9=organic U product from the partial partitioning cycle

10= $\text{HNO}_3$  solution containing a reductant

11=aqueous U+Pu stream

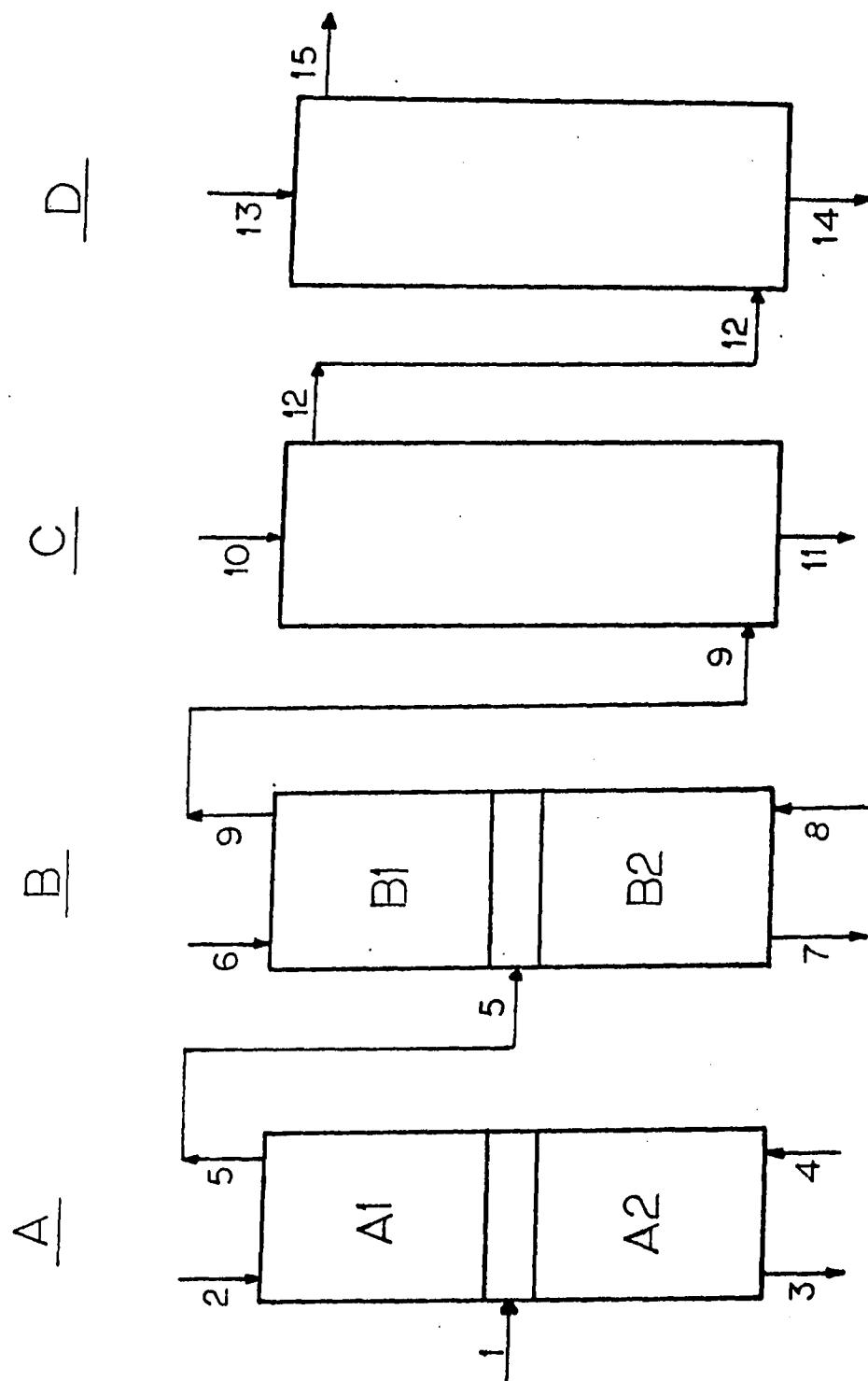
12=organic U product from the finish partitioning cycle

13=strip solution (dilute  $\text{HNO}_3$ )

14=aqueous U product

15=used organic solvent (to used solvent treatment)

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#### 4. FLOW SHEET CALCULATIONS

##### 4.1. Calculation of an Extraction-Scrubbing Cascade

###### 4.1.1. Assumptions and Approximations

(1) The solubility of H<sub>2</sub>O in TBP and of TBP in H<sub>2</sub>O is neglected.

As seen in Table 5, at 25 °C the solubility of pure TBP in H<sub>2</sub>O is 0.42 g/lit, which is obviously a negligible amount. The solubility of H<sub>2</sub>O in 30 v/o TBP in n-dodecane (7.2 g/lit) can also be neglected if it is considered that 1 lit of 30 v/o TBP in n-dodecane, which contains 1.095 moles TBP, is capable of extracting up to 215.7 g uranyl nitrate (UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>) as UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>.2TBP.

(2) Solvent degradation is not taken into account.

As mentioned in Section 3.3.1., degradation of TBP results in formation of DBP and MBP in the organic phase. It has been reported that when 30 v/o TBP was exposed to 0.2 Wh/lit of radiation for 30 min in mixer-settlers processing 240-day cooled fuel, 20 to 30 mg DBP per liter was produced [21]. Then, it should be a justifiable assumption that when processing 10-year cooled fuel in pulse columns, solvent degradation effects will not be significant.

(3) In the aqueous phase all U is maintained as U(VI), which is extracted into the solvent as UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>.2TBP.

The two stable oxidation states of U that can exist in aqueous solution are tetravalent, as U<sup>4+</sup>, and hexavalent, as (U<sup>6+</sup>O<sub>2</sub>)<sup>2+</sup> states [5,22]. The solution resulting from dissolution of UO<sub>2</sub> in HNO<sub>3</sub> is a

stable uranyl nitrate ( $\text{UO}_2(\text{NO}_3)_2$ ) solution. During the reduction of Pu(IV) to Pu(III) in the complete partitioning and finish partitioning cycles, by proper choice of a reductant, reduction of U(VI) to U(IV) can be prevented because the redox potential<sup>1</sup> for Pu(IV)-Pu(III) reduction is more positive than that for U(VI)-U(IV) reduction.

Although, in general, the extraction mechanism is not well understood and several discrepancies exist in the literature [13,23], many authors have accepted that TBP extracts U from uranyl nitrate solutions in the form of a neutral complex,  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ , according to Reaction (3.2) [5,13,24,25].

(4) In the aqueous phase all Pu is maintained as either Pu(IV) or Pu(III). The kinetics of Pu(IV)-to-Pu(III) reduction is not considered.

In aqueous solution the most stable oxidation state of Pu is the tetravalent state,  $\text{Pu}^{4+}$ . However, the trivalent, tetravalent, pentavalent, and hexavalent states of Pu can exist in aqueous solution at the same time because there are only small differences in the oxidation-reduction potentials of these states. The stability of a valence state can easily be affected by small changes in the oxidation-reduction potential of the solution due to the presence of alpha radioactivity and nitrate reduction products ( $\text{NO}$ ,  $(\text{NO}_2)^-$ ,  $\text{N}_2\text{O}_4$ ).

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<sup>1</sup>Redox potential is a measure of relative oxidizing and reducing tendencies of chemical species. Redox half reactions are, in general, written as oxidant + ne = reductant; ( a ), where a is the redox potential in volts for the reaction. For two given redox half reactions, A + ne = Al; ( +a ) and B + ne = Bl; ( +b ), if a > b, A can oxidize Bl.

Notwithstanding, experimental data of Katz and Seaborg show that tetravalent Pu in HNO<sub>3</sub> solutions remains stable for several days [22].

In the feed adjustment step of the Purex method, addition of a valence adjusting agent like nitrite ion into the SF solution brings all the Pu in the solution into the tetravalent state by reducing Pu(VI) and oxidizing Pu(III) [5,25]. In the codecontamination and partial partitioning cycles it is assumed that all the Pu in the system is tetravalent Pu, which is extracted by TBP as Pu(NO<sub>3</sub>)<sub>4</sub>.2TBP according to Reaction (3.4). In the complete partitioning and finish partitioning cycles, upon addition of a reducing agent, preferably hydroxylamine, Pu(IV) is reduced to Pu(III). Although the rate of reduction with hydroxylamine is slow compared to other suitable reductants mentioned in Section 3.3.4.b. [17], it will be assumed that in the finish partitioning contactor all the Pu in the system is trivalent Pu because the amount of Pu being dealt with in this contactor is very small and involvement of the kinetics of the Pu(IV)-Pu(III) reduction would considerably complicate the calculations.

(5) Fission products are represented by 3 groups: (a) Zr group (containing Zr, Nb, and Ce), (b) Ru group (containing Ru and Rh), and (c) RE group (containing rare earths and all others).

As seen in Figure 17, among the FPs, Zr and Ru show the highest distribution coefficients in TBP. Nb, Rh, and Ce display relatively low but still considerable distribution coefficients for TBP. Rare

earths are practically inextractable. Most of the others are absolutely inextractable. Since it is almost impossible to deal with FPs one by one in the solvent extraction calculations (even if equilibrium data were available for each FP), grouping them according to extractability behavior should be a reasonable way to approach the problem.

For the first group, the Zr group, the group's distribution coefficient is taken to be that of Zr. For the second group, the Ru group, the group's distribution coefficient is taken to be that of Ru. For the third group, the RE group, the group's distribution coefficient is taken to be that of rare earths. This way of grouping FPs will result in conservative values for the DFs from FPs because distribution coefficients of several FPs are overestimated.

(6) Actinides other than U and Pu are not taken into account.

Except for U and Pu, the only actinide that may be of importance is Np. However, because the relative amount of Np in SF is not significant and Np is not considered as a contaminant in the product streams, Np will not be taken into account in the flow sheet calculations. Qualitatively speaking, the route of Np in the coprocessing flow sheet is as follows. In the adjusted SF solution most of the Np will be in the inextractable pentavalent state and leave the codecontamination cycle with the FP waste stream [15]. Most of the Np extracted into the organic phase (tetravalent and hexavalent Np) in the codecontamination cycle will be washed back to the aqueous phase in

the partial partitioning cycle and leave the cycle in the U+Pu product stream. Almost all of the Np going into the finish partitioning cycle in the organic stream will remain in the organic phase during the finish partitioning because the reductant used to reduce Pu(IV) to Pu(III) will also reduce Np to the extractable Np(IV) [15]. This Np in the organic stream leaving the finish partitioning cycle, a very small portion of that in SF, will be stripped into the aqueous phase during the U stripping and leave the system with the aqueous U product.

(7) A column contactor is assumed to have discrete theoretical stages in each of which the equilibrium of phases is reached.

When the number of theoretical stages required for a certain separation job is known, the required height of the column contactor can be estimated by multiplying the number of the theoretical stages by the height equivalent to a theoretical stage (HETS). The HETS data are available in the literature for several contactor operating conditions and solutions [6,26]. In any case, pilot plant studies are required for accurately determining the dimensions of a contactor for a given set of operating conditions. Estimations of dimensions of contactors based on calculated numbers of theoretical stages and the HETS data available in the literature are assumed to be sufficient for preliminary design purposes.

(8) Expressions used to calculate the equilibrium concentrations of solutes and densities of phases have satisfactory but limited accuracy.

These expressions and their accuracy will be discussed in Section 4.1.2. and Appendices 10.1. and 10.3.

#### 4.1.2. Equilibrium Relations

The expressions for distribution coefficients of solutes of interest are presented in this section. The solutes under consideration are  $\text{HNO}_3$ , U(VI), Pu(IV), Pu(III), and Zr, Ru, and RE groups of fission products.

4.1.2.a.  $\text{HNO}_3$  and U(VI) Distribution Five correlations for distribution coefficients of  $\text{HNO}_3$  and U(VI) were tested using the experimental data of Codding, Haas, and Heumann [27]. These correlations are: (1) Goldberg, Benedict, and Levi [28], (2) Cleveland [16], (3) Mailen [29,30], (4) Katoch, Kiyose, and Yamamoto [31], and (5) Benedict, Pigford, and Levi [5]. The experimental data consisted of 32 measurements for distribution of  $\text{HNO}_3$  and U(VI) between aqueous solutions and 30 v/o TBP in a hydrocarbon; however, 6 of these measurements were not considered in the numerical comparisons because they did not seem to be accurate. Among the correlations tested, those derived by Goldberg, Benedict, and Levi [28] resulted in the lowest average deviation from the experimental data for both  $\text{HNO}_3$  and U(VI) distribution coefficients and were chosen to be used in this study.

The correlations of Goldberg, Benedict, and Levi are given in detail in Appendix 10.1.

The general form of the expressions of Goldberg, Benedict, and Levi is

$$f_1(x_H, x_U) = g_1(y_H, y_U) \quad (4.1)$$

$$f_2(x_H, x_U) = g_2(y_H, y_U) \quad (4.2)$$

where  $x_H$  = molality of  $\text{HNO}_3$  in aqueous phase,

$x_U$  = molality of U(VI) in aqueous phase,

$y_H$  = molality of  $\text{HNO}_3$  in organic phase,

and  $y_U$  = molality of U(VI) in organic phase.

These coupled non-linear equations can be solved implicitly for  $x_H$  and  $x_U$  when  $y_H$  and  $y_U$  are known, or for  $y_H$  and  $y_U$  when  $x_H$  and  $x_U$  are known. The Newton-Raphson method of successive approximations was used for solution of Eqs (4.1) and (4.2). See Appendix 10.2. for a detailed description of the method of solution.

Goldberg, Benedict, and Levi state [28]:

the results obtained from these expressions are restricted to aqueous solutions whose content of other cations is only a few percent of the sum of the hydrogen and uranyl ion content, to temperatures in the neighborhood of 25 °C, and to hydrocarbon diluents predominantly  $C_{12}$  napthenes and paraffins.

These restrictions are to be considered while specifying the process conditions.

4.1.2.b. Pu(IV) and Pu(III) Distribution      Distribution of  
Pu(IV) was predicted using the following expression [5].

$$\frac{y_{P4}}{x_{P4}} = D_U [0.2 + 0.55V^{1.25} + \frac{0.0074(x_N)^2}{(1 - 0.031x_N - 0.0104x_U - 0.006x_{P4} - 0.0001x_H)^2}] \\ \exp[2700(1/298 - 1/T)] \quad (4.3)$$

where  $D_U$ =distribution coefficient of U(VI),

$y_U$ =molarity of U(VI) in organic phase,

$x_U$ =molarity of U(VI) in aqueous phase,

$y_{P4}$ =molarity of Pu(IV) in organic phase,

$x_{P4}$ =molarity of Pu(IV) in aqueous phase,

$x_N$ =molarity of nitrate ion in aqueous phase,

$x_H$ =molarity of hydrogen ion in aqueous phase,

$v$ =volume fraction of TBP in solvent phase,

and  $T$ =temperature in  $^{\circ}\text{K}$ .

Eq. (4.3) is plotted in Figure 9 for temperatures of 25, 40, and  $55^{\circ}\text{C}$ .

For Pu(III) distribution, Eqs. (4.4), (4.5), and (4.6) were obtained by a least squares fit to the relevant curve in Figure 7.

$$\frac{y_{P3}}{x_{P3}} = D_U(0.112 - 0.038x_N) \quad (4.4)$$

for  $x_N \leq 2.9$ ,

$$\frac{y_{P3}}{x_{P3}} = D_U(6.2819E-3 - 1.5455E-3x_N) \quad (4.5)$$

for  $2.9 \leq x_N \leq 4.06$ ,

$$\frac{y_{P3}}{x_{P3}} = 7.17E-6D_U \quad (4.6)$$

for  $x_N \geq 4.06$ ,

where  $D_U$ =distribution coefficient of U(VI),

$y_{P_3}$ =molarity of Pu(III) in organic phase,  
 $x_{P_3}$ =molarity of Pu(III) in aqueous phase,  
and  $x_N$ =molarity of nitrate ion in aqueous phase.

4.1.2.c. Distribution of Fission Products      Distribution of  
fission products were predicted from the following expressions, derived  
by least squares fits to the relevant curves in Figure 7.

$$\frac{y_{Zr}}{x_{Zr}} = 0.18585(0.438-y_U)+\exp(-7.419+0.865x_H) \quad (4.7)$$

$$\frac{y_{Ru}}{x_{Ru}} = 0.3724(0.438-y_U)+\exp(-4.33589-0.7856x_H) \quad (4.8)$$

$$\frac{y_{RE}}{x_{RE}} = 0.00043+0.04904(0.355875-y_U) \quad (4.9)$$

for  $y_U \leq 0.355875$ ,

$$\frac{y_{RE}}{x_{RE}} = 0.0003 \quad (4.10)$$

for  $y_U > 0.355875$ ,

where  $y_U$ =molarity of U(VI) in organic phase,  
 $x_H$ =molarity of hydrogen ion in aqueous phase,  
 $y_{Zr}$ =molarity of Zr group in organic phase,  
 $x_{Zr}$ =molarity of Zr group in aqueous phase,  
 $y_{Ru}$ =molarity of Ru group in organic phase,

$x_{Ru}$ =molarity of Ru group in aqueous phase,  
 $y_{RE}$ =molarity of RE group in organic phase,  
and  $x_{RE}$ =molarity of RE group in aqueous phase.

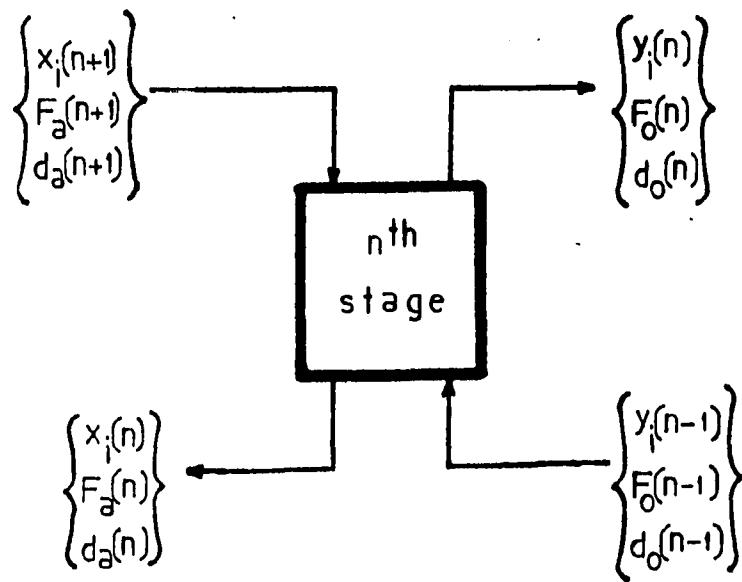
#### 4.1.3. Flow Rate and Density Calculations

During a solvent extraction process mass transfer between phases occurs causing densities of phases to change, which is accompanied by changes in volumetric flow rates of phases. For a complete evaluation of a solvent extraction cascade it is required to take into account flow rate changes.

Neglecting transfer of  $H_2O$  into the TBP phase and of TBP into the  $H_2O$  phase, relative volumetric flow rates of streams in a solvent extraction cascade can be calculated based on changes in densities of phases. The calculational procedure applied and the expressions for calculating aqueous and organic phase densities are presented in Appendices 10.3. and 10.5.

#### 4.1.4. Cascade Calculations

4.1.4.a. Calculation of a Single Stage A single stage equilibrium is shown in Figure 14. When compositions and relative flow rates of the two streams at either end of a stage are given, compositions and relative flow rates of both streams at the other end can be computed using the equilibrium relations and mass balance expressions.




---

y=molarity in organic phase  
 x=molarity in aqueous phase  
 F=relative volumetric flow rate  
 d=density

---

Subscripts: a=aqueous phase  
 o=organic phase  
 i=each solute of interest

---

Numbers in parentheses=the number of the stage that the stream under consideration is leaving (note that it is assumed that stage numbers increase upward).

---

**FIGURE 11. Designation of Streams in Single Stage Equilibrium**

For given  $y_i(n-1)$ ,  $F_{Or}(n-1)$ ,  $x_i(n)$ , and  $F_{aq}(n)$  (see Figure 11 for nomenclature), the calculational procedure is as follows.

1. Calculate  $d_{Or}(n-1)$  and  $d_{aq}(n)$  from the density correlations (Appendix 10.3.).
2. Calculate  $y_i(n)$  from the equilibrium relations (Section 4.1.2. and Appendices 10.1. and 10.2.).
3. Calculate  $d_{Or}(n)$  from the organic-phase density correlation (Appendix 10.3.).
4. Calculate  $F_{Or}(n)$  as described in Appendix 10.5.
5. Make an initial guess for  $F_{aq}(n+1)$ , calculate  $x_i(n+1)$  from mass balance, calculate  $F_{aq}(n+1)$  as described in Appendix 10.5., and successively displace  $F_{aq}(n+1)$  until it converges.

For given  $y_i(n)$ ,  $F_{Or}(n)$ ,  $x_i(n+1)$ , and  $F_{aq}(n+1)$ , the calculational procedure is very similar to that above.

1. Calculate  $d_{Or}(n)$  and  $d_{aq}(n+1)$  from the density correlations.
2. Calculate  $x_i(n)$  from the equilibrium relations.
3. Calculate  $d_{aq}(n)$  from the aqueous-phase density correlation.
4. Calculate  $F_{aq}(n)$ .
5. Make an initial guess for  $F_{Or}(n-1)$ , calculate  $y_i(n-1)$  from mass balance, calculate  $F_{Or}(n-1)$ , and successively displace  $F_{Or}(n-1)$  until it converges.

It should be noted that because the equilibrium relations for U and  $HNO_3$  employ molalities, it is required to convert molarities of U

and  $\text{HNO}_3$  to molalities and vice versa before and after applying the equilibrium relations. Molarity to/from molality conversion for aqueous and organic phases is described in Appendix 10.4.

**4.1.4.b. Calculation of a Simple Cascade** A simple cascade is a cascade performing only one of the basic processes (extraction, scrubbing, or stripping) in the solvent extraction method. This implies that all the streams, including feed solution, enter or leave a simple cascade from either end, as shown in Figure 15. In the Purex method the stripping process is usually performed in a simple cascade.

When the number of stages and compositions and relative flow rates of the two streams at either end are given, compositions and relative flow rates of all the other streams leaving and entering each stage of a simple cascade can be computed by subsequently applying the single-stage calculation, described in Section 4.1.4.a., to each stage throughout the cascade.

**4.1.4.c. Calculation of a Compound Cascade** A compound cascade is a cascade that performs two of the basic processes of the solvent extraction method at one time. Aqueous or organic feed solution enters a compound cascade near the midpoint. An extraction-scrubbing compound cascade with aqueous feed is shown in Figure 12.

**FIGURE 12. An Extraction-Scrubbing Compound Cascade**

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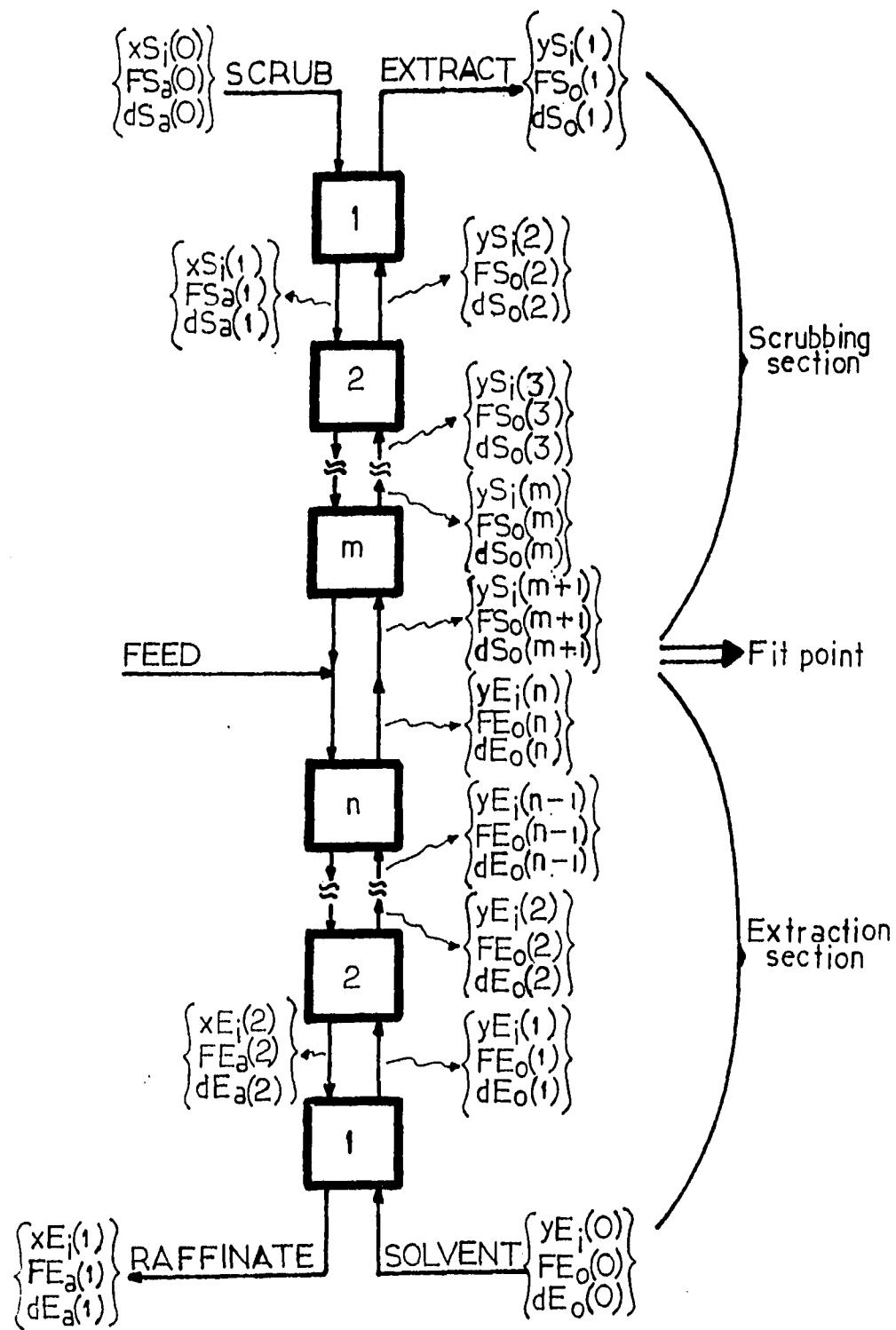
**First letters:** x=molarity in aqueous phase  
y=molarity in organic phase  
F=relative volumetric flow rate  
d=density

**Second letters:** S=scrubbing section  
E=extraction section

**Subscripts:** i=each solute of interest  
a=aqueous phase  
o=organic phase

**Numbers in parentheses**=the number of the stage that the stream under consideration is leaving (note that it is assumed that in the extraction section there are n stages and stage numbers increase upward, in the scrubbing section there are m stages and stage numbers increase downward).

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In the Purex method decontamination and partitioning (complete, partial, or finish) cycles usually consist of a compound cascade with aqueous and organic feed, respectively.

As seen in Figure 12, in an extraction-scrubbing cascade with aqueous feed, the organic stream leaving the extraction section from the top is in fact the same stream entering the scrubbing section from the bottom. Specification of numbers of extracting and scrubbing stages ( $n$  and  $m$ , respectively) determines the location of "organic fit point" ("aqueous feed point" as well), at which the organic streams leaving the extraction section and entering the scrubbing section should be identical, that is,  $FE_{Or}(n) = FS_{Or}(m+1)$  and  $yE_i(n) = yS_i(m+1)$  for each  $i$  (see Figure 12 for nomenclature).

In a compound cascade calculation, the objective is to compute compositions and relative flow rates of extract and raffinate streams for given numbers of extracting and scrubbing stages and compositions and relative flow rates of feed, solvent, and scrub streams.

In the case of aqueous feed this problem can be approached in the following way.

1. Guess compositions and relative flow rates of extract and raffinate streams.
2. Apply the simple-cascade calculation, described in Section 4.1.4.b., to the extraction and scrubbing sections separately for computing compositions and relative flow rates of the aqueous and organic streams at the fit point.

3. If compositions and relative flow rates of the organic streams at the fit point are not identical, properly revise compositions and/or relative flow rates of extract and/or raffinate phases and repeat the simple-cascade calculations.

4. Repeat step 3 until the fit is accomplished.

Because it is not possible to relate the "guessed" to the "calculated" by numerical expressions, the guessing part of the procedure cannot be incorporated into a computer program, but should be done manually by the operator observing guessed-calculated relations.

Another difficulty arises from the fact that composition and relative flow rate of feed solution should be at least roughly prespecified. After the completion of a compound cascade calculation, composition and relative flow rate of feed solution can be calculated from mass balance at the aqueous fit point. If calculated values significantly differ from prespecified ones, it will be required to repeat the whole trial-error procedure for varied compositions and/or relative flow rates of extract and/or raffinate phases, until calculated composition and relative flow rate of feed solution fit prespecified values. This difficulty can be overcome in the following manner.

- Prespecified composition of feed solution: Initial guesses for compositions of extract and raffinate streams are made considering prespecified composition of feed solution and expected recoveries of the solutes. Then, if guessed

concentrations of U and Pu in the extract stream and of fission products in the raffinate stream are held constant during the trial-error procedure, calculated feed composition will approximate prespecified feed composition to a satisfactory extent. The reason for this is that, as discussed in Section 3.3.2., most of the U and Pu in the aqueous feed will transfer into the organic phase and leave the cascade in the extract stream while most of the fission products in the aqueous feed remain in the aqueous phase and leave the cascade in the raffinate stream.

