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ABSTRACT

Uranium fuels containing ^{235}U at enrichments from 1.1% to 94% are processed and recovered, along with neptunium and plutonium byproducts, in one of the separations areas (H-Area) at the Savannah River Plant.

The fuels to be processed are dissolved in nitric acid. Aluminum-clad fuels are dissolved using a mercury catalyst to give a solution rich in aluminum. Fuels clad in more resistant materials are dissolved in an electrolytic dissolver. The resulting solutions are subjected to head-end treatment, including clarification and adjustment of acid and uranium concentration before being fed to solvent extraction.

Uranium, neptunium, and plutonium are separated from fission products and from one another by multistage countercurrent solvent extraction with dilute tri-n-butyl phosphate (TBP) in kerosene. Nitric acid is used as the salting agent in addition to aluminum or other metal nitrates present in the feed solution. Nuclear safety is maintained through conservative process design and the use of monitoring devices as secondary controls.

The enriched uranium is recovered as a dilute solution and shipped off-site for further processing. Neptunium is concentrated and sent to HB-Line for recovery from solution. The relatively small quantities of plutonium present are normally discarded in aqueous waste, unless the content of ^{238}Pu is high enough to make its recovery desirable. Most of the ^{238}Pu can be recovered by batch extraction of the waste solution, purified by counter-current solvent extraction, and converted to oxide in HB-Line. By modifying the flowsheet, ^{239}Pu can be recovered from low-enriched uranium in the extraction cycle; neptunium is then not recovered.

The solvent is subjected to an alkaline wash before reuse to remove degraded solvent and fission products. The aqueous waste is concentrated and partially deacidified by evaporation before being neutralized and sent to the waste tanks; nitric acid from the overheads is recovered for reuse.

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1. INTRODUCTION

1.1 BACKGROUND AND SCOPE

Nuclear products from the Savannah River reactors are recovered in the F and H separations areas. Original operations in both areas were confined to the recovery of plutonium from irradiated natural uranium by the Purex process, in which the two elements are separated and individually purified by solvent extraction with tri-n-butyl phosphate (TBP). The introduction of enriched uranium fuels into Savannah River reactor operations made possible the production of a greater variety of products, but also presented problems in recovering unburned uranium from spent fuels, since the available facilities were not critically safe for large quantities of enriched uranium. Accordingly, a modified (HM) process was developed by the Savannah River Laboratory for the recovery of enriched uranium in existing canyon equipment by solvent extraction with more dilute TBP, and H-Area operations were converted to this process. Subsequent modifications have made possible the recovery of ^{237}Np from irradiated ^{235}U, and the efficient processing of moderately enriched uranium fuels from off-site reactors. This manual describes the operations involved in recovering enriched uranium and its byproducts from spent fuel. It includes, in addition to the technology for processing Savannah River fuel, dissolving methods and flowsheet modifications used in processing off-site fuels.

1.2 HISTORY

The basic HM solvent extraction process for the recovery of enriched uranium was developed at the Savannah River Laboratory as the result of studies there and elsewhere on the solvent extraction of uranium with TBP. Process criteria included:

- Decontaminating uranium from fission products; the factors required may be as high as 10^8 in some cases.
- Maintaining nuclear safety in recovering and purifying nearly fully enriched ^{235}U.

- Using existing canyon equipment, including mixer-settlers, insofar as possible.

- Using a system with TBP as extractant and acidifying with nitric acid in order to maintain chemical compatibility of solutions with equipment, to retain compatibility with existing methods of recovering solvent and treating waste, and to take advantage of the understanding of such systems developed over the years at Savannah River.

These goals were achieved by a process that differed from Purex in several ways:

- The concentration of TBP in the organic phase was decreased from the 30% concentration used in Purex to lower concentrations in the range 2% to 7.5%, with the intention of decreasing the capacity of this phase for uranium and improving decontamination from fission products.

- Aluminum present in the feed as a consequence of dissolving the fuel in acid serves as a salting agent in the first cycle solvent extraction.

- Flow rates and other solvent extraction parameters are designed to limit the concentration of uranium achieved during solvent extraction to no more than that of the feed so as to ensure nuclear safety.

The HM process was put into operation in 1959 in the H-Area canyon, which had previously been used for Purex processing of natural uranium fuels. The process was modified to provide for the recovery of neptunium in 1963. The electrolytic dissolver was put into operation for the dissolution of off-site fuel in 1969. The relatively low ^{235}U enrichment of some off-site fuels led to the development of flowsheet modifications for such fuels, including in particular the use of 7.5% TBP in the first solvent extraction cycle. The first flowsheet of this type was put into use in 1972, and it has subsequently been adapted to processing highly enriched Savannah River fuels.

2. SUMMARY

Uranium fuels containing ^{235}U at enrichments from 1.1% to 94% are processed and recovered, along with neptunium and plutonium byproducts, in one of the separations areas (H-Area) at the Savannah River Plant.

The fuels to be processed are dissolved in nitric acid. Aluminum-clad fuels are dissolved using a mercury catalyst to give a solution rich in aluminum. Fuels clad in more resistant materials are dissolved in an electrolytic dissolver. The resulting solutions are subjected to head-end treatment, including clarification and adjustment of acid and uranium concentration before being fed to solvent extraction.

Feed preparation and solvent extraction steps are shown schematically in Figures 2.1-2.3. Uranium, neptunium and plutonium are separated from fission products and from one another by multistage countercurrent solvent extraction with dilute tri-n-butyl phosphate (TBP) in kerosene. Nitric acid is used as the salting agent in addition to aluminum or other metal nitrates present in the feed solution. Nuclear safety is maintained through conservative process design and the use of monitoring devices as secondary controls.

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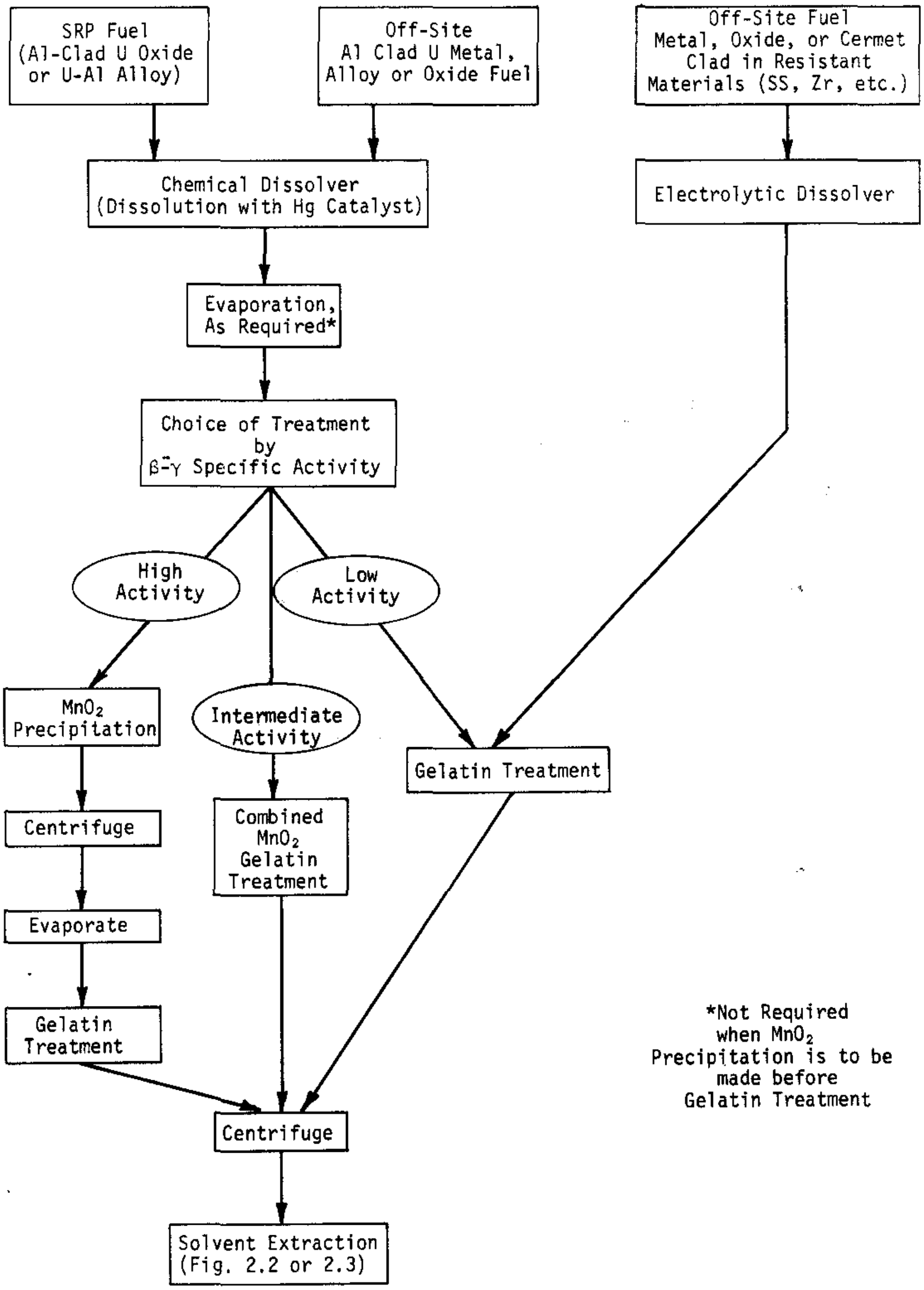
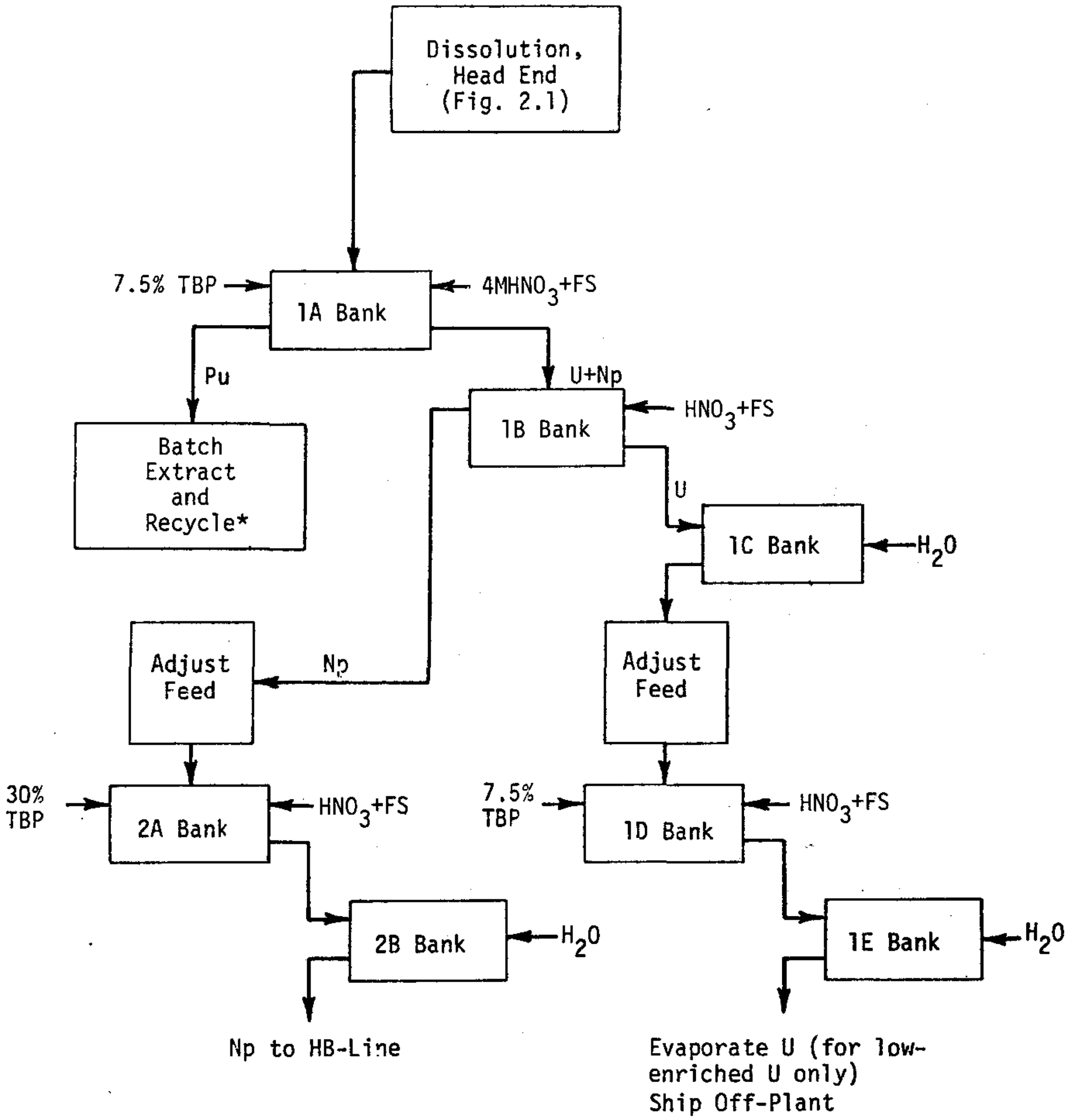


*Not Required when MnO_2 Precipitation is to be made before Gelatin Treatment

FIGURE 2.1 Dissolution and Head-End Treatment



*Pu-U Process in First Cycle
FS = Ferrous Sulfamate

FIGURE 2.2 HM Solvent Extraction Process with Neptunium Recovery

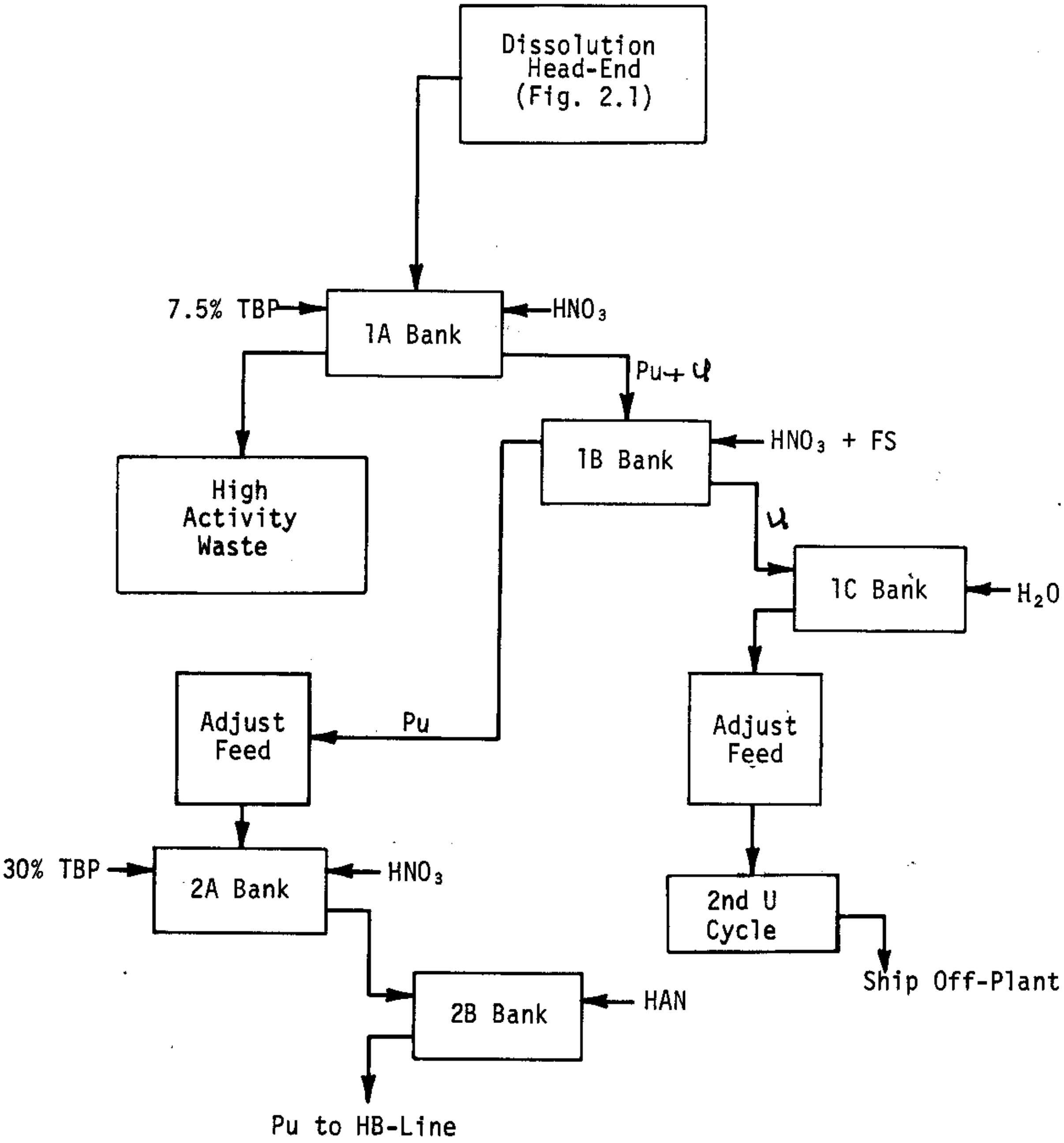


FIGURE 2.3 H-Area Solvent Extraction Process for Plutonium Recovery with Neptunium Absent or Discarded

3. NUCLEAR PROPERTIES AND NUCLEAR SAFETY

3.1 PROPERTIES OF URANIUM, NEPTUNIUM, AND PLUTONIUM ISOTOPES

Various considerations in the processing of enriched uranium fuels depend on the nuclear properties of the nuclides involved; these are summarized in Table 3.1 for uranium isotopes and in Table 3.2 for neptunium and plutonium isotopes. Absorption of neutrons by ^{235}U predominantly leads to fission, as indicated by the cross sections in Table 3.1, but a significant amount of capture also occurs, leading to ^{238}Pu production in the following sequence:

$$^{235}U(n,\gamma)\ ^{236}U(n,\gamma)\ ^{237}U \xrightarrow{\beta^-} {}^{237}Np(n,\gamma)\ ^{238}Np \xrightarrow{\beta^-} {}^{238}Pu$$

For long irradiations, ^{236}U will accumulate, and significant amounts of ^{237}Np will be formed. The ^{238}Pu formed will be diluted by ^{239}Pu produced from the ^{238}U present:

$$^{238}U(n,\gamma)\ ^{239}U \xrightarrow{\beta^-} {}^{239}Np \xrightarrow{\beta^-} {}^{239}Pu.$$

Thus, the ratio of ^{238}Pu to ^{239}Pu will vary greatly with the degree of enrichment and the irradiation history of the sample. For production of plutonium containing mainly ^{238}Pu, it is necessary to separate and irradiate the ^{237}Np precursor.

3.2 GENERAL NUCLEAR SAFETY CONSIDERATIONS

The large quantities of ^{235}U processed present a problem in maintaining nuclear safety in process equipment; it is not generally possible to maintain the quantity of uranium in a given part of the process below that which could conceivably form a critical mass. Nuclear safety is based on administrative controls which take into account the characteristics of the process and the specific designs of the individual pieces of process equipment. These controls may be based on "ever-safe" mass, geometric, or concentration limits[3,4] (Table 3.3), or on conservative calculation of the properties of a particular piece of equipment using accepted

TABLE 3.1

Nuclear Properties of Uranium Isotopes 235 Through 238[a]

	Isotopes			
	235	*236*	*237*	*238*
Natural Abundance, %	0.72	-	-	99.3
Half-Life	$7.1\text{x}10^{8}$y	$2.4\text{x}10^{7}$y	6.7d	$4.5\text{x}10^{9}$y
Decay Mode	α	α	β^{-}	α
Thermal Neutron Cross Section, barns				
Capture	101	6	(Total 370)	2.73
Fission	577	-		-

---

[a] Values from Reference 1 except ^{237}U cross section from Reference 2.

TABLE 3.2

Nuclear Properties of Neptunium and Plutonium Isotopes[a]

	^{237}Np	^{238}Np	^{238}Pu	^{239}Pu
Half-Life	$2.14\text{x}10^{6}$y	2.10d	86.4y	24,390y
Decay Mode	α	β^{-}	α	α
Thermal Neutron Cross Section, barns				
Capture	170	Unknown	500	274
Fission	0.019	1600	16.8	741

---

[a] Values from Reference 1.

TABLE 3.3

Single Parameter Limits[3] for Uniform Aqueous Solutions Containing ^{235}U

The limits in this table are valid when the effects of neutron reflectors and other nearby fissionable materials are no greater than reflection by an unlimited thickness of water.

Parameter	*Subcritical Limit*
Mass of ^{235}U, kg	0.76
Solution Cylinder diameter, cm	13.9
Solution Slab Thickness, cm	4.6
Concentration of ^{235}U, g/ℓ	11.5
Areal density of ^{235}U, g/cm^2	0.40

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Solution Slab Thickness, cm	4.6
Concentration of ^{235}U, g/ℓ	11.5
Areal density of ^{235}U, g/cm^2	0.40

methods.[5] In general, the policy is followed that at least two independent controls prevent the aggregation of a critical configuration, so that a single administrative error or the failure of a single instrument cannot cause a criticality accident.

A detailed study has been made of the nuclear safety hazards associated with each part of enriched uranium processing. Supplementary information is included in appropriate chapters of this report.

Wherever possible the procedures for material handling and process operation have been designed to be conservative and incorporate additional safeguards against the accidental assembly of a critical configuration. Specific examples include:

- *Identification.* When different types of fuel cannot be distinguished from one another by inspection, the fuel is always treated as the most reactive type.

- *Burnup.* No credit is taken for burnup of ^{235}U in dissolving calculations; thus, all fuel of a given type can be handled similarly, regardless of burnup. In subsequent processing, credit for burnup may be taken, up to the least amount associated with the particular batch of fuel; but analytical measurements, wherever possible, are preferred to calculations.

- *Handling.* Fuel assemblies bundled for dissolving shall be fewer than the minimum number that can be made critical if arranged in the most reactive configuration and submerged in water. No more than one bundle may be handled outside the dissolvers or the intermediate storage locations at a time. Individual tubes, when separated from assemblies, shall be considered as complete assemblies for purposes of calculation.

- *Chemicals.* Chemicals authorized for use in processing, or in flushing or decontaminating piping and equipment used for enriched uranium, are specifically named in technical standards. The purpose of this requirement is to provide against unexpected reactions which may precipitate or concentrate uranium.

- *Blanks.* Blanks are provided to block pipelines through which chemicals that might react to concentrate uranium could be introduced to the process. Before each campaign, the nuclear safety blanks required are reviewed and their location physically verified. The design of these blanks is such as to prevent their ready removal. The construction of nuclear blanks is given in Chapter IV.

- *Dissolving.* For each type of fuel, it is necessary to demonstrate that preferential dissolution of cladding does not lead to the accumulation of a dangerous quantity of uranium-rich fragments. Where this sort of accumulation is considered possible, even though unlikely, it is necessary to provide a secondary control. For example, in the dissolution of off-site fuels, using the electrolytic dissolver, a soluble neutron poison has been used as a secondary control.

3.3 FISSION PRODUCTS

The fission products in fuel are principally responsible for the penetrating radiation emitted from fuel and process solution, and thus for the shielding requirements for processing.

Specific noteworthy aspects of some of these fission products are as follows:

- ^{85}Kr, ^{133}Xe. These noble gases are quantitatively volatilized and released to the atmosphere. Due to their lack of chemical reactivity, their biological effect is relatively small.
- ^{131}I. A significant amount of this isotope will be volatized from short-cooled fuels as elemental iodine or as organic iodides. Due to the short half life of ^{131}I, this release of activity can be made negligible by cooling the fuel for a sufficiently long time.
- ^{103}Ru, ^{106}Ru. Because of its complex chemical behavior, ruthenium is difficult to separate from uranium with high efficiency. The volatile form RuO_4 may be produced in strongly oxidizing conditions and released to the atmosphere.
- ^{90}Sr, ^{137}Cs. These long-lived isotopes, which are principally removed from uranium in the first solvent extraction cycle, are major contributors to the activity of aged fission products and are of primary concern in managing aged nuclear wastes.

The specification for the fission product level in purified enriched uranium is a maximum of 3.5 Ci per metric ton. This necessitates an overall fission product decontamination exceeding 10^5. For most isotopes this is fairly easily achieved in two cycles of solvent extraction; ^{95}Zr and the ruthenium isotopes are the most difficult to remove and are therefore of greatest concern to the process.

3.4 References

1. C. M. Lederer, J. M. Hollander, and I. Perlman. *Table of Isotopes*. John Wiley and Sons, New York (1967).

2. W. R. Cornman, E. J. Hennelly, and C. J. Banick. *Nucl. Sci. Eng. 31*, 47 (1968).

3. American National Standard N. 16-1-1969. "Nuclear Criticality Safety in Operations with Fissionable Materials Outside Reactors." American National Standards Institute, Inc., New York (1970).

4. H. C. Paxton. *Criticality Control in Operations with Fissile Material*. USAEC Report LA-3366, Los Alamos Scientific Lab., Los Alamos, NM.

5. H. K. Clark. *Handbook of Nuclear Safety*. USAEC Report DP-532, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC.

4. FACILITIES AND EQUIPMENT

4.1 GENERAL

Enriched uranium is recovered at Savannah River in the 221-H canyon building originally designed for recovering plutonium from irradiated natural uranium. The location of this building with respect to other facilities in the area and external services is shown in Figure 4.1. Figure 4.2 is an isometric drawing showing the principal features of the canyon building. Separations are conducted in the two heavily shielded canyon facilities in equipment that is operated and maintained by remote control, using a shielded crane for access to the equipment.

4.2 BUILDING OPERATION

4.2.1 Labeling and Identification

A specific system of identifying canyon equipment has been developed to ensure clarity in references to such equipment. Canyon vessels are numbered by building section and location in the section; hot canyon vessels in each section are numbered .1 to .4, warm canyon vessels .5 to .8. In addition, the following types of equipment are identified by suffixes:

Mixer-Settler	M
Evaporator	E
Dissolver	D
Centrifuge	C
Decanter (Separator)	S
Filter	F
Iodine Reactor	R

Thus, as an example, the head-end evaporator, located on module three of Section 11 in the hot canyon, is identified as 11.3E.

Jumper assemblies (pipes connecting the vessel and wall nozzles) are identified by the tank number, wall nozzle, and tank nozzle to which they are connected. Rack piping is identified by building section, rack position, and the nozzles to which it is connected.

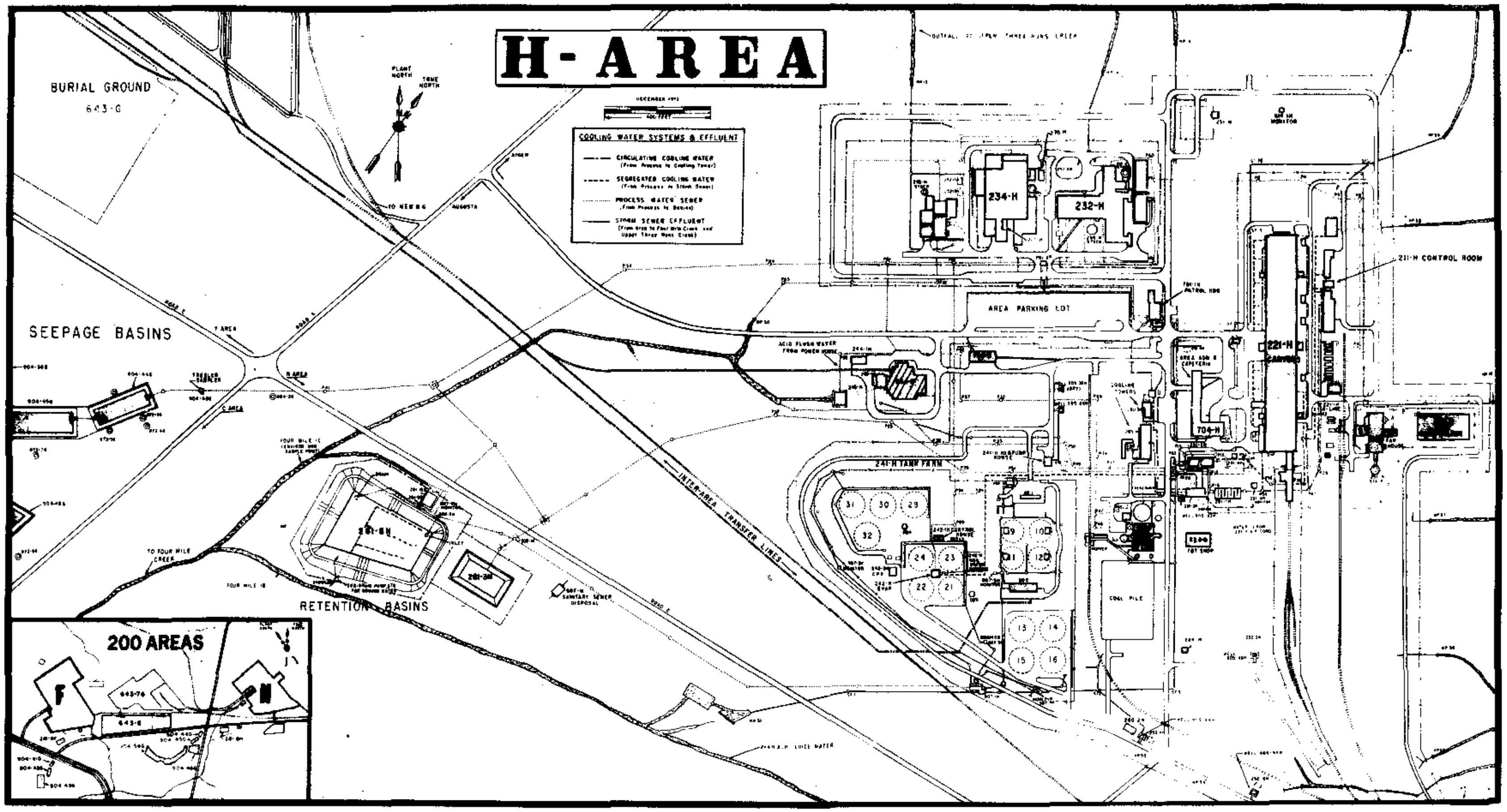


FIGURE 4.1 H-Area Map Showing Location of 221-H Canyon Building

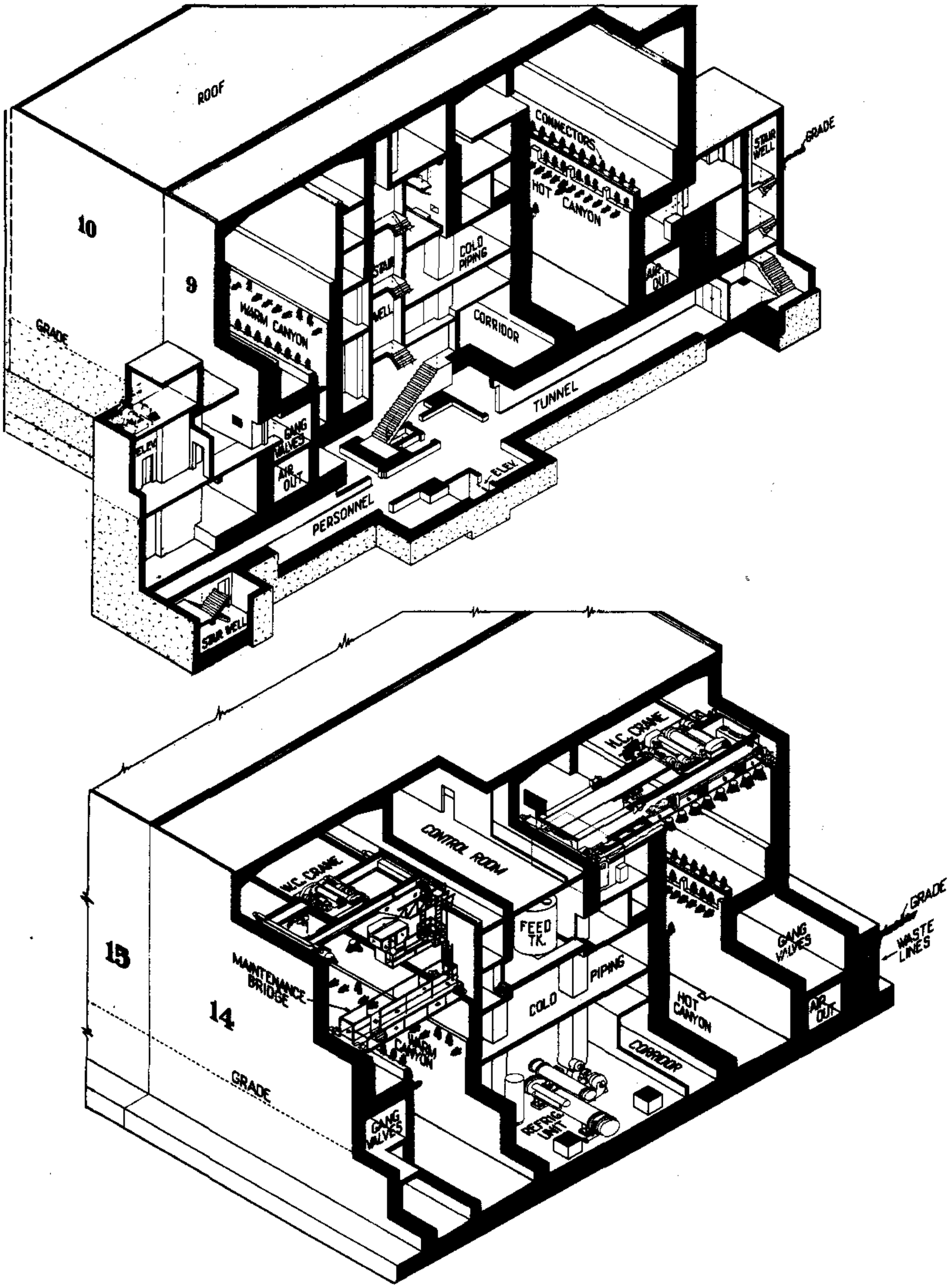


FIGURE 4.2 Isometric of Building 221-H

Equipment in the canyons is identified by painting according to a code that provides good visibility and rapid identification. The canyons themselves are finished to a level just above the pipe rack in white Amercoat 1574 (a coating resistant both to nitric acid and organic solvent): vessels, wall nozzles, and piping are numbered in black; bails, lifting trunnions, and positioning guides are yellow; and hooks are red.

4.2.2 Ventilation and Process Off-Gas Systems

Six individual systems are provided in Building 221-H to protect personnel from airborne radioactivity. In general, air flows from zones of lower to higher contamination. The static pressure in any zone is greater than that in adjacent zones of higher contamination and less than that in adjacent zones of lesser contamination. Blowers, which maintain the required air flow and differential pressures, are located in 292-H fan house and discharge directly to the 291-H exhaust stack. Figure 4.3 is a block diagram of the ventilation and off-gas system;

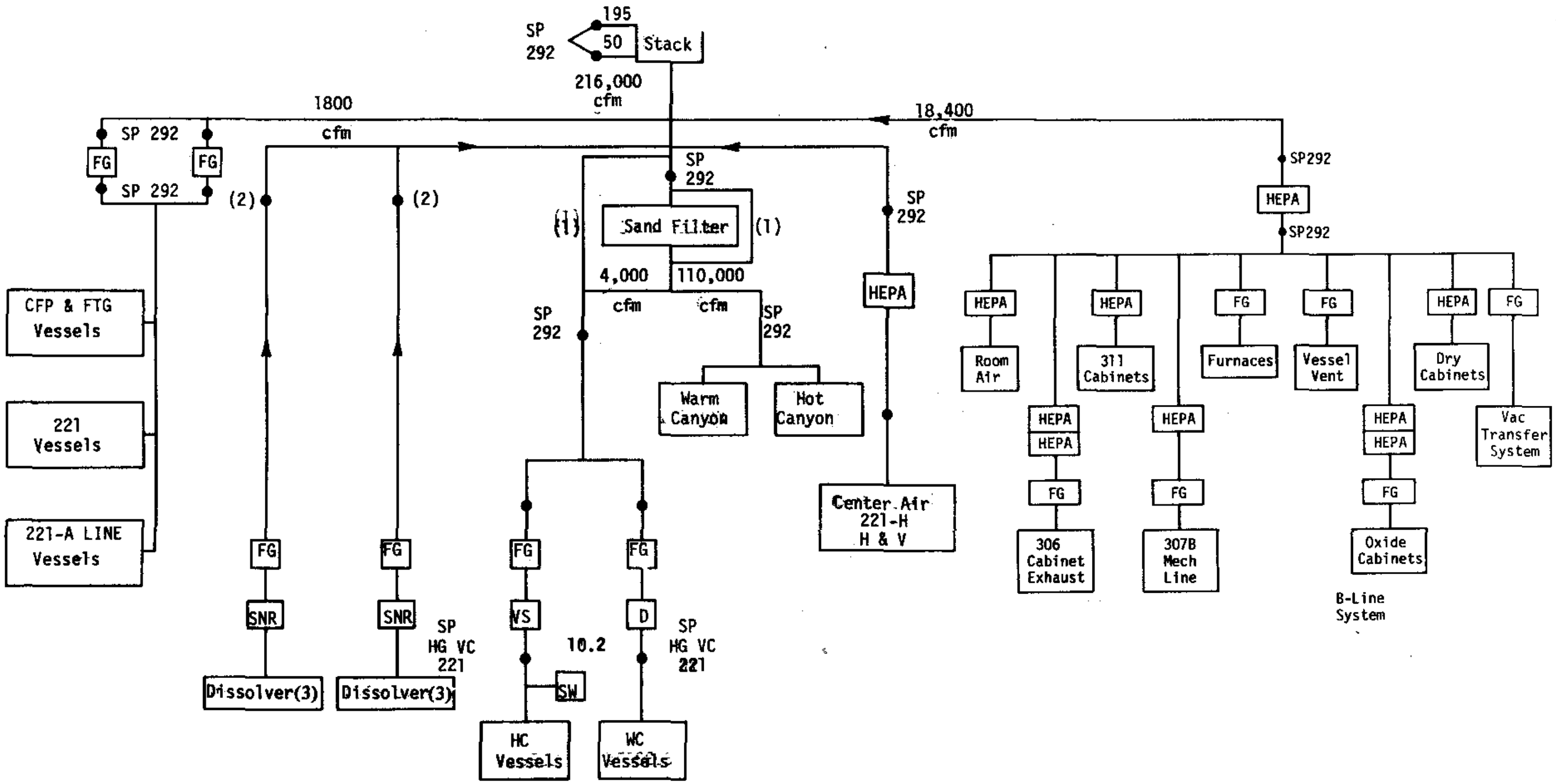
Figure 4.4 illustrates typical air flow patterns.

Central Air System

The central air system provides a continuous supply of conditioned fresh air to the nonregulated and regulated work areas of the building which normally have no, or very little, airborne contamination. Air flows from the clean first and fourth levels of 221-H into work areas with progressively greater potential for contamination. The exhaust from this system passes through a HEPA filter before discharge from 291-H.

Canyon Air System

Individual systems are provided to maintain the required air flow and pressure differentials in the hot and warm canyons. This air also serves those work areas directly associated with the canyons which are permanent sources of high contamination and radiation. In areas requiring personnel access, a system of air locks segregates cannon air from central air. Canyon air exhaust passes through the 294-H sand filter for decontamination before exiting from the 291-H stack.



(1) Bypass - Not Normally Used
(2) Dissolver Off Gas Sampling System Currently Being Installed
(3) Electrolytic Dissolver vented to Either Dissolver Off-Gas System

HEPA	HEPA Filter
SNR	Silver Nitrate Reactor
FG	Fiberglass Filter
SW	Steel Wool Filter (Vessel 10.1)
VS	Vent Scrubber
D	Dehumidifier

HGVC	Hot Gang Volve Corridor
WGVC	Warm Gang Valve Corridor
FTG	Feed Tank Gallery
CFP	Cold Feed Preparation Area
SP	Sample Point

FIGURE 4.3 Ventilation and Off-Gas Systems, 221-H

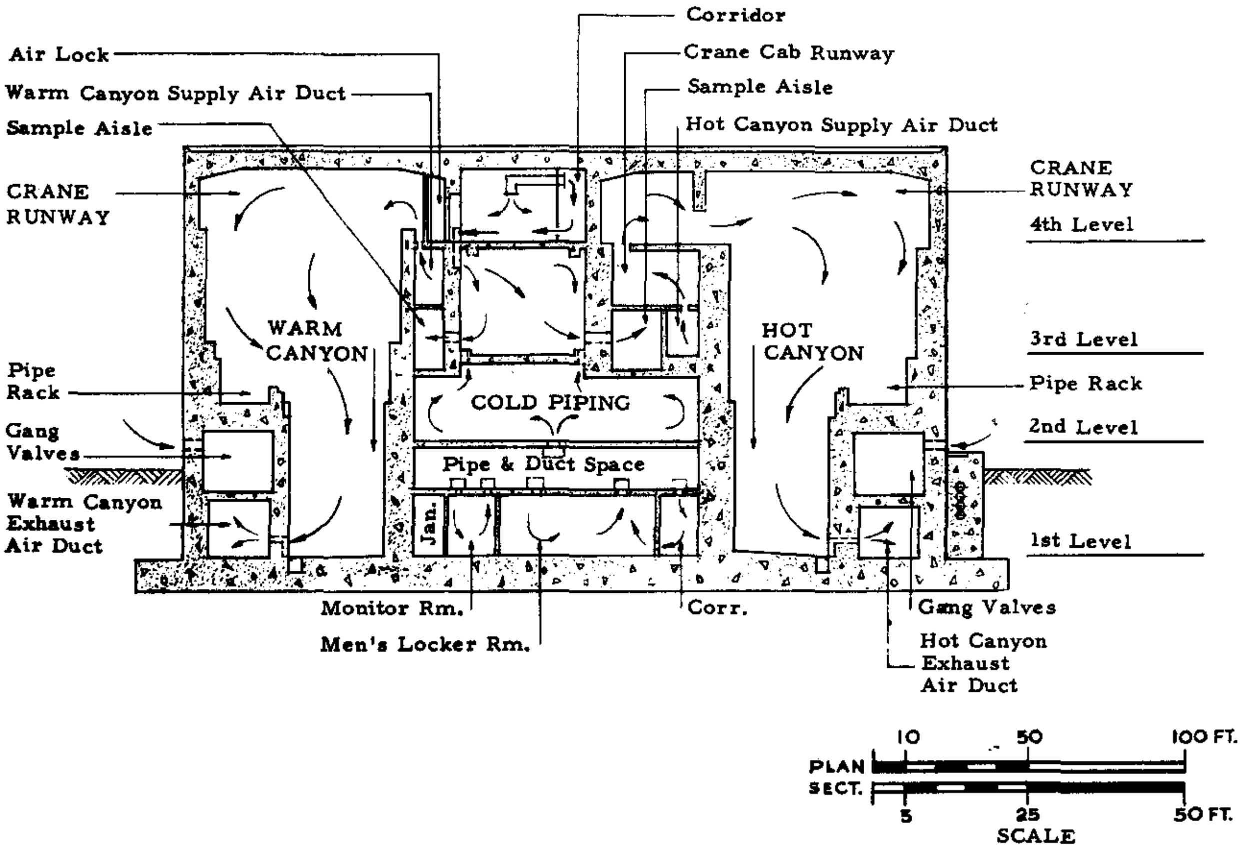


FIGURE 4.4 Ventilation Air Flow, 221-H

Process Vessel Vent System

A constant flow of air is maintained through process vessels and associated facilities in the hot and warm canyons to maintain them at a slightly negative pressure relative to their surroundings. In this manner, airborne radioactivity is swept from the process equipment into the process vessel vent (PVV) system.

The hot canyon PVV system has a stainless steel wool filter (vessel 10.1) interposed between the head-end strike tank (10.2) and the hot canyon vessel vent header to absorb the comparatively large amount of ruthenium volatized from 10.2 (see Section 6.3.3). The hot canyon vessel vent air passes into the vessel vent scrubber (7.3) that contains a bed of stainless steel Raschig rings which can be continuously sprayed with water or solutions. After passing through a fiberglass filter (7.2) the hot canyon PVV off-gas combines with that from the warm canyon before final decontamination by 294-H sand filter and exiting the 291-H stack.

The warm canyon PVV air passes through a dehumidifier (5.6) where it is cooled to condense contaminated water vapor and passed through a fiberglass filter (5.7). The condensate from the dehumidifier is collected in a canyon tank from which it is periodically sent to low-activity waste evaporation. Off-gas from the warm canyon PVV header combines with that from the hot canyon PVV header before the combined PVV off-gases join with the canyon air system before entering the 294-H sand filter.

Recycle Vessel Vent System

Tanks used for cold or warm solutions (gallery, cold-feed preparation, 211-H tanks) are vented through a common header called the recycle vessel vent (RVV) system. This off-gas stream passes through a fiberglass filter before exiting the 291-H stack. Currently, the vacuum produced by the RVV blowers is used to pull air samples in the 292-H fan house. Therefore, the RVV system, itself is not sampled.

Dissolver Off Gas System

Off-gas from the dissolvers first passes into a silver nitrate reactor to remove iodine and then through a fiberglass filter before exiting from the 291-H stack. The acid absorber, previously used in the dissolver off-gas system, has been dismantled. An air sampling system is currently being installed.

B-Line Off Gas System

Containment vessels in HB-line, under slightly negative pressure, are vented to the B-line off-gas system that has two stages of HEPA filtration before exhausting from the 291-H stack.

4.2.3 Water Utilities

A flow diagram for the water utilities in 200-H Area is shown in Figure 4.5 Three separate water systems supply 221-H: cooling water, fire water, and domestic water. Water is obtained from five deep wells, two of which pump 1000 gpm continuously through heat exchangers at Building 241-H to the Building 285-H cooling tower; the remaining three supply two constant level reservoirs.

Cooling Water Supply

Four pumps operating in parallel pump water from the cooling tower to a main header which supplies a normal header and an independent header. Both headers have branch lines serving the entire 200-H Area. In the event of cooling water pressure failure, a valve in the normal header closes and diverts all available cooling water to the independent header. The purpose of the independent system is to allow continued operation of important equipment (e.g., air compressors, evaporators, evaporator columns (during a failure of short duration or to provide for a controlled shutdown of key facilities during an extended failure.

Cooling Water Return

Cooling water leaves 221-H in three main streams. Clean cooling water from air conditioning units and air compressors and stream condensate from the center section is returned to the 285-H cooling tower without monitoring. Regulated cooling water which has been used in the single-purpose coils of canyon vessels and condensate from stream supply headers in the gang valve corridors is monitored at Building 281-4H and pumped to the cooling tower if free of contamination. Segregated cooling water (Figure 4.6) which has been through dual-purpose coils (heating and cooling) in canyon vessels is monitored at Building 281-6H and discarded to the river if free of contamination. In the event of leaks in dual-purpose coils, water in the segregated system is especially prone to contamination by suck-back of process solution when steam in the coil is followed by cooling water; to minimize this possibility of contamination, all dual-purpose coils are equipped with an air-pressurization system which maintains a minimum coil pressure of 8 psig at all times. The value of this system has been borne out

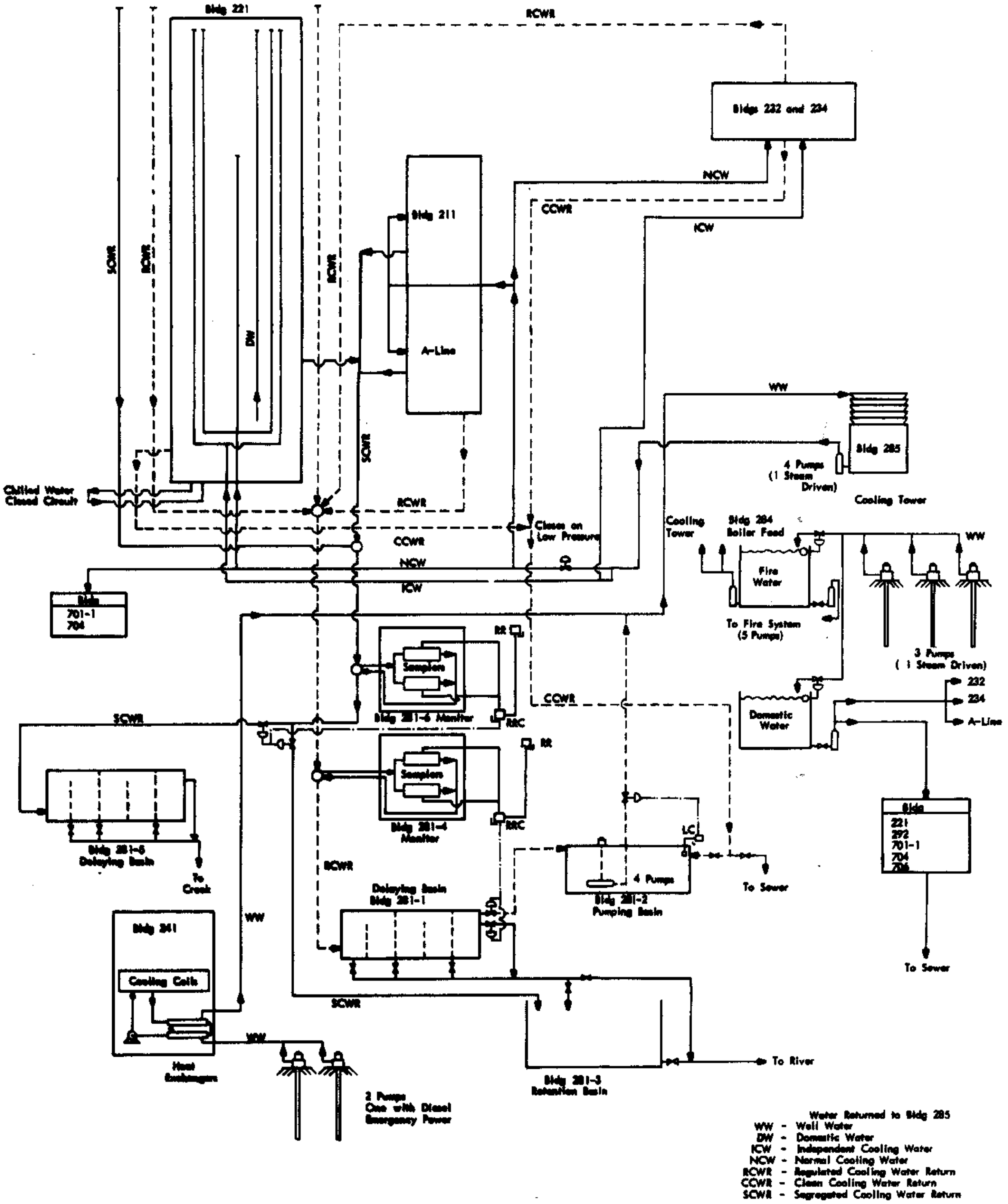
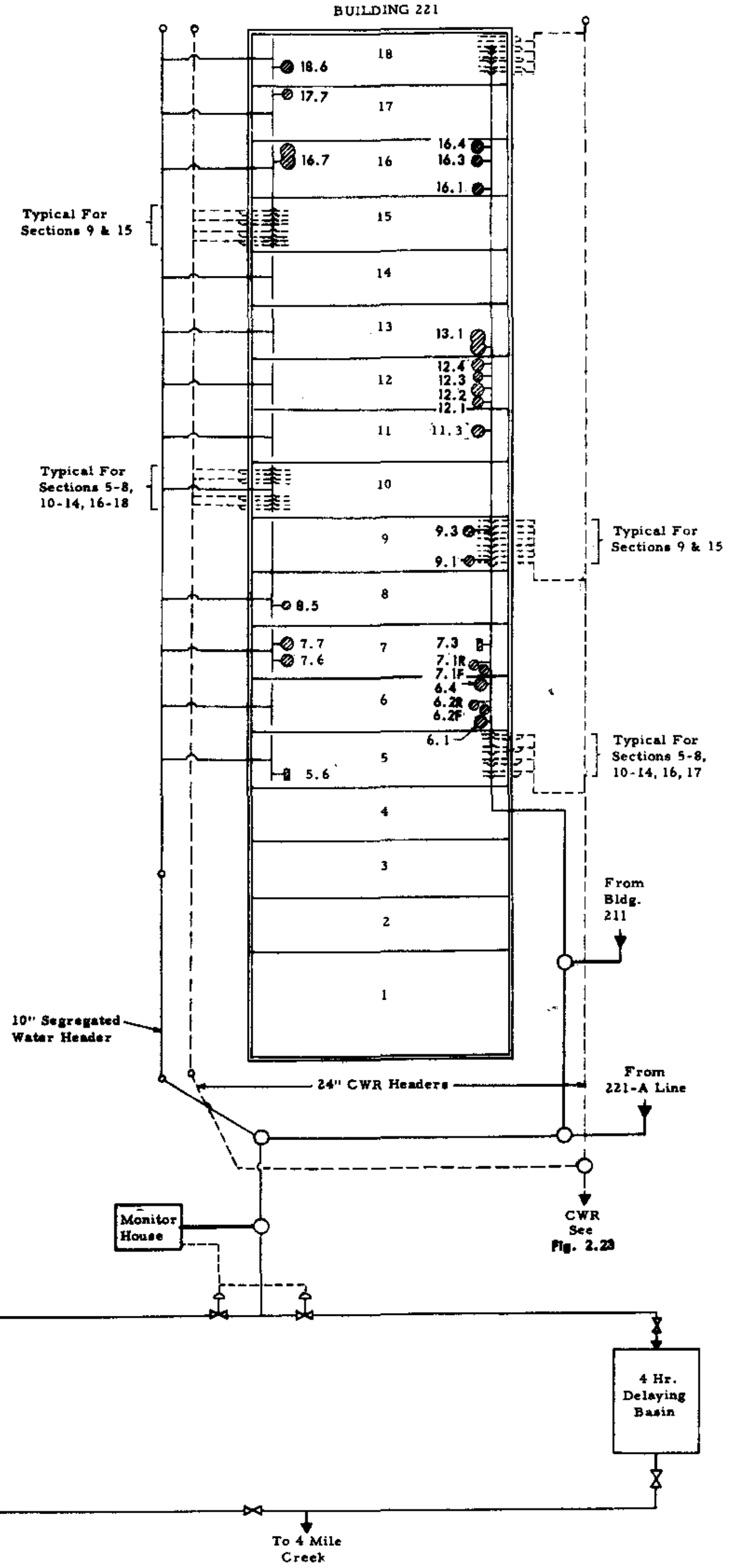


FIGURE 4.5 200-Area Water Utilities

Equipment Connected to Segregated Water System

No.	Name
5.6	L. A. Process Vent Dehumidifier
6.1	Dissolver
6.2F	Filter
6.2R	Reactor
6.4	Dissolver
7.1F	Filter
7.1R	Reactor
7.3	H. A. Process Vent Dehumidifier
7.6	L. A. Waste Batch Evaporator
7.7	L. A. Waste Batch Evaporator
8.5	L. A. Waste Continuous Evaporator Reboiler
9.1	H. A. Condensate Continuous Evaporator Reboiler
9.3	H. A. Waste Continuous Evaporator Reboiler
11.3	Head End Batch Evaporator
12.1	Cake Slurry Hold Tank
12.2	Head End Strike Tank
12.3	Head End Filter
12.4	1AF Solution Adjustment Tank
13.1	1AF Feed Tank
16.1	Rerun Batch Evaporator
16.3	Rerun Hold Tank
16.4	H. A. Rerun Run Tank
16.7	1DF Feed Tank
17.7	1CU Continuous Evaporator Reboiler
18.6	Lab Waste Batch Evaporator
	Hydrate Evaporators (A-Line)



LEGEND

Segregated Water Return

Regulated Cooling Water System

FIGURE 4.6 Segregated Water Return, Buildings 221 and 211 by the large number of evaporator coil failures which resulted in only one case of segregated cooling water contamination and was coincident with malfunctioning of the pressurization system. If either alpha or beta-gamma contamination is detected in the regulated or segregated water streams, it is diverted to Building 281-3H retention basin (capacity 964,000 gallons) until the presence of contamination is confirmed or the source of the trouble is located.

Provision for Electrical Power Failure

In case of electrical power failure, cooling water to the normal system is automatically shut off. In this event, the independent-cooling water system is supplied by a steam-driven pump. Water for the fire protection system is supplied by five 2,000-gpm pumps; three of these are steam driven and are, therefore, independent of electrical failure.

One of the two wells that supplies cooling water to Building 241-H is protected by a Class I (blast resistant) structure. A diesel engine can be coupled directly to the protected well pump, so that cooling water supply to the waste tanks is independent of both electrical and steam failure.

4.3 PROCESS EQUIPMENT

The operation of process equipment for the various steps of enriched uranium processing is described in the chapters dealing with the process, Chapters 5 through 11. In this chapter, additional information is given on specific equipment used in enriched uranium processing, specifically jets and pumps, in-canyon monitoring equipment, and the use of nuclear blanks.

4.3.1 Jets and Pumps

Transfers of solution in the canyon are made by steam jets or centrifugal pumps. The use of pumps for transfers is necessary in several cases: where dilution of the solution by steam is unacceptable, where heating the solution is undesirable, or where a wide range of flow rates is required. The pumps used are of centrifugal, single-stage, submerged type with the shaft common to both pump and motor. The motor and bearings are located on the top of the tank; no packing or bearings are exposed to process solution. A typical pump of this type is shown in Figure 4.7. Spent solvent flow to the 1CW washers and from the 1CW and 1EW washers is controlled at a constant rate by means of a fixed orifice

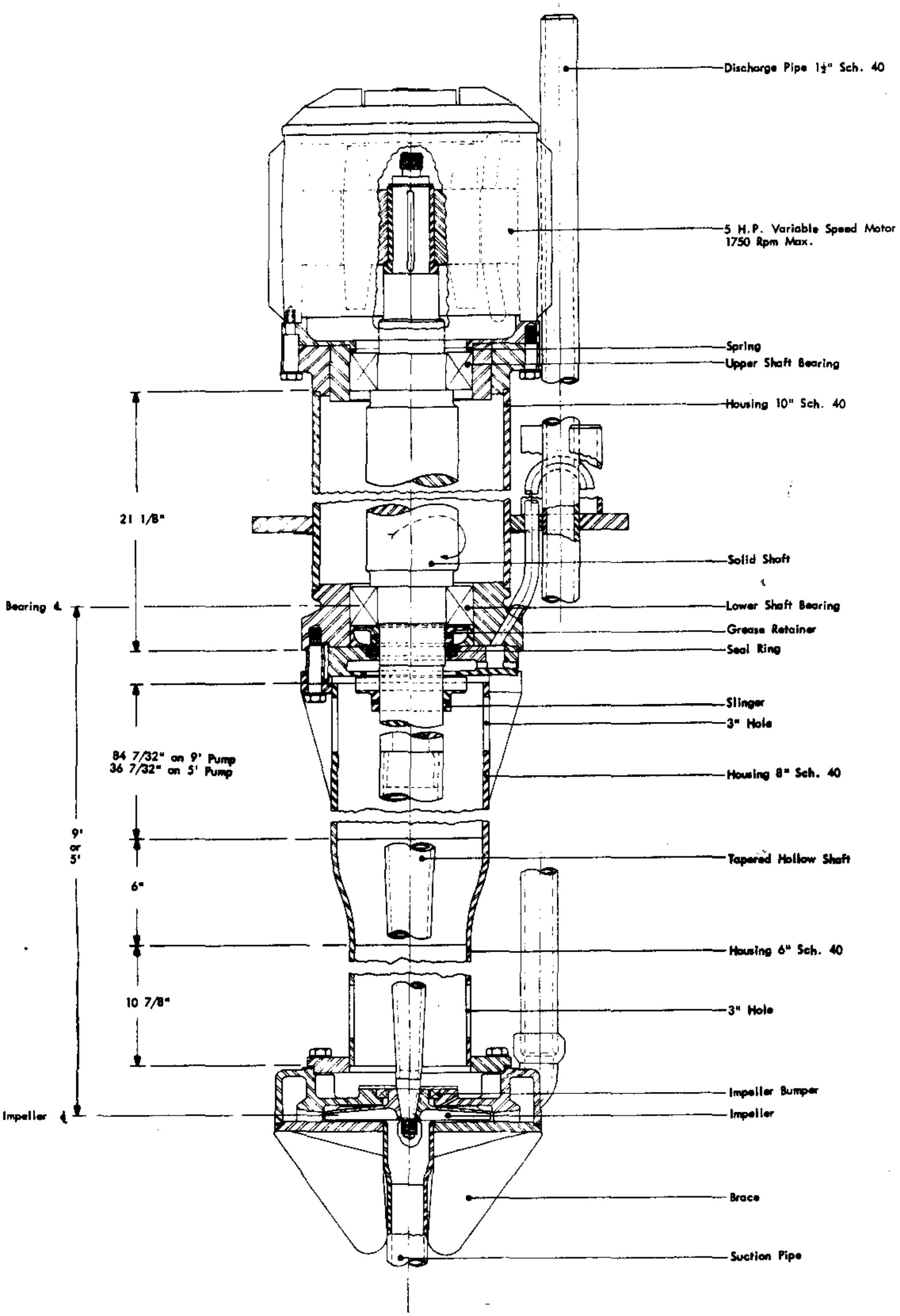


FIGURE 4.7 Canyon Pump

in the discharge of a constant speed pump. Process solution can be fed to the 1D mixer-settler by pump or by jet. Feed rate to the 1D bank is regulated by a control valve in the discharge of a constant speed pump. The control valve takes its signal from a flow measuring device (rotameter or Hackman Hat) in the pump discharge line.

