

# Nuclear Criticality Safety Engineering Training

## Module 11<sup>1</sup>

### Criticality Safety in Material Processing Operations - Part 2<sup>2</sup>

#### 1.0 LESSON OBJECTIVE

This module continues the review of chemical separation processes that was started in Nuclear Criticality Safety Engineering Training (NCSET) Module 10. This module describes how the fundamental chemistry of plutonium and uranium is applied to each unit operation of the PUREX process, including subsequent purification. Criticality safety issues are discussed for each unit operation described in this module.

#### 2.0 REFERENCES

- 1) David G. Karraker, William J. Crooks III, Jeffery L. Siler, Mitchell R. Hartman, Thomas G. Campbell, Carlisle E. Pickett, G. Jimmy Winkler, James W. (Chip) McClard, Alice M. Murray, Norman E. Barnett, "F-Area Processing/Chemical Compatibility Overview," WSRC-MS-2002-0385S, May 1, 2002.
- 2) Major C. Thompson, William J. Crooks III, Jeffery L. Siler, Mitchell R. Hartman, Thomas G. Campbell, Carlisle E. Pickett, G. Jimmy Winkler, James W. (Chip) McClard, Alice M. Murray, Norman E. Barnett, "H-Area Processing/Chemical Compatibility Overview," WSRC-MS-2002-0386S, May 1, 2002.
- 3) T. P. McLaughlin, S. P. Monahan, N. L. Pruvost, V. V. Frolov, B. G. Ryazanov, and V. I. Sviridov, *A Review of Criticality Accidents*, LA-13638, 2000 Revision, Los Alamos National Laboratory, Los Alamos, New Mexico.

#### 3.0 Unit Operations and Criticality Safety

The processing and stabilization of nuclear materials or the reprocessing of spent nuclear fuels is complicated by many factors including radiation exposure, nuclear criticality safety controls, chemical reactivity hazards, solvent degradation, remote multi-stage operations, and waste treatment and disposal. Each unit operation presents its own challenges to criticality safety, and details of the controls usually vary according to specific installations. An attempt is made in this

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module to describe the functions of several unit operations in the PUREX process, identify the typical operating conditions, and focus on conditions that are important to criticality safety.

### 3.1 Dissolving Process

As the name implies, dissolving is the unit operation that transforms reactor fuel (or other nuclear materials) into a solution that can be readily transported through piping between unit operations. For PUREX processing (see NCSET Module 10), basic (caustic) solutions, such as NaOH, are used to dissolve the aluminum cladding of depleted uranium targets into soluble sodium aluminate ( $\text{NaAlO}_2$ ), and then the bare uranium targets are separately dissolved in concentrated nitric acid solutions. There are many competing oxidation and reduction reactions that occur during decladding and dissolving, but the net result is that uranium exits the process as  $\text{UO}_2(\text{NO}_3)_2(\text{aq})$  and plutonium as  $\text{Pu}(\text{NO}_3)_4(\text{aq})$ .

For HM processing (see NCSET Module 10), the Al cladding and Al-U alloy are co-dissolved in nitric acid using a mercuric nitrate catalyst in a single step. As in the PUREX process, the uranium is converted to  $\text{UO}_2(\text{NO}_3)_2(\text{aq})$ .

For dissolving, nuclear material is added to either a pot or annular dissolver via ports. Figure 1 shows a typical annular dissolver. As a criticality safety control, the material charging bundle may be placed in an “insert” (perforated fuel bucket) that provides separation between bundles, and thus geometry control during dissolution. Figure 2 shows an idealized model of the dissolution process. As nuclear material dissolves, the fragments pass through the perforations into the annulus.

#### 3.1.1 Criticality Safety Controls during Dissolving Operations

Obviously, there are a lot of potential situations during the dissolving operation that require criticality safety controls: large quantities of fissile material, solution chemistry, precipitation potential, loss of neutron poison, etc. The following list shows the numerous controls used during dissolution.

- Limiting the fissile mass of charging ports, per dissolver; use blocked dissolver ports to limit fissile mass per zone
- Concentration limits in dissolver (high nitric acid concentration required to prevent Pu polymer formation and maintain acceptable Pu and U concentrations)
- Geometrically-favorable dissolver dimensions (e.g., slab tanks); configurations such as the annulus design are a control feature
- Sufficient solution conditions to dissolve (e.g.,  $\text{HNO}_3$ ,  $\text{F}^-$ , time, temperature); flow sheet validation for off-normal materials
- Water-soluble neutron poison (B as boric acid, Gd as  $\text{Gd}^{3+}$ , U as  $\text{UO}_2^{2+}$ )
- Control fluoride concentration in acid:  $\text{KBF}_4$  can precipitate under certain conditions with potential loss of soluble B