- Prespecified relative flow rate of feed solution: The relative flow rate of the aqueous phase leaving the scrubbing section is nearly equal to that of the scrub solution because in the scrubbing section the rate of mass transfer between the phases is not high enough to give rise to significant changes in flow rates of phases. However, in the extraction section, where the primary mass transfer occurs, the relative flow rate of the aqueous phase will decrease considerably while it proceeds downward. The rate of decrease in the aqueous-phase flow rate while progressing down in the extraction section can be predicted by a simple-cascade calculation. Having predicted approximate flow rates of the aqueous phases at the feed point, it is possible to estimate the relative flow rate of the feed solution before starting the compound-cascade calculation.

It should be noted that for preliminary design purposes rigorous prespecification of feed composition and relative flow rate is not required; small changes in prespecified values are acceptable.

As mentioned earlier, a compound-cascade calculation can be performed for given numbers of extracting and scrubbing stages. In practice, numbers of extracting and scrubbing stages are unknown. Therefore, a compound-cascade calculation is done based on assumed numbers of extracting and scrubbing stages and may have to be repeated for different numbers of extracting and scrubbing stages until the resulting recoveries and decontamination factors are found satisfactory.

In the case of an organic feed solution, all the procedures described above for aqueous feed remain unchanged in principle. However, because organic feed solution enters a compound cascade from the organic-stream side, fits of aqueous phases instead of organic phases are sought.

Two separate computer programs were developed for calculation of a simple extraction cascade with given solvent and raffinate streams and for calculation of a simple scrubbing cascade with given scrub and extract streams. These were incorporated into a main program for a compound-cascade calculation.

#### 4.2. Results for the Coprocessing Flow Sheet

The simple cascade and compound cascade calculations, described in Sections 4.1.4.b. and 4.1.4.c., were applied to the cycles of the proposed Purex flow sheet, depicted in Figure 10. The results obtained are presented in this section.

##### 4.2.1. Results for the Codecontamination Cycle

The results obtained for the codecontamination cycle are shown in Figure 13 and Table 6.

The following prespecifications were made for the codecontamination cycle. Solvent used is 30 v/o TBP in n-dodecane. In the feed solution mole ratios of U to Pu, U to FP, RE group to Ru group, and RE group to Zr group are 106.0, 13.5, 6.46, and 2.69, respectively. These are the mole ratios in a typical PWR fuel exposed to a burnup of 33,000 MWD/MT [5]. Concentrations of U and HNO<sub>3</sub> in the feed solution are 1.7 to 2.0 M and 3.0 to 3.5 M, respectively. The scrub solution is a 2.9 to 3.0 M HNO<sub>3</sub> solution. The relative flow rates of the solvent and scrub solution are 5.50 and 1.00, respectively, based on a feed solution flow rate of 1.00. Recoveries expected for U and Pu are above 99.5 %, with U recovery being a little greater than Pu recovery.

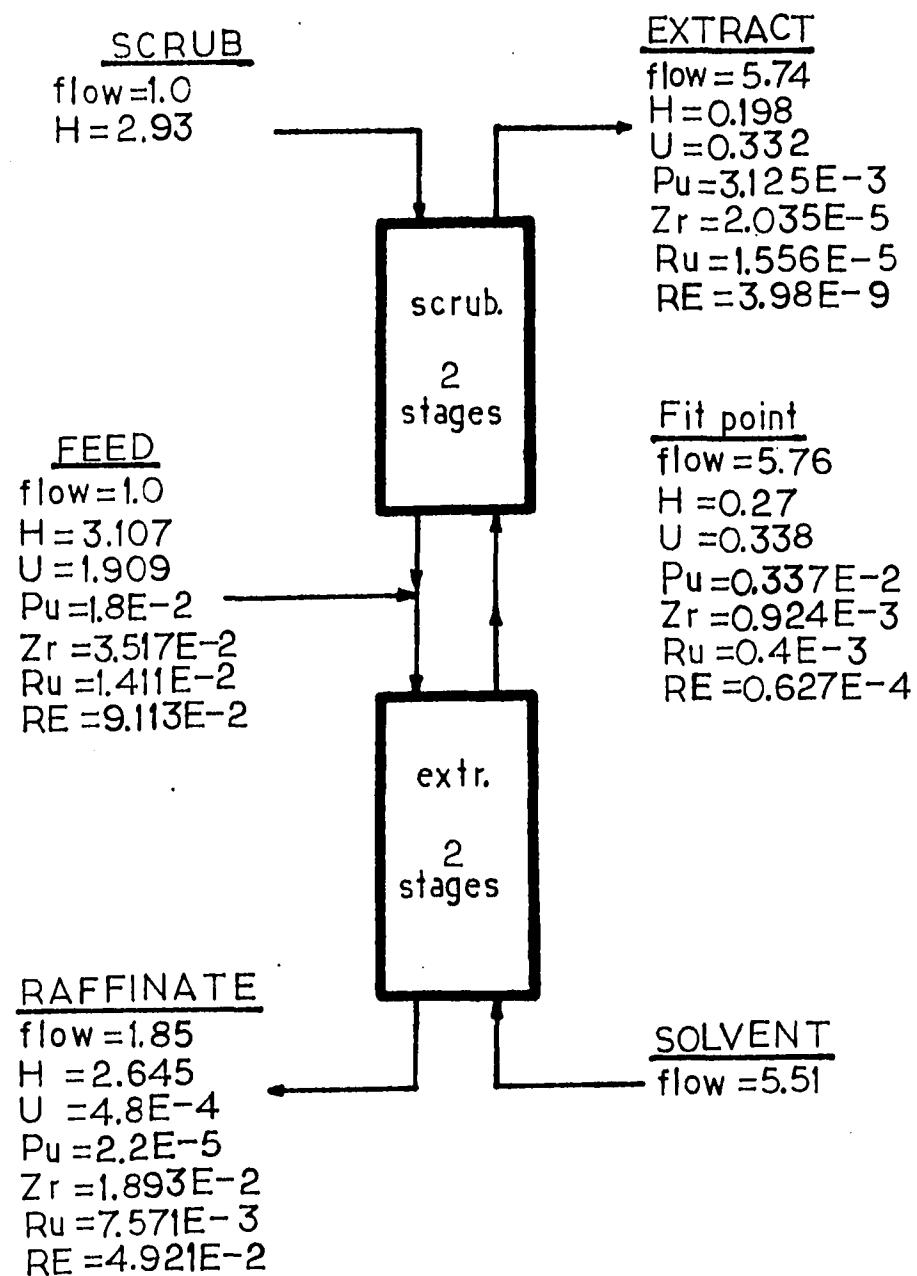


FIGURE 13. Results for the Codecontamination Cycle

TABLE 6. Recoveries and DFs Obtained in Codecontamination Cycle

U recovery = 99.95 %
Pu recovery = 99.77 %
DF <sub>U-Zr</sub> = 300
DF <sub>U-Ru</sub> = 160
DF <sub>U-RE</sub> = 4.0E+6

#### 4.2.2. Results for the Partial Partitioning Cycle

The results obtained for the partial partitioning cycle are presented in Figure 14.

In the partial partitioning cycle FPs are not considered in the calculations because, as will be shown later, after the first cycle the additional DF<sub>U-FP</sub> required is around 12 and the required DF<sub>Pu-FP</sub> is already achieved. It can easily be shown that a DF<sub>U-FP</sub> much greater than 12 will readily be obtained in the partial partitioning cycle. There is no need to calculate DF<sub>U-FP</sub> and DF<sub>Pu-FP</sub> for the partial partitioning cycle.

The two important specifications to be ensured in the partial partitioning cycle are (1) the aqueous U+Pu product stream should contain 5 to 6 % Pu and (2) at least 90 to 95 % of the Pu in the organic feed solution should be transferred to the aqueous product solution. Several numerical fits were needed to meet these

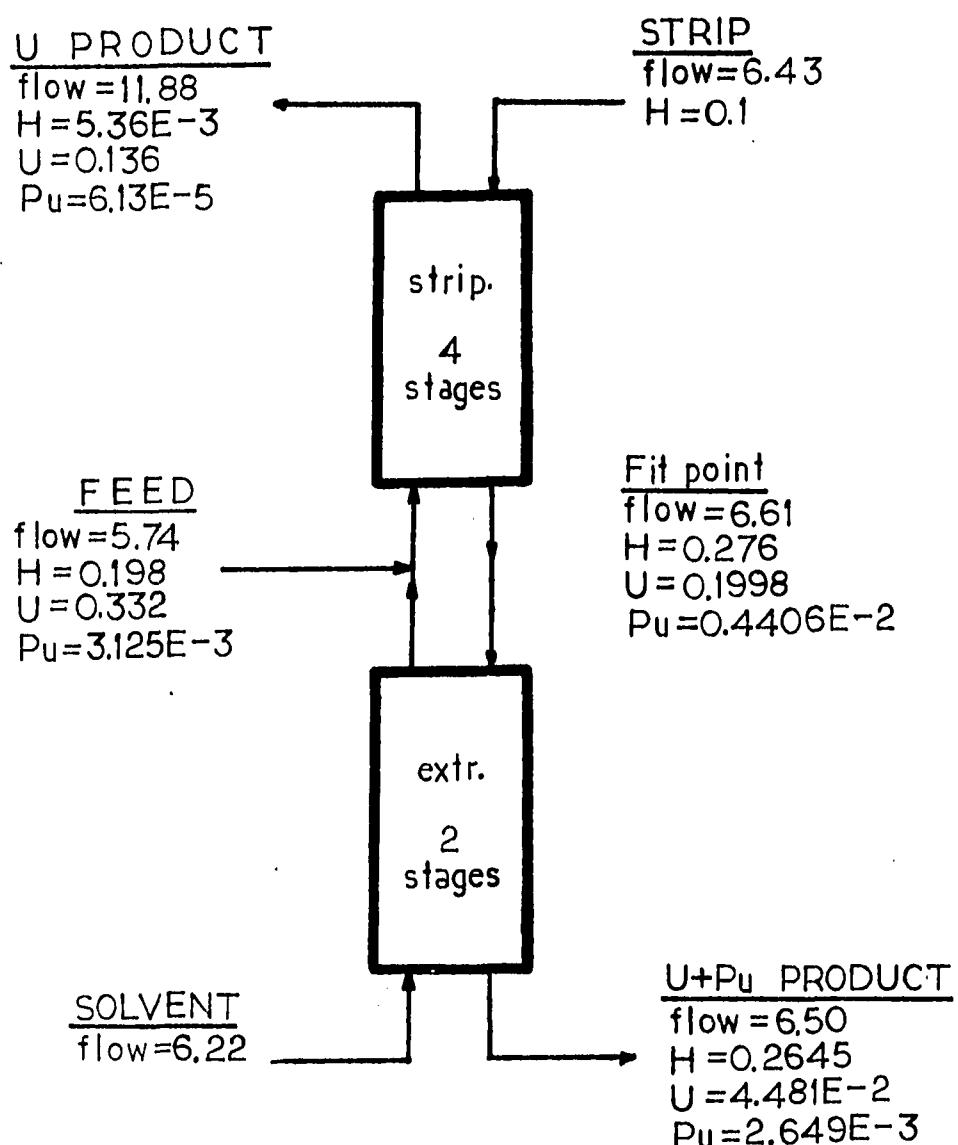


FIGURE 14. Results for the Partial Partitioning Cycle

specifications. The plots in Figure 15, showing how U-to-Pu mole ratio in the aqueous product stream and Pu recovery into the aqueous product stream change with relative flow rates and number of extracting and scrubbing stages, were derived from these numerical fits.

Other specifications adopted for the partial partitioning cycle are as follows. Solvent used is again 30 v/o TBP in n-dodecane. The scrub solution is a 0.1 M HNO<sub>3</sub> solution. Relative flow rates of the solvent and scrub solution are 1.0 to 1.2 based on an organic feed flow rate of 1.00.

#### 4.2.3. Results for the Finish Partitioning Cycle

The results obtained for the finish partitioning cycle are presented in Figure 16.

#### 4.2.4. Results for the U Stripping Cycle

The results obtained for the U stripping cycle are shown in Figure 17.

#### 4.2.5. Discussion of the Results

For 150-day and 10-year cooled fuels the activities and FP contents of the several streams in the coprocessing flow sheet are given in Table 7. As can be seen in Table 7, for 10-year cooled fuel the U and Pu product specifications set in Section 2.3. are met by the 4-cycle coprocessing flow sheet; no purification cycles are required.

For the 150-day cooled fuel, the FP activity in the organic product stream leaving the first cycle (9430.0  $\mu$ Ci/g U) is 1275 times

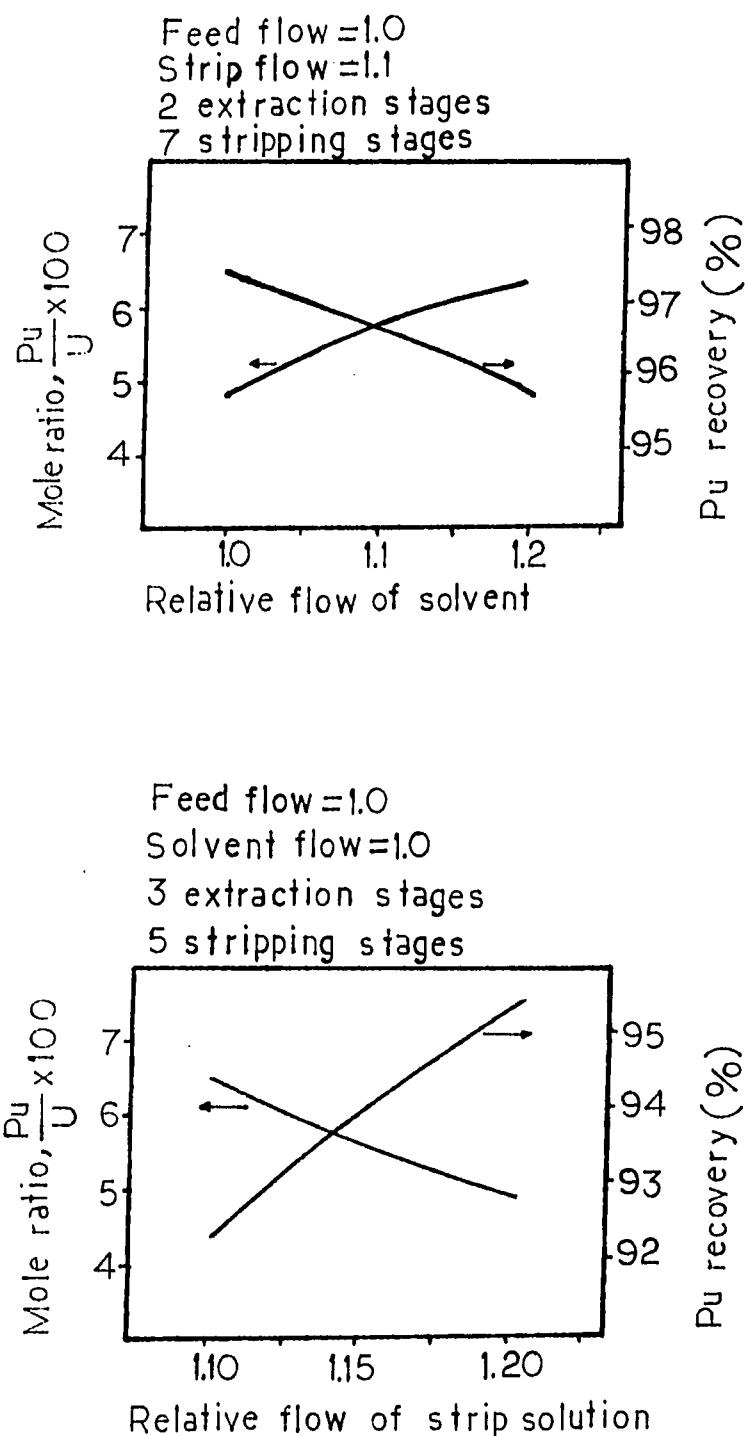


FIGURE 15. U-to-Pu Mole Ratio in the U+Pu Product and Pu Recovery as a Function of Flow Rates and Number of Scrubbing Stages in the Partial Partitioning Cycle

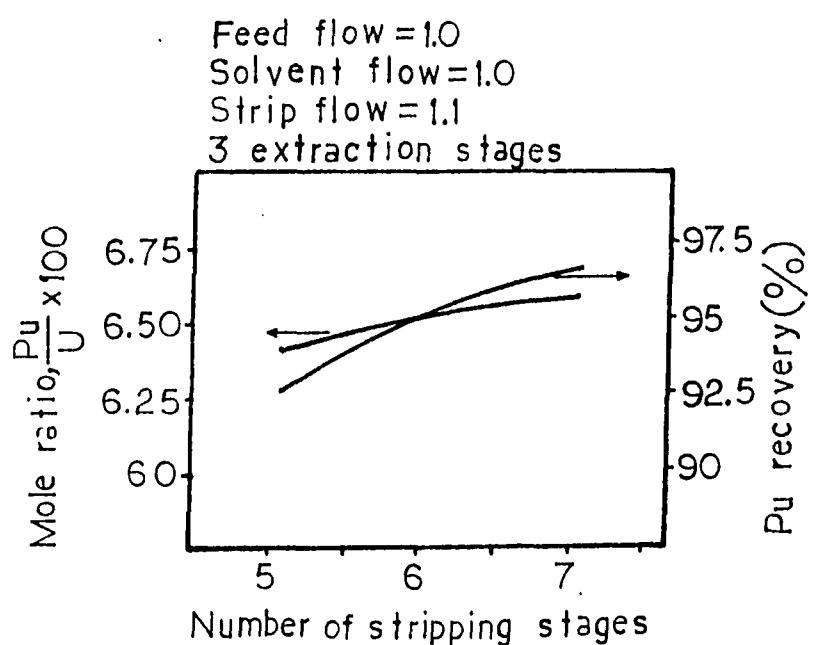
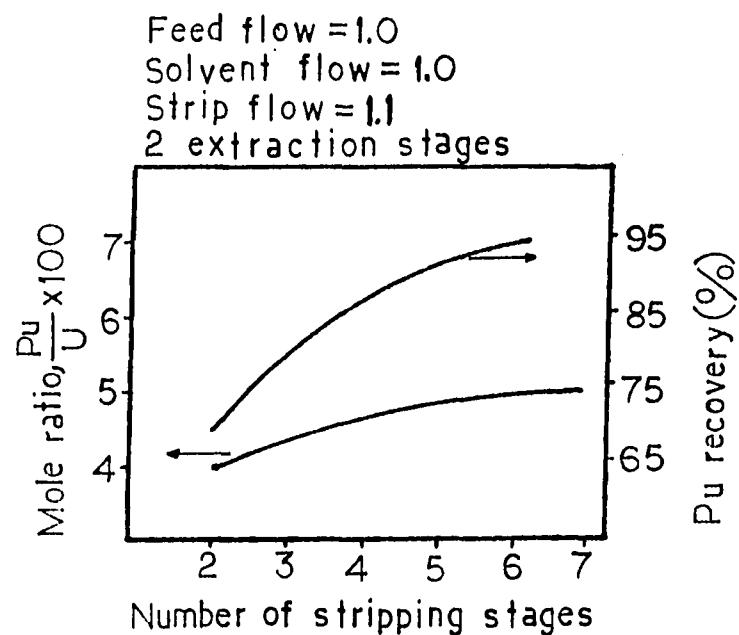


FIGURE 15 (continued)

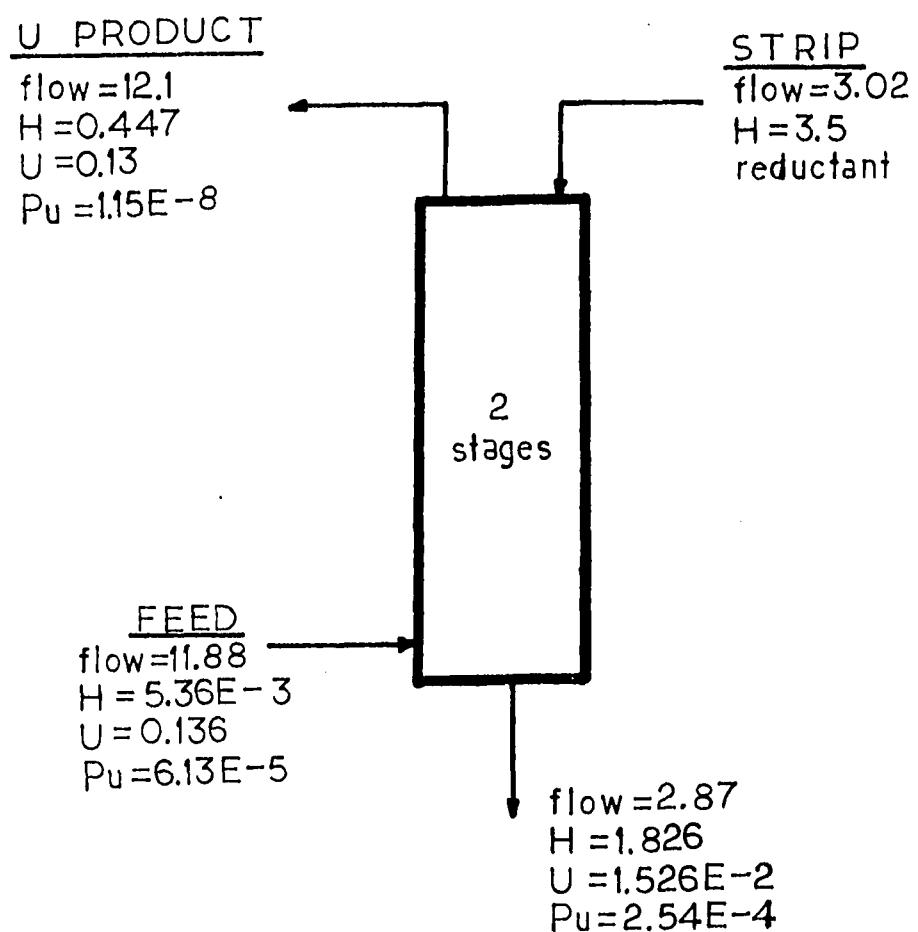


FIGURE 16. Results for the Finish Partitioning Cycle

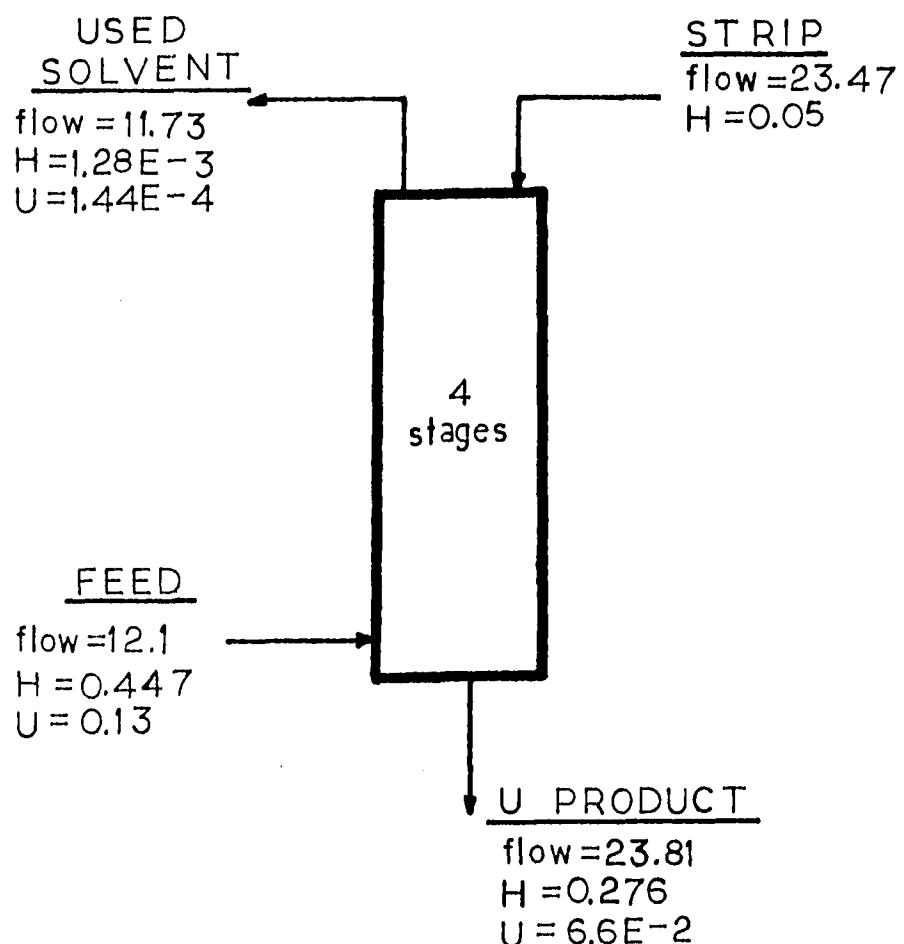


FIGURE 17. Results for the U Stripping Cycle

higher than that for the 10-year cooled fuel ( $7.4 \mu\text{Ci/g U}$ ), although the FP activity of the 150-day cooled fuel is only 13 times higher than that of the 10-year cooled fuel. This drastic difference stems from the fact that in the 10-year cooled SF almost all of the overall FP activity is attributed to the RE group, which consists of practically inextractable FPs, whereas in 150-day cooled SF the Zr and Ru groups, which contain relatively extractable FPs, are responsible for more than one third of the overall FP activity. For the 150-day cooled SF, two purification cycles should be added to achieve the additional decontamination of U from FPs.

It should also be noted that for 150-day cooled fuel the amount of Pu  $\beta$  activity remaining in the organic U-product stream leaving the finish partitioning cycle is nearly two times higher than the permissible level ( $0.68 \mu\text{Ci/g U}$ ); see Section 2.3.1.

The results of these calculations therefore show that a relatively simple, 4-cycle process as adopted for this work is sufficient to achieve the desired goals of separation: isolation of U and U+Pu of sufficient purity to be directly reusable, and recovery of U and Pu with a very high process yield.

TABLE 7. Activities of Several Streams in the Coprocessing Flow Sheet  
for 150-day and 10-year Cooled Fuel

		ACTIVITY ( $\mu\text{Ci/g U}$ )			
		Stream <sup>a</sup>			
Contaminant	Cooling Period	codec a. f.	codec o. p.	p. p. o. p.	f. p. o. p.
Zr	150-day	8.40E5	2807	---	---
	10-year	2.86	9.50E-3	---	---
Ru	150-day	1.05E6	6626	---	---
	10-year	1153	7.30	---	---
RE	150-day	2.50E6	0.626	---	---
	10-year	3.30E5	0.083	---	---
FP total	150-day	4.38E6	9430	---	---
	10-year	3.33E5	7.40	---	---
Pu- $\beta$	150-day	1.08E5	1.08E5	5167	1.034
	10-year	6.53E4	6.53E4	3125	0.610
Pu-a		4732	4732	226	0.045

<sup>a</sup> codec=codecontamination, p. p.=partial partitioning  
f. p.=finish partitioning, a. f.=aqueous feed, o. p.=organic product.

## 5. PLANT DESIGN

### 5.1. Process Description

A simplified flow chart for the fuel reprocessing system is exhibited in Figure 18.

The following process areas are contained in the plant.

1. Fuel receipt and storage
2. Shear-leach and feed preparation
3. Solvent extraction separations
4. Calcination of U product solution
5. Calcination of U+Pu product solution
6. Used solvent treatment
7. High level waste (HLW) treatment
8. Low level waste (LLW) treatment and acid recovery
9. Solid intermediate level waste treatment
10. Off-gas treatment

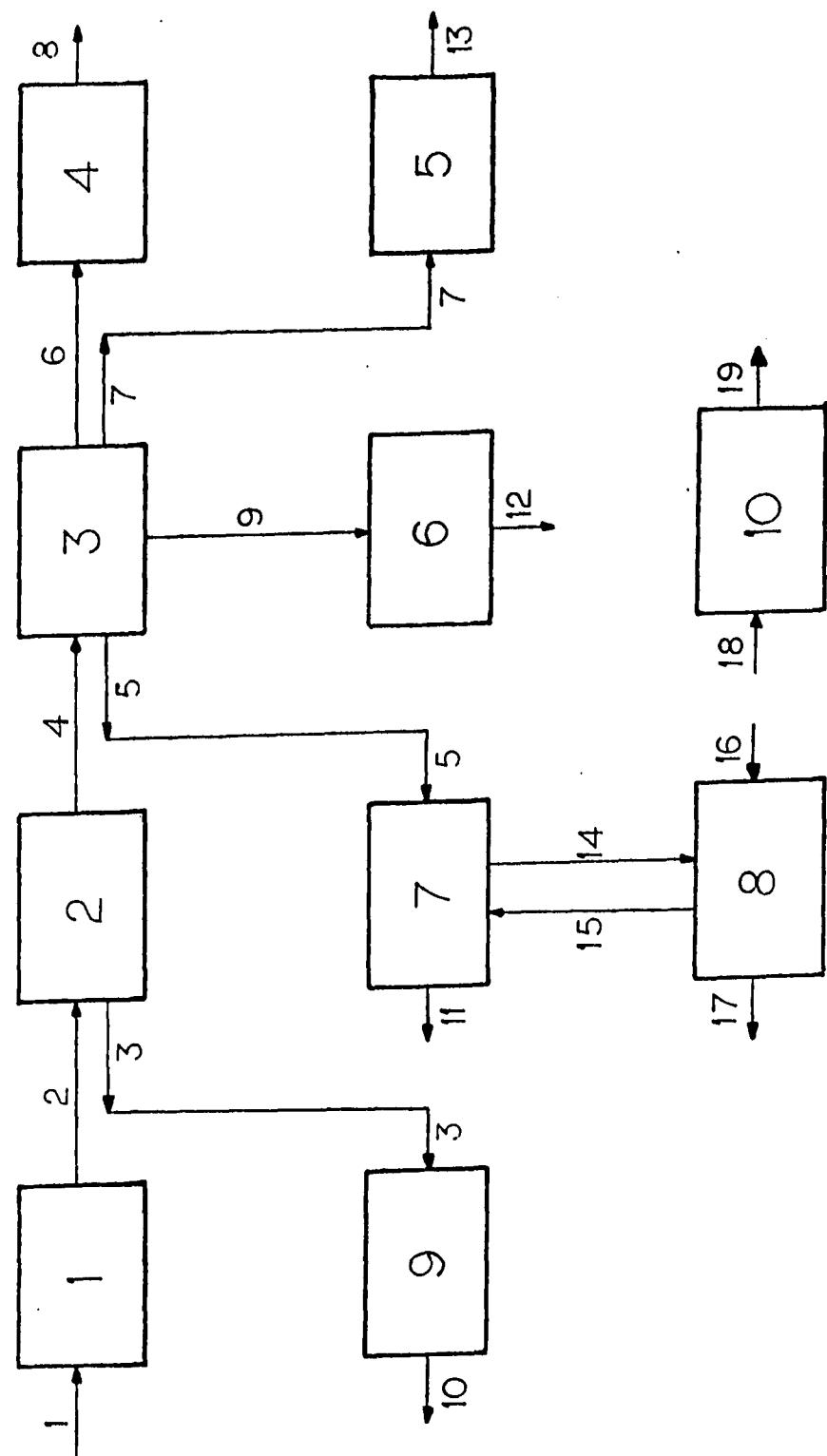
This section describes the above processes.