4.3.2 Monitoring Instruments

A number of monitoring instruments are used on the process equipment to assure that the concentrations of solute do not exceed permissible limits; these include instruments for measuring nitric acid concentration, uranium concentration, boron concentration, and the neutron emission from fissile material. A brief description of each follows.

Nitric Acid Monitor

The concentration of nitric acid is measured by electrodeless conductivity cells that monitor the 1DS, 1CU, and 1EU streams. The introduction of more concentrated acid into these dilute acid streams (which could lead to excessive uranium inventory in the bank concerned) is readily detected by the conductivity of the solution.

Uranium Colorimeter

The uranium concentration of the 1CU and 1EU streams is continuously monitored by a dual-beam colorimeter. This instrument was designed to measure uranium concentrations up to 10^{-} g/ℓ in the normal range of operation. Higher concentrations up to 10 g/ℓ in the upper range with reduced resolution. The higher concentration range is required for processing low-enriched uranium from off-site.

Neutron Monitor

Neutron monitors are installed in the 1A, 1B, 1C, 1D, and 1E banks to detect the neutrons emitted from uranium (and plutonium) as a qualitative measure of the concentration of fissile material. Neutron emission is induced by a small neutron source that is part of the monitor system. The monitors are installed at Stage 12 in the 1C and 1E banks and at Stage 2 in the other banks. At normal uranium concentrations, the neutron emission is low, and the detectors are near background; process upsets causing significant increases in uranium concentration in the banks produce a readily perceived increase in the signal.

The monitors detect neutrons through the pulses they produce in a BF_3 counter tube. The tube is connected to an integrating circuit that provides a continuing indication of count rate. The circuit allows the use of fast (15 sec) or slow (330 sec) time constants in averaging; the slow constant is normally used in plant operation.

Boron Concentration Monitor

As described in Chapter V, boric acid is used as a secondary nuclear safety control in the electrolytic dissolution of off-site uranium oxide fuels. A boron detector is used to monitor the head tank from which nitric acid is added to the dissolver, in order to assure that the boric acid is actually present in the dissolver at all times.

The boron monitor consists of a 2-Ci Pu-Be neutron source and a BF_3 neutron detector. These are placed within the 6A head tank about 5 inches from one another. The neutrons emitted from the source are absorbed by the boron in the solution, and the detector signal is thereby attenuated. For boron concentrations in the range of interest (2 to 3 g/ℓ) the accuracy of the detector is ±0.2 g/ℓ.

Interaction of the boron monitor with process equipment is shown in Figure 4.8. If the boron concentration in the tank is below a certain concentration, the solenoid valve will not permit the solution to be added to the dissolver, nor can current be fed to the electrodes of the dissolver.

4.3.3 Nuclear Blanks

Nuclear blanks are installed in process and service piping where the inadvertent addition of the wrong reagent might cause the concentration of enriched ^{235}U with the potential for an accidental nuclear criticality (see Chapter III). Examples of the unsafe conditions that might result from inadvertent addition of materials include:

- Precipitation of uranium,
- Dilation of salting agent for extraction, with consequent uranium reflux in the aqueous phase, and
- Addition of salting agent to stripping streams in solvent extraction, causing reflux in the organic phase.

These blanks are closures bolted to the flange of the piping, and held in place by loops of rod that encircle the pipe; the loops are welded in place and must be cut to remove the blank. Removal of a blank is governed by procedures that require special approval from supervision. An illustration of the nuclear blank is shown in Figure 4.9.

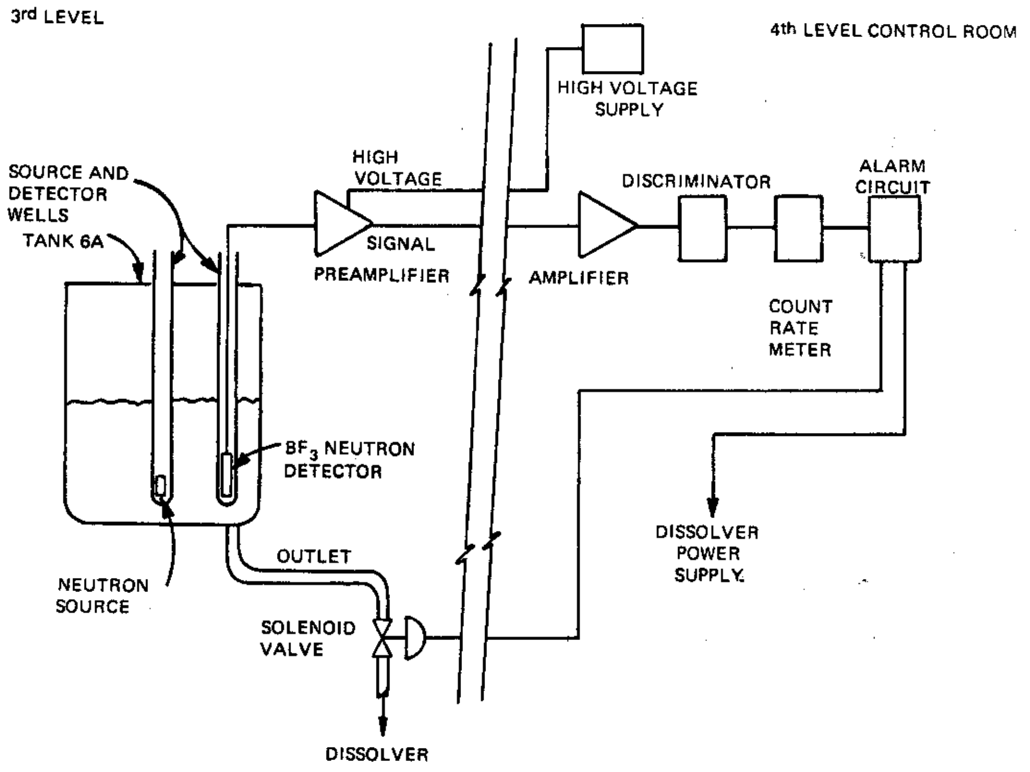


FIGURE 4.8 Interaction of Boron Monitor with Process Equipment

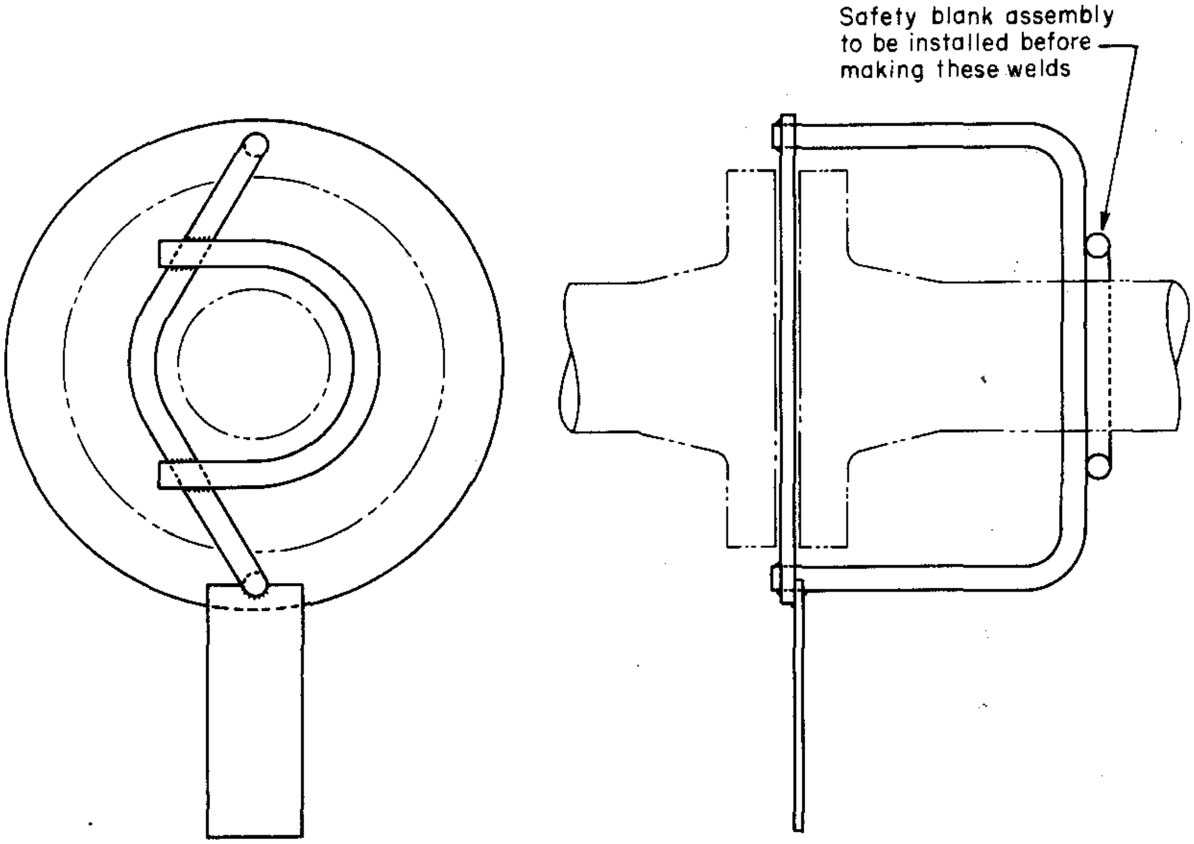


FIGURE 4.9 Nuclear Blank, Shown Installed at a Pipe Joint

5. DISSOLUTION

5.1 GENERAL

Irradiated or unirradiated enriched uranium fuel elements or uranium scrap are dissolved in nitric acid to provide an aqueous solution suitable for processing to decontaminate and recover the enriched uranium, neptunium, and plutonium. Two types of dissolvers are used: a chemical dissolver is used for Al-clad SRP or off-site fuels; and an electrolytic dissolver is used for off-site fuels in resistant cladding (stainless steel, zircaloy, etc.). Chemical dissolution involves dissolving the entire fuel element in nitric acid with mercuric nitrate added as a catalyst to promote the dissolution of the aluminum. In electrolytic dissolution, the fuel is held submerged between two electrodes which create a potential gradient within the solution. This potential creates potential differences between the fuel and solution that suffice to dissolve the resistant cladding metals electrolytically and expose the core metal or oxides to chemical attack. The two types of dissolution are treated individually in Sections 5.2 and 5.3. Both types of dissolution produce a nitric acid solution containing cladding, actinides, and fission products, and an off-gas containing nitrogen oxides, gaseous fission products, and traces of hydrogen. Volatilized iodine is adsorbed on silver nitrate to minimize release of this fission product to the atmosphere. Nuclear safety is ensured by a combination of equipment design, batch size, and operating procedures that are based on thorough and conservative nuclear safety analyses. A flow diagram for chemical dissolution of U-Al fuel is shown in Figure 5.1; the equipment services and instrumentation are listed in Table 5.1. A typical dissolution material balance is presented in Table 5.2.

TABLE 5.1

Equipment Services and Instrumentation for Dissolution Treatment

VESSEL IDENTIFICATION						INSTRUMENTATION									SERVICES							
NO.	FUNCTION	EP No.	PROCESS PIPING DIAGRAM	INSTRUMENT DIAGRAM	ELECTRICAL DIAGRAM	Liquid Level	Sp. Gr.	Temperature	Pressure	Differential Pressure	Radiation	Sparge Flow	Cooling Water Flow	Foam Level	Sampler	Agitator	Microphone	Coil(s)	Recirculating Jet	Other Jets (Number)	Sparge	Other
6.1D 6.4D	Dissolvers	361.1-1 361.1-2	W163293	W145599 149907	W147419	R,I	RI	R	R L, H***	-	R	SI AI	-	R,H	X	-	X	S_m W_i A	-	C(2)	S_m V	A
	Column Condensers					-	-	Water RC Gas R,H	-	R,H	-	-	R	-	-	-	-	W_i	-	-	-	-
6.2R 7.1R	Iodine Reactors	341.86-2 341.86-2	163293	145603 145631	147419 147420	-	-	R,L	-	-	R	-	-	-	-	-	-	S_h	-	-	-	-
6.2F 7.1F	Off-Gas Filters	353.52-1 353.52-2	163293	145602 146155	147419 147420	-	-	R,L	I*	-	R,** H	-	-	-	-	-	-	S_g	-	-	-	-
8.3	Raw Metal Solution Hold Tank	371.79	W163293	146208	147420	R,I L,H	R,I	R	-	-	R	-	-	-	X	X	X	W	X	C(2)	-	-

SYMBOLS:

I	- Indicator	S_m	- Steam, medium pressure	W	- Cooling Water
R	- Recorder	S_h	- Steam, high pressure	W_i	- Independent Cooling Water
C	- Controller	H	- High Alarm	V	- Vent
S	- Steam, low pressure	L	- Low Alarm	X	- Present
		A	- Air		

* Both inlet and outlet pressure

** Off-gas line.

*** High pressure interlocked to stack jet.

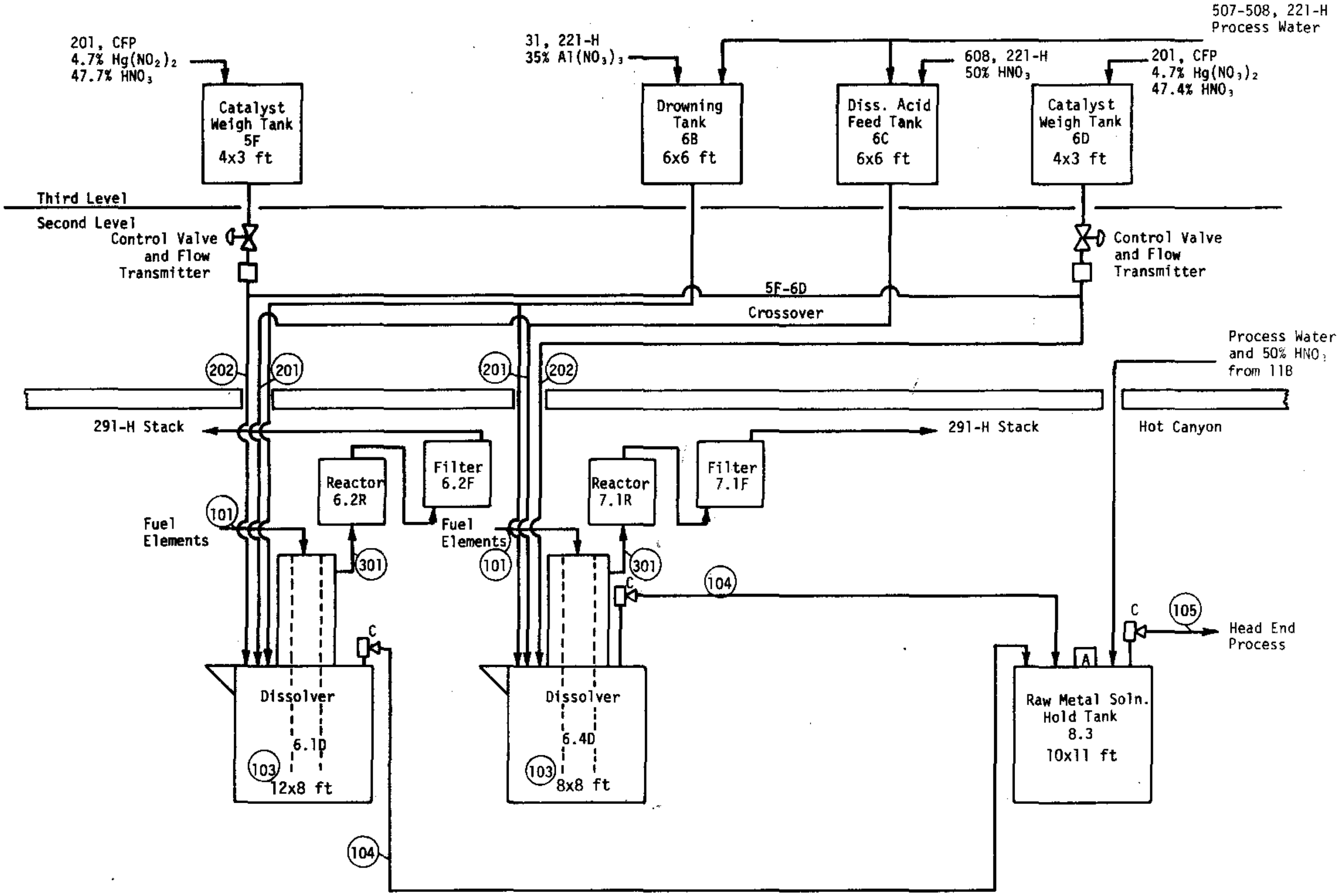


FIGURE 5.1 Dissolving Process Flowsheet

TABLE 5.2

Dissolution Material Balance

Stream Number	Stream Description	Process Material													
		lbs. Al	lbs. SiO_2	lbs. $Al(NO_3)_3$	% $Al(NO_3)_3$	lbs. $UO_2(NO_3)_2$	lbs. $Hg(NO_3)_2$	lbs. HNO_3	lbs. NO	lbs. N_2O	lbs. H_2	lbs. H_2O	lbs. Total	Sp. Gr.	Solution Volume Gallons
101	Fuel Elements and Bundles	1000	3	-	-	-	-	-	-	-	-	-	1094	-	-
103	Dissover Solution	-	3	7898	25.46	146	24	779	-	-	-	22172	31025	1.255	2962
104	Raw Metal Solution	-	3	7898	25.06	146	24	779	-	-	-	22664	31517	1.250	3021
105	Head End Feed Solution	-	3	7898	24.66	146	24	779	-	-	-	23173	32026	1.245	3082
201	Nitric Acid Solution	-	-	-	-	-	-	9200	-	-	-	18918	28118	1.194	2822
202	Catalyst Solution	-	-	-	-	-	24	1008	-	-	-	2216	3248	1.194	326
301	Dissolver Off-Gas	-	-	-	-	-	-	-	645	245	3	-	893	-	-

* Includes dilution of 2 volume % for transfer jets or 3 volume % for rate jets with each transfer.

5.2 CHEMICAL DISSOLVERS

5.2.1 Elements

Aluminum-clad fuels from both SRP reactors and off-site sources are dissolved in the chemical dissolvers. Regardless of their source, the elements are processed similarly, but with different charge sizes and reagent concentrations depending on their size and their chemical and isotopic composition. Typical SRP fuel elements include:

> *Mark VI.* A single fuel tube 14 ft long and 3.0 in. OD with an enriched uranium-aluminum alloy core clad in Type 1100 aluminum.
>
> *Mark 16.* Three concentric fuel tubes 14 ft long with cores of enriched U-Al alloy. The tubes are clad with Type 8001 aluminum. This assembly has an OD of 3.70 in.
>
> *Mark 22.* Two concentric fuel tubes 163 in. long with cores of enriched U-Al alloy. The tubes are clad with Type 8001 aluminum. The assembly has an OD of 3.2 in.

Off-site reactor fuels processed at SRP vary widely in shape, dimension, and composition. The following are representative types of off-site fuels that are dissolved chemically at SRP:

Source	Cladding	Core
Research and Test Reactors	Al	U-Al Alloy
High Flux Isotopes Reactor	Al	U_3O_8-Al Cermet
Power Reactors (Piqua)	Al	U-Mo-Al Alloy

Many of the fuels with U-Al alloy cores are of the same design as the Materials Testing Reactor (MTR) fuel. A typical MTR type assembly is approximately 48 x 3 x 3 in. with an active core containing about 200 g ^{235}U in up to 19 curved plates about 2 ft. long. Core alloy compositions vary around 19% U-81% Al; cladding is Type 1100 aluminum.[1]

A High Flux Isotopes Reactor (HFIR) fuel assembly consists of two concentric annular fuel elements. Each inner and outer element is a ring of thin, Al-clad, curved plates containing fully enriched uranium as U_3O_8-Al cermet; these plates are held in place by aluminum shrouds. An unirradiated HFIR assembly contains about 10 kg U and 129 kg Al and is about 17" OD x 31" long.[2]

5.2.2 Charging the Chemical Dissolvers

Irradiated fuel elements are normally cooled several months before reprocessing begins. The purpose of this cooling period is to allow the fission products to decay, so that the solution fed to the solvent extraction system (1AF) contains beta-gamma activity of less than 3×10^{11} dis/(min-ml). SRP experience indicates that extended processing at higher fission product levels degrades the organic extractant too rapidly.

Irradiated fuel elements are shipped in casks on railroad cars to the 221-H facility for processing. SRP elements are in open framework, aluminum bundles* that hold the elements in a line; the number of elements in a bundle varies with different fuels. The bundle design for Mark VI fuel is illustrated in Figure 5.2; bundles for Mark VI, Mark 16, and Mark 22 fuels are similar. Off-site fuels are bundled as their special shape and dimensions require. For instance some MTR fuels use a "square tube" bundle, a 3.5x3.5x175.5-in. aluminum can that holds about 6 stacked, cropped fuel assemblies. Occasionally, it is necessary to package assemblies in special bundles that contain the same number or fewer assemblies that a standard bundle; in such a case, the handling and processing rules for a standard bundle apply. HFIR assemblies are not bundled; they are disassembled into an inner element and an outer element that are charged to the dissolver on special aluminum carriers.

Bundled elements may be stored vertically in the water-filled storage cell in Building 221-H, if a safety analysis of such storage has been made, or may be charged directly from the railroad shipping cask to the dissolver. Each bundle is identified by a number to show the type of fuel element because the fuel exterior appearance often does not permit identification.

Normally fuel shipments to the canyon include only one fuel type. For operating efficiency, however, it is sometimes necessary to ship different fuels together in a cask. In all cases, strict procedural control is imposed to ensure that the cask is loaded properly at the point of origin; and in the case of mixed fuel shipments, all fuels in the cask are unloaded, stored, and charged according to rules and conditions that ensure nuclear safety at all times for the most reactive fuel in the shipment.

Elements are charged vertically into an insert in the dissolver. Four different inserts may be available. The

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* The term bundle applies to both the aluminum framework and a framework containing fuel.

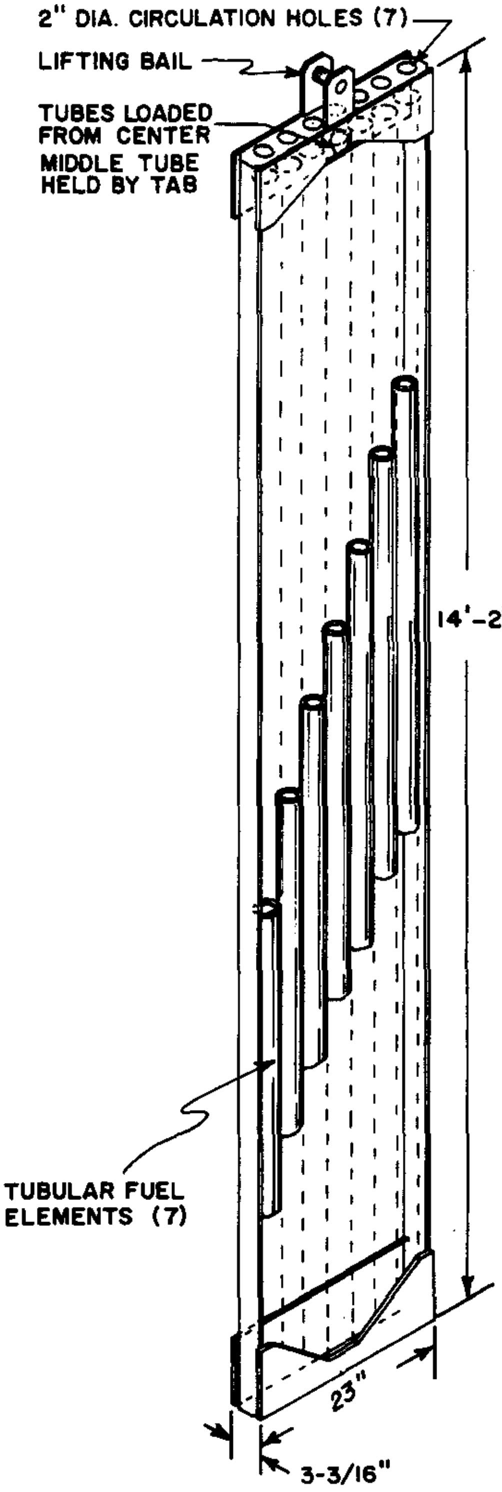


FIGURE 5.2 Mark VI Fuel Elements in a Mark VI Bundle

Mark VI and XII inserts (Figure 5.3) can accommodate four bundles of elements; the bundles and fuel elements are confined in two, rectangular, parallel slots that have space for two bundles each. The slots are slightly thicker than a bundle and slightly wider than two bundles. A partition in the middle of each slot divides the slot into two bundle compartments or quadrants. The slots are perforated on the bottom and sides to a height of 5 ft to allow solution to flow around the tubes; additional perforations are provided near the top of the insert to discharge foam and off-gas. The slots in the Mark VI insert are slightly narrower than those of the Mark XII insert.[3]

The Ten-Well insert can accommodate one fuel assembly or column of fuel in each of ten spaced, parallel, cylindrical wells.[4] The wells are in a rectangular 2 x 5 array and are perforated to allow free flow of dissolvent (Figure 5.4).

The HFIR insert (Figure 5.5) can accommodate one HFIR core or assembly, consisting of an inner element and an outer element, in two parallel cylindrical wells. HFIR fuel must be dissolved in the HFIR insert only.

Nuclear safety considerations often limit the number of bundles of fuel that can be charged to the available space in an insert. When all four quadrants of the Mark VI or XII insert or all ten wells of the Ten-Well insert cannot be used for nuclear safety reasons, all unused quadrants or wells must be blocked by plugs to prevent overcharging. The insert probe, described below, may be used to block a quadrant or a well.

Off-site fuel bundles are usually small enough that several bundles can be charged to one insert quadrant. In such cases, strict procedural control ensures that the safe number of bundles per quadrant is not exceeded.

The quantity of fuel that may be charged to the chemical dissolvers varies depending on the type of fuel, the insert, and which of the two differently sized dissolvers is to be used. For example:

> *Mark VI.* Four bundles (28 tubes) may be charged to either dissolver, one bundle per quadrant of the Mark VI insert.
>
> *Mark 16 or 22.* Three bundles (12 assemblies) may be charged to the larger dissolver. Only one bundle (4 assemblies) may be charged to the smaller dissolver, Mark 16 assemblies will not fit into the Mark VI insert; the Mark XII insert must be used. Either insert may be used for Mark 22 dissolution.

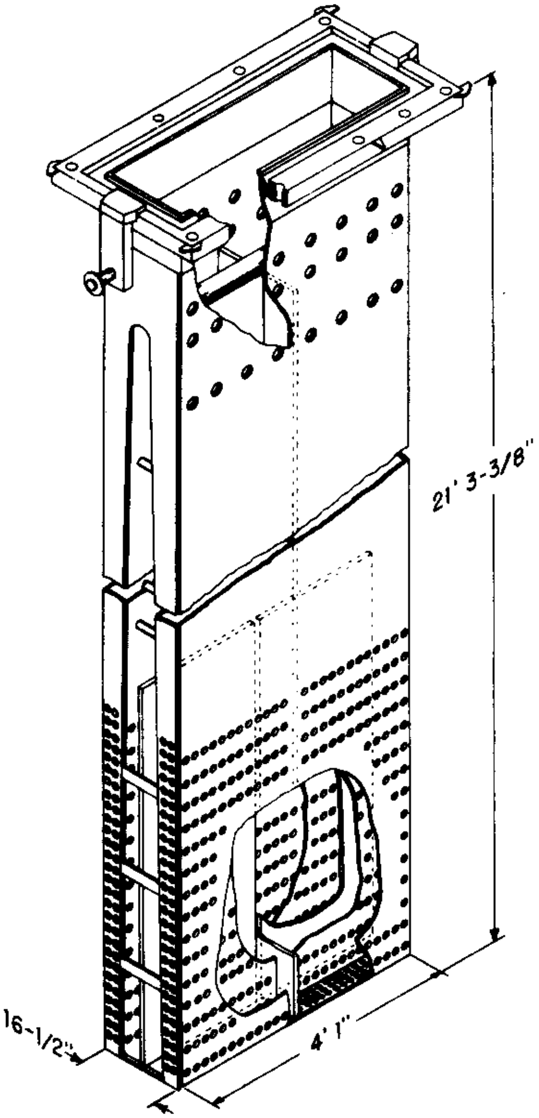


FIGURE 5.3. Mark VI Dissolver Insert

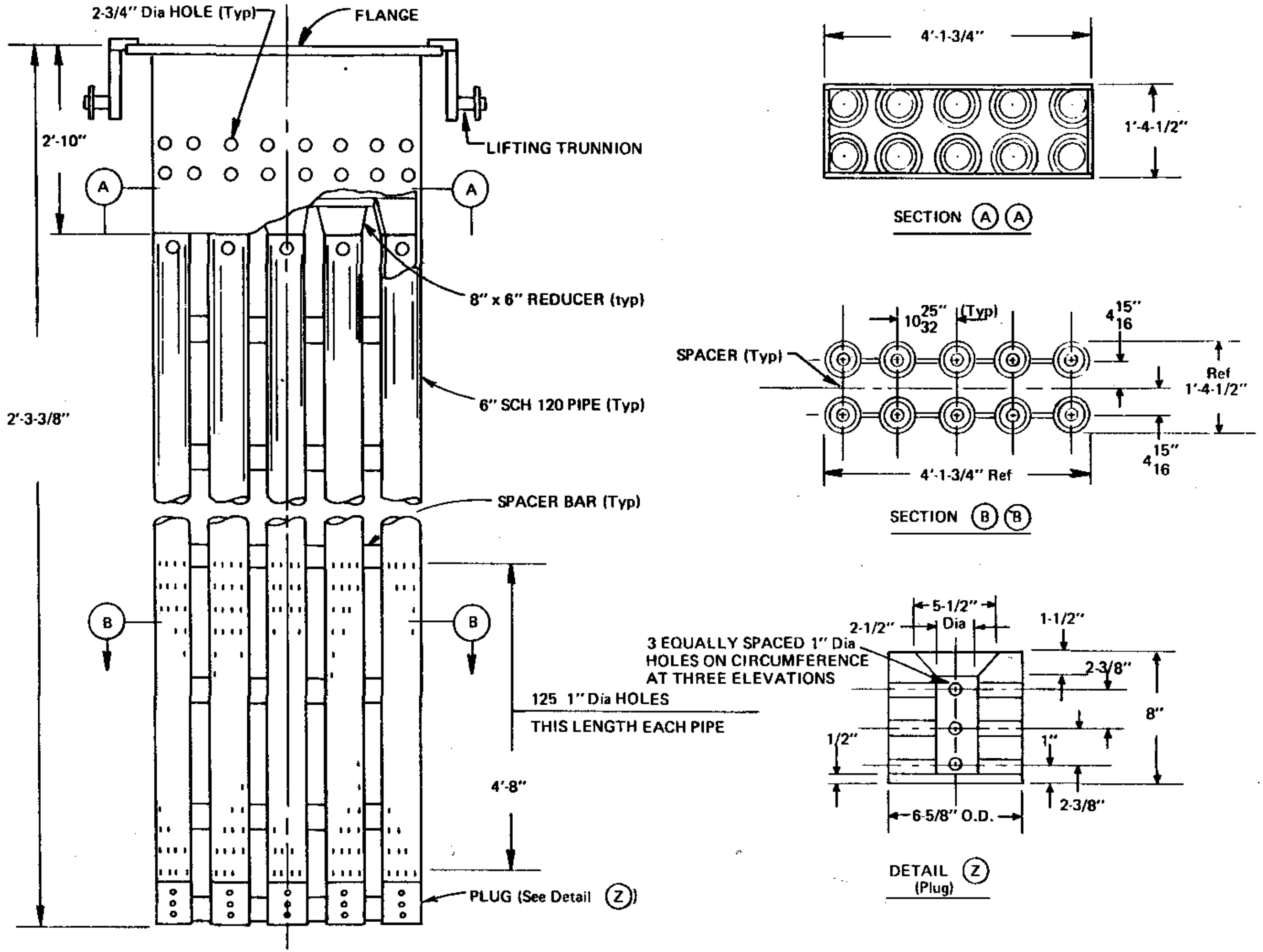


FIGURE 5.4 Ten-Well Column Insert

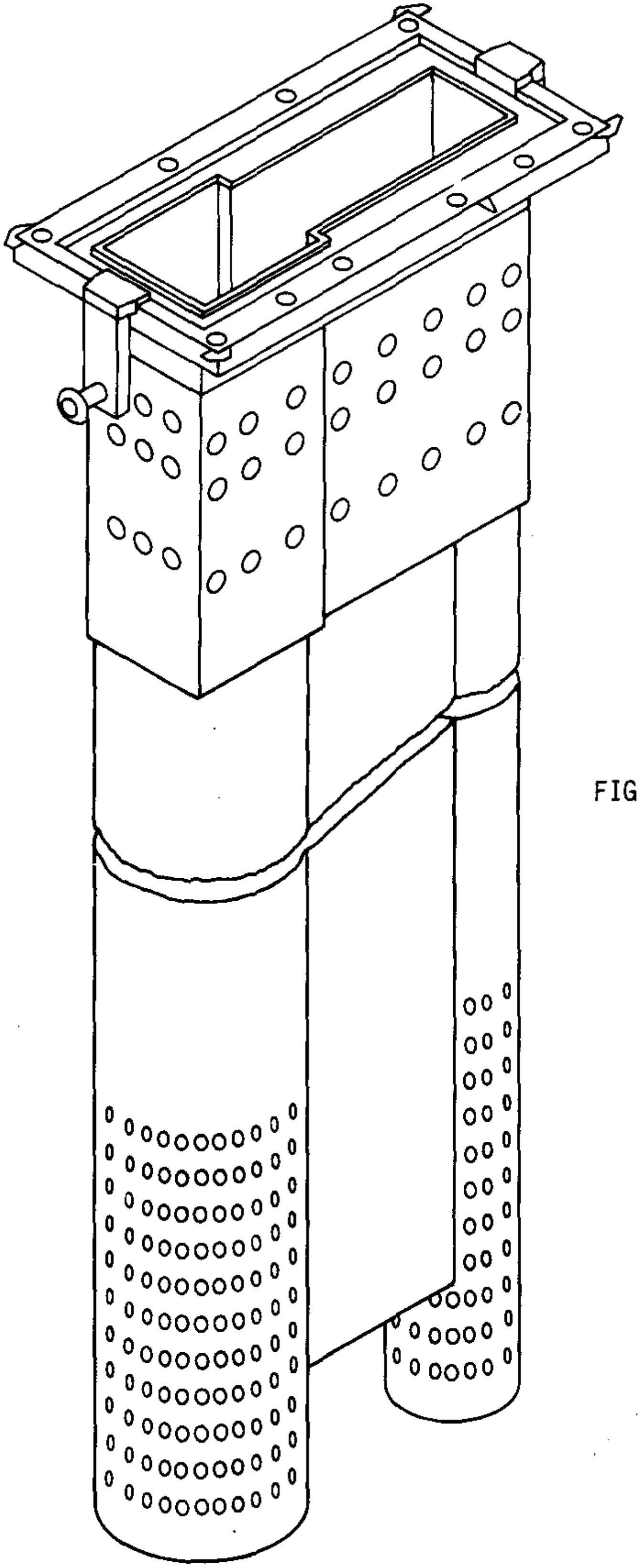


FIGURE 5.5 HFIR Insert

MTR Type. The number of bundles varies inversely with ^{235}U content of the fuel. Four to twelve bundles may be charged to either dissolver, one to three bundles per quadrant of the Mark VI insert. Up to ten square-tube bundles at a time may be charged to the Ten-Well insert, one bundle per well.

HFIR. One inner element an one outer element may be charged to either dissolver, one element per well of the HFIR insert.

The Ten-Well insert may be used to dissolve any fuel that will fit into the 5.5 in. ID wells, so long as the fuel package is long enough to make immediately obvious any attempt to charge more than the safe number of bundles of that fuel.[4]

The maximum number of elements allowable in any dissolver charge in any insert is determined by the largest whole number of elements that contain less than 50.6 kg ^{235}U (larger dissolver) or 25.3 kg ^{235}U (smaller dissolver). These ^{235}U limits in turn are based on the maximum safe concentration[5] of 11.5 g $^{235}U/\ell$ and the minimum volumes (for accidental evaporation) of 4400 and 2200 ℓ, respectively.

Before charging, it is verified that no excessive quantity of metal remains in the insert from previous runs and that the solution has been removed from the dissolver. The absence of excess metal heel ensures that the fresh charge can be inserted without mechanical difficulty and without exceeding the permissible ^{235}U loading. Usually, fresh solution is added to the dissolver before charging to prevent charged fuel from overheating itself. After fuel is charged to the dissolver, the column lid is replaced to seal the dissolver. A small partial vacuum is then established in the dissolver to ensure that the lid has been replaced properly and to minimize the release of gases into the canyon during dissolution.

5.2.3 Element Dissolution in the Chemical Dissolvers

Fuel elements and aluminum bundles are dissolved in a solution of nitric acid and mercuric nitrate. The quantity and concentration of these reagents vary with the size of the fuel charge and the dissolver. Sufficient nitric acid is normally used so that the final solution requires minimum adjustment to meet requirements for feed (1AF) to the first solvent extraction cycle. The minimum concentration in 1AF containing at least 1M Al is 0.5M HNO_3. Adequate dissolving rates are usually attained with initial HNO_3 concentrations in the range of 4 to 8M. A final concentration of at least 0.3M HNO_3 is required in the dissolver to prevent precipitation of aluminum, uranium, or plutonium compounds. The maximum concentrations of HNO_3 and Al in the final solution depend on their mutual solubility and are a function of temperature (Figure 5.6). However, the maximum concentration of ^{235}U in the dissolver solution is limited to the value specified in the applicable nuclear safety analysis. Consequently, the maximum concentration of Al in Figure 5.6 may not be allowable for fuels with high $^{235}U/Al$ ratios.

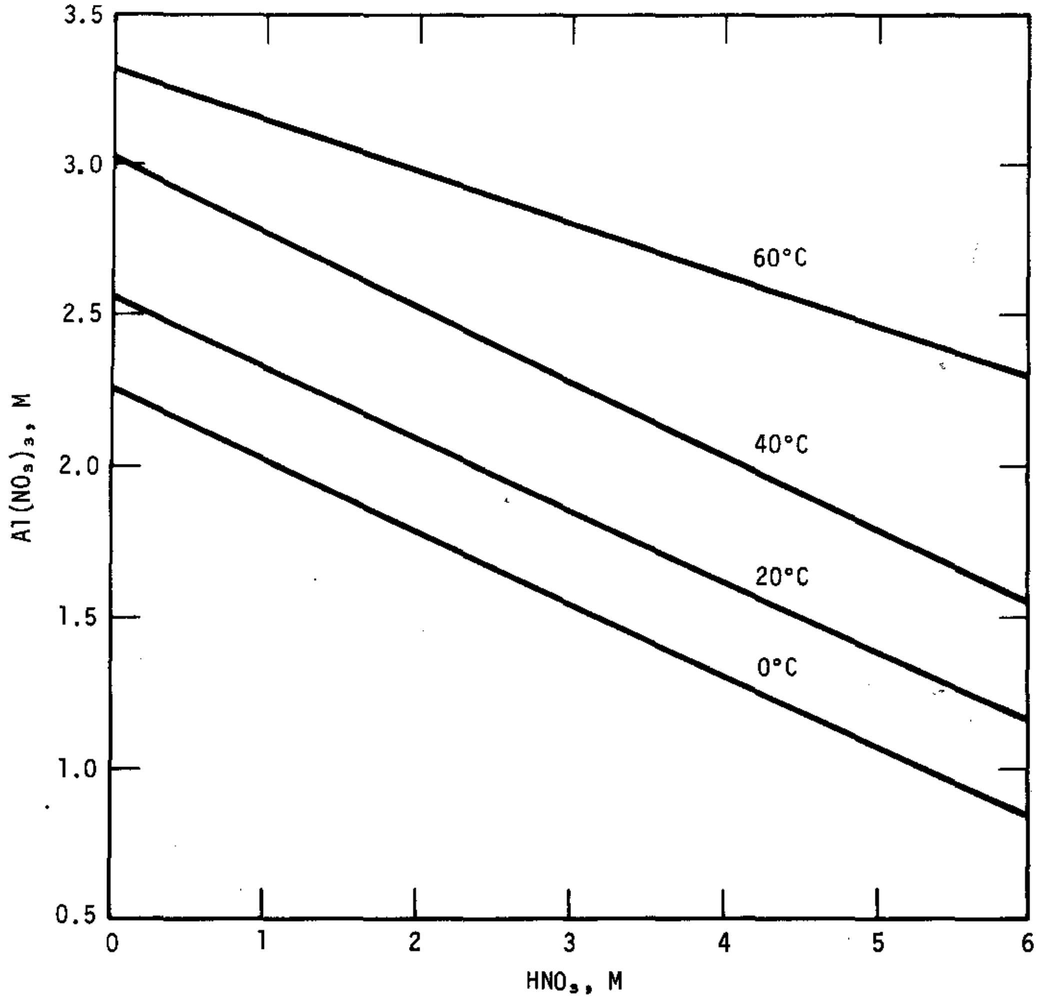


FIGURE 5.6 Solubility of $Al(NO_3)_3$ in Aqueous Solutions of HNO_3. (Region of Complete Solubility is Below and Left of the Applicable Curve.)

Mercuric nitrate acts as a catalyst in the dissolving reaction. As shown in Figure 5.7, the dissolving rate increases with increasing mercury concentration. Aluminum and U-Al alloy do not dissolve at an acceptable rate in pure nitric acid, because aluminum oxide formation produces a passive surface. In the presence of mercuric ion, aluminum forms an amalgam that is rapidly dissolved by nitric acid. The amalgam formation rate can therefore control the rate of dissolution.[6] Since amalgam formation requires the reduction of mercuric ion to metallic mercury, high concentrations of an oxidant, such as nitrate ion from either HNO_3 or $Al(NO_3)_3$, can reduce the amalgam formation rate significantly. As shown in Figure 5.7, the dissolving rate is slower at the higher $Al(NO_3)_3$ concentration. Consequently, a rapid reaction can be depressed by adding either $Al(NO_3)_3$ or HNO_3 to the dissolver solution. However, at the nearly constant nitrate concentration during a dissolution, the gradual decrease in dissolving rate (Figure 5.8) is due to the gradual decrease in HNO_3, the gradual increase in $Al(NO_3)_3$, and the accompanying decrease in the rates of HNO_3 attack on the amalgam and uranium.

The composite reactions (at HNO_3 concentrations around 4M) are approximately represented by the following equations:[6]

$$Al + 3.75\ HNO_3 \xrightarrow{Hg^{++}} Al(NO_3)_3 + 0.225\ NO + 0.15\ N_2O + 0.11\ N_2 + 1.9\ H_2O + 190\ \text{kcal/mole Al} \qquad (1)$$

$$U + 4\ HNO_3 \rightarrow UO_2(NO_3)_2 + 2NO + 2H_2O \qquad (2)$$

Nitric acid utilization depends on the efficiency of conversion of the nitrogen oxides to HNO_3 in the off-gas condenser:

$$2NO + O_2 \rightarrow 2NO_2 \qquad (3)$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad (4)$$

The dissolving rate is also dependent on temperature, the surface area of undissolved metal that is exposed to the solution (element submergence), and the irradiation history of the fuel. Increasing irradiation decreases the dissolution rate,[7] but this has caused no problem in the plant. Figure 5.9 shows the effect of irradiation on initial dissolving rate. Increasing temperature increases the dissolving rate; hence, the temperature is maintained as high as possible by boiling the dissolvent.

Dissolver operation consists of three phases: startup, dissolving, and shutdown.

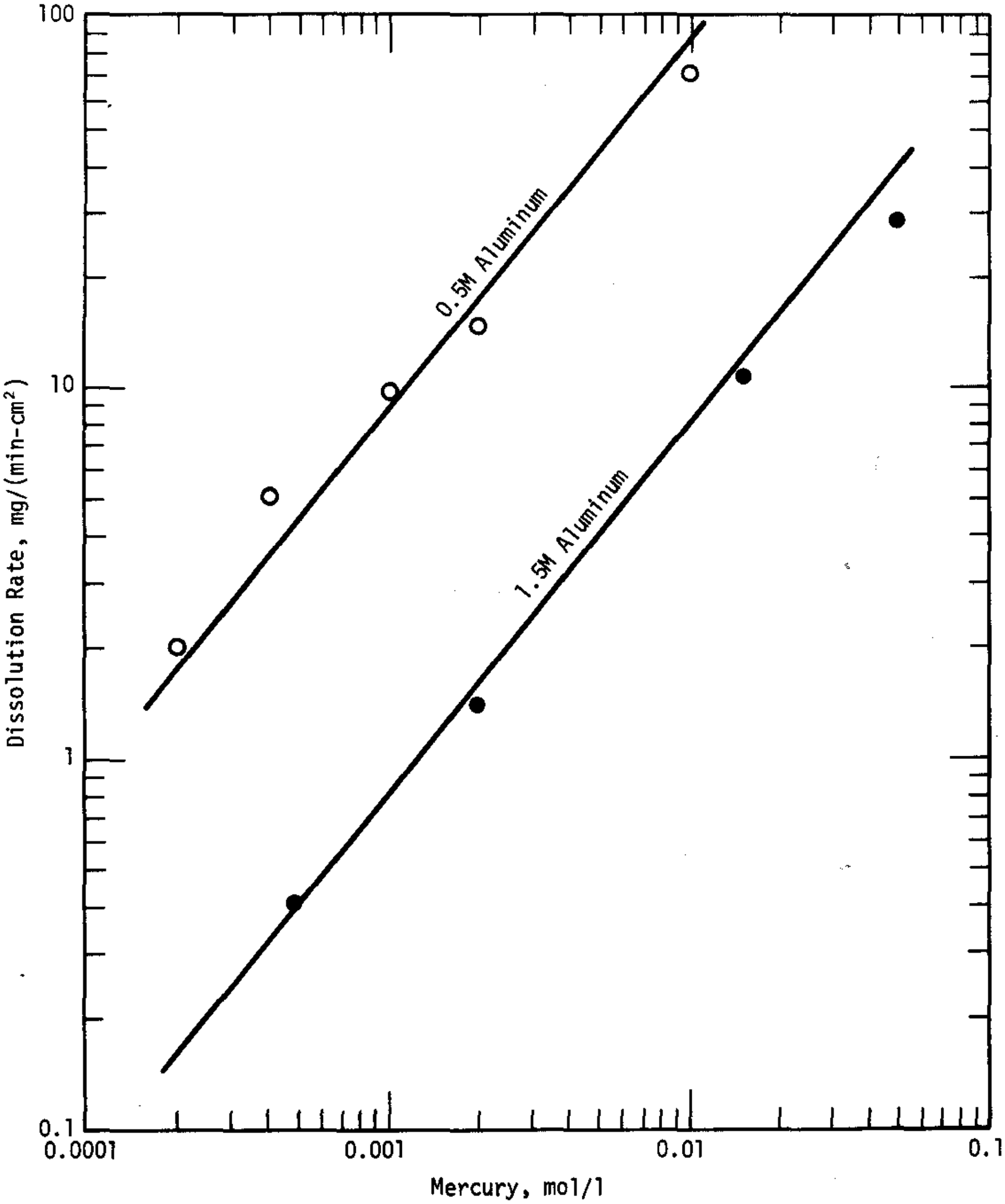


FIGURE 5.7 Effect of Catalyst Concentration on Dissolving Rates of Unirradiated Mark VI Tubes in 6M HNO_3

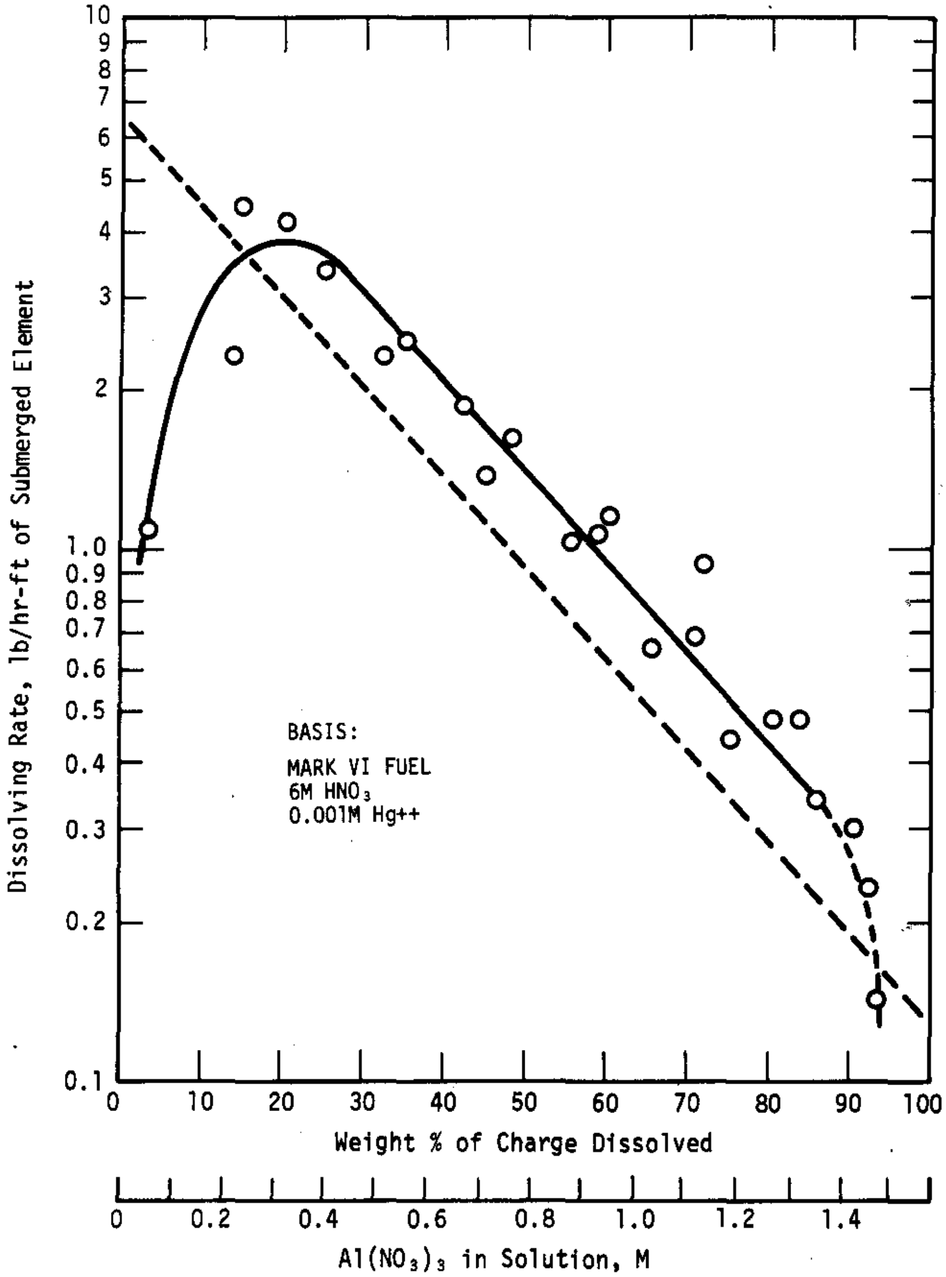


FIGURE 5.8 Typical Dissolving Rate Curve

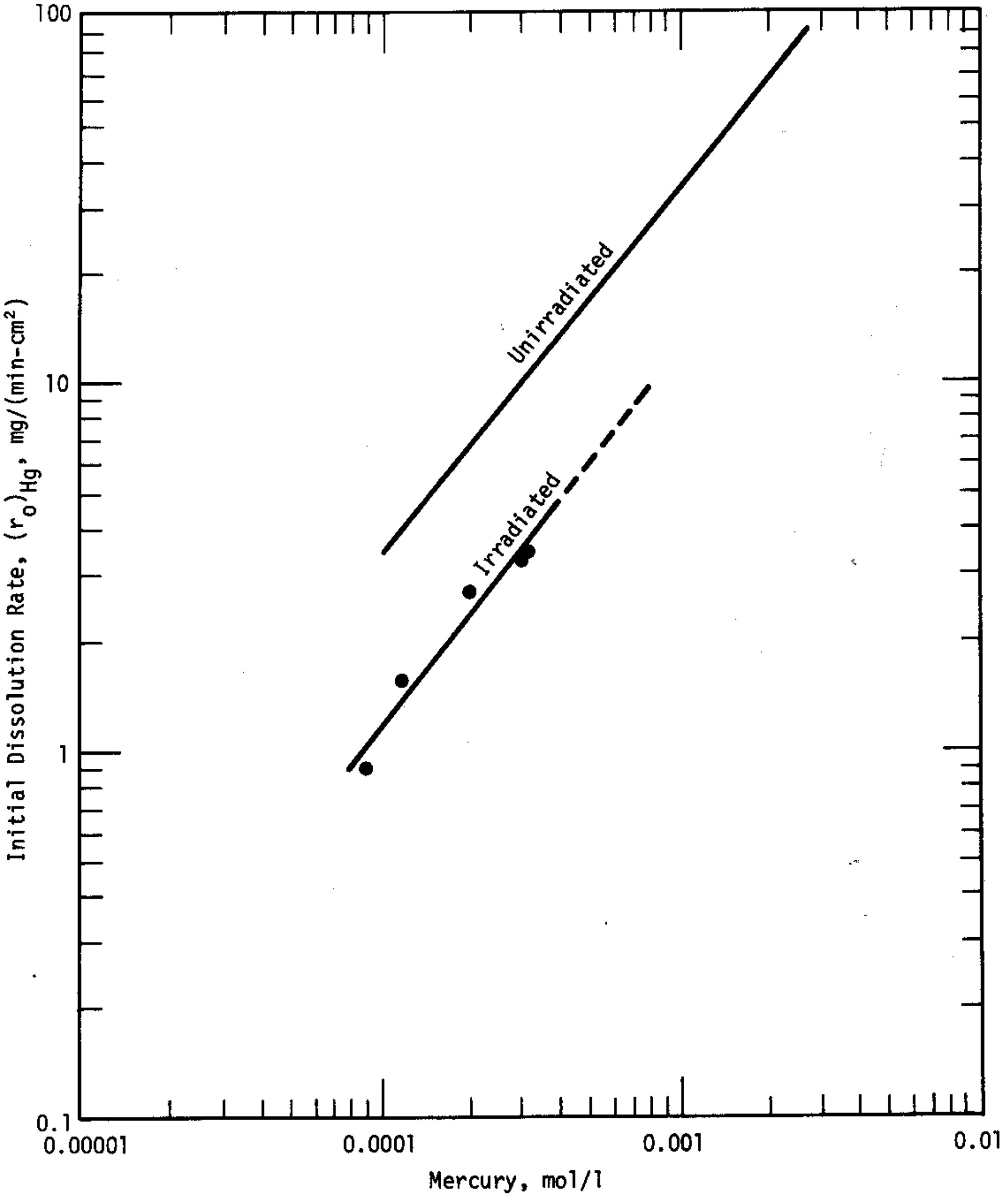


FIGURE 5.9 Effect of Irradiation on Initial Dissolving Rate of Mark VI Tube in 6M HNO_3

The HNO_3 solution is heated to boiling and, after any reaction at 80 to 105°C has subsided, a solution of mercuric nitrate and nitric acid is added at a slow rate that controls the initial dissolving rate and maintains, in conjunction with the vacuum capability of the off-gas system, the dissolver at a pressure below atmospheric. For example, to dissolve Mark 16 fuel, a 4.7 wt % $Hg(NO_3)_2$ - 47 wt % HNO_3(Sp. Gr. = 1.35) solution is usually added in several increments, each over a period of 60 to 100 minutes, to a final concentration of 0.012M Hg^{2+}. The dissolver is maintained at boiling throughout catalyst addition and for a pre-established time thereafter. Boiling times depend on the dissolver being used and the fuel. About 18 hours is usually required to dissolve a charge of Mark 16 fuel. The initial dissolution of aluminum is vigorous and is accompanied by foaming. The dissolver inserts are designed to direct the foam up and out through foam ports near the top of the inserts for return to the dissolver pot, so some dissolving occurs in the insert above the nominal solution level. As the dissolution proceeds, the nitric acid concentration decreases and the aluminum nitrate concentration of the solution increases; this tends to suppress the reaction rate and reduce foaming, as shown in Figure 5.8.

As the nitric acid attacks the submerged portion of the bundles and tubes, the submerged aluminum cladding dissolves, the exposed core dissolves, and the partially dissolved tubes slide into the dissolvent until all of the tubes are covered by nitric acid solution. Partially dissolved tubes have been inspected and appear uniformly thinned at the submerged end with little or no evidence of localized attack that might lead to early collapse or fragmentation.[8] Figure 5.10 shows an idealized dissolution model.[8]

After a predetermined boiling period, usually several shifts, the dissolved metal solution is cooled to less than 60°C, and the dissolver is probed mechanically to measure the height of the metal heel in the insert. If the metal heel does not exceed the Technical Standard limit, the solution is transferred to a hold tank for sampling; otherwise, dissolution is resumed. For example, the maximum height of residual fuel fragments from a Mark 16 dissolving is 9 inches in the Mark VI or XII inserts and from HFIR, 5 inches.

Occasionally, extra cleanout of the dissolver is required at the end of a process campaign to preserve the isotopic composition of uranium in the next campaign. In such cases, the last dissolution is extended about six hours and the dissolver is flushed with dilute acid (process water).

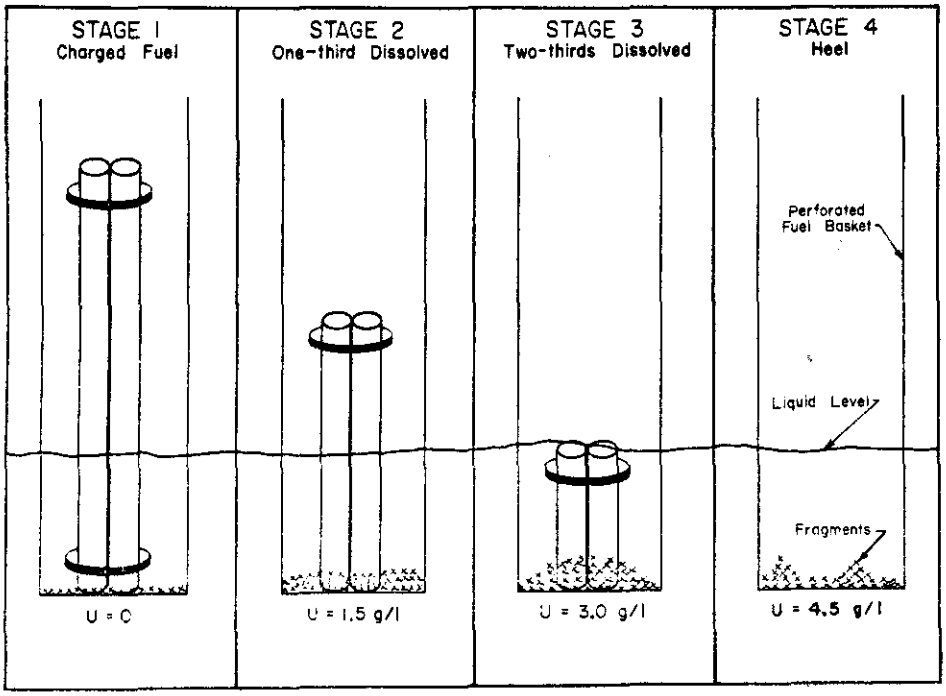


FIGURE 5.10 Idealized Dissolving Model

5.2.4 Dissolver Off-Gas

The off-gases liberated from dissolution contain NO, N_2, N_2O, and traces of H_2, plus fission product iodine, krypton, and xenon. These gases pass successively through a condenser, heated iodine reactor, and a filter before leaving the canyon. The condenser is a downdraft type through which the off-gas and condensate flow downward concurrently. Thus, the coolest condensate is in contact with the coolest gas for most efficient absorption and conversion of NO_2 to HNO_3. A condensate of weak nitric acid is returned to the dissolver pot for maximum utilization of acid during the dissolution. N_2, NO, N_2O, H_2, and rare gases are vented. The temperature of the off-gas leaving the condenser is maintained below 60°C to limit the quantity of condensable vapor leaving the dissolvers. Iodine escaping the dissolver is removed by absorption in the iodine reactor, which contains Berl saddles coated with silver nitrate. Iodine absorption would be incomplete at temperatures below 180°C and silver nitrate melts at 212°C, so the iodine reactor is maintained in the temperature range of 180° to 200°C by heating with steam at 195 psig (196°C). The reactions that occur in this reactor are not fully understood and are probably cyclic in nature. A probable reaction is:

$$6AgNO_3 + 3I_2 + 3H_2O \longrightarrow 5AgI + AgIO_3 + 6HNO_3$$

A glass wool filter downstream of the reactor is designed to collect any particulate matter. The filter is heated with 15-psig steam to avoid pluggage of the filter by condensation from water vapor.

5.2.5 Safety

Safety considerations associated with charging the dissolver and dissolution are: 1) criticality, 2) pressurization of the dissolver tank, 3) evolution of hydrogen, and 4) evolution of radioactive gases. These hazards and control methods are described below.