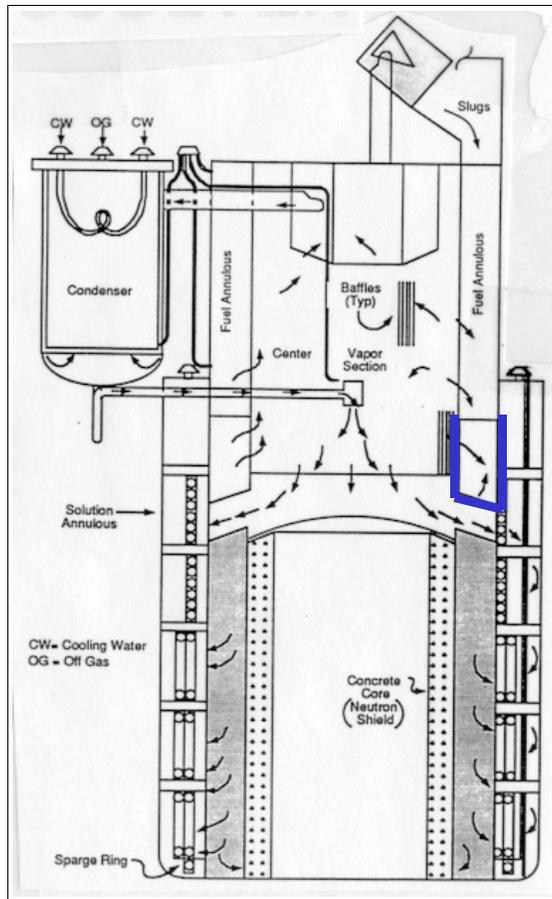


Figure 1. Sketch of Typical Dissolver with Condenser

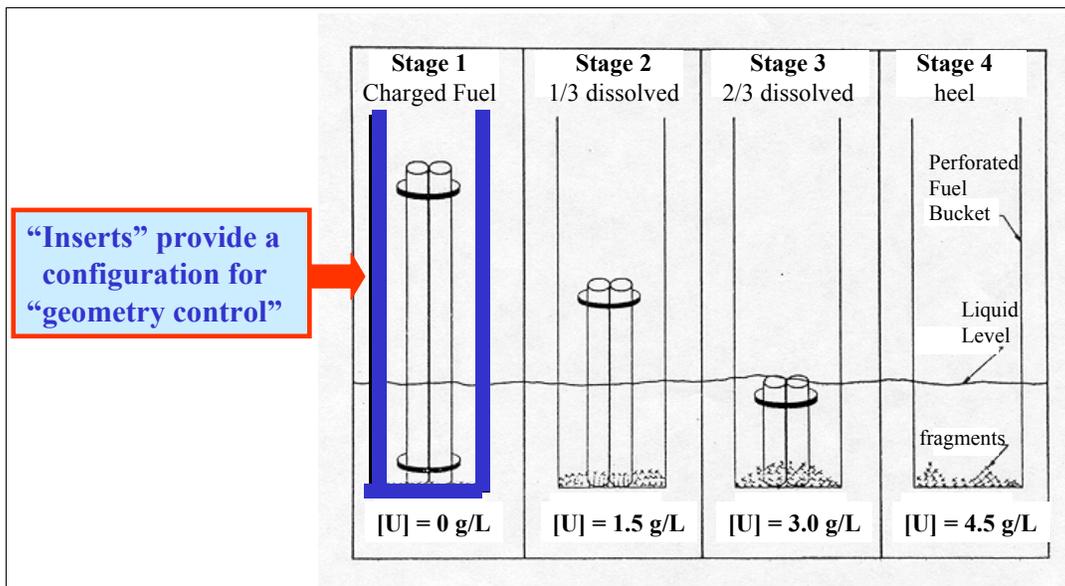


Figure 2. Idealized Dissolving Model of a Nuclear Fuel Bundle

- Maintain MC&A records for charge, yields, losses [e.g., heel in tank, spills, mistakes (over-charges of material)], and measurement uncertainties
- Solids control: avoid undissolved material such as PuO<sub>2</sub> fines, and post-precipitate material such as the KBF<sub>4</sub> issue

## 3.2 Head-End Process

As described earlier, the key to separation in the PUREX process is the control of oxidation (or valence) states. Head-End is the unit operation where chemical adjustments are made to control valence and other solution conditions. Once adjusted, the solution serves as “feed” to another unit operation (e.g., solvent extraction or ion exchange). For valence state adjustments, oxidizing and reducing agents are used. These reactions may be energetic and require controlled addition rates within acceptable concentration ranges. Improper feed adjustments can lead to undesirable chemical processes that could result in a nuclear criticality. Plutonium precipitation is a major concern in the Head-End process.

### 3.2.1 Criticality Safety Controls during Head-End Operations

Nuclear criticality safety controls for the Head-End process include:

- analysis of solution after chemical adjustments (i.e., Pu content, acidity) to verify that solutions are within concentration limits;
- mass balance determination to verify all Pu is in solution.

## 3.3 Solvent Extraction Process

Solvent extraction is a multi-stage operation, composed of “extraction banks” in series (see Figures 1 and 2, NCSET Module 10). Actinide extraction into the organic phase is driven by a high nitric acid concentration that results in “salting out” of actinide nitrate from the aqueous phase and extraction into the organic phase.

To reduce the radiation dose to the organic solvent in the PUREX process, fission products are removed first. The solvent extraction equipment is separated into banks (A, B, etc.). Each bank is part of a step-wise purification process. In bank A of the First Solvent Extraction Cycle at SRS, a rapid separation is achieved using centrifugal contactors. In a continuous, counter-current, multi-stage process, the solvent and aqueous phases are mixed and are subsequently separated by centrifugal force.

After the highly radioactive fission products have been removed in the First Solvent Extraction Cycle, additional purification in the second cycles (i.e., the additional Uranium and Plutonium solvent extraction cycles) is achieved with mixer-settlers, also in a continuous, counter-current, multi-stage process. In a mixing section, solvent and aqueous phases are rapidly stirred, and

subsequently, the phases are allowed to disperse in a long settling section, and the separated phases flow to the next stage in opposite directions. The idealized operation of the mixer-settler process of a single solvent extraction stage is illustrated in Figure 3.

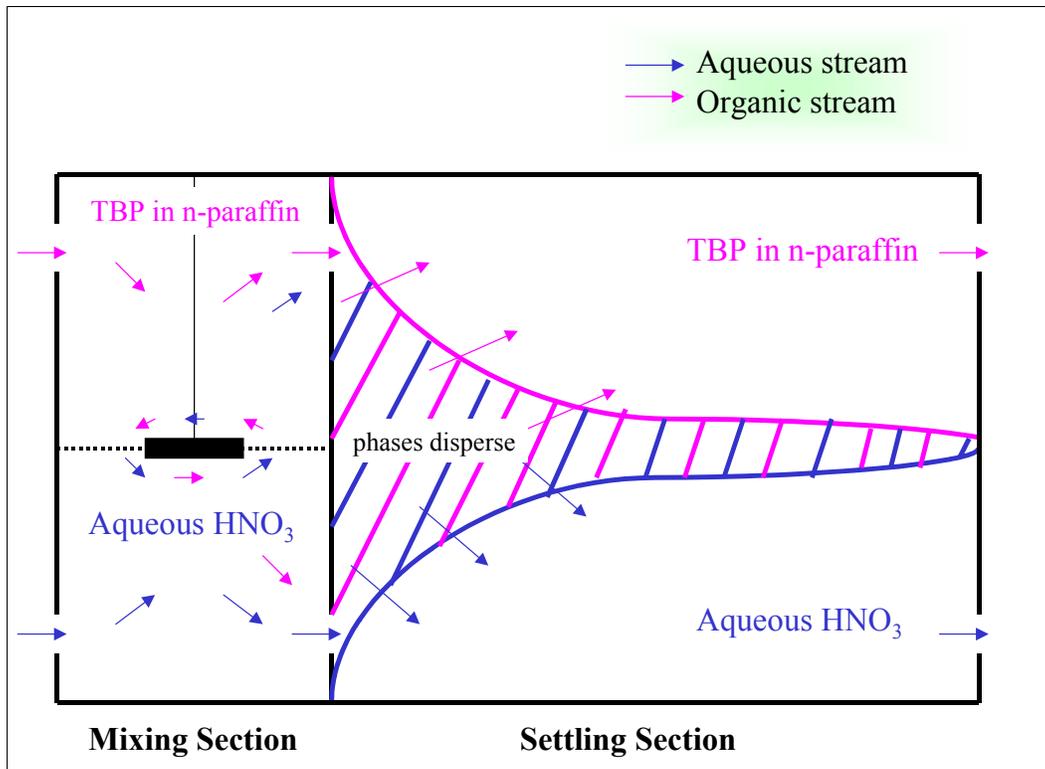


Figure 3. Idealized Mixer-settler Operation

### 3.4 Normal Operation, First Solvent Extraction Cycle of the PUREX Process

At SRS, nuclear material streams are processed through a first (solvent extraction) cycle to rapidly separate fission products from Pu and U, followed by separation of Pu (and/or Np) and U. The PUREX process is separated into banks A, B, and C as shown in Figure 4.