#### 5.1.1. Fuel Receipt and Storage

Spent fuel assemblies are received in shielded casks at the fuel receipt port of the plant. The cask is washed down, inspected for damage, monitored for contamination, and then transferred to a position beneath a cask unloading cell. The cask lid is opened and fuel assemblies are removed into the cask unloading cell. After inspection, the assemblies are placed in baskets and moved into an air-cooled

FIGURE 18. A Simplified Flow Chart for the Reprocessing System

Step no.	Step	Stream no.	Stream
1	Fuel receipt and storage	1	SF transportation cask
2	Shear-leach and feed preparation	2	SF assemblies
3	Solvent extraction separations	3	Solid ILW waste
4	Calcination of U product solution	4	SF solution
5	Calcination of U+Pu product solution	5	HLW solution
6	Used solvent treatment	6	U product solution
7	HLW treatment	7	U+Pu product solution
8	LLW treatment and acid recovery	8	Solidified U product
9	Solid ILW treatment	9	Used solvent
10	Off-gas treatment	10	Cemented solid ILW
		11	Glassified HLW
		12	Cleaned solvent
		13	Solidified U+Pu product
		14	Decontaminated HNO <sub>3</sub>
		15	Contaminated HNO <sub>3</sub>
		16	LLW solution
		17	Recovered HNO <sub>3</sub>
		18	Off-gases
		19	Cleaned off-gases



storage cell. The emptied cask is inspected, decontaminated, if necessary, and shipped back. Liquid wastes arising from washdown and decontamination operations are monitored and discharged to a liquid waste treatment system.

#### 5.1.2. Shear-Leach and Feed Preparation

A flow chart of the shear-leach and feed preparation process is shown in Figure 19.

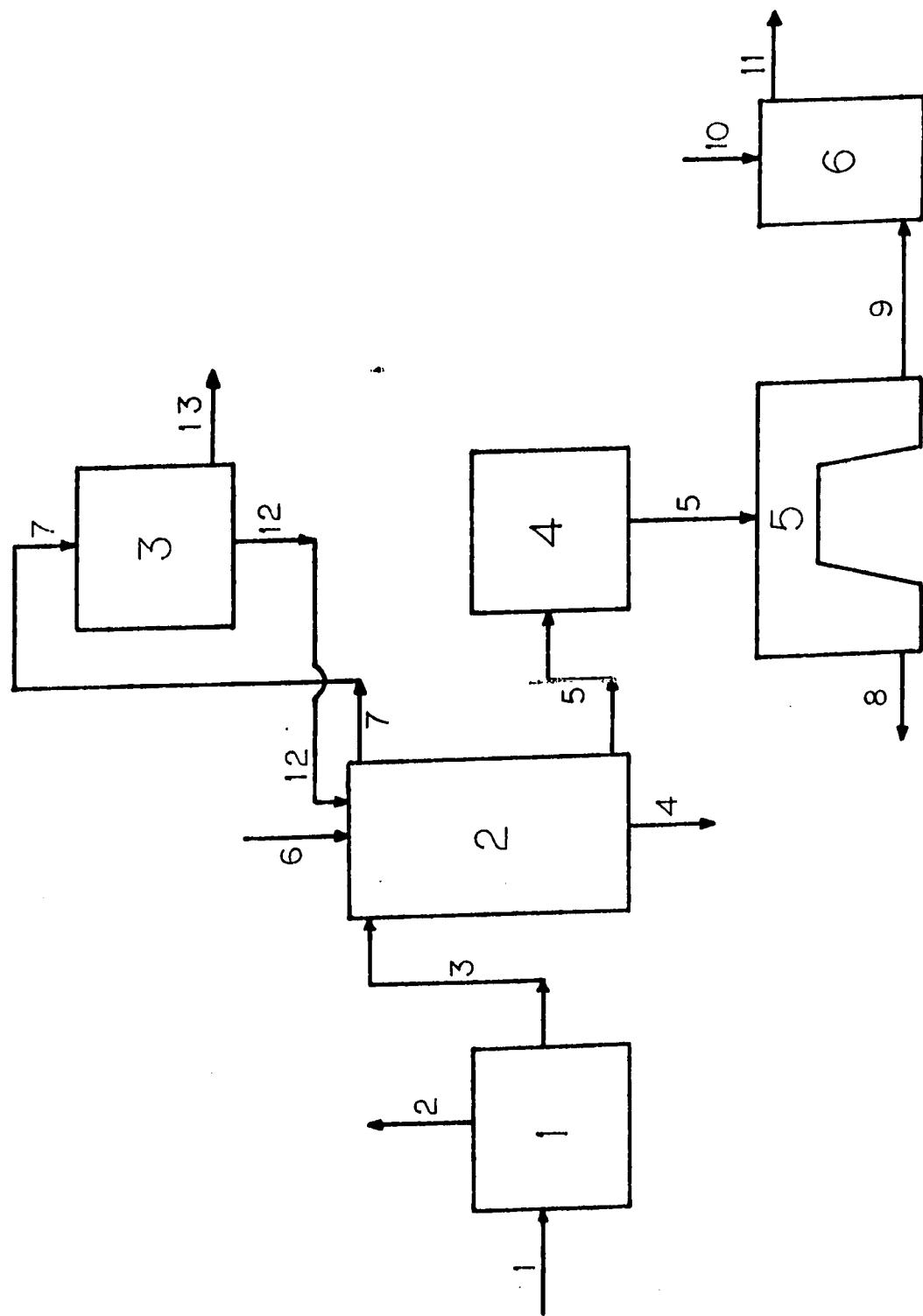
Fuel assemblies are first sheared into 2 to 4 cm. pieces by a hydraulic shear exerting up to 320 tons of force on the shear blade [32]. Sheared fuel assemblies are fed into one of the leachers by a diverter. In the leacher, sheared fuel is contacted with a  $\text{HNO}_3$  solution. U, Pu, other actinides, and fission products in the spent fuel are dissolved in  $\text{HNO}_3$  leaving the cladding hulls and fuel hardware as solid. Less than 0.05 % of U and Pu in the fuel is expected to remain with the solids [14,15]. The solids from the leacher are monitored for their U and Pu content and sent to the solid ILW treatment system.

The leacher solution is transferred into an accountability tank where input quantities of U and Pu are determined. Then the solution is centrifuged to remove suspended solids in it, which are sent to the solid ILW treatment process, and fed into a feed adjustment tank. In the feed adjustment step acidity of the solution and concentrations and oxidation states of the solutes are adjusted to obtain a suitable solution for the solvent extraction process. As mentioned in

FIGURE 19. Shear-Leach and Feed Preparation Process

Step no.	Step	
1	Shear	
2	Leacher	
3	Downdraft condenser	
4	Accountability	
5	Centrifugation	
6	Feed adjustment	
Stream no.	Stream	Contents <sup>a</sup>
1	SF elements	U, Pu, other actinides, FP, cladding, fuel hardware
2	Off-gases from shear	FP gases
3	Sheared fuel elements	Same as Stream 1
4	Solid ILW waste	Cladding, fuel hardware, FP, (U), (Pu), (other actinides)
5	SF solution	HNO <sub>3</sub> , U, Pu, FP, other actinides
6	HNO <sub>3</sub> solution	
7	Off-gases from leaching	HNO <sub>3</sub> and H <sub>2</sub> O fumes, NO <sub>x</sub> , FP gases
8	Filtrate from centrifuge	Suspended solids
9	Clarified SF solution	HNO <sub>3</sub> , FP, U, Pu, other actinides
10	Valence adjusting NaNO <sub>2</sub> agent	
11	Adjusted SF solution	HNO <sub>3</sub> , FP, U, Pu, other actinides
12	Condensate	HNO <sub>3</sub> solution
13	Non-condensible off-gases	FP gases, NO <sub>x</sub>

<sup>a</sup> Materials in parentheses are present in trace quantities.



Chapter 3, the desirable valence states of U and Pu in the solvent extraction feed solution are 6+ and 4+, respectively. These valence states can be obtained by addition of NaNO<sub>2</sub> to the spent fuel solution [13,25]. Composition of the feed solution adopted in this study is as follows: U(6+) = 1.9089 M, Pu(4+) = 1.7988E-2 M, FPs = 1.404E-1 M, and HNO<sub>3</sub> = 3.107 M. Although lower U and HNO<sub>3</sub> concentrations in the feed solution have been more often used in the existing flow sheets, it has been shown that high concentrations of U and HNO<sub>3</sub> in the feed solution results in a decrease in the amount and rate of formation of zirconium dibutylphosphate (a TBP degradation product) precipitate, which can be a major problem when mixer-settler contactors are employed in the solvent extraction system [15]. A high acidity is also favorable with regard to low Pu losses [15].

Off-gases from the leaching, which contain HNO<sub>3</sub> and H<sub>2</sub>O vapors, nitrogen oxides (NO<sub>x</sub>), and FP gases, are passed through a downdraft condenser to absorb NO<sub>x</sub>. Oxygen or air is fed into the downdraft condenser to improve absorption by converting NO to NO<sub>2</sub>. HNO<sub>3</sub> solution recovered in the downdraft condenser is sent back to the leachers. Absorption of NO<sub>x</sub> gases in the leacher off-gases reduces HNO<sub>3</sub> makeup and prevents acid contamination of environment. NO<sub>x</sub> gases can also interfere with iodine and rare gas retention processes and reduce performance and life of particulate filters in the off-gas treatment system [32]. Off-gases from the shearing are mixed with all other vessel off-gases in the plant and routed to the off-gas treatment process.

### 5.1.3. Solvent Extraction Separations

The solvent extraction system consists of 4 cycles: codecontamination, partial partitioning, finish partitioning, and U stripping. Descriptions of these cycles have been given in Chapter 4. A flow chart of the solvent extraction system is shown in Figure 20. Compositions and relative flow rates of the streams are given in Table 8.

The solvent extraction process generates the following streams, which are to be further processed.

- U product solution
- U+Pu product solution
- Used solvent
- High level waste solution

### 5.1.4. Calcination of U Product Solution

A flow chart of the U calcination process is exhibited in Figure 21. U product solution leaving the U stripping cycle is concentrated to a syrupy liquid in an evaporator system consisting of an evaporator, a deentrainment column, and an overhead condenser, and calcined into oxide form in a fluidized bed calciner. Calcined product, approximately  $\text{UO}_3$ , is packaged and sent to the U product storage and shipment area.

Condensate streams from the condensers of the evaporator and calciner, taken to be contaminated  $\text{HNO}_3$  solutions, are sent to the acid recovery process. Non-condensable off-gases from the condensers are

FIGURE 20. Solvent Extraction Separations

Step no.	Step
7	Solvent extraction (codecontamination)
8	Solvent extraction (partial partitioning)
9	Solvent extraction (finish partitioning)
10	Stripping
Stream no.	Stream
11	Adjusted SF solution
14	Organic solvent
15	HLW solution
16	Scrub solution
17	Extract phase from codecontamination
18	Solvent
19	U+Pu product solution
20	Scrub solution
21	Extract phase from partial partitioning
22	Raffinate phase from finish partitioning
23	Scrub solution
24	Extract phase from finish partitioning
25	U product solution
26	Strip solution
27	Used solvent

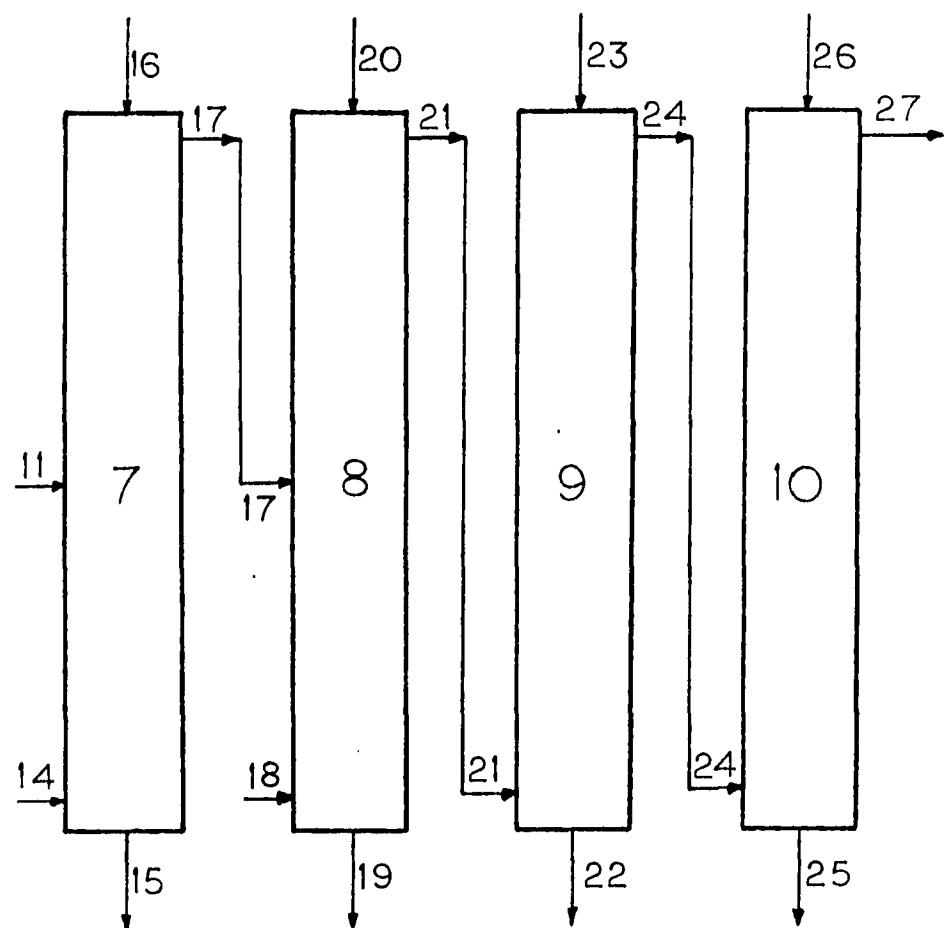


TABLE 8. Description of Streams in the Solvent Extraction System

Stream no.	Phase <sup>a</sup>	Relative <sup>b</sup> flow	HNO <sub>3</sub> moles/lt	U moles/lt	Pu moles/lt	FP moles/lt
13	Aqueous	1.00	3.11	1.91	1.8E-3	1.404E-1
14	Organic	5.51				
15	Aqueous	1.85	2.65	4.8E-4	2.2E-5	7.57E-2
16	Aqueous	1.00	2.93			
17	Organic	5.74	0.198	0.332	3.13E-3	3.59E-5
18	Organic	6.22				
19	Aqueous	6.50	0.264	4.48E-2	2.65E-3	Trace
20	Aqueous	6.43	0.10			
21	Organic	11.89	5.36E-3	0.136	6.13E-5	Trace
22	Aqueous	2.87	1.826	1.53E-2	2.54E-4	Trace
23 <sup>c</sup>	Aqueous	3.02	3.50			
24	Organic	12.10	0.447	0.13	1.15E-8	Trace
25	Aqueous	23.81	0.276	6.6E-2	Trace	Trace
26	Aqueous	23.47	0.05			
27	Organic	11.73	1.28E-3	1.44E-4	Trace	Trace

<sup>a</sup> Organic phase contains 30 volume % TBP in n-dodecane.  
 Aqueous phase is a HNO<sub>3</sub> solution.

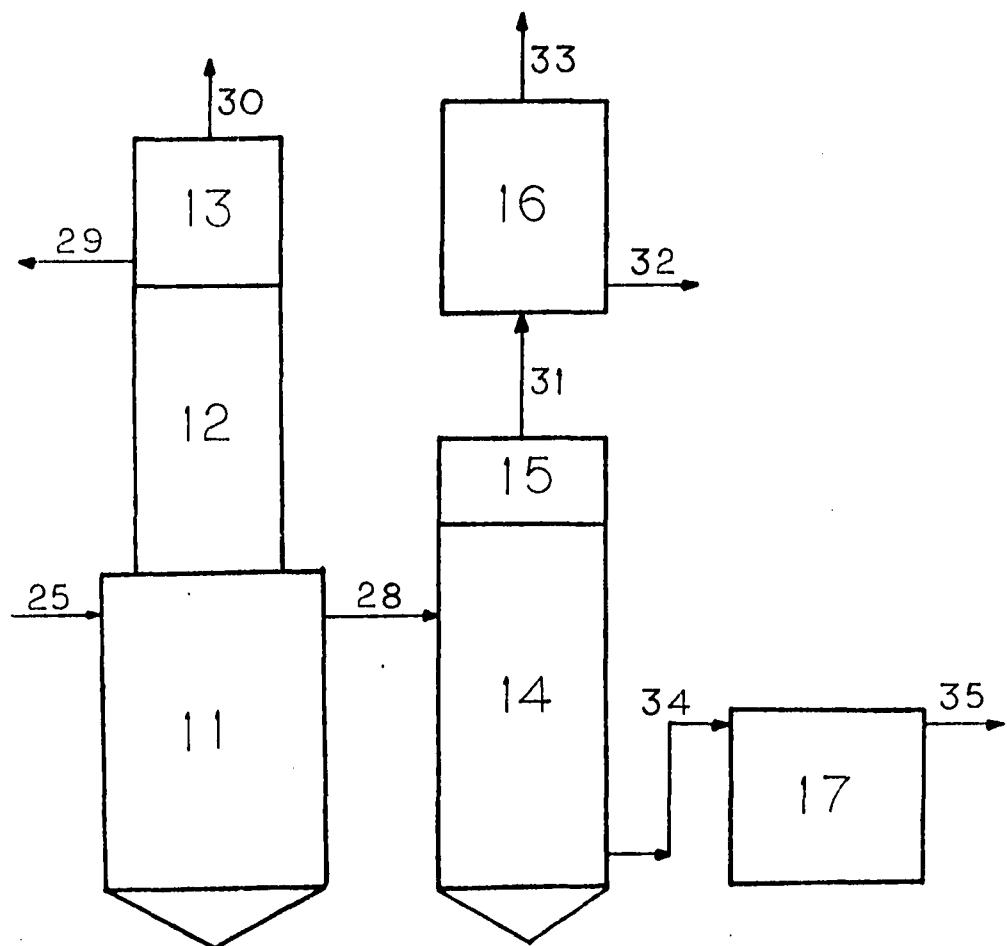
<sup>b</sup> Flow 1.00 corresponds to a volume flow rate of 233 lt/hr.

<sup>c</sup> Stream 23 contains hydroxylamine as a reducing agent and hydrazine as a holding agent.

FIGURE 21. Calcination of U Product Solution

Step no.	Step	
11	Evaporator	
12	Deentrainment column	
13	Condenser	
14	Fluidized bed calciner	
15	Porous filters	
16	Condenser	
17	Packaging	
Stream no.	Stream	Contents <sup>a</sup>
25	U product solution	U, HNO <sub>3</sub> , (Pu), (FP)
28	Concentrated U solution	Same as Stream 25
29	Condensate	HNO <sub>3</sub>
30	Non-condensable off-gases	FP, NO <sub>x</sub>
31	Off-gases from calciner	FP, NO <sub>x</sub> , HNO <sub>3</sub> and H <sub>2</sub> O vapors
32	Condensate	HNO <sub>3</sub>
33	Non-condensable off-gases	FP, NO <sub>x</sub>
34	U oxide product	UO <sub>3</sub>
35	Packaged U oxide	UO <sub>3</sub>

<sup>a</sup> Materials in parentheses are present in trace quantities.



mixed with other vessel off-gases and routed to the off-gas treatment system.

#### 5.1.5. Calcination of U+Pu Product Solution

A flow chart of U+Pu calcination process is shown in Figure 22. The process is basically the same as U calcination process, with U product solution replaced by U+Pu product solution. U+Pu product solution is calcined to obtain  $\text{UO}_3+\text{PuO}_2$  product.

#### 5.1.6. Used Solvent Treatment

A flow chart of the used solvent treatment process is exhibited in Figure 23. Used solvent leaving the U stripping cycle contains  $1.44\text{E-}4$  M U,  $1.283\text{E-}3$  M  $\text{HNO}_3$ , less than  $1.0\text{E-}9$  M Pu, trace amounts of FP, and TBP degradation products (DBP and MBP, produced from radiolysis and hydrolysis of TBP). The used solvent is washed first with a dilute  $\text{HNO}_3$  solution to remove major portions of solutes in it and then with a carbonate solution to remove TBP degradation products and remaining amounts of solutes. Washed solvent is filtered through stainless steel filters and sent to a makeup tank.

$\text{HNO}_3$  washings are concentrated in an evaporator system and recycled to the solvent extraction system. The condensate stream, contaminated  $\text{HNO}_3$ , is sent to the LLW treatment and acid recovery process.

Carbonate washings are distilled in a high pressure distillation system. Distillate containing solvent degradation products is

FIGURE 22. Calcination of U+Pu Product Solution

Step no.	Step	
Stream no.	Stream	Contents <sup>a</sup>
18	Evaporator	
19	Deentrainment column	
20	Condenser	
21	Fluidized bed calciner	
22	Porous filters	
23	Condenser	
24	Packaging	
19	U+Pu product solution	HNO <sub>3</sub> , U, Pu, (FP)
22	Raffinate from finish partitioning	Same as Stream 19
36	Condensate	HNO <sub>3</sub> solution
37	Non-condensable off-gases	FP, NO <sub>x</sub>
38	Concentrated U+Pu solution	Same as Stream 19
39	Off-gases from calciner	FP, NO <sub>x</sub> , HNO <sub>3</sub> and H <sub>2</sub> O vapors
40	Condensate	HNO <sub>3</sub>
41	Non-condensable off-gases	FP, NO <sub>x</sub>
42	U+Pu oxide product	UO <sub>3</sub> +PuO <sub>2</sub>
43	Packaged U+Pu oxide	UO <sub>3</sub> +PuO <sub>2</sub>

<sup>a</sup> Materials in parentheses are present in trace quantities.

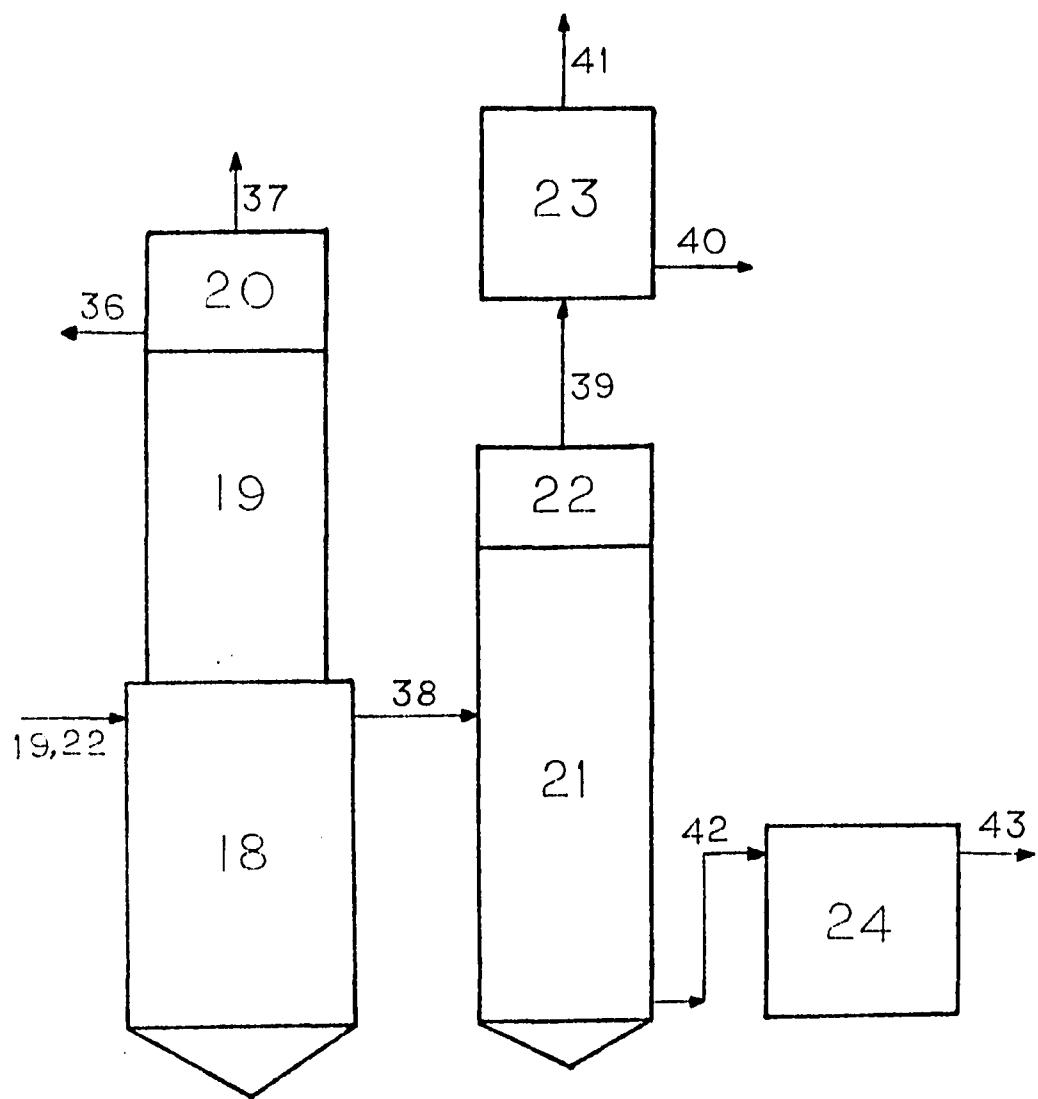
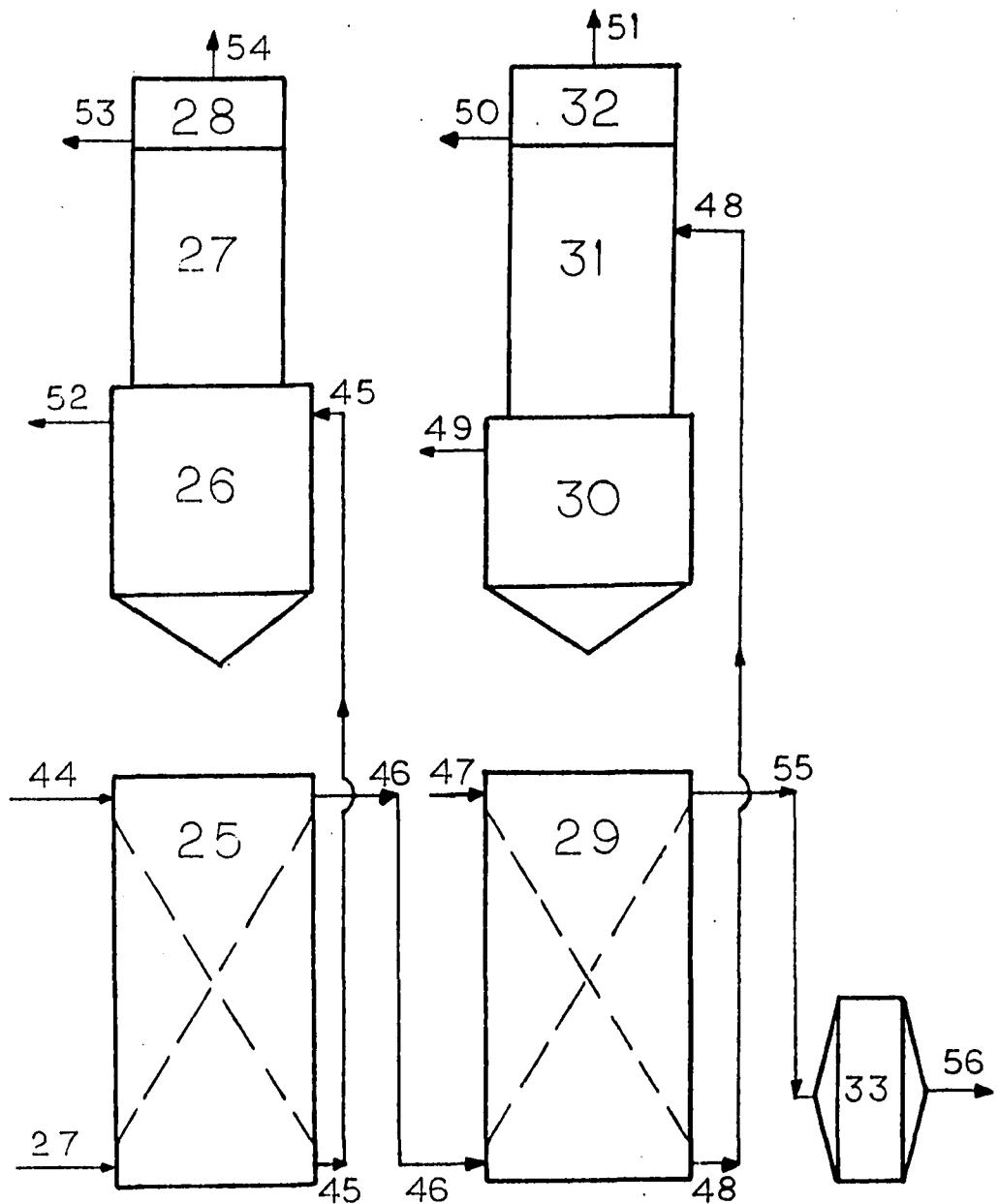


FIGURE 23. Used Solvent Treatment

Step		
25	Washing with $\text{HNO}_3$	
26	Evaporator	
27	Deentrainment column	
28	Condenser	
29	Washing with a carbonate solution	
30	Reboiler	
31	Distillation column	
32	Condenser	
33	Stainless steel filter	
Stream		Contents
27	Used solvent	Sdp <sup>a</sup> , solutes
44	$\text{HNO}_3$ wash solution	0.01 M $\text{HNO}_3$
45	$\text{HNO}_3$ washings	$\text{HNO}_3$ , solutes
46	Solvent washed with $\text{HNO}_3$	Sdp
47	Carbonate wash solution	0.2 M $\text{Na}_2\text{CO}_3$
48	Carbonate washings	Sdp, solutes
49	Bottom solution	$\text{Na}_2\text{CO}_3$
50	Distillate	Sdp
51	Non-condensable off-gases	FP, $\text{NO}_x$ , hydrocarbons
52	Concentrated $\text{HNO}_3$ washings	Same as Stream 45
53	Condensate	$\text{HNO}_3$ , FP
54	Non-condensable off-gases	FP, $\text{NO}_x$
55	Solvent washed with carbonate solution	
56	Filtered solvent	

<sup>a</sup> Sdp = Solvent degradation products.



transferred to a miscellaneous waste treatment process to be burned. The bottoms from the distillation system is recycled to the solvent extraction process.