Criticality

Dissolution of enriched uranium requires controls for the safe handling of ^{235}U.[9] SRP administrative controls involve the mass of uranium charged to the dissolver, the volume of dissolvent, and the heel of undissolved fuel. Administrative controls also avoid conditions that lead to precipitation of fissile material from solution. The principal mechanical control is the dissolver insert. The insert is necessary to ensure that fuel tubes remain in a row and that any fuel tube fragments created during the dissolution are confined in proper configuration and can be detected. Administrative controls are based on nuclear safety calculations made for each fuel in the appropriate insert to determine the safe combination of ^{235}U in the fuel charge, ^{235}U concentration in solution, quantity of ^{235}U in fragmented tubes in the insert, and dissolvent volume.

The charge size including any heel is limited to satisfy all of the nuclear safety requirements listed below:

- The mass of ^{235}U must be dissolved into the normal dissolvent volume without exceeding the ^{235}U concentration assumed for the nuclear safety analysis.
- The possible combinations of ^{235}U concentration in the normal dissolvent volume and of the remaining height of intact, partially submerged fuel tubes plus fragments generated must be safe (Δk_{eff} 0.05) throughout the entire dissolution.
- In addition to the requirements for normal operating conditions listed above, the concentration of ^{235}U in solution must not exceed[5] 11.5 g/ℓ in the event that the dissolver solution is inadvertenly concentrated by evaporation from the normal volume to the minimum volume attainable with installed heating coils (4400 ℓ in the larger dissolver and 2200 ℓ in the smaller dissolver). Consequently, at no time should the mass of ^{235}U exceed 50.6 kg in the larger dissolver or 25.3 kg in the smaller dissolver.

The normal volume of dissolver solution is well in excess of the minimum volume by virtue of the quantity and concentration of nitric acid solution needed for complete charge dissolution. Appreciable boildown could be achieved only if the condenser cooling water supply were lost, and the dissolver continued to boil despite the instrument interlocks that should shut off the steam and despite several indications of an abnormal situation, e.g., high off-gas temperature, the decrease in solution level, and the increase in solution specific gravity. Design features have been incorporated in the dissolvers to physically limit the volume of dissolver solution to a safe minimum. First, dissolver steam service is connected only to the upper coils, the bottoms of which are 24 inches from the bottom of the dissolver pot. The minimum volume of dissolver solution possible by evaporation with the steam coils is then defined as the level at which the upper coils would come out of solution (44 ℓ in the large dissolver and 2200 ℓ in the smaller dissolver). Since undissolved metal is confined within the insert, no dissolution can take place when the insert is not submerged.

During normal operation, i.e., when the insert is partly submerged, the minimum volume of dissolvent must be controlled so that the concentration of ^{235}U in solution does not exceed the maximum value assumed in the nuclear safety analysis for the fuel being dissolved. At higher concentrations, the nuclear safety analysis is not valid. The maximum volume of dissolvent must also be controlled so that the depth of submergence of fuel assumed in a nuclear safety analysis is not exceed. At larger submergence depths, the nuclear safety analysis is not valid.

Nuclear safety in the dissolution also depends on control of the quantity of fuel element fragments[8] because fuel fragments may assume a configuration more reactive than tubes. The control used during startup of enriched uranium processing in 221-H Building, a heel cleanout after each dissolution,[11] was later replaced to increase dissolving capacity by control of the height of residual fragments, or heel, allowable in the insert when fresh fuel is charged. Subsequently, nuclear safety analyses determine a maximum height of residual fragments to be measured by mechanical probing of each insert compartment before fresh fuel is charged. Fragments can be formed by two methods:

- Fuel elements thinned by dissolution collapse because of the weight of undissolved metal above them. These fragments continue dissolving and have a transient existence.

- Some fuel sections may be relatively passive to further dissolution because of irradiation effects or impurities introduced during fabrication. These residual fragments form the heel carried to subsequent charges.

Nuclear safety analyses recognize both types of fragments to ensure subcriticality throughout the dissolution, because transient fragments cannot be controlled or monitored.

Core fragmentations were not detected during dissolver inspections in the plant nor during prototype dissolution of unirradiated fuel tubes. Partially dissolved tubes have been shown to become very thin before any evidence of fragmentation appeared, so no significiant mass of ^{235}U in fragment form is likely.[3,8] However, the possibility of the presence of both transient and residual fragments in the insert is included in each nuclear safety analysis, and a conservative dissolution model has been developed (Figure 5.10), based on observed dissolving behavior.[8] It is assumed that no significant quantity of fragments escapes the insert. Some conservative features normally included in nuclear safety calculations are:

- No allowance is made for burnup of ^{235}U.

- No allowance is made for neutron absorptions (poisoning) by fission products, nitrate, aluminum, or mercury.

- No credit is taken for the boron poison plates on some inserts (except for the posts inside the HFIR insert).
- The ^{235}U content of any fuel element is assumed to be the maximum for that type element.
- Fragment heights measured by probing the dissolver insert are assumed to be filled with fragments of unirradiated core material at the optimum packing density.

Precipitation of uranium or plutonium from the dissolver solution represents a potential nuclear safety hazard. Administrative controls must ensure that a minimum concentration of 0.3M HNO_3 is always present to avoid hydrolysis and precipitation of fissile material. Inadvertant addition of a precipitating chemical, such as NaOH, must also be prevented by a combination of nuclear blanks in process lines from certain cold feed tanks and by administrative controls.

Pressurization of the Dissolver

Pressurization of the dissolver could occur from excessive dissolution rates or from failure of the normally dependable off-gas jets. Pressurization could release contaminated vapors and gases into the hot canyon and the ventilation system, and could contaminate the crane and crane cab runway. Thus, the dissolver is operated with a small partial vacuum, and mercury catalyst is added at a carefully controlled rate.

In the event that normal techniques are unsuccessful in reducing the reaction rate and maintaining the dissolver vacuum, the dissolver may be flooded with a solution of aluminum nitrate from a cold feed tank on the third level. This addition cools the solution and abruptly increases the aluminum concentration which, as Figure 5.6 indicates, effectively decreases the dissolution rate.

Hydrogen Evolution

The noncondensable portion of the dissolver off-gas can contain up to 7% hydrogen by volume (air free basis). To maintain the off-gas hydrogen content of the off-gas well below the lower explosive limit of 4 volume %, the off-gas is diluted by a continuous air purge in addition to any air inleakage.[11]

Evolution of Fission Product

Krypton, xenon, and some iodine are released with the dissolver off-gas. The amount of radioiodine (^{131}I) present in the enriched fuel elements when processed is small because of its 8-day half-life. The mercury present in the dissolver solution greatly reduces iodine evolution by forming complexes, such as HgI_3^-. The iodine reactors are capable of removing greater than 99% of any iodine in the off-gas, even at much higher than expected concentrations of this fission product. Consequently, little iodine is evolved from the dissolver system.

Krypton and xenon are not absorbed by the body and therefore are not a biological problem after dilution with other effluent gases during discharge from the stack. Essentially all of the krypton and xenon isotopes present in cooled fuel are released; all except ^{85}Kr and short-lived ^{133}Xe are stable.

5.2.6 Equipment

The equipment used in chemical dissolving operations includes facilities for bundle storage, two dissolvers, several dissolver inserts, insert spacers, insert probes, and a solution hold tank. An iodine reactor and a filter are provided in the off-gas system for each dissolver.

Bundle Storage

Up to ten bundles of irradiated SRP fuel may be stored under water on a rack in Section 3 of the hot canyon. The storage rack holds two rows of five bundles vertically with a surface-to-surface spacing of 24 in. between bundles for nuclear safety.

Three HFIR inner elements and three HFIR outer elements may be stored under water in a line on posts in Section 2. These posts are spaced at least 27 in. center-to-center.

Experience in the plant has shown that the heat load from 10 bundles of irradiated SRP fuel or from three HFIR assemblies does not increase the temperature of the water in the storage cells excessively.

Dissolver Inserts

Each dissolver that is used for enriched uranium fuels must have a nuclear safety device called a dissolver insert. This device contains several compartments into which the fuel is charged and in which the fuel remains confined until it dissolves. Some inserts available are the Mark VI insert, the Mark XII insert, the HFIR insert, and the Ten-Well insert.

Mark VI and Mark XII Inserts

Two inserts, having slightly different dimensions, and designated as the Mark VI and the Mark XII inserts respectively, are available for dissolving SRP and compatible off-site fuels. Each of these inserts has two parallel slots about 21 ft deep and 50 in. wide. Partitions divide each slot into 2 slab-shaped compartments or quadrants that confine the fuel (see Figure 5.3).

The following as-fabricated insert dimensions were used in making the nuclear safety calculations for dissolution of SRP fuels.

	Mark XII Insert	Mark VI Insert
a. Reference Drawing	D 139026	D 110473
b. Inside width of fuel compartment, inches:		
1. at bottom	4.25 max.	3.625 max.
2. 6 ft above bottom	4.7 max.	4.5 max.
c. Distance between insides of adjacent surfaces of fuel compartments on opposite sides of poison plates, inches:	6.75 min	8.0 min.

HFIR Insert

The HFIR insert (Figure 5.5) consists of two cylindrical compartments or wells, one constructed to contain one (and only one) HFIR inner element and one constructed to contain one (and only one) HFIR outer element. The bottom 31 in. of each well is carefully machined and fitted with a machined center post of 1/4-in.-thick boron-stainless steel clad with 1/8-in.-thick 304L stainless steel. The center-to-center distance of the two wells is 32 in.

Each well is provided with an external neutron isolation shield over about 1/3 of its circumference on the sides between the wells. The shield is of the same composition as the center post and is spaced one inch from the outer surface of the well to permit liquid circulation.

The nuclear safety study of HFIR fuel dissolving established that 1% boron is required in 1/4-in.-thick boron-stainless steel poison in the wells to ensure nuclear safety during fuel dissolution. This requirement is met by the center posts. An additional margin of safety is provided by the external neutron isolation shield, but no credit was taken for this shield in the nuclear safety calculations.

The following as-fabricated insert dimensions were used in making the nuclear safety calculations for dissolution of HFIR fuel.

		HFIR Insert	
a.	Reference Drawing	S5-2-3612	
b.	Dimensions	Inner Section Well	Outer Section Well
	Post ID, in.	3.25	9.00
	Post OD, in.	4.245±0.005	9.995±0.005
	Outer wall ID, in.	12.245±0.005	17.545±0.005
	Outer wall OD, in.	13.0	18.875

Ten-Well Insert

The Ten-Well insert consists of a 2x5 rectangular array of 10 cylindrical fuel compartments or wells about 18 ft. deep and 5.5 in. ID. The following insert dimensions were used in making nuclear safety calculations for this insert.

Maximum Inner Well Radius, cm	7.304
Minimum Well Wall Thickness, cm	0.793
Minimum Well Bottom Thickness, cm	0.635
Maximum Open Area for Perforated Regions, %	15.0
Nominal Center-to-Center Well Spacing	
Width, cm	25.082
Length, cm	27.386

Insert Spacers

Insert spacers are nuclear safety devices that are placed in the Mark VI and XII insert compartments to provide maximum separation between fuel bundles in a slot, thereby improving the nuclear safety margin for the system. In those nuclear safety evaluations that assume the spacers are installed, the spacers must be used or the nuclear safety evaluation is not valid.

Insert Probes

Before fresh fuel is charged to a dissolver insert, the height of fragments in each insert compartment must be measured to ensure subsequent nuclear safety. This measurement is made with an insert probe, a device that has the same shape and dimensions as the bottom of the insert compartment. There is at least one probe available for each insert. The crane operator lowers the probe into the insert as far as possible and determines the fragment height by a variety of techniques, depending on the probe used. The simplest technique involves a calibration mark (on the handle of the probe) that is visible to the crane operator. For nuclear safety calculations, the measured heel height is assumed to be packed with fuel fragments of the same composition as the unirradiated fuel core. If the fragment height measured by probing a well exceeds the maximum allowable height determined in the nuclear safety analysis for the fuel being dissolved, fresh fuel may not be charged to that well.

Chemical Dissolvers

The two chemical dissolvers are of almost identical construction except for the pot diameters. The smaller dissolver is shown in Figure 5.10; the dissolver pot is 8 ft in diameter by 8 ft high. Each dissolver is normally charged with dissolvent to achieve about 48 in. of fuel submergence. At that level the dissolvers are about 75% full with 7400 ℓ in the smaller dissolver and 15,000 ℓ in the larger dissolver.

Each dissolver is equipped with a rectangular column and two, parallel, downdraft condensers (Figure 5.12). The rectangular column accepts a perforated insert that has slots or wells into which fuel bundles are charged. Ports are provided in the top of the insert to allow off-gas to flow into the rectangular annulus between the insert and the column wall. Off-gas flows from the column into the condensers through two six-inch pipes per condenser. Noncondensables pass down over the condenser coils and leave through nozzles near the bottom of each condenser. Condensate returns to the dissolver through a pipe in the bottom of each condenser. The condensers are of a downdraft type in which the off-gas and condensate flow downward concurrently, so that the coolest reflux is in contact with the coolest off-gas for most efficient absorption of NO_2 gas at the off-gas exit. A liquid seal in the condensate return line prevents off-gas from bypassing the condensers.

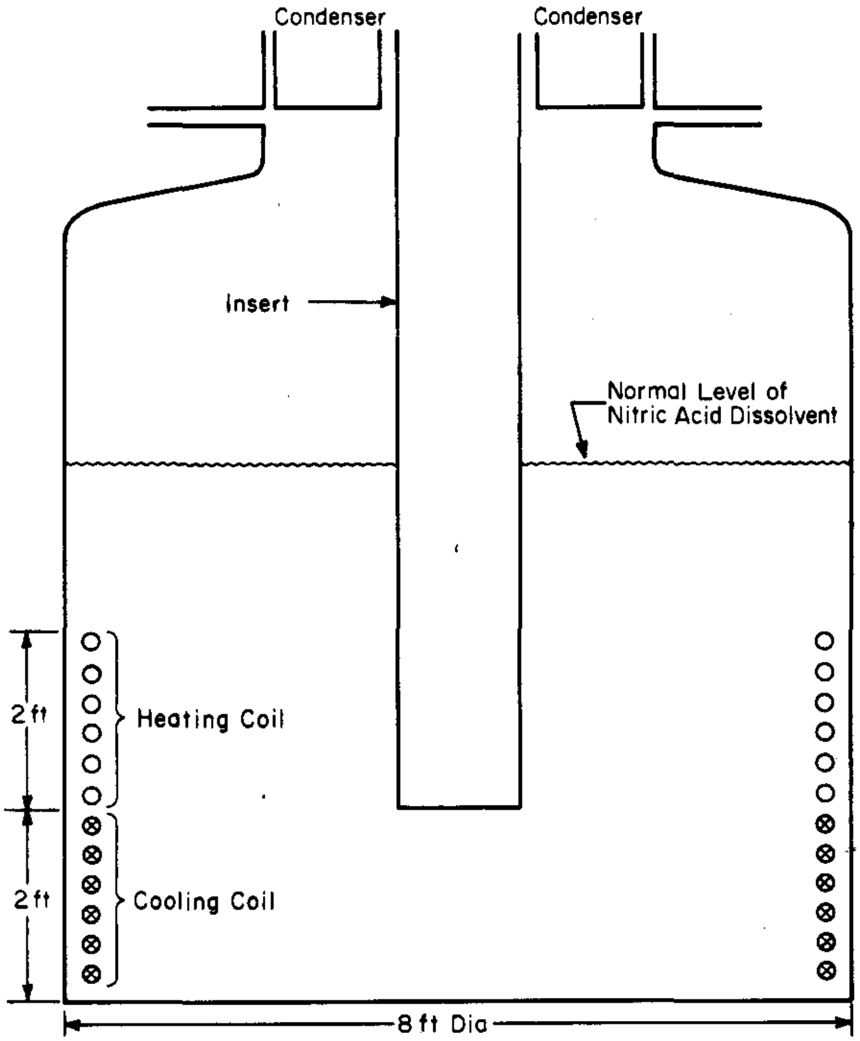


FIGURE 5.11 Schematic View of HM Dissolver with Mark VI Insert

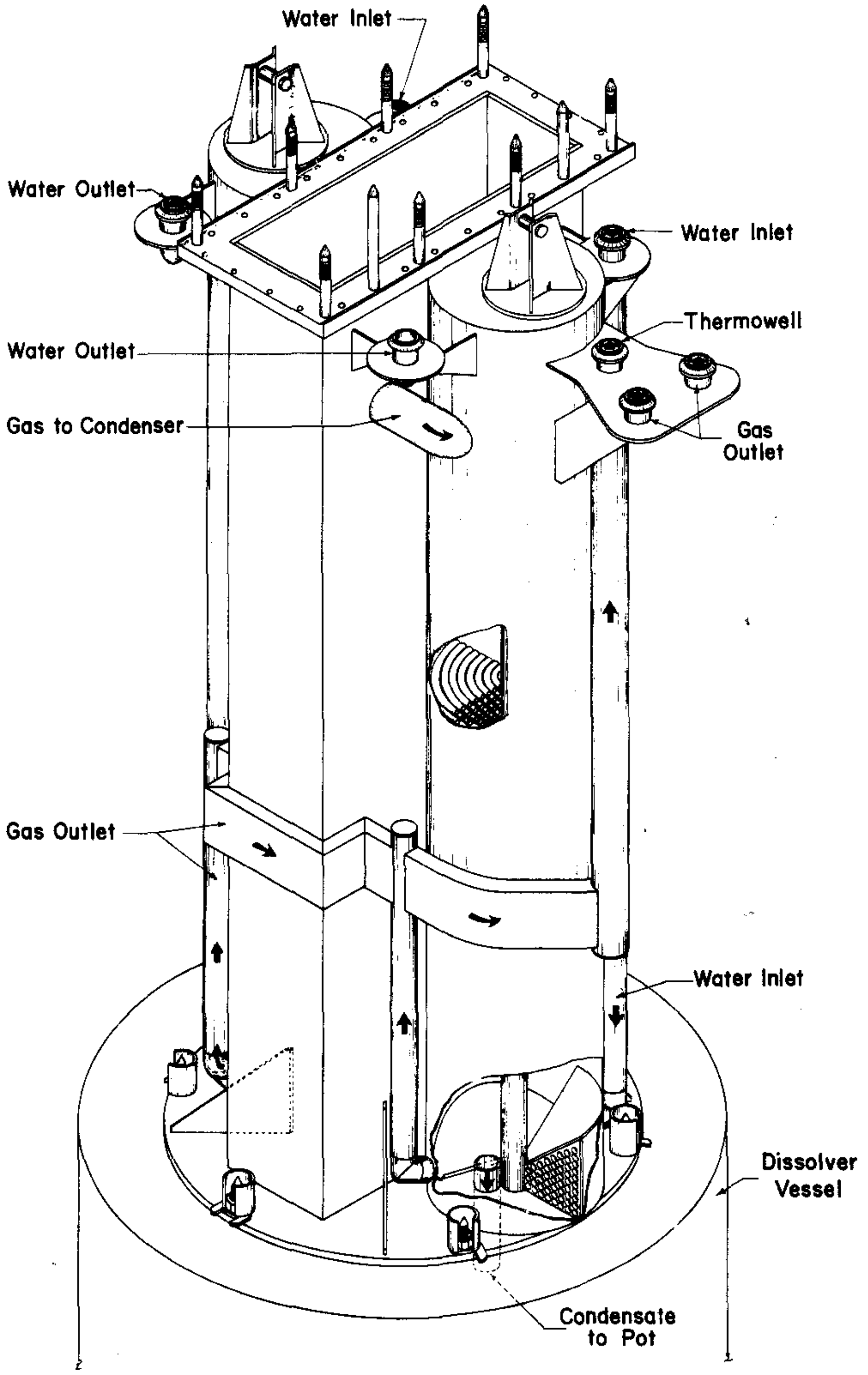


FIGURE 5.12 Dissolver Column for Enriched Tubes

Storage of Dissolver Solution

The dissolver solution hold tank receives the final dissolver solution. It is a standard canyon tank 10 ft in diameter by 11 ft high equipped to measure the volume of the solution and to sample the solution.

Off-Gas System

The heated iodine reactors and glass-wool filters used with dissolver off-gases are located in the hot canyon. The exhaust jets are adjacent to the stack at Building 291-H.

The off-gas heater and iodine reactor are combined in one unit as shown in Figure 5.13. The steam jacket is heated with 195-psig steam to provide a temperature of 196°C. The inner vessel is packed with 1/2-in. Berl saddles that have been coated with silver nitrate. The off-gas filter shown in Figure 5.14 is packed with four layers of fiberglass to remove particulate matter from the off-gas. The filter jacket is heated with 15-psig steam. A diagram of the off-gas system is shown in Figure 4.7.

5.3 ELECTROLYTIC DISSOLVER

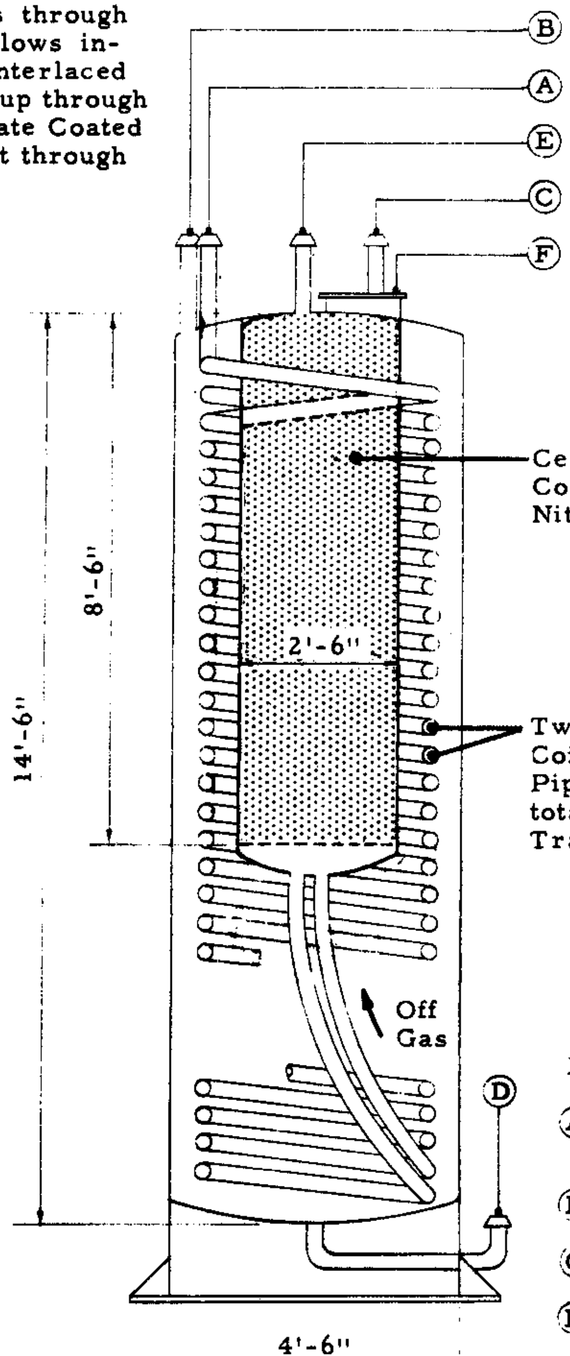
5.3.1 Fuel Description

Many power reactor fuels contain either stainless or zirconium components, neither of which can be dissolved in nitric acid. They must be dissolved by electrolytic dissolution. Hydrochloric acid, hydrofluoric acid, sulfuric acid, or aqua regia could be used, but would require new dissolvers made of corrosion-resistant alloys. A large number of power fuels contain UO_2 pellets swaged into stainless steel or Zircaloy tubes. Some others are mixtures of UO_2 and stainless steel powder, some are U-Zr alloys, and others are uranium alloys bonded to stainless steel tubes with sodium.

UZr_3 (referred to as the "epsilon phase" in U-Zr alloys and the "delta phase" in U-Zr-Nb alloys) is an intermetallic compound that detonates under some oxidizing conditions.[12] The compound is present in some zirconium-containing fuel, and it has not been shown that such fuel can be processed safely by electrolytic dissolution. Extremely close scrutiny of zirconium fuels is therefore necessary to ensure that only fuel essentially free of UZr_3 is processed.

Stainless-steel-clad sodium-bonded fuels may be dissolved electrolytically at a sufficiently low temperature (<60°C) and sodium exposure rate [<2.5 g sodium/ (min-ft^2) of electrode cavity cross section].[13]

Off Gas enters through Nozzles (A), flows inside the two interlaced Helical Coils, up through the Silver Nitrate Coated Packing and out through Nozzles (C).



Ceramic Packing Coated with Silver Nitrate

Two Interlaced Helical Coils, 4 inch Sch. 40 Pipe, 14 turns per Coil, total of 28 turns, Heat Transfer Area 330 sq.ft.

LEGEND

Ⓐ	**Dissolver Off Gas Inlet**
Ⓑ	**Steam Inlet**
Ⓒ	**Gas Outlet**
Ⓓ	**Condensate Outlet**
Ⓔ	**Thermowell**
Ⓕ	**Access Hatch for installing Packing**

Equipment Insulation Not Shown

FIGURE 5.13 Dissolver Off-Gas Heater and Iodine Reactor

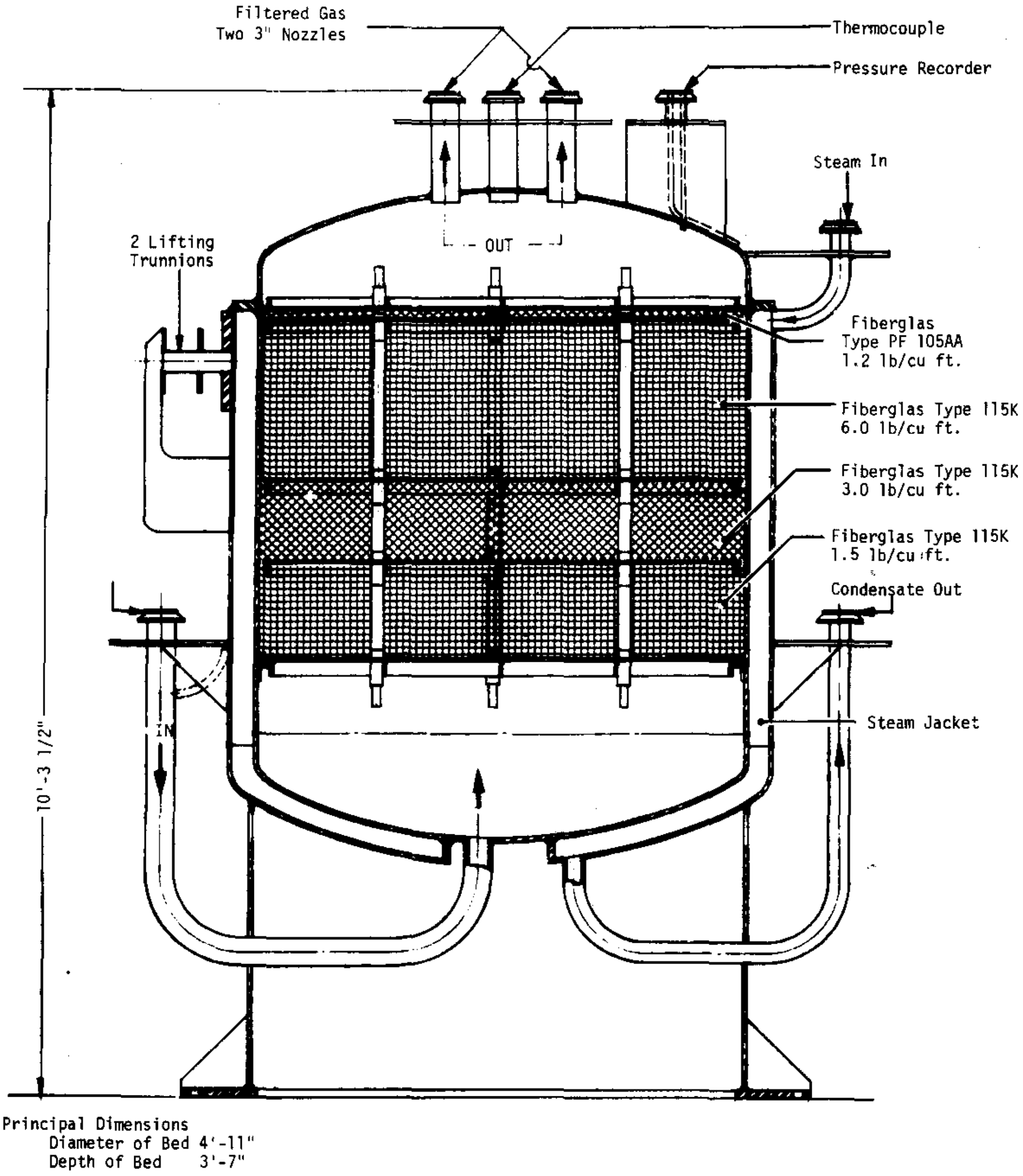


FIGURE 5.14 Dissolver Off-Gas Filter

In addition to intact fuel assemblies, fuel scrap in steel cans may be charged and processed electrolytically. Shipping and charging limitations due to nuclear safety analyses apply to scrap as well as to intact fuel assemblies.

5.3.2 Charging

Off-site fuel is stored at the Receiving Basin for Off-Site Fuel (RBOF), Building 244-H. Because of the variety of fuel types and fuel dimensions, there is no standard fuel container (bundle) in which these fuels (or scrap) are shipped to 221-H. The type of shipping container is dictated by fuel type and dissolver chute geometry. Often a square-tube bundle (Section 5.2.2) is used. The shipping cask inventory and container arrangement are dictated by a nuclear safety analysis for each type of fuel to be processed. Each container must be properly identified as to number, fuel type (or scrap type), stainless steel, zircaloy, or aluminum content, total uranium and ^{235}U content before loading in the shipping cask.

The fuel is transported to 221-H from RBOF and charged directly to the dissolver. Fuel types may be mixed in a fuel shipment or dissolver charge if rules and limits for the operation are based on the type of fuel that is most restrictive. The quantity of fuel charged and its physical configuration in the dissolver insert is governed by a nuclear safety analysis for each type of fuel. Fuel baskets and basket liners (referred to as trash baskets) are employed to ensure critically safe geometry throughout dissolution for a variety of fuel containers, to retain short segments of fuel tubes (loose) at the end of dissolution and to retain insoluble foreign material (such as thermocouples) present in the fuel.

5.3.3 Fuel Dissolving

Stainless steel, zirconium, and aluminum cladding are dissolved anodically in the electrolytic dissolver; and the core material dissolves chemically, or in the case of cermet cores, both anodically and chemically. The use of nitric acid as the electrolyte permits recovery of fissile materials by conventional solvent extraction flowsheets using existing stainless steel equipment.

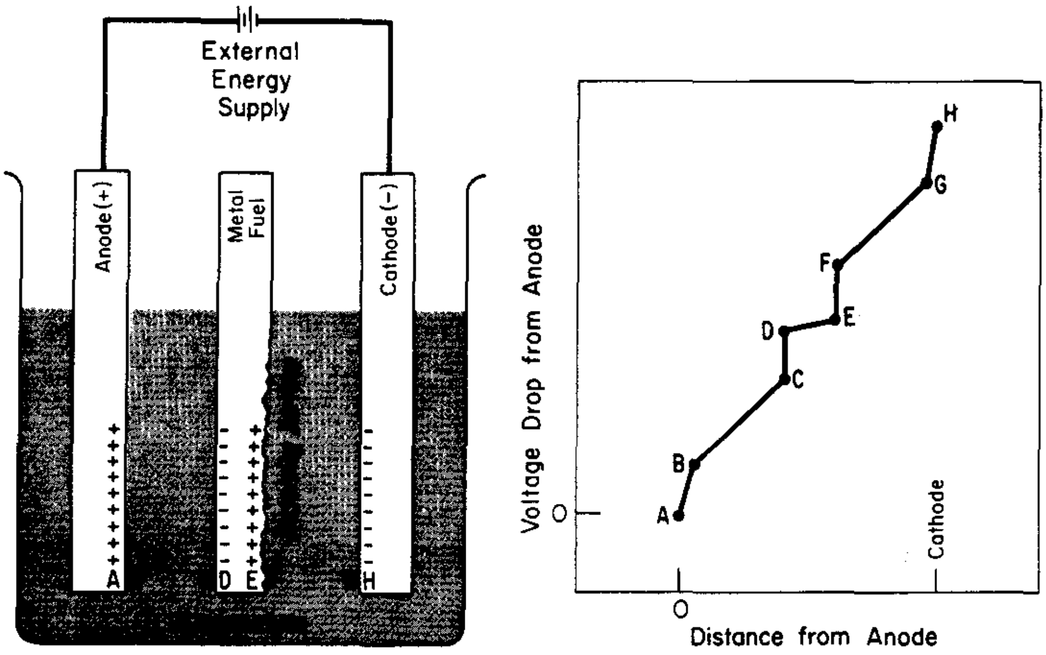
Thermodynamically, nitric acid should dissolve many of the candidate fuel claddings, but in most cases the metal surface is protected by oxide films. When the electrochemical potential at a metal-solution interface is increased by applying an external source of electrical energy, passive films can be destroyed.

When directly connected to the electrical supply as the anode, stainless steel electrolytically dissolves in nitric acid at the theoretical rate of 0.59 g/(amp-hr) (equivalent to 30 mil/hr at a current density of 1 amp/cm^2); zirconium and aluminum are dissolved at 0.85 and 0.33 g/(amp-hr), respectively.[13]

Because direct electrical connection with the fuel is difficult to maintain in a remotely operated production facility,[14] contact is established through the electrolyte with the dissolving fuel suspended between two electrodes. The liquid-contact principle is shown schematically in Figure 5.15. The current produces oxygen as it passes out of the anode into the electrolyte and enters the adjacent surfaces of the fuel by one of two competing cathodic reactions: either the reduction of nitrate ion, or the formation of hydrogen gas. The surface of the fuel adjacent to the cathode becomes anodic by association and dissolves as the current passes out of it and back into the electrolyte. The current is accepted at the cathode, and nitrogen oxides and/or hydrogen are produced.

The primary disadvantage of the liquid-contact technique is that there are two parallel paths for current flow, one through the fuel assembly and one directly through the electrolyte. Because the resistance of the electrolyte is relatively high (0.98 ohm-cm for 8M HNO_3 at 50°C compared to 6×10^{-5} ohm-cm for stainless steel), most of the current will flow through and dissolve the fuel assembly as long as the voltage drop through an equivalent distance of the electrolyte (typically 2.5 volt/inch at a current density of 1 amp/cm^2) exceeds the sum of the anodic and cathodic reaction potentials. The combined reaction potentials of several metals are shown in Table 5.3. If the combined reaction potential is too high or if the electrodes are wider than the dissolving metal, a fraction of the current will flow between the electrodes and will not be used in dissolution. Liquid-contact dissolution of stainless steel normally results in a current utilization of over 80% (0.47 kg stainless steel/1000 amp-hr), while zirconium is dissolved with only 25% efficiency (0.21 kg Zirconium/1000 amp-hr).[13] In nitric acid concentrations ranging from 4 to 16M, approximately 85% of the zirconium is electrolytically converted[15] to an insoluble surface layer of ZrO_2, which is responsible for the relatively high reaction potentials and resulting poor current utilization.

Almost all of the power required to operate the cell is dissipated as heat in the nitric acid electrolyte. If the heat is not removed, the acid will boil and blanket the electrode with vapor, causing a rapid increase in resistance.[16] The result is that a maximum current density is reached for a given electrode-fuel assembly configuration and bulk temperature. The limiting current density can be increased by lowering the temperature of the bulk electrolyte and/or by increasing the flow of the electrolyte past the electrode.



VOLTAGE DISTRIBUTION

A to B - Reaction potential at the surface of the anode
B to C - Voltage drop across the electrolyte
C to D - Reaction potential at the cathode surface of the fuel
D to E - Voltage drop across metal fuel
E to F - Reaction potential at the anodic surface of the fuel
F to G - Voltage drop across the electrolyte
G to H - Reaction potential at the surface of the cathode

FIGURE 5.15 Liquid Contact Principle

TABLE 5.3

Reaction Potential Required for Electrolytic Dissolution in Nitric Acid

Material	*Combined Reaction Potential, volts*
Stainless Steel	1.1
Aluminum	1.95
Zirconium	3 to 4

Current density is limited only by the area of the platinum anode. Maximum current densities for platinum anodes are shown in Figure 5.16 as functions of the height of the electrode and the difference between the temperature of the electrolyte and its boiling point. At a given temperature difference, the taller the electrode, the lower the maximum current density.

Platinum is used in the electrolytic dissolver as the anode cladding because it is the only material that is not severely corroded during anodic reaction in nitric acid; the cathode is clad in platinum to reduce the extent of hydrogen embrittlement in case of unexpected operation with dilute (<6M) electrolyte. Tests of the corrosion of platinum electrodes in nitric acid showed that platinum is not a completely passive electrode material and that significant rates of attack can occur. The rate of corrosion of the anode increases rapidly with increasing temperature and decreasing acidity (Figure 5.17), whereas the corrosion rate of the cathode is only slight (protected by negative potential). The platinum corrosion rate is not significantly affected by the presence of dissolved stainless steel or uranium. Under the operating conditions in the dissolver (6 to 10M HNO_3, 50 to 60°C), the rate of attack is not excessive, averaging 1.8 mil/yr for the anode and 0.5 mil/yr for the cathode.[13]

Bundles or cans of fuel and scrap are charged to the dissolver by stacking the fuel vertically in the basket and chute. Nitric acid, generally at an initial concentration of 10 to 14M, is employed as the electrolyte. The nitric acid level covers the electrodes and recirculation ports in the electrodes. During dissolution, cooling water flow through the dissolver coils and jacket is maintained to remove the electrical heat input and maintain an electrolyte temperature at 60°C. The charge size and electrolyte volume are adjusted for each run to ensure that: 1) the ^{235}U concentration in the electrolyte does not exceed the arbitrarily selected nuclear safety control guide of 4.6 g/l, 2) stainless steel and other components do not exceed the solubility limit, 3) the final acid concentration after dissolution is not less than 6.0M to minimize corrosion of the platinum anode and hydrogen embrittlement of the columbium cathode, and 4) the mass of ^{235}U is critically safe for the ^{235}U concentration in the pot.

Dissolution is initiated by adjusting the anode potential to ∿40 volts, causing current to pass through the electrolyte and fuel assemblies. As the assembly cladding dissolves at the sloped side facing the cathode and consequently moves down filling the space between the electrode, the resistance is lower and a corresponding increase in amperage occurs rapidly. Therefore, the anode potential must be reduced to maintain the current below the 10,000-amp operating limit.

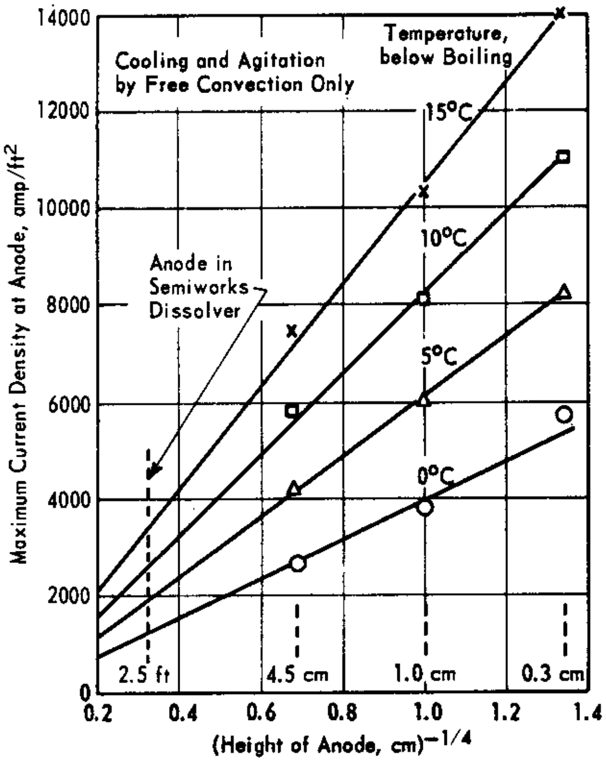
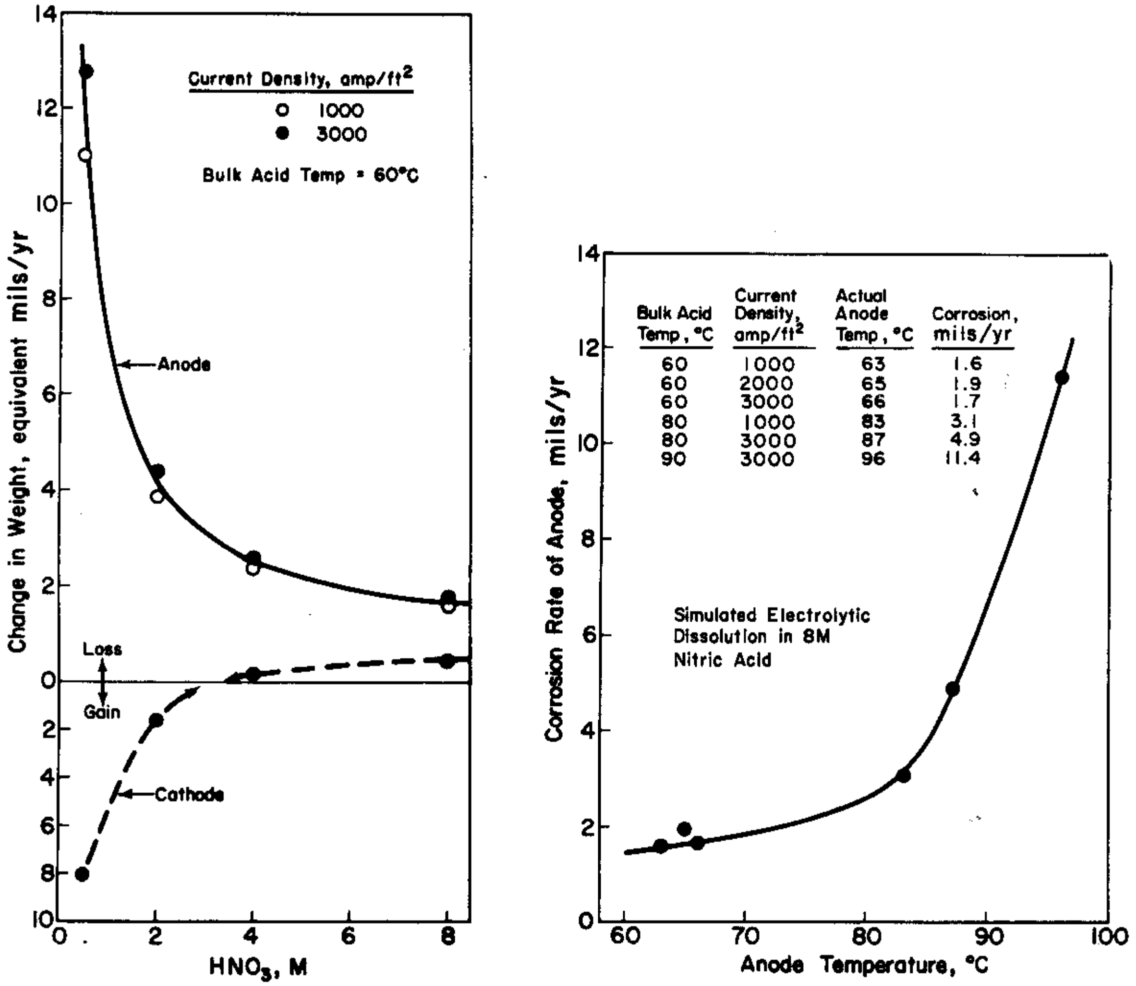


FIGURE 5.16 Maximum Current Density at Platinum Anode



Bulk Acid Temp, °C	Current Density, amp/ft²	Actual Anode Temp, °C	Corrosion, mils/yr
60	1000	63	1.6
60	2000	65	1.9
60	3000	66	1.7
80	1000	83	3.1
80	3000	87	4.9
90	3000	96	11.4

FIGURE 5.17 Corrosion of Platinum Electrodes

Dissolver operation is to be controlled within the guides shown below. These guides control nuclear safety, prevent damage to the equipment and prevent escape of gases to the canyon air system.

Electrolytic Dissolver Operating Guides

		Min.	*Max.*	*Units*	*Reason for Limits*
1.	Vacuum in dissolver	>0	45	inches water	Operating experience under DPSTS-221H-HM-1.03
2.	Concentration of ^{235}U in dissolver solution	-	4.6	g/l	Extent of safety analysis
3.	Final HNO_3 concentration	6.0	-	molarity	To prevent hydrogen embrittlement of columbium cathode
4.	Potential difference between anode and cathode (at top)	-	45	volts	To prevent excessive corrosion of the columbium anode
5.	Sustained current flow	-	10,000	amperes	To prevent damaging rectifier**
6.	Electrolyte Bulk Temperature	-	60	°C	To maintain efficient chemical dissolution without excessive corrosion
7.	Concentration of metal in electrolyte	-	Figures 5.18 and 5.19		To avoid exceeding solubility of somponents in electrolyte
8.	Electrolyte solution level	63	-	inches	To allow removal of heat by electrolyte circulation through port in electrode shields
9.	Voltage difference between top of cathode bus bar and				Higher values indicate undesirable current loss and possible electrical malfunction
	a. Tank	-	3	volts	
	b. Ground	-	3	volts	
10.	Air sparges:				To remove heat from electrodes and provide agitation
	cathode	1	-	scfm	
	anode	1	-	scfm	
	basket	1	-	scfm	
	ring	10	-	scfm	

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* The maximum *initial* HNO_3 concentration must ensure the solubility of the boric acid as is required by the nuclear safety analysis. See Section 5.3.8 and Figures 5.25 and 5.26. The maximum *final* HNO_3 concentration must ensure the solubility of the metals in solution. See Figures 5.18 and 5.19.

** Occasional current flow in excess of 10,000 amps is permitted and will not cause the rectifier protection circuit to shut down the dissolver.

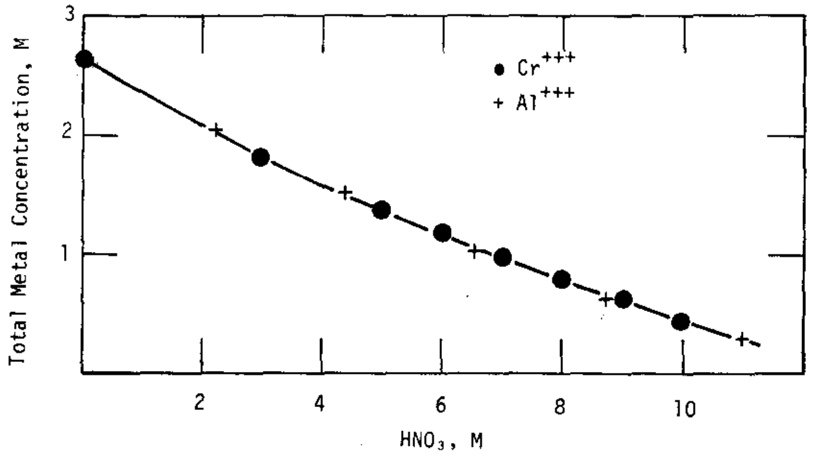

FIGURE 5.18 Solubility Guideline for Fully Enriched Fuels (T ⩾ 20°C)

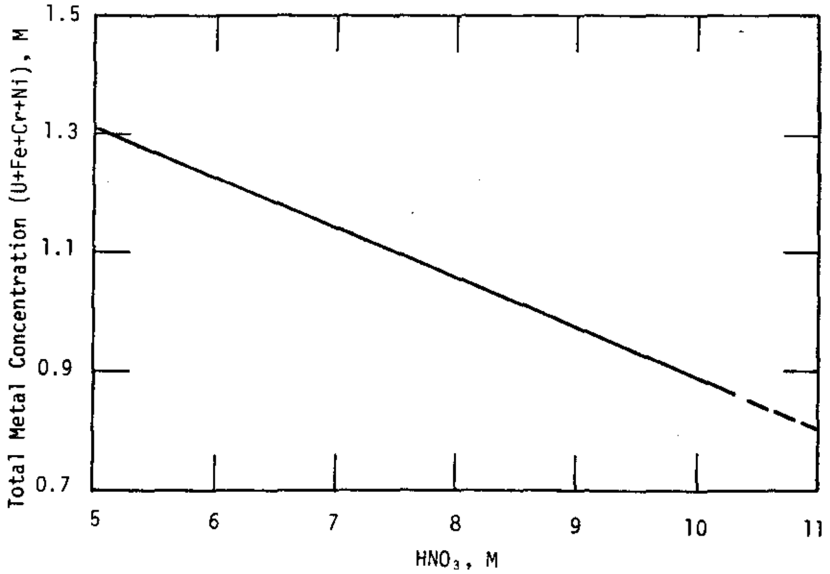

FIGURE 5.19 Solubility Guideline for Low Enriched Fuels (T ⩾ 20°C)

Assuming the basket is filled with fuel, the following dissolving rates are attainable:[13]

0.5 g stainless steel/(amp-hr)

0.25 g zirconium/(amp-hr)

2.5 g uranium/(amp-hr)

0.3 g aluminum/(amp-hr)

The dissolver capacity is limited by the ability to remove electrical heat. The dissolving rates given above assume that current densities of 2000 to 3000 amp/ft^2 of submerged platinum anode are attained at a potential of about 25 volts and that the electrolyte can be circulated sufficiently to remove the generated heat.

5.3.4 Sludge Generation

During electrolytic dissolution, less than 2 wt % of the stainless steel tubing falls to the bottom of the dissolver as very small grains to form a sludge, whereas about 7 wt % of the stainless steel in a cermet fuel appears as sludge.[13] Conversely, 85 wt % of zirconium is anodically oxidized in the form of an insoluble ZrO_2 film, which spalls off of the base metal and accumulates at a rate of 15 gal/100 lb of zirconium processed. The characteristics of the two types of sludge are shown in Table 5.4. Tests have shown that less than 0.5% of the uranium charged to the dissolver remains with the sludge following a normal rinse procedure.

TABLE 5.4

Characteristics of Electrolytic Dissolver Sludge

Elements Dissolved	*Stainless Steel - UO_2 Cermet*	*Zircaloy-Clad UO_2*
Fraction of charge converted, wt %	7	85
Sludge form	Stainless steel grains	ZrO_2 flakes
Bulk density, g/cm^3	4	0.9
Size distribution, wt %		
U. S. Standard Sieve		
+40	6	8
- 40 +80	7	47
- 80 +100	5	15
-100 +200	13	22
-200 +325	29	5
-325	40	3

Sludge must be removed from the dissolver periodically (more frequently during the dissolution of zirconium-clad fuel as opposed to stainless steel clad fuel) to ensure good circulation in the dissolver vessel and prevent accumulations of material near the electrodes.

5.3.5 Dissolver Off-Gas

The air sparges (providing bulk agitation and circulation in the electrode cavity) are the primary contributors to the volume of off-gas. A lesser volume of oxides of nitrogen is produced by the reduction of the nitrate ion at the cathode. If the electrolyte concentration is maintained above the specified limit (6M HNO_3), essentially no H_2 formation will occur at the cathode.[15] Oxygen is produced at the theoretical rate at the anode. These gases pass through a reflux condenser, heated iodine reactor, and high-efficiency fiberglass filter with subsequent discharge to the environs via the 291-H stack. The iodine reactor and fiberglass filter are common to both the chemical dissolvers and the electrolytic dissolver.

The temperature of the off-gases leaving the condenser should be less than 60°C to limit the quantity of condensable vapor leaving the dissolvers. Iodine is effectively removed by absorption in the iodine reactor, which contains Beryl saddles coated with silver nitrate. The reactor is operated at 175 to 195°C to achieve maximum absorption efficiency.

5.3.6 Safety

Safety considerations associated with the dissolution are: 1) criticality, 2) pressurization, 3) hydrogen evolution, 4) evolution of radioactive gases, and 5) sodium-acid reaction. These hazards and the methods of their control are discussed below.

Criticality

Processing of enriched uranium fuel requires rigid controls for the safe handling of the fissile ^{235}U. These controls include: 1) limitation of the mass of uranium in the dissolver, 2) limitation of the mass of uranium in the dissolver chute, 3) selection of the volume of dissolvent, and 4) the dissolver insert design which controls the geometry of whole or partially dissolved fuel. These variables are interrelated since each dissolution involves a series of conditions starting with the initial undissolved charge moderated by a surrounding dissolvent and procressing through the partially dissolved charge surrounded by dissolvent of increasing uranium concentration, to the final completed dissolution with all the uranium in solution. A nuclear safety analysis must be made for every fuel type since there is such a variety of nonproduction fuels of varying geometry and ^{235}U content.

The fuel charge size is limited to satisfy all of the nuclear safety requirements listed below:

- Unless specific nuclear safety calculations at specific ^{235}U concentrations are made, the charge in the dissolver insert must be safe ($\Delta k_{eff}>0.05$) when surrounded by a solution containing the maximum terminal ^{235}U concentration.
- The mass of ^{235}U must be dissolved into the normal dissolvent volume without exceeding the maximum ^{235}U concentration assumed for the nuclear safety analysis.
- The possible combination of ^{235}U concentration in the normal dissolvent volume and of that ^{235}U in the remaining intact, partially submerged fuel must be safe throughout the entire dissolution.
- The possible combination of the maximum terminal ^{235}U concentration in the dissolvent volume and the maximum anticipated concentration of ^{235}U in a maximum possible volume of sludge must be critically safe ($\Delta k_{eff} \geq 0.05$).

The normal dissolvent volume must be maintained throughout the dissolution to ensure the maximum permissible ^{235}U concentration (4.6 g/ℓ) is not exceeded. Accidental evaporation of the dissolver solution due to loss of cooling water is prevented by design features, including a nuclear safety control blank in the steam supply to the dissolver cooling coils,* a reflux condenser, a liquid level monitor, temperature monitors, flow monitors, etc., with corresponding interlock systems as described in Section 5.3.8.

Fuel fragmentation may occur when dissolving stainless-steel-clad, low-enrichment UO_2 fuels. Since some UO_2 can escape the dissolver insert when the cladding is breached, the nuclear safety analyses must assume the highly unlikely event of escape of the total UO_2 charge. Also, it must be assumed that the UO_2 fines agglomerate in the most reactive array. Accordingly, additional measures (such as addition of a soluble poison to the electrolyte) must be taken as secondary nuclear safety controls to ensure that a nuclear excusion cannot occur (see Section 5.3.8 and Figures 5.25 and 5.26).

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* Steam supply is required to process $BeO-UO_2$ fuels such as GCRE and ML-1.

All credible accidents that may occur during loading or unloading operations as well as shipping must be considered in the nuclear safety analysis. A separate analysis must be made for each type of fuel shipment.

Fuel bundles or fuel containers should be constructed to ensure that the fuel contained in these bundles or containers retain a critically safe configuration until the assemblies are dissolved between the electrodes. An exception to this is the case of processing low-enriched UO_2 fuels where the UO_2 is assumed to be loose in the most reactive array.

Pressurization

Dissolver pressurization may occur due to failure of the off-gas steam jet, pluggage of the off-gas system, or excessive dissolution rates. The air sparges (providing bulk agitation and circulation in the electrode cavity) are the primary contributors to the expected volume of off-gas. Unexpected dissolution rates are avoided, since the maximum rate of dissolution for the cladding material is fixed by the design current, anode surface area, ability to remove the heat near the surface of the electrodes, and electrode submergence.

In the event of failure of the off-gas jet or pluggage, the dissolver would vent via the dissolver chute plug into the canyon until the electrolysis is stopped and air sparges are stopped. Approximately 0.1 psig pressure will lift the chute cover.

Evolution of Hydrogen

The hydrogen content of the dissolver off-gas must be well below the lower explosive limit for hydrogen in air (4 vol %).[11] Previous tests using nitric acid as the electrolyte indicate that hydrogen actually accounts for less than 2% of the total cathode gas.[15] The preferred cathode reaction is reduction of nitrate to the oxides of nitrogen. Laboratory studies indicate that if the total nitrate concentration is maintained above 7M and contains at least 6M HNO_3, hydrogen evolution is insignificant.[15] Even in dilute nitric acid (<2M), where hydrogen is evolved at the significant theoretical rate, the nominal air sparges required for heat dissipation would maintain the hydrogen concentrations less than the explosive limit. Electrolyte concentration below 6M HNO_3 must also be avoided to prevent embrittlement of the cathode by atomic hydrogen.[17]

Evolution of Fission Product Gases

During the electrolytic dissolution, fission-product gases such as ^{85}Kr, ^{133}Xe, and radioiodine are released to the off-gas system. The $AgNO_3$ reactor is capable of removing 99% of any iodine in the dissolver off-gas. Krypton and xenon are released to the atmosphere. Fuel to be processed electrolytically should have sufficient cooling time so that together with other anticipated releases in the 200 Area processes they do not exceed the plant operating guides.

Sodium-Nitric Acid Reaction

The dissolution of sodium-bonded fuels requires special precautions to ensure that the operating temperature is held below the 60°C plastic point of sodium. A temperature above this limit might allow the entire load of sodium present in the dissolver fuel charge to flow into the nitric acid electrolyte causing a violent chemical reaction. Sodium-bonded fuels may be safely processed at sodium exposure rates less than 2.5 g of sodium per minute per square foot of electrode cavity cross section. (The total electrode cavity cross section is about 4.75 ft^2.) At this rate, $\sim$1.2 ℓ H_2/(min-ft^2 of electrode cavity cross section) will be released to the dissolver off-gas, and an air purge of 30 ℓ/(min-ft^2 of electrode cavity cross section) is required to maintain the hydrogen concentration below the lower explosive limit.[13]

The electrolyte temperature between the electrodes must be maintained below stated limits throughout the dissolution; consequently, cooling systems must be efficient, dependable, and redundant. During dissolution, the primary (and backup) cooling system must be capable of removing fuel decay heat I^2R loss and heat of reaction. Dissolver controls enable immediate shutdown of the power to the electrodes if the temperature exceeds the decay heat from the maximum fuel charge in the event both water cooling systems fail.

Under no circumstances may NaK bonded fuels (such as SRE power fuel) be charged to the dissolver. NaK has a melting point of 10°C, and the entire NaK content would be released to the electrolyte as soon as the outer cladding dissolved, causing a violent reaction and probably damage to the dissolver.

5.3.7 Equipment

The electrolytic dissolver (6.3) is located in module 6.3 of the hot canyon in Building 221-H and is vented to a chemical dissolver. The electrolytic dissolver vessel is an 8-ft-high by 8-ft-diameter jacketed pot constructed of 304L stainless steel. Assembly views are shown in Figures 5.20. Major components of the dissolver are as follows:

- Internal coils for cooling (and heating as required).
- Electrode assembly consisting of a niobium anode and cathode with platinum surfaces for transfer of current between electrodes.
- Ceramic fuel basket to retain the fuel bundles between the electrodes.
- Trash basket.
- Fuel charging chute lined with electrical insulation.
- Necessary insulators between tank, anode, cathode, and basket.
- Air spargers on tank bottom.
- Annular heat removal jacket.
- Reflux condenser.
- Sludge removal system.
- Services and instrumentation are listed in Table 5.5.