In the 1A bank, Pu and U are extracted (using centrifugal contactors) into an organic phase containing tri-n-butyl phosphate in n-paraffin (1AP) from a nitric acid feed solution (1AF), and inextractable fission products are rejected to the aqueous phase (1AW). The 1AP organic phase is then transferred to the 1B bank for separation of U and Pu.

Certain chemical conditions can lead to a build up of fissile nuclear material that could lead to a criticality. As a first example, consider the details of the equipment and chemistry in the 1B bank. The typical feeds are shown in Figure 5. In the high stage numbers, the feeds are designed to retain uranium (“extracted”) in the organic phase and to reductively strip Pu from the organic phase into the aqueous phase. In the lower stages, the uranium is retained in the organic

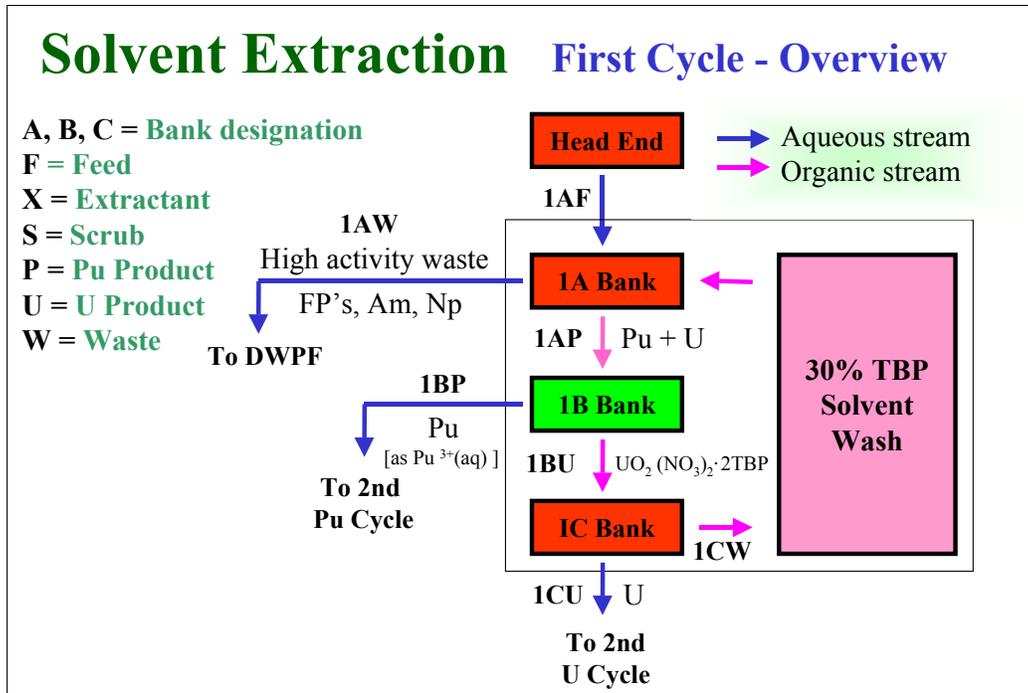


Figure 4. Additional Details of the First Solvent Extraction Cycle in PUREX

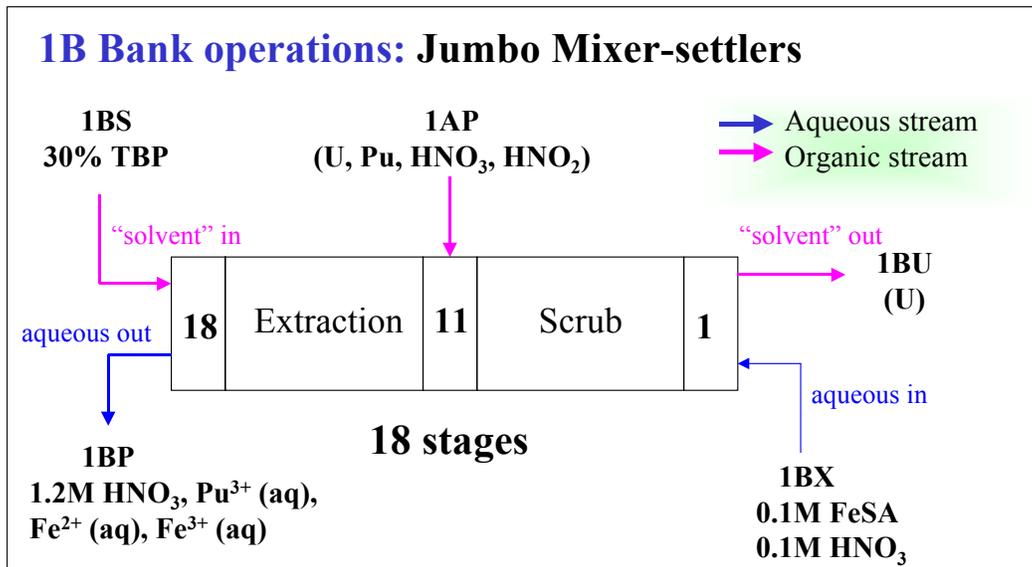


Figure 5. Typical Feeds to the 1B Bank of the First Solvent Extraction Cycle of PUREX

phase and residual amounts of plutonium are scrubbed (reductively with FeSA). Figure 6 shows a typical mixer-settler flow path (here, for the 1B bank), including the relationship between counter-current stages.