Non-condensable off-gases from the evaporation and distillation systems are routed to the off-gas treatment process after being mixed with other vessel off-gases.

#### 5.1.7. HLW Treatment

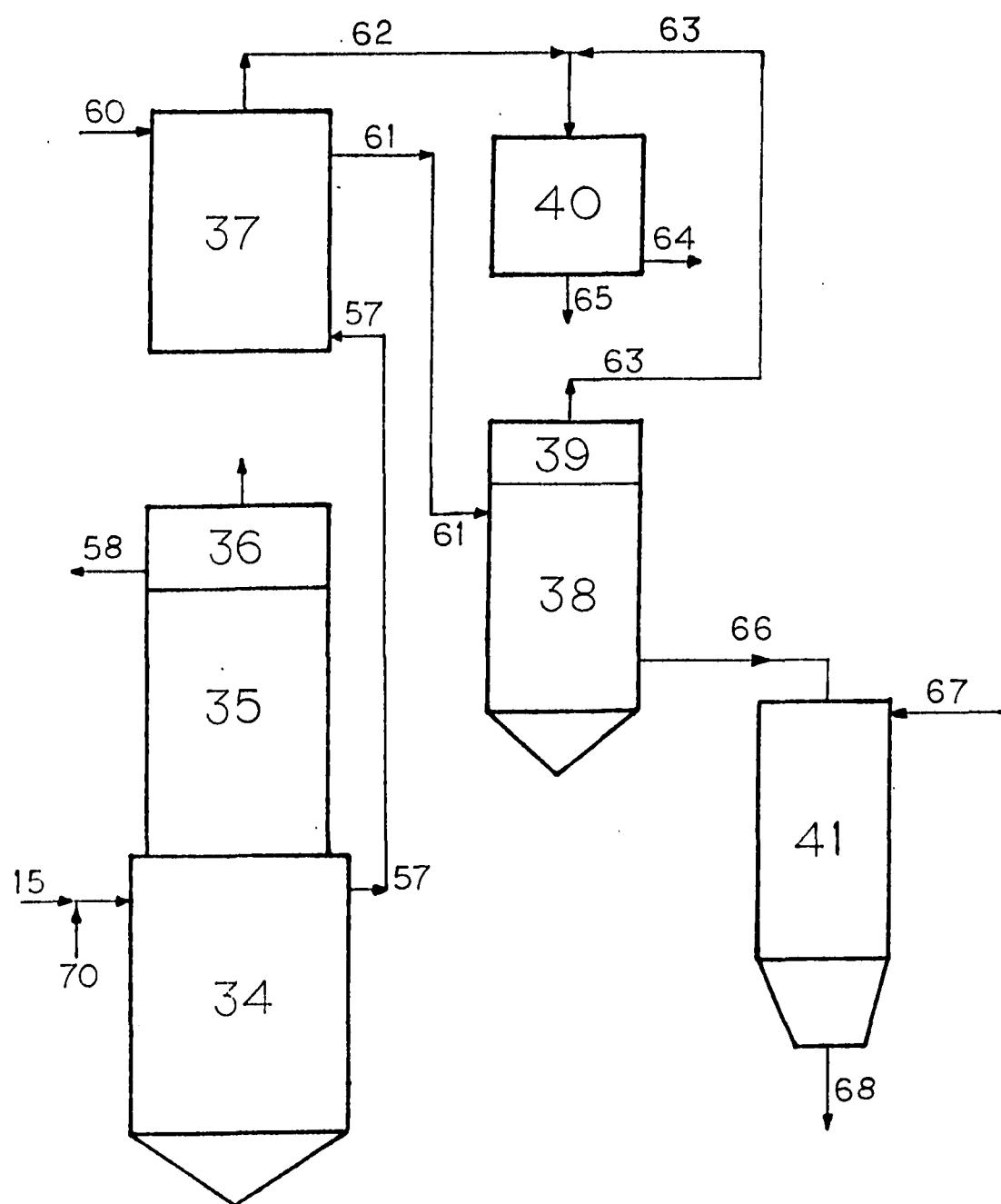
A flow chart of the HLW treatment process is shown in Figure 24. The HLW stream, composition of which is given in Table 8, from the codecontamination cycle of the solvent extraction system is concentrated to nearly 7.0 M HNO<sub>3</sub> in an evaporator system containing an evaporator, a deentrainment column, and an overhead condenser [5]. The concentrated HLW solution is transferred to a denitration reactor, where it is denitrated by use of an organic reducing agent. Above 80°C denitration with formaldehyde, for example, can reduce the acidity to 1 M in 1 to 2 hr [5]. The condensate stream from the overhead condenser, a slightly below 2.65 M contaminated HNO<sub>3</sub> solution, is sent to the LLW treatment and acid recovery process.

Denitrated HLW solution is calcined in a fluidized bed calciner to produce waste oxides. Waste oxides, granular solids, are mixed with glass frit. This mixture is heated in a glass-forming vessel which drains into glassified-HLW containers [33,34].

Off-gases from the denitration reactor and calciner are passed through a condenser and sent to the off-gas treatment system together

FIGURE 24. HLW Treatment

Step no.	Step
34	Evaporator
35	Deentrainment column
36	Condenser
37	Denitration reactor
38	Fluidized bed calciner
39	Porous filters
40	Condenser
41	Glass forming vessel
Stream no.	Stream
15	HLW solution from solvent extraction system
57	Concentrated HLW solution
58	Condensate ( $\text{HNO}_3$ solution)
59	Non-condensable off-gases
60	Organic reducing agent (formaldehyde)
61	Denitrated HLW solution
62	Off-gases from denitration
63	Off-gases from calciner
64	Non-condensable off-gases
65	Condensate ( $\text{HNO}_3$ solution)
66	Solidified HLW (waste oxides)
67	Glass frit
68	Glassified HLW
70	Concentrated LLW solution from LLW evaporator



with off-gases leaving the overhead condenser in the HLW evaporation system. The condensate stream from the condenser of the denitration reactor and calciner is routed to the LLW treatment process.

#### 5.1.8. LLW Treatment and Acid Recovery

A flow chart of the process is exhibited in Figure 25. All LLW streams generated in the plant process areas are fed into a feed tank. LLW solution is concentrated in an evaporator system consisting of an evaporator, a deentrainment column, and an overhead condenser. Bottoms from the evaporator, a contaminated HNO<sub>3</sub> solution, are transferred into the HLW evaporator feed tank. The overhead stream, a decontaminated HNO<sub>3</sub> solution, is fractionated into nearly 50 % HNO<sub>3</sub> (15 M, concentration of the HNO<sub>3</sub>-H<sub>2</sub>O azeotrope) and H<sub>2</sub>O in an acid fractionator. Non-condensable off gases from the overhead condenser are routed to the off-gas treatment system.

#### 5.1.9. Solid ILW Treatment

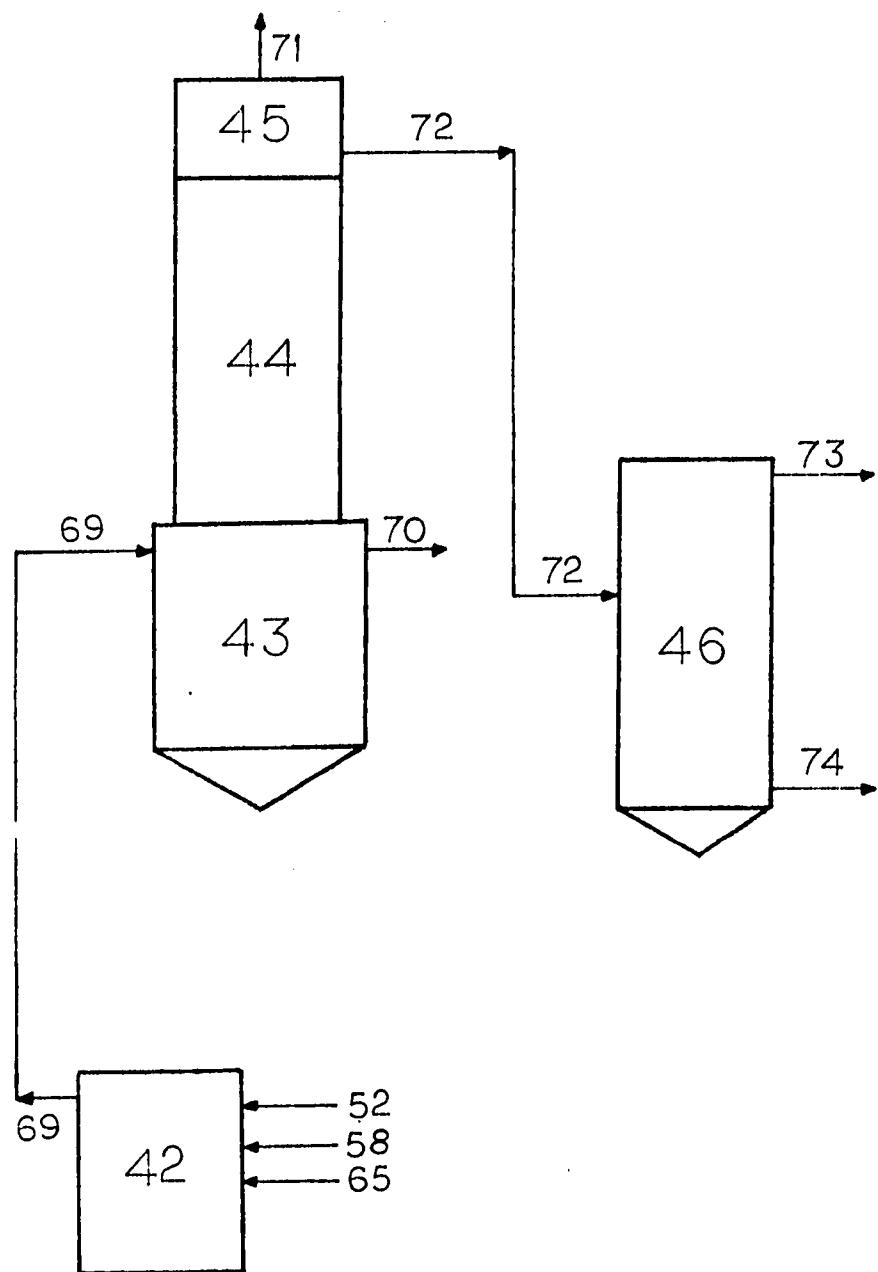
Solid ILW includes cladding hulls and fuel hardware from the leaching step and filtrate phase from the centrifugation of feed solution. Solid ILW is leached with HNO<sub>3</sub> and cemented into stainless steel containers to be shipped to a waste repository. HNO<sub>3</sub> solution generated from leaching the solid ILW is monitored for its U and Pu content. If significant amounts of U and Pu are detected, which is not normally expected, the solution is recycled to the feed preparation step; otherwise, it is routed to the HLW treatment process.

FIGURE 25. LLW Treatment and Acid Recovery

Step no.	Step
42	Feed tank
43	Evaporator
44	Deentrainment column
45	Condenser
46	HNO <sub>3</sub> fractionator

Stream no.	Stream
52	Concentrated HNO <sub>3</sub> washings from used solvent treatment
58	Condensate from HLW evaporator
65	Condensate from condenser of denitrator and calciner in HLW treatment
69	LLW solution
70	Concentrated LLW solution (to HLW treatment)
71	Non-condensable off-gases
72	Condensate (recovered HNO <sub>3</sub> )
73	HNO <sub>3</sub> solution (approximately 50 %)
74	H <sub>2</sub> O



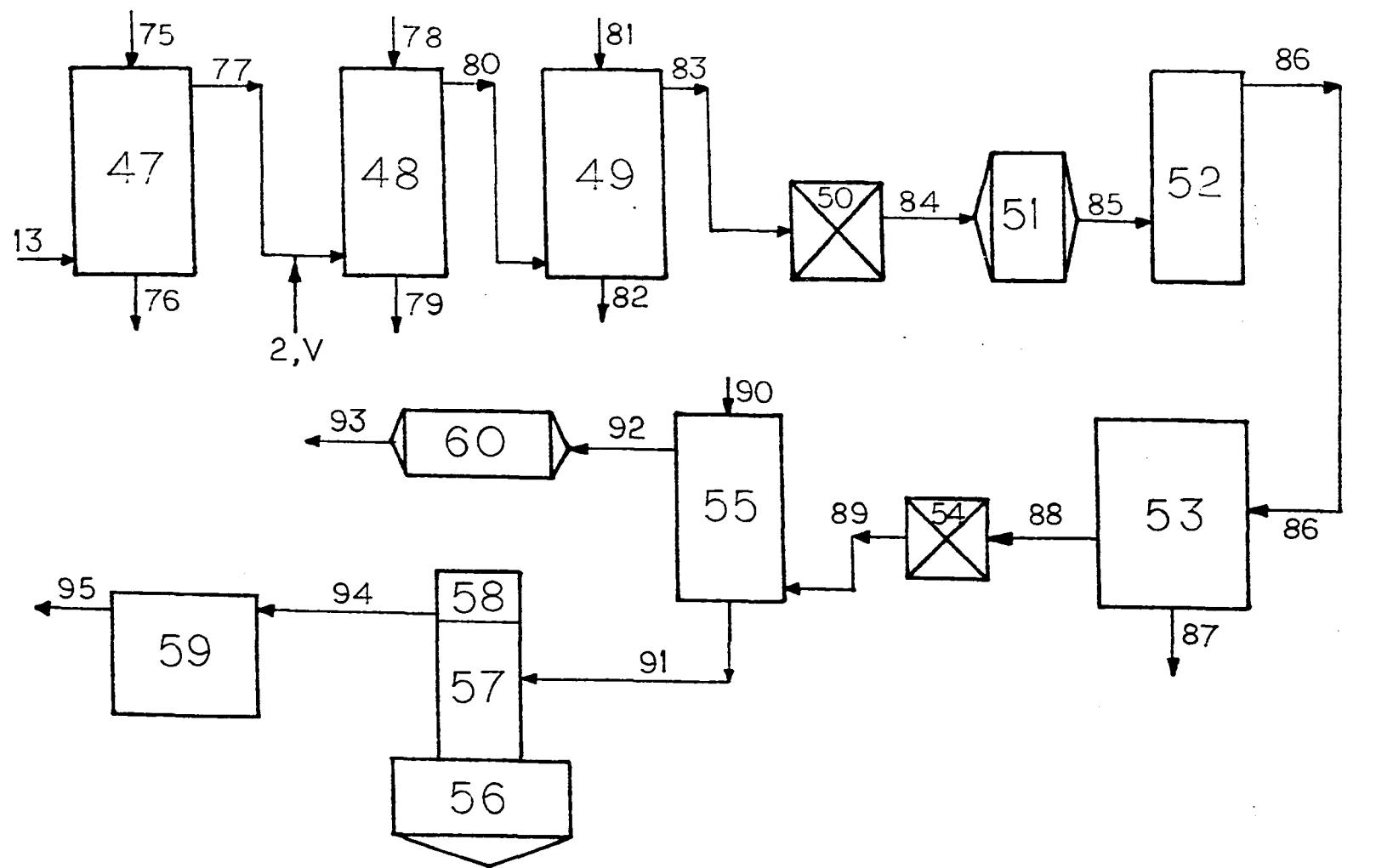
#### 5.1.10. Off-Gas Treatment

Off-gases to be treated include leacher, shear, and vessel off-gases. Leacher off-gases have already been passed through a downdraft condenser for NO<sub>x</sub> absorption in the shear-leach step. It is required to remove iodine, rare gases, and particulate from the off-gases before releasing them into the atmosphere. Since the spent fuel being processed is long-cooled (longer than 200 days), the radioactivity hazard associated with iodine is not of main concern; however, the biological toxicity of iodine still necessitates its retention from the off-gases. Removal of rare gases is required because of the activity of Kr-85. In the iodine and rare gas removal processes significant amounts of ruthenium, carbon-14 dioxide, and hydrocarbons are also removed from the off-gases. The off-gas treatment system consists of the following processes: iodine removal, rare gas recovery, and HEPA (high efficiency particulate air) filtration. A flow chart of the off-gas treatment process is shown in Figure 26.

Leacher off-gases are scrubbed by caustic containing thiosulfate to reduce iodine and iodate to iodide. Caustic scrubber removes more than 90 % of iodine and Ru and about 80 % of carbon-14 dioxide [32]. Vessel and shear off-gases are mixed with the leacher off-gases leaving the caustic scrubber. Combined off-gases are passed through a H<sub>2</sub>O scrubber for NO<sub>x</sub> absorption and sent to a second caustic scrubber for additional iodine removal. Then the off-gases are heated, filtered, and passed through a silver zeolite adsorbent column, operated at 200 °C, to achieve a total iodine DF of approximately 1.0E5 [32].

FIGURE 26. Off-Gas Treatment

Step no.	Step	Stream no.	Stream
47	Caustic scrubber	2	Shear off-gases
48	H <sub>2</sub> O scrubber	13	Leacher off-gases from the downdraft condenser
49	Caustic scrubber	V	Vessel off-gases
50	Preheater	75	Caustic containing thiosulfate
51	Protective filter	76	Caustic containing iodine
52	Ag-zeolite adsorbent column	77	Off-gases scrubbed with caustic
53	Prepurification	78	H <sub>2</sub> O
54	Precooler	79	HNO <sub>3</sub> solution
55	Condensation column	80	Off-gases scrubbed with H <sub>2</sub> O
56	Reboiler	81	Caustic containing thiosulfate
57	Fractional distillation column	82	Caustic containing iodine
58	Condenser	83	Off-gases scrubbed with caustic
59	Bottling station	84	Heated off-gases
60	HEPA filters	85	Pre-filtered off-gases
		86	Off-gases leaving the Ag-zeolite adsorbent column
		87	CO <sub>2</sub> , NO <sub>x</sub> , H <sub>2</sub> O, hydrocarbons
		88	Pre-purified off-gases
		89	Cooled off-gases
		90	Liquid N <sub>2</sub>
		91	Condensed off-gases (Kr, Xe, O <sub>2</sub> , N <sub>2</sub> , Ar)
		92	Non-condensed off-gases (H <sub>2</sub> , N <sub>2</sub> )
		93	Filtered off-gases
		94	Kr, Xe, and O <sub>2</sub> fractions
		95	Bottled Xe and Kr



The off-gases leaving the adsorbent column enter the rare gas recovery process. Rare gas recovery is accomplished by a cryogenic method. After a prepurification step, which removes remaining amounts of CO<sub>2</sub>, NO<sub>x</sub>, H<sub>2</sub>O vapor, and hydrocarbons, the off-gases are precooled to -160 °C and fed into a condensation column, in which they are contacted with liquid nitrogen [35]. Condensed off-gases leaving the condensation column, which contain Kr, Xe, O<sub>2</sub>, N<sub>2</sub>, and Ar, are sent to the cryogenic fractional distillation column and fractionated into Kr, Xe, and O<sub>2</sub> fractions. The Kr and Xe fractions are bottled, O<sub>2</sub> fraction is partially recycled. More than 99.9 % of Kr and Xe in the off-gases can be recovered by this method [35,36]. Because the Xe to Kr ratio in the FPs is around 15, the separation of Kr and Xe is favored in order to reduce ultimate storage requirements for containing Kr [35,36]. The cryogenic method, which is fully developed and commercially demonstrated, presents an efficient and reliable approach for recovery of rare gases from the off-gases of a reprocessing plant [35].

Non-condensed off-gases leaving the condensation column, which mainly contain H<sub>2</sub> and vaporized N<sub>2</sub>, are passed through two HEPA filters in series for particulate removal and released into the atmosphere through a high stack. The first HEPA filter removes more than 99.9 % of the particulate, and the second one in series around 98.0 % [32].

## 5.2. Plant Description

### 5.2.1. General Comments

The reprocessing plant being designed is to handle approximately 10-year cooled LWR fuel, the composition and activity of which are given in Tables 8 and 9.

The plant is designed for a capacity of 960 MTHM SF/year. With an assumed capacity factor of 0.83 (nearly 300 days of operation in a year) it is required to process about 2.67 MTHM SF per day. The specified U concentration in the feed solution is 1.9089 M. The amounts of fuel contained in a PWR and a BWR fuel assembly are 0.70 to 1.0 and 0.30 to 0.35 tons, respectively [37]. Then, the plant will process approximately 3 to 5 PWR, or 8 to 10 BWR fuel assemblies, or 5600 liter SF solution per day.

Plant life is assumed to be 25-30 years. This is the life of a similar chemical plant dealing with nonradioactive materials [38,39].

Since the fuel to be processed is long-cooled, there is no need for on-site cooling of spent fuel before reprocessing. This reduces requirements for on-site storage of SF. Assuming that SF will be received at the plant at least once every 15 days, a maximum of 50 tons of SF will be stored on-site at any given time. Liquid HLW will be solidified immediately after being generated, requiring no temporary storage facilities. The products ( $\text{UO}_3$  and  $\text{UO}_3 + \text{PuO}_2$ ), solidified HLW, and bottled rare gases are to be stored at the plant for no longer than 5 days.

### 5.2.2. Maintenance Approach

There are 2 basic maintenance approaches that can be considered in the design of a reprocessing plant: contact maintenance and remote maintenance.

Contact maintenance requires in-situ decontamination of process equipment to permit personnel entry for repair and/or replacement of failed equipment. Equipment is contained in heavily shielded cells which are equipped with remote decontamination sprays installed on cell walls.

Remote maintenance process cells are designed such that equipment in the cells is remotely replaceable using remote bridge cranes, manipulators, and/or robots. Remote cells are usually located adjacent to one another in a heavily shielded structure called a canyon, which is surrounded by service corridors. No human entry into remote cells is permitted under normal conditions.

Both approaches have been applied in varying degrees at reprocessing plants. Based on experiences gained in the past, the following conclusions can be arrived at.

- There is a direct correlation between the plant operating efficiency and degree of remote maintenance. Plants in which most radioactive equipment is remotely maintained have reported high operating efficiencies and long plant life times [40,41].

- Construction costs and cost and design complexity of equipment are less for a contact maintenance plant because there is no need for special remote features and the cell size is reduced. A remote maintenance plant requires a large and massive building, close toleranced process equipment, and several remote features such as pipe jumpers and special connectors. Extensive engineering and craft support is also required for a remote maintenance plant.
- Repairing or replacing equipment in a contact cell usually results in an outage time of 3 months to 1 year [42,43]. In order to reduce the downtime of a contact plant (or to keep the downtime at a reasonable level), it is usually required to place a small amount of equipment in each cell and to have installed spare equipment in separate cells [40]. This necessitates the construction of many small contact cells, thus offsetting the main advantages of contact maintenance mentioned above.
- The 2 most successful reprocessing plants in the world (Savannah River and Hanford plants), both remotely maintained, have reported that equipment could be remotely decontaminated in a cell adjacent to a remote cell and then repaired by contact means at about 15 % of the original equipment cost [40,41]. At Hanford, every type of major process equipment was replaced at least once, and the outage time for replacement ranged from 2 days to 2 weeks [40].

- Besides lengthy plant downtimes, other basic disadvantages of contact maintenance are summarized as follows: large amounts of liquid and solid wastes produced during decontamination operations, spread of contamination throughout the building because of the entry into cells, and gradually increasing activity levels in the equipment and cells making decontamination less effective [40].
- Regardless of which maintenance approach is applied, equipment malfunctions (leaks, plugging) should be expected and provisions should be made.
- The designers of the Barnwell plant<sup>2</sup> aimed at a minimum maintenance plant. At Barnwell, highly radioactive equipment is contained in contact or remote cells depending on the probability of failure. This approach probably would result in reduced costs and also reduced operating efficiencies compared to a remote maintenance plant because of repairing and replacing equipment in contact cells. However, experience has shown that even carefully designed equipment with assumedly low probability of failure cannot be considered

---

<sup>2</sup>The Barnwell plant, the latest nuclear reprocessing plant in the U.S.A., was built by Allied-General Nuclear Services at Barnwell, South Carolina. When construction of the plant was completed in 1976, commercial reprocessing in the U.S.A. was deferred by government decisions. The Barnwell plant was not permitted to begin hot start-up. It has been stated in several reports that at the Barnwell the newest design concepts were utilized and significant engineering effort was applied in order to arrive at a low-cost and high-operating efficiency plant [44,45].

maintenance free for a long period. In one study, it was speculated that operating efficiency of Barnwell plant would not have exceeded 50 % if allowed to be operated [40].

In this study, taking into account the above considerations, the remote maintenance approach has been adopted. All the equipment involving highly and moderately active materials is to be remotely maintained and colocated. Failed equipment in remote maintenance areas is going to be replaced by means of remote bridge cranes, robots, and/or manipulators. No human entry into remote cells is permitted.

Contact maintenance is to be applied only to equipment whose activity is low enough to decontaminate in a short period to allow human approach.

Table 9 lists the processes in the plant according to the maintenance approach applied.

TABLE 9. Contact and Remote Maintenance Processes in the Plant

Remote Maintenance Processes	Contact Maintenance Processes
Cask unloading and fuel storage	U stripping (4th SE <sup>a</sup> cycle)
Shear-leach and feed preparation	Calcination of U product solution
1st 3 cycles of SE	Used solvent treatment
Calcination of U+Pu product solution	LLW treatment and acid recovery
HLW treatment	Off-gas treatment
Solid ILW treatment	

<sup>a</sup> SE=Solvent Extraction.

### 5.2.3. Plant Layout

A layout of the process buildings is shown in Figure 27.

Figure 28 exhibits a layout of the basement process areas. The main processes are carried out in 2 buildings located adjacent to each other and partitioned by a common wall. All high and medium activity processes are housed in the "west" building while low activity processes are contained in the "east" building. Such an arrangement of processes provides a clear line of demarcation between the low activity and high activity process areas and is expected to result in increased operating and maintenance efficiency, reduced personnel requirements and exposure, and improved safeguardability features [25,46].

5.2.3.a. Remote Maintenance Canyon (RMC)      The remote maintenance canyon is a heavily shielded (about 1.5 m thick), nearly L-shaped reinforced concrete structure located at grade level in the west building. The RMC houses 4 process cells partitioned by thin walls and also includes a robot station, equipment replacement hatches, and crane maintenance areas. A layout of the RMC is shown in Figure 29.

Cask unloading and fuel storage, shear-leach and feed preparation, solvent extraction (the first 3 cycles), and U+Pu calcination processes are contained in the process cells of RMC. RMC equipment is replaced using overhead bridge cranes and robots mounted on rails. The L-shaping of the RMC not only allows convenient location of a robot station at the center but also results in a more compact building.