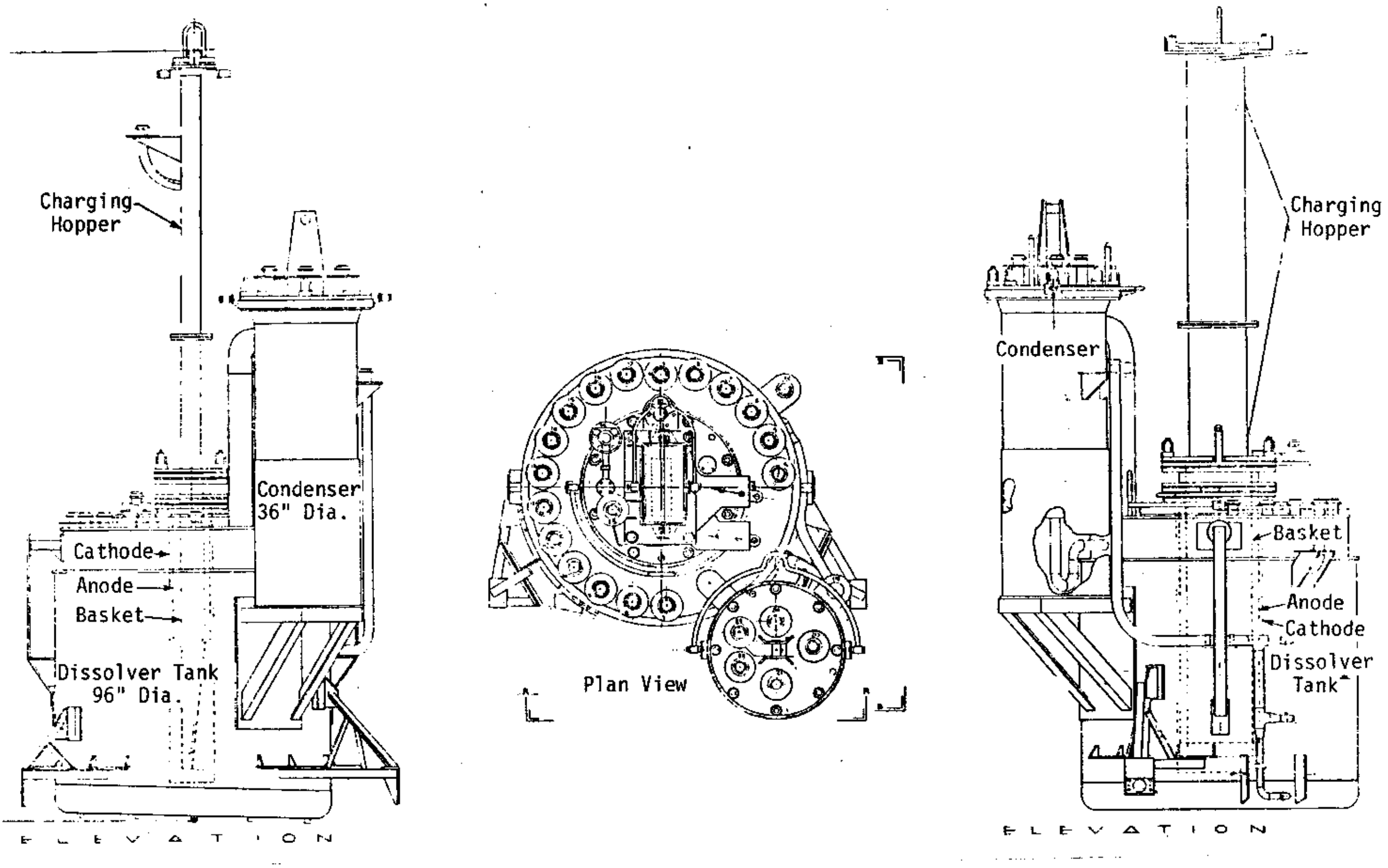

FIGURE 5.20 Assembly View of Electrolytic Dissolver

TABLE 5.5

Electrolytic Dissolver Services and Instrumentation

Services

- Process Cooling Water to Tank Coils, Annular Jacket and Rectifier
- Steam to Coil (normally blanked with a Nuclear Safety Blank)
- Air Sparge to Sludge Spray Ring
- Air Sparge to Electrode Assembly
  (1) Behind anode (2) Behind cathode (3) Center of Electrode Cavity
- Air Purge to Dissolver Chute (Blanked)
- Nitric Acid
- Vent to Chemical Dissolver

Instrumentation

- Liquid Level
- Specific Gravity
- Temperature
  - (1) Bulk Electrolyte
  - (2) Electrolyte between Electrodes[a]
  - (3) Rectifier Cooling Water
  - (4) Dissolver Off-Gas
  - (5) Tank and Condenser Exit Cooling Water
- Dissolver Vacuum
- Current Flow and Power Consumption
- ΔP Across Condenser
- Cooling Water Flow
- ΔV between Reference Cathode Flange and,[b]
  - (1) Anode Flange
  - (2) Anode Face
  - (3) Basket
  - (4) Tank
  - (5) Cathode Face

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[a] Thermohms, used to measure the electrolyte temperature between the electrodes, failed during early operation and could not be replaced. Operating temperature has been controlled based on the temperature difference between the bulk electrolyte and that between the electrodes observed during demonstration test and is adequate control as long as sodium bonded fuels are not processed.

[b] Instrumentation has failed due to acid attack. Currently monitors voltage differentials between the cathode busbar and (1) the vessel, and (2) ground.

Dissolver Vessel

The dissolver vessel consists of a 7-ft-5-in.-diameter stainless steel tank (in which the electrode assembly is suspended), which in turn is inside an 8-ft-diameter tank. The annulus between the two tanks serves as an emergency heat-removal jacket and provides secondary containment. A 12-ft-tall chute is placed on top of the electrode-basket assembly and permits charging the fuel assemblies above the active dissolution zone. The dissolver is also equipped with a large condenser to minimize evaporative loss of electrolyte.

Electrode Assembly

The platinum-bonded niobium electrodes are designed to be massive enough to give strength and high conductance to the electrode assembly and resist electrochemical and chemical attack. The electrode configuration (Figure 5.21) allows the fuel assembly to remain close to the electrodes at all times without touching them. Contact between the fuel and electrodes is prevented by placing the charge in a perforated basket located between the electrodes and electrically insulated from them (Figure 5.22). As a charge dissolves and moves downward, it takes the shape of the electrode cavity and always remains close to each electrode providing a low resistance path for current flow. The cathode is extended at the bottom to a position under the anode to ensure against a slowly dissolving tip on the charge limiting the rate of downward movement.

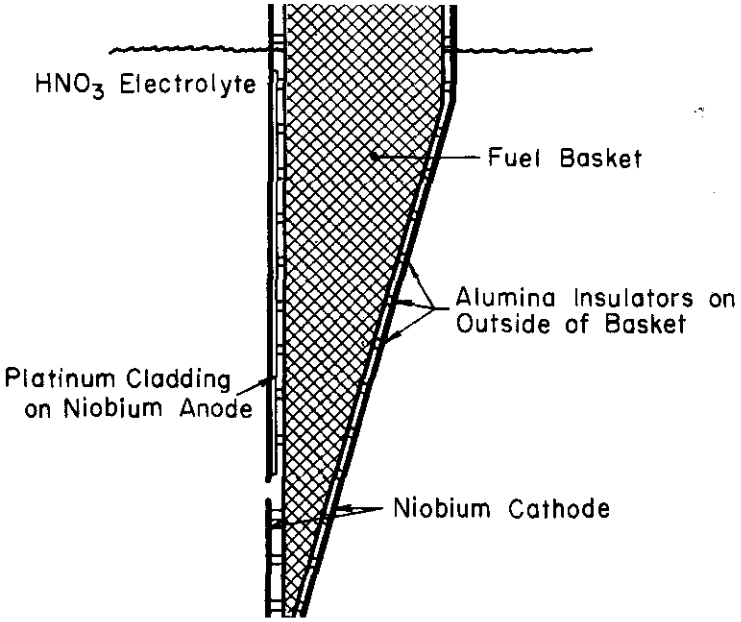

FIGURE 5.21 Electrode Configuration

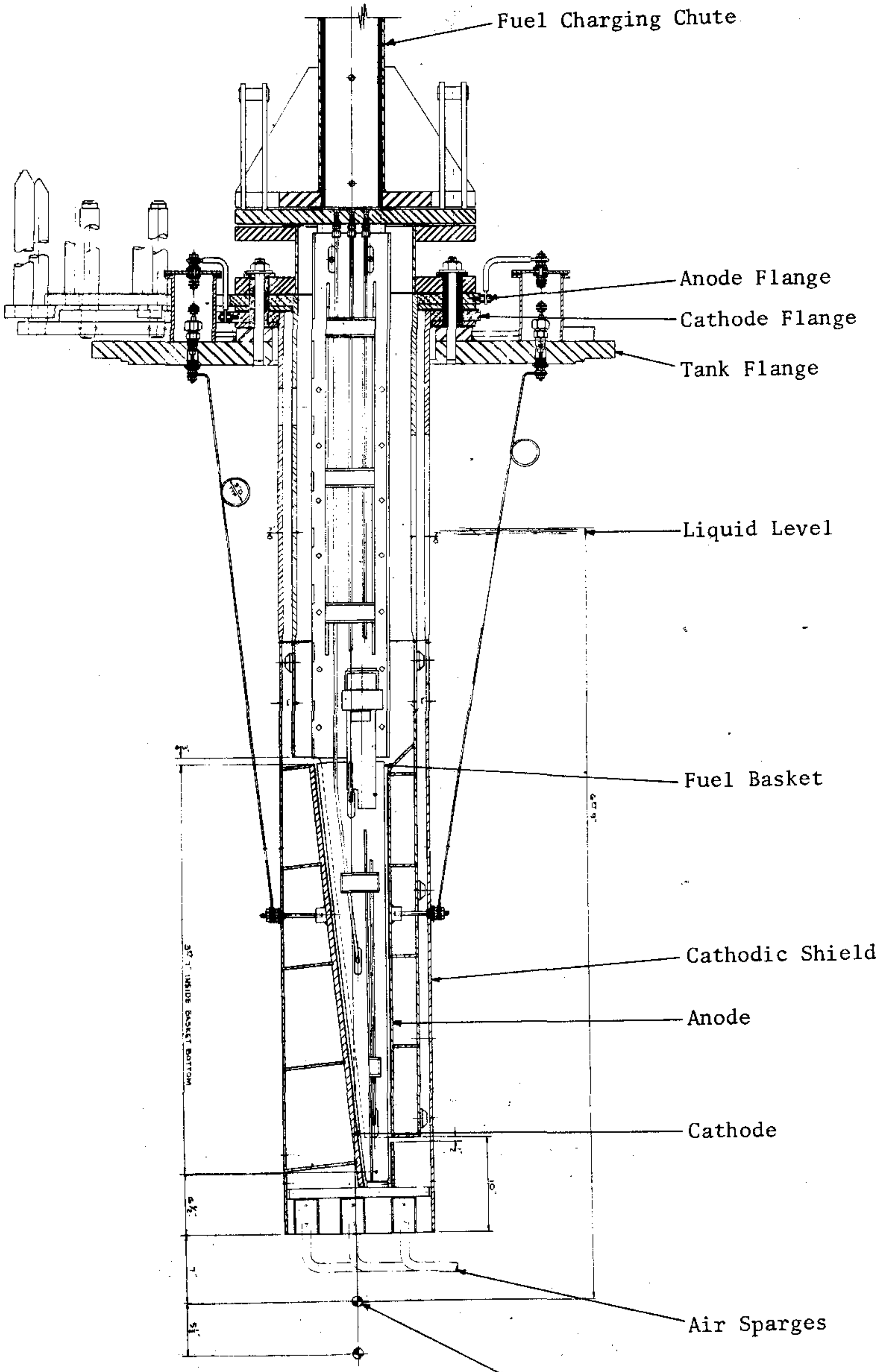

FIGURE 5.22 Electrode Assembly of the Electrolytic Dissolver

The active dissolution zone, which is theoretically restricted vertically to the platinum-clad area of the anode and is laterally confined by the shape of the fuel basket, is 19 in. wide, tapers from 5½ in. to 1 in. thick, and is approximately 3½ ft deep.

Fuel Basket

The fuel to be dissolved is vertically supported between the two electrodes by an insulating basket. The backet (Figure 5.23) consists of ceramic alumina insulators supported on a nondissolving metal frame and has an open area of about 50%.

Certain metals can be considered to be inert to anodic dissolution in nitric acid because a nonporous oxide film is formed. Electrolytically these inert metals are rectifiers in that they allow current flow as a cathode but not as an anode. If the anodic potential is sufficient, the oxide films can be broken down, and the resulting current flow will cause severe corrosion of the base metal. As shown in Table 5.6, both niobium and tantalum are reported to have high breakdown potentials and are suitable metals for construction of the basket frame. Titanium forms a similar oxide layer, but the breakdown potential is too low for practical use. Contrary to reported values, studies at Savannah River indicate that significant amount of current will not flow from niobium anodes at potentials up to 100 volts in HNO_3 solutions ranging from 0.1 to 10M. Although tantalum has a higher breakdown potential, the basket frame was fabricated from niobium because of its lower cost. An all-columbium fuel basket was fabricated to replace the ceramic basket if structural failure

TABLE 5.6

Breakdown Potential for Anodically Passive Metals

Material	*Breakdown Potential,*[a] *volts*
Titanium	10
Niobium	50
Tantalum	180

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[a] Potential required to pass current of 1 mamp/cm^2 in 70% HNO_3 at 25°C when as an anode.

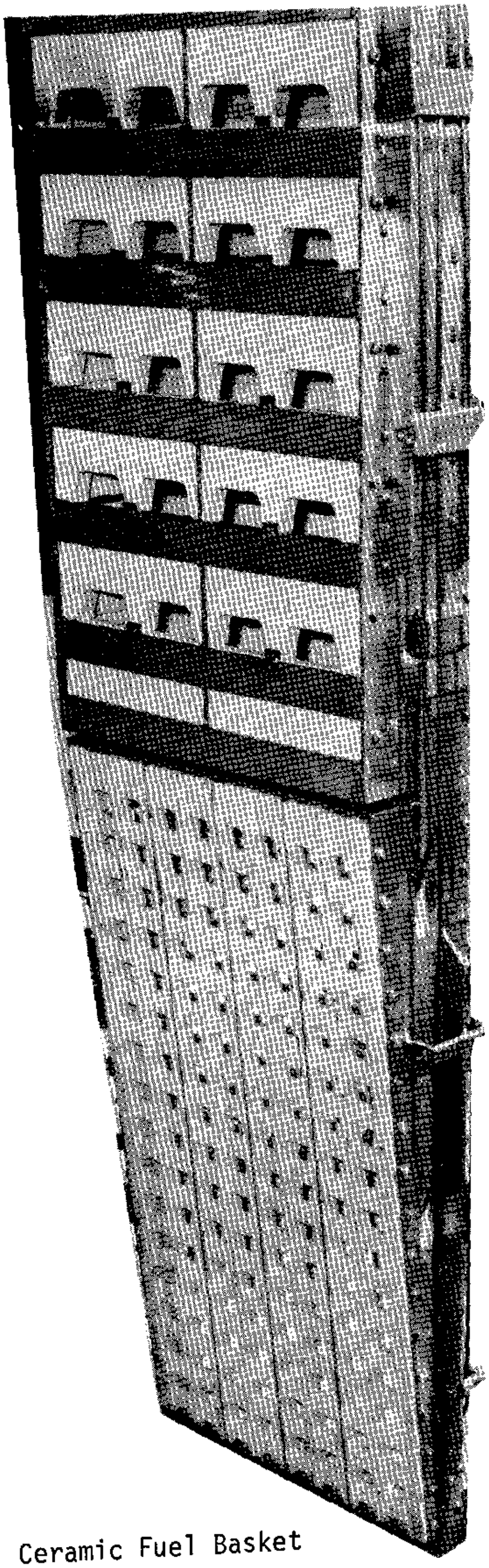

FIGURE 5.23 Ceramic Fuel Basket

of the brittle ceramic components should occur. The lower section of the metal basket (Figure 5.24) consists of louvers that prevent pieces of the charge from falling through openings and touching the electrode. The rectifying characteristic of niobium causes the metal basket to become anodically charged, and when intimate metallic contact is made with the dissolving fuel it discharges. Electrical arcing occurs at the point of discharge and causes some damage to the metal basket and fuel as evidenced during performance test with the dissolver.

Trash Basket

The trash basket is used to ensure critically safe geometry throughout dissolution for a variety of fuel containers, to retain short (loose) segments of fuel tubes at the end of dissolution, and to retain insoluble foreign material (such as thermocouples) present in the fuel. The trash basket has its lower section tapered to fit into the dissolver basket and a straight upper section. The lower section is fabricated entirely of niobium metal and is perforated on both sides with holes 1/8 in. in diameter to attain ∿90% open wall area. Each section is partitioned into wells that facilitate a variety of charging geometries. Nuclear safety analyses must be made for each type of fuel charge and trash basket geometry.

Cathodic Shield

Corrosion caused by stray currents is eliminated by enclosing the back and the bottom of the anode in a shield at cathode potential (Figure 5.22). Development studies with a prototype dissolver showed that the stainless steel dissolver tank could be anodically corroded by stray currents. Localized anodic corrosion of the tank was noted after long operation, particularly on the bottom behind the cathode. The cathodic shield allows the tank to "see" only one electrode, and all current flow is confined within the electrode assembly. An alternative method of protection from corrosion would be to connect the tank to the cathode. Cathodic shielding is used because stainless steel corrodes cathodically (about 1/10 of the anodic rate). This cathodic corrosion should be small and should be uniform over the tank. A summary of corrosion rates experienced while testing the various methods of protection has been previously reported.[13]

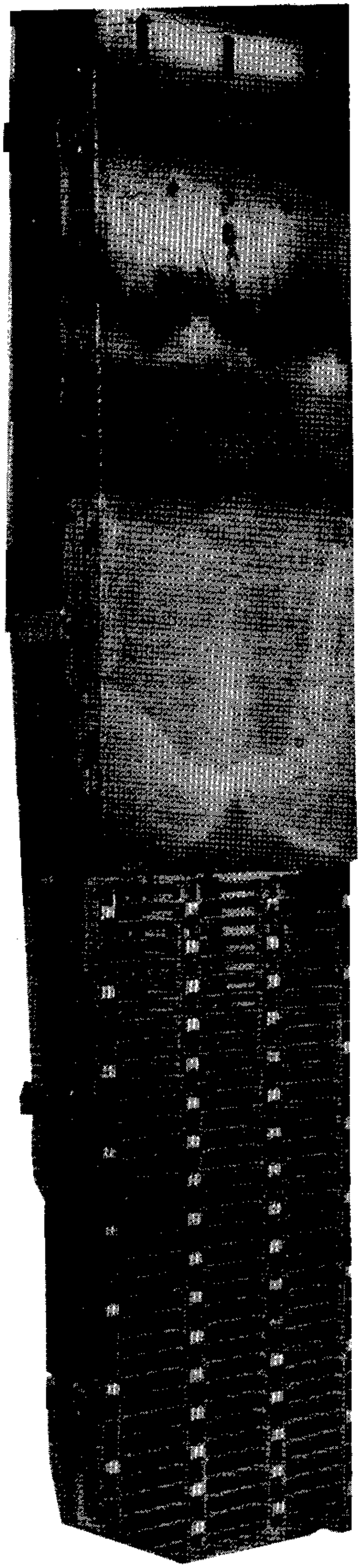

FIGURE 5.24
Metal Fuel Basket

Power Supply

Power is supplied to the dissolver by a 600-kw Westinghouse Transformer-Rectifier that produces 10,000 amps of direct current from a six-phase, double-wye circuit containing a total of 96 silicon diodes. Power controls can automatically maintain either constant current or voltage. Electrical connection in the remote production facility is made by two 3 x 5-in. aluminum buses. The buses are bolted to tabs on the flanges that support each electrode. The electrode flanges are composed of two pieces: 1) a ½-in. columbium plate that is welded to the vertical niobium electrode for support, and 2) a 1-5/32-in. thick aluminum insert that laterally distributes the current and is mechanically connected to the lower niobium plate. The aluminum and niobium contact surfaces were painted with gold to prevent atmospheric oxidation; and "Conducto-Lube,"* which is micronized silver in a petroleum spreader, was applied between them to increase contact area in case of surface irregularities.

Sludge Removal System

Two concentric water spray rings and a steam jet pump were installed in the bottom of the dissolver tank to remove sludge. Development studies[13] showed that during electrolytic dissolution, less than 2 wt % of the stainless steel (∿7 wt % for cermet fuel) fell to the bottom of the dissolver as very small metallic grains to form a sludge.[13] Conversely, 85 wt % of zirconium is anodically oxidized in the form of an insoluble ZrO_2 film, which spalls away from the base metal and accumulates at a rate of 15 gal/100 lb of zirconium processed. The characteristics of the two types of sludge are shown in Table 5.4.

Sixteen nozzles, which each supply 10 gal/min at 60 psig in the form of a flat 160° spray, are installed on the bottom of the concentric spray rings (5 inner and 11 outer).

Before removal, the sludge is rinsed and agitated by a dilute acid spray. The sludge is then flushed toward the suction of the steam jet pump, which is located on the low side of the sloped dissolver bottom, by intermittent water spraying. The sludge is continuously removed as a 1 wt % slurry at a rate of 100 gal/min. Multiple cycles of intermittent spraying are required to remove any sizable amount of sludge that may occur with each zirconium dissolution or after numerous stainless steel dissolutions.

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* Registered tradename of the Conducto-Lube Company, Portland, Oregon.

Heat Removal System

The dissolver vessel is equipped with a heat removal system since almost all of the power required to operate the dissolver is dissipated as heat in the nitric acid electrolyte. Additional heat is generated by fission-product decay in the fuel assembly. If the heat is not removed, the acid will boil and blanket the electrodes with vapor, causing a rapid increase in resistance. Lowering the temperature of the bulk electrolyte permits increasing the amount of current that can be supplied for dissolution.

A total heat transfer surface of 600 ft^2 is provided by the outer tank jacket and a double set of 2-in. cooling coils. The bulk electrolyte is agitated by 10 scfm of air which is distributed through the nozzles on the sludge spray rings. The electrolyte is forced upward over the electrodes and fuel assembly by injecting 3 scfm of air into the solution at each of three points below the electrode assembly: behind the anode, behind the cathode, (both anode and cathode contain circulation holes and are inside the cathodic shield) and into the center of the electrode cavity. The effective density of the solution within the electrode assembly is decreased below that electrolyte outside the electrode and is displaced by it. The lighter solution flows upward and out of the electrode assembly through circulation ducts cut into the top portion of the electrodes. Although the current density of the electrodes of the dissolver is not expected to be above 2000 amp/ft^2, operation of the prototype dissolver equipped with a similar heat removal system was successfully demonstrated at 3500 amp/ft^2.

Sludge Tank

The electrolytic dissolver sludge tank is a 6-ft high by 6-ft diameter vessel constructed of 304L stainless steel. The vessel is equipped with an inlet jumper from the dissolver and a decant jet out leg positioned ∿3 ft off the vessel bottom. Also included is a liquid level monitor and a specific gravity monitor.

Following a transfer of sludge from the electrolytic dissolver, the slurry is allowed to stand for solid settling. The supernate is subsequently jetted to a vessel for neutralization before transfer to the waste tank farm. When the tank is filled with sludge and allowed to dry, it will be removed from the canyon for disposal.

5.3.8 Electrolytic Dissolver Instrumentation and Interlocks

The guides outlined in Section 5.3.3 of this manual must be followed to avoid equipment damage, contamination dispersion, and product loss from electrical shorting, electrode corrosion, chemical explosion or nuclear excursion.

Accordingly, the dissolver is instrumented and interlocked to facilitate monitoring as well as automatic power shutdown if the necessity arises. The alarm and interlocks for the dissolver are listed in the following table.

Electrolytic Dissolver Alarm and Interlock System

Condition	*Alarm*	*Interlock*
Cooling Coil-Low Flow	X	
High Electrolyte Temp.	X	X
Tank Sparge, Low Flow	X	X
Cathode Sparge, Low Flow	X	X
Anode Sparge, Low Flow	X	X
Basket Sparge, Low Flow	X	X
Jacket Cooling Water High Pressure	X	
Jacket Cooling Water Low Flow	X	
Boron Detector	X	X

As previously indicated (Section 5.3.6), a soluble poison, boric acid, is added as a secondary nuclear safety control in the dissolution of oxide fuels. The presence of the poison in the dissolver must be established before each dissolution to ensure safe operation. A special system of instrumentation, controls, and interlocks is provided to monitor the addition of reagents and confirm the presence of the required concentration of soluble poison (Figures 5.25 and 5.26). These interlocks prevent the operation of the dissolver in the absence of the poison.

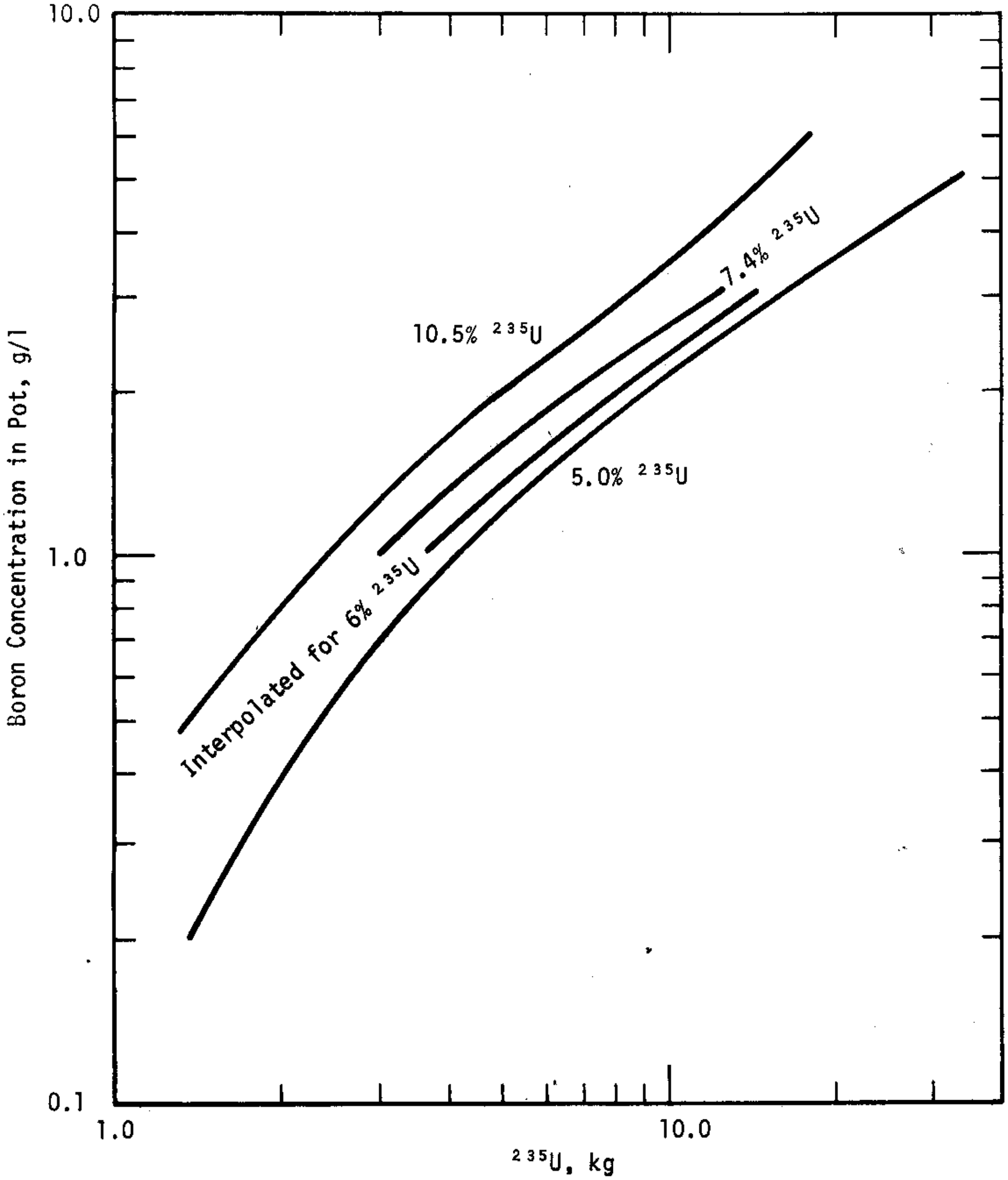

FIGURE 5.25 Minimum Boron Concentration in Dissolver Pot as a Function of Mass of ^{235}U to Keep $\Delta k_{eff} > 0.10$ in an Expanding Sphere Regardless of Uranium Concentration

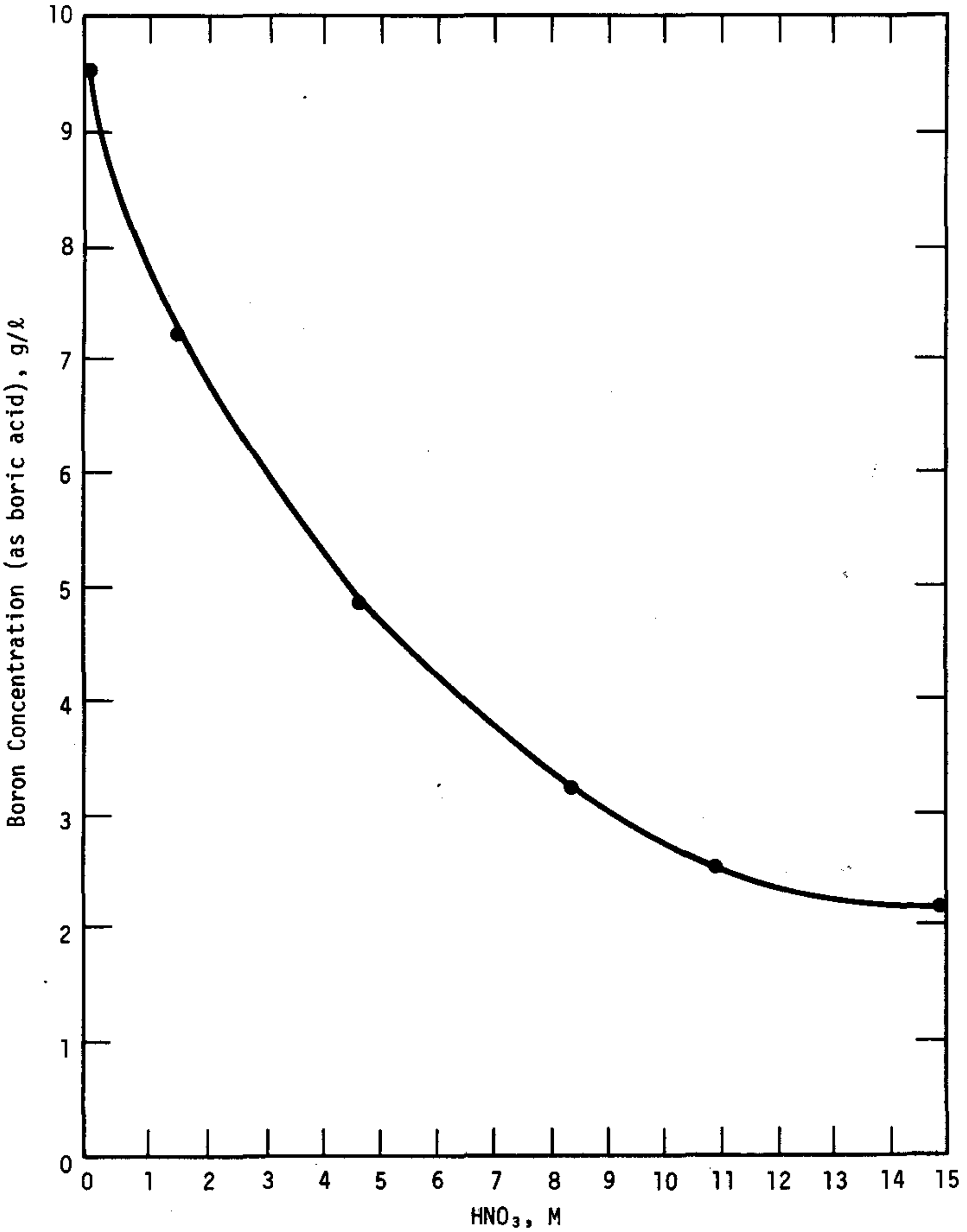

FIGURE 5.26 Solubility of Boric Acid in Nitric Acid at 25°C

Addition of reagents to the dissolver may be made only under controlled conditions. Electrolyte containing boric acid is added only through one specified head tank. All other connections to the chemical addition line to the dissolver are either severed or blanked with nuclear safety blanks. Nuclear safety blanks are installed in the cooling water line to the dissolver chute and in the process water line to the pot spray system to ensure that water does not enter the dissolver from these sources. Electrolyte is prepared in a specified cold feed tank and delivered to the designated head tank through a header isolated for this purpose.

An instrument in the head tank indicates the amount of boron in all electrolyte dropped to the dissolver. The instrument consists of:

1) A neutron source (two Ci Pu-Be),
2) A neutron detector (a BF_3 tube) located 5 in. from the source, and
3) The electronics required to indicate boron concentration in the range of 2 to 3 g/ℓ with an accuracy of ±0.2 g/ℓ.

The boron detector is interlocked with a control valve in the only chemical addition line to the dissolver and with the electrical supply circuit for the dissolver. Any signal from the detector outside established control points closes the control valve and shuts off the dissolving current. The boron detector interlock system is physically disconnected when poisoned electrolyte is not required; the disconnecting operation is administered the same way as nuclear safety blanks. A visual panelboard signal indicates activation of the boron detection system.

5.3.9 Raw Metal Solution and Waste Handling

The solutions resulting from electrolytic dissolution of stainless steel are corrosive to stainless steel under the conditions existing in an evaporator. The heating coils in SRP evaporators are particularly vulnerable to attack. Consequently, evaporation of raw metal solutions or of waste solutions, such as 1AW, from the recovery process for stainless steel fuels should be avoided. First cycle waste (1AW) from these fuels is normally neutralized and discarded as high-level waste without evaporation.

The corrosion rate of stainless steel in boiling nitric acid is accelerated by the presence of hexavalent chromium, Cr(VI), in the solution. The stainless steel cladding of most power fuels contains significant quantities of chromium; Cr(VI) is formed by the reaction between noncorrosive trivalent chromium, Cr(III), and HNO_3 at elevated temperatures. The degree of conversion of Cr(III) to Cr(VI) depends on the temperature of the solution and the time at elevated temperature. Prolonged boiling, as in an evaporator bottom, can result in practically complete conversion. Therefore, the concentration of total chromium, regardless of valence, can ultimately determine the corrosion rate in an evaporator.[14,18]

Traces of chromium routinely appear in process solutions from nitric acid corrosion of process vessels. Corrosion of evaporator coils by Cr(VI) from this source is inherent to the process. The lower limit of detection by colorimetric methods is about 0.001 g/l; at this concentration the corrosion due to Cr(VI) is no worse than the corrosion due to HNO_3.[19]

The corrosion of stainless steel is also enhanced by intergranular attack at the high concentrations of iron and nitric acid produced in evaporator bottoms.[18,19]

Corrosion rates of stainless steel surfaces in the electrolytic dissolver itself are significantly lower than those in an evaporator. The lower operating temperature of the dissolver is inadequate to oxidize Cr(III) significantly. Also, the oxides of nitrogen produced at the dissolver electrodes effectively maintain chromium in the reduced state.[20]

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6. HEAD-END TREATMENT

6.1 GENERAL

In head end operations, the raw metal solution from the dissolver is clarified and adjusted as required for feed to the first cycle of solvent extraction. A manganese dioxide precipitation may also be made if required to remove zirconium and niobium activities from the solution and to reduce the specific activity of fission products to tolerable levels. Formation of a precipitate for clarification or decontamination is commonly referred to as a "strike"; hence the several operations of this type performed in head end operation have acquired the following designations:

- Gelatin strike: Treatment of the solution with gelatin to coagulate and remove silica impurities.
- Combined strike: Simultaneous formation of silica and MnO_2 precipitates for removal of silica and fission products.
- Double strike: Sequential treatment of the solution with MnO_2 precipitated and removed first, followed by gelatin treatment.

The MnO_2 is normally formed by the "reverse strike" method of oxidizing manganous nitrate with potassium permanganate. "Reverse" in this sense refers to the order of addition of reagents, which is chosen to avoid oxidizing the volatizing fission product ruthenium.

The individual process operations in head end are 1) concentration, 2) precipitation, 3) centrifugation, and 4) cake disposal. These steps are described in detail in the following section. The head end process is shown schematically in Figure 6.1, and the equipment used and its arrangement is shown in Figure 6.2.

6.2 PROCESS DESCRIPTION AND CHEMISTRY

6.2.1 Concentration of Raw Metal Solution

Raw metal solutions ordinarily contain high concentrations of aluminum, from chemical dissolution of aluminum-clad fuel, or of iron, chromium, and nickel from electrolytic dissolution of

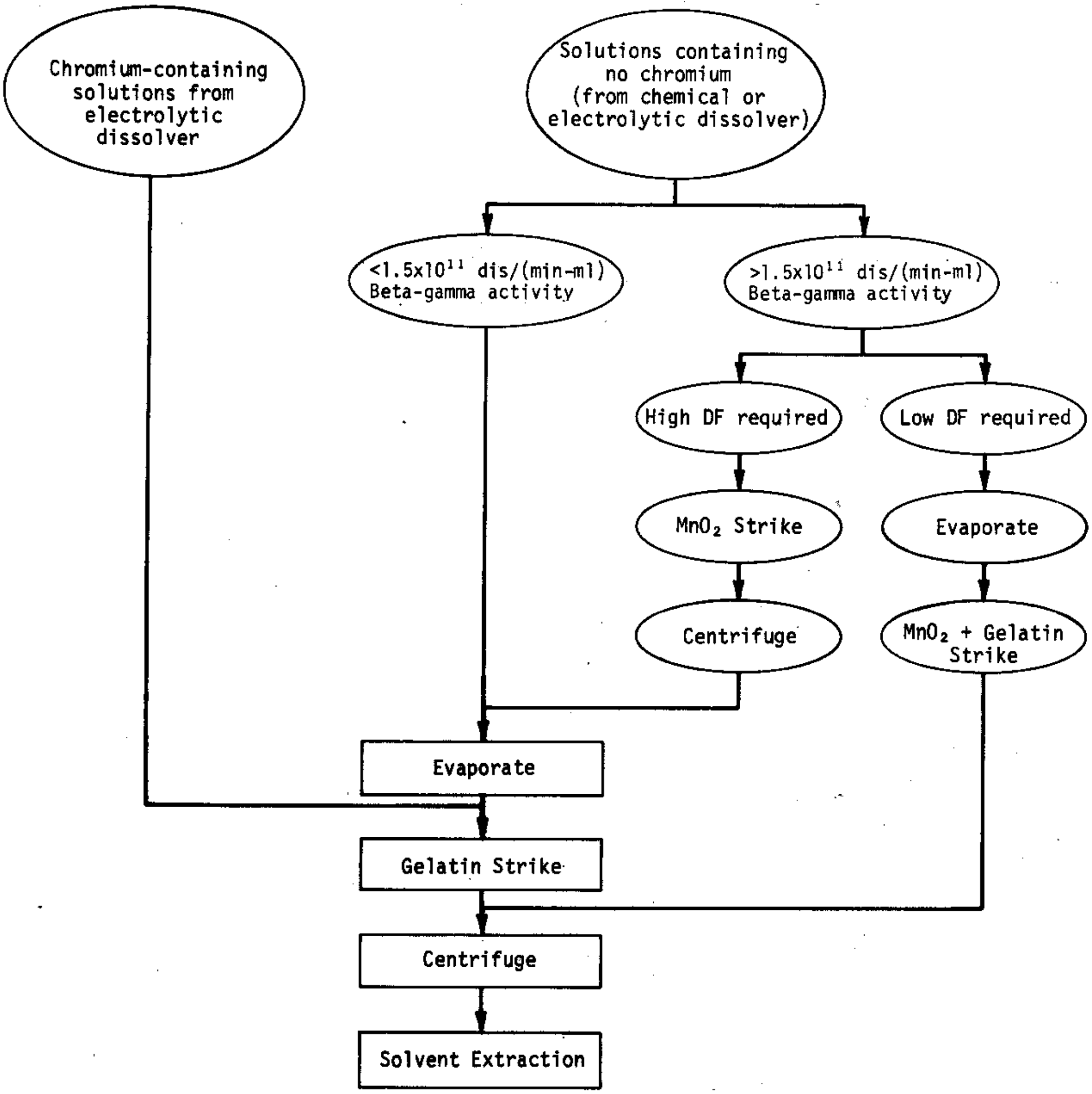

FIGURE 6.1. Head-End Process Flow Diagram

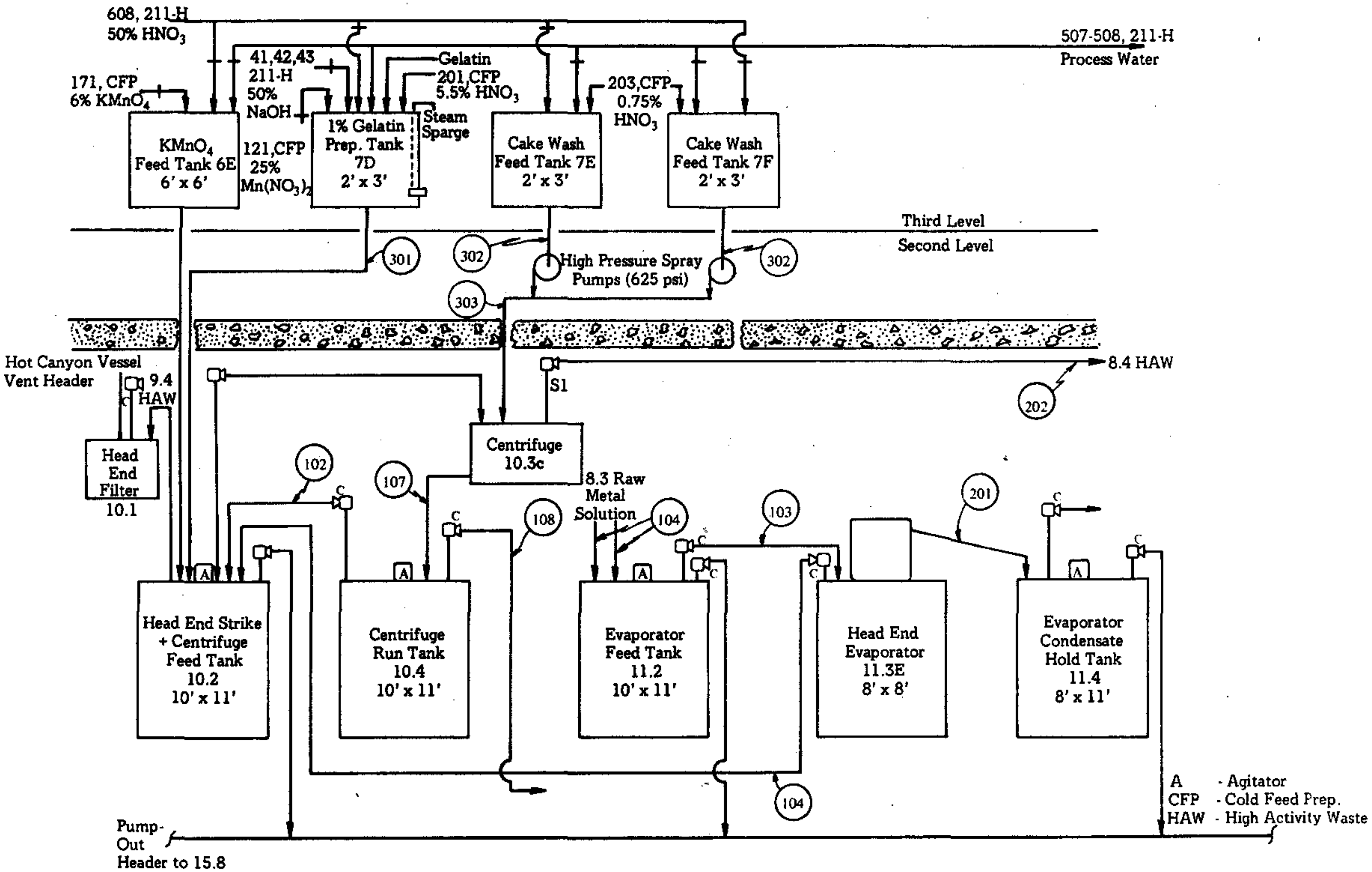

FIGURE 6.2. Head-End Process Equipment Layout

stainless steel.* The latter class of solutions must be fed to solvent extraction without concentration, since the hexavalent chromium present would cause severe corrosion of stainless steel evaporators. Aluminum-bearing solutions are normally evaporated to an aluminum concentration of about 1.8M; the solution is subsequently diluted by transfer with jets and by strike solutions before solvent extraction.

Evaporation is performed in a standard canyon evaporator. Normally a batch of solution from the dissolver is transferred into the evaporator feed tank; the evaporator is then filled from this tank, and brought to boiling. The balance of the feed solution is fed into the evaporator as required to maintain a nearly constant volume; when the entire batch has been fed, evaporation is continued to the desired concentration as determined by specific gravity measurements. The concentrate is then cooled and jetted to the strike tank for further treatment. Overheads are collected and further decontaminated by another evaporation and sent to acid recovery.

Safety concerns related to evaporation are treated in Section 6.3.

6.2.2 Precipitation

Gelatin Strike

Silicon is present in aluminum-clad fuels as an impurity in the aluminum and as a product of nuclear transmutation of the aluminum by neutron irradiation. On dissolution of the aluminum in nitric acid, silicon forms colloidal silica or polymeric silicic acids. These substances collect at the phase interface in solvent extraction, cause emulsions, form precipitates, and lower the operating efficiency of the extraction process.

Gelatin reacts with silica and polysilicic acid to form an insoluble complex. This probably involves hydrogen bonding between the peptide nitrogens of the gelatin and the siloxane oxygen of the polysilicic acid, or the silonal groups on the surface of colloidal silica particles,[1] as illustrated here schematically:

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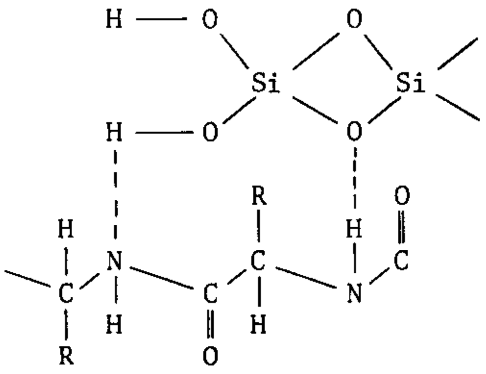
*At the time of writing, little experience had been obtained with the head-end treatment of solutions resulting from electrolytic dissolution of zirconium-clad fuel.



The large molecules thus formed agglomerate and precipitate from solution. The requirements for complex flocculation in a given solution vary and are dependent on the initial molecular weights of the silica species and the gelatin. However, acidic, highly-salted solutions promote formation of silica-gelatin complexes; because silicic acid polymerization increases with increasing acidity and the high salt content of the solution tends to dehydrate the gelatin, making it more reactive toward silica. A reasonably complete precipitation is ensured by using an excess of gelatin; the unreacted gelatin remains in solution but does not affect solvent extraction processing.

Plant experience has shown that gelatin concentrations of about 50 mg/ℓ are effective in removing silica with digestion at 50 to 80°C for 30 minutes or longer.

Combined Strike

The combined strike is used for fuels containing more than 1.5×10^{11} dis/(min-ml) of beta-gamma activity. The feed solution along with any cake washes returned from the previous head end batch is jetted into the strike tank, 10.2. Manganous nitrate is added as a 25% solution to a Mn^{++} concentration of about 0.014M, and the solution is heated to 70 to 75°C. Enough gelatin is added as a 1% solution to give 50 mg gelatin per liter. A 3% potassium permanganate solution is then added at a rate of 10 to 15 lb per minute. The quantity of $KMnO_4$ added is calculated to react with 90% of the manganous ion present, according to the equation:

$$3Mn(NO_3)_2 + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2 + 2KNO_3 + 4HNO_3$$

The nitric acid concentration for this step generally is in the range 1.5 to 2.5M. The resulting slurry, which may contain up to 60 lb of precipitate, is heated at 70 to 75°C for one hour, cooled to about 40°C, and centrifuged. The rate of permanganate addition and agitation are controlled to avoid evolution of ruthenium, as described in Section 6.3. The manganese dioxide precipitate should not be allowed to stand because radiolytic effects dissolve MnO_2 releasing fission products. Partial dissolution of the cake may occur at shorter times with highly radioactive solutions.

The fission products removed by sorption on manganese dioxide are those that form readily hydrolyzed polyvalent ions, chiefly zirconium and niobium. The decontamination factor achieved for these ions with a combined strike is 1.2 to 6; the factor achieved varies inversely with the acidity and aluminum concentration of the solution.[1,2]

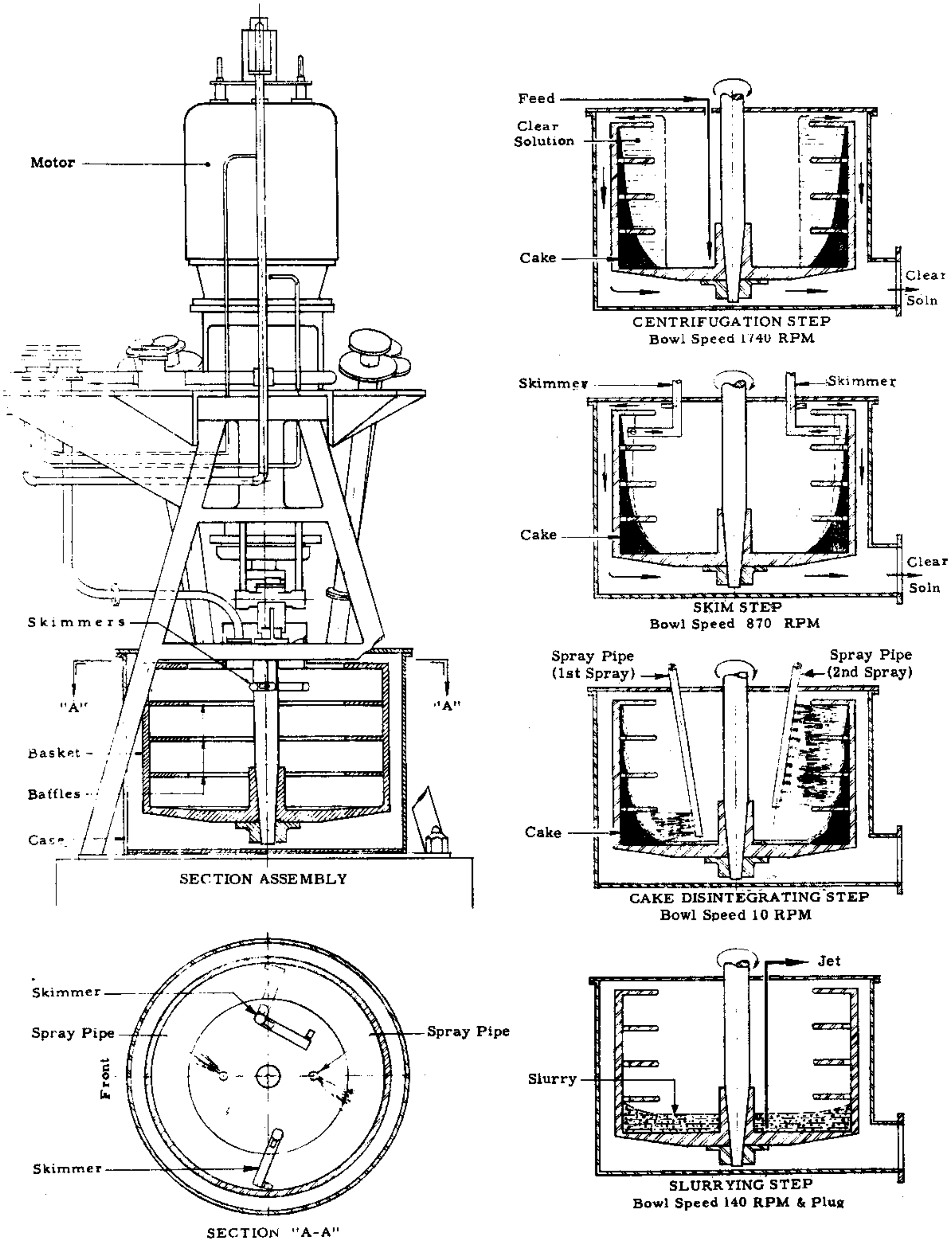
Double Strike

In the double strike, manganous nitrate and potassium permanganate are added to the unevaporated feed in the manner described above. The MnO_2 is removed by centrifugation; the solution is then evaporated and given a gelatin strike. This treatment produces greater decontamination from zirconium and niobium (a decontamination factor up to 20) and is therefore used for solutions of very high specific activity where the benefits to be gained outweigh the additional time and cost required for two separate strike steps.

6.2.3 Centrifugation

The digested solution containing the suspended manganese dioxide and/or gelatin is centrifuged to yield clarified liquid and a cake by the operations described below. Figure 6.3 shows the construction of the centrifuge and illustrates the various steps.

With the centrifuge bowl rotating at 1740 rev/min (1730 times the force of gravity) the slurry is jetted from the centrifuge feed tank into the centrifuge at up to a maximum rate of 12 gal/min for MnO_2 or 20 gal/min for gelatin only. The clarified solution overflows from the centrifuge bowl and flows by gravity to the centrifuge run tank. A feed rate of 12 gal/min provides a residence time of feed solution in the bowl that varies from 6 to 4 min during the period of accumulation of the cake. A feed rate of 20 gal/min provides a residence time of feed solution in the bowl of about 3 min during the period of accumulation of the cake. The cake deposited in the centrifuge bowl occupies a volume of 13 to 20 gal, depending on the type and conditions of the strike, and contains up to 60 lb of manganese dioxide. After all solution has been fed to the centrifuge, the product is removed from the run tank. The final volume of liquid retained in the bowl is then reduced from 40 gal to 6 to 8 gal by



SECTION ASSEMBLY

SECTION "A-A"

CENTRIFUGATION STEP
Bowl Speed 1740 RPM

SKIM STEP
Bowl Speed 870 RPM

CAKE DISINTEGRATING STEP
Bowl Speed 10 RPM

SLURRYING STEP
Bowl Speed 140 RPM & Plug

FIGURE 6.3. Centrifuge

reducing the centrifuge speed to 870 rev/min and skimming to the run tank. The cake is then washed five times to remove the heel of uranium solution by successive dilution and skimming; these washes are also sent to the run tank. Before each wash the cake is dislodged by high-pressure sprays that spray about 20 gal of 0.75% nitric acid into the bowl compartments at 600 psig while the bowl is rotating at 10 rev/min. The wash solution is divided between the two spray pipes by automatically timed valve operation. The first third of the wash solution is sprayed through the pipe that serves the lower compartment; after a time delay, the remainder of the wash solution is sprayed through the other pipe which serves the upper three compartments. When the spray cycle is complete, the slurry is recentrifuged (1740 rev/min), and the wash solution is skimmed *870 rev/min) to the centrifuge run tank. Following the final wash the cake is broken up again by spraying with approximately 20 gal of 0.75% nitric acid (10 rev/min), the speed is increased to 140 rev/min, the centrifuge is stopped, and the slurry is jetted from the bowl to the high-activity waste neutralization tank for disposal.

The washing procedure successively dilutes the uranium solution left with the cake and decreases the uranium loss from about 2% to less than 0.1% of the total amount of uranium fed to the centrifuge. (Figure 6.4). The washes do not remove significant amounts of sorbed fission product activity from the cake if a small amount of acid is present in the wash solution to prevent peptization of the cake. The skim solution and the cake washes are normally recycled to the strike tank to prevent any entrained cake from reaching the solvent extraction process.

The washed MnO_2 or MnO_2-silica-gelatin cakes typically contain 10 to 50 g of uranium. Washed silica-gelatin cakes typically contain 5 to 15 g or uranium.

6.2.4 Disposal of Cake

The cake containing most of the Zr-Nb fission products is received as a slurry in the high-activity waste neutralization tank. The slurry is neutralized with caustic and jetted directly to the high-level waste storage tank. Uranium losses to the cake are determined at intervals by dissolving the cake with sodium nitrite and nitric acid:

$$MnO_2 + NaNO_2 + 2HNO_3 \rightarrow Mn(NO_3)_2 + NaNO_3 + H_2O$$

At the present time, a batch of cake is dissolved to permit sampling and analysis by adding 50% nitric acid to the slurry followed by H_2O and 30% sodium nitrite metered in at about 26 lb/min. If the uranium content is acceptably low, the solution is neutralized by the addition of 50% sodium hydroxide to a pH above 8 and transferred directly to high-level waste storage.

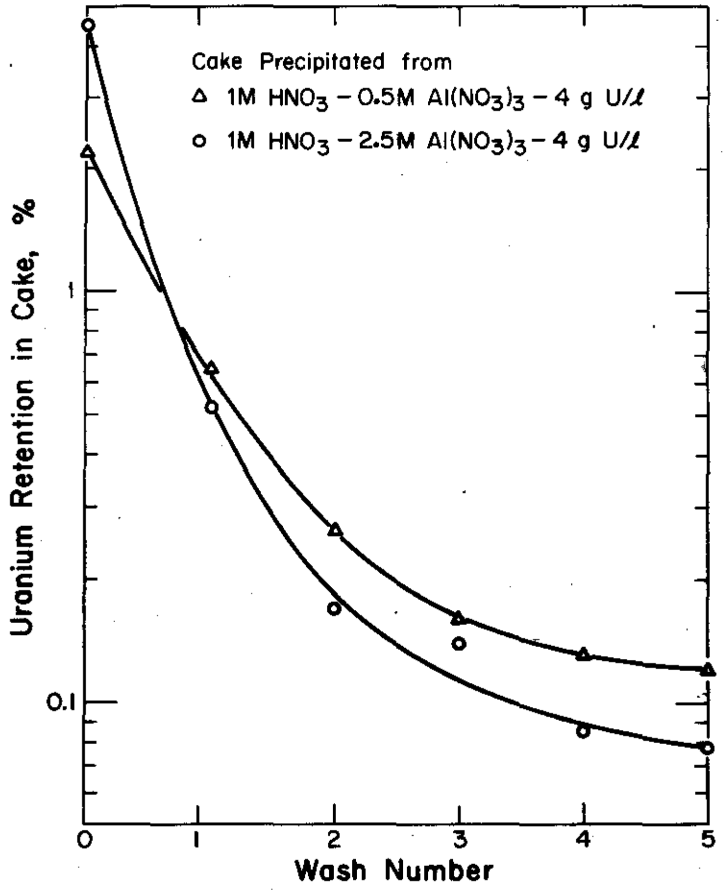


FIGURE 6.4 Efficiency of Cake Washing

6.3 Safety

6.3.1 Items Considered

The potential accident conditions with the head end process are: 1) criticality caused by excessive boildown in the evaporator, by boildown in the strike step, or by precipitation of excess uranium in the cake disposal step, 2) evolution of ruthenium, 3) foaming of the MnO_2 waste slurry and pressurization of the tank during cake dissolution, and 4) pressurization of the evaporator. These hazards and control methods are described below.

6.3.2 Criticality

Evaporation of uranium solutions provides a mechanism for reaching an unsafe ^{235}U concentration in the head end system. The concentration is limited by temperature controls and by the presence of aluminum nitrate, which raises the boiling point as the solution is concentrated. Further, the total quantity of ^{235}U that may be contained in the head end evaporator and its feed tank is limited to ensure that the total in the evaporator does not exceed the safe loading of 336 gram-equivalents[3] of ^{235}U per square foot above any bottom surface on which it might settle if precipitated. (The quantity in the strike tank, which is heated only to approximately 70°C, is not so limited.) The evaporator temperature instrumentation is interlocked to cut off the steam supply so the concentration of fissile material cannot exceed the maximum subcritical concentration for any of the fuels processed. The specific gravity instrumentation alarms and cuts off the steam supply if the specific gravity indicates overconcentration.

The steam supply would also be cut off in the event of cooling water failure to the condenser either by the failure itself or by the high vent temperature which would result. There is little likelihood that these mechanical limitations will actually be needed because the evaporation is conducted under strict procedural control, and the head end operation receives essentially continuous coverage by the assigned operating personnel.

The possibility of overconcentration in the strike step is even less likely because of the lower operating temperature, but equivalent safeguards are still provided. The steam to the tank coils is automatically cut off by high temperature or low liquid level.

The normal quantity of ^{235}U associated with a washed centrifuge cake is less than 50 g. Each cake slurry is mixed with high-activity waste, neutralized with caustic, and transferred to waste storage. The number of slurries in each waste batch is limited to restrict the ^{235}U content.

6.3.3 Evolution of Ruthenium

Although the reverse strike process retains most of the fission product ruthenium in the process slurry, up to 1% of it does escape from the feed solution as volatile ruthenium tetroxide. This volatized ruthenium is highly radioactive and can pass through filters.

Accumulation in process equipment of ruthenium dioxide (which is formed by decomposition of the ruthenium tetroxide) would also complicate replacement and servicing of the equipment. The principal zones of evolution of ruthenium are the head end strike tank, the centrifuge, and the cake disposal tank. The head end tank would evolve relatively large amounts of ruthenium tetroxide if manganous nitrate were absent, if the rate of addition of potassium permanganate were excessive, or if the temperature were higher than about 80°C.

To minimize such evolution, the addition of potassium permanganate is made at a controlled rate and with the maximum agitation, and the temperature of the precipitation and simmer is kept at about 70°C. The off-gases from the head end tank are routed through a ruthenium absorber (described in Section 6.4) which typically removes most of the ruthenium before the off-gases reach the main exhaust manifold for the hot canyon process vessels.

6.3.4 Foaming During Slurry Dissolving

Nitrous acid (formed by the addition of sodium nitrite to dilute nitric acid) decomposes with evolution of nitrogen oxides. Too rapid an addition of sodium nitrite results in excessive gas evolution and foamover of cake slurry to the canyon sump. This problem is minimized by maintaining as low a temperature as possible during dissolution to increase the solubility of nitrous acid and/or nitrogen oxides, and by adding the sodium nitrite at a low rate.

6.3.5 Pressurization of Evaporator

The evaporator could be pressurized by rapid reaction of organic materials, such as solvent entrained in solutions recycled from other steps of the separation process. Consequently, the evaporator temperature is limited to 120°C; the evaporator coil steam pressure is limited to 25 psig. Under these conditions the possibility of excessively rapid reactions is remote.[4] The amount of entrained solvent in evaporator feeds is normally limited to 0.5% to minimize the quantity of organic material in the evaporator; however, dissolver solutions are assumed to be free of organic material. Materials transferred from rerun to head-end must be analyzed to assure the absence of organic material. The evaporator feed tank is emptied as much as possible after each batch to assure that no organic material is present to accumulate.

Evaporation of solutions containing more than trace quantities of potentially explosive materials, such as ammonium salts, if not permitted, as discussed in Section 7.3.4 and 11.3.2.

6.4 EQUIPMENT

6.4.1 Equipment Used in the Process

The equipment used in the head end operation includes facilities for concentrating the raw metal solution, precipitation of silica with gelatin or MnO_2, centrifugation, washing, dissolution, and removal of the cake, and decontamination of vented gases. Table 6.1 shows the head end equipment, services, and instrumentation.