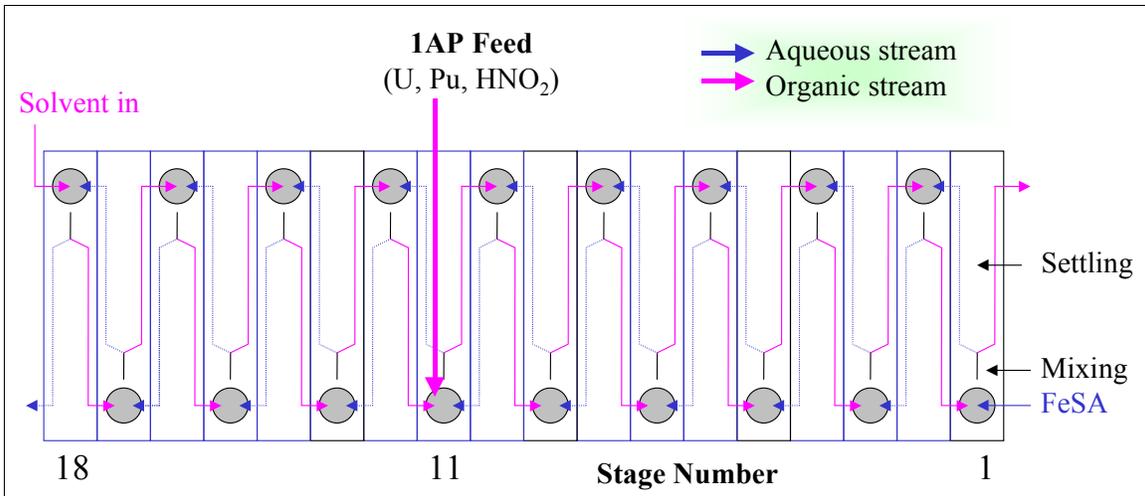


Figure 6. Flow Path of the 1B Bank of the First Solvent Extraction Cycle of PUREX

One of the complications in normal operations is that nitrous acid ( $\text{HNO}_2$ ) is formed by irradiation of nitric acid solutions. With a sufficient supply of ferrous sulfamate ( $\sim 0.1\text{M FeSA}$ ) entering the 1B Bank, the  $\text{Fe}^{2+}$  reduces the Pu (IV) to inextractable Pu (III) and the sulfamate destroys  $\text{HNO}_2$  in order to protect the Pu (III) from reoxidation, as designed. For the ideal process, the chemical changes occurring throughout the mixer-settler stages are illustrated in Figure 7.

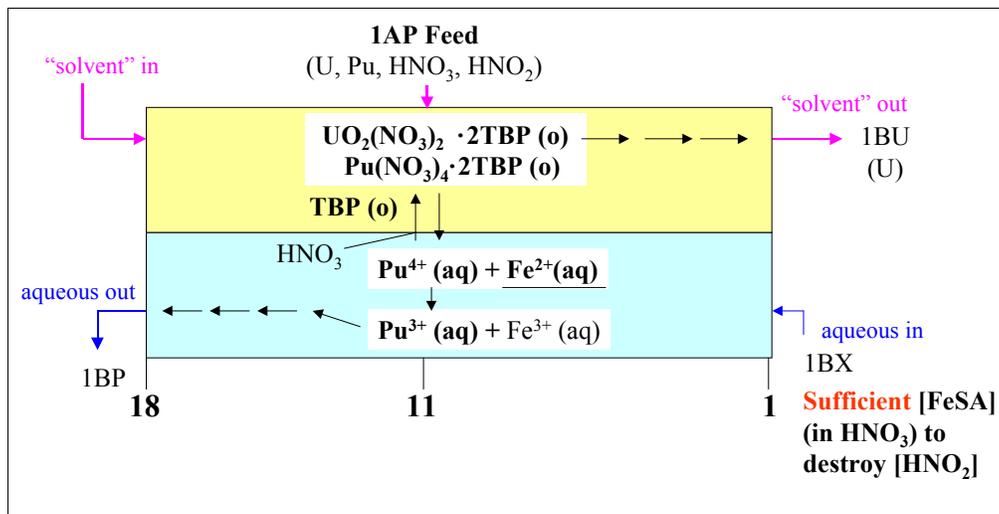


Figure 7. Illustration of Reductive Stripping of Pu in the 1B Bank of PUREX

### 3.4.2 Nuclear Criticality Safety Issues in the PUREX 1B Bank Process

With no FeSA entering the 1BX stream, the Pu (IV) would remain in the organic phase (1BU), and the U and Pu would not be separated. On the other hand, when an insufficient supply of FeSA is present, a nuclear criticality issue arises in the 1B bank. In this scenario, Pu (IV) in the feed is initially reduced by  $\text{Fe}^{2+}$  in the lower stage numbers but once the sulfamate is consumed by  $\text{HNO}_2$ , the Pu (III) is reoxidized to Pu (IV) in the higher stage numbers. The result is the Pu is “refluxed” or cycled between the organic and aqueous phases in the bank, with the potential to build up an inventory of Pu in the middle stages. The phenomenon of Pu reflux during solvent extraction is illustrated in Figure 8.

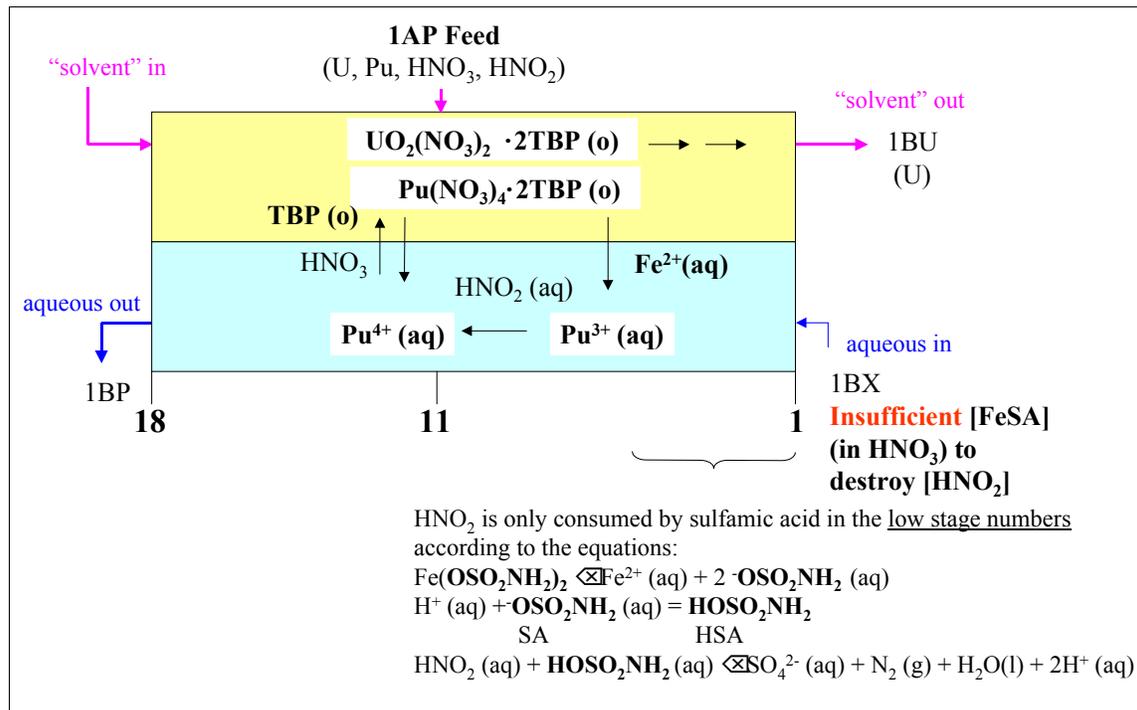


Figure 8. Illustration of Pu Reflux in the 1B Bank of the PUREX Process.