FIGURE 27. Layout of Process Buildings: Grade Level

Area no.	Area
1	Cask receipt and handling area
2	Service area (maintenance, health physics laboratory)
3	Robot station and maintenance area, laboratory
4	Control rooms
5	Robot maintenance area and manipulator port
6	Solidified HLW storage cell and shipment port
7	U-Pu product storage vault and shipment port
8	Remote maintenance canyon (RMC)
9	Service galleries and/or corridors
10	Chemicals storage and cold feed preparation area
11	Analytical laboratory
12	Personnel area
13	Maintenance area
14	Change room and laundry
15	Equipment replacement aisle
16	Contact maintenance process area (CMPA)
17	Miscellaneous waste handling area
18	U product storage and shipment port
19	Bottled rare gases storage and shipment port
W	West building
E	East building

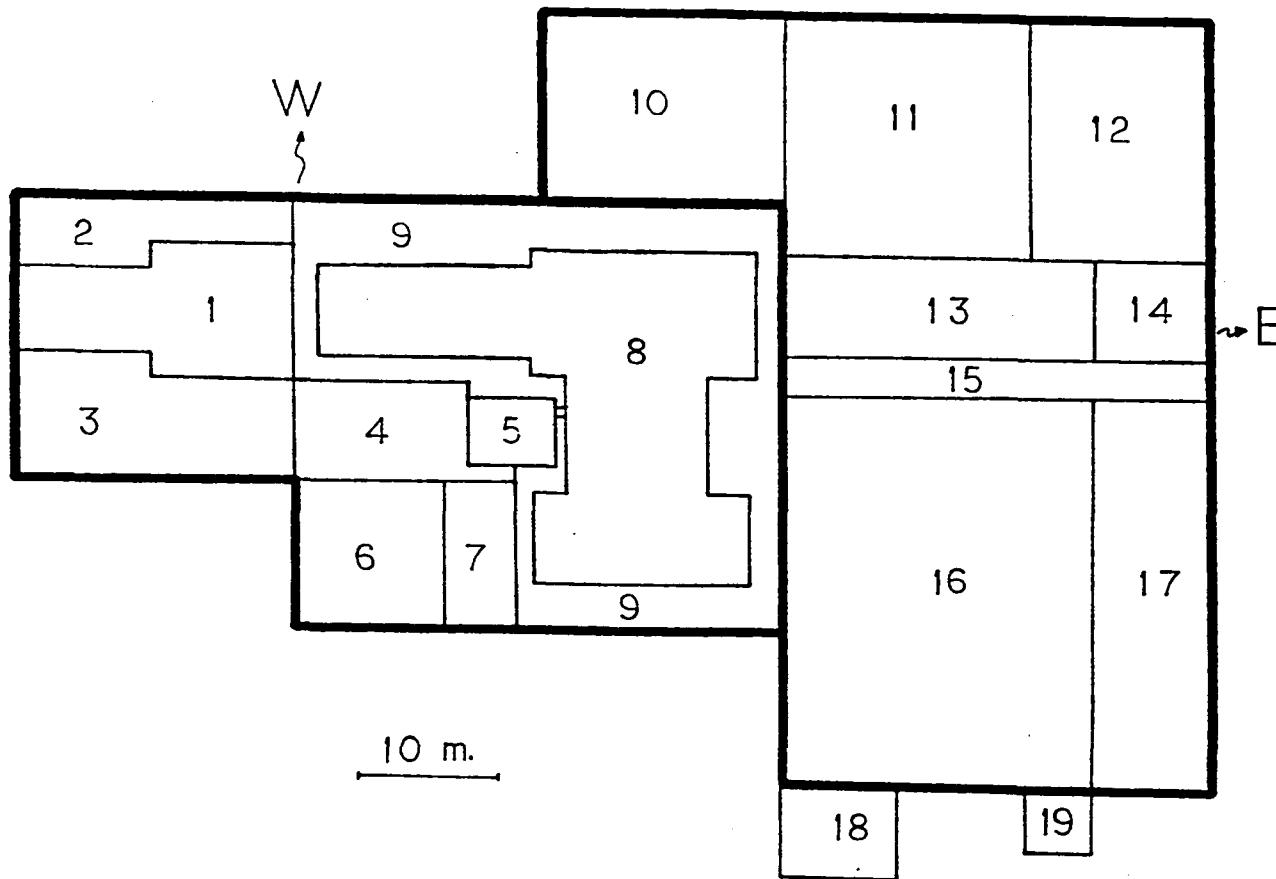
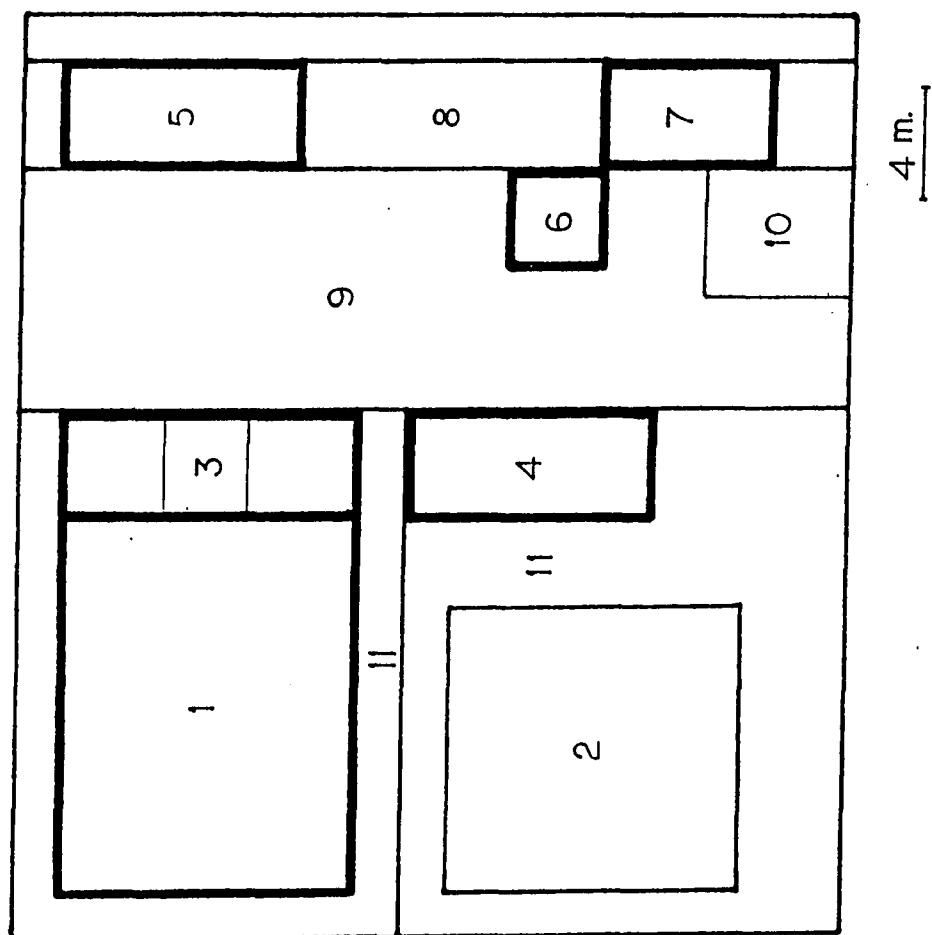


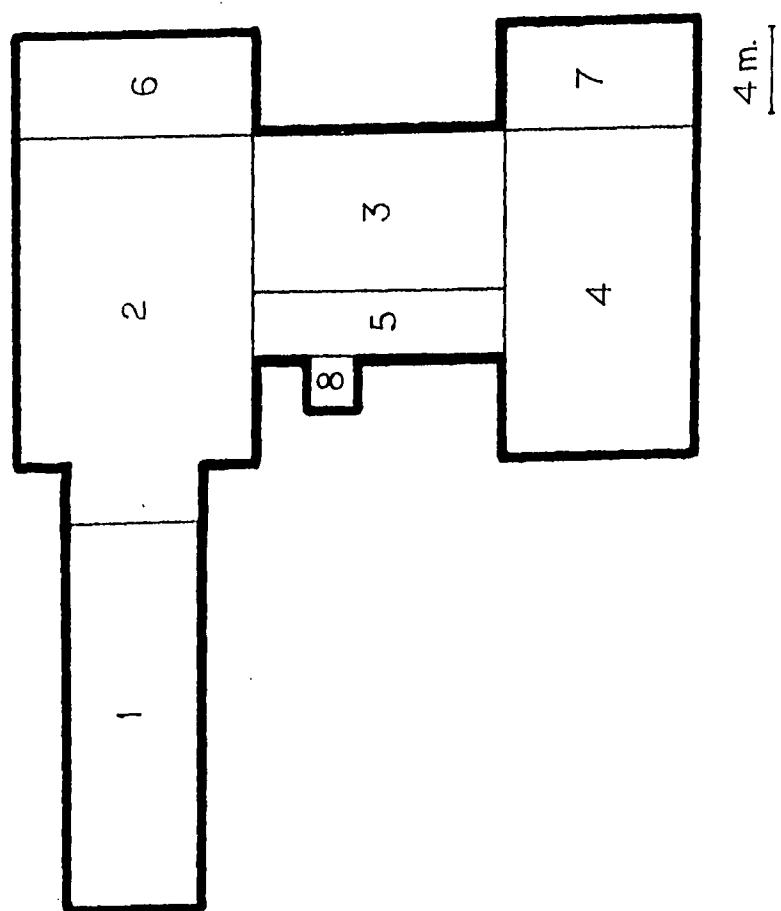
FIGURE 28. Layout of Process Buildings: Basement

Area no.	Area
1	HLW treatment cell
2	LLW treatment and acid recovery process area
3	Decontamination and maintenance room for HLW treatment
4	Solid ILW treatment cell
5	Decontamination room for shear-leach and feed preparation
6	Decontamination room for solvent extraction
7	Decontamination room for U+Pu calcination
8	Maintenance area
9	Equipment transfer aisle
10	Equipment discharge room
11	Service galleries and/or corridors



**FIGURE 29.** Layout of the RMC

<b>Area no.</b>	<b>Area</b>
1	Cask unloading and fuel storage cell
2	Shear-leach and feed preparation cell
3	Solvent extraction cell
4	U+Pu calcination cell
5	Robot station
6	Equipment replacement and crane maintenance area
7	Equipment replacement and crane maintenance area
8	Airlock door to robot maintenance area



Robot entry into the cells is through remotely operated sliding doors. In addition to robots moving on the canyon floor, "monkey" robots, which are capable of climbing a post, are used for reaching upper parts of canyon equipment. Robot posts near each equipment rack are provided.

Shear-leach and feed preparation and U+Pu calcination cells include equipment replacement hatches with removable floors opening to heavily shielded decontamination rooms located in the basement.

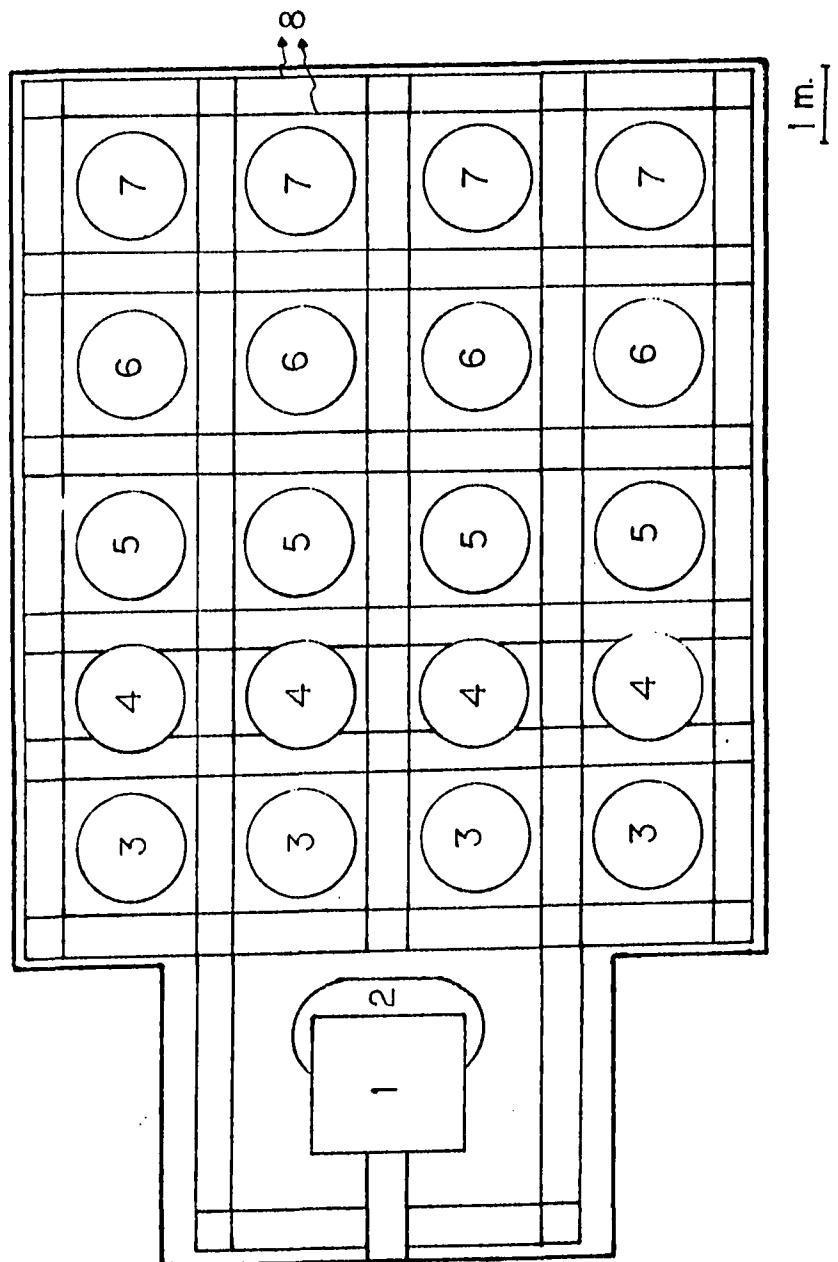
A crane maintenance area equipped with manipulators is contained at the top part of each equipment replacement hatch. The solvent extraction cell is provided with a manhole on the floor for equipment replacement. The manhole, around 75 cm in diameter, also opens to a heavily shielded decontamination room in the basement. Failed equipment in the RMC process cells is immediately transferred to decontamination rooms in the basement through the hatches or manhole. Repaired or new equipment is brought into the RMC by the same route. Enough overhead space is provided in the RMC for equipment replacement. It is expected that replacement of a failed unit of equipment in the RMC will not take longer than 15 days.

Listing and arrangement of equipment in the RMC process cells, except cask unloading and fuel storage cell, are exhibited in Figures 30, 31, and 32.

Mixer-settlers, pulse columns, or centrifugal contactors can be used as contacting equipment in the solvent extraction processes.

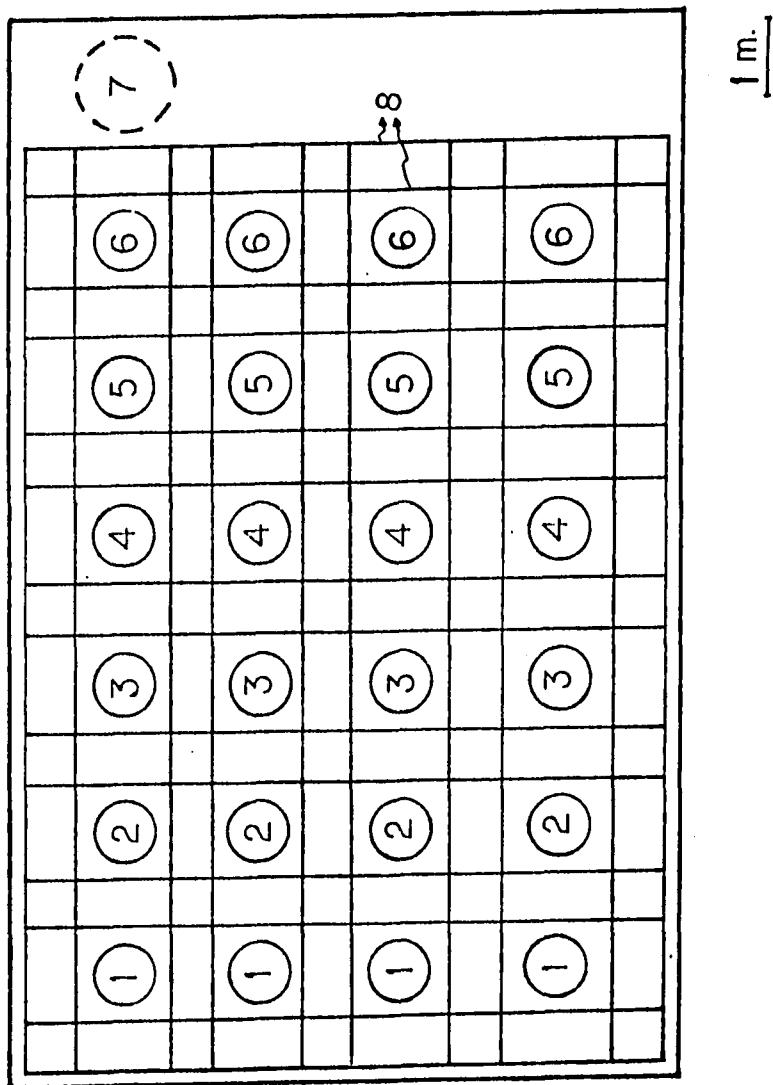
**FIGURE 30. Equipment Arrangement in Shear-Leach and Feed Preparation Cell**

- 
- 1. Shear
  - 2. Diverter
  - 3. Leacher
  - 4. Downdraft condenser
  - 5. Accountability tank
  - 6. Centrifuge
  - 7. Feed adjustment tank
  - 8. Robot rails
-



**FIGURE 31. Equipment Arrangement for Solvent Extraction Cell**

- 
- 1. Holdup column
  - 2. Pulse column (codecontamination)
  - 3. Holdup column
  - 4. Pulse column (partial partitioning)
  - 5. Holdup column
  - 6. Pulse column (finish partitioning)
  - 7. Manhole
  - 8. Robot rails
-



**FIGURE 32. Equipment Arrangement for U+Pu Calcination Cell**

- 
- 1. Feed tank**
  - 2. Evaporator system**
  - 3. Holdup tank**
  - 4. Fluidized bed calciner**
  - 5. Packaging station**
  - 6. Robot rails**
-

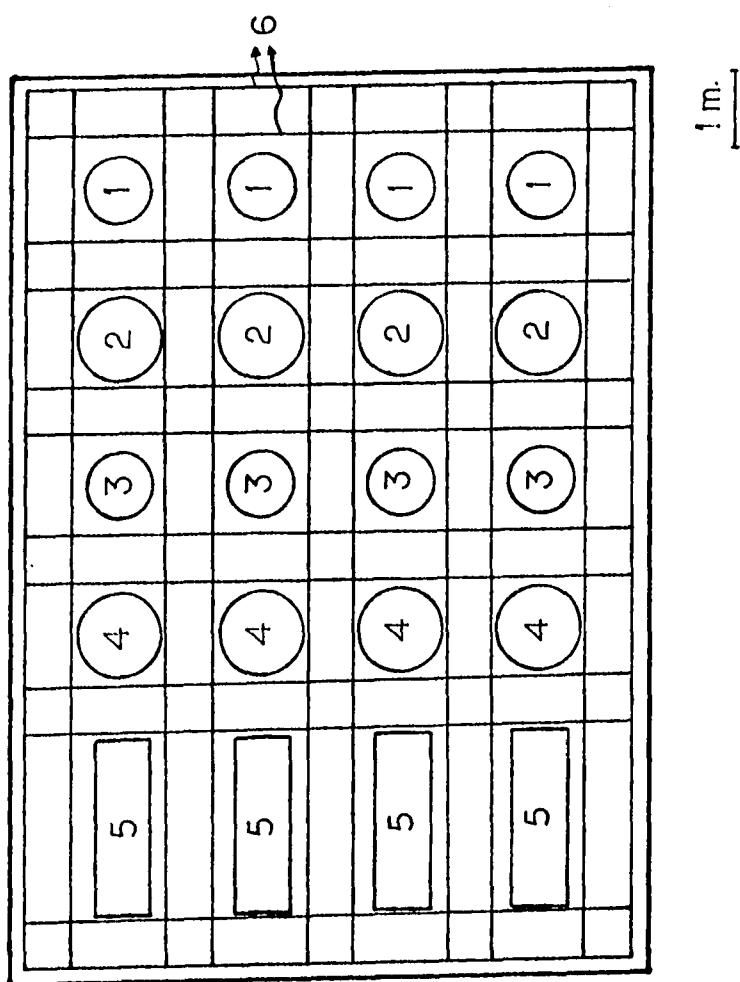


TABLE 10. Dimensions of Pulse Columns

Pulse Columns				
	1st cycle (codec.)	2nd cycle (p. p.)	3rd cycle (f. p.)	4th cycle (U strip)
Diameter (cm)	10.0	15.0	15.0	20.0
Separating height (m)	7.5	9.0	3.0	6.0

Because pulse columns do not occupy much space, have no moving parts, and are relatively inexpensive, they have been the choice for contacting equipment in the solvent extraction processes in this study. Dimensions of the pulse columns, approximately calculated from the number of theoretical stages contained in each column and HETS and flow rate data [6,26], are given in Table 10. Since the pulse columns employed are quite tall, the use of modular columns is proposed. Each column is composed of approximately 3-m segments keyed into one another and pressure-sealed using clips. Use of modular columns reduces the overhead space required for column replacement, thus reducing the height of the process cell.

Equipment-to-equipment and equipment-to-wall spacings in the RMC cells are 75 to 90 cm, which provides enough space for robot operations and is also much larger than the minimum distance required between units containing fissile material to prevent any interaction [6].

As seen in Figures 30, 31, and 32, the equipment in the RMC is arranged in 4 parallel lines, each line having one fourth of the plant capacity. This manifolding is expected to result in very high operating efficiencies. When an equipment unit fails, only one line of processing will have to be shut down until the failed unit is replaced, meaning 75 % of the processing capacity will still be available. The 4-line arrangement also gives rise to smaller volumes of equipment, almost totally eliminating the nuclear criticality problem by geometry control. For the same reason, reliability and flexibility features of the design are improved significantly and the equipment replacement burden is eased.

Shielded viewing windows and lighting are provided for each cell in the RMC. Telescopic viewing devices attached to robots and bridge cranes are also utilized.

Liquid transfer in the RMC is by air lift and jet transfer; therefore, no in-cell pumps or motors are required for the process equipment in the RMC.

Spill trays are provided underneath each equipment rack to discharge any spills to the HLW treatment area. Floors and lower portions of interior walls of the RMC are covered by stainless steel lining to prevent the accumulation of radioactivity in pores of the concrete structure.

The RMC is surrounded by 2 to 4 m wide operating galleries and/or corridors, which provide room for sampling, instrumentation, monitoring, observation, piping, and other services that may be needed.

A robot maintenance area is located outside the RMC adjacent to the robot station. Robots needing maintenance are brought into the robot maintenance area from the robot station through an airlock door. Remote and contact maintenance devices are provided for the robot maintenance area. A manipulator port serves the robot maintenance area.

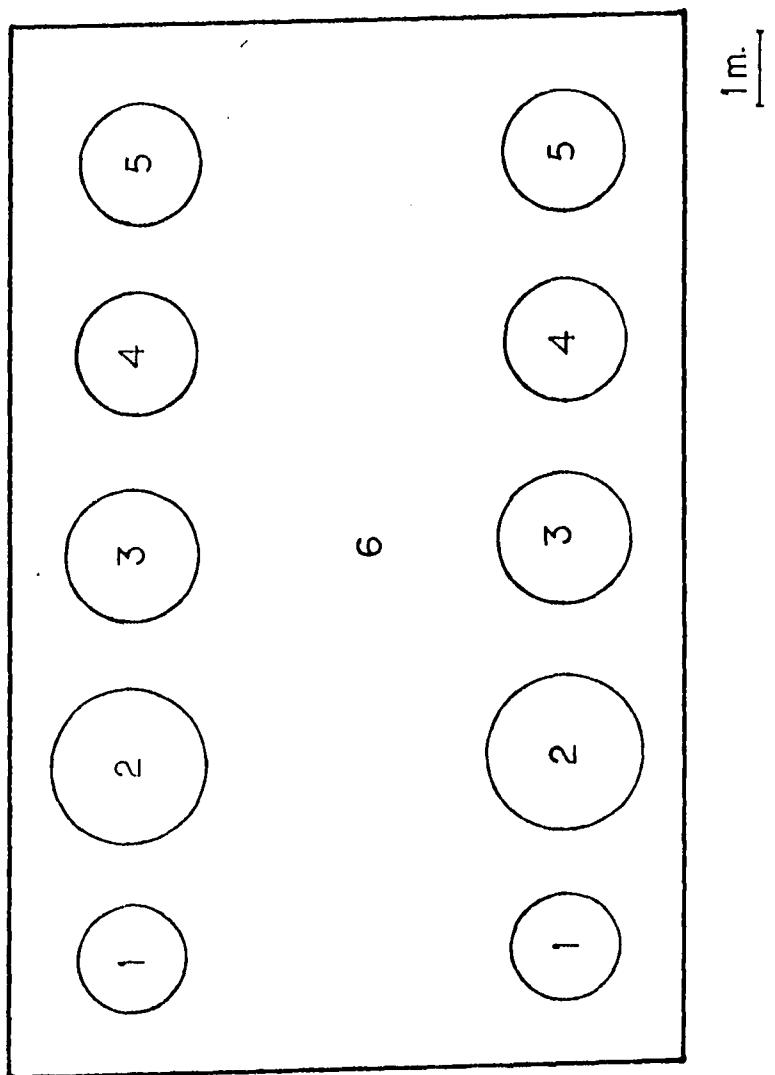
5.2.3.b. Basement Area A layout of the basement process areas was shown in Figure 28. Two remote maintenance cells, a contact maintenance process area, decontamination and maintenance rooms, and an equipment transfer aisle are contained in the basement of the west building.

The remote cells house the HLW treatment and solid ILW treatment processes. The LLW treatment and acid recovery process is located in the contact maintenance process area.

Remote cells are equipped with manipulators and remote bridge cranes to perform maintenance operations. Aisles for replacing failed equipment are provided in the basement process areas since overhead space is limited in the basement. This leads to a 2-line arrangement of processing since 4-line processing would require a larger area than the grade level area of the building. Equipment failure in the basement processes will then cause the shutdown of 2 process lines in the RMC, dropping the plant capacity to 50 % during the equipment replacement operations. Listing and arrangement of equipment for HLW treatment and LLW treatment and acid recovery processes are given in Figures 33 and 34.

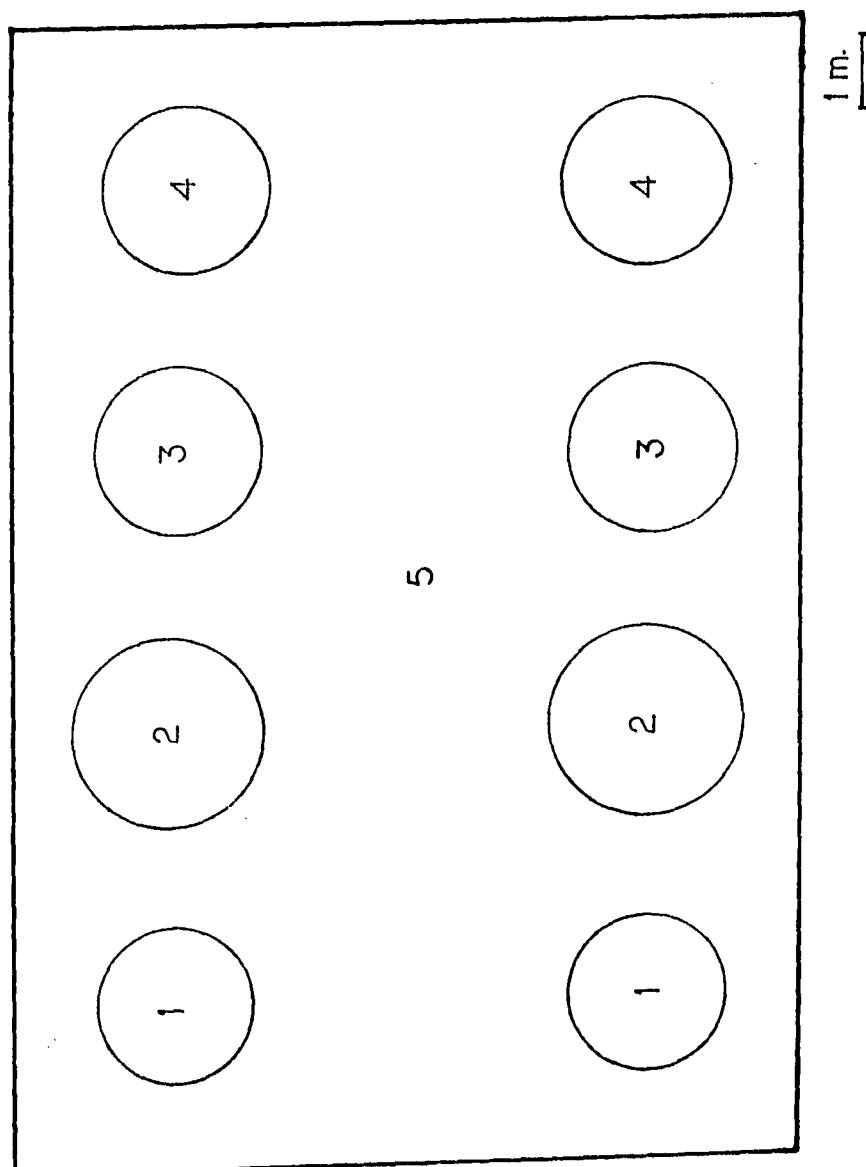
**FIGURE 33. Equipment Arrangement in HLW Treatment Cell**

- 
- 1. HLW feed tank**
  - 2. HLW evaporator system**
  - 3. Denitration reactor**
  - 4. Fluidized bed calciner**
  - 5. Glass-forming vessel**
  - 6. Equipment transfer aisle**
-



**FIGURE 34. Equipment Arrangement in LLW Treatment and Acid Recovery**

- 
- 1. LLW feed tank**
  - 2. LLW evaporator system**
  - 3. Acid Fractionator**
  - 4. Holdup tank**
  - 5. Equipment transfer aisle**
-



Two of the decontamination rooms in the basement are under the equipment replacement hatches, one opening to the manhole in the RMC, and the other one to the equipment replacement aisle of the HLW treatment cell. These decontamination rooms are equipped with high pressure spray nozzles, monitoring devices, shielded windows, and overhead cranes. Each decontamination room is connected to a maintenance room where the repair work can be performed.