6.4.2 Concentration of Raw Metal Solution

The equipment for concentrating raw metal solution consists of an evaporator feed tank, an evaporator, an evaporator concentrate hold tank, and a condensate collection tank. The feed and concentrate tanks are standard canyon tanks, 10 ft in diameter and 11 ft high; the condensate tank is 8 ft in diameter and 11 ft high. The head end evaporator is a standard canyon evaporator.

6.4.3 Precipitation and Off-Gas Decontamination

The equipment for cake precipitation includes a third-level cold-feed mix tank for makeup of the gelatin solution, third level tanks for makeup of 3% $KMnO_4$ and 25% $Mn(NO_3)_3$ solutions, the strike tank, and the ruthenium absorber. The strike tank is a standard canyon tank, 10 ft in diameter and 11 ft high. It is maintained under a negative pressure with respect to the canyon. The ruthenium absorber is between the strike tank and the vessel vent header. It is a standard canyon tank, 10 ft in diameter and 6 ft high, packed with a knitted stainless steel "demister" screen. The flow of gas through the packing is radial toward the axis of the tank. The large surface area of the packing effectively absorbs any ruthenium and filters entrained activity from the ventilation air which sweeps the liquid surface in the strike tank.

TABLE 6.1

Head-End Equipment Services and Instrumentation[a]

Vessel Identification						*Instrumentation*								*Services*						
No.	*Function*	*EP. No.*	*Process Piping Diagram*	*Instrument Diagram*	*Electrical Diagram*	*Liquid Level*	*Sp. Gr.*	*Temperature*	*Pressure*	*Differential Pressure*	*Radiation*	*Steam Flow*	*Water Flow*	*Sampler*	*Agitator*	*Microphone*	*Coil (s)*	*Recirculating Jets*	*Other Jets (Number)*	*Other*
10.2	Strike Tank	371.14	W163294	W163351	W147421	R, L, H^b	R	RH^c	R, H^b, I	R, M	R	R, I, C	I, C	X	X	X	S_m W	X	C(2)	-
10.1	Ruthenium Absorber	371.1-2	W163294	W162612	W147421	R, H	-	R	R, I		R	R, C	I, C	-	-	-	S_m W	X	C	-
11.2	Evaporator - Centrifuge Feed Tank	372.56	W163294	W146217	W147422	R, I L, H	I, R	R	-	-	R	-	I, C	X	X	X	W	X	mod Z(4) C	-
10.3C	Centrifuge	420.1-1	W163294	W146214 W146216	W147421 W147422	R, H L	-	R	-	-	R	-	-	-	-	X	-	-	S1	skimmer and spray controls
10.4	Centrifuge Run Tank	372.62	W163295	W146307	W147421	R L, H	R	R	-	-	R	-	I, C	X	X	X	W	X	C(2)	-
11.3E	Evaporator Column	301.20	W163295	W148308	W147422	-	-	R, H, I	I	R	-	-	I, C	-	-	-	W	-	-	-
11.3E	Evaporator	311.22	W163295	W148308	W147422	R L, H	R H^c	R, I	S_m R, I	-	R	R, I, C	I, C	X	-	-	S_m W	-	C(1)	-
11.4	Condensate Tank	372.91	W163295	W162255	W147422	R L, H	R	R	-	-	R	-	I, C	X	X	-	-	X	C(1) mod F(1)	-

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a. I, Indicator; H, High Alarm; A, Air; R, Recorder; L, Low Alarm; W, Cooling Water; S_m, Steam, medium, pressure; M, Manometers, 2nd level; X, Present; C, Control Manual.

b. Low alarm interlocked to shut off coil steam.

c. High alarm interlocked to shut off coil steam.

6.4.4. Centrifugation and Cake Disposal

The equipment used for centrifugation consists of standard third-level cold-feed tanks, high-pressure pumps, a centrifuge feed tank, a centrifuge, and a centrifuge run tank. The centrifuge feed tank is a standard canyon tank, 10 ft in diameter and 11 ft high; it also serves as the strike tank during that phase of the head end operation. The centrifuge feed jets are of the modified Z type. The performance curve for this type of jet is the same as the curve for jets used in solvent extraction for ICU service (see Figure 7.41).

Construction and operation details of the centrifuge are shown in Figure 6.3. The centrifuge bowl is 40 in. in diameter and has four horizontal compartments for cake collection and a total dynamic volume of 60 gal. The feed enters through nozzles near the bottom center of the bowl, and the clarified solution overflows from the bowl to the centrifuge casing and discharges by gravity to the centrifuge run tank. The centrifuge run tank is a standard canyon tank, 10 ft in diameter and 11 ft high. The bowl skimmers, when operated, are turned slowly by an electric linkage toward the outside of the upper compartment. As the nozzle enters the path of the rotating solution, the centrifugal velocity of the solution forces the solution through the skimmer pipe to the centrifuge casing. As solution is skimmed out of the upper compartment, solution in the lower compartments flows upward through holes in the baffles enabling the entire bowl to be skimmed. Two spray pipes are used to break up and wash cake. One spray pipe extends to the bottom of the bowl and has four spray nozzles that direct spray into the lower compartment. The other spray pipe has twelve nozzles, arranged so that four nozzles spray each of the upper three compartments. The centrifuge spray pumps are triplex, single-acting, power pumps that develop the required spray pressure of 600 psig. The centrifuge is equipped with a single S-1 type (25 gal/min) transfer jet to transfer cake slurry and bowl rinses to the high-activity waste tank where the cakes are neutralized.

6.5 REFERENCES

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7. SOLVENT EXTRACTION

7.1 GENERAL

The solvent extraction process separates plutonium, neptunium, and enriched uranium from gross contaminants, from fission products, and from each other. The actinides are recovered in aqueous solutions suitable for further processing. The overall process consists of a first cycle for primary decontamination and separation and two second cycles for final decontamination. One second cycle is for uranium; the other is for neptunium or plutonium. Each cycle involves extracting the actinides from an aqueous feed stream into an immiscible organic solvent, scrubbing the resulting product bearing solvent to purify it, and stripping the product back into an aqueous stream. The transfer of uranium, plutonium, and neptunium between phases is controlled by adjustment of the concentration of aluminum nitrate, other metal nitrates, or nitric acid in the feed, and the flow ratios in the mixer settlers.

Neptunium is maintained in the Np(IV) valence state through the entire solvent extraction process. Plutonium valence is adjusted to either Pu(III) or Pu(IV) depending on whether it is to be extracted or not.

The extraction, scrubbing, and stripping are operated as continuous processes with tri-n-butyl phosphate (TBP) diluted with refined kerosene as the solvent. Overall recovery is greater than 99% for uranium and greater than 95% for neptunium. The radiation from fission products is reduced by at least 10^6 for uranium, and by 10^5 for neptunium or plutonium. Fission products and other inorganic contaminants are removed as aqueous waste. The solvent is washed to remove impurities after each pass through the process and reused.

Since procedures may be altered to meet new conditions or to test promising variations, only nominal procedures are given, and the flowsheets should be considered as typical but not fixed. Flow diagrams for typical process cycles are presented in Figures 7.1 through 7.4.

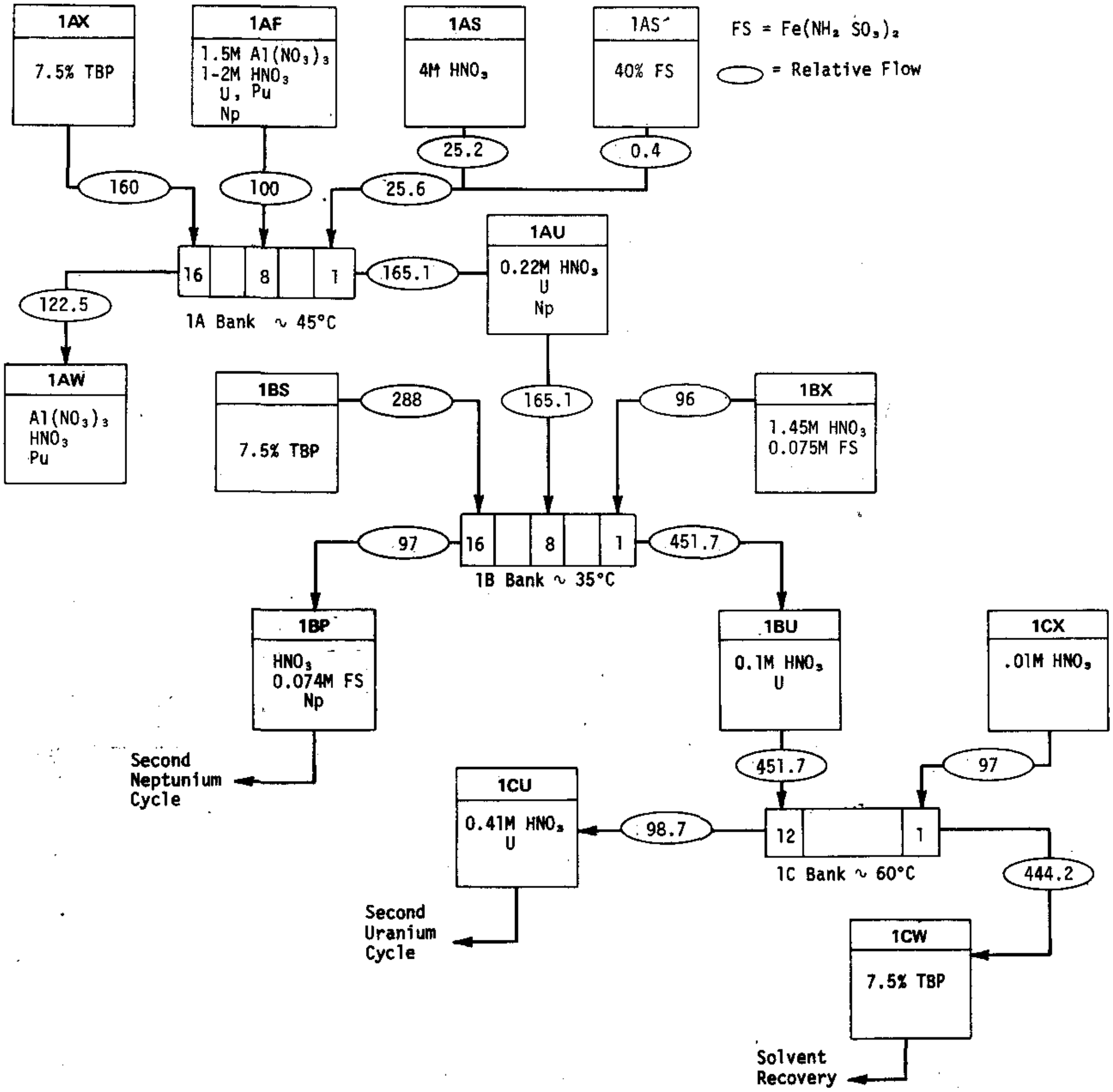


FIGURE 7.1 First Cycle Flowsheet, Modified HM Process for Highly Enriched Uranium

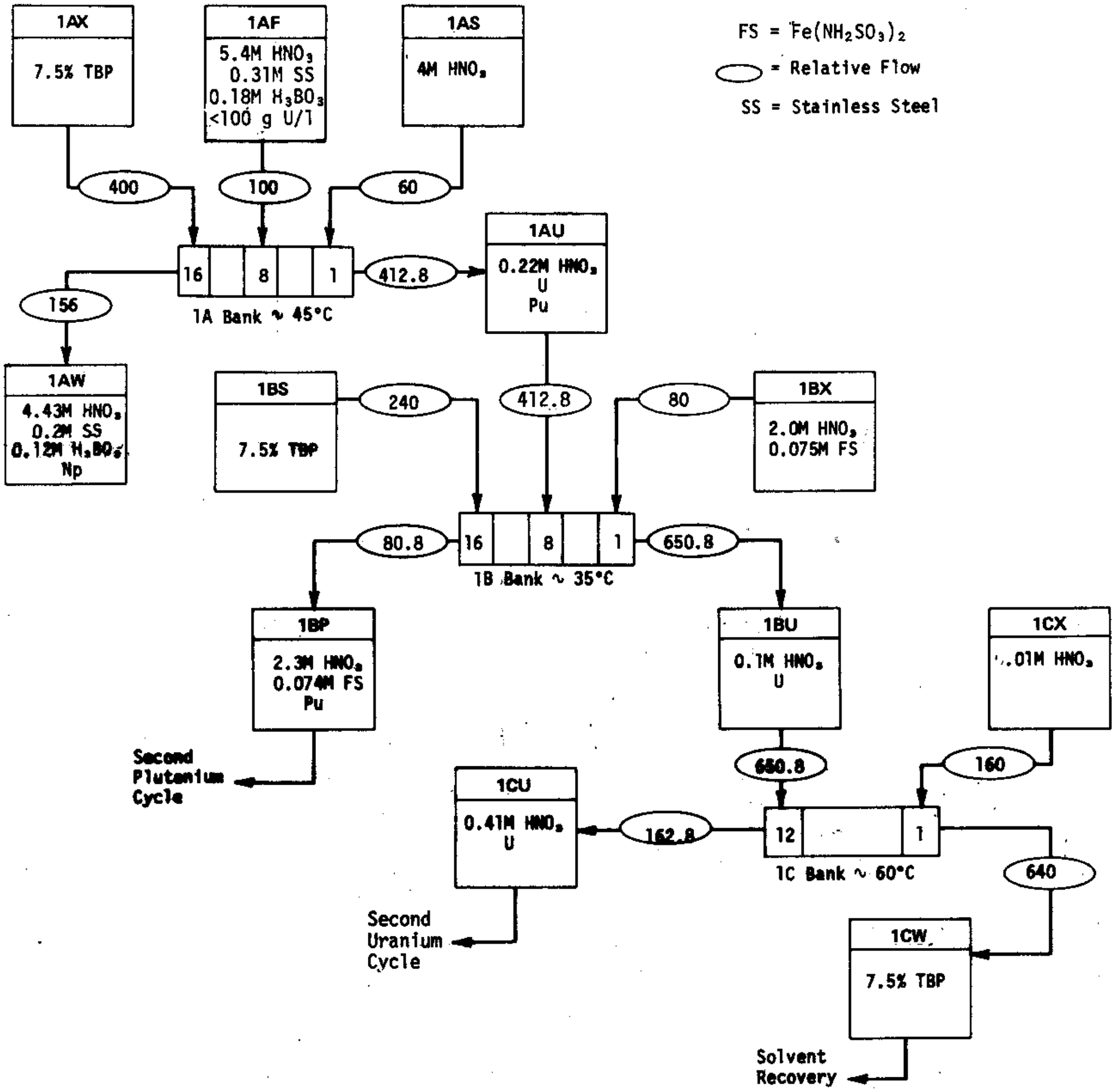


FIGURE 7.2 First Cycle Flowsheet for Low Enrichment Uranium, Modified HM Process

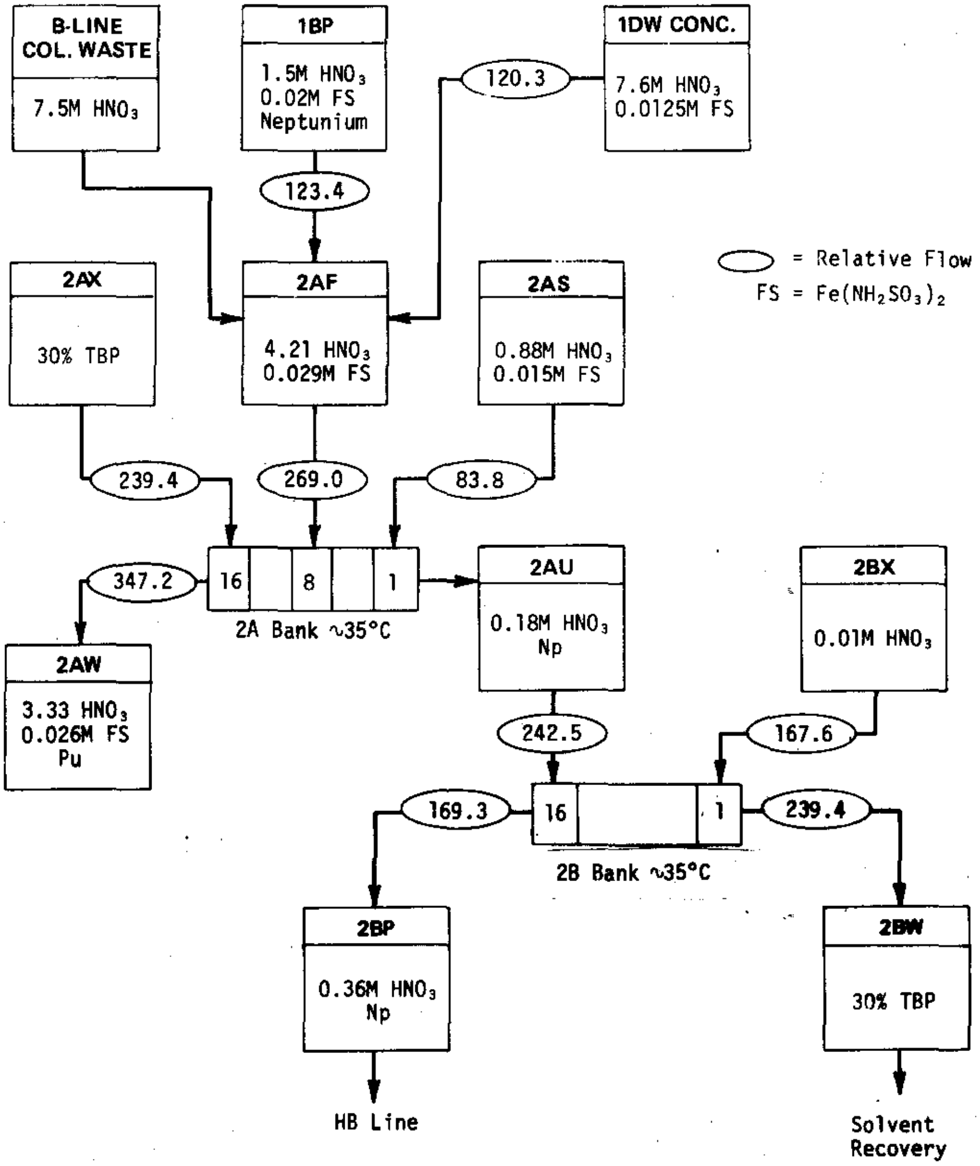


FIGURE 7.3 Nominal Second Neptunium Cycle Flowsheet, HM Process

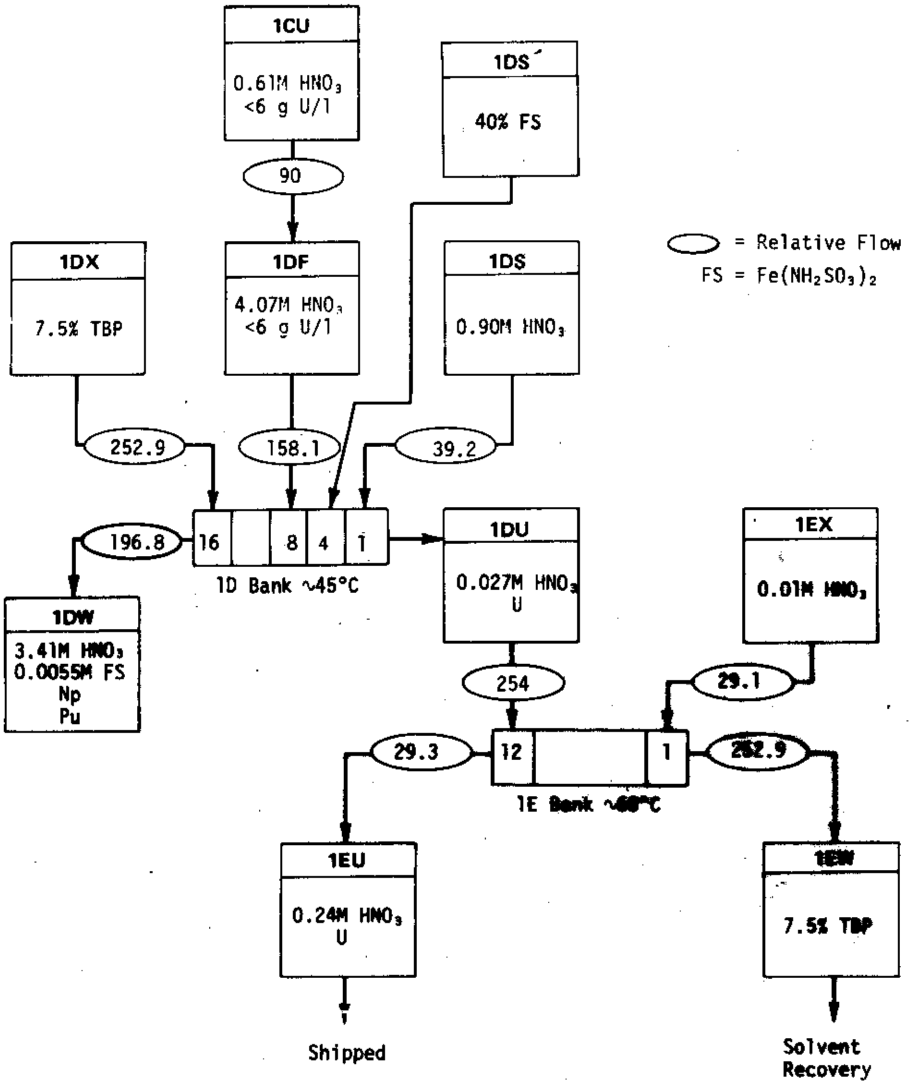


FIGURE 7.4 Nominal Second Uranium Cycle Flowsheet, HM Process

7.2 PROCESS DESCRIPTION AND CHEMISTRY

The solvent extraction separations are conducted in "banks" which are multistage mixer-settlers through which organic and aqueous streams flow countercurrently (see Section 7.4). The 1A, 1D, and 2A banks are divided into extraction and scrub sections. In the extraction section, the product is quantitatively extracted into the organic stream. This stream then enters the scrub stages where less extractable impurities are stripped from the organic phase and removed. The 1B bank, where uranium and neptunium (or plutonium) are partitioned, is also divided into scrub and extraction sections.

The first cycle of solvent extraction uses 7.5% TBP as the extractant and 4.0M nitric acid as the scrubbing agent. In principle, any TBP concentration can be used for uranium purification provided feed concentrations are adjusted accordingly; 7.5% was selected on the basis of experience with this concentration in the second uranium cycle. Aluminum nitrate in the feed solution is formed by dissolution of the original fuel elements and their bundles (see Chapter V). Feed solutions where aluminum is not present, or is dilute, contain nitric acid and other metal nitrates, e.g., iron and nickel. Since aluminum, iron, and nickel are not appreciably soluble in the extractant, they are separated effectively from the product in the first cycle and are retained in the waste stream. Use of nitric acid as the salting agent in solvent extraction minimizes waste volume. Nitric acid is not separated completely from the uranium or neptunium during the cycle, but low concentrations of acid in the product do not interfere with subsequent processing steps.

Nitric acid and some metal ions interact with TBP to form complexes that are soluble in organic solvents such as kerosene. A few of these ions, in order of decreasing tendency to complex are: U(VI), Pu(IV), Np(VI), Np(IV), Pu(VI), HNO_3, Zr(IV), Pu(III), and Np(V). The most important reactions can be represented as follows:

$$UO_2^{++} + 2NO_3^- + 2TBP \rightarrow UO_2(NO_3)_2 \cdot (TBP)_2 \qquad (1)$$

$$Np^{4+} + 4NO_3^- + 2TBP \rightarrow Np(NO_3)_4 \cdot (TBP)_2 \qquad (2)$$

$$H^+ + NO_3^- + TBP \rightarrow HNO_3 \cdot (TBP) \qquad (3)$$

$$Pu^{4+} + 4NO_3^- + 2TBP \rightarrow Pu(NO_3)_4 \cdot (TBP)_2 \qquad (4)$$

When recovery of neptunium from the feed solution is desired, reducing reagents are added to all cycles of solvent extraction to maintain plutonium in the Pu(III) valence state and neptunium in the Np(IV) state. Thus, the small amount of plutonium present will remain with the fission products in the waste streams, and neptunium will be extracted into the TBP.

When recovery of plutonium is desired and the neptunium may be discarded, mild oxidizing conditions are maintained in the first cycle. Plutonium is extracted in the first set (1A Bank) of mixer-settlers as Pu(IV) and separated from uranium in the second set (1B Bank) of mixer-settlers by reducing it to Pu(III); neptunium, if present in the feed, remains as Np(V) and is rejected to the aqueous waste stream.

Valence adjustment for neptunium and plutonium is carried out using ferrous sulfamate.[1] The principal reactions involved are as follows:

$$NpO_2^{+} + Fe^{2+} + 4H^{+} \rightarrow Np^{4+} + Fe^{3+} + 2H_2O \qquad (5)$$

$$NpO_2^{++} + 2Fe^{2+} + 4H^{+} \rightarrow Np^{4+} + 2Fe^{3+} + 2H_2O \qquad (6)$$

$$Pu^{4+} + Fe^{2+} \rightarrow Pu^{3+} + Fe^{3+} \qquad (7)$$

$$NH_2SO_3^{-} + NO_2^{-} \rightarrow N_2 + SO_4^{=} + H_2O \qquad (8)$$

$$Fe^{2+} + NO_2^{-} + 2H^{+} \rightarrow NO + Fe^{3+} + H_2O \qquad (9)$$

The ferrous ion reduces both Pu(IV) and Np(V). The sulfamate ion reacts with nitrite ion formed by radiolytic degradation of nitric acid and prevents nitrite reaction with ferrous ion. (Ferrous ion is, however, oxidized at a significant rate by radiolysis,[2] as described below.)

Plutonium(IV) can also be reduced by hydroxylamine sulfate or nitrate as follows:

$$2Pu^{4+} + 2NH_3OH^{+} \rightarrow 2Pu^{3+} + N_2 + 2H_2O + 4H^{+} \qquad (10)$$

Hydroxylamine can only be used in low nitric acid concentrations since it reacts with nitric acid autocatalytically.[3] The rate of reduction of Pu(IV) by hydroxylamine is slowed by the presence of sulfate, due to the stabilization of Pu(IV) by sulfate complexation. Sulfate ion aids in stripping Pu(IV) from TBP; however, it interferes with subsequent ion exchange processing.

Using strong oxidants (Ce^{4+}, $K_2Cr_2O_7$, MnO_2), both neptunium and plutonium can be oxidized to their respective VI valence states, NpO_2^{2+} and PuO_2^{2+}. These states are extractable. For successful extraction, oxidizing conditions must be maintained with excess oxidant or by addition of sulfamic acid to protect Np(VI) and Pu(VI) from reduction by radiolytically produced nitrite ions. Np(VI) extracts better than Np(IV); however, Pu(VI) is not as extractable as Pu(IV). Oxidation is necessary when high ferric or sulfate concentrations prevent reduction by ferrous sulfamate or when both neptunium and plutonium must be recovered.

Two terms often used in describing solvent extraction processes are the distribution coefficient ($D_o/_a$) and the extraction factor (E_f). If an aqueous solution is mixed with an organic solvent until equilibrium is reached, then the distribution coefficient for Component A ($D_o/_a$) is defined as:

$$D_{o/a} = \frac{\text{Concentration of Component A in solvent phase}}{\text{Concentration of Component A in aqueous phase}}$$

The distribution coefficient does not depend on the relative volumes of the two phases. A term that takes the volume of the phases into consideration is the extraction factor (E_f) (for Component A) which is defined as:

$$E_f = D_{o/a} \text{ (for Component A) } x \frac{\text{volume of solvent phase}}{\text{volume of aqueous phase}}$$

Distribution data, which take into account the mutual effects of temperature, solvent concentration, salting agent concentration, and component concentration, are shown in Figures 7.5 to 7.14.[4-6] The uranium distribution coefficient varies inversely with temperature. The nitric acid distribution coefficient is essentially unaffected by temperature. Specific applications of these data may be found in subsequent sections. It is convenient to express the removal of fission products from uranium in the various steps of the separations process in terms of decontamination factor (DF), or by log DF. These terms are defined as follows:

DF (from Step A to Step B) = Fission product activity per unit of uranium, plutonium, or neptunium at Step A, divided by fission product activity per unit or uranium, plutonium, or neptunium at Step B.

Example: Removal of all but 0.0001%, or one millionth, of the activity originally present corresponds to a DF of 10^6 or a log DF of 6.

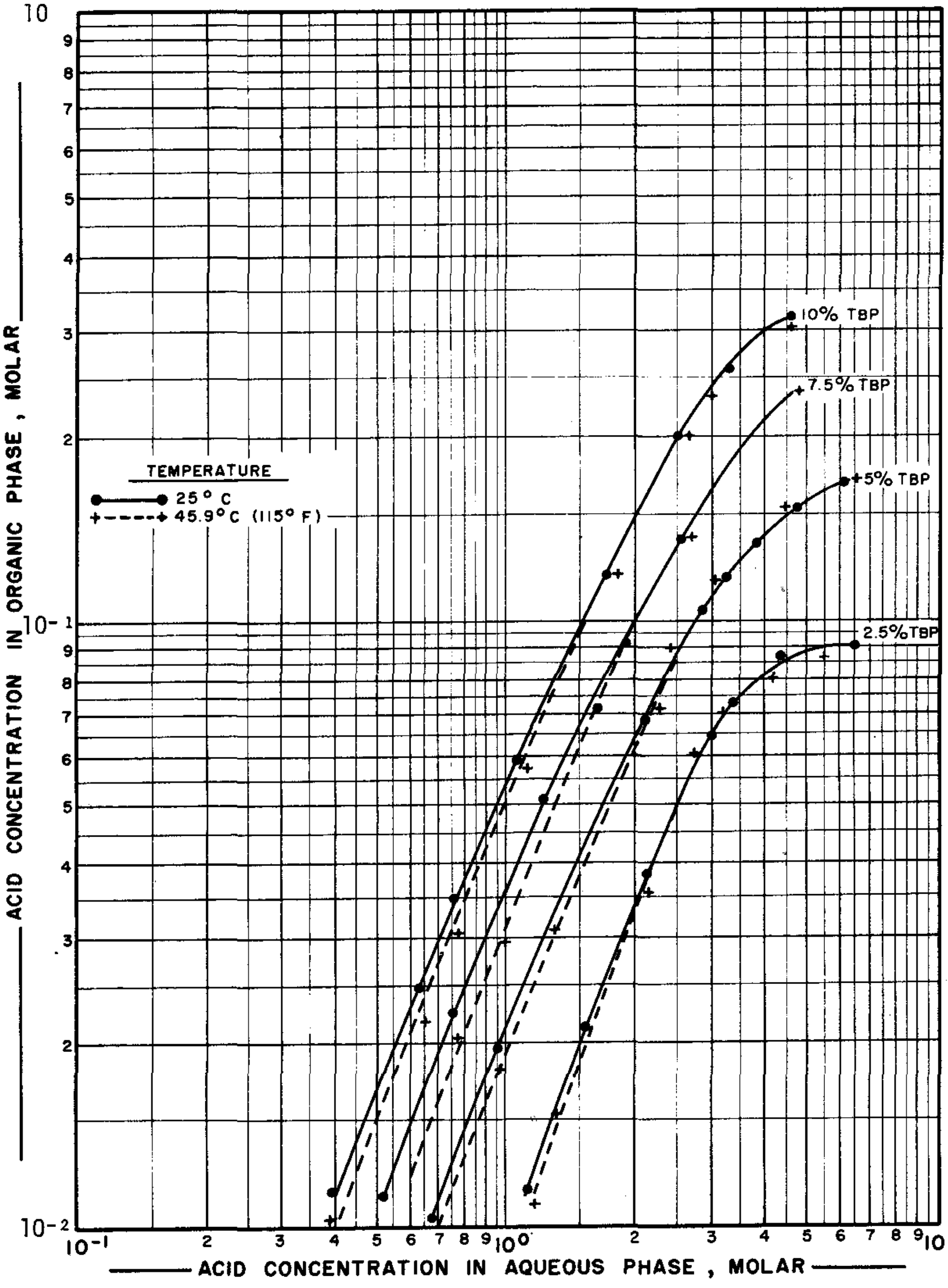


FIGURE 7.5 Nitric Acid Distribution as a Function of Nitric Acid and TBP Concentration

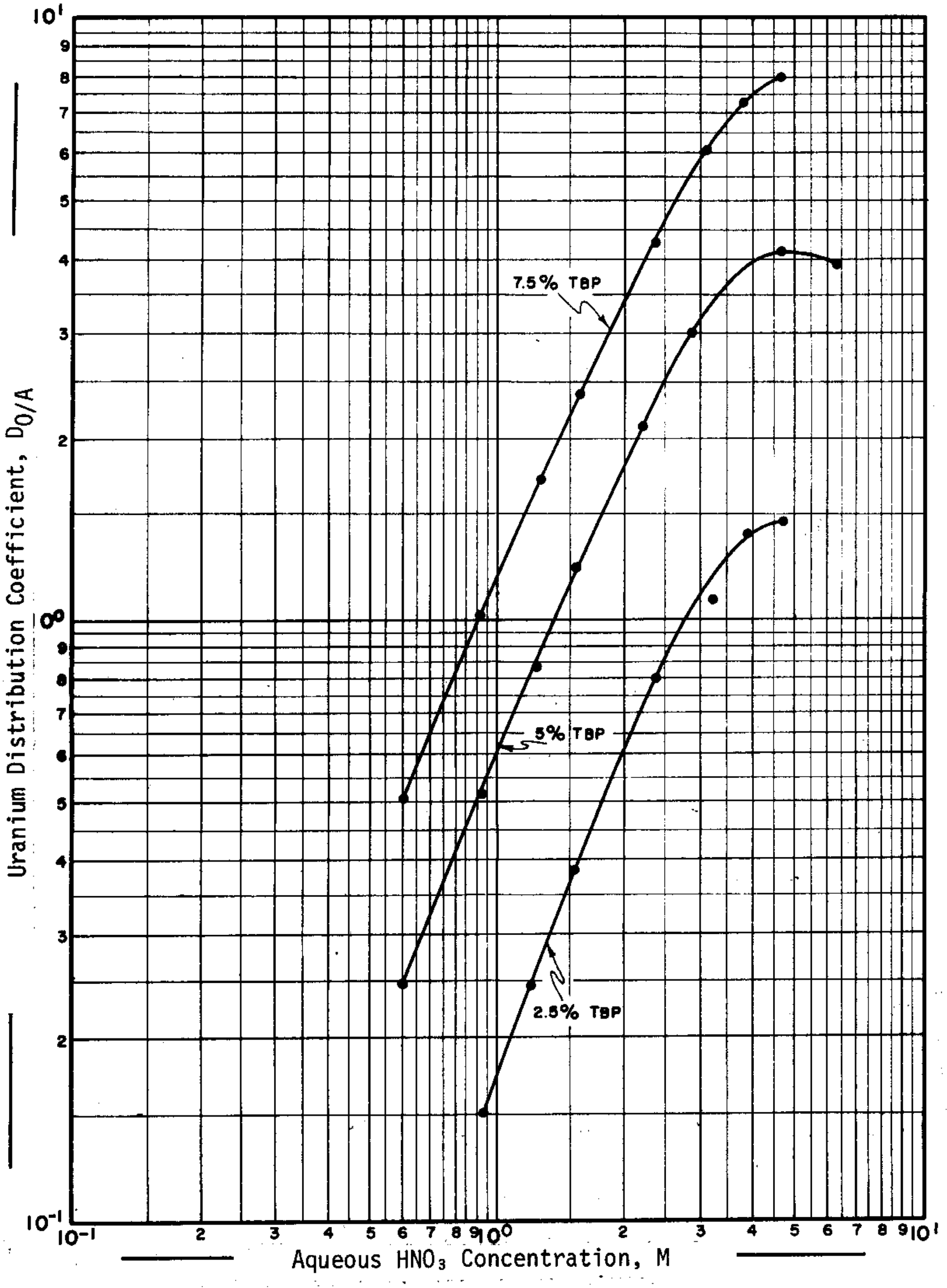


FIGURE 7.6 Uranium Distribution as a Function of Nitric Acid and TBP Concentrations at Low Concentrations of Uranium and at 25°C

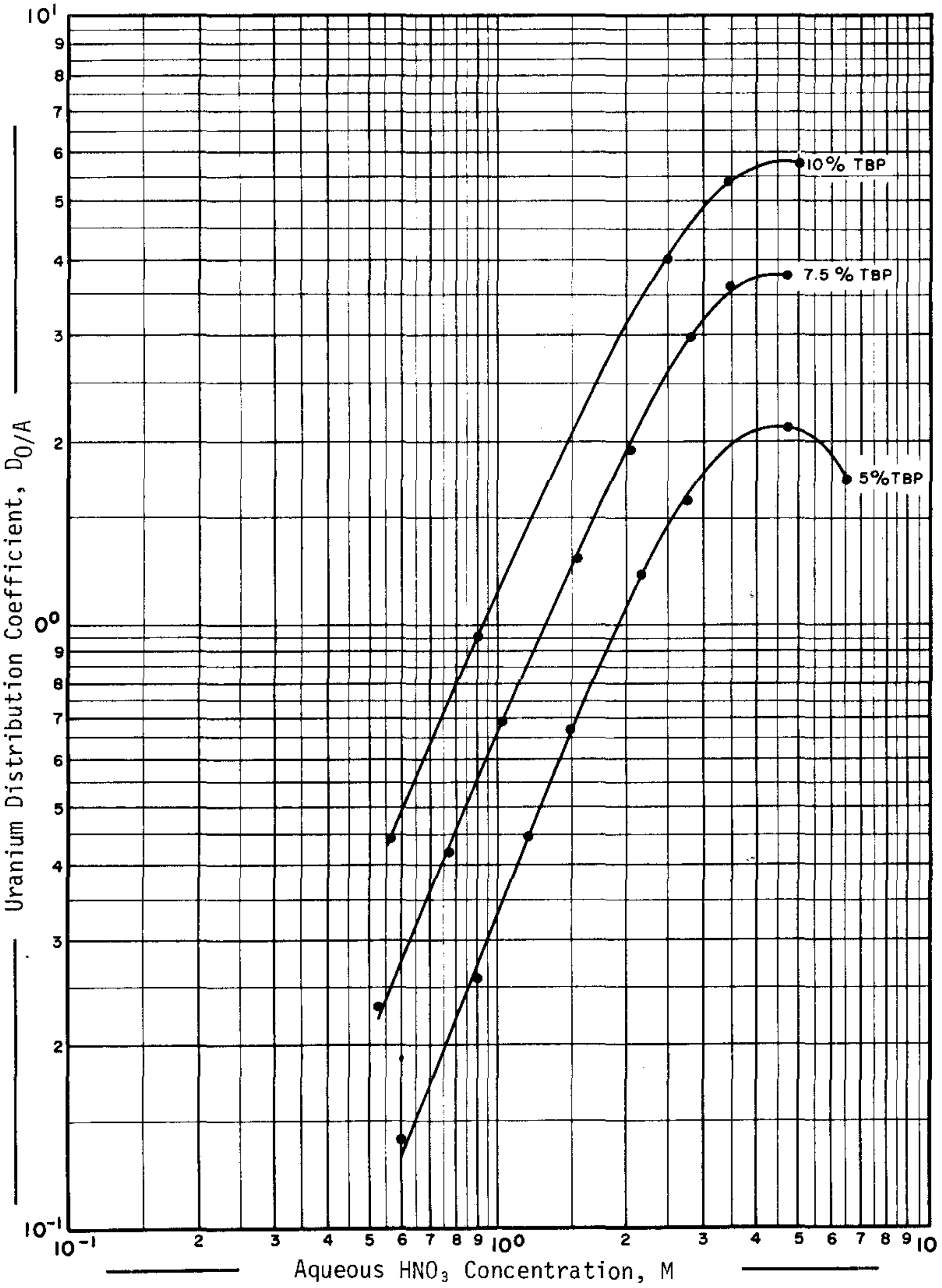


FIGURE 7.7 Uranium Distribution as a Function of Nitric Acid and TBP Concentrations at Low Concentrations of Uranium and at 45.9°C

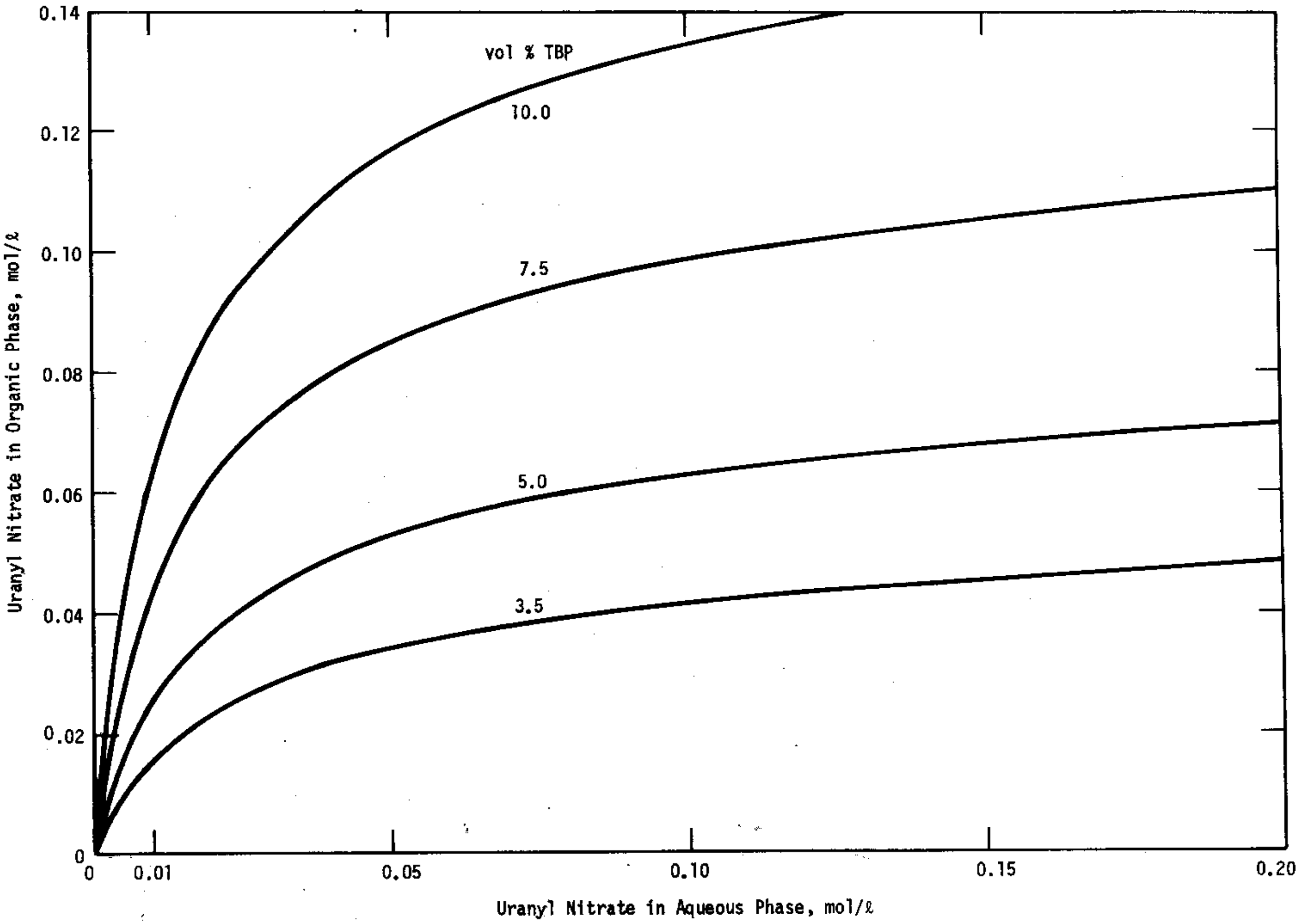


FIGURE 7.8 Equilibrium Distribution of Uranyl Nitrate Between TBP and 4M Nitric Acid at 25°C

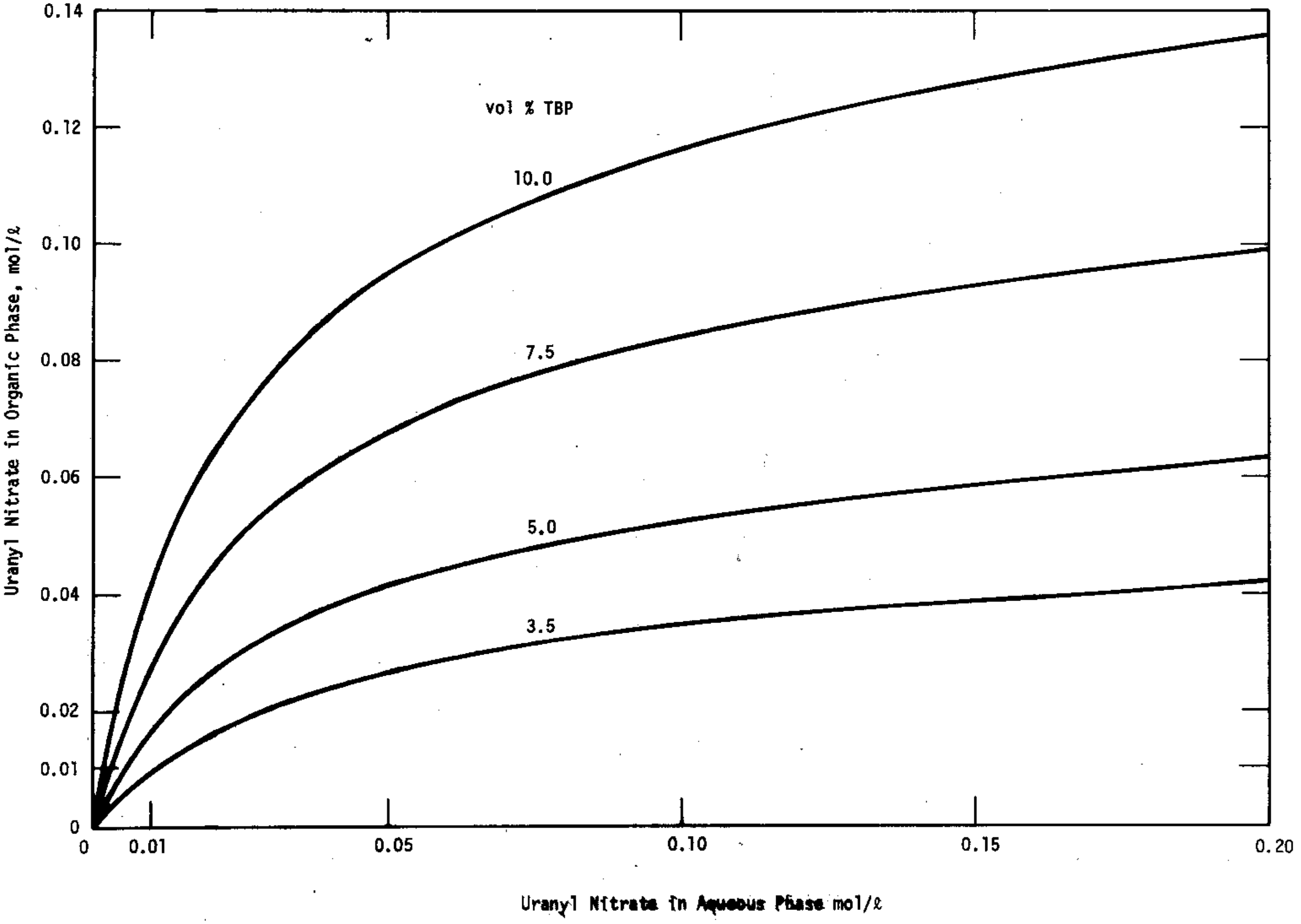


FIGURE 7.9 Equilibrium Distribution of Uranyl Nitrate Between TBP and 4M Nitric Acid at 45°C

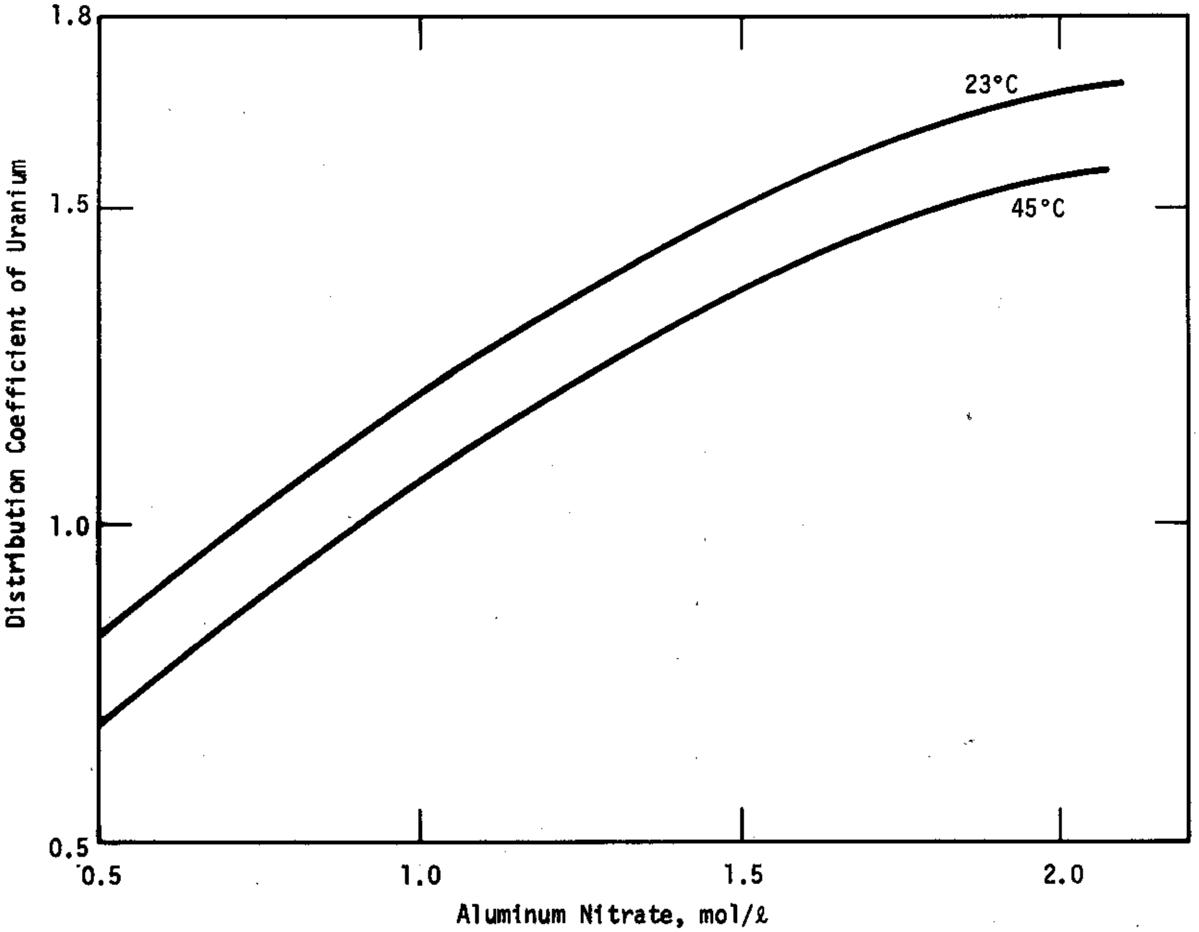


FIGURE 7.10 Uranium Distribution Between 7.5% TBP and Aqueous Aluminum Nitrate Solutions at Constant Nitric Acid Concentration (0.5M) and Initial Uranium Concentration (45 g/l) at 23 and 45°C

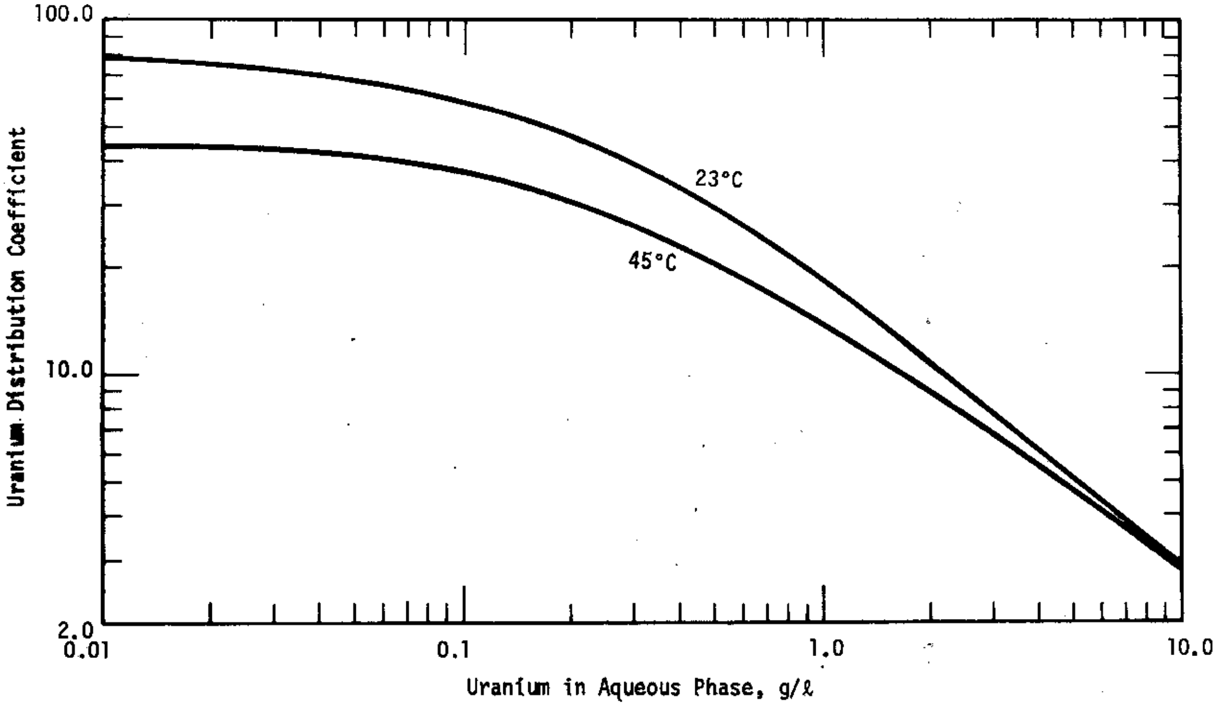


FIGURE 7.11 Distribution of Uranium in 7.5% TBP as a Function of Uranium in 1.6M $Al(NO_3)_3$ - 0.5M HNO_3

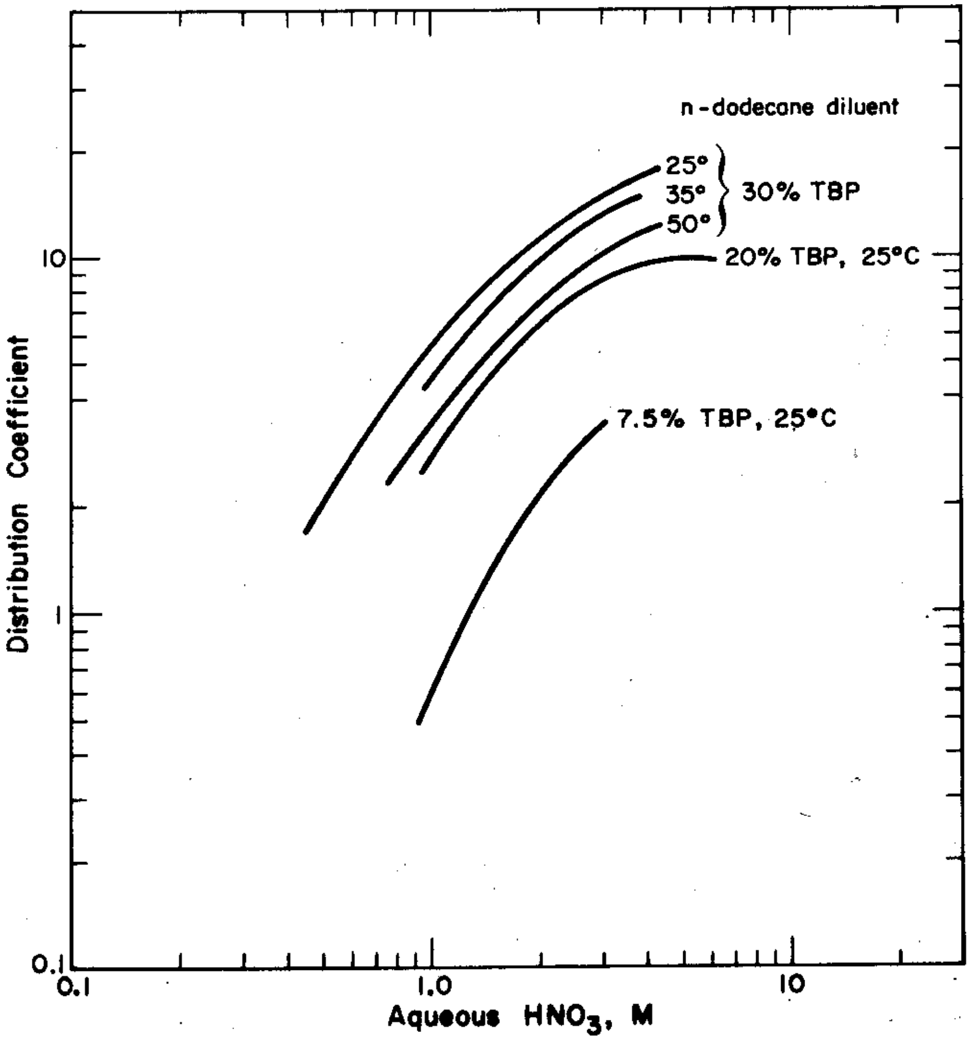


FIGURE 7.12 Extraction of Np(VI) by TBP from HNO$_3$

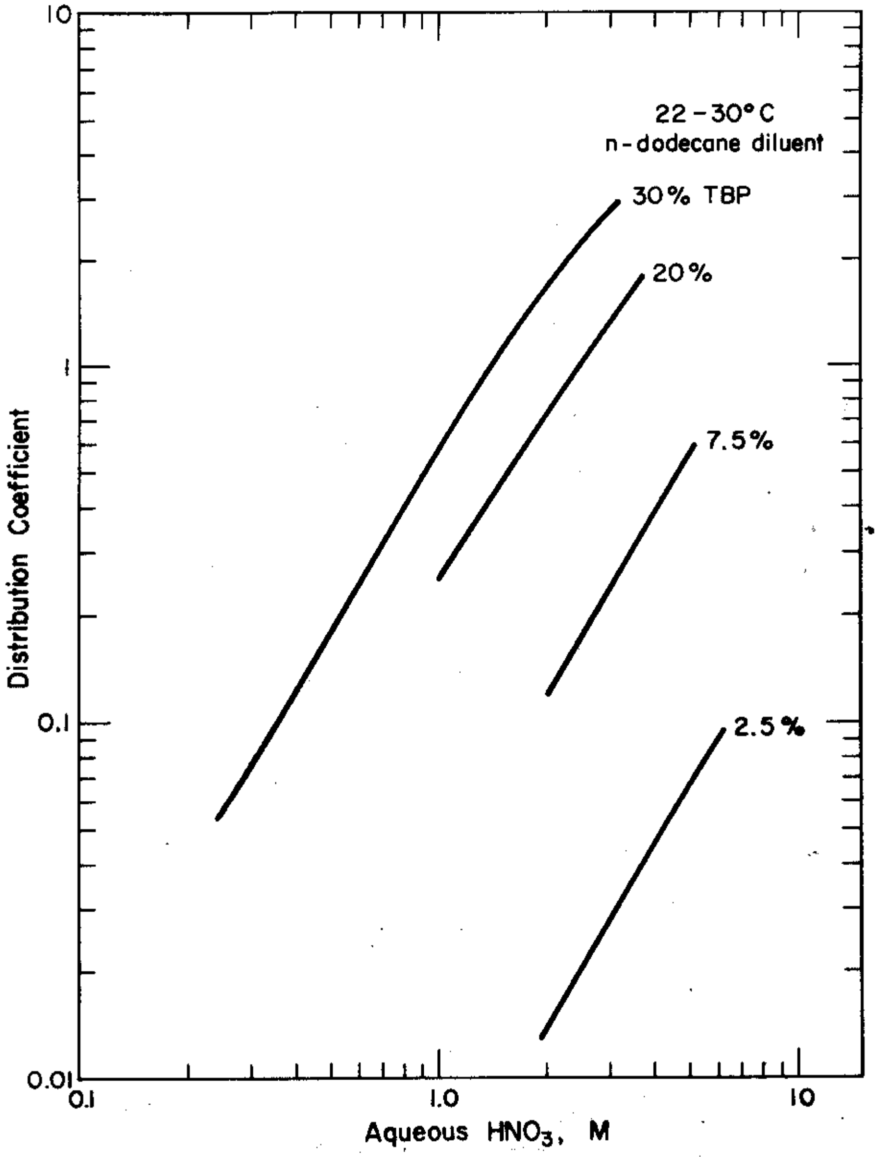


FIGURE 7.13 Extraction of Np(IV) by TBP from HNO_3

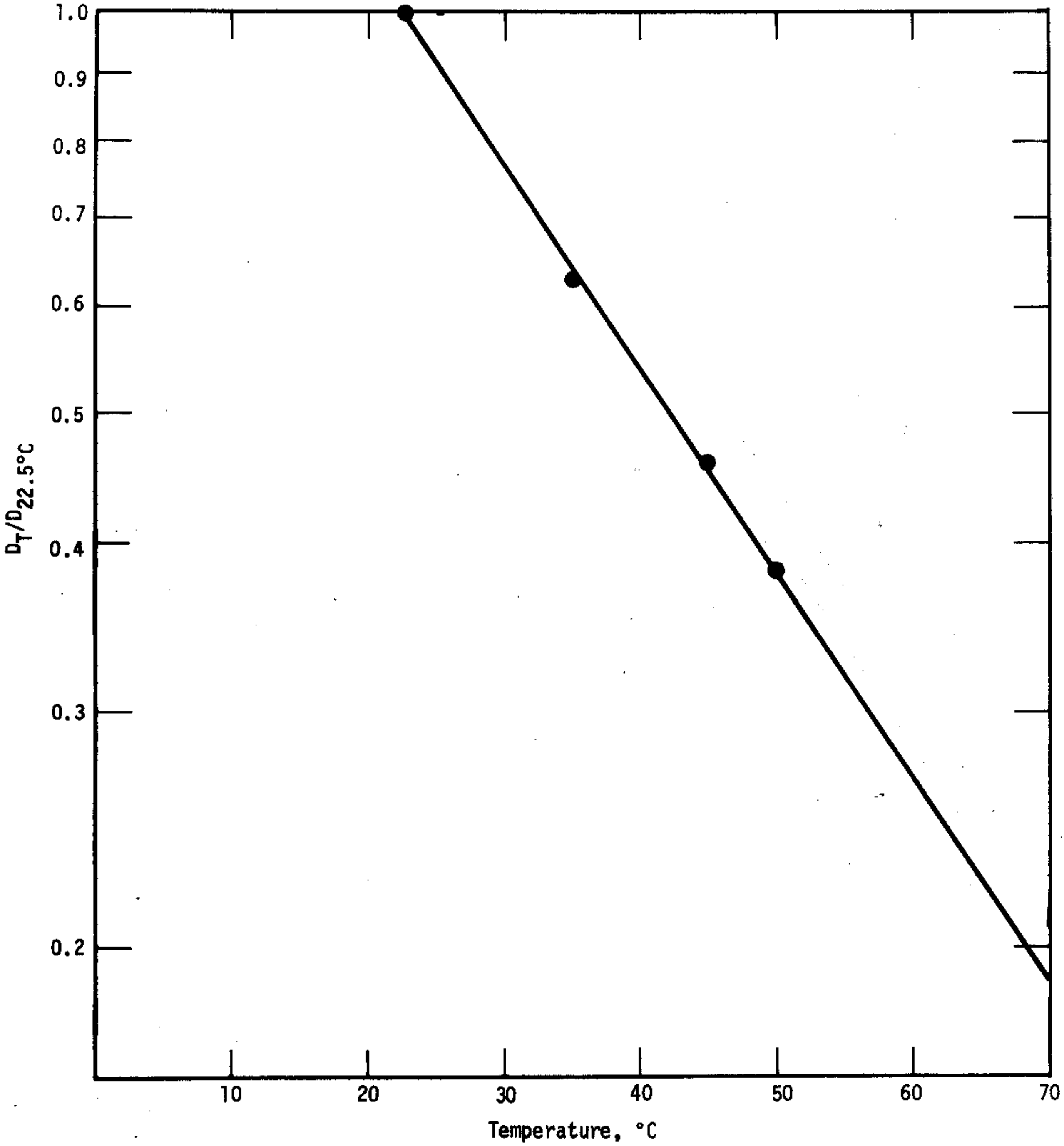


FIGURE 7.14 Effect of Temperature on Tracer U(VI) Extraction

7.2.1 Process Chemicals

Properties of the Solvent

The process solvent (Table 7.1) is a solution of tributyl phosphate in a normal paraffin. The concentration of TBP in the solvent is 7.5% by volume in the first cycle, 7.5% in the second uranium cycle, and 30% TBP in the second neptunium cycle or second plutonium cycle. Pure TBP is not useful for solvent extraction because its high viscosity and density give it poor hydraulic characteristics. (The density, 0.97 g/ml at 25°C, is only slightly less than that of water.) The extractive capacity of undiluted TBP is far in excess of that required for the process.