### 3.5 Some Nuclear Criticality Safety Issues in the HM Process

As mentioned in NCSET Module 10, SRS also uses a modified PUREX process for enriched uranium fuel elements, called the HM process. In addition to many criticality safety concerns that are common to the PUREX and HM processes, the HM process presents a few that are unique to its chemistry.

### 3.5.1 First Solvent Extraction Cycle (HEU and LEU Flowsheets)

The first solvent extraction cycle for the high enriched uranium (HEU) and low enriched uranium (LEU) flowsheets are shown in Figures 9 and 10, respectively. For both flowsheets, common nuclear criticality issues arise in the 1AS, 1BX, and 1CX streams, and are discussed below.

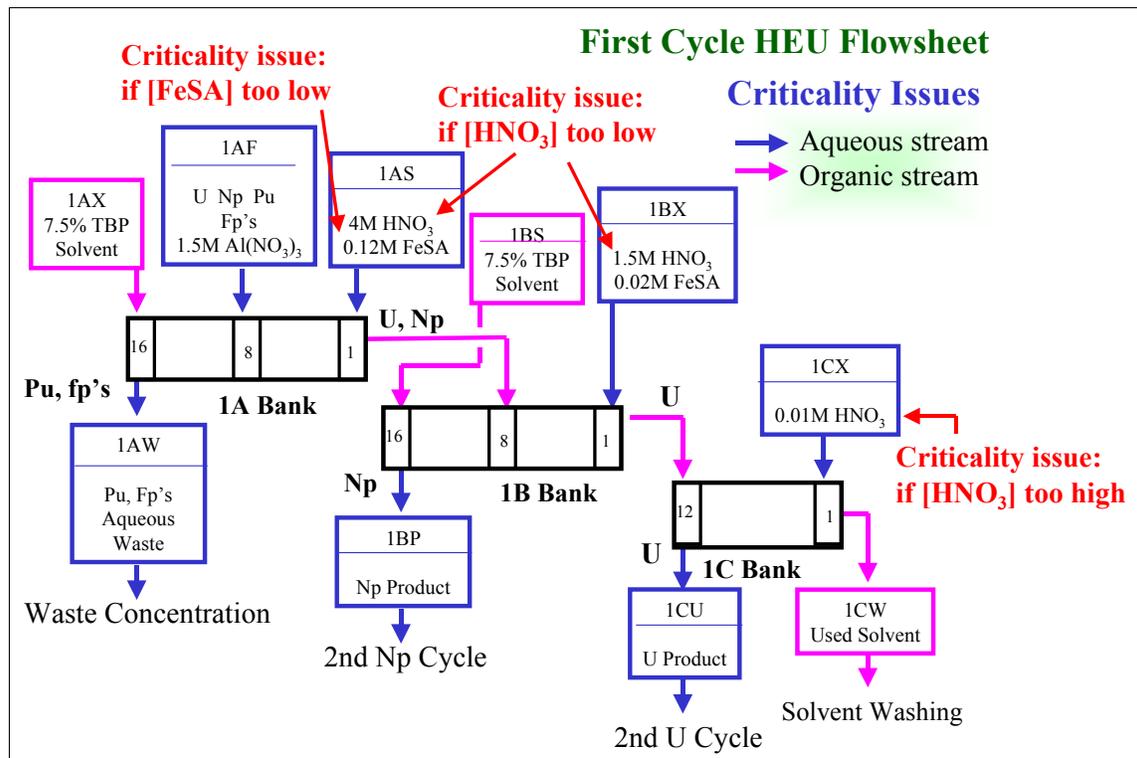


Figure 9. First Solvent Extraction Cycle for the HM Process (HEU)

#### Stream 1AS

Low nitric acid concentration will shift the  $\text{UO}_2^{2+}$  extraction equilibrium towards the aqueous state, resulting in a potential buildup of U in the 1AW stream which could be a criticality safety concern in subsequent evaporation.

#### Stream 1BX

Low nitric acid concentration will shift the  $\text{UO}_2^{2+}$  extraction equilibrium towards the aqueous state, resulting in a buildup of uranium in the 1BP stream, causing potential criticality safety concerns for downstream Np processing.