A wide aisle (4 to 6 m) is provided in the basement for equipment transfer. A remote fork lift is operated in this aisle. At the south end of the aisle is an equipment discharge room, where the equipment to be discharged is broken into pieces and packaged.

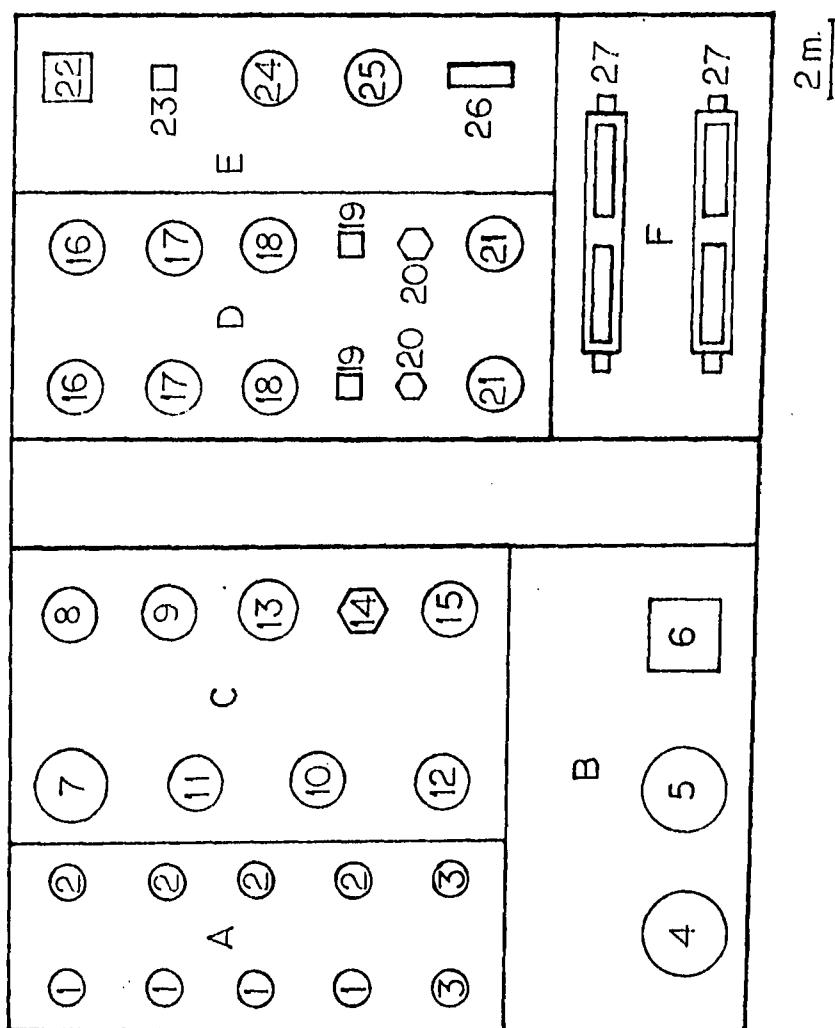
5.2.3.c. Contact Maintenance Process Area (CMPA) The CMPA, located in the east building, houses the following processes: U stripping (the 4th cycle of the solvent extraction separations), U calcination, used solvent treatment, and off-gas treatment. Listing and arrangement of equipment in the CMPA is given in Figure 35.

The CMPA is partitioned into several process cells by nearly 30 to 50 cm thick walls. Service aisles are provided between the cells. Failed equipment can be replaced through the aisles using overhead cranes. The cells are equipped with high pressure spray nozzles for decontamination operations, when necessary, to permit human entry.

The U stripping, U calcination, and used solvent treatment processes are 1-line processes; no manifolding is applied and no spare lines are provided. Provisions should be made for temporary holdup of

**FIGURE 35. Arrangement of Equipment in the CMPA**

- 
- |                                       |   |
|---------------------------------------|---|
| <b>A. U stripping area</b>            | <b>D. Off-gas treatment area</b>                |
| 1. Holdup column                      | (iodine removal and NO <sub>x</sub> absorption) |
| 2. Pulse column (U stripping)         |   |
| <b>B. U calcination area</b>          | <b>16. Caustic scrubber</b>                     |
| 3. Feed tank                          | 17. Water scrubber                              |
| 4. Evaporator system                  | 18. Caustic scrubber                            |
| 5. Fluidized bed calciner             | 19. Heater                                      |
| 6. Packaging station                  | 20. Prefilter                                   |
| <b>C. Used solvent treatment area</b> | 21. Adsorbent column                            |
| 7. Feed tank                          | <b>E. Off-gas treatment area</b>                |
| 8. Wash column                        | (cryogenic distillation)                        |
| 9. Holdup tank                        | 22. Prepurification step                        |
| 10. Distillation system               | 23. Precooler                                   |
| 11. Evaporator system                 | 24. Condensation column                         |
| 12. Holdup tank                       | 25. Fractional distillation system              |
| 13. Wash column                       | 26. Bottling station                            |
| 14. Metal filters                     | <b>F. Off-gas treatment area</b>                |
| 15. Holdup tank                       | (HEPA filtration)                               |
|                                       | 27. HEPA filters                                |
|                                       | <b>G. Equipment transfer corridor</b>           |
-



process streams in order to prevent the plant shutdown in case of a failure of equipment in these processes. Temporary storage rooms are provided in the basement of the CMPA. A temporary storage (or holdup) capacity of 15 days is made available; that is, the plant can be operated for 15 days with these 1-line processes shutdown. It is expected that 15 days should be more than enough for repairing or replacing a failed equipment unit in the CMPA.

Under normal conditions human entry into the contact cells is not required for process operations. Entry is permitted for maintenance and equipment replacement after monitoring and decontaminating the cell, if necessary.

The off-gas treatment system includes iodine removal, rare gas recovery, and HEPA filtration processes, which are all 1-line processes. A spare line is provided for the iodine removal and HEPA filtration processes to ensure that equipment failure in these processes will not cause any plant downtime. No spare line is provided for the rare gas recovery process. In case of equipment failure in this process, it is simply bypassed. The off-gases containing rare gases can be safely discharged into the atmosphere through a high stack for several weeks [32].

5.2.3.d. Other Areas      A maintenance area, located adjacent to the CMPA, includes a decontamination room and several repair ports. A change room is provided near the maintenance area.

To the south of the CMPA are temporary storage (for about 5 days) rooms and shipping ports for the packaged U product and bottled rare gases.

The east building also houses the following areas: chemicals storage and cold feed preparation area, analytical laboratory, miscellaneous waste handling area and personnel area.

The west building also includes a cask receipt and handling area, a storage cell for packaged HLW, a storage vault for packaged U+Pu product, shipping ports, and an analytical laboratory.

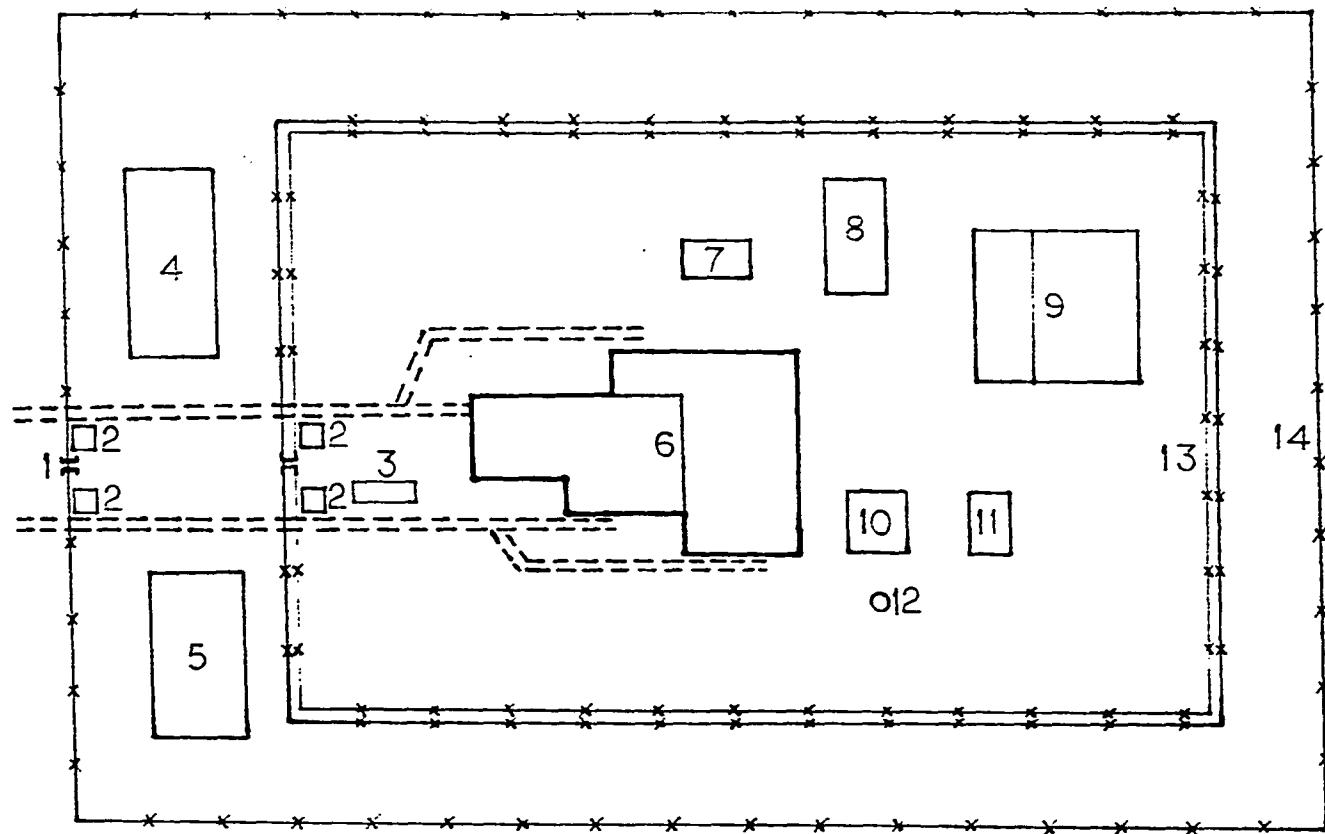
#### 5.2.4. Site Layout

The site layout, adapted from Reference [47], is shown in Figure 36. Except for the administration building and general store, all the other facilities are located within an inner perimeter, which is established by a double fence system with area monitors. The whole plant site is surrounded by an outer fence. Guard check stations for control of personnel access are located at entrance points at the inner and outer perimeter.

For this layout, site security considerations are discussed in detail in Reference [47]. It will suffice here to state that the site layout presented provides satisfactory external physical protection from a safeguardability standpoint and does not interfere with process building design [47].

**FIGURE 36. Site Layout**

- 
- 1. Entrance
  - 2. Guard check station
  - 3. Guard center
  - 4. Administration building
  - 5. General store
  - 6. Main process building
  - 7. Electrical substation
  - 8. Water, compressed air, and diesel electric generator area
  - 9. Warehouse and shops
  - 10. Heating and air-conditioning building
  - 11. Ventilation building
  - 12. Exhaust stack
  - 13. Double fence system with area monitors
  - 14. Outer fence
-



20m

roads == =  
fences -x-x-

## 6. COST ESTIMATION

A cost estimation of the plant designed will be made in this chapter. A complete cost estimation involves determination of the fixed capital cost (FCC) and total product cost (TPC). The FCC includes the total direct plant cost and indirect costs. The TPC consists of operating costs and general expenses. These costs will be broken down and presented in this chapter.

### 6.1. Fixed Capital Cost

The breakdown of the FCC for a nuclear reprocessing plant is shown in Table 11. In general, major components of the FCC for a nuclear reprocessing plant and a conventional chemical plant can be assumed to be the same; however, in the case of nuclear reprocessing, radioactivity and criticality considerations lead to inclusion of additional items.

A study estimate, or factored estimate, of the FCC, which is based on the cost of major process equipment delivered, will be made. In a simple study estimate, the FCC is calculated by multiplying the delivered equipment cost (DEC) by an appropriate factor (Lang factor). Probable accuracy of a study estimate is stated as  $\pm 30\%$  [38]. A more accurate study estimate can be obtained by using a separate subfactor for each component of the FCC, shown in Table 11. The sum of these subfactors is the Lang factor for the project in question. Noting the difficulty in deciding on a single value for a subfactor,

Miller suggests picking up a high, probable, and low value for each subfactor [48]. This results in a maximum, most likely, and minimum estimate of the FCC.

The first step in estimating the FCC is to determine the DEC. Published data have been used for this purpose. Almost all published costs are Free On Board (FOB) prices, which include loading charges but not freight charges. Freight charges can be taken as 5 % of the published costs (7 % for western locations) [39]. Cost of major process equipment is presented in Table 12. Capacity (or size) and time corrections for the cost data have been made using scaling factors and Marshall and Swift cost indexes [49].

Costs of some items in Table 12 for which published cost data are not available have been estimated considering costs of similar items. A  $\pm$  25 % accuracy is assumed for cost of such an item. This results in an accuracy of  $\pm$  12 % in the total DEC. After adding a contingency allowance of 20 % [39] for miscellaneous unlisted items, the total DEC is estimated to be 17,455,000 to 22,030,000 \$ in 1987.

The second step in estimating the FCC is to choose the subfactors for the components of the FCC presented in Table 11. The subfactors used and the estimation of the FCC based on them are presented in Table 13. A high and a low subfactor have been picked up for each component of the FCC after due consideration of the subfactors given for conventional chemical plants and nuclear reprocessing plants in the literature. Because of the stringent specifications of a nuclear

reprocessing plant, usually the most conservative (highest) values for the subfactors have been chosen.

Costs for support systems and buildings have been determined separately. An Argonne National Laboratory study [50] is the main source for the cost of the support systems. Building costs have been calculated using the data given in References [39,51]. Time corrections for the building costs were made using Chemical Engineering Plant cost indexes [52]. Estimation of building costs is discussed in Appendix 10.6.

The indirect costs are estimated as 54 % of the direct costs, which is higher than the maximum value suggested for ordinary chemical plants (45 %) and consistent with the values used in the old (late 1950s and 1960s) cost studies of nuclear reprocessing plants [6,25,46]. Notwithstanding, because some studies of 1970s estimate the indirect costs of reprocessing plants as more than 100 % (up to 149 %) of the direct costs [32,53], the FCC estimate with the indirect costs as 149 % of the direct costs is also included.

Based on the high value of the DEC (22,030,000 \$ in 1987), the total direct costs have been estimated to be 141 to 194 million \$ in 1987. The estimates of the FCC are 257 million \$ (217 to 297 million \$) with the indirect costs as 54 % of the direct cost and 417 million \$ (351 to 483 million \$) with the indirect cost as 149 % of the direct cost. Although, in a study estimate where information is not complete, it is likely that the estimated cost will be lower than the

actual cost, the above direct cost estimate ought to be an overestimate rather than an underestimate: it is based on conservative values of the subfactors and the high estimate of the DEC.

TABLE 11. Breakdown of Fixed Capital Cost

---

**A. DIRECT PLANT COSTS**

1. Delivered equipment cost (FOB cost + freight charges)
  2. Special cost for equipment (remote maintenance features, quality assurance)
  3. Installation cost (installation of process equipment, equipment foundations and structural supports, insulation of equipment)
  4. Piping cost (process piping, insulation of piping, fittings, valves, hangers, jumpers, connectors)
  5. Electrical auxiliaries (electrical equipment, materials, and labor)
  6. Instrumentation and controls (instruments and installation)
  7. Support systems (robot systems, manipulators, remote bridge cranes, samplers, etc.)
  8. Main plant building and services
    - a. Heavily shielded areas (heavy shielding, crane maintenance caves, shielded windows, air-lock openings, services, etc.)
    - b. Other areas (including services)
  9. Auxiliary buildings and services (administration building, warehouses, general store, guard houses)
  10. Services (electrical substation and distribution system, air compression, refrigeration, water distribution, steam and gas distribution, fuel, fire protection, etc.)
  11. Site development (clearing, landscaping, roads and walks, fencing, parking lots, etc.)
  12. Land purchase
- 

**B. INDIRECT COSTS**

1. Engineering and supervision
  2. Construction expenses
  3. Contractor's fee
  4. Contingency
-

TABLE 12. Cost of Major Process Equipment

Equipment unit <sup>a</sup>	Capacity <sup>b</sup> or size	Unit FOB cost (x1000 \$)	Date	Ref.	Unit FOB cost in 1987 (x1000 \$)	Number of units	Total FOB cost in 1987
<b>Feed preparation equipment</b>							
Shear and diverter <sup>c</sup>						1	475-725
Dissolver <sup>3</sup>	35 kg/h				270-450	4	1080-1800
Downdraft condenser	100 sf	6.00	1979	38	9	4	36
Accountability tank	100 gal	4.40	1979	38	7	4	28
Centrifugal filter	D=18 in	30.00	1979	38	43	4	172

<sup>a</sup> All the equipment is made of stainless steel (mostly 316, rarely 304 or unspecified, depending on the cost data available).

<sup>b</sup> The following units have been used to express capacity (or size) of equipment, depending on the type of equipment and cost data:  
processing rate in kg/h, lb/h, lt/h, or cf/min,  
heat transfer area in sf,  
filter area in sf,  
diameter (D) in cm or in,  
height (H) in m or ft,  
weight in lb,  
volume in gal.

<sup>c</sup> For these items, no published cost data have been found. The cost estimates are based on costs of similar items and a probable accuracy of  $\pm 25\%$  is assumed.

TABLE 12 (continued)

Equipment unit <sup>a</sup>	Capacity <sup>b</sup> or size	Unit FOB cost (x1000 \$)	Date	Ref.	Unit FOB cost in 1987 (x1000 \$)	Number of units	Total FOB cost in 1987
Feed adjustment tank	100 gal	4.40	1979	38	7	4	28
<b>Subtotal</b>							<b>1819-2789</b>
<b>Solvent extraction equipment</b>							
Holdup column	370 lb	7.18	1979	38	11	4	44
Holdup column	660 lb	10.37	1979	38	15	4	60
Holdup column	220 lb	5.33	1979	38	8	4	32
Holdup column	580 lb	9.78	1979	38	14	4	56
Codec. column	D=10 cm H=7.5 m	13.30	1982	23	14	4	56
Partial part. column	D=15 cm H=9.0 m	21.40	1982	23	23	4	92
Finish part. column	D=15 cm H=3.0 m	11.20	1982	23	12	4	48
U strip. column	D=20 cm H=6.0 m	21.80	1982	23	24	4	96
<b>Subtotal</b>							<b>484</b>
<b>U+Pu calcination equipment</b>							
Feed tank	200 gal	4.33	1979	38	7	4	28

TABLE 12 (continued)

Equipment unit <sup>a</sup>	Capacity <sup>b</sup> or size	Unit FOB cost (x1000 \$)	Date	Ref.	Unit FOB cost in 1987 (x1000 \$)	Number of units	Total FOB cost in 1987
Evaporator	1525 lb/h	34.00	1961	55	117	4	468
Deent. column	900 lb H=5 ft	17.50	1979	38	26	4	104
Condenser	130 sf	6.50	1979	38	10	4	40
Holdup tank	200 gal	4.33	1979	38	7	4	28
Fluidized bed reactor <sup>c</sup>	30 lt/h				38-62	4	162-248
Dust collector	1000 cfm	20.00	1979	38	29	4	116
Packaging station <sup>c</sup>					110-190	4	440-760
Subtotal							1386-1792
<b>HLW treatment equipment</b>							
Feed tank	100 gal	2.60	1979	38	4	2	8
Evaporator	1560 lb/h	36.00	1961	55	124	2	248
Deent. column	900 lb H=5 ft	17.50	1979	38	26	2	52
Condenser	150 sf	8.00	1979	38	12	2	24
Denitr. reactor	40 gal	9.50	1979	38	14	2	28
Fluidized bed reactor <sup>c</sup>	70 lt/h				62-104	2	124-208

TABLE 12 (continued)

Equipment unit <sup>a</sup>	Capacity <sup>b</sup> or size	Unit FOB cost (x1000 \$)	Date	Ref.	Unit FOB cost in 1987 (x1000 \$)	Number of units	Total FOB cost in 1987
Dust collector	2000 cfm	25.00	1979	38	36	2	72
Glass forming vessel	20 kg/h	220.00	1986	34	223	2	446
<b>Subtotal</b>							<b>1002-1086</b>
<b>LLW treatment and acid recovery equipment</b>							
Feed tank	2000 gal	13.73	1979	38	20	2	40
Evaporator	14385 lb/h	128.00	1961	55	441	2	882
Deent. column	1800 lb H=8 ft	27.00	1979	38	39	2	78
Condenser	500 sf	16.00	1979	38	23	2	46
Fractionator	14000 lb/h	128.00	1961	55	430	2	860
Holdup tank	2000 gal	13.73	1979	38	20	2	40
<b>Subtotal</b>							<b>1946</b>
<b>U calcination equipment</b>							
Feed tank	2000 gal	13.73	1979	38	20	2	40
Evaporator	15400 lb/h	133.50	1961	55	460	1	460
Deent. column	1800 lb H=8 ft	27.00	1979	38	39	1	39
Condenser	500 sf	16.00	1979	38	23	1	23

TABLE 12 (continued)

TABLE 12 (continued)

Equipment unit <sup>a</sup>	Capacity <sup>b</sup> or size	Unit FOB cost (x1000 \$)	Date	Ref.	Unit FOB cost in 1987	Number of units	Total FOB cost in 1987 (x1000 \$)
<b>Off-gas treatment equipment<sup>d</sup></b>							
Caustic scrubber	17.95	1976	32	31		2	62
Water scrubber	17.95	1976	32	31		1	31
Preheater	1.00	1976	32	2		1	2
Protective filter	4.00	1976	32	7		1	7
AgZeo adsorption column	208.00	1970	54	556		1	556
Cryogenic distill. system	711.75	1976	32	961		1	961
HEPA Filters	37.40	1960	54	130		2	260
<b>Subtotal</b>							<b>1879</b>
<b>Other equipment<sup>e</sup></b>							
Temporary storage tanks							930-1400

<sup>d</sup> The costs of off-gas treatment equipment have been adapted from References [32,54], which present the equipment costs for a certain plant capacity, without specifying the capacity or size of equipment. When required, corrections for the plant capacity have been made assuming an exponential factor of 0.6.

<sup>e</sup> Costs for these items are based on an average capacity and approximate number of units required. A probable accuracy of  $\pm 25\%$  is assumed.

TABLE 12 (continued)

Equipment unit <sup>a</sup>	Capacity <sup>b</sup> or size	Unit FOB cost (x1000 \$)	Date	Ref.	Unit FOB cost in 1987 (x1000 \$)	Number of units	Total FOB cost in 1987 (x1000 \$)
Pumps							1200-1800
Compressors							500-800
Blowers							400-600
ILSW processing equipment							190-310
Chemicals storage tanks							560-910
<b>Subtotal</b>							<b>3780-5820</b>
FOB cost of main plant items							13960-17625
Miscellaneous unlisted items (20 % of FOB cost [39])							2795-3525
<b>Total FOB cost</b>							<b>16755-21150</b>
Freight charges (5 % of FOB cost [39])							700-880
<b>Total DEC cost</b>							<b>17455-22030</b>

TABLE 13. Estimation of the FCC

Component <sup>a</sup>	Subfactors (percentage of DEC) low / high	Sources	Cost (million \$)	
			low	high
<b>A. Direct Costs</b>				
1.DEC	100		22.03	
2.Special cost for equipment <sup>b</sup>	—	25	4.82	
3.Installation	40.0 / 53.0	38,48	8.81 / 11.68	
4.Piping	80.0 / 150.0	48,56	17.62 / 33.05	
5.Electrical	5.5 / 11.0	25,56	1.21 / 2.42	
6.Instrumentation	18.0 / 37.0	48	3.97 / 8.15	
7.Support systems	—	25,50	15.00 / 20.00	
8.Main process building <sup>c</sup>				
a.Heavily shielded areas	—	32	32.00 / 40.00	
b.Other areas	—	51	7.00 / 17.00	
Total			39.00 / 57.00	
9.Auxiliary buildings <sup>c</sup>	—	51	6.00 / 8.00	
10.Services	80.0 / 90.0	56	17.62 / 19.83	
11.Site development	20.0 / 25.0	56	4.41 / 5.51	
12.Land purchase	4.0 / 8.0	38	0.88 / 1.76	

<sup>a</sup> See Table 11 for a description of the cost components.

<sup>b</sup> 80 % of cost of remote maintenance equipment (4,600,000 to 6,100,000 \$ in 1987) [25].

<sup>c</sup> See Appendix 10.6 for a description of building costs.

TABLE 13 (continued)

Component <sup>a</sup>	Subfactors (percentage of DEC) low / high	Sources	Cost (million \$) low / high
<b>TOTAL direct costs</b>			<b>141.37 / 194.25</b>
<b>B. Indirect Costs (54 % of direct costs)</b>			
1.Engineering and supervision (15 % of direct costs)	25,38	21.20 / 29.14	
2.Construction (20 % of direct costs)	25,38	28.27 / 38.85	
3.Contractor's fee (6 % of direct costs)	38	8.48 / 11.66	
4.Contingency (13 % of direct costs)	38	18.38 / 25.25	
<b>TOTAL indirect costs (54 % of direct costs)</b>		<b>76.14 / 104.76</b>	
<b>TOTAL FCC (with indirect costs as 54 % of direct costs)</b>		<b>217.00 / 297.00</b>	
<b>Indirect costs<sup>d</sup> (149 % of direct costs)</b>	32	210.00 / 289.0	
<b>TOTAL FCC (with indirect costs as 149 % of direct costs)</b>		<b>351.00 / 483.00</b>	

<sup>d</sup> The breakdown of the indirect costs (149 % of the direct costs) is given as follows [32].

#### Percentage of the direct costs

Engineering and supervision	15
Construction and contractor's fee	20
Engineering design	19
Quality assurance	6
Other owner's cost	10
Contingency	40
Interest during construction	39

### 6.2. Total Product Cost

The TPC consists of operating cost, general expenses, and financing cost. The operating costs are divided into three categories: (1) direct operating costs, (2) fixed charges, and (3) overhead costs. The general expenses include administrative costs, distribution and marketing expenses, and research and development expenses. Financing cost (interest on borrowed capital) is in fact a fixed charge; however, whether or not it should be included in the TPC is questionable [38]. Thus, the financing cost is considered here as a separate expense. The TPC with and without financial cost will be estimated. Table 14, condensed basically from the data given in Reference [38], exhibits a detailed breakdown of the TPC.

Estimation of the total product cost on an annual basis is presented in Table 15. The annual TPC is estimated as 72,000,000 \$ without financing cost, 87,000,000 \$ with 5 % financing cost, and 102,000,000 \$ with 10 % financing cost when the FCC estimate is 257,000,000 \$, and 106,000,000 \$ without financing cost, 131,000,000 \$ with 5 % financing cost, and 156,000,000 \$ with 10 % financing cost when the FCC estimate is 417,000,000 \$. The estimates of the total product costs with and without financing cost on annual and unit-of-product bases are exhibited in Table 16.

TABLE 14. Breakdown of Total Product Cost<sup>a</sup>

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A. Operating Cost

1. Direct Operating Costs

- a. Raw materials, catalysts, and solvents
- b. Operating labor
- c. Supervision and clerical labor
- d. Maintenance and repairs
- e. Utilities
- f. Operating supplies
- g. Laboratory charges

2. Fixed Charges

- a. Depreciation
- b. Annual payment to establish a fund for decommissioning
- c. Property taxes
- d. Insurance

3. Plant Overhead Costs (medical, safety and protection, payroll overhead, general plant overhead, packaging, restaurant, recreation, control laboratories, plant superintendence, storage facilities)

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B. General Expenses

1. Administrative Costs (executive salaries, clerical wages, engineering costs, office maintenance, communications)

2. Distribution and Selling Costs

3. Research and Development

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C. Financing Cost (interest)

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<sup>a</sup> Source: Reference [38] (pages 192, 207, and 208).

TABLE 15. Estimation of Total Product Cost

Component <sup>a</sup>	Method of Estimation	Sources	Annual Cost in 1987 (million \$)	
			FCC <sup>b</sup>	
			257	417
<b>A.1</b>				
1.a.	Material balance and prices of chemicals (see Appendix 9)	—	3.9	3.9
1.b.	Manpower estimate and average wage rates <sup>c</sup>	—	1.8	1.8
1.c.	25 % of 1.b.	38	0.5	0.5
1.d.	3 % of FCC	25, 38	7.7	12.5
1.e.	20 of TPC without financing	38	14.3	21.2
1.f.	20 % of 1.d.	38, 48	1.5	2.5
1.g.	60 % of 1.d.	25	4.6	7.5
<b>A.1. Total</b>			<b>34.3</b>	<b>49.9</b>
<b>A.2.</b>				
2.a.	Straight-line method over 30 years	39	8.6	13.9

<sup>a</sup> Refer to Table 14 for a description of components of the TPC.