TABLE 7.1

Physical Properties of Process Solvent

	n-Paraffin
Flashpoint of Diluent, °C	84
Flashpoint of 30% TBP - 70% Diluent, °C	89
Density of 7.5% TBP - 92.5% Diluent at 25°C, g/ml	0.774
Density of 30% TBP - 70% Diluent at 25°C, g/ml	0.821
Density at 25°C, g/ml	0.760
Density of TBP at 25°C, g/ml	-
Viscosity TBP at 25°C, millipoises	-
Viscosity of Diluent at 25°C, millipoises	0.17
Interfacial Tension of 7.5% TBP - 92.5% Diluent at 25°C, dynes/cm	13.0
Interfacial Tension of 30% TBP - 70% Diluent at 25°C, dynes/cm	10.0
Solubility of TBP in water at 20°C - 7.5% TBP - 92.5% Diluent, g/1	0.18
Solubility of TBP in water at 20°C - 30% TBP - 70% Diluent, g/1	0.32
Vapor pressure of TBP at 25°C, mm Hg	0.006
Vapor pressure of TBP at 100°C, mm Hg (calculated)	1.0
Molecular Weight of TBP $(n\text{-}C_4H_9O)_3PO$	266.32

Dilution of the TBP with an inert material of low density, viscosity, and polarity, such as kerosene, yields a process solvent which separates well from aqueous solutions. The process solvent undergoes some degradation during each cycle of use in the process, so it is purified after each cycle. Objectionable compounds result from hydrolysis, acidolysis, and radiolysis of TBP and radiolysis of the diluent. The hydrolysis products of TBP are formed slowly under a variety of conditions and include in order of abundance: butanol, dibutyl phosphate, monobutyl phosphate, and phosphoric acid. The acidolysis products are butyl nitrate and phosphoric acid. These impurities are removed during the washing step of solvent recovery; if allowed to accumulate, they would adversely affect decontamination, product recovery, and phase disengagement. Some of the products of degradation of the hydrocarbon diluent are not completely removed in the solvent recovery operations.

The most noticeable effect of these degradation products is the extraction of zirconium and ruthenium along with uranium or neptunium, and subsequent release of these contaminants to the aqueous product streams in the stripping banks. The solvent remains serviceable for an extended period in normal use in which provisions are made for prompt cleanup, but it may become seriously degraded in a few weeks when stored in contact with solutions that contain nitric acid and/or nitrous acid.

A particular source of degraded solvent is the entrained solvent that accumulates in tanks above stored aqueous solutions, and then is returned to the process when these solutions are processed. When too much degraded solvent is present, normal methods of rejuvenating the solvent may not restore it to acceptable performance, and it must be discarded.

Aqueous Phase Chemicals

Several chemicals may be used in the aqueous streams during solvent extraction. These are aluminum nitrate, nitric acid, ferrous sulfamate, sodium nitrite, and hydroxylamine sulfate or nitrate.

Aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$, M.W. 375.13] forms colorless, rhombic crystals. It is deliquescent; it melts in its water of crystallization at 73°C and decomposes at 135°C; and it is soluble in water, alcohol, and acetone. The aqueous solution is weakly acidic because of hydrolysis of the aluminum ion.[7] Its solubility and density in water and nitric acid at different temperatures are shown in Figures 7.15 and 7.16.

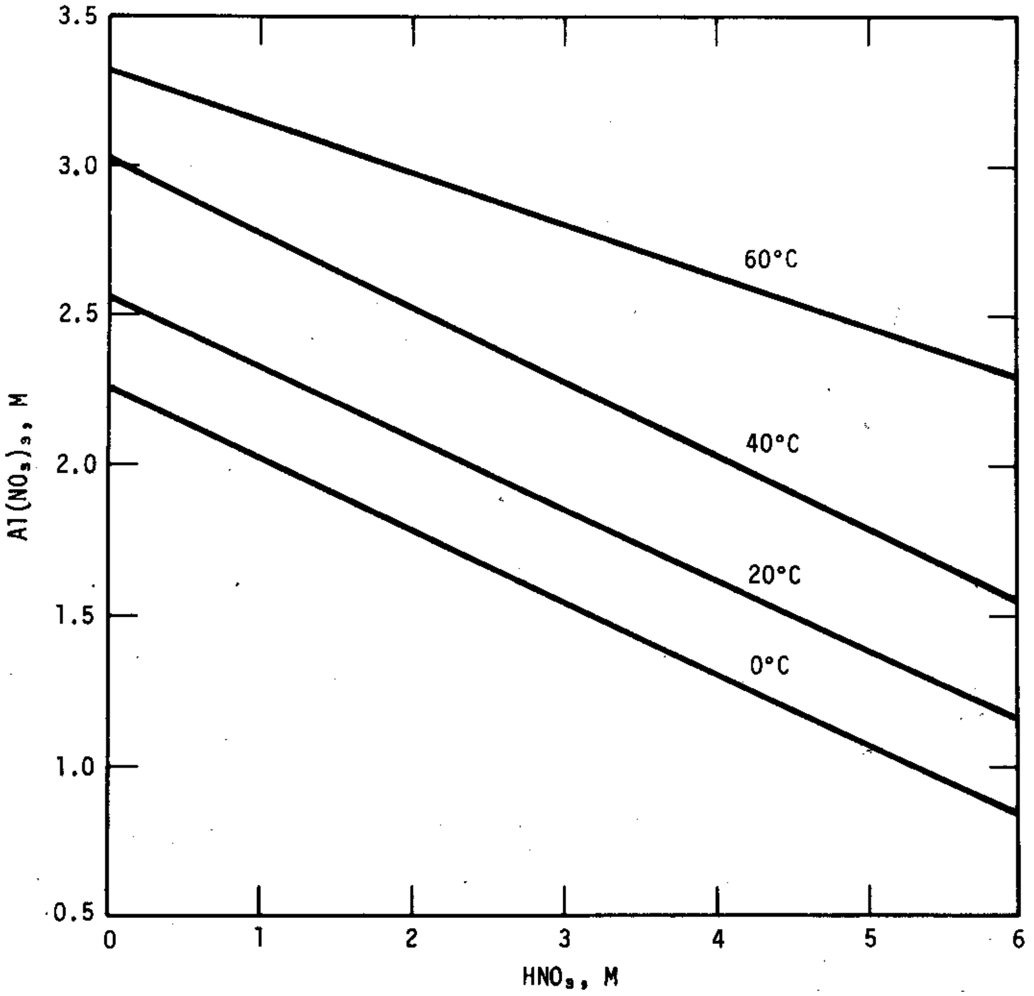


FIGURE 7.15 Solubility of $Al(NO_3)_3$ in Solutions of HNO_3

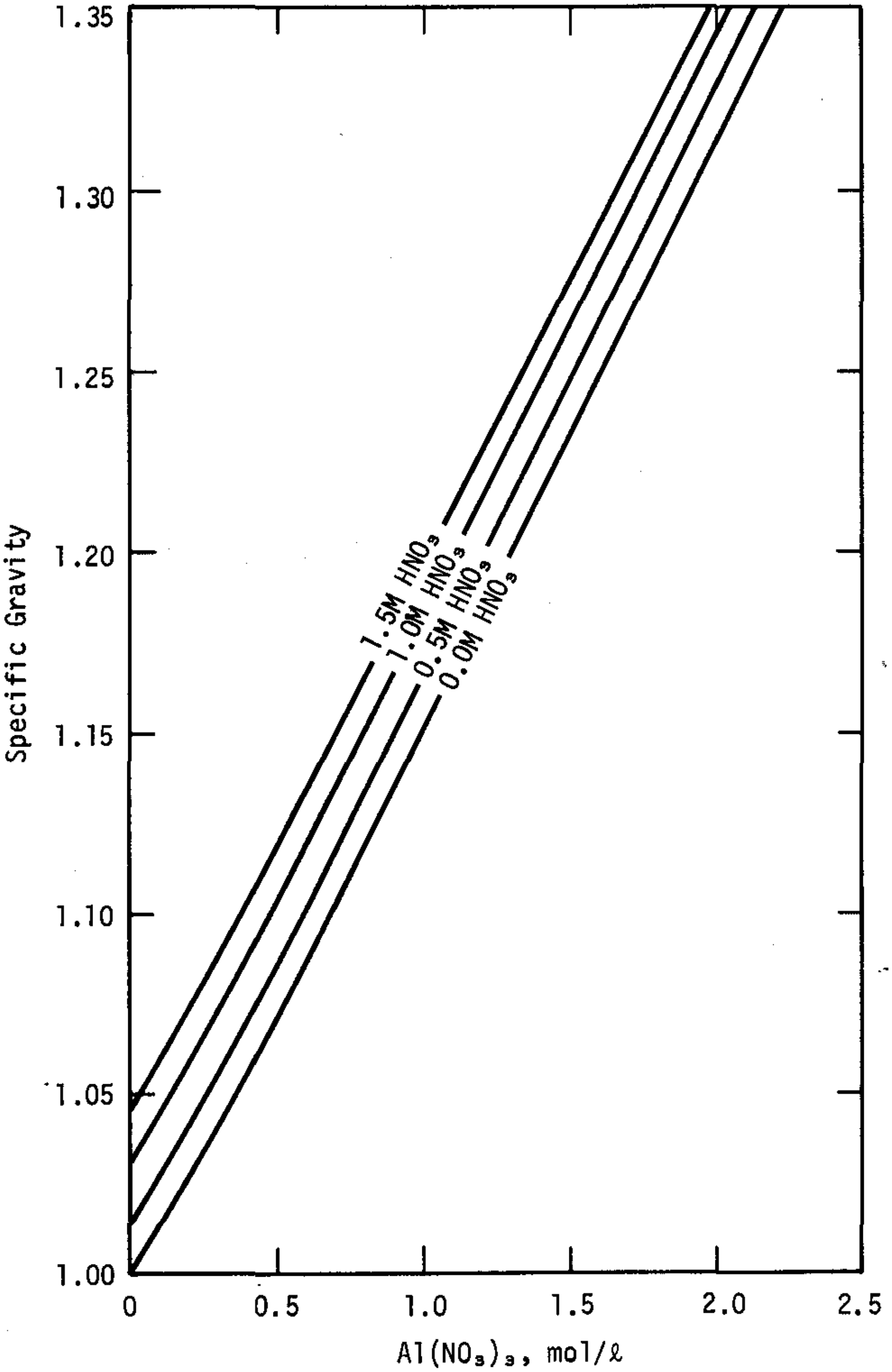


FIGURE 7.16 Specific Gravity of $Al(NO_3)_3$ - HNO_3 Solutions at 20°C

Nitric acid is obtained in various concentrations from commercial sources or SRP acid recovery operations. It forms an azeotrope with water at a concentration of 68.8% after boiling at 122°C. The densities of aqueous solutions at various temperatures are shown in Figure 7.17.

In general, the reactions of nitric acid may be classified conveniently into three groups: 1) reactions as an acid (formation of inorganic nitrates), 2) reactions as an oxidizing agent, and 3) organic reactions.

Nitric acid is a strong, monobasic acid. It reacts readily with alkalies, oxides, and basic materials to form nitrate salts.

Concentrated nitric acid is a strong oxidant. Organic materials such as turpentine, charcoal, and charred sawdust are violently oxidized, while alcohol may react explosively. For rocket propulsion, nitric acid has been used as an oxidant with such organic materials as furfuryl alcohol and aniline. Most metals, with the exception of the platinum metals and gold, are oxidized and dissolved by nitric acid; some are converted into oxides (arsenic, antimony, and tin), but most others are converted to nitrates. Exceptions are aluminum and chromium steel, which may become passivated by the acid and show very little attack. The oxides, sulfides, etc., of the lower oxidation states of most elements can be readily oxidized to higher oxidation levels by concentrated nitric acid.

The activity of nitric acid as an oxidizing agent apparently requires the presence of free oxides of nitrogen. Pure nitric acid does not attack copper, for example, but when oxides of nitrogen are introduced, the reaction is at first slow and then proceeds with great rapidity and violence. The reduction products of nitric acid vary with the concentration of the acid and the strength of the reducing agent with which it reacts. A mixture of oxides is generally produced; dilute nitric acid tends to give a predominance of nitric oxide while concentrated acid produces a mixture richer in nitrogen dioxide. Very dilute acid reacting with a strong reducing agent such as metallic zinc produces a mixture of ammonia and hydroxylamine.

For all temperatures, viscosities of solutions of nitric acid reach a maximum at a concentration of about 68% acid. At 20°C this maximum is 2.0 cP, the viscosity decreases from this value to about 0.9 cP for 100% acid and 1.0 cP for pure water.

Ferrous sulfamate [$Fe(NH_2SO_3)_2$] is a strong reducing agent prepared by dissolution of iron in sulfamic acid solution, and is used in the dissolved form. The maximum concentration obtainable is ∿50 wt %. Solutions are unstable to oxidation by air in the presence of light. Storage for more than a few months even in the absence of oxygen is not recommended.

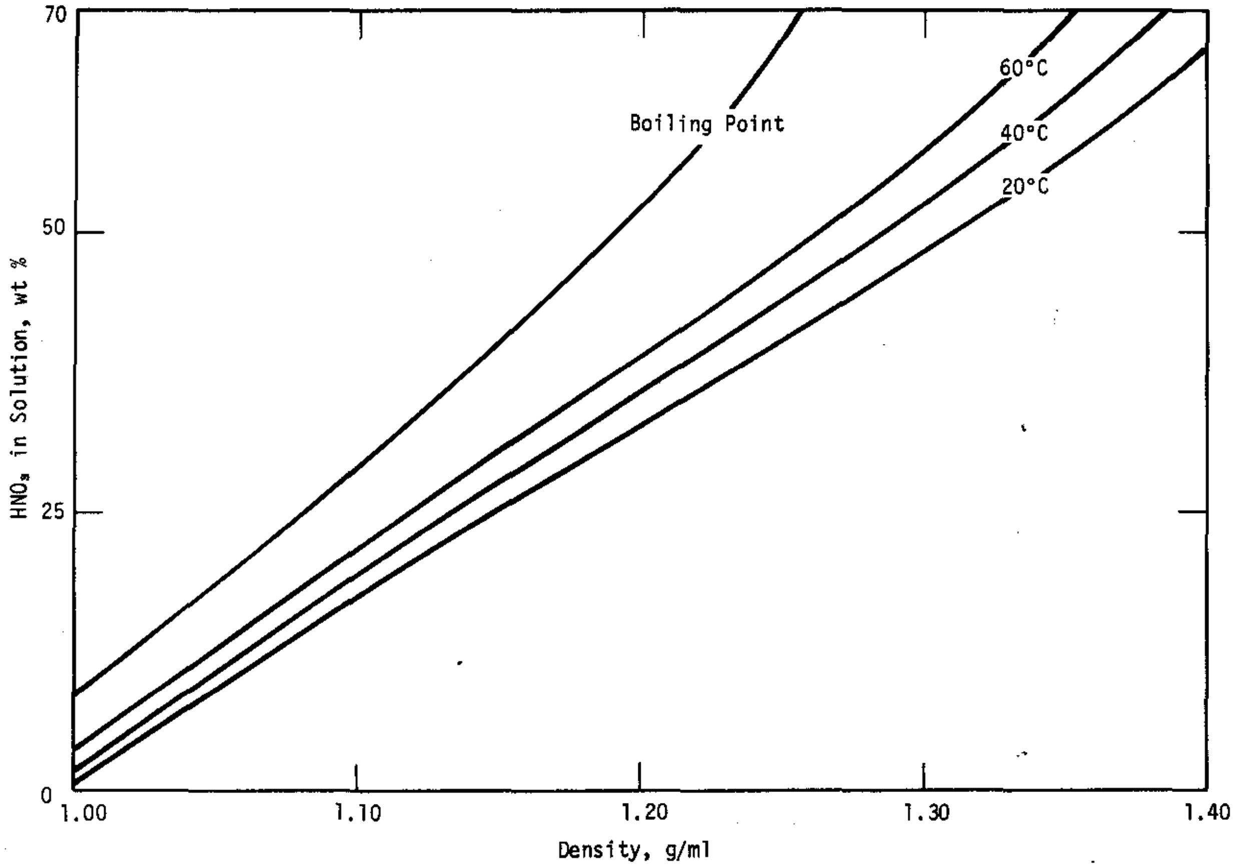


FIGURE 7.17 Density of Solutions as a Function of Nitric Acid Concentration and Temperature

Ferrous sulfamate is oxidized by nitric acid under the concentration and temperature conditions of the process.[8] The oxidation of the ferrous ion is first order with respect to ferrous ion. Therefore, the concentration of ferrous at any time in the absence of radiation can be calculated from

$$C = C_o e^{-kt}$$

where C is the concentration at time t, C_o is the initial concentration, and k is the reaction rate constant. The rate constants as a function of temperature and acid concentration are given in Figures 7.18 and 7.19. The half-life of ferrous sulfamate as a function of temperature and acid concentration is shown in Figure 7.20.

Ferrous sulfamate in nitrate solutions is rapidly destroyed by the products of ionizing radiation. Ferrous ion is destroyed more rapidly than sulfamate; the rates of destruction are 0.013M ferrous ion and 0.006M sulfamate ion oxidized per megarad of radiation. The hydroxyl radical is believed responsible for the oxidation of ferrous ion, and hydrogen peroxide may also be involved.[2] Sulfamate is destroyed by radiolytically produced nitrite ion, and perhaps by other reactions.

Sodium nitrite ($NaNO_2$) is a colorless or yellowish transparent solid; it is very hydroscopic, and is soluble in water and in liquid ammonia. Sodium nitrite has a specific gravity of 2.168 at 0°C, a melting point of 284°C, and heat for formation, ΔH_j = -85,900 cal/mole.[7] Sodium nitrite is not oxidized by air at any appreciable rate at ambient temperature. When heated, it begins to decompose at 320°C giving off N_2, O_2, and NO and leaving a residue of Na_2O. When dissolved in water, sodium nitrite has a heat of solution of -3570 cal/mole. The solubility in water is shown in Figure 7.21 and solution density is shown in Figure 7.22.[7] Sodium nitrite decomposes to NO and NO_2 in the presence of strong acids, such as nitric acid.

Sodium nitrite is toxic. The tolerance limit for bare skin to aqueous $NaNO_2$ is 1.5 wt %.[7] Stronger solutions, even as dilute as 2.0 to 2.5% $NaNO_2$, can cause inflammation of the skin and blisters. More severe nitrite intoxication produces such symptoms as insomnia, headache, rapid fatigue, and loss of appetite. The method of manufacture causes sodium carbonate to be the principal impurity. A 30 wt % solution is used in plant applications.

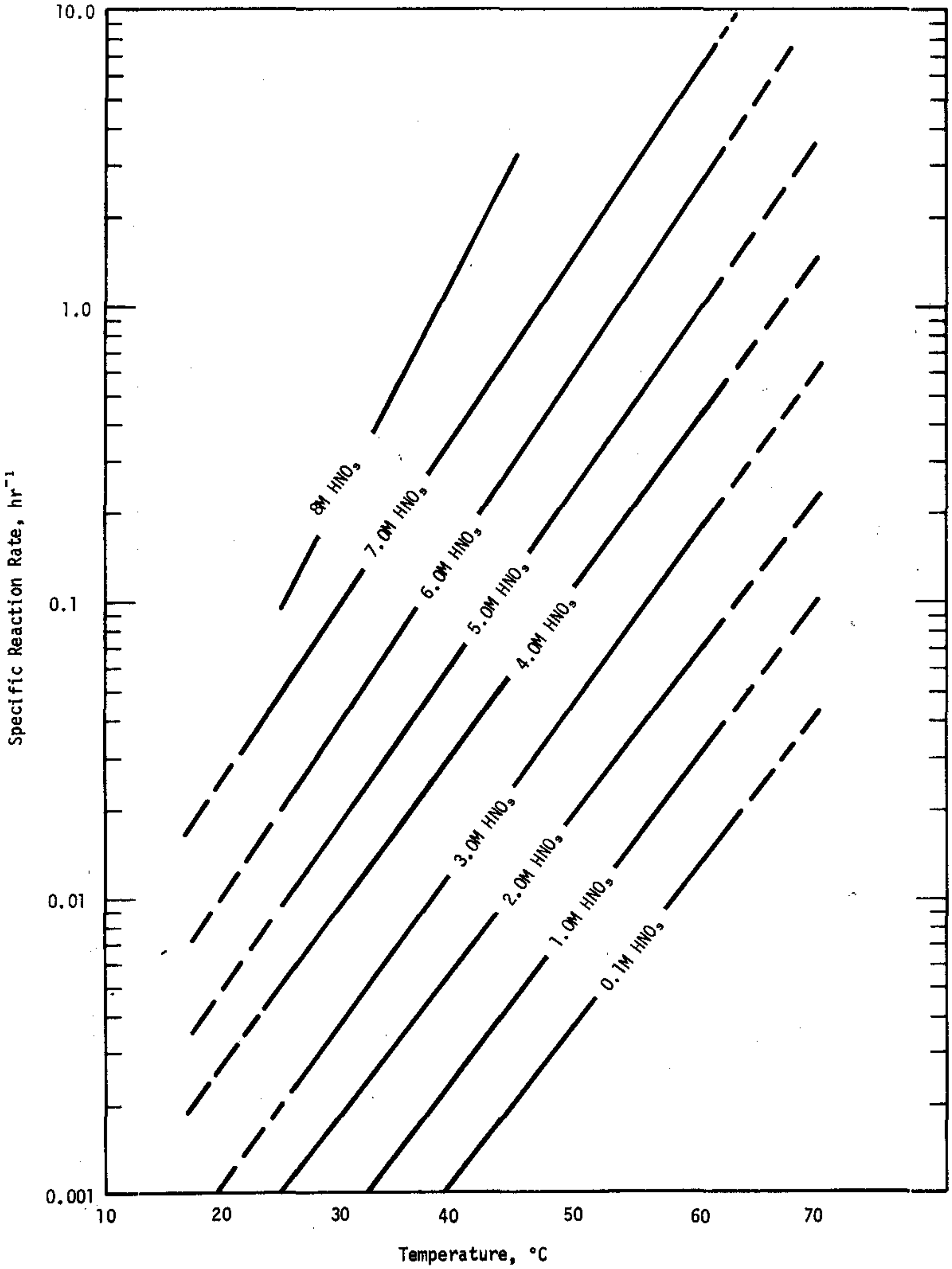


FIGURE 7.18 Ferrous Sulfamate Stability in HNO_3 as a Function of Temperature

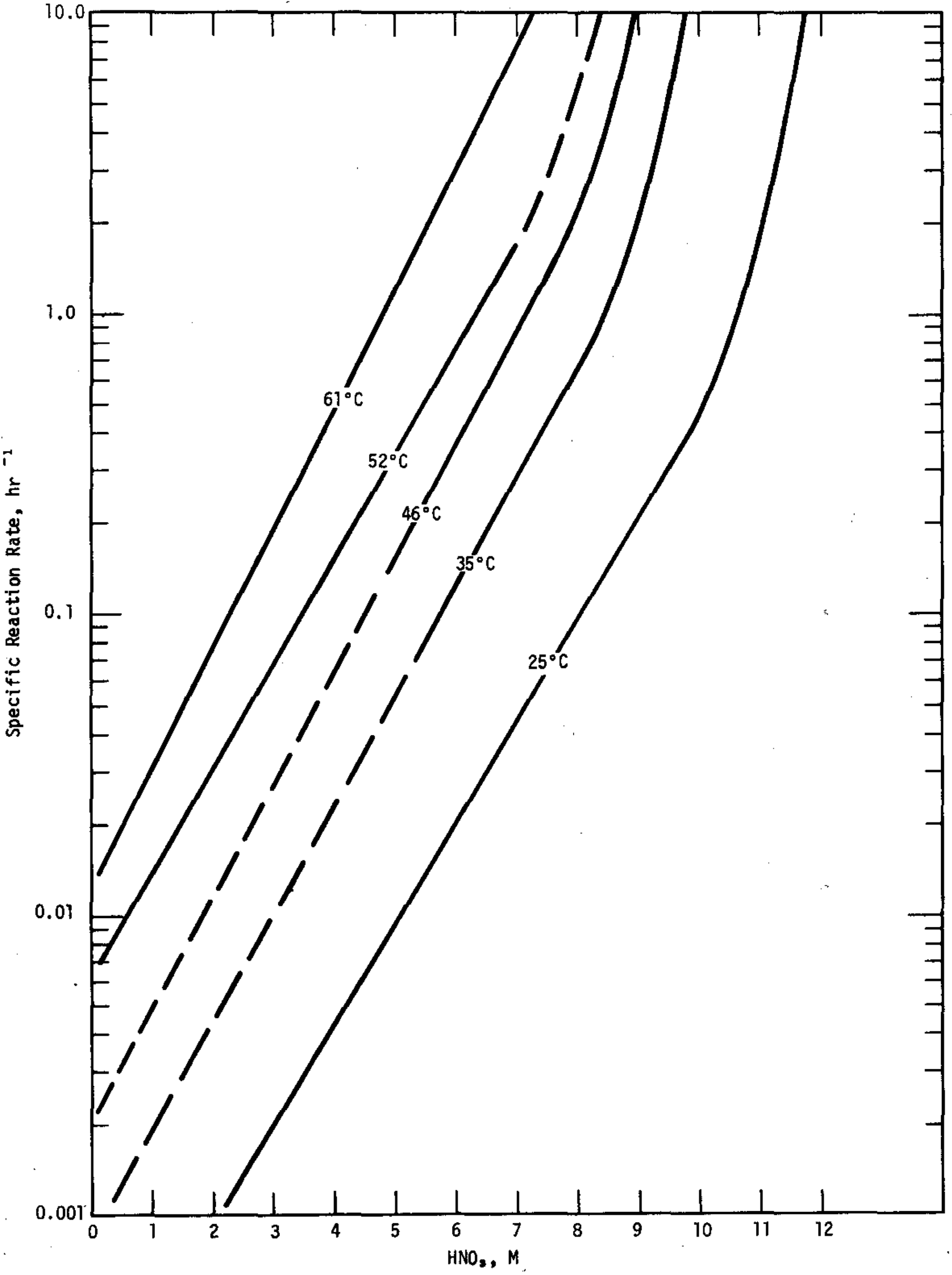


FIGURE 7.19 Ferrous Sulfamate Stability in HNO_3 as a Function of Acid Concentration

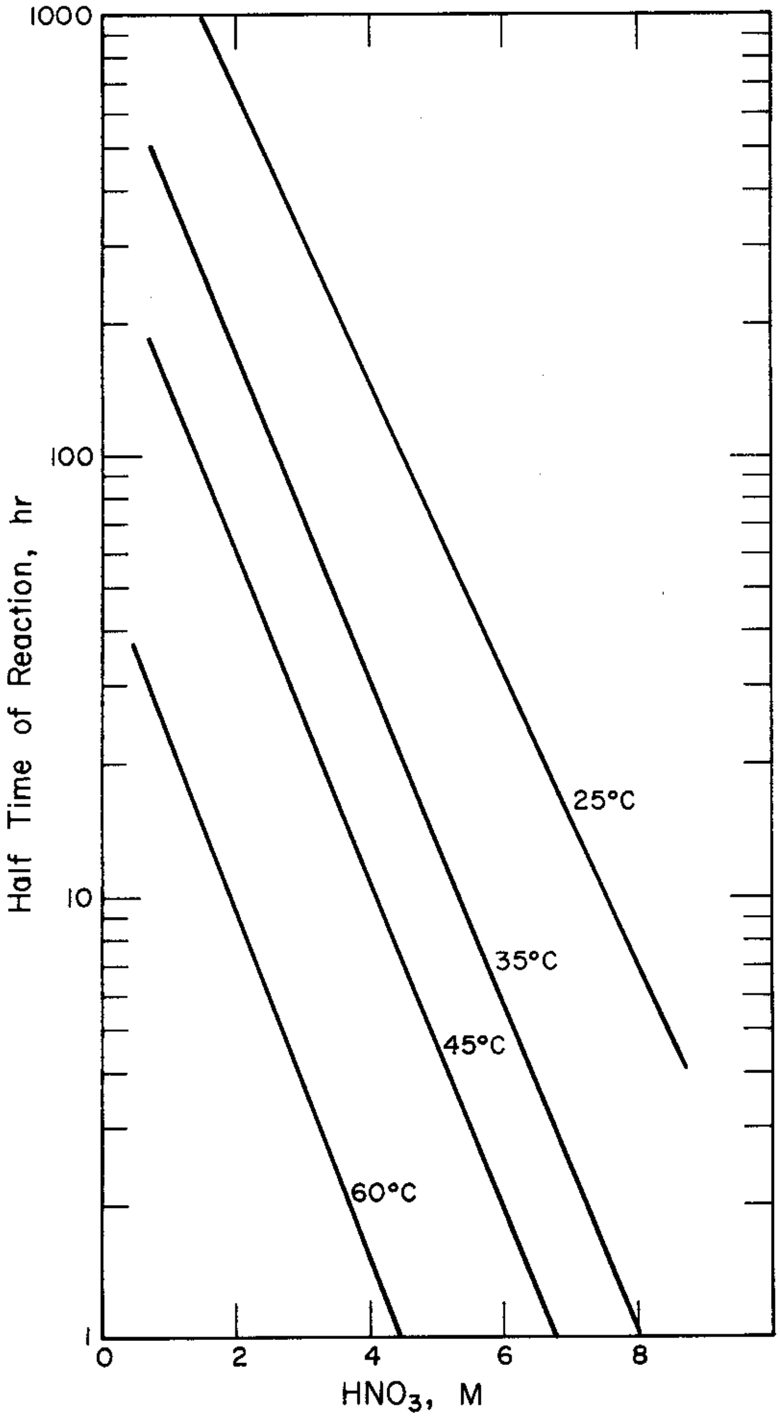


FIGURE 7.20 Half Time of Reaction of Ferrous Sulfamate with HNO_3 as a Function of Acid Concentration

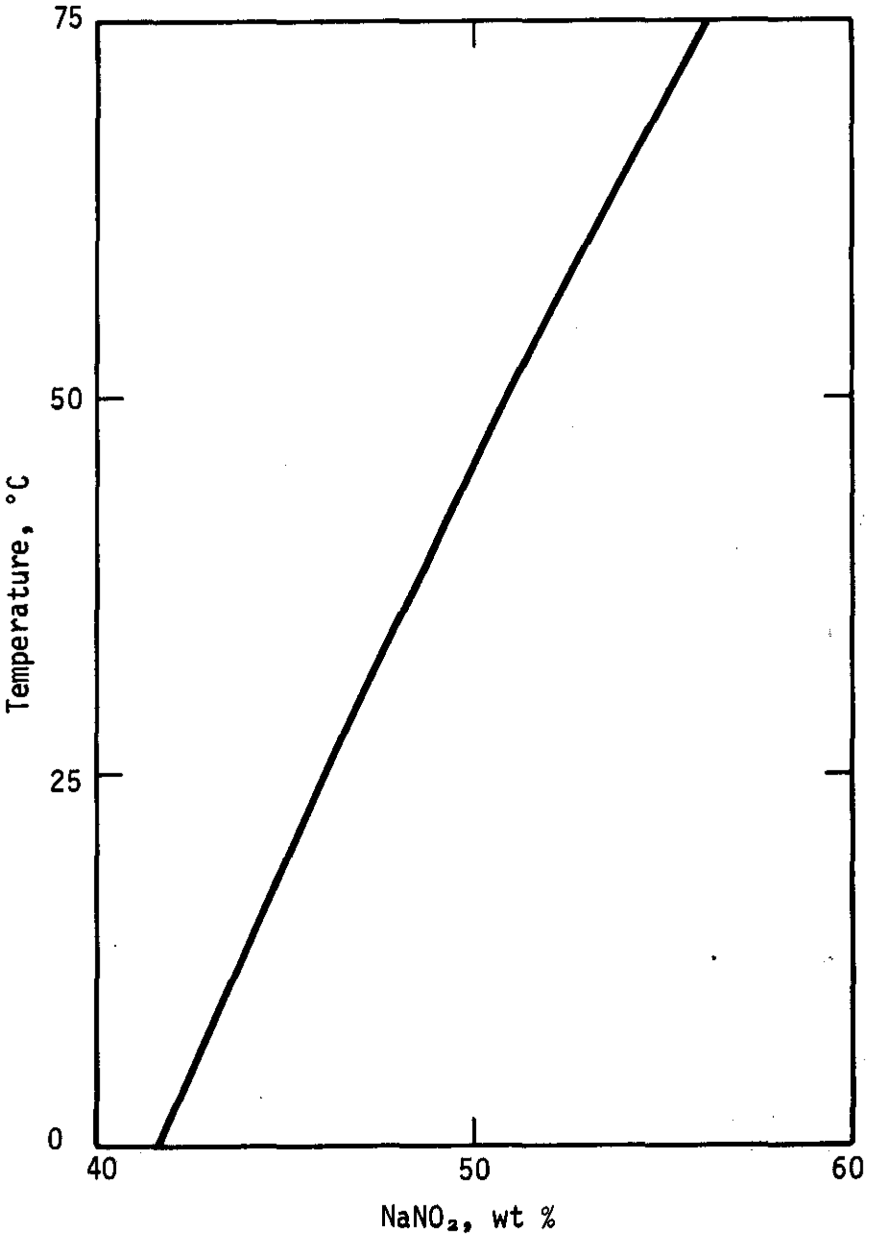


FIGURE 7.21 Solubility of Sodium Nitrite in Water as a Function of Temperature

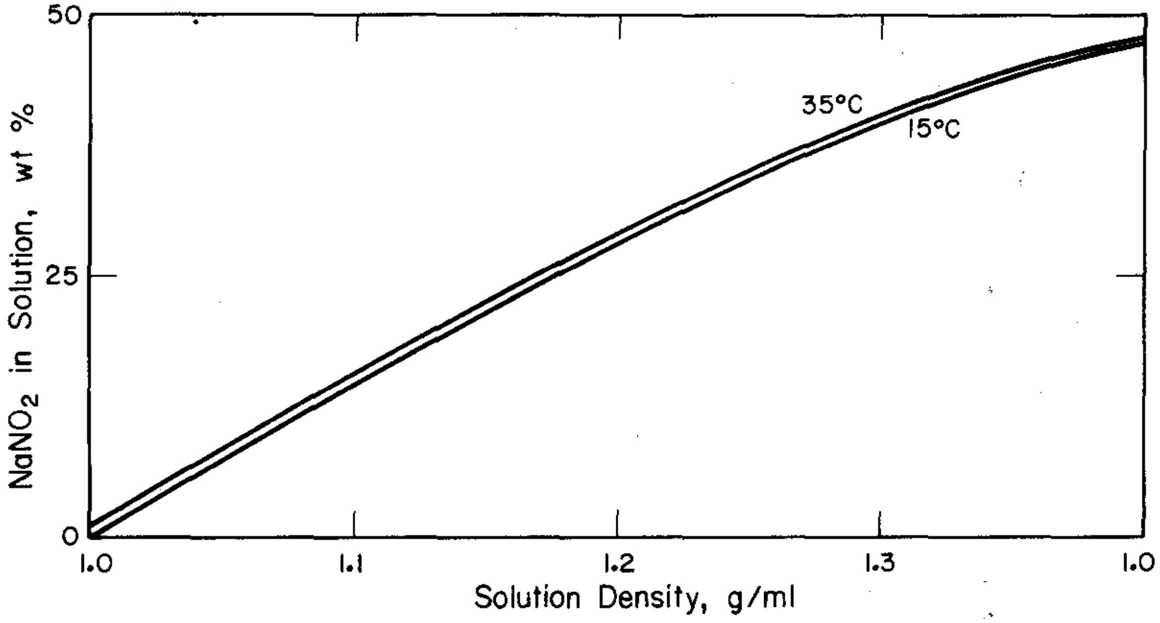


FIGURE 7.22 Density of Sodium Nitrite Solutions

Hydroxylamine (NH_2OH) is a colorless, hygroscopic crystalline solid. As shown by its formula, hydroxylamine is closely related to ammonia and exhibits many of the basic properties of ammonia. In plant operations it is handled as the sulfate or nitrate salts. The salts are much more stable than the free base. Hydroxylamine can function as both an oxidizing and reducing agent. As a reducing agent, it reacts to form nitrogen or oxides of nitrogen. Hydroxyl ammonium salts decompose on heating, and above 200°C the decomposition can become violent even when the salts are unconfined. The products of decomposition are similar to those of hydroxylamine, namely ammonia and nitrogen or nitrous oxide. Hydroxylamine nitrate begins to decompose into nitrogen, oxygen, and water at 60°C. Storage of these hygroscopic salts in a cool, dry place is recomemdned and should present no hazard. However, airtight containers, particularly if they contain hydroxyl ammonium acid sulfate, may build up internal pressure which should be relieved by occasional venting. Hydroxylamine nitrate is also available as an aqueous solution shipped in polyethylene containers at a maximum concentration of 16%. This form also must be kept at temperatures below 60°C.

Hydroxylamine and its salts are moderately toxic substances which may cause both irreversible and reversible changes in the body. Care should be taken to avoid oral ingestion or breathing of the dust from the dry salts. Exposure of the skin to either the dry salts or their solutions may cause mild dermatitis in some persons.[9]

7.2.2 Process Variables

The successful operation of the solvent extraction process depends largely on close control of compositions of solutions and rates of flow.[1,10-44] Control of temperature is comparatively less critical, but temperature must be taken into account in setting flow rates. Some of the requirements for close control of compositions and flow rates become apparent from an examination of Figures 7.5 to 7.14, which show the dependence of distribution coefficients on a number of variables. Due to the interdependence of some variables, mutual effects must also be considered in determining operating conditions (Figures 7.23-7.30).

7.2.3 First Cycle[1,12]

The first cycle of the solvent extraction process accomplishes the primary separation of uranium and neptunium (or plutonium) from each other and from fission products and inorganic salts (primarily aluminum, iron, and mercuric nitrates).

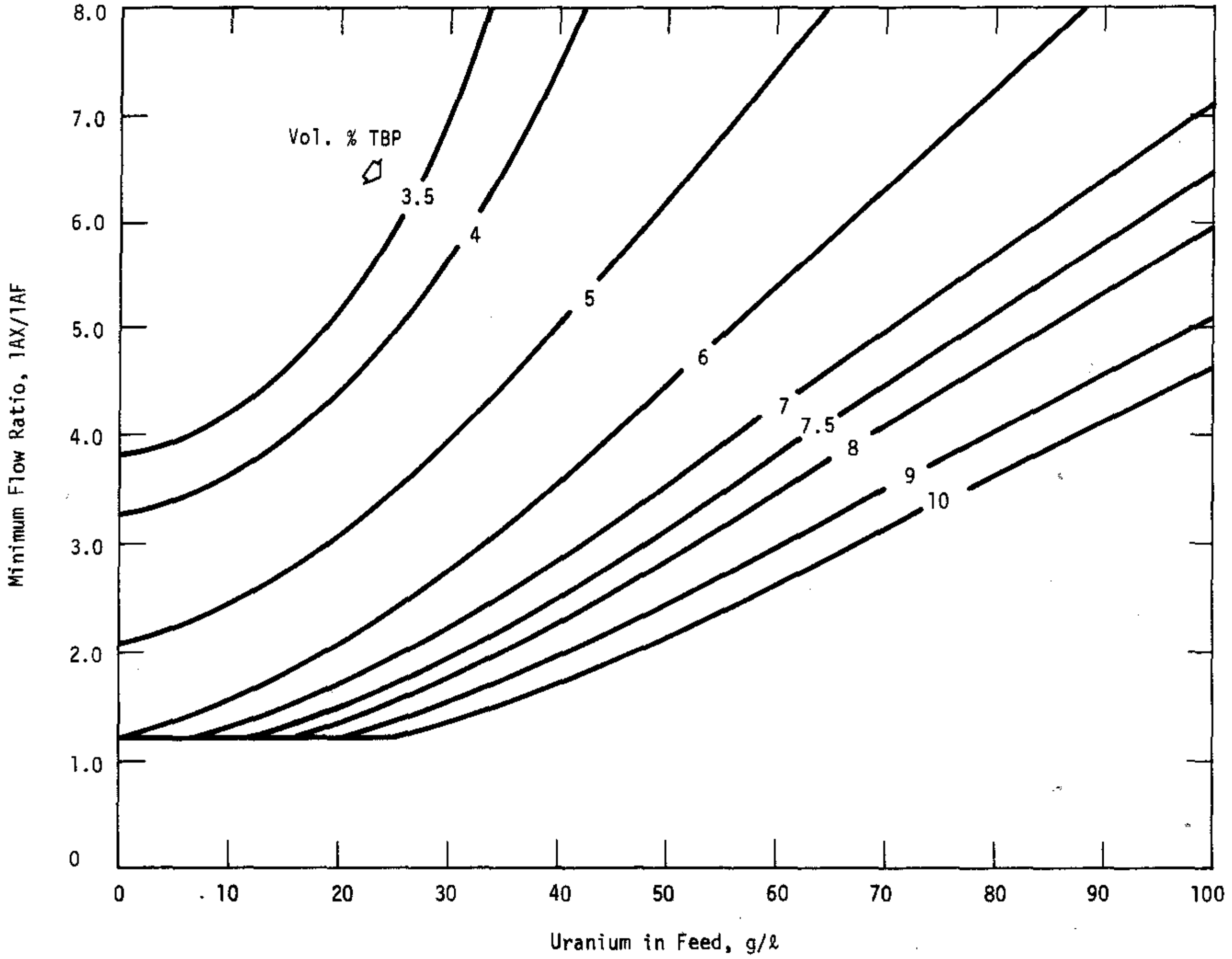


FIGURE 7.23 Limits of 1AX/1AF Flow Ratio as a Function of TBP and Uranium Concentrations (HNO_3 in 1AF and 1AS = 4.0M; Temperature $<$ 45°C; Ratio 1AS/1AX = 0.115 to 0.17)

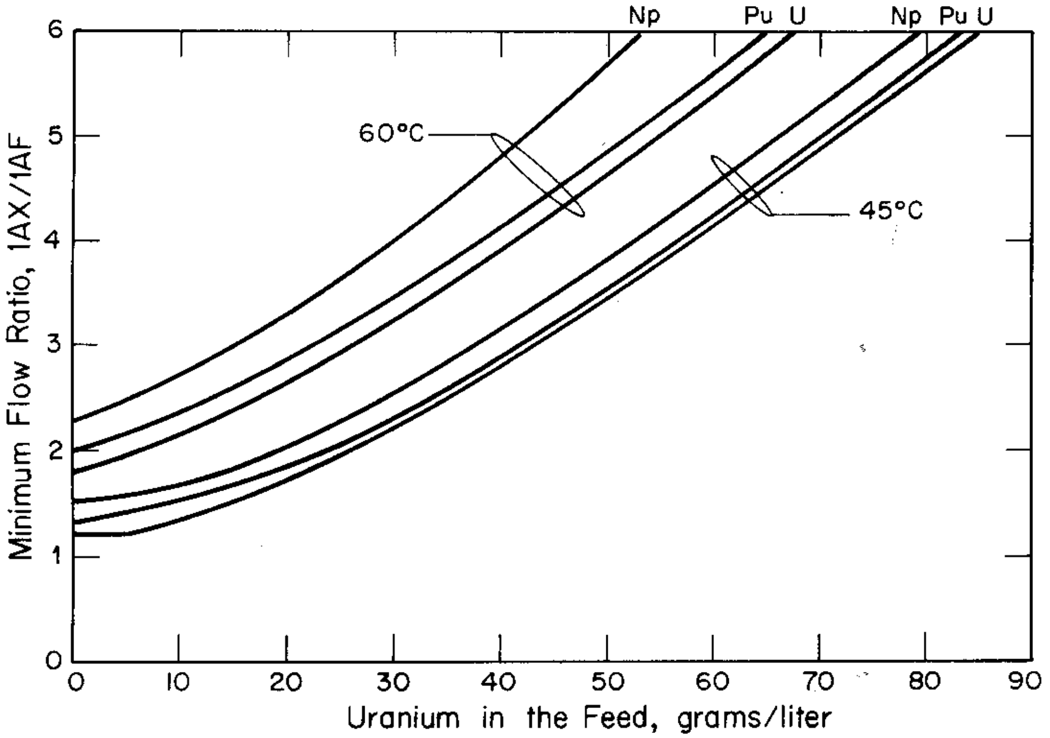


FIGURE 7.24 Limits of 1AX/1AF Flow Ratio as a Function of Uranium Concentration in the Feed (1AF) for Recovery of Uranium, Plutonium, and Neptunium with 7.0% TBP. HNO_3 in 1AF and 1AS = 3.8 M. Ratio 1AS/1AX = 0.17.

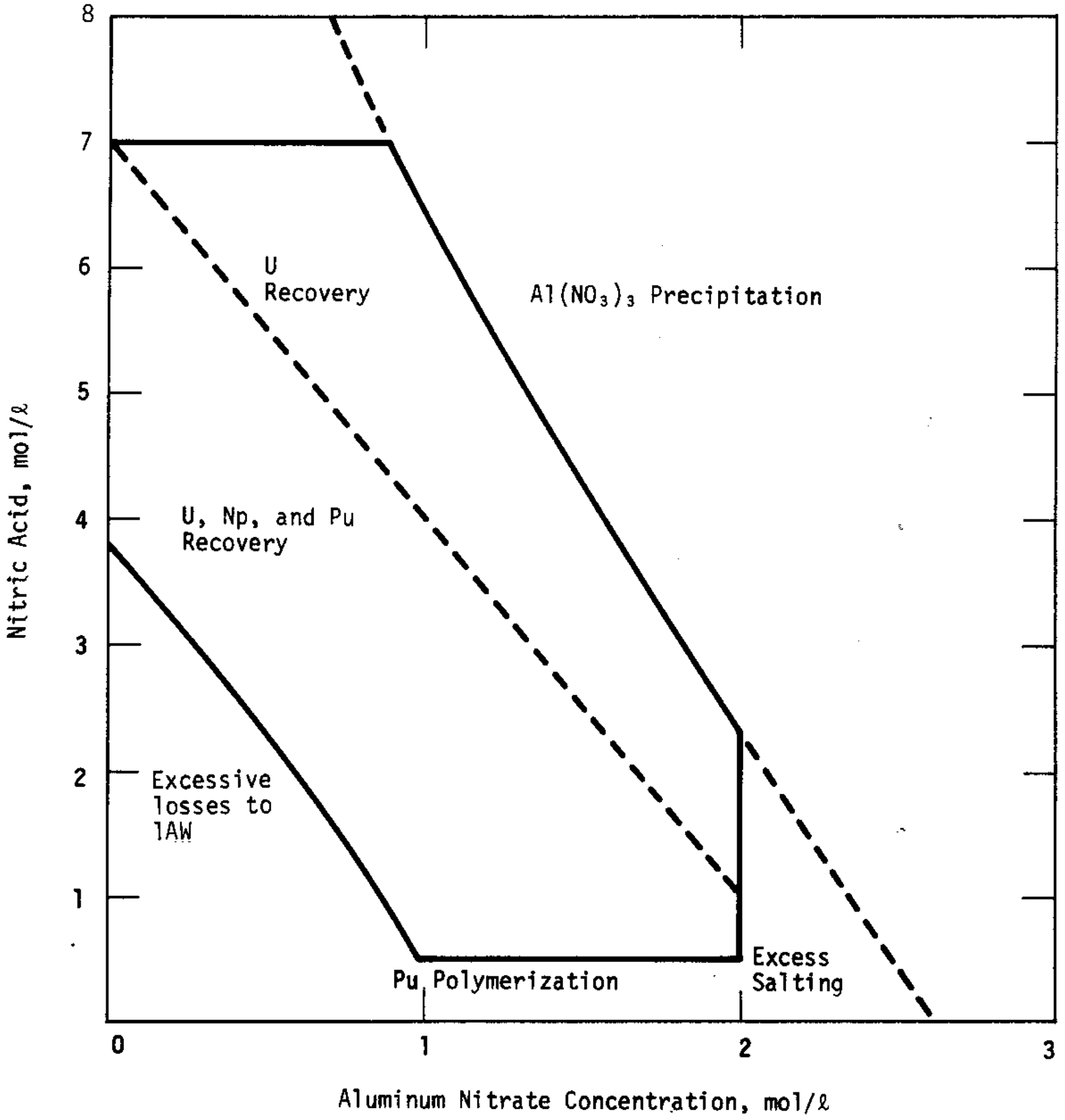
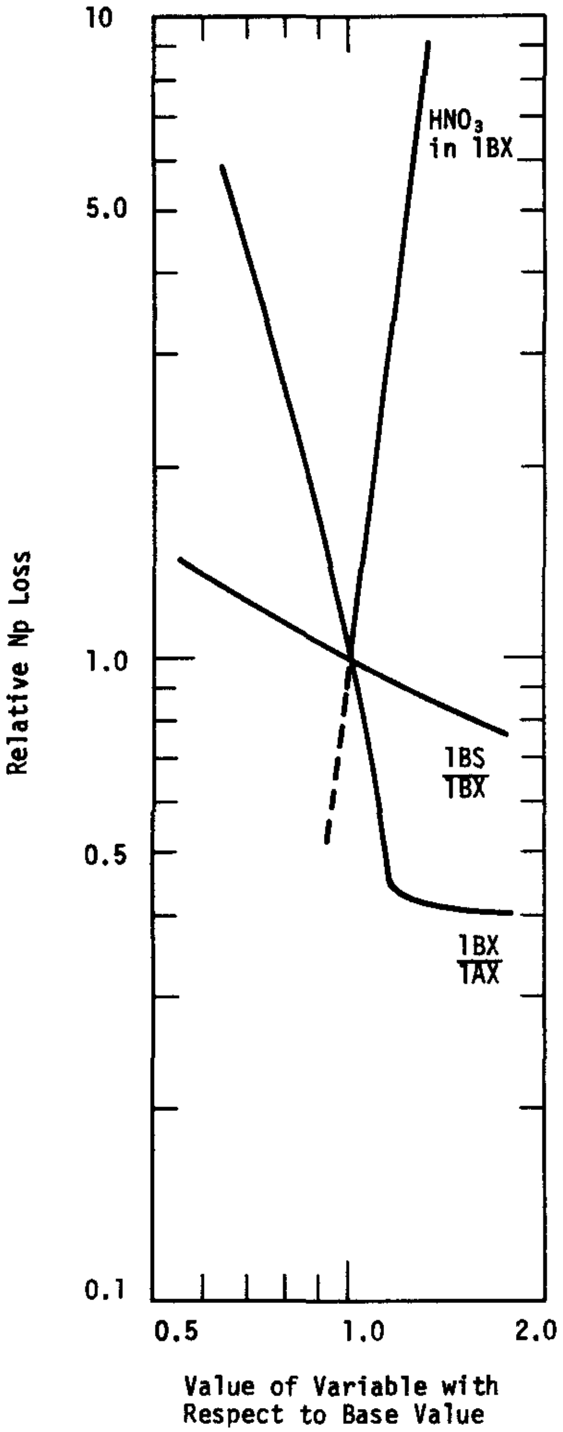


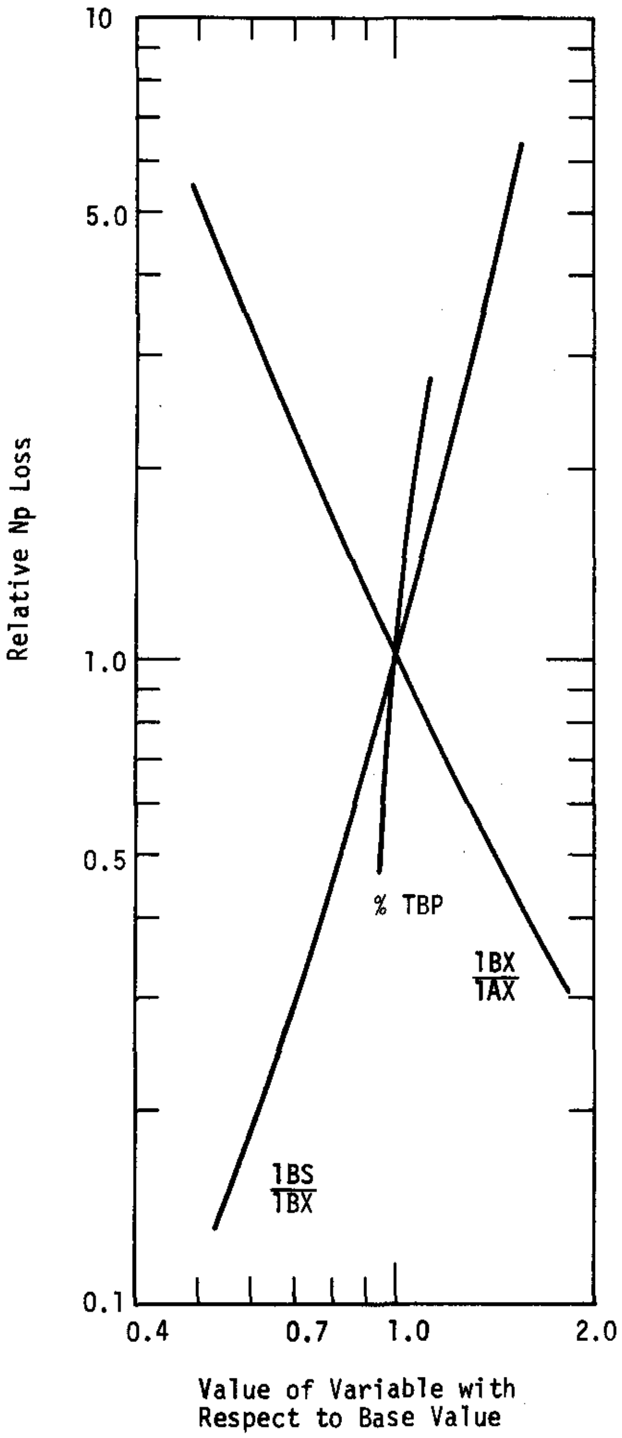
FIGURE 7.25 Concentration Limits for First Cycle Solvent Extraction Feed Solution (1AF)



Base Conditions

1BX/1AX ratio = 0.6
1BS/1BX ratio = 3
1BX acid = 1.30M
Np Loss to 1CU = 0.97%
U in BP ≤0.01% for
1BX/1AX & 1BS/1BX lines
only 7.5% TBP

FIGURE 7.26 Relative Neptunium Loss to the 1CU as a Function of Change in 1BX Acid Concentration and Organic-to-Aqueous Flow Ratios in the 1B-Bank



Base Conditions

1BX/1AX ratio = 0.6
1BS/1BX ratio = 3
1BX acid = 1.56M
Np Loss to 1CU = 4.11%
U in BP ⩽0.01%
7.5% TBP

FIGURE 7.27 Relative Neptunium Loss to the 1CU as a Function of Change in Organic-to-Aqueous Flow Ratios in the 1B-Bank with Constant Acid Concentration in the 1BX

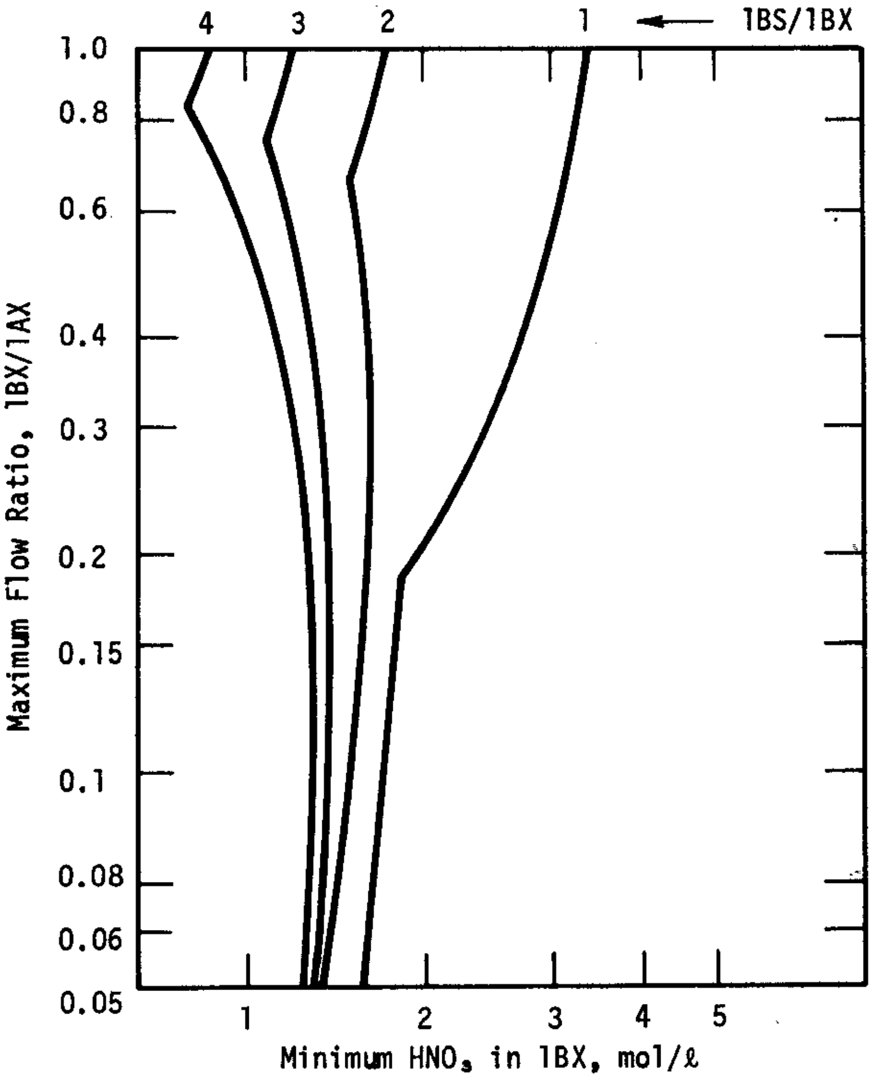


FIGURE 7.28 Minimum HNO_3 in 1BX at 7.5 vol % TBP and at <45°C

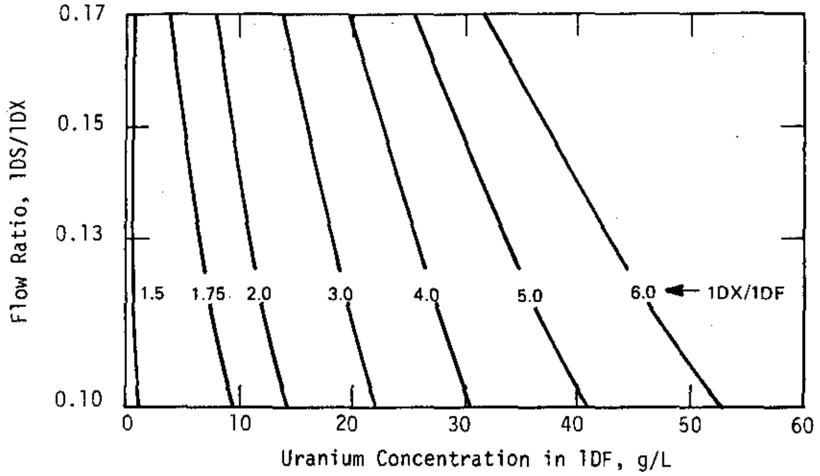


FIGURE 7.29 Limits of 1DS/1DX Flow Ratio as a Function of Uranium Concentration in the Feed (1DF) and 1DX/1DF Flow Ratio. (7.0 vol % TBP in 1DX; HNO_3 in 1DX = 0.8M; Temperature = 45°C)

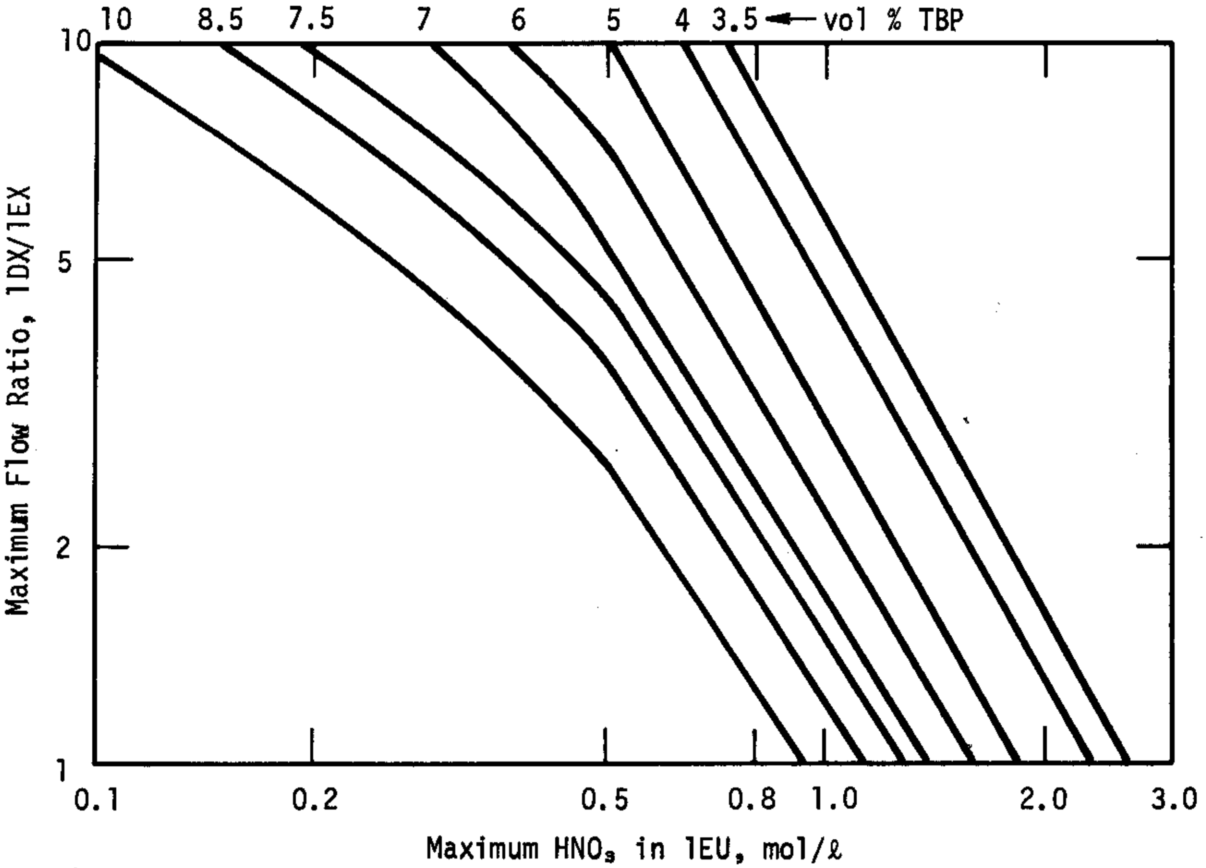


FIGURE 7.30 Limits of 1DX/1EX Flow Ratio as a Function of TBP in 1DX and HNO_3 in 1EU at 45°C

The feed solution from the head end step (see Chapter VI) is adjusted to the proper nitrate concentration with nitric acid and water (see Figure 7.25). The adjusted feed (1AF) is fed to the mixing section of stage 8 of the first mixer-settler unit (1A bank). The organic extractant (1AX) and the aqueous scrub solution (1AS) are pumped to stages 16 and 1, respectively. In the extraction section of the bank (stages 8 through 16), uranium and neptunium or plutonium are selectively extracted into the organic phase, while the bulk of the fission product remains in the aqueous phase and leave the process with the waste stream. In the scrub section (stage 1 through 7), the organic solution bearing uranium and neptunium or plutonium is washed by 4.0M HNO_3 solution (1AS) for additional fission product removal.