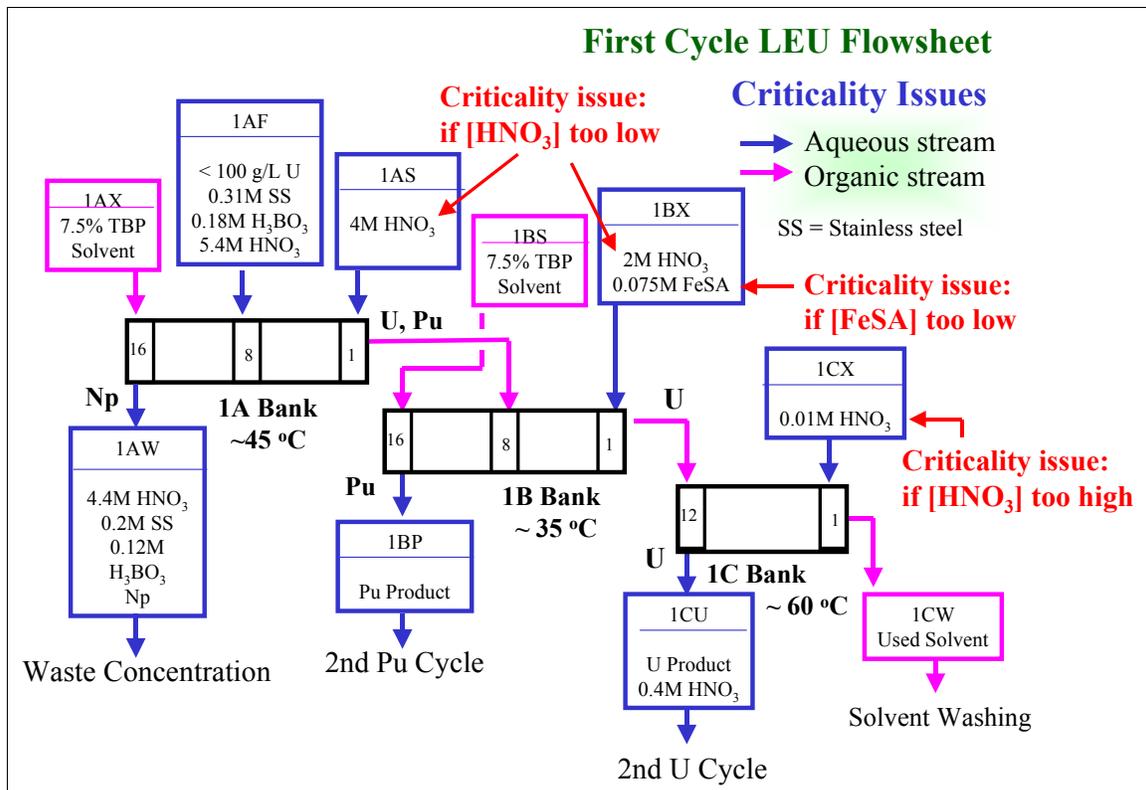


Figure 10. First Solvent Extraction Cycle for the HM Process (LEU)

### Stream 1CX

If the nitric acid concentration is too high, the  $\text{UO}_2(\text{NO}_3)_2$  (aq) tends to remain as is and does not dissociate into the separate ions  $\text{UO}_2^{2+}$  (aq) and  $\text{NO}_3^-$  (aq). Under these conditions, U cannot be stripped from the organic phase and the  $\text{UO}_2(\text{NO}_3)_2$  (aq) is extracted by TBP into the organic phase. This allows an inventory of U to build up in the 1CW stream, the used solvent, which is next washed with sodium carbonate during recycling operations. The uranium can collect in the solvent washing vessel, and can accumulate with successive carbonate washings, creating a nuclear criticality hazard.

### Streams 1AS and 1BX

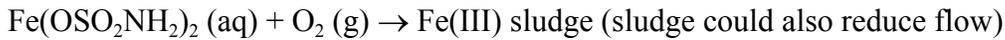
For the HEU process (Figure 9), Pu is reductively stripped from the organic phase into the aqueous phase in the 1A bank, whereas for the LEU process (Figure 10), this exchange is carried out in the 1B bank. Nuclear criticality safety issues exist if the ferrous sulfamate (FeSA) concentration is low during reductive stripping as described below for the 1AS and 1BX streams.

Low ferrous sulfamate concentrations lead to Pu reflux which could lead to a build up of Pu inventory in the middle stages of the solvent extraction banks of the first cycle for the HM

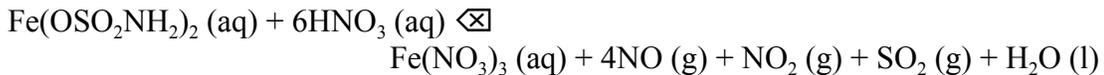
process. This phenomenon was illustrated earlier for the 1B bank of the PUREX process. In the first cycle LEU process (Figure 10), boron (added as boric acid) serves as a soluble neutron poison during the dissolving process, but does not function as a control in solvent extraction. Possible ways that the FeSA can be depleted during the process include:

1) Incorrect make-up concentration;

2) Reaction with oxygen;



3) Reaction with nitric acid.



Administrative controls (e.g., independent verification) are used to ensure the proper concentration of FeSA in make-up tanks. Fresh solutions (limits oxygen exposure) are prepared in dilute (slows rate of reaction) nitric acid.

#### Stream 1AF

If the boric acid concentration is low or absent (e.g., due to precipitation as  $\text{KBF}_4$ , volatilization, or inadvertently not added to the feed), this nuclear criticality control is lost. Compounded with other adverse conditions (e.g., fissile solid build-up or Pu reflux), a nuclear criticality is possible.

### 3.5.2 Second Uranium Solvent Extraction Cycle

Fission products and other metal cations are separated from uranium in the first solvent extraction cycle. The purpose of the second uranium (solvent extraction) cycle (see Figure 11) is to increase the purity of the uranium product stream (1CU). The purification is achieved using banks 1D and 1E. In the 1D bank, FeSA is used to reductively strip any remaining Pu, Np and fission products. Since  $\text{UO}_2^{2+}$  is the one of the most extractable species into the organic phase, it is efficiently extracted with relatively dilute nitric acid (0.9M). In the 1E bank, the  $\text{UO}_2^{2+}$  is from the organic phase into the aqueous by using a dilute nitric acid wash (0.01M). Under the dilute nitrate conditions, the uranyl ions are solvated by water (denoted as  $\text{UO}_2^{2+} \text{ (aq)}$ ) and partition into the aqueous phase rather than being complexed by nitrate and extracted. Two situations are possible that could lead to a nuclear criticality due to the chemistry of the second uranium solvent extraction cycle.

#### Stream 1DS

A low nitric acid concentration in the 1DS stream could reduce the amount of extraction of  $\text{UO}_2^{2+}$  into the organic phase. With an insufficient concentration of nitrate,  $\text{UO}_2^{2+}$  and  $\text{NO}_3^-$  ions tend to remain separated in the aqueous phase instead of complexing with TBP into the organic phase. This results in the potential for fissile U buildup in the 1DW stream.