<sup>b</sup> The average estimates of the FCC are 257 and 417 million \$ in 1987 (Table 13) when the indirect costs are calculated as 54 and 149 % of the direct costs, respectively.

<sup>c</sup> Operating labor has been estimated as 225 employee hours/day and average hourly wage rate of craft labor has been taken as 22 \$, including fringe benefits and employer's burden [38].

TABLE 15 (continued)

Component <sup>a</sup>	Method of Estimation	Sources	Annual Cost in 1987 (million \$)	
			FCC <sup>b</sup>	
			257	417
2.b.	0.8 % of FCC <sup>d</sup>	57	2.1	3.3
2.c.	2 % of FCC	38,48	5.1	8.3
2.d.	1 % of FCC	38,48	2.6	4.2
A.2. Total			18.4	29.7
A.3.	70 % of (1.b.+1.c.+1.d.)	38	9.7	13.1
A. TOTAL			62.4	92.7
B.				
1.	15 % of (1.b.+1.c.+1.d.)	38	2.1	2.8
2.	5 % of TPC without financing	38	3.6	5.3
3.	5 % of TPC without financing	38	3.6	5.3
B. TOTAL			9.3	13.4
TPC (without financing)			71.7	106.1
C.	5 % of total capital cost <sup>e</sup>	15.0	25.0	
	10 % of total capital cost	30.0	50.0	
TPC (with 5 % financing) <sup>f</sup>		87.0	131.0	
TPC (with 10 % financing)		102.0	156.0	

<sup>d</sup> Decommissioning cost of a nuclear reprocessing plant is estimated as 20 % of the FCC [57].

<sup>e</sup> Total capital cost (TCC) is the FCC plus working capital, which is estimated as 15 % of the TCC [38].

<sup>f</sup> Rounded values.

TABLE 16. Summary of Total Product Costs

	TPC (1987) <sup>a,b</sup>					
	without financing		with 5 % financing		with 10 % financing	
	<sup>FCC<sup>c</sup></sup>					
	257	417	257	417	257	417
Annual (million \$)	72	106	87	131	102	156
\$/kg U in SF	94	138	114	172	132	204
\$/kg U originally loaded	90	132	109	164	126	195
\$/kg UO <sub>2</sub> originally loaded	79	116	96	145	111	172

<sup>a</sup> Rounded values.

<sup>b</sup> Based on a design capacity of 960 MT U (originally loaded) per year and a capacity factor of 0.83.

<sup>c</sup> The average estimates of the FCC are 257 and 417 million \$ in 1987 (Table 13) when the indirect costs are calculated as 54 and 149 % of the direct costs, respectively.

## 7. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Purex reprocessing of 10-year cooled LWR fuel has been investigated in the foregoing chapters. The three major areas of research have been (1) process description and flowsheet calculations, (2) plant design, and (3) cost estimation.

Involvement of nearly 13 times less radioactivity in the 10-year cooled fuel than that in the 150-day cooled fuel, and the adoption of coprocessing of U and Pu in a new flow sheet rather than the complete partitioning of the standard purex method have resulted in several simplifications in the process and design over the standard purex method reprocessing 150-day cooled fuel, leading to a simpler and more economic design for reprocessing. The conclusions arrived at and recommendations for future work are discussed in this chapter.

### 7.1. Conclusions

It is a prime requirement that a reprocessing plant should be designed to achieve the necessary decontamination factors (DFs) for the U and Pu products. The necessary DFs mainly depend on amount and type of initial activity in the SF, which is strictly dependent on the length of the cooling period prior to the reprocessing, and the subsequent use of the U and Pu products, and determine the number of the extraction cycles needed. Because the U product of the reprocessing is going to be handled by direct contact, a high degree of decontamination of U from FPs is required. The necessary DFs are

$DF_{U-FP} = 7.0E6$  for 150-day cooled fuel, and  $DF_{U-FP} = 5.0E5$  for 10-year cooled fuel. If the Pu product of the reprocessing is going to be used as fuel, after being mixed with certain amounts of U in a MOX fuel fabrication plant, the complete separation of U from Pu, which is one of the basic processes included in the standard purex method, is not needed. Thus, requirements for obtaining an almost completely U-free Pu product are eliminated. A Pu product containing 94 to 95 % U as LWR fuel (or 75 to 80 % U as FBR fuel) is aimed at in the reprocessing. What governs the DF required for this U+Pu product is Pu activity. Because the activity of the Pu itself in the SF is quite high compared to that of the FPs, relatively mild decontamination of FPs from the U+Pu stream is sufficient: this calls for a  $DF_{Pu-FP}$  of 500 to 1500. By contrast, in a standard reprocessing plant designed to produce highly pure Pu the required  $DF_{Pu-FP}$  is  $1.0E6$  to  $1.0E7$  and more than 0.1 w/o U in the Pu product is not tolerable [5,6].

In a standard plant, processing 150-day cooled fuel to produce completely separated and highly pure U and Pu streams, the solvent extraction separations process basically consists of the following cycles : codecontamination, complete partitioning, U stripping, U purification, and Pu purification. Very often a stripping (back-washing) cycle is added between the codecontamination and complete partitioning cycles. This serves the purpose of reducing the solvent degradation due to radiolysis by decreasing the contact time between the solvent and radioactivity. For the proposed design

handling long-cooled fuel, the flowsheet calculations have been performed to determine the DFs achieved in each extraction cycle. The results show that a solvent extraction separations process composed of 4 cycles (codecontamination, partial partitioning, finish partitioning, and U stripping) is sufficient to achieve the necessary DFs together with high process yields. The purification cycles in the standard flowsheet are not needed, both because of the reduced decontamination requirements and because nuclides that are hard to remove quantitatively no longer dominate the FP activity for long-cooled fuel. Moreover, the additional stripping cycle between the codecontamination and partitioning cycles is not necessary at all because solvent radiolysis is not a serious problem in the case of the long-cooled fuel. Table 17 summarizes the results of the flowsheet calculations for the codecontamination cycle and compares the DFs for the long- and short-cooled fuels.

Degradation of the organic solvent (TBP) under intense radiation fields can give rise to poor decontamination factors and formation of solids which may eventually cause the plugging of the extraction equipment. The TBP degradation is a more serious problem in the case of the short-cooled fuel, which involves higher radiation levels, and has led to the use of more complicated and expensive contactors (centrifugal contactors) with short-contact times. Although a quantitative study of the TBP degradation has not been made here, it can certainly be stated that, when reprocessing the long-cooled fuel,

TABLE 17. The DFs Required and Results from the Flowsheet Calculations for the Codecontamination Cycle

	Standard Plant (150-day cooled fuel)	Proposed Plant (10-year cooled fuel)
DF <sub>U-FP</sub>	7.0E6	5.0E5
DF <sub>U-a</sub>	2.0E4	2.0E4
DF <sub>Pu-FP</sub>	1.0E6-1.0E7	500-1500
Tolerable amount of U in Pu	< 0.1 w/o	94-95 w/o

Contaminant	Cooling period	Activity ( $\mu\text{Ci/g U}$ ) Codecontamination cycle Aq feed      Org product	DF achieved
Zr	150 day	8.40E5      2.81E3	300
	10 year	2.86      9.50E-3	300
Ru	150 day	1.05E6      6.60E3	160
	10 year	1.15E3      7.3	160
Rare earths	150 day	2.50E6      0.626	4.00E6
	10 year	3.30E5      0.083	4.00E6
Total FPs	150 day	4.38E6      9.43E3	465
	10 year	3.30E5      7.4	4.64E4

the TBP degradation is not as serious a problem as is in the case of the short-cooled fuel. Therefore, simpler and cheaper but more dependable contactors (pulse columns, or even mixer-settlers) with longer-contact times than centrifugal contactors can be employed with success. In general, for the same type of contactor, better performance, more regular extraction behavior, and higher efficiency are achieved when processing less-active fuel.

As can be seen in Table 17, the codecontamination cycle achieves a much higher DF from the FPs when processing the long-cooled fuel than that when processing the short-cooled fuel. This stems from the fact that the Zr and Ru groups of FPs, which are the most difficult ones to remove by the solvent extraction, are the major contributors to the overall FP activity in the short-cooled fuel. The FPs (Cs, Ba, Sr, etc.) that can be easily removed by solvent extraction are responsible for the major portion of the FP activity in the long-cooled fuel.

In the complete partitioning cycle of the standard flowsheet, it is required to reduce all the Pu to the inextractable trivalent state. This is done by the addition of a reducing agent. Because of the competing oxidation-reduction reactions, re-oxidation of the Pu(III) is hard to prevent. Therefore, the complete partitioning process is considered to be the most difficult one to control. In order to avoid major process upsets, reduction methods which require complicated and expensive equipment (reduction with U(IV), or electrolytic reduction), instead of a simple reducing agent like hydroxylamine, have been used

and/or proposed for use in the complete partitioning cycle. The partial partitioning cycle, in the form suggested in several other studies [8,9,18], also involves the addition of a reductant, which can very likely exhibit the same difficulties as in the complete partitioning cycle. Our flow sheet calculations have shown that the partial partitioning of U and Pu can be accomplished merely by adjusting the flow rates and compositions of the streams, without needing reduction of the Pu. Such a partial partitioning process requires close control of the flow rates and compositions of the streams and makes use of the differences between the distribution coefficients of U(VI) and Pu(IV) to produce an aqueous U+Pu product solution, and an organic U product solution for which the necessary decontamination has not yet been accomplished at this stage. The partial partitioning process also obtains a better decontamination for U from the FPs than the complete partitioning process in the standard flowsheet because it employs a dilute HNO<sub>3</sub> solution as the scrub solution instead of a HNO<sub>3</sub> solution of an intermediate concentration in the complete partitioning process. As discussed in Chapter 3, except for Ru almost all the FPs exhibit lower distribution coefficients at lower HNO<sub>3</sub> concentrations.

The organic U solution from the partial partitioning is then processed in a cycle called finish partitioning for removing the remaining amounts of Pu. Although a reductant must be used in the finish partitioning contactor, the difficulties arising from the

reduction of Pu are relatively insignificant because, compared to the complete or partial partitioning cycles, only very small amounts of Pu are present in the finish partitioning cycle. A simple reductant like hydroxylamine can be satisfactorily used in the finish partitioning cycle. The finish partitioning cycle, by removing additional amounts of the FPs from the U stream, also improves the decontamination of U from FPs to such an extent that the necessary  $DF_{U-FP}$  is achieved at the end of the finish partitioning process. No purification cycles are required for the organic U product leaving the finish partitioning cycle.

In summary, in the proposed flowsheet, the partial partitioning process is divided into 2 less complicated steps: partial partitioning (main partitioning of U and Pu to produce a mixed U+Pu stream and a U stream without reducing Pu to the Pu(III)), and finish partitioning (decontamination of U stream from Pu and additional removal of FPs by reducing Pu to the Pu(III) with hydroxylamine). Such an arrangement of the partitioning process not only results in relatively trouble-free operation with high efficiency but also improves the  $DF_{U-FP}$  significantly.

As mentioned earlier, the adoption of coprocessing gives rise to reduced decontamination requirements for the Pu product so that the necessary  $DF_{Pu-FP}$  is easily accomplished in the codecontamination cycle; this eliminates the Pu purification cycles required in the standard flowsheet. The elimination of the Pu purification cycles is a

major simplification, which also leads to better safeguardability features. In the coprocessing flowsheet, the principal flows of Pu are handled in a minimum number of process vessels, which can be located together in the same process area. This reduces surveillance requirements and makes it easier to obtain a draw-down inventory of Pu more frequently with less uncertainty than in a flowsheet containing a larger number of process vessels handling Pu.

Another advantage from the safeguardability standpoint results from the fact that the coprocessing flowsheet never completely separates U and Pu. It is more difficult and takes longer for a diverter to obtain weapons material from a mixed U+Pu product than from a pure Pu product. In the SAFAR project [9] the desirability of the several process materials to a potential diverter was measured by a factor named relative attractiveness factor (RAF). The RAF, which is a measure of the relative degree of protection that should be provided for that particular material, is defined as the product of three attribute factors: density, gamma activity, and time factors. Table 18 lists the RAFs for the Pu-bearing streams produced in a standard purex flowsheet and a purex coprocessing flowsheet. The RAF for the material produced in a coprocessing flowsheet (  $(U,Pu)O_x$ , or  $(U,Pu)(NO_3)_x$  ) is half or less of that for the corresponding material produced in a standard flowsheet (  $PuO_2$ , or  $Pu(NO_3)_4$  ), as seen in Table 18.

In addition to the solvent extraction separations process consisting of the 4 cycles, the following processes are included in the

TABLE 18. Relative Attractiveness Factors for the Pu-Bearing Streams<sup>a</sup>

	Materials Attribute Factors			RAF
	Density	Gamma	Time	
Pure Pu metal	1.0	1.0	1.0	1.0
PuO <sub>2</sub>	0.7	1.0	0.9	0.63
(U,Pu)O <sub>2</sub>	0.4	1.0	0.65	0.25
Pu(NO <sub>3</sub> ) <sub>4</sub> solution	0.25	1.0	0.8	0.2
(U,Pu)(NO <sub>3</sub> ) <sub>x</sub> solution	0.15	1.0	0.7	0.1

<sup>a</sup> Source: Reference [9].

plant: shear-leach and preparation, U calcination, U+Pu calcination, intermediate level solid waste (ILSW) treatment, HLW glassification, LLW treatment and acid recovery, used solvent treatment, and off-gas treatment (including iodine retention and rare-gas recovery). The plant was designed as an integrated facility which contains all the above processes housed in 2 adjacent buildings.

Since the SF is already long-cooled, technically there is no need for the on-site storage of the SF and liquid HLW. The liquid HLW generated in the separations process can be immediately glassified. The storage capacity provided for the SF, glassified HLW, and products is minimized. A maximum of 50 tons of SF (17-day supply) is stored in an air-cooled cell. The outputs from the plant (calcined U and U+Pu

products, classified HLW, bottled rare gases, and packaged solid wastes) are stored on-site for only 5 days. All the storage functions can be arranged as extensions of the related processes and contained in the main process buildings because they do not require much room. A standard plant usually includes separate facilities for the storage of the SF (in large pools with a capacity of up to 2,000 tons) and liquid wastes (in large tanks with a capacity of up to 10,000 m<sup>3</sup>). It should be noted that, when processing the short-cooled fuel, the liquid HLW generated in the separations process should be cooled (stored) for 5 years before it is glassified because of the high heat liberation rate in it. In an integrated plant with minimum storage of the inputs and outputs and no storage of the intermediate streams, pumping, piping, and shielding requirements are considerably reduced compared to that in a plant composed of separate facilities with large storage capacities for the inputs, outputs, and intermediate streams.

One of the major problems that reprocessing plants, especially the commercial ones, have had is low operating efficiency. Several commercial plants have operated at 10 to 35 % of rated capacity due to equipment malfunction problems and had to be shut down in 9 years or fewer [40]. These commercial plants usually did not apply a high degree of remote maintenance. The West Valley plant was rated at 35 % remote maintenance and most others applied even less remote maintenance than West Valley [40]. On the other hand, some government plants with a high degree of remote maintenance, the Savannah River and Hanford

plants particularly, have experienced operating efficiencies of nearly 80 % and have operated longer than 30 years. In general, a direct correlation between the degree of remote maintenance and plant operating efficiency can be observed; consequently, a plant with a high degree of remote maintenance, where most radioactive equipment is maintained by remote means, is favored.

One process building is designed to house all the high and moderate activity processes, which are to be remotely maintained. Except for the HLW glassification process, all the other remote-maintenance processes, including the cask unloading and SF storage, are contained in a L-shaped remote canyon at grade level surrounded by operating corridors and served by robots and remote bridge cranes. The remote canyon opens through air-lock doors to several maintenance and decontamination rooms located in the basement. In the basement are also a large center-aisle remote cell for the HLW glassification, a small remote cell for the solid waste treatment, and a direct-maintenance process area for the LLW treatment and acid recovery. The L-shaping of the remote canyon and placement of the waste treatment facilities and maintenance rooms in the basement lead to a relatively compact structure and reduce the transfer lines for streams and equipment to be replaced.

In order to decrease the plant downtime during the equipment replacement operations, the remote canyon equipment is arranged in 4 parallel lines, each line carrying one fourth of the plant capacity.

On one hand, this manifolding increases the number of equipment units, requirements for connections and piping, and the necessary canyon volume; on the other hand, it improves the operating efficiency significantly and results in smaller-volume equipment, which is critically safe and easy to replace. The application of a high degree of remote maintenance and manifolding of process lines in the high and moderate activity processes ensure that the operating efficiency of the plant would not be much impaired by failure of equipment.

The low activity processes (U stripping, U calcination, used solvent treatment, and off-gas treatment) are contained in a large direct maintenance process area housed in the other building, located contiguous to the remote maintenance building. The direct maintenance processes do not require heavy shielding and can be handled almost like conventional chemical processes, especially when the fuel is long-cooled. Several equipment units are placed in the same room surrounded by light shielding and equipped with spray nozzles and radiation monitors in case decontamination of the room is required before human entry.

The capital cost and total product cost for the plant designed were estimated using a factored cost estimation method. The capital cost estimates are summarized in Table 19. An approximate breakdown of the direct cost is given in Table 20.

Table 21 lists capital costs of several reprocessing plants. The values adjusted to 1987 prices and a design capacity of 920 ton U/year

TABLE 19. Capital Cost Estimates for the Proposed Plant

	Million \$ in 1987		
	low	average	high
Direct cost	141	168	194
Indirect costs (as 53 % of the direct cost)	75	89	103
Indirect costs (as 149 % of the direct cost)	211	251	290
Fixed capital cost (with indirect costs as 53 % of the direct cost)	217	257	297
Fixed capital cost (with indirect costs as 149 % of the direct cost)	351	417	483

are also included for comparing to the costs estimated in this study. The plants listed in Table 21 are essentially the ones for which cost estimates are available in the literature. A direct comparison of the costs is not possible because not every plant contains the same facilities and features and/or follows the same design philosophy, and several uncertainties arise from lack of complete cost data.

The AEC, Dupont, and ORNL plants are the standard base-case reprocessing plants, which do not include U conversion, Pu conversion, HLW solidification, and rare gas recovery (in the off-gas treatment)

TABLE 20. An Approximate Breakdown of the Direct Plant Cost for the Proposed Plant

	Percentage of Direct Plant Cost
SF receipt and storage	4.8
Head-end and feed preparation	17.5
Solvent extraction	4.9
U conversion	4.5
U+Pu conversion	12.0
HLW glassification	8.2
LLW treatment and acid recovery	7.6
Used solvent treatment	3.9
Off-gas treatment	7.4
ILSW treatment	1.8
Cold feed preparation, chemicals storage, final products storage, temporary storage of some intermediate streams	7.2
Laboratories, maintenance and personnel areas, auxiliary buildings, services, site improvements, land, etc.	20.2

TABLE 21. Capital Costs of Several Reprocessing Plants

	AEC	Dupont	ORNL	Barnwell <sup>a</sup>	SAFAR
Date	1957	1961	1973	1987	1982
Design capacity (ton U in SF/y)	360	3600	1500	1800	2160
References	[25]	[46]	[32]	[4]	[9]
Original capital cost (million \$)	41	60	125	1,400	2,000 to 2,700
Adjusted capital cost (1987 prices and 920 ton U/y capacity) <sup>b</sup>	174	171	275	1,275	1,500 to 2,000
Indirect costs (% of direct cost)	54	22	149	--	--
Adjusted indirect costs (million \$)	61	31	165	--	--
Adjusted direct cost (million \$)	113	140	110	--	--

<sup>a</sup> The cost estimate of the Barnwell plant, with an added HLW conversion facility, is given as 1,400 million \$ in 1987 in Reference [4].

<sup>b</sup> An exponential factor of 0.14 was used for cost-capacity adjustments, as suggested in the Dupont study [46].

processes. The estimates of the direct plant costs for these 3 plants are in fairly good agreement, as can be seen in Table 21.

Compared to a standard base-case plant, the major simplifications in the proposed design through which substantial savings can be expected are the elimination of the U and Pu purification cycles and storage needs for liquid HLW and liquid products and replacement of the large-capacity SF storage pools by a small-capacity, air-cooled cell. On the other hand, the proposed plant includes additional facilities and features, which will increase the costs (or offset the savings). These additions are U conversion, U+Pu conversion, HLW glassification, and rare gas recovery processes and the manifolding of process lines in most of the remote maintenance processes. It can be assumed that the cost of the support systems is not affected significantly. Taking the Dupont plant, for which nearly complete cost data are available, as the representative of the standard base-case plants, the incremental and decremental direct plant costs due to the above simplifications over and additions to a standard plant can be estimated. The results, exhibited in Table 22, show that the savings which can be achieved through the simplifications are offset by the additional facilities and features included and the direct costs for the two plants should be nearly the same. In fact, the direct cost of the proposed plant (141 to 194 million \$ in 1987) is a little higher than that of the Dupont estimate (140 million \$, as adjusted); however, the difference between the two is well acceptable considering all the uncertainties

involved. It can be concluded that the direct cost of the proposed plant will probably not exceed that of a standard base-case plant by more than 35 %.

TABLE 22. Comparison of the Direct Costs of the Dupont Plant and the Proposed Plant

	Adjusted Direct Costs (million \$)		
	Dupont plant	Proposed plant	Cost differential
SF receipt and storage	20.1	8.0	- 12.1
U conversion	--	7.5	+ 7.5
Pu conversion	--	20.2	+ 20.2
Off-gas treatment	3.0	12.5	+ 9.5
Head-end, feed preparation, and solvent extraction	69.0	37.6	- 31.4
HLW solidification	--	13.8	+ 13.8
Liquid HLW storage	12.6	--	- 12.6
ILSW treatment	--	2.9	+ 2.9
Total	104.7	102.5	- 2.2

The Barnwell and SAFAR cost estimates are very high compared to the other plants listed in Table 19. Because detailed cost data are not available for the Barnwell and SAFAR designs, a quantitative comparison of the costs cannot be made. The comparatively very high costs for the Barnwell and SAFAR can be, in general, attributed to additional facilities and features included and higher indirect costs.

In an attempt to explain the difference between the costs of the SAFAR plant and the proposed plant, a qualitative comparison of the two is made below.

The SAFAR design includes a separate fuel receiving and storage facility, which contains a fuel receiving and transfer area, a cask unloading cell, a 4-segment pool for storage of SF and solidified HLW, and its own support facilities. The pool (390x150 ft, 30 ft below grade, 5 ft thick walls) has a capacity of 600-ton SF plus 10-year solidified HLW [9,10]. The SF receiving and storage facility of the SAFAR accounts for one third of the total plant cost (1.5 to 2.0 billion \$, as adjusted) [9]. In the proposed design, fuel receiving and storage functions are contained in the remote maintenance building (a storage capacity of 50 ton SF is found adequate) and their contribution to the overall cost is not more than 8 %.

In addition to all the processes included in the proposed design, the SAFAR plant also contains UO<sub>3</sub>-to-UF<sub>6</sub> conversion, UF<sub>6</sub> purification, and fluoride off-gas treatment processes.

Although the SAFAR design employs a coprocessing flowsheet that has fewer process steps than a conventional purex flowsheet, it still includes two U purification and one Pu purification cycles. The total number of process steps required to obtain decontaminated liquid products is nearly 32 in the SAFAR flowsheet. The 4-cycle solvent extraction process adopted in this study also requires 32 process steps because of the 4-line arrangement. This implies that each process step in the proposed flowsheet has a capacity of one fourth of that in the SAFAR flowsheet. Besides, more complicated and expensive equipment (centrifugal contactors employed in the Pu cycle, concentrators required in the purification cycles) is used in the SAFAR flowsheet.

The SAFAR plant contains several storage functions (a liquid HLW surge cell with a capacity of 30,000-gal, two 100,000-gal liquid ILW storage tanks located in a separate cell, and storage tanks for liquid U+Pu product) that are not considered necessary in the proposed plant.

In the SAFAR plant, the liquid U+Pu product is converted to  $(U,Pu)O_2$  spheres, which are fed to a colocated spherepac fuel fabrication facility. Compared to the direct calcination process used in the proposed plant, the sphere formation process requires a much greater number of process steps, and more complicated and expensive equipment. We consider sphere formation, if adopted, to be part of the fabrication process, and terminate the reprocessing when shippable and workable products are formed.

All the above differences between the two plants contribute to the higher cost of the SAFAR plant. In addition, the following uncertainties, which are closely related to the cost estimation and adjustment methods and hinder a better comparison of the costs, exist. The maximum indirect costs for the proposed design were estimated as 60 % of the fixed capital cost (or 149 % of the direct plant cost), as suggested in Reference [32]. It is very likely that in the SAFAR project the indirect costs are responsible for a larger fraction of the fixed capital cost. The cost-capacity adjustments were made using an exponential factor of 0.14, which is suggested by the Dupont study of 1961 [46]. Although the Dupont study is considered to be the most thorough cost study of reprocessing plants, the applicability of this exponential factor to the cost-capacity adjustments of the modern-day plants, which contain different facilities and features, is questionable. An INFCE-IAEA (International Fuel Cycle Evaluation-International Atomic Energy Agency) study of 1980 suggests an exponential factor of 0.63 for the standard base-case reprocessing plants [58]. Noting that the average exponential factor for the conventional chemical plants is 0.60, it seems that an exponential factor of 0.63 is rather high for the reprocessing plants because the reprocessing plants contain more items independent of the plant capacity than do chemical plants. Using a cost-capacity adjustment factor of 0.63, the adjusted (to a capacity of 920 ton U/year from 2100 ton U/year and to 1987 prices from 1982 prices) cost of the SAFAR

project is calculated to be 930 to 1,250 million \$, which is to be compared to 1.5 to 2.0 billion \$, calculated using a cost-capacity adjustment factor of 0.14. As seen, the adjusted cost varies significantly depending on the choice of the cost-capacity factor. It can be speculated that the actual cost-capacity factor for the modern reprocessing plants is probably higher than 0.14 and lower than 0.63.

A comparison of the estimated product costs to the published estimates will not be attempted here because: (1) the qualitative comparisons made for the capital costs are also valid for the product costs since the product costs, to an appreciable extent, depend on the capital costs; and (2) complete and comparable data are not available, the uncertainties involved, making it almost impossible to obtain adjusted (comparable) values, prevent a meaningful comparison.

Notwithstanding, it can be noted that, in general, the older (1960s) estimates of the annual total product cost (TPC) assume low fixed charge rates and no financing cost, and range from 20 to 25 % of fixed capital costs (FCCs) while the newer estimates (1970s, 1980s) assume relatively high fixed charge rates together with a considerable amount of financing cost, and range from 30 to 50 % of FCCs [6,25,46,54,58].

The estimates of the product costs for the proposed design have been presented in Table 6, Chapter 6. Because several components of the product costs are estimated as percentages of the FCC, different product cost estimates were obtained for each of the FCC estimates (257 and 417 million \$ with indirect costs as 54 and 149 % of the direct

costs, respectively). Besides, the financing charge on borrowed money was estimated as a separate annual expense (5 and 10 % of the total capital cost (TCC)), which also resulted in considerably different product cost estimates. Assuming 5 % financing charge on the TCC (government-type financing [58]), the TPCs were estimated to be 109 and 126 (1987) \$/kg U (originally loaded) with the FCC being 257 and 417 million \$, respectively. Assuming 10 % financing charge on the TCC (in the lower range of industrial-type financing [58]), the TPCs were estimated to be 164 and 195 (1987) \$/kg U (originally loaded) with the FCC being 257 and 417 million \$, respectively. The value of the reprocessing products is estimated as  $180^3$  (1987) \$/kg U (originally loaded).

Annual rate of return on investment (ROI) is defined as the ratio of annual expected profit to TCC and a measure of the profitability of a project. Most chemical companies aim at at least 20 % pretax annual ROI [39]. Table 23 lists the reprocessing charges (or selling prices of the products) required for obtaining a 20 % annual pretax ROI. As seen in Table 23, the unit reprocessing charge, 184 to 285 \$/kg U originally loaded (with 5 % financing cost and for 20 % ROI), exceeds the unit value of the products, 180 \$/kg U originally loaded. This

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<sup>3</sup>This is an approximate value based on the 1983 prices of 1 kg natural U and 1 g fissile Pu. U and fissile Pu are priced at 60 \$/kg and 24 \$/g (1983 prices), respectively [59]. Note that the U product of the plant is very slightly richer in U-235 than the natural U and the Pu product is mixed with U (5-6 % Pu in U). The reprocessing products contain nearly 0.95 kg U and 5.2 g fissile Pu per kg of U originally loaded.

leads to the conclusion that, even with the government-type financing (5 %), the proposed project is not profitable enough to attract private sector. Direct support or participation of the government is required.

TABLE 23. Unit Reprocessing Charges for 0 and 20 % Annual ROI

TCC <sup>b</sup>	Reprocessing Charge (\$/kg U originally loaded)					
	Annual pretax ROI		0 %		20 %	
	Financing cost <sup>a</sup>		Financing cost			
	5 %	10 %	5 %	10 %		
302	109	126	184	202		
491	164	195	285	314		

<sup>a</sup> Financing cost is charged on the total capital cost annually.