In the 1AS stream, used for scrubbing fission products from the uranium-bearing solvent phase, 4M HNO_3 will not strip uranium from the organic phase in the scrub stages of the 1A bank. The streams coming into the 1A Bank (1AF, 1AS, and 1AX) may be heated to improve the decontamination from fission products and to improve hydraulic behavior following the bank to run efficiently at the highest possible flow rates.

The scrubbed organic phase (1AU) emerges from the 1A bank and flows by gravity to the mixing section of stage 8 of the second mixer-settler unit (1B bank). The organic scrub solution (1BS) and the aqueous strip solution (1BX) are pumped to stages 16 and 1, respectively. In the stripping section of the bank (stages 1 through 8) neptunium or plutonium is stripped into an aqueous stream of nitric acid and ferrous sulfamate, while the uranium remains in the organic phase and is carried to the 1C bank. The aqueous neptunium or plutonium stream is washed in the scrub section of the bank (stages 9 through 16) with fresh solvent to remove any trace of uranium; the stream is then sent to the second neptunium or plutonium solvent extraction cycle. The uranium-bearing stream (1BU) flows by gravity to the third mixer-settler unit (1C bank), where the uranium is stripped from the organic phase into a very dilute solution of nitric acid (1CX). The aqueous uranium stream (1CU) from the 1C bank is sent to the second uranium solvent extraction cycle. The 1CU may be evaporated. The stripped solvent (1CW) from the 1C bank is sent to solvent recovery (see Chapter IX). The gross gamma decontamination factor for this cycle is normally 25,000 to 50,000 for uranium and 200 to 300 for neptunium.

In order to convert most of the uranyl nitrate, plutonium nitrate, and neptunium nitrate into extractable TBP complexes, it is necessary (see Equations 1, 2, and 4) to provide a large excess of nitrate ion. Aluminum nitrate or other metal nitrates produced by dissolution of the original fuel elements and their bundles are usually present in the first solvent extraction feed solution in sufficient concentrations for extraction. Additional nitric acid is added to prevent the precipitation of mercuric sulfamate. Figure 7.31 shows how the solubility product constant for mercuric sulfamate varies with acid concentration. When neptunium is being recovered, neptunium is reduced from Np(VI) and Np(V) to Np(IV) as shown in Equations 5 and 6 by the addition of ferrous sulfamate to the 1AS stream. Ferrous sulfamate, if added to the feed solution, is destroyed by radiolysis (see Section 7.2.1), which allows plutonium and neptunium to rapidly reoxidize to Pu(IV) and Np(V). The radiation dose rate for plant fuel solutions is typically 0.1-0.2 mrad/hr. Ferrous sulfamate in the scrub (1AS) solution reduces neptunium and plutonium in the mixer-settler, ensuring neptunium extraction into the organic phase and plutonium rejection to the aqueous waste. Since ferrous sulfamate is unstable in nitric acid solution (see Section 7.2.1 and Figures 7.18 and 7.19), ferrous sulfamate must be added to the scrub section of the 1A bank or the scrub solution as a separate stream immediately before the scrub solution enters the 1A bank.

Plutonium must be in the most extractable, Pu(IV), valence state for best recovery; however, small amounts (<10%) of Pu(VI), which is about one-fifth as extractable as Pu(IV), do not cause excessive loss of plutonium. In some unadjusted feeds where Pu(IV) is the principal species, no valence adjustment is required. When Pu(III) or Pu(V) and Pu(VI) are present, addition of nitrite ion alone or ferrous sulfamate followed by nitrite ion may be necessary to properly adjust (and stabilize) the plutonium valence to Pu(IV).

Sodium nitrite alone will oxidize Pu(III) to Pu(IV) in a few minutes and will reduce Pu(V) and Pu(VI) to Pu(IV) also in a few minutes provided a sufficient concentration of one or more catalysts such as U(VI) or Fe(III) is present to accelerate the reaction.[14] In the absence of catalysts the reaction is slow and may require several hours. Heat (e.g., to 40°C) and/or longer agitation may compensate for the absence or inadequacy of catalyst. The maximum sodium nitrite in the feed must be limited because excesses will increase the nitrite extracted (as nitrous acid) by the solvent to mixer-settler 1B where the nitrite may interfere with reduction and partitioning of the plutonium.

Ferrous sulfamate will reduce all plutonium in solution to Pu(III) and sodium nitrite will subsequently oxidize all Pu(III) to Pu(IV); both reactions proceed rapidly and require no catalysts. Ferrous sulfamate must be limited to avoid excess sulfate (from destruction of sulfamate ion) which complexes plutonium and interferes with solvent extraction. The sodium nitrite is limited as explained above.

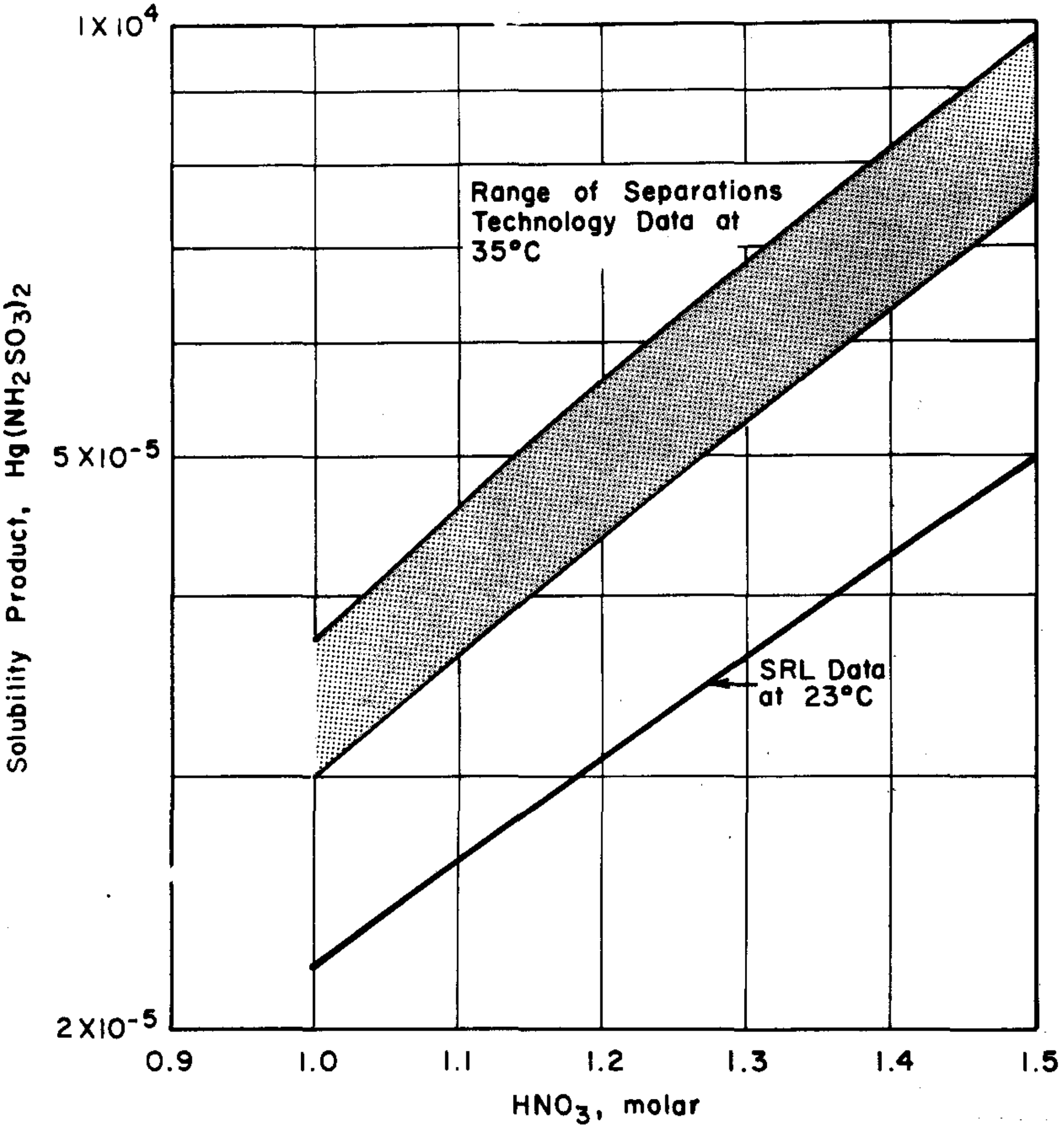


FIGURE 7.31 Solubility of Mercuric Sulfamate in Nitric Acid Solutions

For aluminum-containing fuels, the feed is adjusted with acid and/or water until the aluminum nitrate concentration meets specifications for the 1AF stream, >1.1M aluminum nitrate. For stainless steel, nichrome, and other metal clads or cores, the total nitrate in the feed is adjusted to maximize the extraction of uranium and neptunium. The maximum nitrate concentration must be limited to prevent formation of the inextractable $Np(NO_3)_6^=$ complex which has a maximum concentration at 7.5 to 8M total nitrate. Limiting total nitrate to ≤6M when neptunium is present maximizes neptunium extraction.

The distribution of uranium between the organic and aqueous phases is dependent on the uranium concentration, the TBP concentration, the temperature at which the extraction takes place, and the nitrate concentration in the aqueous phase (see Figures 7.5 to 7.14). The uranium distribution coefficient decreases with temperature; at 45°C, it is about half that at room temperature. Therefore, with feed solutions containing greater than 10 g/ℓ uranium, recovery is more efficient at 45°C than at 60°C. In addition, the flow rate of the extractant (1AX) must be increased as uranium concentration in the feed increases in order to efficiently recover uranium (see Figure 7.23). Higher extractant (1AX) rates are required if neptunium is to be recovered efficiently (see Figure 7.24). The flow rates in Figure 7.24 may be linearly interpolated to obtain flow rates for temperatures between 45 and 60°C.

When plutonium is being recovered, B-bank conditions need only assure that uranium does not reflux. When neptunium is being recovered, B-bank conditions must be closely controlled to prevent uranium reflux and neptunium loss to the 1CU. Therefore, the flows of all streams and the acid concentration in the 1BX cannot be allowed to vary without increasing neptunium losses (see Figures 7.26 and 7.27).

7.2.4 Second Uranium Cycle

The second uranium cycle further decontaminates the uranium to meet product specifications and to permit direct handling during the finishing operations. The decontamination factor achieved in this cycle is normally 300 to 500.

The uranium-bearing aqueous solution (1CU) from the first cycle stripping bank (1C) flows by gravity into a tank-type decanter in which entrained organic phase disengages. An air lift on the decanter returns the organic phase to the 1C mixer-settler. Normally the aqueous solution is transferred to the 1DF adjustment tank where nitric acid is added as the salting agent for second cycle extraction. If the uranium concentration is low, the solution can be evaporated to increase the uranium and nitric acid concentrations. The adjusted feed (1DF) is next transferred to the 1DF feed tank from which it is delivered continuously to the mixing section of stage 8 of the second cycle mixer-settler bank (1D). Organic extractant (1DX) is pumped to stage 16. A small amount of ferrous sulfamate is added at stage 4 (1DS') to ensure that any plutonium present in the feed solution will remain in the aqueous phase in the unextractable trivalent state; the ferrous sulfamate also maintains the neptunium in the tetravalent state. The uranium is extracted into the organic phase; the fission products, any plutonium as Pu(III), and 80 to 90% of the neptunium remain in the aqueous phase and leave the bank at stage 16 in the aqueous waste stream (1DW). The acidity of the scrub and the flow ratios of extractant to scrub streams are adjusted to reject Np(IV) to the aqueous waste stream.

The organic solution of uranium, while flowing toward stage 1, is scrubbed with a solution of nitric acid (1DS) for further separation from fission products. The organic product stream (1DU) emerges from the bank at stage 1 and flows by gravity to stage 12 of the 1E bank. In the 1E bank the uranium is stripped from the organic phase into a countercurrent stream of water slightly acidified with nitric acid (1EX). The resulting aqueous solution of uranium (1EU) is evaporated if necessary and shipped. The stripped solvent (1EW) is discharged from stage 1 and is sent to solvent recovery (see Chapter X).

Flow and concentration control for the second solvent extraction cycle are more exacting than those for the first cycle. First, the flow rates are moderately higher and, since the equipment is no larger, a deviation from the specified conditions will cause mixer-settler disturbances to occur more rapidly and to a greater degree. A further complication introduced is that nitric acid, the salting agent for the second cycle, is itself complexed by TBP (Equation 3), so the distribution coefficient of nitric acid and the effects of nitric acid concentration on the distribution coefficient of uranium must be considered. In the first cycle extraction, a moderate deviation in the concentration of the nitric acid salting agent in either the feed or the scrub stream would cause only a minor shift in the 1A bank stage uranium concentrations; in the second cycle, a deviation in the corresponding nitric acid concentration would be reflected by changes in concentration of both uranium and nitric acid in every stage of both extraction and stripping mixer-settler banks. A controlled degree of uranium reflux exists in the scrub stages of the 1D bank because of variation in the nitric acid concentration in these stages. This reflux is controlled so that the uranium concentration in the feed at normal operating conditions is not exceeded. As a result, there is a peak uranium concentration at about stage 5. Deviation from specified operating conditions could cause increased reflux and dangerously high uranium concentration in this region of the bank.

Another factor which makes a high quality of operating control desirable pertains to the location of the second cycle solvent extraction in the overall process. The second cycle contributes the last large decontamination. Its product stream must meet the specifications not only for fission products, but also for inorganic solids. On occasion, feed material of subnormal quality may be fed to the second cycle and produce a satisfactory product. If the uranium solution delivered from the second cycle is below specifications, there is no recourse except to reprocess.

7.2.5 Second Neptunium Cycle

Reducing Flowsheet

The neptunium streams from the first cycle (1BP), solvent washes, and the second uranium cycle (1DW) are processed in the second neptunium cycle, along with plutonium free wastes from HB-line, for additional decontamination and concentration of the neptunium. The 1DW (3M HNO_3) and solvent washes are evaporated batch-wise to 5 to 8M HNO_3 and combined with the 1BP (1.5M HNO_3) to give a resulting feed solution (2AF) 4M in HNO_3. Ferrous sulfamate is added to maintain the neptunium in the Np(IV) valence state. The 2AF is transferred continuously into the mixing section of stage 8 of the 2A mixer-settler. The neptunium is extracted into the organic phase (30 vol % TBP) (2AX); fission products and other salts are scrubbed into the aqueous phase by the (2AS) scrub stream and leave the bank in the aqueous waste stream (2AW). The organic solution of neptunium flows by gravity to the 2B bank where the neptunium is stripped from the organic phase into the slightly acidified aqueous stream (2BX). The stripped solvent (2BW) is discharged through a decanter to solvent recovery. The aqueous neptunium solution (2BP) is evaporated and stored in the evaporator. As a general rule, the neptunium concentrate will require additional decontamination before being shipped to B-line. In this case, the concentrate is periodically returned to the second neptunium cycle for one or two additional passes to achieve the desired decontamination. The processing of 1BP and 1DW may be temporarily delayed while reprocessing the concentrate.

The second neptunium cycle extractant (30% TBP) can retain significant quantities of neptunium in combination with dibutyl phosphate (DBP), a hydrolysis and radiolysis product of TBP. This Np-DBP compound is not decomposed by aqueous acid but is destroyed by basic solutions. The neptunium is stripped in the solvent washers, and the washes must be recycled to recover the neptunium.

This cycle does not separate neptunium from any uranium that may be present. The amount of uranium increases with recycle since B-line wastes that contain traces of uranium are also recycled. (Wastes containing ^{238}Pu are not recycled.) The uranium is allowed to accumulate before a special solvent extraction run is made in the second neptunium cycle mixer-settlers to purge the uranium. The uranium is extracted into 30 vol % TBP in the 2A bank, stripped into dilute nitric acid in the 2B bank, and sent to the first solvent extraction cycle for recovery.

Oxidizing Flowsheet

The reducing flowsheet described above for neptunium purification does not separate neptunium and thorium. If significant thorium contamination is present in the neptunium, an oxidizing solvent extraction flowsheet is used. Neptunium is oxidized to its most extractable state [Np(VI)] by addition of ceric ammonium nitrate to the feed solution. The feed solution (2AF) is jetted continuously to the mixing section stage 8 of the 2A bank. In the extraction section the nitric acid concentration and the relative flow rates of feed and extractant are adjusted to extract neptunium into the organic phase; thorium remains in the aqueous phase and leaves the bank in the aqueous waste stream (2AW). In the scrub section of the 2A bank, the organic phase is scrubbed with dilute acid (0.5M HNO_3) to remove residual thorium and fission products. The organic solution of neptunium flows by gravity to the 2B bank where neptunium is stripped from the organic phase into the slightly acidified aqueous stream (2BX). Cerium extracts and follows neptunium into the 2BP. The 2BP from the oxidizing runs is recycled to a reducing run to remove cerium. The gamma decontamination factor from oxidizing runs is low. Entrained 2AS must be minimized to prevent interference from sulfate ion during subsequent recycle. Sulfate ion complexes Np(IV), prevents complete extraction, and causes excessive loss of Np to waste. When significant sulfate ion is present in the 2BP, the 2BP may require dilution before recycle. The stripped solvent is treated as described earlier. The aqueous neptunium solution is concentrated by evaporation and stored for later processing in B-line.

7.2.6 Second Plutonium Cycle

The second plutonium cycle concentrates and decontaminates the plutonium product of the first cycle to meet direct handling requirements and other product specifications; no removal of uranium is achieved. The product 1BP from the first cycle is treated with sodium nitrite to destroy the residual ferrous sulfamate and to oxidize the plutonium to the extractable Pu(IV) state. After adjustment to the proper concentration of nitric acid, the feed solution (2AF) is jetted at a controlled rate to the center stage of the 2A bank. The plutonium and any uranium are extracted into the organic phase (2AX); the fission products, iron, and other inorganic contaminants remain in the aqueous phase and leave the process in the aqueous waste stream (2AW). The organic solution of plutonium is scrubbed with dilute nitric acid (2AS) for additional removal of ^{234}Th and fission products, and the emergent organic stream (2AP) flows by gravity to the 2B bank. In the 2B bank, the plutonium is reduced by, and stripped into, an aqueous solution of hydroxylamine sulfate or nitrate. The decontamination factor across the second plutonium cycle is about 1000. The product stream (2BP) contains plutonium that has been decontaminated from fission products by a factor of about 10^7. The solution is transferred to storage. The stripped solvent (2BW) is sent to solvent recovery.

The valence adjustment of the feed solution for the second cycle involves the stepwise oxidation of sulfamate ($NH_2SO_3^-$), Fe^{2+}, and Pu^{3+} ions. The sulfamate must be completely destroyed before the iron and plutonium can be oxidized. This reaction can be represented by the following simplified equation:

$$NH_2SO_3^- + NO_2^- \rightarrow N_2 + SO_4^= + H_2O$$

After destruction of the sulfamate, a small excess of nitrite is sufficient for the catalysis of the oxidation of the iron and plutonium by nitric acid. The overall reactions for the destruction of ferrous sulfamate and adjustment of the plutonium valence can be represented as follows:

$$3Fe(NH_2SO_3)_2 + 6NaNO_2 + 4HNO_3 \rightarrow Fe(NO_3)_3 + Fe_2(SO_4)_3$$
$$+ 3Na_2SO_4 + 6N_2 + NO + 8H_2O$$

$$3Pu(NO_3)_3 + 4HNO_3 \rightarrow 3Pu(NO_3)_4 + NO + 2H_2O$$

The use of a large excess of nitrite is undesirable, because it is almost completely extracted as nitrous acid by the solvent. In the solvent, nitrous acid degrades the diluent and follows the solvent into the 2B bank where it consumes an equivalent amount of the hydroxylamine reductant. It is therefore important to operate with a minumum amount of nitrite in the feed (2AF).

Therefore, after nitrite addition, a sample of 2AF is tested in the sample aisle with an indicator sensitive to nitrite.[13] The indicator used is a mixture of tris(o-phenanthroline) iron(II) sulfate and sodium indigotin-6,6'-disulfonate (indigo carmine dye). Indigo carmine is blue in color and changes to light yellow on reaction with nitrite ion in acid solution (nitrous acid). Tris (o-phenanthroline) iron(II) sulfate is red in color and is not affected by nitrous acid, but merely provides proof that indicator is present. Thus, a positive test for excess nitrite in the 2AF consists of a color change in solution from blue to red. The plant has shown that the reaction of nitrite with indigo carmine is affected by acid concentration in solution. The effective range for instantaneous reaction is between 2 and 4M HNO_3. Below 2M HNO_3, the reaction proceeds very slowly and a large amount of nitrite is required to produce complete reaction. Above 4M HNO_3, nitrite is decomposed autocatalytically, and high acid destroys the tris(o-phenanthroline) iron(II) complex ion. The acid concentration of the 2AF must be adjusted before nitrite addition.

Ruthenium removal is most effective at high acidity, and the removal of zirconium, niobium, and thorium is most effective at low acidity. Hence, a highly acidic feed and a low acidic scrub most effectively decontaminate plutonium from fission products and thorium.

Selection of operating conditions for the 2A bank is governed by the tendency of plutonium to reflux in the bank. Plutonium tends to be stripped out of the solvent in the scrub section and to move in the aqueous phase to the extraction section where it is re-extracted by the solvent. Equilibrium is established only when the concentration of plutonium in the scrub section is considerably higher than it is in the feed. The extent of this reflux is determined by the acidity of the scrub stream and the relative rates of flow of the streams entering the bank. Close control of the scrub acidity is particularly important, because the plutonium inventory of the bank increases rapidly as the acidity of the scrub falls below about 0.5M.

Since Pu(IV) and thorium are complexed by sulfate, the effect of sulfate in the 2AF is to decrease the distribution coefficients of both elements. This decrease is beneficial to decontamination from thorium but detrimental to the recovery of plutonium. The 2AF plus the 2AS contain 0.03M sulfate and 2.8M nitric acid. Under these conditions, the plutonium distribution coefficient is 10 and the extraction factor is 5.7.

In the 2B bank, hydroxylamine sulfate functions as a stripping agent for plutonium by two mechanisms. First, sulfate strongly complexes Pu(IV) at low acidity. Sulfate alone can strip plutonium. Secondly, in dilute (less than about 0.6M nitric acid, plutonium is reduced by hydroxylamine. Pu(III) has a distribution coefficient of only about 0.01, and it therefore is strongly retained by the aqueous stream.

Hydroxylamine nitrate in the 2B bank strips plutonium by only one mechanism, reduction of Pu(IV) to Pu(III). This reaction is more rapid in the absence of sulfate. The nitric acid must be dilute to prevent autocatalytic reaction of hydroxylamine with nitric acid.

Typical operation of the second plutonium cycle is as follows. Aqueous plutonium nitrate is received from the first cycle into the 1BP receiving tank from which it is transferred periodically to the 2AF adjustment tank. This solution is diluted, according to the plutonium content of the original fuel elements, such that the plutonium concentration in the 2AF will be approximately 0.5 g/ℓ. (Higher concentrations are being tested in order to increase bank capacity subject to bank inventory criticality limits.) Sodium nitrite is added to oxidize plutonium to Pu(IV) and to destroy the ferrous sulfamate added in the first cycle; the quantity of sodium nitrite may be varied for test programs or for special conditions such as process startup. Adjusted feed is transferred to stage 8 of 2A bank. Organic solvent (2AX) is fed continuously from a header to stage 16, and the aqueous scrub (2AS) is fed from a gallery tank to stage 1. The aqueous waste stream is collected in the 2AW decanter where it is sampled and transferred, under normal conditions, to the low-activity waste feed tank; batches containing excessive amounts of plutonium are normally recycled. The Pu-containing organic stream (2AP) flows by gravity to stage 16 of 2B bank; the aqueous strip (2BX) is pumped to stage 1. The stripped organic stream is collected in the 2BW run tank and pumped to solvent recovery. The plutonium product stream (2BP) is collected, evaporated, and stored or sent to B-Line.

7.3 SAFETY

The safety considerations associated with the solvent extraction process include the possibility of: 1) accumulation of critical amounts of enriched uranium or plutonium, 2) exposure of personnel to radiation, 3) ignition of the solvent, and 4) rapid pressurization of evaporators.

7.3.1. Criticality

The most serious nuclear safety hazard encountered in the solvent extraction process is fission of ^{235}U or ^{239}Pu as a result of accumulation of a critical concentration or configuration of the material at some point in the system. Such an accident could result in equipment damage and/or release of fission products. The provision of safeguards to ensure that such a situation will never arise is paramount in the entire separations process.[10]

The consideration has special significance in the solvent extraction cycles because of two factors. First, since the process is inherently continuous, it is not possible to establish a batch size, whereby the quantities of available material are restricted to critically safe limits. Second, the concentrations of enriched uranium in the individual stages of the banks are variable and sensitive to process changes.

The basis of all safeguards for prevention of nuclear incident in the solvent extraction process is concentration control; the concentration of fissile material in solution is maintained below the minimum critical concentration for any fissile material or mixture of fissile materials. Additional control is provided by geometry and mass limits. Figures 7.32-7.36 depict the uranium concentrations anticipated at each stage of each mixer-settler under flowsheet conditions of operation with 3.5% TBP. The concentration profiles with 7.5% TBP are the same although the absolute concentrations will depend on flow rates.

Under normal flowsheet operation, a dangerous buildup of uranium concentration in a mixer-settler, by foreseeable circumstances, is not possible because organic-to-aqueous flow ratios and salting agent concentrations are limited to maintain the concentration of uranium less than the feed concentration. However, it is essential that bank operation be maintained constantly within specifications to avoid hazard. As an example, consider Figure 7.35 in which the stage concentrations of uranium are plotted for the ID bank for flowsheet conditions. If the concentration of nitric acid in the IDS stream is allowed to decrease from the specified 0.9M to 0.5M, the aqueous phase concentrations will increase to the values shown by the dotted lines. Low salting strength in the IB bank or high salting strength in the IC bank could also cause a reflux of uranium which could result in a nuclear incident. The safe salting strengths for the 1B and 1C banks are shown for various conditions in Figures 7.28 and 7.30 for 7.5% TBP. Extreme reliability is demanded of the flow measuring instruments and of the concentration analyses; in most cases this reliability is achieved through use of duplicate instrumentation.

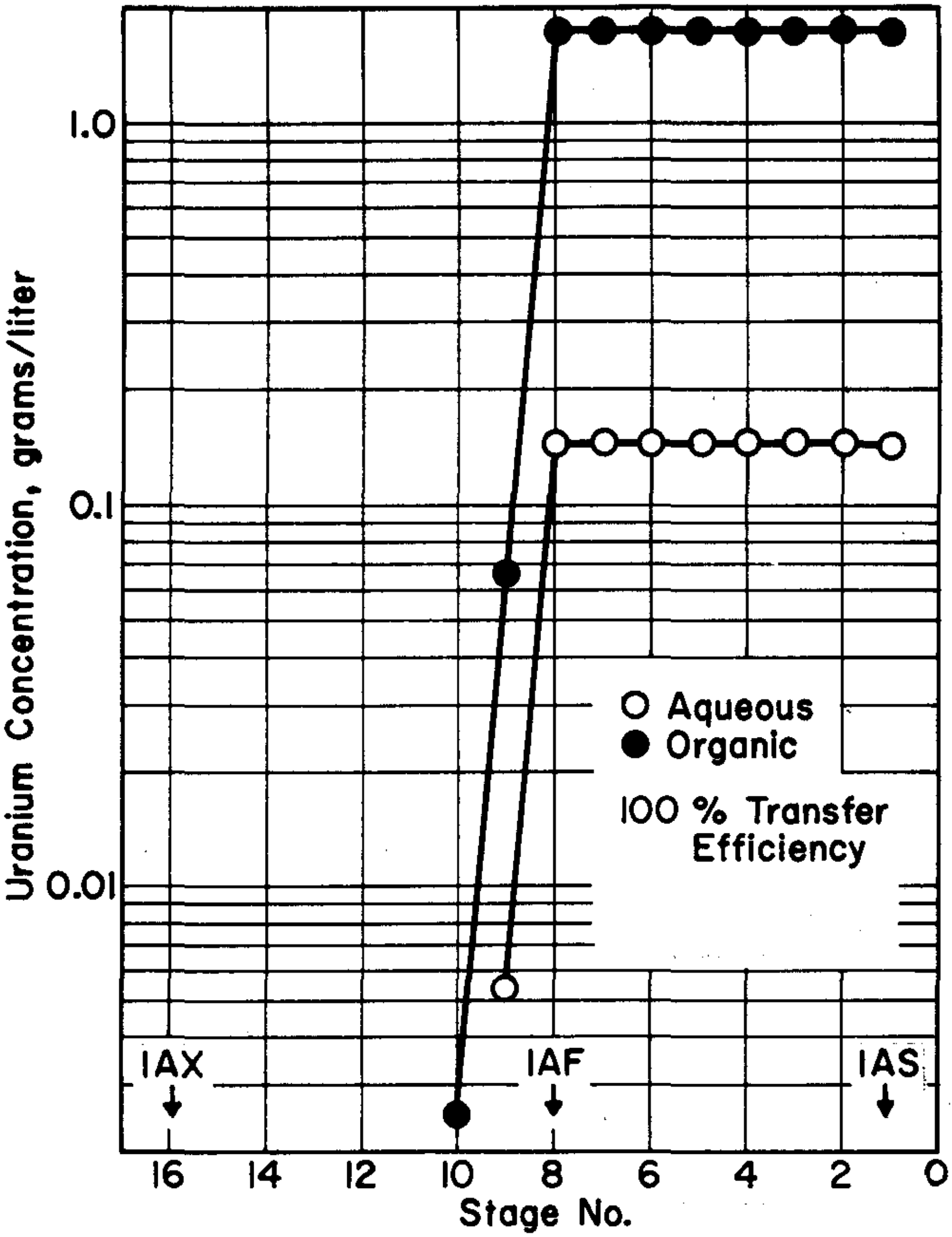


FIGURE 7.32 1A Mixer-Settler Uranium Distribution

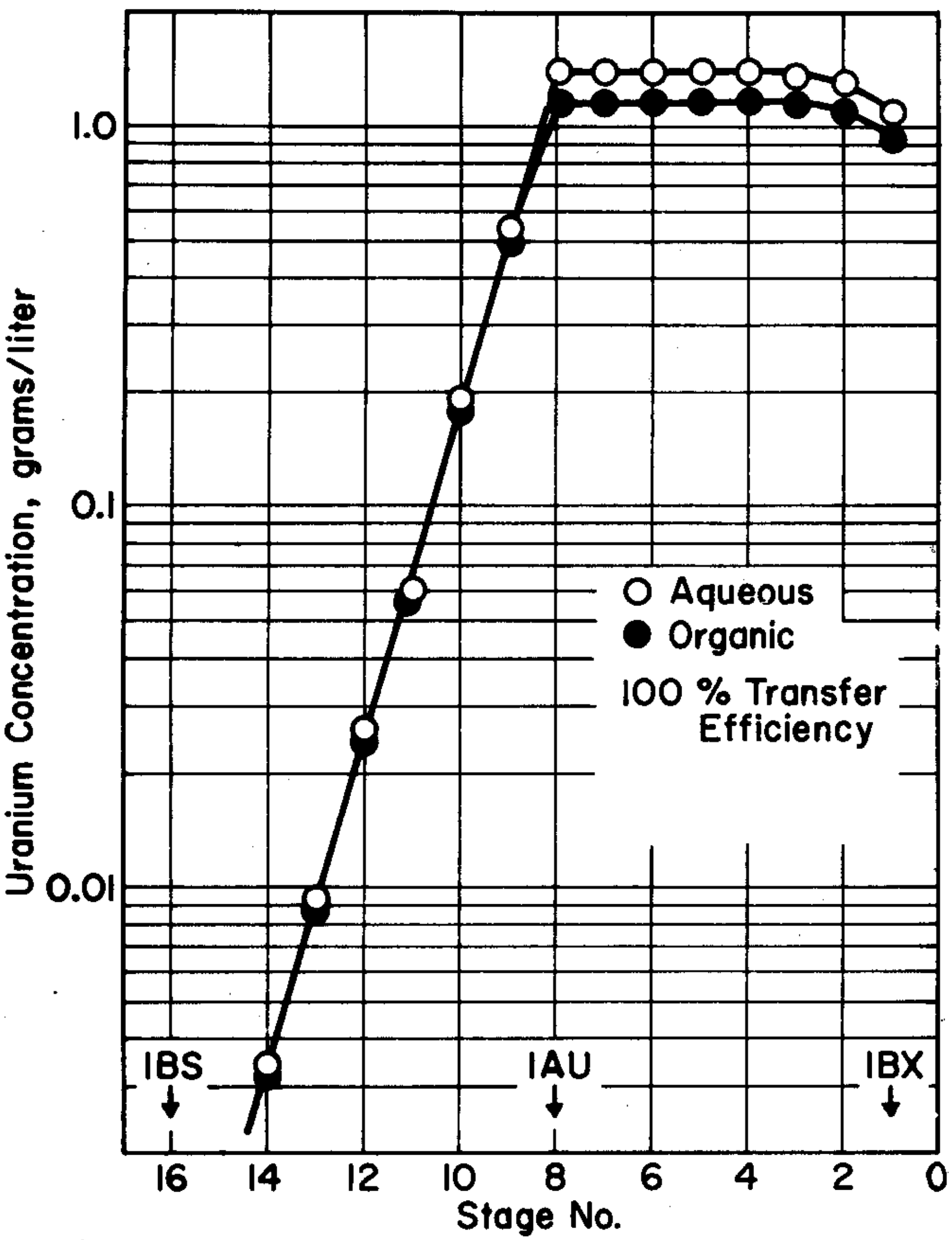


FIGURE 7.33 1B Mixer-Settler Uranium Distribution

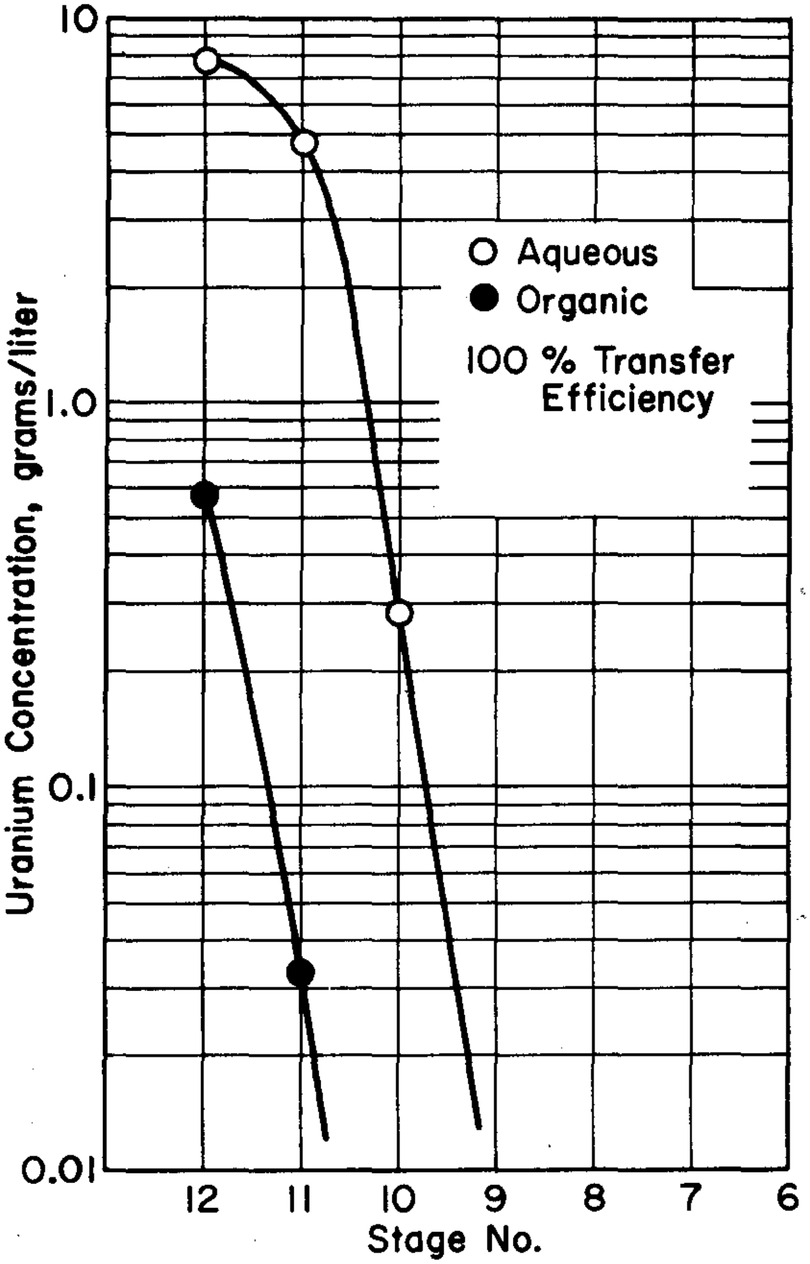


FIGURE 7.34 1C Mixer-Settler Uranium Distribution

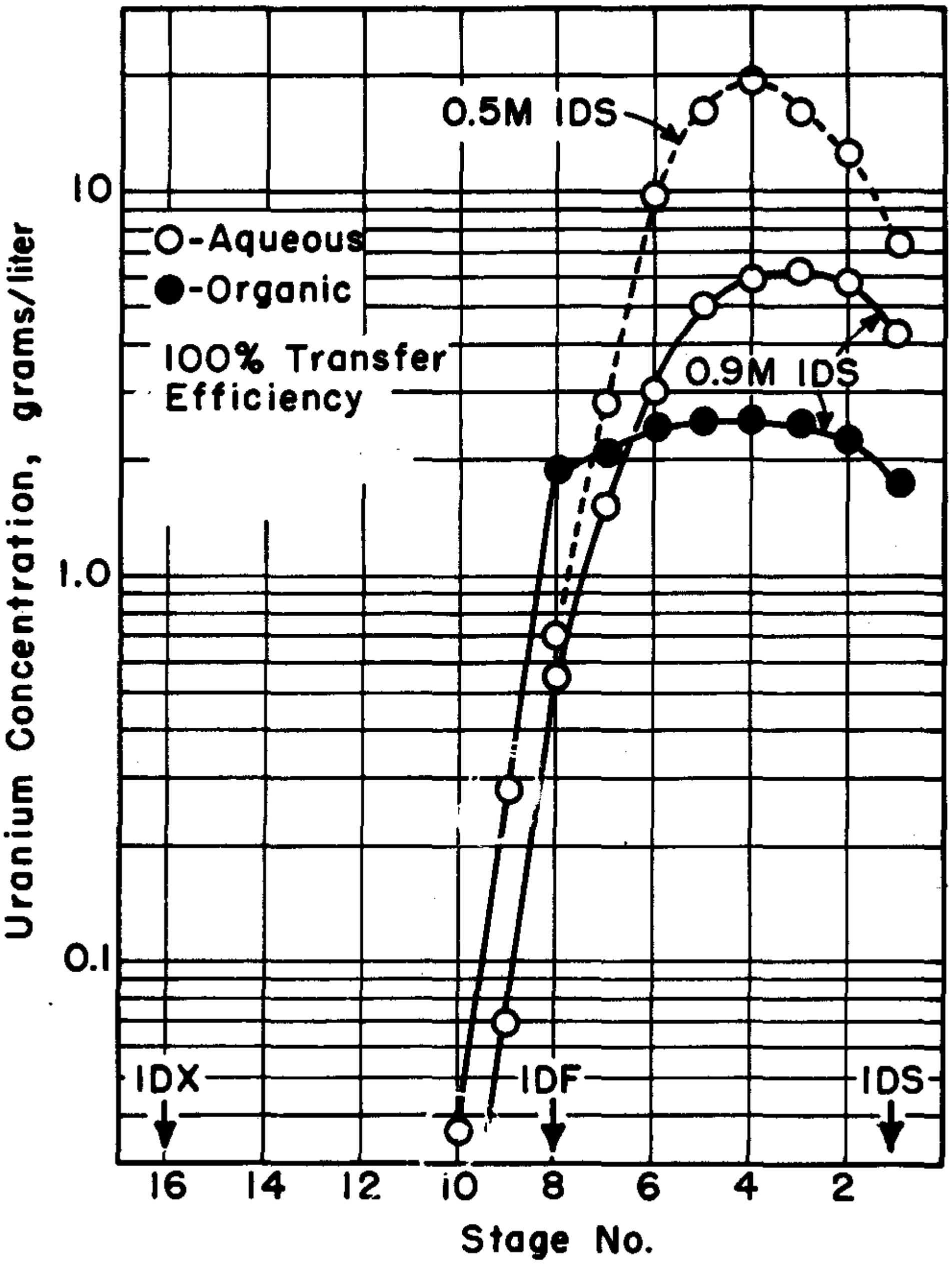


FIGURE 7.35 1D Mixer-Settler Uranium Distribution

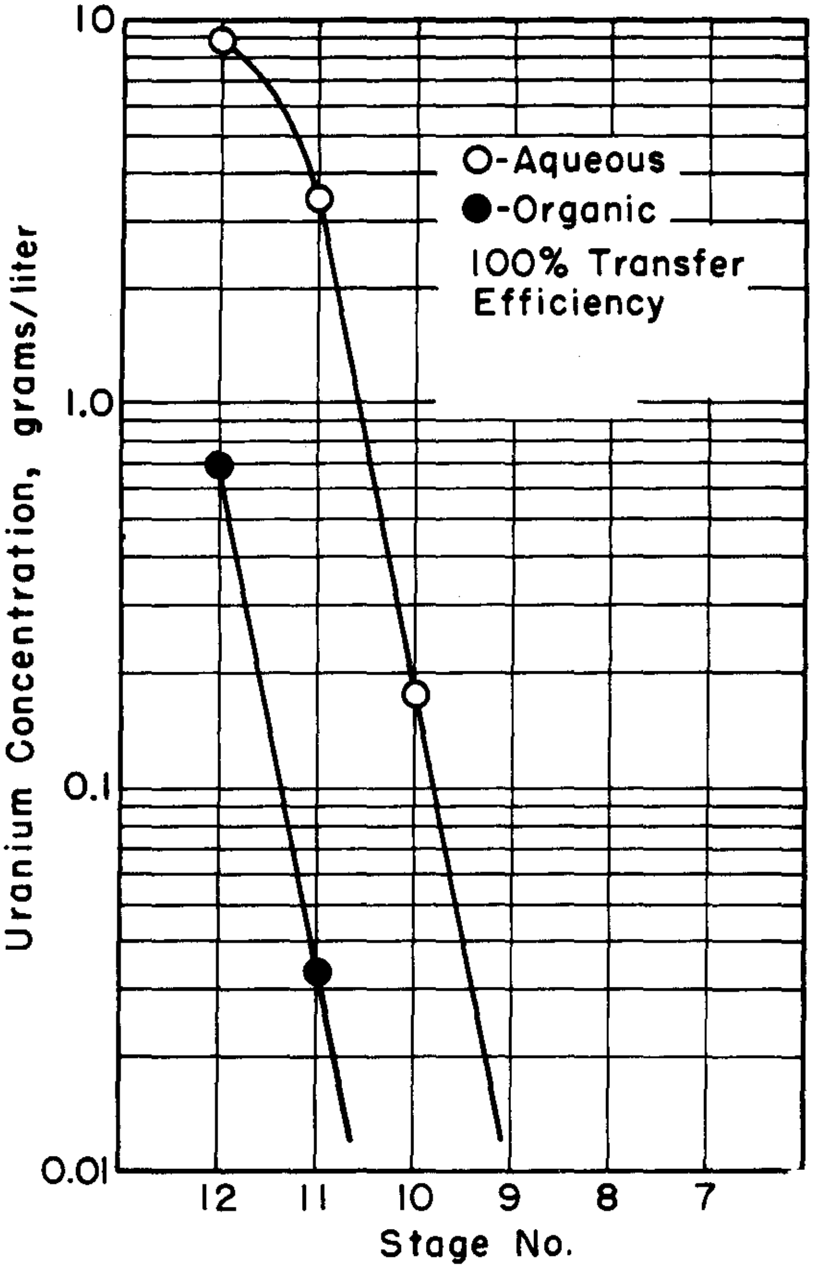


FIGURE 7.36 1E Mixer-Settler Uranium Distribution

The correct concentration of salting agent in the banks must be maintained in order to avoid reflux and the resultant criticality hazard. The hazard from this particular type of maloperation is both serious and insidious; the ultimate result of the action is not immediately obvious. There are several other types of maloperation that could force the uranium concentration to high levels, but in every case (other than abnormal salting strength) the nature of the hazard is clearcut. For example, operation of either of the stripping banks with no aqueous flow would not be innocently tolerated because it is so apparent that, with no uranium leaving the bank, the uranium concentration in the bank would have to be increasing continuously.

The effect of substituting water for aluminum nitrate or HNO_3 as a 1AS stream has been demonstrated in a semiworks mixer-settler. Natural uranium was used in the tests. It was established that there were two separate phenomena. First, the water stripped the uranium from the solvent in the scrub stages, carried the uranium down the bank, and caused a peak concentration of about 38 g/ℓ to be reached at stage 8 about 90 minutes after the water flow started. Second, with uranium continuing to enter the feed stage, but being prevented by the water scrub from leaving the bank in the solvent stream, the uranium refluxed and accumulated around the feed stage. After 6 hours, the aqueous concentration had reached 25 g/ℓ and was continuing to increase. Under these conditions in the processing of enriched uranium, the 1A bank would eventually accumulate a critical concentration. Similar behavior would occur in the 1A bank with 7.5% TBP and the 1D bank if water were substituted for the acid scrub solution.

Dual flow measuring instrumentation is installed on each of the mixer-settler feed streams. For the 1AX, 1AS, 1BX, 1BS, 1DX, and 1DS streams, each pair of instruments is in the feed lines to the canyon; for the 1CX and 1EX, there is a flow recorder on the cold stream, and the duplicate flow instrument is in the canyon on the 1CU and 1EU stream. For any stream, both instruments are connected into alarm systems so that a deviation from specifications indicated by either instrument will actuate an alarm. Composition of cold feeds is determined by routine laboratory analysis, and some of the vessels are equipped with instruments that provide warning if the contents are not within specifications. For example, if the specific gravity of the 1AS feed tank contents is less than that of 4.0M HNO_3, the instrument will actuate an alarm. Uranium concentrations of solutions of 1CU and 1EU are monitored continuously by colorimetric analyzers. Conductivity meters which indicate acid strength are also located on the 1CU and 1EU streams to detect any increase in acid concentration in the stripping banks.

As a backup to all of the other safeguards, each bank is equipped with dual neutron monitors and a neutron source. These monitors measure neutron multiplication by the fissile material in the bank and thus provide an independent indication of uranium concentration. The extraction bank monitors are mounted adjacent to stage 2; stripping banks have monitors beside stage 12. The 1B bank monitors are beside stage 2.

The quantity of ^{235}U in the second neptunium cycle is limited to a quantity that is subcritical even in the most favorable configuration for criticality.

In the 2A bank, the refluxing of plutonium is sensitive to acidity and flow rate of the scrub stream (2AS). Close control of nitric acid concentration is particularly important, since the plutonium concentration in stages 3, 4, 5, and 6 increases rapidly below 0.5M nitric acid. In the case of no acid in the scrub stream, the plutonium would accumulate in these stages at approximately the input rate, and criticality would be approached within a few hours. The controls include careful adjustment of the acidity of the scrub stream and close accounting of the plutonium discharged by the cycle.

7.3.2 Radiation Exposure

Exposure of personnel to excessive amounts of radiation from equipment in the solvent extraction cycles has been largely eliminated by design of the plant shielding. Precautions must be taken to avoid excessive amounts of fission product activity in the 1EU and 2BP which are removed from the shielded canyons for subsequent direct handling. These precautions include monitoring and strict adherence to specifications of purity for these streams. Likewise, the radiation level from washed solvent must be monitored to avoid excessive exposure of personnel during solvent handling in 211-H Building and recycle to the third level feed tanks (see Chapter IX).

7.3.3 Ignition of Solvent

The process solvent is flammable because of the volatility of the hydrocarbon diluent. The flash point of vapor and air for dry "Ultrasene" is 70 to 75°C; the same limit is valid for solvent containing up to 7.5% TBP. The flash point for n-paraffin is 84°C and those of its TBP solutions are correspondingly higher. The flash point for 30% TBP - 70% "Ultrasene" is 75 to 80°C. Serious hazards are avoided by minimizing spillage in the working area and by keeping the solvent below its flash point at all times.

7.3.4 Evaporator Pressurization

The extensive use of evaporators in the solvent extraction process entails the hazard of pressurization through rapid reaction of nitric acid with excessive amounts of entrained solvent. Safeguards limit entrained solvent in evaporator feed to 0.5 vol %, steam pressure to 25 psig, and evaporator temperature to 120°C, as discussed in Section 6.3.5. Special operating procedures avoid buildup of organic material in the evaporator feed tank.

Dried ammonium nitrate is potentially explosive, especially if heated with organic matter. This does not represent a hazard because (1) solutions cannot be evaporated to dryness; (2) organic material is controlled to <0.5 vol %; and (3) the amount of ammonium ion in the evaporator is small. This ammonium ion originates in reagents ($\sim$0.02% in fresh 64% HNO_3) and in hydrolysis of sulfamate during evaporation of solutions containing this material. Destruction of sulfamate with sodium nitrite before evaporation significantly reduces the formation of ammonium ion.

Solutions of hydroxylamine nitrate (HAN) are increasingly unstable at acid concentrations above 0.1M. Once initiated in boiling acidic solution, HAN decomposition proceeds autocatalytically and completely, releasing large volumes of gas.[3] This reaction can be prevented by destroying the HAN with sodium nitrite ($NaNO_2$) before evaporation. Although one mole of sodium nitrite can destroy one mole of HAN, three moles of sodium nitrite are added per mole of HAN in nitric acid solution because some nitrite is destroyed by side reactions. Alternatively, the decomposition of HAN can be controlled by feeding the HAN solution to an evaporator containing boiling high strength acid (>2M) which destroys the HAN as it enters.

Evaporation of other hazardous materials is discussed in Section 11.3.2.

7.4 EQUIPMENT

The principal items of equipment in the solvent extraction process are the seven mixer-settler banks. Facilities are also provided for the preparation and transfer of aqueous and organic feed streams, for concentration of product streams, and for storage of product, solvent, and waste solutions. First cycle equipment is located in the hot canyon, while both second cycles are in the warm canyon.

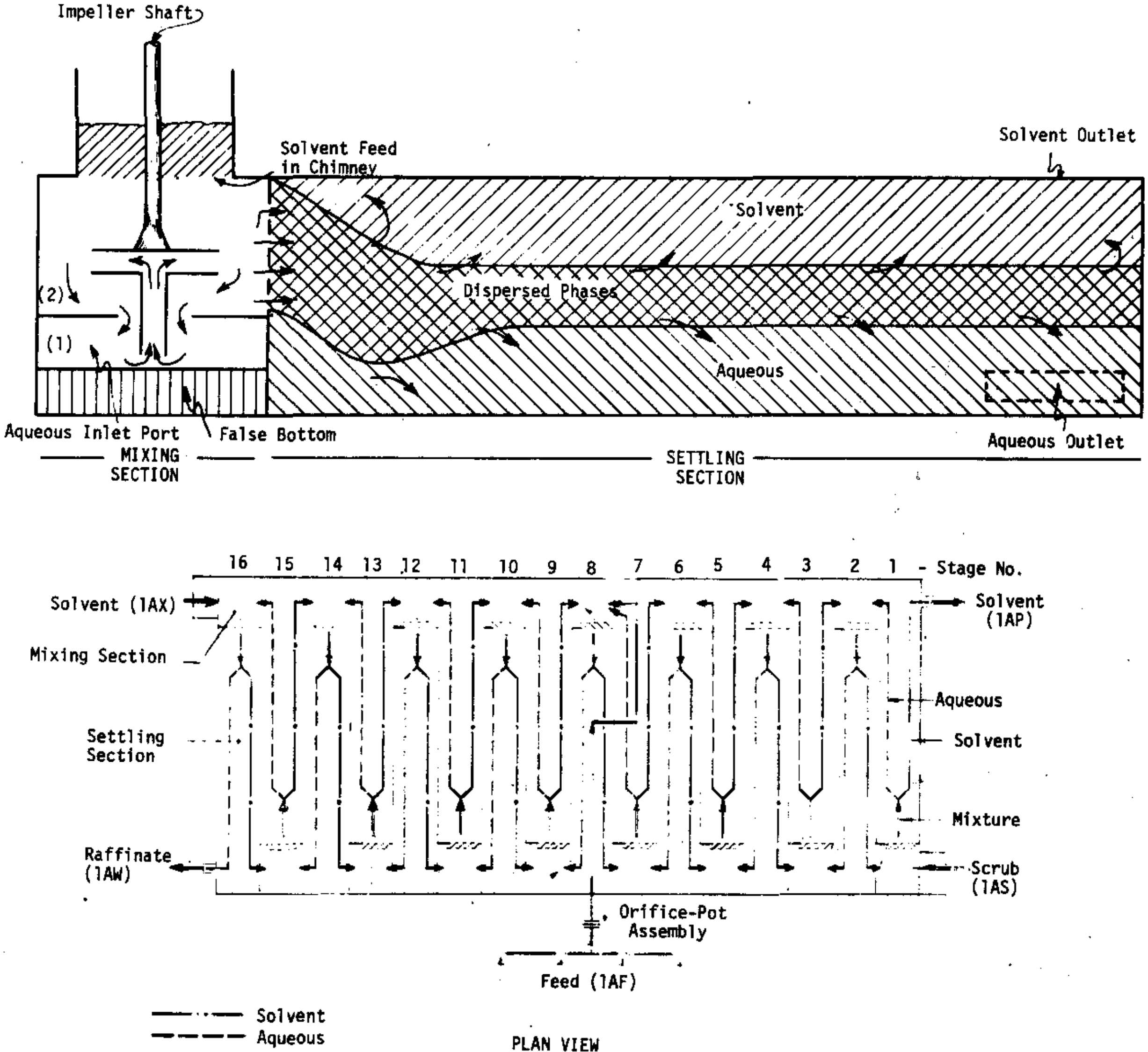
7.4.1 Mixer-Settlers

The mixer-settlers, generally termed "banks," are multistage, countercurrent liquid-liquid contactors. Each stage consists of a mixing and a settling section. The aqueous and organic phases flow concurrently from the mixing section through the settling section within a given stage, but countercurrently between adjacent stages. The pattern of flow of aqueous and organic streams through a type 1A bank is illustrated in Figure 7.37.

Each mixer-settler stage is a long rectangular box divided into a mixing and a settling section by a louvered opening. The settling sections vary in length, depending on the type of bank. A mixer-settler bank is a combination of these stages, so connected that the mixing section of a given stage joins the settling section of the two adjacent stages.

The settling section of a stage is totally enclosed except for openings with louver-type baffles that admit liquid from the mixing section with a minimum of turbulence, and the exit ports which allow liquid to flow to the mixing sections of the two adjacent stages. The mixing section of a stage is subdivided into three parts, one above the other. At the bottom is an aqueous inlet compartment, above it is the mixing compartment, and at the top is the chimney. The chimney is a large pipe (open at the top, and roughly equal in diameter to the width of the stage) that supports the mixer motor above the mixing section. The organic phase port from the settling section of one of the adjacent stages delivers organic phase into the side of the chimney; aqueous phase is delivered from the settling section of the other adjacent stage to the aqueous inlet compartment. Figure 7.38 illustrates both the details of a stage and arrangement by which stages are coupled together.