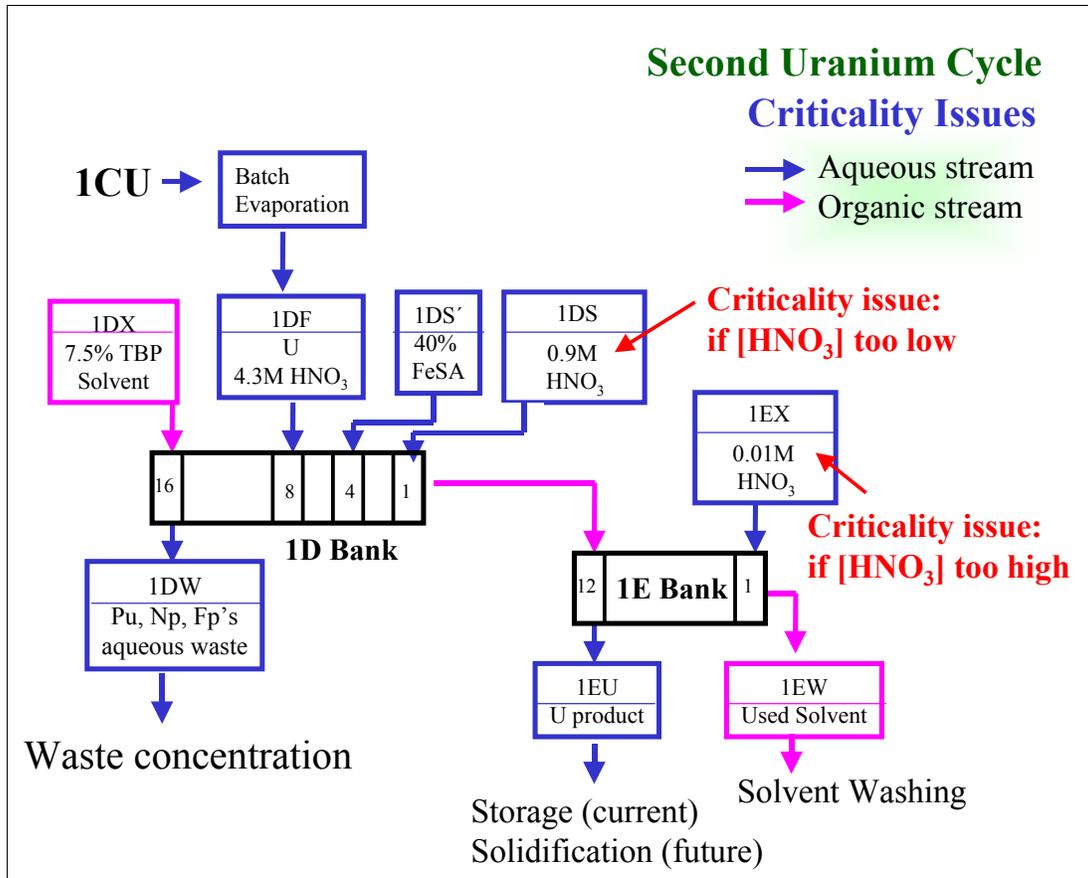


Figure 11. Second Uranium Solvent Extraction Cycle

### Stream 1EX

U stripping is designed to occur in the 1EX bank using dilute nitric acid (essentially acidified water). A high nitric acid concentration will shift the  $\text{UO}_2^{2+}$  complexation equilibrium toward formation of the extractable nitrate complex. An inventory of U may build up in the 1EW stream, the used solvent, which is next washed with sodium carbonate as part of recycling operations. The uranium can collect in the solvent washing vessel, and accumulate with successive carbonate washing, creating a nuclear criticality hazard.

### 3.5.3 HM Process Second Plutonium Cycle

The purpose of the second plutonium (solvent extraction) cycle (see Figure 12) is to increase the purity of the plutonium product stream (2AF). The purification is achieved using two sets of solvent extraction banks, 2A and 2B. In the 2A bank, the aqueous feed enters at stage 8 and the Pu is extracted into the organic phase from 4M nitric acid. The 2AS scrub at stage 1 employs 0.66M nitric acid to retain Pu in the organic phase and to scrub impurities into the aqueous

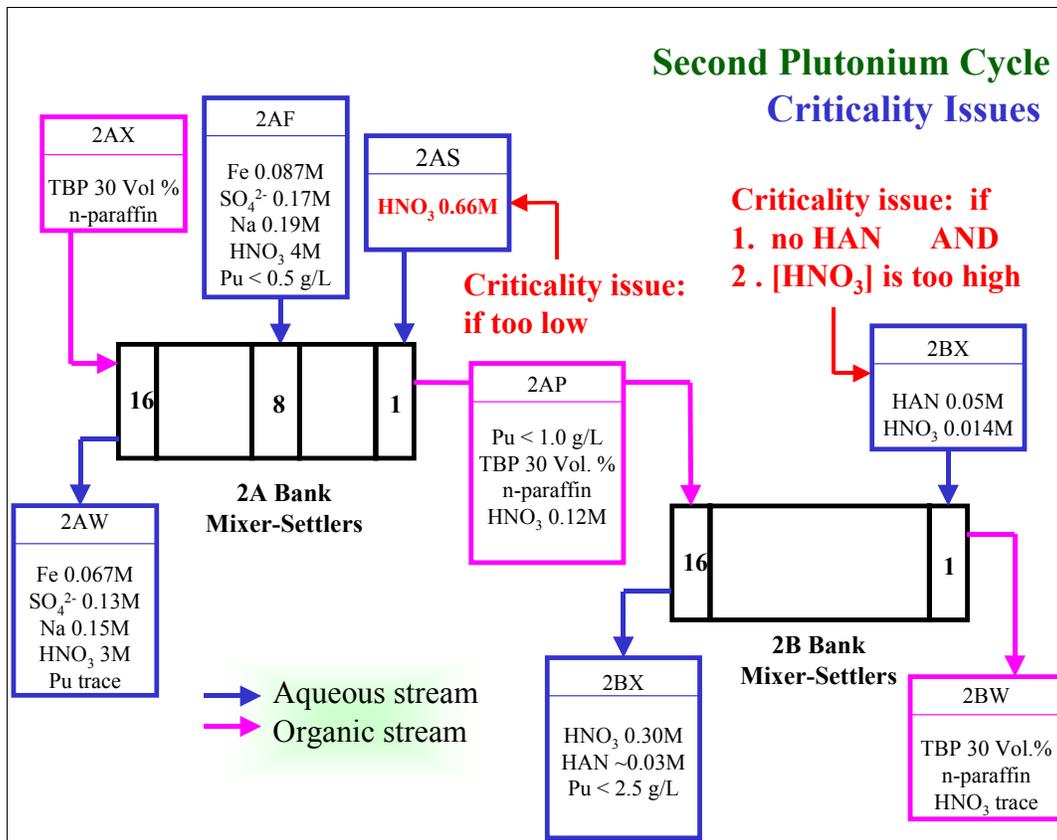


Figure 12. Second Plutonium Solvent Extraction Cycle

phase. In the 2B bank, the Pu is reductively stripped from the organic phase into the aqueous phase with hydroxylammonium nitrate (HAN) and dilute nitric acid. Out-of-normal chemical conditions can lead to two situations that could lead to a nuclear criticality accident.