<sup>b</sup> Total capital cost (TCC) includes the fixed capital cost (FCC) and the working capital (WC), which is estimated as 15 % of the TCC [38]. The TCC estimates are 302 million \$ (FCC=257, WC=45, with the indirect costs as 54 % of the direct cost) and 491 million \$ (FCC=417, WC=74, with the indirect cost as 149 % of the direct cost).

In parallel with this study, a project concerned with the economics of the nuclear waste disposal was performed by J. Roglans at I.S.U. in 1987 [3]. One of the conclusions that Roglans reached is that, for a waste repository of 72,000 MTHM SF or equivalent glassified

HLW, average potential cost reductions achievable in the waste disposal stage for selecting a regular reprocessing cycle over the once-through are 872 million \$ for a repository in salt, 615 million \$ in basalt, 579 million \$ in granite, and 440 million \$ in tuff in 1987 [3]. A 72,000 MTHM SF-capacity waste repository accommodates 3 reprocessing plants each having an actual annual capacity of 800 MTHM SF (or MT U originally loaded) and a life of 30 years. For one reprocessing plant, processing 24,000 MTHM SF during its operating life, the above cost reductions will be 291 million \$ in salt, 205 million \$ in basalt, 193 million \$ in granite, and 147 million \$ in tuff in 1987. If it is assumed that these savings achieved in the waste disposal stage through the adoption of reprocessing are invested in the design and construction of a government-owned reprocessing plant, then the net total capital expenditure of the reprocessing plant on which the annual financing cost is charged will be reduced considerably, leading to reduced unit product costs. The resulting unit product costs (in \$/kg U originally loaded, with 5 % financing charge on the TCC, and for a TCC of 491 million \$ for the reprocessing plant) and overall savings are shown in Table 24. As seen in Table 24, the total combined savings from one waste repository with a capacity of 72,000 MT U (originally loaded) and three accommodating reprocessing plants, which can be achieved by choosing the reprocessing cycle over the alternative once-through cycle, are 1.87, 2.09, 2.16, and 2.52 billion \$ in 1987 for a repository medium of tuff, granite, basalt, and salt,

respectively. It should be noted that the above values for the savings are based on a conservative estimate of the TCC for the reprocessing plant designed, which assumes that the indirect costs are 149 % of the direct cost; therefore, these savings should be considered as minimum achievable. Additional savings are possible if the reprocessing plants are colocated with the waste repository: then, because of the common support facilities, reprocessing costs will be reduced.

#### 7.2. Summary of Major Conclusions

- In a plant processing long-cooled fuel to produce a mixed U+Pu stream and a pure U stream, the required decontamination factors for the products are considerably reduced compared to those in a standard plant, processing short-cooled fuel to produce completely separated and highly pure U and Pu streams. The product purification cycles in the standard flowsheet are eliminated. A 4-cycle (codecontamination, partial partitioning, finish partitioning, and U stripping) solvent extraction flowsheet is adequate to achieve the necessary decontamination factors.
- The proposed 4-cycle flowsheet is expected to require less complicated and less expensive equipment and to perform better than does the standard flowsheet because (1) the rate of solvent degradation is lower in the case of long-cooled fuel, and (2) the difficulties arising from the reduction of Pu are

TABLE 24. Unit Product Costs for Reprocessing and Overall Savings  
 (Considering the Waste Disposal Savings Achievable through  
 the Adoption of Reprocessing)

	TCC <sup>a</sup> on which 5 % annual financing cost is charged				
	w/o waste disposal savings	w/ salt	w/ basalt	w/ granite	w/ tuff
	491	200	286	298	344
Unit product cost, \$/kg U (originally loaded)	164	145	150	151	154
Profit <sup>b</sup> , \$/kg U (originally loaded)	16	35	30	29	26
Overall Savings <sup>c</sup> , million \$ (from 24,000 MT U originally loaded)	384	840	720	696	624
Overall savings <sup>d</sup> , billion \$ (from 72,000 MT U originally loaded)	1.15	2.52	2.16	2.09	1.87

<sup>a</sup> Capital cost figures are in million \$ in 1987. The TCC estimate of the reprocessing plant is 491 million \$, with the indirect costs as 149 % of the direct costs. When considering the waste disposal savings, the TCC on which 5 % financing cost is charged is taken as the difference between the TCC of the reprocessing plant and the waste disposal savings.

<sup>b</sup> Profit is the difference between the unit value of the products (assumed to be 180 \$/kg U originally loaded, see footnote on page 172) and the unit product cost.

<sup>c</sup> These are the total combined savings from one reprocessing plant and the corresponding waste disposal capacity (24,000 MT U originally loaded).

<sup>d</sup> These are the total combined savings from a waste repository with a capacity of 72,000 MT U (originally loaded) and three accommodating reprocessing plants.

decreased since Pu is reduced in the finish partitioning contactor only, where, compared to that in the complete or partial partitioning contactors, very small amounts of Pu are present. In addition, the elimination of the Pu purification cycles and fact that U and Pu are never completely separated enhance the safeguardability features.

- An integrated plant with minimum storage of the inputs and outputs and no storage of the intermediate streams can be designed to produce calcined U+Pu and U products, classified HLW, and bottled rare gases. All the high and moderate activity processes are maintained by remote means (remote bridge cranes, robot systems, manipulators) and housed in a remote canyon and basement cells in a remote maintenance building. To keep operating efficiency high, process lines are manifolded in most of the remote maintenance processes. An adjacent building houses all the low activity processes, which can be handled almost like conventional chemical processes because the fuel is long-cooled.
- The fixed capital cost of the plant is estimated to be 257 (217 to 297) million \$ if the indirect costs are calculated as 54 % of the direct costs, or 417 (351 to 483) million \$ if the indirect costs are calculated as 149 % of the direct costs. A comparison of the estimated direct cost of the plant to that of a standard base-case plant results that the costs of the

additional facilities and features included slightly exceed the savings that can be achieved through the simplifications in the flowsheet and design. The conclusion is that the direct cost of the proposed plant will probably not exceed that of a standard base-case plant by more than 35 %. Compared to a modern-day plant like SAFAR, which includes all the functions in the proposed design and some additional ones, the capital cost of the project is appreciably lower. Quantitative comparisons between the cost estimates are hindered because of the lack of complete cost data and uncertainties involved in the cost estimation and adjustment methods.

- The unit product costs are estimated to be 109 and 126 \$/kg U originally loaded, with 5 % financing cost and fixed capital cost estimate being 257 and 417 million \$, respectively, or 169 and 195 \$/kg U originally loaded, with 10 % financing cost and fixed capital cost estimate being 257 and 417 million \$, respectively. The unit value of the products is estimated as 180 \$/kg U originally loaded. When the capital costs and unit value of the products are taken into account, it is found that the unit product costs are too high to obtain a reasonable (at least 20 %) pretax annual return on investment. Therefore, it seems that the proposed project is not attractive enough for private industry to be interested in. Direct support or participation of the government is necessary.

- Compared to the once-through cycle, a reprocessing cycle results in substantial savings in the waste disposal stage [3]. For a government-owned reprocessing plant, assuming that the savings achieved in the waste disposal stage through choosing a reprocessing cycle are spent on the capital cost of the reprocessing plant, the unit product costs are lowered because the net capital expenditure on which the financing cost is charged is reduced. For a waste repository with a capacity of 72,000 MT U originally loaded and three accommodating reprocessing plants, the minimum achievable savings for selecting the reprocessing cycle over the once-through range from 1.87 to 2.52 billion \$ in 1987 depending on the repository medium.

### 7.3. Recommendations for Future Work

- Experimental work is needed to show that the 4-cycle solvent extraction flowsheet adopted will perform as indicated.
- A quantitative study of the effect of solvent degradation on the performance of various solvent extraction contactors is recommended. Such a study would improve the evaluation of the differences between the solvent extraction processing of short- and long-cooled fuels.
- A more detailed and thorough analysis of capital and product costs of reprocessing plants is required to eliminate the

uncertainties (or conflicts) met when comparing cost estimates of several plants. Major conflicts existing in published data are related to the indirect costs and cost-capacity adjustments, further investigation of which is especially recommended.

- A complete optimization study of the whole back-end of the nuclear fuel cycle is needed. Such a study would combine the findings of this study and the waste disposal study [3], and look further into (1) the spent fuel storage costs, probably reaching an economically optimum spent fuel cooling period, (2) the effect of colocation of the facilities on the economics, and (3) the fabrication and enrichment costs for the reprocessing products.

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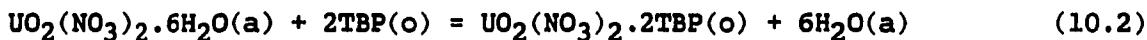
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## 10. APPENDIX

## 10.1. Correlations of Goldberg, Benedict, and Levi for Distribution

Coefficients of HNO<sub>3</sub> and U(VI) in TBP

The distribution of HNO<sub>3</sub> and U(VI) in TBP is expressed by the following reactions, adapted from Reference [28].



where (a) and (o) denote aqueous and organic phases, respectively.

Equilibrium constants ( $K_H$  and  $K_U$ ) for the above reactions are defined as follows.

$$K_H = \frac{[\lambda_H(y_H, y_U)]y_H}{[a_H(x_H, x_U)]y_{\text{TBP}}[\lambda_{\text{TBP}}(y_H, y_U)]} \quad (10.3)$$

$$K_U = \frac{[\lambda_U(y_H, y_U)]y_U[a_{\text{H}_2\text{O}}(x_H, x_U)]^6}{[a_U(x_H, x_U)][\lambda_{\text{TBP}}(y_H, y_U)]^2(y_{\text{TBP}})^2} \quad (10.4)$$

where  $y$ =organic phase molality,

$x$ =aqueous phase molality,

$a$ =chemical activity in aqueous phase,

$\lambda$ =chemical activity coefficient in organic phase,

TBP=uncomplexed TBP.

The activity coefficient ratios ( $L_H$  and  $L_U$ ) in organic phase are defined by the following equations.

$$L_H(y_H, y_U) = \frac{K_H[\lambda_{TBP}(y_H, y_U)]}{[\lambda_H(y_H, y_U)]}$$

$$= \frac{y_H}{[a_H(x_H, x_U)](3.75493 - y_H - 2y_U)} \quad (10.5)$$

$$L_U(y_H, y_U) = \frac{K_U[\lambda_{TBP}(y_H, y_U)]^2}{[\lambda_U(y_H, y_U)]}$$

$$= \frac{y_U[a_{H_2O}(x_H, x_U)]^6}{[a_U(x_H, x_U)](3.75493 - y_H - 2y_U)^2} \quad (10.6)$$

Rearranging Equations (10.5) and (10.6), the following equations are obtained.

$$a_H(x_H, x_U) = \frac{y_H}{[L_H(y_H, y_U)](3.75493 - y_H - 2y_U)} \quad (10.7)$$

$$\frac{a_U(x_H, x_U)}{[a_{H_2O}(x_H, x_U)]^6} = \frac{y_U}{[L_U(y_H, y_U)](3.75493 - y_H - 2y_U)^2} \quad (10.8)$$

After correlating  $a_H$ ,  $a_U$ , and  $a_{H_2O}$  as functions of  $x_H$  and  $x_U$ , Equations (10.7) and (10.8) can be solved for  $y_H$  and  $y_U$  when  $x_H$  and  $x_U$  are known, or for  $x_H$  and  $x_U$  when  $y_H$  and  $y_U$  are known.

Correlations for  $a_H$ ,  $a_U$ , and  $a_{H_2O}$  are given below.

$$\begin{aligned}
 a_H(x_H, x_U) = & x_H(x_H+2x_U) \exp\left\{2\left[-\frac{s(x_H+2x_U)^{1/2}}{1+A_2(x_H+2x_U)^{1/2}} + 2B_2x_H\right.\right. \\
 & + (3/2)C_2x_H^2 + (4/3)D_2x_H^3] \\
 & + x_U[R + R_Hx_H + (R_U/2)x_U \\
 & + (R_{HU}/2)x_Hx_U + R_{HH}x_H^2 \\
 & \left.\left.+ (R_{HHU}/2)x_H^2x_U\right]\right\} \quad (10.9)
 \end{aligned}$$

$$\begin{aligned}
 a_U(x_H, x_U) = & x_U(x_H+2x_U)^2 \exp\left\{3\left[-\frac{2s(3x_U)^{1/2}}{1+A_3(3x_U)^{1/2}} + 2B_3(3x_U)\right.\right. \\
 & + (3/2)C_3(3x_U)^2 + (4/3)D_3(3x_U)^3] \\
 & + x_H[R + (R_H/2)x_H + R_Ux_U + (R_{HU}/2)x_Hx_U \\
 & + (R_{HH}/3)x_H^2 + (R_{HHU}/3)x_H^2x_U] \\
 & \left.\left.+ 3\left[-\frac{2s(x_H+3x_U)^{1/2}}{1+A_2(x_H+3x_U)^{1/2}} + \frac{2s(3x_U)^{1/2}}{1+A_2(3x_U)^{1/2}}\right]\right]\right\} \quad (10.10)
 \end{aligned}$$

$$a_{H_2O}(x_H, x_U) = [a_{H_2O}(x_H, x_U=0)] [a_{H_2O}(x_H=0, x_U)]$$

$$\left\{ \frac{[1+A_2(x_H)^{1/2}][1+A_2(3x_U)^{1/2}]}{1+A_2(x_H+3x_U)^{1/2}} \right\}^{[4S/(A_2^{355}.509)]}$$

$$\exp \left\{ \frac{2S}{55.509} \left[ - \frac{x_H(x_H)^{1/2}}{1+A_2(x_H)^{1/2}} + \frac{(x_H+3x_U)(x_H+3x_U)^{1/2}}{1+A_2(x_H+3x_U)^{1/2}} \right] \right\}$$

$$- \frac{3x_U(3x_U)^{1/2}}{1+A_2(3x_U)^{1/2}} + \frac{4S}{A_2^{355}.509} [- (x_H)^{1/2}]$$

$$+ (x_H+3x_U)^{1/2} - (3x_U)^{1/2} - \frac{x_Hx_U}{55.509} [R + R_Hx_H]$$

$$+ R_Ux_U + (3/4)R_HUx_Hx_U$$

$$+ R_{HH}(x_H)^2 + (2/3)R_{HHU}(x_H)^2x_U] \} \quad (10.11)$$

$$\begin{aligned}
 a_{H_2O}(x_H, x_U=0) = & \exp \left\{ - \frac{2x_H}{55.509} \left[ 1 - \frac{s}{A_2^3 x_H} (1 + A_2(x_H)^{1/2} \right. \right. \\
 & - 2 \ln(1 + A_2(x_H)^{1/2}) \\
 & \left. \left. - \frac{1}{1 + A_2(x_H)^{1/2}} \right] + B_2 x_H + C_2(x_H)^2 \right. \\
 & \left. + D_2(x_H)^3 \right\} \quad (10.12)
 \end{aligned}$$

$$\begin{aligned}
 a_{H_2O}(x_H=0, x_U) = & \exp \left\{ - \frac{3x_U}{55.509} \left[ 1 - \frac{2s}{A_3^3 (3x_U)} (1 + A_3(3x_U)^{1/2} \right. \right. \\
 & - 2 \ln(1 + A_3(3x_U)^{1/2}) - \frac{1}{1 + A_3(3x_U)^{1/2}} \\
 & \left. \left. + B_3(3x_U) + C_3(3x_U)^2 + D_3(3x_U)^3 \right] \right\} \quad (10.13)
 \end{aligned}$$

where  $A_2 = 1.118816 \text{ (kg/mole)}^{1/2}$   
 $A_3 = 1.395422 \text{ (kg/mole)}^{1/2}$   
 $B_2 = 11.82976 \text{ E-2 kg/mole}$   
 $B_3 = 9.236731 \text{ E-2 kg/mole}$   
 $C_2 = -6.985887 \text{ E-3 (kg/mole)}^2$   
 $C_3 = -6.755264 \text{ E-3 (kg/mole)}^2$   
 $D_2 = 1.288488 \text{ E-4 (kg/mole)}^3$

$$\begin{aligned}
 D_3 &= 1.284050E-4 \quad (\text{kg/mole})^3 \\
 S &= 1.1696 \quad (\text{kg/mole})^{1/2} \\
 R &= 1.01085 \quad \text{kg/mole} \\
 R_H &= -0.143084 \quad (\text{kg/mole})^2 \\
 R_U &= -0.323067 \quad (\text{kg/mole})^2 \\
 R_{HU} &= 0.0365150 \quad (\text{kg/mole})^3 \\
 R_{HH} &= 0.00301169 \quad (\text{kg/mole})^3 \\
 R_{HU} &= 0.000215242 \quad (\text{kg/mole})^4.
 \end{aligned}$$

Correlations for  $L_H$  and  $L_U$ , for 30 v/o TBP, are as follows.

$$L_H(x_H, x_U) = 0.6634 \exp[-0.5994y_H - 0.6264(2y_U)] \quad (10.14)$$

$$\begin{aligned}
 L_U(y_H, y_U) &= 34.57 \exp[-1.534y_H - 0.0831(2y_U) + 0.000534y_H(2y_U) \\
 &\quad + 0.4748(y_H)^2 + 0.06656(2y_U)^2]
 \end{aligned} \quad (10.15)$$

Inserting Eqs (10.12) and (10.13) into Eq (10.11),

Eq (10.9) into Eq (10.7),

Eqs (10.10) and (10.11) into Eq (10.8),

Eq (10.14) into Eq (10.7), and Eq (10.15) into Eq (10.8), Eqs (10.7) and (10.8) are obtained in the following form.

$$f_1(x_H, x_U) = g_1(y_H, y_U) \quad (10.16)$$

$$f_2(x_H, x_U) = g_2(y_H, y_U) \quad (10.17)$$

Eqs (10.16) and (10.17) can be solved implicitly for  $x_H$  and  $x_U$  if  $y_H$  and  $y_U$  are known, or for  $y_H$  and  $y_U$  if  $x_H$  and  $x_U$  are known.

### 10.2. Newton-Raphson Method of Successive Approximations

For solution of Eqs (10.16) and (10.17), the Newton-Raphson method of successive approximations (displacements) was used in the following manner.

Assume that  $x_H$  and  $x_U$ , i.e., the right-hand sides of (10.16) and (10.17), are known; then the 2 non-linear equations to be solved for  $y_H$  and  $y_U$  are

$$C_1 - g_1(y_H, y_U) = 0 \quad (10.18)$$

$$C_2 - g_2(y_H, y_U) = 0 \quad (10.19)$$

where  $C_1$  and  $C_2$  are known constants.

Expanding  $g_1$  and  $g_2$  into series, and taking only first order derivatives, the following expressions are obtained.

$$C_1 - g_1(y_H^O, y_U^O) - \left[ \frac{\partial g_1}{\partial y_H} \right] (y_H - y_H^O) - \left[ \frac{\partial g_1}{\partial y_U} \right] (y_U - y_U^O) = 0 \quad (10.20)$$

$$C_2 - g_2(y_H^O, y_U^O) - \left[ \frac{\partial g_2}{\partial y_H} \right] (y_H - y_H^O) - \left[ \frac{\partial g_2}{\partial y_U} \right] (y_U - y_U^O) = 0 \quad (10.21)$$

First order derivatives are approximated as

$$\frac{\partial g}{\partial y} \approx \frac{g(y+\Delta y) - g(y-\Delta y)}{2\Delta y}$$

The calculational procedure used is as follows.

(1) Guess or specify  $y_U$ . Obtain Eq (10.20) in the following form.

$$c_1 - g_1(y_H^O) - \left[ \frac{\partial g_1}{\partial y_H} \right] (y_H - y_H^O) = 0 \quad (10.22)$$

(2) Starting with an initial guess,  $y_H^O$ , calculate  $y_H$  from Eq (10.22) and replace it with  $y_H^O$  successively in Eq (10.22) until it converges.  $y_H$  is calculated for the guessed or specified value of  $y_U$ .

(3) With known  $y_H$ , obtain Eq (10.21) in the following form.

$$c_2 - g_2(y_U^O) - \left[ \frac{\partial g_2}{\partial y_U} \right] (y_U - y_U^O) = 0 \quad (10.23)$$

(4) Calculate  $y_U$  from Eq (10.23) by successive displacements (inner loop) in the same fashion as  $y_H$  is calculated in step(1). If the value of  $y_U$  calculated here is different from the guessed or specified value in step (1), insert it into Eq (10.20) to get Eq (10.22).

(5) Repeat steps (2) through (4) until the  $y_U$  value in the outer loop converges.

### 10.3. Expressions for Aqueous and Organic Phase Densities

The organic phases is a 30 v/o TBP in n-dodecane solution which may contain  $\text{HNO}_3$  and nitrates of U, Pu, and FP. The aqueous phase is a  $\text{HNO}_3$  solution, which may contain nitrates of U, Pu, and FPs In the density calculations, the concentrations of Pu and FP nitrates are included in the concentration of U nitrate for simplicity.

The following expressions have been derived from the related figures in Reference [6] for estimating the densities of the phases.

$$d_o = 0.814 + 0.318y_U + 0.03y_H \quad (10.24)$$

$$d_a(100^\circ\text{C}) = 0.006(H_{w/o} - 10) + \exp(-0.023842 + 0.0112 U_{w/o}) \quad (10.25)$$

for  $U_{w/o} \geq 10$  and any  $H_{w/o}$

$$d_a(100^\circ\text{C}) = 0.006(U_{w/o} + H_{w/o} - 5) + 1 \quad (10.26)$$

for  $5 < U_{w/o} < 10$  and any  $H_{w/o}$

$$d_a(100^\circ\text{C}) = 0.005 H_{w/o} - 0.01319 + \exp(-0.023842 + 0.0112 U_{w/o}) \quad (10.27)$$

for  $U_{w/o} \leq 5$  and  $H_{w/o} > 7.33$

$$d_a(100^\circ\text{C}) = 0.97 + 0.0040927 H_{w/o} + 0.006 U_{w/o} \quad (10.28)$$

for  $U_{w/o} \leq 5$  and  $H_{w/o} \leq 7.33$

$$d_a(t^\circ\text{C}) = d_a(100^\circ\text{C}) + a(100 - t) \times 10^{-4} \quad (10.29)$$

where  $d_o$ =organic phase density

$d_a$ =aqueous phase density

$H=\text{HNO}_3$

$U=UO_2(NO_3)_2$

w/o=weight percent

y=molarity in the organic phase

t=temperature in  $^{\circ}C$

a=18.2 + 0.141 H<sub>w/o</sub>.

Since in the case of the aqueous phase the H<sub>w/o</sub> is usually unknown, it is necessary to apply an iterative procedure to calculate the density. Based on an initially guessed density value, knowing molarities of all the solutes in the aqueous phase, H<sub>w/o</sub> can be calculated. Then, the density of the solution is obtained from the applying equation above. The density value is successively displaced until converges.

#### 10.4. Molality to/from Molarity Conversion

The equations used for molality to/from molarity conversion in the aqueous and organic phases are given below. In these equations m = molality, M = molarity, MW = molecular weight, and d = density of the phase.

The aqueous phase molality of a solute is defined as g-mole of that solute per kg H<sub>2</sub>O in the solution and the conversion equation for solute i is as follows.

$$m_i = \frac{M_i}{\sum_i (M_i \cdot MW_i)} \quad (10.30)$$

$$d_a = \frac{d_o - \frac{[d_o - \frac{1000}{1000}](0.35825)}{1000}}{1000}$$

The organic phase molality of a solute is defined as g-mole of that solute per kg TBP in the solution and the conversion equation for solute *i* is as follows.

$$m_i = \frac{M_i}{\sum_i (M_i \cdot MW_i)} \quad (10.31)$$

$$[d_o - \frac{1000}{1000}](0.35825)$$

Note that in 1 kg 30 v/o TBP + n-dodecane 0.35825 kg TBP is present.

In a solution whose density is unknown, in order to convert molalities of solutes to molarities, the density of the solution is initially guessed: based on the guessed density, molarities are calculated, and knowing molarities, the density of the solution is calculated. An iterative procedure is applied until the density value converges.

#### 10.5. Relative Volumetric Flow Rate Calculation

Neglecting transfer of H<sub>2</sub>O into the TBP phase and of TBP into the aqueous phase, relative volumetric flow rates of streams in a solvent extraction cascade can be calculated based on changes in densities of phases.

An example calculation for the extraction section shown in Figure 12 is given below. Refer to Figure 12 for nomenclature of streams. All  $x_i$ 's,  $dA(1)$ ,  $dA(n+1)$ ,  $FA(1)$ , all  $y_i$ 's,  $dO(0)$ ,  $dO(n)$ , and  $FO(n)$  are known.  $FA(n+1)$  and  $FO(n)$  are to be calculated. The procedure to calculate  $FA(n+1)$  is as follows.

1. Calculate total mass of solutes per liter of  $FA(1)$  stream,  $TOTS(1)$ .
2. Calculate total mass of  $H_2O$  per liter of  $FA(1)$  stream,  $TOTW(1)$ .
3. Calculate total mass of solutes per liter of  $FA(n+1)$  stream,  $TOTS(n+1)$ .
4. Calculate total mass of  $H_2O$  per liter of  $FA(n+1)$  stream,  $TOTW(n+1)$ .
5. Calculate  $FA(n+1)$  from the following equation.

$$FA(n+1) = FA(1) \left\{ 1 + \frac{[TOTW(1) - TOTW(n+1)][1 + \frac{TOTS(n+1)}{TOTW(n+1)}]}{1000 dA(n+1)} \right\} \quad (10.32)$$

$FO(n)$  is calculated in the same fashion: simply replacing mass of  $H_2O$  per liter with mass of (TBP+n-dodecane) per liter.

### 10.6. Estimation of Building Costs

Estimation of building costs are presented in the following tables.

TABLE 25. Cost of Main Plant Buildings: Regular Areas

Area	Floor Area (sf) <sup>b</sup>	\$/sf <sup>a</sup> in 1987	Cost in 1987 (1000 \$)
Process <sup>c</sup>	13,200	250	3300
Maintenance	1,940	114	221
Storage and shipment	1,640	114	187
Laboratory	3,880	187	726
Personnel	5,810	122	709
Cold feed preparation	3,450	84	290
Fuel receipt	13,950	114	1590
<b>TOTAL</b>	<b>43,870</b>		<b>7023</b>

<sup>a</sup> sf=ft<sup>2</sup>.

<sup>b</sup> Except for process area, \$ per sf prices were estimated using the method and cost data of Guthrie (1969) [39,51] and adjusted to 1987 prices using the Chemical Engineering Plant cost index [52]. Services are included.

<sup>c</sup> The unit cost of process area (\$/sf) was estimated using the cost data given in References [32,39,51].

TABLE 26. Cost of Main Plant Buildings: Heavily Shielded Areas

Area	Dimensions (ft)	Volume <sup>a</sup> (cf) <sup>a</sup>	Cost <sup>b</sup> in 1987 (million \$)
Cask unloading and fuel storage	52.5x23.0x32.8	39,550	2.37
Shear-leach and feed preparation	65.6x32.8x49.2	106,000	6.36
Solvent extraction	32.8x32.8x65.6	70,620	4.24
U+Pu calcination	59.1x26.3x49.2	76,207	4.58
HLW treatment	39.4x36.1x49.2	70,000	4.20
ILSW treatment	29.5x16.4x32.8	15,900	0.95
Maintenance rooms	13.1x13.1x49.2 23.0x13.1x49.2 29.6x13.1x49.2 36.1x16.4x49.2	8,443 14,824 19,078 29,128	
total		71,423	4.29
Storage		64,650	3.89
TOTAL		515,000	30.88
Services <sup>c</sup>			6.00
TOTAL with services			36.88

<sup>a</sup> cf=ft<sup>3</sup>.

<sup>b</sup> 1 cf of the heavily shielded area was costed at 60 \$ in 1987. This value is obtained converting the 1976 estimate given in Reference [32], 35 \$/cf of heavily shielded area in 1976.

<sup>c</sup> Services were estimated as 20 % of the cost of buildings [39].

TABLE 27. Cost of Auxiliary Buildings

Building	Floor area (sf) <sup>a</sup>	\$/sf <sup>b</sup> in 1987	Cost in 1987 (1000 \$)
Administration	20,000	118	2360
General store	12,200	105	1281
Electrical substation	3,000	105	315
Water, compressed air, etc.	6,000	107	642
Heating, ventilation, air conditioning	5,000	107	535
Warehouses and shops	20,000	105	2100
<b>TOTAL</b>			<b>7223</b>

<sup>a</sup> sf=ft<sup>2</sup>.

<sup>b</sup> \$ per sf prices were estimated using the method and cost data of Guthrie (1969) [39,51] and adjusted to 1987 prices using the Chemical Engineering Plant cost index [52]. Services are included.

## 10.7. Cost of Raw Materials

Cost of chemicals (or raw materials) are presented in Table 28.

TABLE 28. Cost of Raw Materials<sup>a</sup>

Material	Quantity required per MTU in SF	Unit price \$/unit	Cost (\$/MTU in SF)
TBP	500 gal	1.77/gal	885
n-dodecane	950 gal	1.50/gal	1350
HNO <sub>3</sub>	1140 lb	0.28/kg	320
Hydroxylamine	10 lb	0.83/lb	8
Hydrazine	10 lb	1.25/lb	13
Formaldehyde	40 lb	0.11/lb	4
Glass mixture	140 kg	0.50/kg	70
Sodium carbonate	50 kg	0.39/kg	20
Sodium nitrite	100 lb	0.37/lb	37
Sodium hydroxide	100 kg	0.20/kg	20
Others (liquid nitrogen, AgZeO, containers, filters, cement, bottles, etc.)			1200
<b>TOTAL</b>			<b>3920</b>

<sup>a</sup> Source: Reference [60].