#### Stream 2AS

A low nitric acid concentration in the 2AS stream can cause the Pu<sup>4+</sup> and NO<sub>3</sub><sup>-</sup> ions to remain separated in the aqueous phase instead of becoming Pu(NO<sub>3</sub>)<sub>4</sub> and complexing with TBP into the organic phase. Under these conditions, a large portion of the Pu is stripped (without reduction) back into the aqueous phase and a buildup of Pu can occur in the 2AW stream.

#### Stream 2BX

The low nitric acid concentration (0.014M) limits the formation of the extractable neutral Pu tetranitrato complex, Pu(NO<sub>3</sub>)<sub>4</sub>. The purpose of the HAN in 2BX is to reduce Pu to inextractable Pu (III). If the 2BX has no HAN and a high acid concentration, the plutonium, as Pu (IV), will be extracted into the organic phase. Under these conditions, a large portion of the Pu is retained in the organic phase and a build-up of Pu inventory can occur in the 2BW stream.

### 3.6 Other Chemical Issues Leading to Nuclear Criticality Concerns

#### 3.6.1 Poor Phase Separation in Solvent Extraction

Poor phase separation and formation of emulsions (as illustrated in Figure 13) can lead to Pu and/or U carry-over to subsequent stages and may lead to a buildup of fissile material.

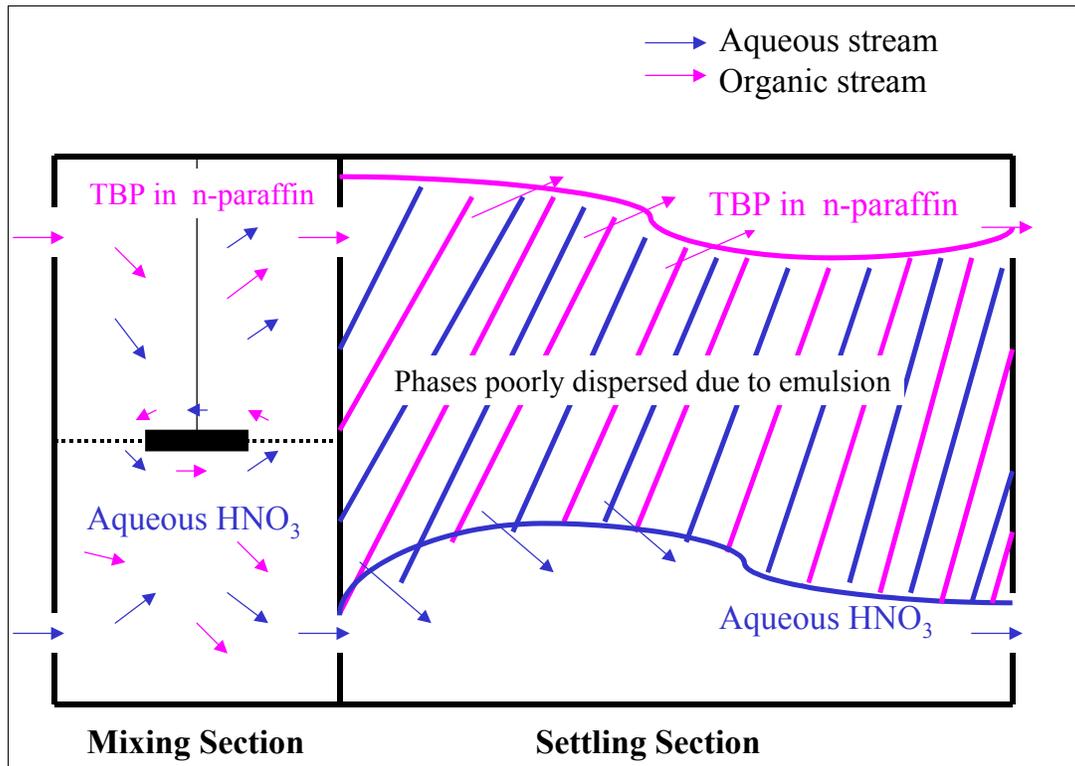


Figure 13. Illustration of Poor Phase Separation during Mixer-settler Operation

One cause of emulsion formation is the presence of amorphous silicates or “silica”, present as a neutron activation product of <sup>27</sup>Al and as an impurity in Al. Silica acts as a surfactant during mixer-settler operation, causes emulsions, and reduces the separation efficiency of aqueous and organic phases. Silica can be removed by coagulating it in a solution of warm gelatin, followed by centrifugation (called a “gelatin strike”) as part of the feed preparation in the Head End unit operation.

#### 3.6.2 Acid Reflux in Solvent Extraction

Analogous to Pu reflux, “acid reflux” can alter the chemical composition of solvent extraction stages. However, acid reflux results from higher than normal organic to aqueous flow rates. The phenomenon is illustrated in Figure 14.



### Potassium Tetrafluoroborate (KBF<sub>4</sub>)

For difficult-to-dissolve materials, a high concentration of potassium fluoride (KF) in nitric acid is required to achieve dissolution. Under certain chemical conditions, boron in solution may precipitate as potassium tetrafluoroborate (KBF<sub>4</sub>). In process streams where the boron is used as a criticality control, this precipitation removes the boron and thus the nuclear criticality control is lost.

One defense to prevent the precipitation of boron during full-scale process operations is to verify the acceptability of the proposed flowsheet used to process any unusual materials on a laboratory scale prior to implementing that process for plant operations. Another defense to prevent KBF<sub>4</sub> precipitation is to use calcium fluoride (CaF<sub>2</sub>) as the fluoride source rather than KF, since Ca<sup>2+</sup> does not form a sparingly soluble salt like KBF<sub>4</sub>.

### Di-n-Butyl Phosphate (DBP)

During solvent extraction, radiolytic and chemical degradation of TBP leads to formation of di-n-butyl phosphate (DBP). In nitric acid, the DPB will exist as the acid form, HDBP (di-n-butyl phosphoric acid). In the presence of HDBP and dilute nitric acid, UO<sub>2</sub><sup>2+</sup> and/or Pu<sup>4+</sup> can precipitate as UO<sub>2</sub>(DBP)<sub>2</sub> or Pu(DBP)<sub>4</sub> creating a potential nuclear criticality safety issue.

The solvent quality is preserved by washing the used solvent with carbonate and bicarbonate solutions to strip the HDBP (and other degradation products) out of the organic solvent into the aqueous phase. Carbonate washing is also effective in stripping the DBP complexes of Pu and U from the used solvent.

## 3.7 Process Accidents and Lessons Learned

There have been a number of criticality accidents in nuclear material process facilities. With one exception, they have all involved solution operations. A review of the conditions leading to these accidents provides an excellent overview of what not to do during process operations. Reference 3 provides details of each of the historical criticality accidents and includes a summary section on lessons learned.