An important feature of the mixer-settlers is the use of a centrifugal-type impeller which mixes both phases in the mixing compartment and also serves as a pump to lift the aqueous phase flowing from one settling stage into the mixing section of the next. Figure 7.37 illustrates the general pattern of flows within a stage. The impeller is suspended in the mixing section from a variable-speed electric motor mounted on the top of the chimney. The impeller has a hollow shaft, which extends into the aqueous inlet compartment. During operation, aqueous phase flows from one adjacent stage settling section into the aqueous inlet compartment, is sucked up the shaft, and is discharged into the mixing compartment. The aqueous phase mixes with organic phase that comes from the settling section of the other adjacent stage. The impeller has considerably more than adequate aqueous pumping capacity, so a portion of the mixed phases in the mixing compartment is sucked down through an opening around the shaft into the



PLAN VIEW
Showing Flow Through
Type 1A Mixer-Settler

FIGURE 7.37 Mixer-Settler Flow Patterns

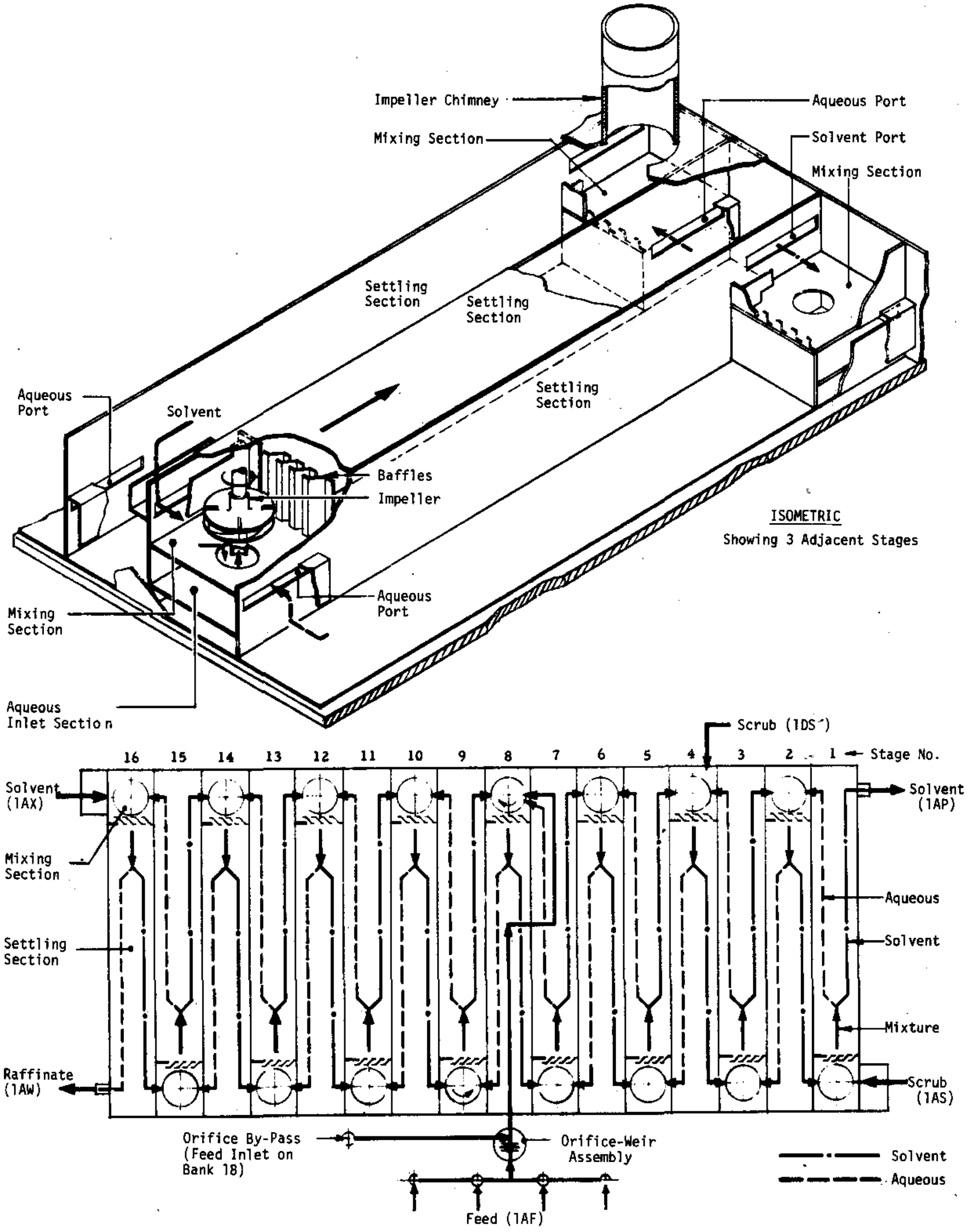


FIGURE 7.38 Mixer-Settler Stage Details

aqueous inlet compartment and back up through the impeller shaft together with fresh aqueous phase. The remaining mixed phase material is discharged from the mixing compartment through the baffles into the settling section.

An orifice cap is placed on the end of the hollow impeller shaft to limit the pumping capacity of the impeller so that, over the range of speed necessary for achieving adequate mixing, the impeller will not draw so much aqueous phase from the adjacent stage settling section that the interface in that section is lowered to a point where organic phase would also be withdrawn. In the extraction banks, the aqueous flow rate is considerably larger in the extraction section (from the combination of feed and scrub streams) than in the scrub section. Because the impellers all operate at the same speed, the orifice caps in the scrub section have smaller orifices than in the extraction section to limit the pumping capacity of the impellers. Adequate mixing is achieved in every stage and, at the same time, the pumping rates, which set the interface levels in the preceding stages, are correct. The second neptunium cycle banks do not have orifice caps installed on the impellers since the hydraulic rate through this cycle is generally less than that through either uranium cycle.

The impeller speeds are adjusted to represent an optimum balance between phase mixing (efficiency) and separation (de-entrainment). These optimum speeds vary with process rate and with the condition of the solvent. The increase in entrainment that accompanies increased impeller speed is not a simple function but depends to some extent on the degree of degradation of the solvent, the temperature, and the acidity. In general, adequate phase disengagement is achieved in the settling sections only if the residence time of liquids in the sections is in excess of one minute.

The general overall appearance of an extraction type bank (1A, 1B, 2A, 2B, or 1D) is shown in Figure 7.39. The stripping banks (1C and 1E) differ from the extraction-type banks in that the stages are larger (to allow longer settling times, there are only 12 stages instead of 16, and there is no feed point at the center stage. Typical dimensions of the stages of the two types of mixer-settlers are indicated in Table 7.2.

The size of the settling sections was designed for the Purex process in accordance with the required capacity and the rate at which the phases separate. However, plant experience has demonstrated that the hydraulic behavior is suitable for the enriched uranium recovery process. Generally, the 1C and 1E banks are operated without an impeller in the organic outlet stage. Although this mode of operation effectively reduces the number of stages from twelve to eleven, the loss in stripping efficiency is not

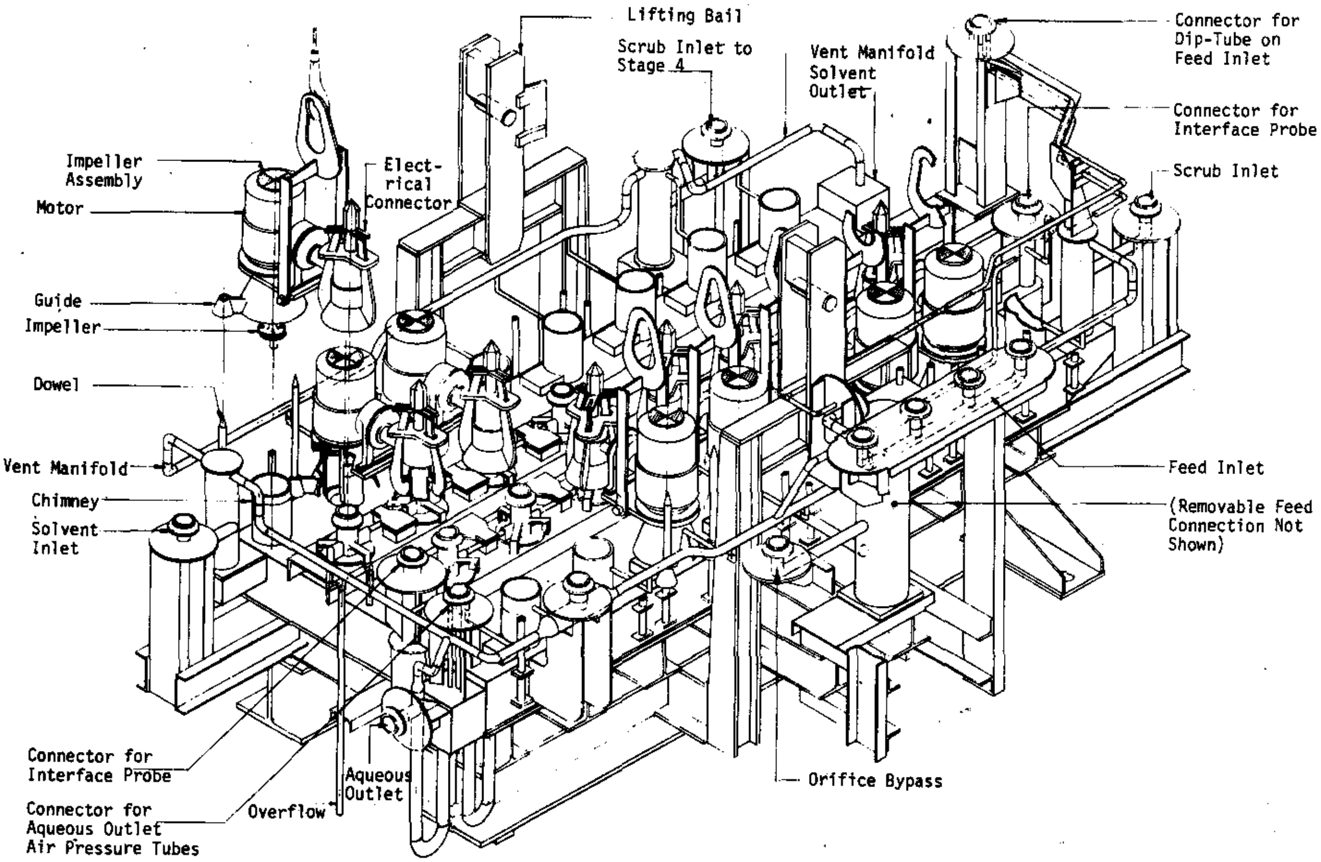


FIGURE 7.39 General Appearance of an Extraction-Type Bank

appreciable, and the increased settling time results in a pronounced improvement in the disengagement of organic and aqueous phases.

TABLE 7.2

Mixer-Settler Dimensions

	Extraction Banks	*Stripping Banks*
Number of Stages	16	12
Settling section (volume in gallons)	16.7	67.3
Settling section (height, width, and length in inches)	10 x 8 x 48	12 x 12 x 108
Mixing section (height, width, and length in inches)	8 x 8 x 9	9.5 x 12 x 13.5
Aqueous inlet compartment (height, width, and length in inches)	2 x 8 x 9	2.5 x 12 x 13.5

7.4.2 Interface Control

As mentioned in the preceding section, the interfaces in the settling sections of stages are maintained at acceptable levels as a result of the pumping action of the mixer impellers. The impeller in stage 2 controls the interface in stage 1, the impeller in stage 3 controls the interface in stage 2, and so on. The position of the interfaces is detected and indicated by electrical resistance probes located in the settling section of the two terminal stages. Since the detector at the organic outlet stage (stage 1) indicates the level as controlled by the impeller in stage 2 and, since the impellers of other stages have approximately equal pumping capacity, this detector also gives a reasonably good indication of the level in these stages (except for the aqueous outlet stage).

The interface level in the aqueous outlet stage is controlled in a different fashion from the interfaces in the other stages since there is no impeller available for control. Figure 7.40 shows the method used for this stage. The control system is based on a balance between the total liquid head inside the stage due to the organic and aqueous phases and the total head in the weir box due to the aqueous phase and the air pressure. Increasing the air pressure will tend to raise the interface level in the stage since a greater stage pressure and hence relatively more of the heavy aqueous phase will be required to force aqueous phase over the weir. Decreasing the air pressure will have the opposite effect, resulting in a lower interface level. Fluctuations in the total organic head above the top of the stage (such as might be caused by changes in the organic flow rate) are compensated automatically by maintaining the weir box air pressure at a constant amount above the organic pressure at the top of the stage. Although the air pressure operated weir arrangement is used as an interface controller, it is actually a differential pressure controller, specifically maintaining a preset difference in pressure between points 1 and 2 on the diagram. It does not sense the interface location and is not connected to the electrical resistance probe circuit, which does sense the interface.

The organic solvent stream is not pumped through the bank by the impellers, but flows by gravity. Since a pressure head is required to produce this gravity flow, a rising organic level is developed toward the organic inlet end of the bank. The true hydraulic head of the organic phase cannot be observed in the covered settling sections, but is evident in the organic level of the vented chimneys on the mixing sections. The chimney level decreases progressively from the organic inlet stage to the organic outlet stage where the organic liquid flows over a vented weir to emerge from the bank. The ultimate rate of organic solvent flow is limited by the total pressure drop across the bank. An attempt to achieve excessive flow would cause the organic solvent to overflow the bank at the organic inlet stage chimney.

The level of the organic solvent in the organic inlet stage chimney is measured. In addition to serving as a monitor for overflow conditions, this measurement provides a sensitive indication of the hydraulic behavior of the mixer-settler. A steady chimney level indicates smooth operation. A high or rising chimney level, indicating an increase in the solvent level gradient across the bank, could be caused by:

- An increase in flow of solvent,
- An increase in emulsion, brought about by excessive impeller speed, low temperature or low acidity, or
- An increase in interface levels brought about by an excessively high rate of aqueous phase flow, low impeller speed or motor failure.

A low or falling chimney level could be caused by a decrease in solvent flow or failure of the mixer motors. Sudden changes in the interface of the aqueous outlet (organic inlet) stage will also affect the chimney level. For example, a rising interface results in increased solvent flow out of the settling section (relative to the feed rate) and results in a higher chimney level until the interface rise stops.

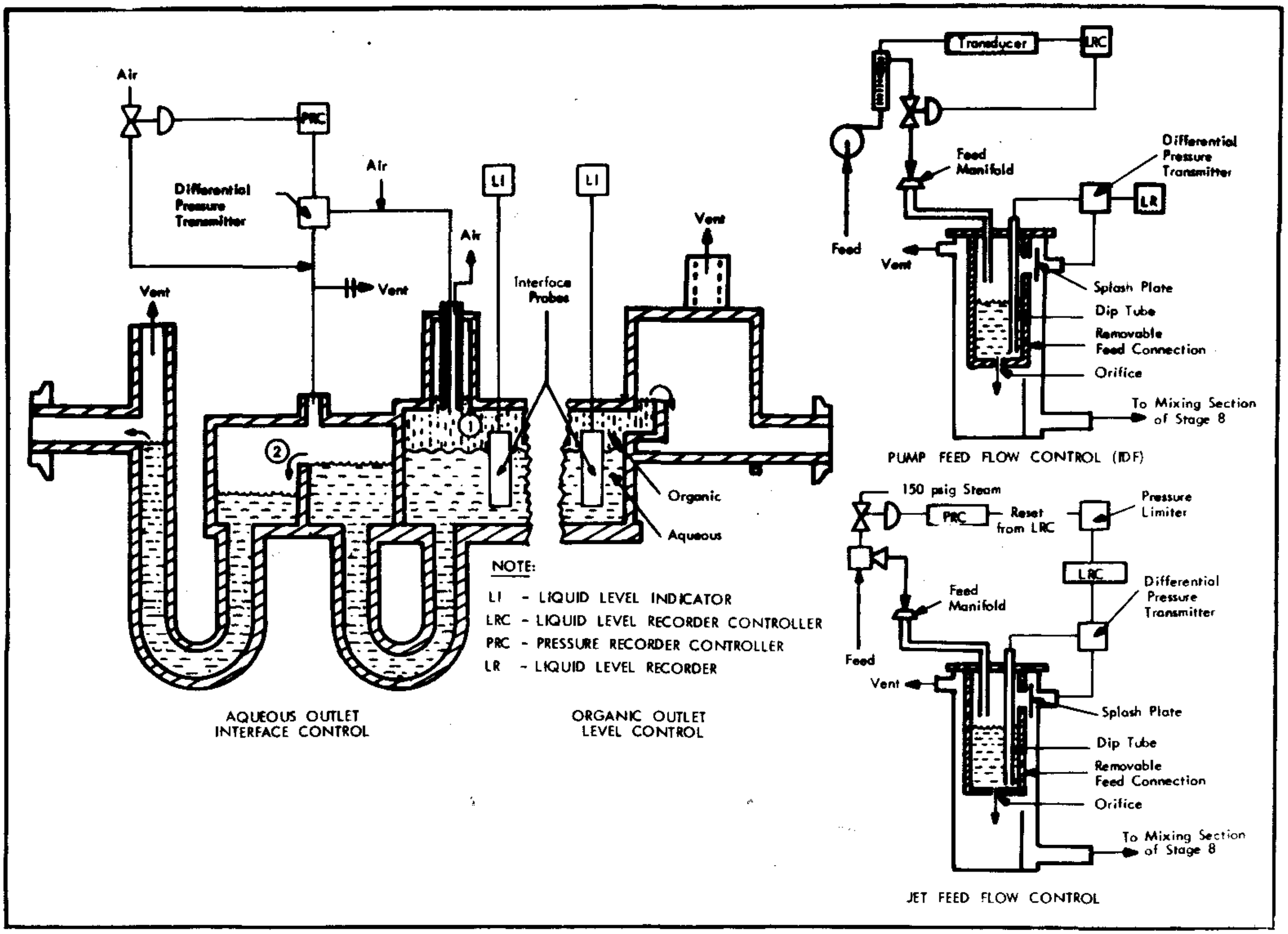


FIGURE 7.40 Mixer-Settler Flow Control Devices

7.4.3 Feed Control

The 1AF and 2AF feed streams flow from feed tanks through heat exchangers to the banks at controlled flow rates by means of rate-type steam jets mounted above the feed tanks. The delivery of a rate-type jet is a function of the steam pressure applied (see Figure 7.41). The feed control instrument system (Figure 7.40) operates on the principle that the flow of liquid through an orifice at the bottom of a standpipe is proportional to the square root of the hydrostatic head above the orifice. Feed solution delivered by a rate-type jet to such a standpipe and orifice mounted above the mixer-settler feed stage establishes an equilibrium level in the standpipe which is measured by a bubbler. The level reading is convertible directly into terms of flow rate. In addition to recording the standpipe level as a flow rate measurement, the level instrument system output is used to direct a pneumatic controller which in turn regulates the steam pressure supplied to the rate jets.

In this way, the complete instrument loop provides automatic control so that feed solution is delivered to the mixer-settler bank constantly at the desired flow rate. The rate jet feed system, although complicated, avoids the necessity of installing equipment containing moving parts in the canyons. A more conventional system, consisting of a pump, flow measuring orifice, and a control valve, is used for 1DF service in the warm canyon with a rate jet as a stand-by.

7.4.4 Flow Control

Most reagent streams to the mixer-settler banks flow from duplicate cold feed tanks on the third level. The tanks permit measurement of depletion rates on these continuous streams. Also, dual flow measuring equipment is installed so as to minimize the possibility that failure of one flow measuring instrument will be undetected for a significant interval and cause a serious bank upset. If the dual flow measuring instruments do not agree, the cause of the discrepancy must be found and corrected or the operation must be shut down to avoid compromise of nuclear safety.

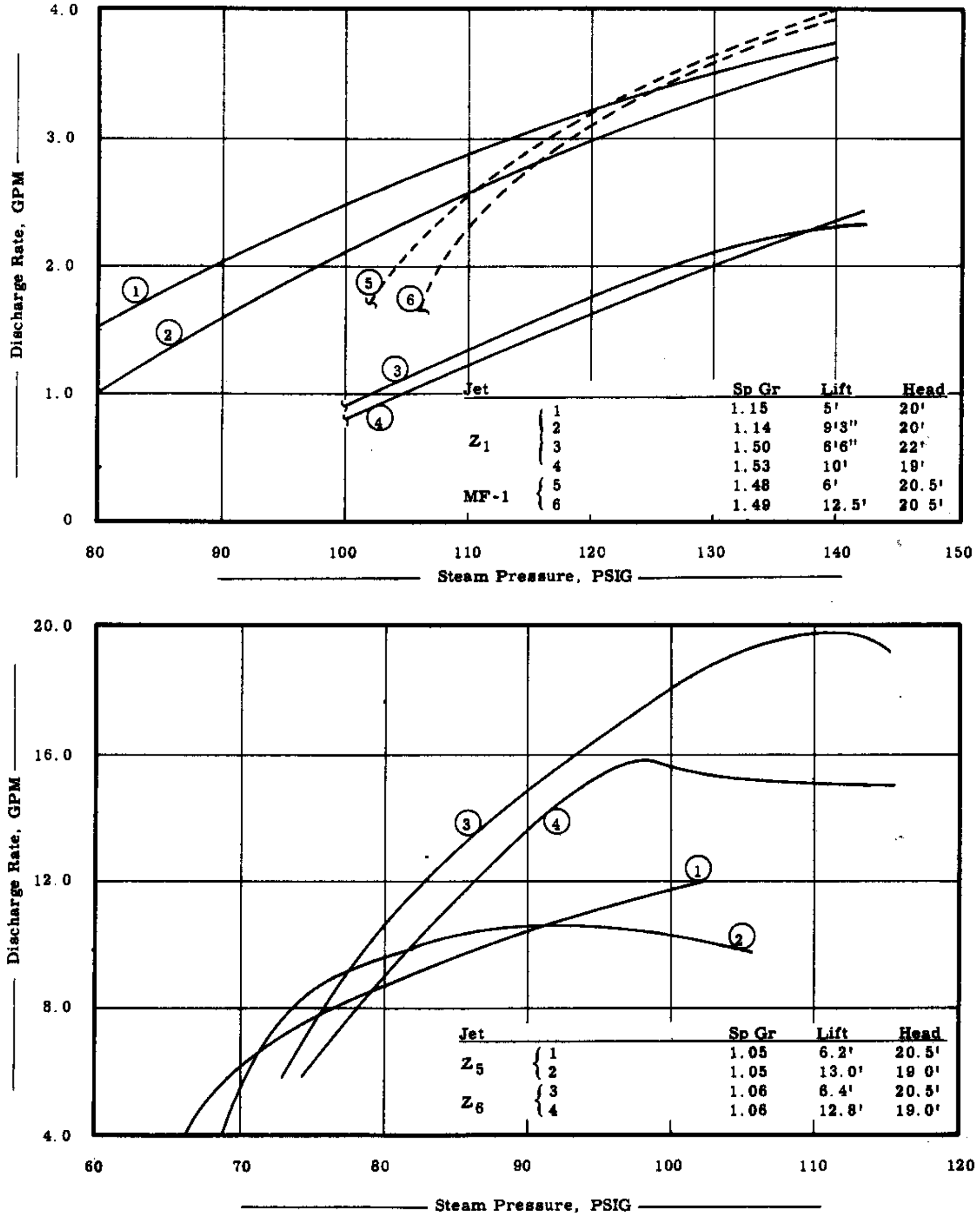


FIGURE 7.41 Typical Rate Jet Performance Curves

7.4.5 Temperature Control

The temperature at which mixer-settlers are operated has an appreciable effect on their performance. The specified operating temperature is obtained by controlling the temperature of the feed streams. The excess heat introduced by the feed jets into the uranium and/or neptunium feed streams to the mixer-settlers is removed by heat exchangers before admitting the streams to the feed flow control standpipes. Reagent feed streams are generally cooler than the desired bank operating temperature, so heat exchangers are provided to warm the solutions as necessary before they enter the canyons.

7.4.6 Decanters

Aqueous streams emerging from the mixer-settler banks are delivered to tank-type decanters to remove gross amounts of entrained solvent. A sketch of this type of decanter is shown in Figure 7.42.

Entrained solvent would create an operating hazard in the operation of evaporators. Solvent disengaged from the aqueous phase in a decanter is periodically transferred to rerun or returned, by means of an air lift, to the mixer-settler. Previous plant performance with the Purex process has demonstrated that the decanters are capable of routinely reducing the entrainment of solvent in aqueous streams below 0.5 vol %.

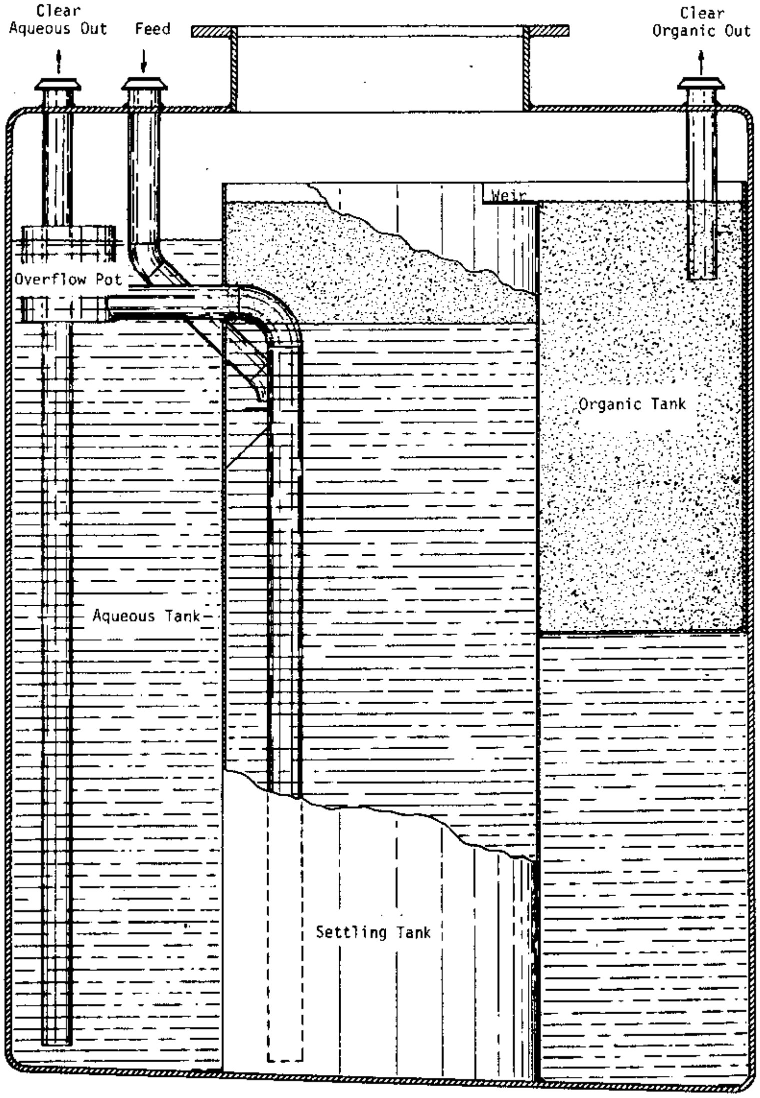


FIGURE 7.42 1EU Tank Decanter

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8. URANIUM PRODUCT STORAGE AND SHIPMENT

8.1 GENERAL

The uranyl nitrate solution (1EU) is pumped from the 221-H canyon to tanks outside the canyon on the east side for storage. The solutions are mixed and sampled as required to confirm that the product meets specifications. Accountability samples are taken during loading into tank trucks. When the product does not meet specifications, it is returned to the canyon. Figure 8.1 shows the outdoor facilities for storage and loading.

8.2 PROCESS DESCRIPTION AND CHEMISTRY

There are no chemical additions or process steps after 1EU is transferred from the canyon. The total mixed fission product activity must not exceed 3.5 µCi/g uranium. Other shipping limits are specified for the concentration of ^{234}U, ^{235}U, ^{236}U, total uranium alpha, and total plutonium alpha.

8.3 SAFETY

The safety concerns associated with the storage and loading facility are the possibility of:

- Accumulation of a critical amount of enriched uranium, and
- Exposure of personnel to radiation and contamination.

8.3.1 Criticality

In the storage and shipping area, two nuclear incident monitors are provided at two appropriate locations for detection of abnormally high levels of gamma radiation such as would result from a nuclear excursion.

The process and the equipment design, along with suitable operating procedures are intended to ensure that a nuclear excursion is not possible. The normal 1EU ^{235}U concentration is maintained at <6 g/l (normally 5 g/l), well below the maximum subcritical concentration of 12 g/l. In addition to normal operation, other situations requiring consideration are:

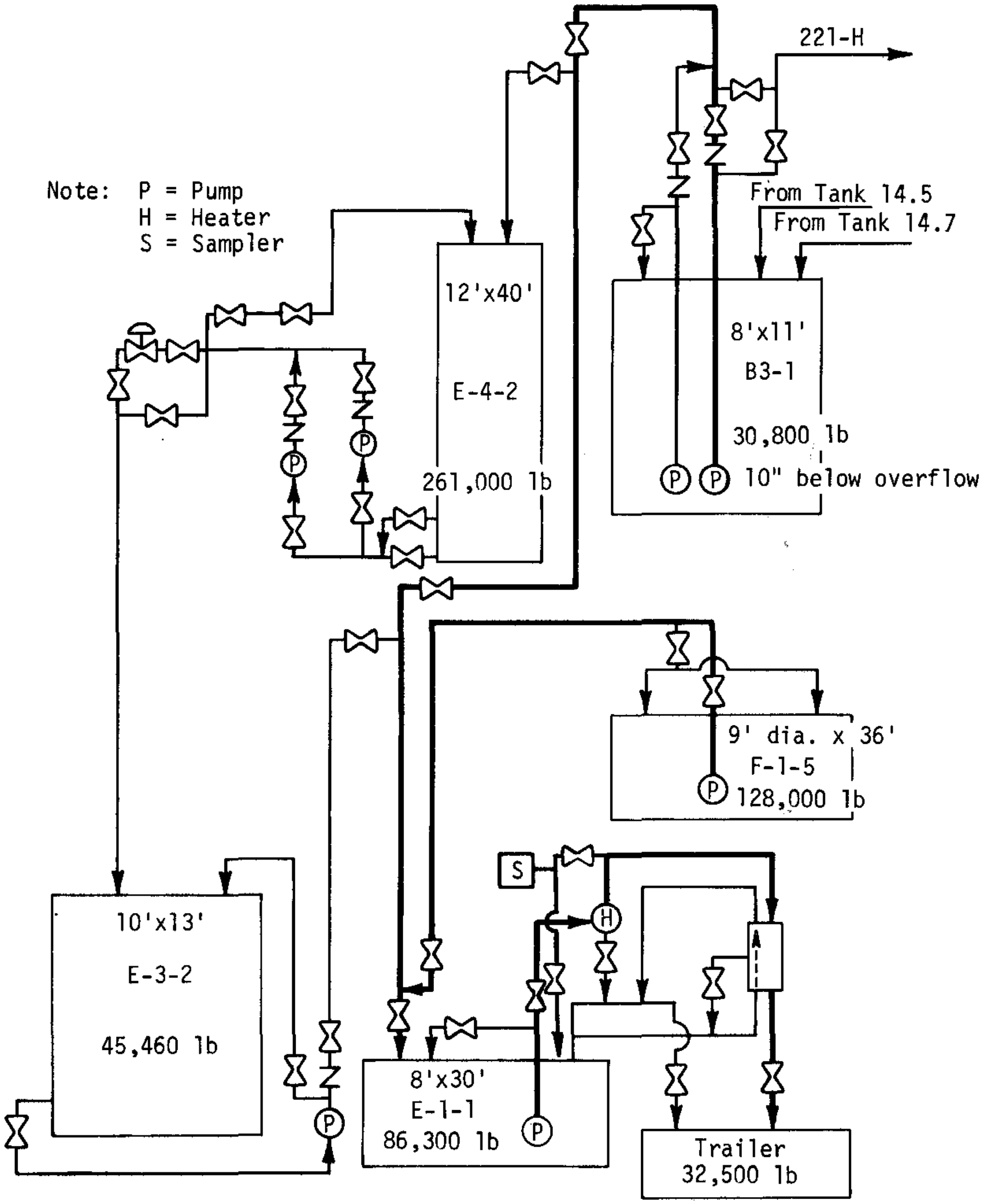

FIGURE 8.1 Uranium Product Storage and Loading System

- Precipitation in any of the process vessels,
- Mixing of uranium solution and a precipitant in the sumps, and
- Accumulation of solvent in process tankage.

The silo tank (E-4-2) is equipped with a steam trace to heat the contents to prevent freezing in cold weather and a consequent risk of uranium concentration. The other process vessels are not heated; thus, in them the possibility of inadvertent concentration of uranium by evaporation is eliminated. The product heater uses hot water rather than steam to heat the solution as it is pumped to the tank truck, so evaporation is not possible in the event of recirculation of solution through the heater by improper valving.

Spills and leaks of uranium solution are flushed into sumps and recycled to avoid possible precipitation by subsequent mixing with precipitant similarly collecting in the sumps. Since the sumps of concern are not of critically safe size from the standpoint of the amount of precipitate that could be formed, these sumps are packed with absorbing Raschig rings. These Raschig rings are made of a cadmium-lead mixture covered with polyethylene to prevent dissolution of the neutron poison. Cadmium is the neutron absorber and is ∿25% of the weight of the ring. The lead increases the specific gravity to >1.5 to ensure that the rings will not float in high-density solutions.

Concentration of uranium in the solvent which collects in the basin transfer tank (B-3-1) and the storage tank (E-4-2) does not present a potential nuclear hazard. The distribution ratio for the prevailing 1EU composition, ∿0.2M HNO_3 and ∿5g $^{235}U/l$, is not favorable for extraction of uranium into the solvent. For 7.5% TBP, the organic uranium concentration in equilibrium with nominal 1EU is ∿0.6 g/l; for 30% TBP it is ∿3.5 g/l. At greater concentrations of HNO_3 and TBP, concentrations of organic uranium exceeding 12 g/l can be attained, but the thin slab configuration of such solvent would provide adequate safety.

8.3.2 Personnel Exposure to Radiation and Contamination

Operating personnel in the facility are exposed to varying degrees of penetrating radiation. Frequent routine monitoring of the facility is used to establish prevailing radiation intensities and the extent of contamination from spills, leaks, etc. This information is used to adjust personnel assignments as may be necessary to avoid undue or excessive exposure.

8.3.3 Corrosive Chemicals

No chemical additions are made in the facility. The uranyl nitrate in dilute nitric acid is handled in a closed system. Procedures are used, and personnel wear protective clothing. Safety showers are provided to minimize the injury from accidental contact with the solution.

8.4 EQUIPMENT

The equipment consists of transfer and storage tanks, a heater, and associated pumps and piping.

8.5 SHIPMENT

1EU Handling

The uranyl nitrate solution (1EU) is transferred from the canyon to a basin transfer tank (B-3-1), which is 8 ft in diameter by 11 ft high and is equipped with two submerged pumps. Normally, solution is transferred to other storage tanks; however, off-standard solution may be returned to the canyon from this tank or from other storage tanks using the basin transfer tank piping. There are several storage tanks. One, which has been termed the "silo", is 12 ft in diameter by 40 ft high. Tank E-3-2 is 10 ft in diameter and 13 ft high. Tank F-1-5 is 9 ft in diameter and 36 ft long. Tank E-1-1 is 8 ft in diameter and 30 ft long. The uranyl nitrate solution is recirculated in tank E-1-1 with pumps for 24 hours before sampling and transfer to the tank trailer. The solution is maintained between 70° and 90°F for sampling and loading. Each of the three tank trailers has a capacity of ∿3900 gal of solution.

Sampling and Loading for Shipment

The 1EU is transferred from canyon tanks into the storage and loading tanks shown in Figure 8.1. Uranyl nitrate solutions are blended and mixed in tank E-1-1. Mixing is marginal in tank E-1-1, so the solution is blended and then mixed for 24 hours. The capacity of E-1-1 is two trailer tank trucks. Tank E-1-1 is sampled for accountability after mixing and from the stream entering the trailer at 1/5, 2/5, 3/5, and 4/5 full. The solution is heated to between 70 and 90°F with hot water if the air temperature is below 70°F. This provides protection against freezing because the solution cools very slowly in the insulated tank truck even in winter.

9. SOLVENT RECOVERY

9.1 GENERAL

The purpose of the solvent recovery process is to remove all deleterious materials, degradation products, and radioactive contaminants from the spent solvent and to return the treated solvent to the extraction process in a uniform and standard composition. If allowed to accumulate, the contaminants would adversely affect decontamination, product recovery, and production capacity. Spent solvents from each of the different segments of the solvent extraction process are treated separately and returned to the respective process streams; any stagnant solvent is collected periodically and isolated for special disposal. All "hot" and "warm" solvent is treated continuously with sodium carbonate and nitric acid or process water. The alkaline reagents remove most of the contaminants and degradation products, and the nitric acid neutralizes any residual alkalinity and enhances the clarity of the purified solvent. Figure 9.1 presents a schematic flow diagram.

9.2 PROCESS DESCRIPTION AND CHEMISTRY

9.2.1 Solvent Deterioration

In the solvent extraction process, the solvent accumulates both radioactive and nonradioactive contaminants, which reduce its effectiveness and render it unsuitable for immediate reuse. The principal radioactive contaminants include zirconium, niobium, and ruthenium; uranium or neptunium may also be present. Radioactive iodine is a potential contaminant, but ^{131}I decays rapidly and no problems have been encountered when processing feed material which has been cooled sufficiently. The nonradioactive contaminants include hydrolysis products of tributyl phosphate (TBP) and various oxidation and nitration products of the hydrocarbon diluent.[1]

The most prominent solvent degradation product, according to laboratory studies, is dibutyl phosphate (DBP).[2] Dibutyl phosphate is produced both by chemical damage (hydrolysis) and by radiation damage, with the relative amounts depending on the specific activity of the radioactive solution processed. DBP is readily removed by

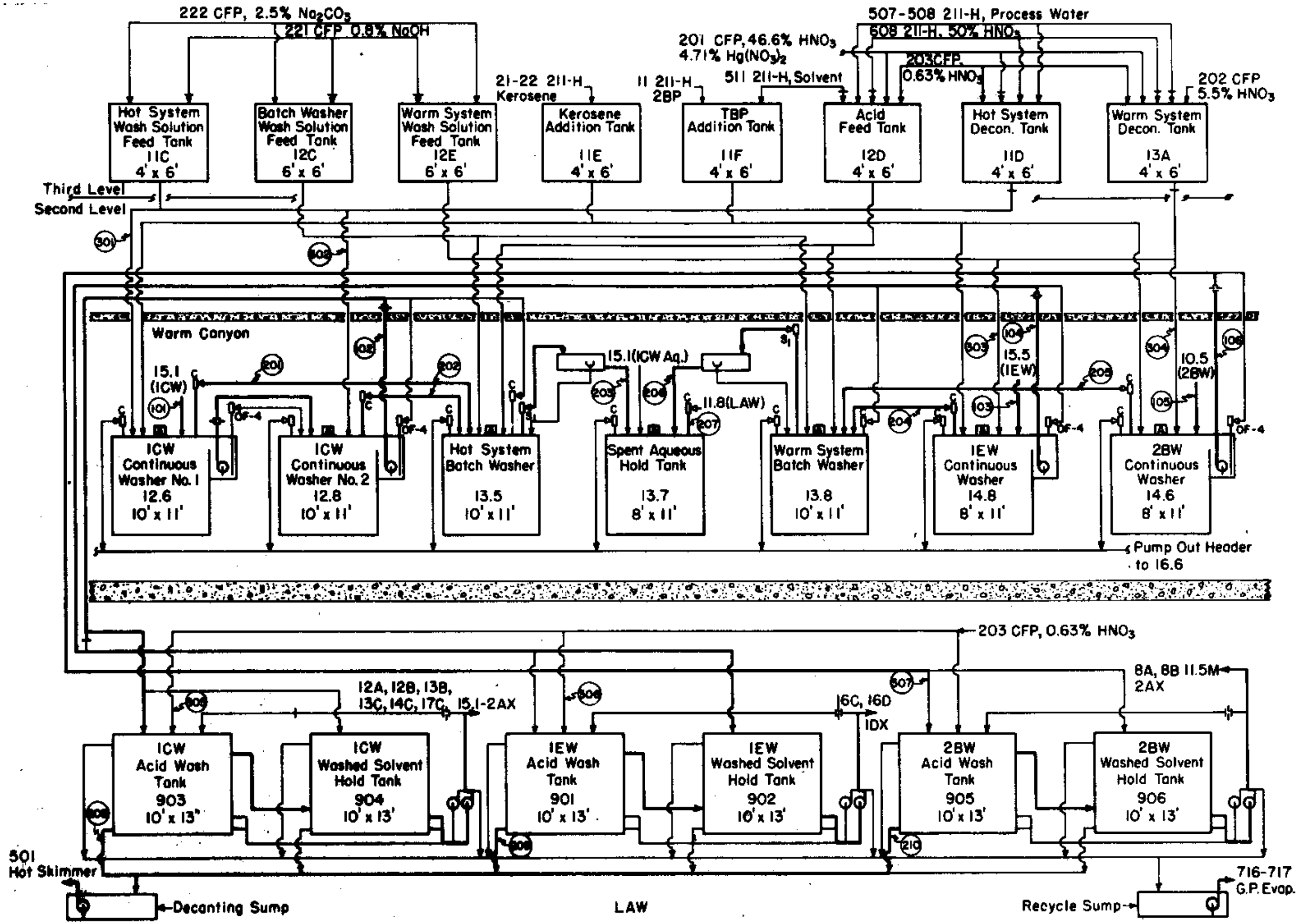

FIGURE 9.1 Solvent Recovery Flow Diagram

alkaline washing and does not tend to accumulate in the solvent during successive passes through the solvent extraction cycle. DBP is preferentially soluble in the organic phase and forms strong complexes with zirconium, uranium (VI), and plutonium (IV). The complex with zirconium causes zirconium to be extracted along with the product in the solvent extraction process.[4] Some of this zirconium is released to the aqueous product streams in the stripping banks and thereby restricts decontamination. DBP also forms solid compounds with aluminum and iron; these solids tend to accumulate at the liquid interface in the mixer-settler and promote emulsion formation. MBP and DBP form strong complexes with neptunium and cause loss to the solvent. These complexes eventually reach the solvent washes and are decomposed there by boiling which degrades MBP and DBP. The boiled solvent washes are recycled to the second neptunium cycle to recover the neptunium. Contacting the solvent with weak acid will not extract the neptunium in the presence of MBP and DBP.

Degradation products of the diluent are not as pronounced in the enriched uranium recovery process as in the Purex process operation. As a result, the residual fission activity and contaminant concentration is much lower in the enriched uranium process solvent than in Purex solvent.[5] Many of the degradation products of the diluent resist removal in the normal recovery operation and tend to accumulate in the solvent. These compounds cause zirconium to extract with the product into streams.[4] Also, some of the activity remains in the solvent even after washing and causes undesirable radiation in the solvent storage area. These degradation products, which act as complexing agents, are associated with the solvent, and may include ketones, diketones, esters, and their polymers. They are formed mainly by exposure of the solvent to nitrite-nitric acid solutions and radiation fields. The formation of these compounds is relatively rapid above 50°C. Several factors which may have contributed to the lower degree of diluent degradation in the enriched uranium process are:

- Lower nitric acid concentration in the first cycle because of the aluminum nitrate present from dissolved fuel
- No nitrite additions to the uranium recovery process - the only nitrite present is that which accompanies nitric acid in the radioactive solutions
- Lower TBP concentration in the first cycle and second uranium cycle solvent - less nitric acid, nitrite and fission products are extracted into the organic phase resulting in a lower exposure of the diluent to these compounds.

The second neptunium cycle solvent, which utilizes 30% TBP and is in contact with high HNO_3 concentration, normally has the highest residual fission product activity of the three solvent systems. Other solvent degradation products cause loss of uranium or neptunium to the spent solvent, affect phase disengagement, and impart a yellow color to the diluent.

The degree of solvent deterioration can be measured by polarographic diffusion current (PDC) and interfacial tension (IT). Both are used as indicators for possible disposal of solvent. The diffusion current is the relative measure of the gross amount of degradation products and has been used as a yardstick for solvent quality. The diffusion current for virgin solvent is zero amp/mℓ. Laboratory studies have shown that the diffusion current has a direct correlation with "Z" number (zirconium retention number) and is simple to determine. The interfacial tension is a measure of the surfactant concentration which affects the hydraulic properties of the solvent, including phase disengagement time and emulsion formation. Interfacial tension is measured against an aqueous phase of 0.7M NaOH. The typical effect of degradation on solvent decontamination is shown in Figure 9.2. Some solvent has been shown to have good extraction properties even though the PDC and IT were poor.[6] The main indicator for disposal of solvent is poor extraction properties as determined by "use" tests; that is, how well the process performs.

9.2.2 Segregation of Solvent

The solvent from each of the three solvent extraction cycles has a separate recovery system. The solvent in each system is segregated from solvent used in the other extraction cycles. This segregation aids in meeting the stringent purity specifications for the final product solutions. Although most of the solvent from the process is washed immediately, floating solvent heels accumulate in the aqueous run tank decanters. This solvent may become seriously degraded and is sent to the rerun station for disposal. Solvent accumulated in the wash change tanks is batch-washed with 2.5% Na_2CO_3 and water, or 2.5% Na_2CO_3-0.8% NaOH and water, and returned to the process via the acid washer of the appropriate system (see Section 9.3).

Solvent accumulated in the rerun station is periodically discarded. This solvent is batch-washed with 5% caustic plus reductant, 5% acid plus oxidant, and oxalic acid. Then all acid is removed by a water wash before the solvent is shipped in a trailer to waste solvent storage tanks at the burial ground.

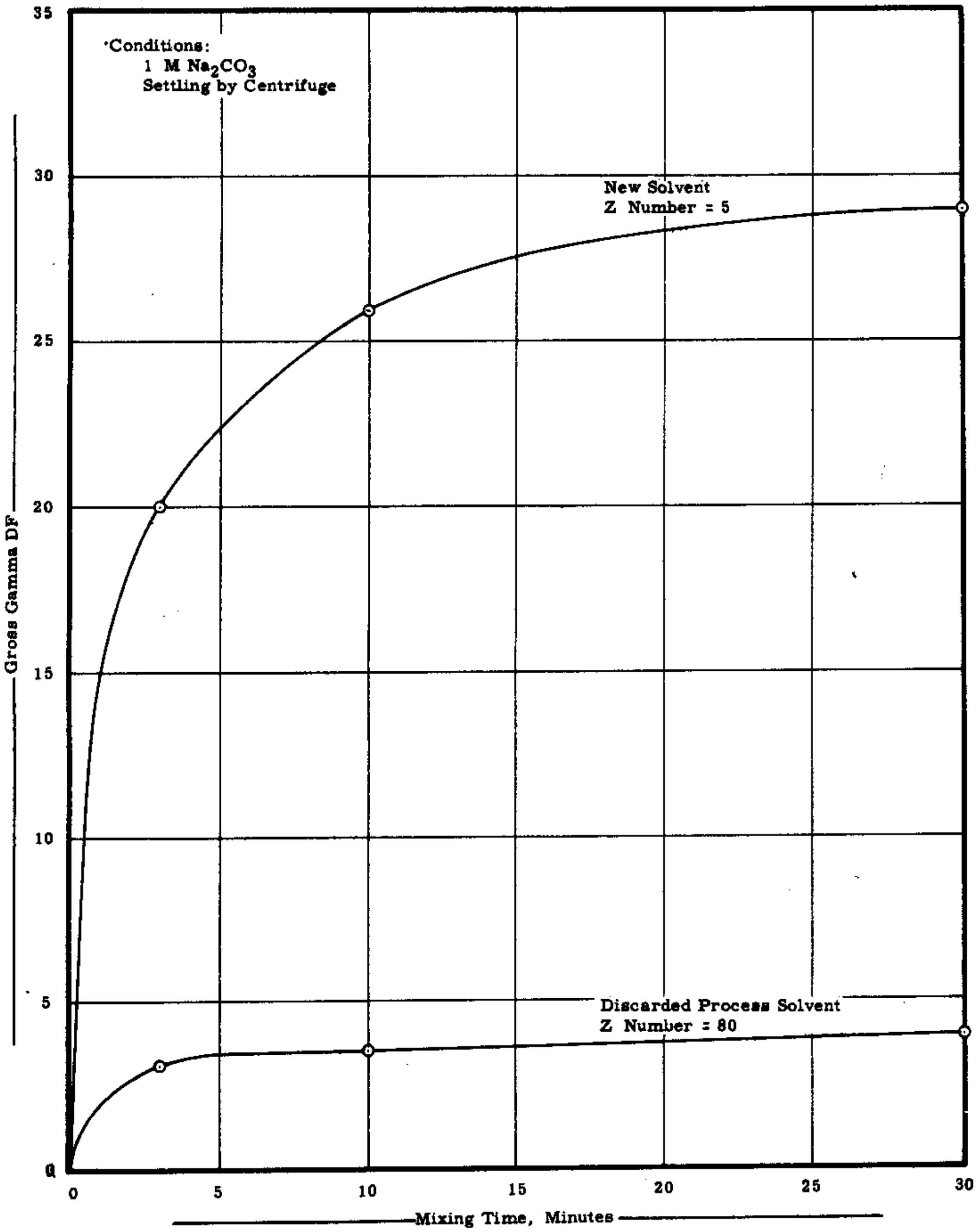

FIGURE 9.2 Typical Effect of Degradation on Solvent Decontamination

9.2.3 Continuous Washing

The spent solvent streams from the first and second cycles are washed continuously with sodium carbonate and then transferred outside to the 211 building for washing with weak nitric acid or process water. As the process solvent inventory decreases due to losses, new solvent is added via the carbonate washer of the appropriate system. The new solvent is washed along with spent solvent to remove impurities such as mono- and dibutyl phosphates, phosphoric acid, and butanol present in the new TBP. Washed solvent is sent to storage tanks for subsequent use. The spent carbonate wash solutions of the first and second cycle solvent washers are replaced every 7 to 14 operating days; the spent acid wash solutions are replaced every 5 to 8 operating days. If the activity level of the solvent is excessive, the wash solutions can be replaced more frequently.

The first cycle spent solvent (1CW) is pumped continuously from the 1CW hold tank and is washed with about 15,000 lb of 2.5 to 5.0% Na_2CO_3 in the first of two identical continuous washers. The solvent is contacted with an equal quantity of Na_2CO_3 solution in the second washer for further removal of degradation products and contaminants. Carbonate is used in both washes to minimize the possibility of precipitating uranium. The washing temperature is usually controlled in the range of 45 to 50°C; a higher temperature (at the tank hot water coils), is not used because of the relatively low flash point of the solvent vapor (see Section 9.3). The alkaline-washed solvent is pumped outside to Building 211 for continuous washing with about 20,000 lb of 0.63% HNO_3 and flows to the 1CW washed solvent hold tank. The spent sodium carbonate wash solution is transferred to the hot system wash change tank for subsequent jetting to a decanter from which the aqueous phase is sent via the spent solvent aqueous hold tank to the low-activity waste hold tank. Carbon dioxide is evolved in the low-activity waste hold tank from the reaction of sodium carbonate in the spent solvent washes and nitric acid in the 2AW. The carbon dioxide is vented to the warm canyon process vent header. The spent acid wash solution is removed from the 1CW acid washer and sent to the waste water skimmer for subsequent transfer to the seepage basin or general-purpose evaporator, depending on the activity level of the solution.

The second uranium cycle spent solvent (1EW) flows by gravity from the 1E bank and is washed with about 10,000 lb of 2.5 to 5.0% Na_2CO_3 in a continuous washer. The wash temperature is maintained at 30 to 45°C by circulating hot water through the washer coils. The alkaline-washed solvent is pumped to Building 211 for continuous washing with about 15,000 lb of 0.63% HNO_3 and then flows to the 1EW washed-solvent hold tank. The spent sodium carbonate wash solution is transferred to the warm system wash charge tank for transfer to a decanter from which the aqueous phase is sent via the spent solvent aqueous hold tank to the low-activity waste hold tank.

The second neptunium cycle spent solvent (2BW) is pumped continually from the 2BW hold tank and is washed with about 10,000 lb of 2.5 to 5.0% Na_2CO_3 in a continuous washer. Since the 2BW washer is not equipped to heat the wash solution, the wash temperature may vary from 30 to 45°C depending on the temperature of the 2BW. The alkaline-washed solvent is pumped to Building 211 for continuous washing with about 15,000 lb of 0.63% HNO_3 and then flows to the 2BW washed-solvent hold tank. If the 2BW wash solutions contain recoverable neptunium, they are boiled and recycled through the second neptunium cycle. If not, they are disposed of in the same manner as the 1EW wash solutions.

Washing of the spent solvent with NaOH would be more effective than washing with Na_2CO_3, but the use of NaOH would increase the nuclear safety hazard (see Section 9.3). Batch washing is also superior to continuous washing; however, batch washing does not provide the capacity required for the process.

9.2.4 Batch Washing

Equipment is provided for batch washing of solvent if desired. Amounts of solvent up to 30,000 lb can be washed with Na_2CO_3 or HNO_3 solutions, and/or water alone.

9.3 SAFETY

Safety problems associated with the solvent recovery process include the possibilities of ignition of the solvent, exposure of personnel to radiation, and nuclear safety.

9.3.1 Ignition of Solvent

The process solvent is flammable due primarily to the volatility of the hydrocarbon diluent. The temperature to obtain the lower explosive limit for vapor and air for dry diluent is 70 to 75°C; this lower explosive limit is also valid for solvent containing up to 7.5% TBP. The lower explosive limit for 30% TBP - 70% diluent is 75 to 80°C. Serious hazards are avoided by minimizing spillage in working areas and by keeping the solvent below its flash point at all times.

9.3.2 Radiation Exposure

While exposure of personnel to excessive amounts of radiation has been largely eliminated by the design of the building, special consideration must be given to the solvent filters, the storage tanks for washed solvent, and the lines for transferring solvent between Building 221 and Building 211. The filters accumulate radioactive solids, particularly from the alkaline solvent, and require shielding to absorb radiation. The storage tanks for the first cycle solvent are also shielded. The solvent piping lines between Building 221 and Building 211 are unshielded and require close observation during solvent extraction upsets when the radiation level has been as high as 400 mrem/hr. The second cycle solvent tanks are not shielded.

9.3.3 Criticality

Accumulation of a critical amount of enriched uranium in the 1CW or 1EW continuous washers through operational errors or unforeseen process conditions should be considered, although such an accumulation is very unlikely. In the event of a total loss of uranium to the solvent washers, the maximum uranium loading of 280 g of uranium per square foot could be reached in 9.2 hours in the first cycle solvent washer, and 5.9 hours in the second uranium cycle solvent washer. Such an event is very unlikely because the normal uranium content of the 1CW and 1EW stream is extremely low. Extraction of uranium into the aqueous 1CU and 1EU streams is so highly favored that only greatly reduced 1CX or 1EX flow rates could cause a significant increase in uranium concentration in the waste solvent streams. Close observations of the main solvent extraction streams by neutron monitors and continuous direct colorimetric analysis for uranium ensure that no major undetected losses to the waste streams will occur. A uranium loss of greater than 20% would quickly be detected by the 1CU or 1EU colorimeter. A sustained uranium loss of 20% would require 1.9 days at the 57.5-kg/day rate to reach the maximum uranium loading in the first cycle washer and 1.2 days in the second uranium cycle washer. The aqueous wash solutions are sampled routinely to prevent any undetected accumulation of uranium in the washers.

Use of sodium carbonate as an alkaline wash solution reduces the criticality hazard below that which would be faced if sodium hydroxide were used. Carbonate forms a soluble complex with uranium; NaOH precipitates sodium uranate. Uranium is soluble to 60 g/l in 2.5% sodium carbonate, whereas uranium is only soluble to about 0.05 g/l in 0.8 wt % sodium hydroxide. A welded blank in the sodium hydroxide line in the cold feed preparation area prevents the addition of caustic to the solvent recovery system. Scheduled, routine dumping of the wash solutions eliminates the potential for a small but prolonged buildup of uranium.

Segregation of the various solvent systems is necessary due to the differences in TBP concentration. The first cycle solvent and the second uranium cycle solvent are 7.5% TBP, and the second neptunium cycle solvent is 30% TBP. Substitution of solvent at a different TBP concentration from that used to determine the operating parameters for the mixer-settlers may in some cases lead to the accumulation of uranium in the mixer-settlers. To prevent this, each solvent extraction cycle has a separate solvent recovery system. Since both the second uranium cycle washer and the second neptunium cycle washer use the same wash charge tank for disposing of spent wash solutions, any solvent accumulated in the wash change tank is returned to the second neptunium solvent system rather than to the second uranium solvent system.

9.4 EQUIPMENT

The equipment in the solvent recovery system includes facilities for collecting, adjusting, washing, decanting, and storing solvent before return to the solvent extraction process. Table 9.1 lists the equipment services and instrumentation. This list was assembled in mid-1975 and may change with time.

9.4.1 Continuous Washing

The "hot" solvent recovery system comprises two continuous washers connected in series for alkaline washing and a continuous washer outside in Building 211 for acid washing. The design of the continuous solvent washer is shown in Figure 9.3. The unit consists essentially of a standard 10 × 11-ft tank with the conventional agitator replaced by a paddle shrouded in a 30-inch pipe at the axis of the tank. Spent 1CW enters the tank continuously, mixes with the wash solution, separates, and overflows into a solvent collection blister from which it is removed by pump or steam jet. The washed solvent is usually pumped to the outside acid wash tanks to avoid diluting and heating the solvent by jet condensate. Rotation of the paddle at 100 rpm provides sufficient pumping capacity to allow considerable recirculation of organic and aqueous phases within the washer. Orifice plates above and below the paddle control the relative rates of recirculation of the two phases. As designed, these orifices provide a minimum mixing ratio of about ten volumes of aqueous phase to one of organic phase. The continuous washer for acid washing of the 1CW is essentially of the same design as the alkaline washers, except the washers are 10 × 13-ft tanks, and the collection blister has been eliminated so that the solvent overflows directly to the solvent storage tanks.

TABLE 9.1

Solvent Recovery Equipment Services and Instrumentation

Vessel Identification						*Instrumentation*							*Services*							
No.	*Function*	*Ep No.*	*Process Piping Diagram*	*Instrument Diagram*	*Electrical Diagram*	*Liquid Level*	*Blister Level*	*Sp. Gr.*	*Temperature*	*Radiation*	*Flow Control*	*Steam Flow*	*Sampler*	*Agitator*	*Microphone*	*Coils (s)*	*Recirculating Jet*	*Other Jets (Number)*	*Pump*	*Gauge Glass*
12.6	1 CW Continuous Washer	372.89-2	W163044	W162339	W147422	RHL I_f- RL	RHL	R	R	R	Jet-C	-	X	X	X	W_h	X	OF-4 C(2)	1	-
12.8	1CW Continuous Washer	372.89-3	W163044	W162336	W147422	RHL I_f- RL	RHL	R	R	R	Jet-C	-	X	X	X	W_h	X	OF-4 C(2)	1	-
13.5	1CW Batch Washer	372.88	W163044	W146440	W147423	RHL	-	R	R	R	-	-	X	X	X	CW	-	S1 C(2)	-	-
13.61S	Decanter	331.4-1	W163045	W162334	W147423	-	-	-	R H	R	-	-	-	-	X	-	-	S1	-	-
13.62S	Decanter	331.4-2	W163044	W162334	W147423	-	-	-	R H	R	-	-	-	-	X	-	-	S1	-	-
13.7	Spent Aqueous Hold Tank	372.90	W163045	W162340	W147423	RHL	-	R L	R	R	-	-	X	X	-	CW	X	C(2)	-	-
13.8	1EW Batch Washer	372.894	W163045	W146438	W147423	RHL	-	R	R	R	-	-	X	X	X	CW	X	S1 C(2)	-	-
14.6	2BW Continuous Washer	395.31-1	W163045	W163077	W147424	RHL I_f- RH	RHL	R	R	R	FC	-	X	X	X	W_h	X	OF-4 C(2)	1	-
14.8	1EW Continuous Washer	395.32	R163090	W163071	W147423	RHL I_f- RL	RHL	R	R	R	Jet-C	-	X	X	X	CW	X	OF-4 C(2)	1	-
901	1EW Acid Wash Tank	373.67-3	W163978	W162064	W144292	IH I_f- IH	-	I	ICH	-	-	IC	X	X	-	SCW	-	-	-	X
902	1EW Washed Solvent Hold Tank	373.67-4	W163978	W162064	W144292	IH	-	I	IH	-	-	-	X	X	-	CW	-	-	2	X
903	1CW Acid Wash Tank	373.67-2	W163978	W162064	W144292	IH I_f- IH	-	I	ICH	-	-	IC	X	X	-	SCW	-	-	-	-
904	1CW Washed Solvent Hold Tank	373.67-1	W163978	W162064	W144292	IH	-	I	IH	-	-	-	X	X	-	CW	-	-	2	2
905	2BW Washed Solvent Hold Tank	373.67-5	W163978	W162064	W144292	IH I_f- IH	-	I	ICH	-	-	IC	X	X	-	SCW	-	-	-	X
906	2BW Washed Solvent Hold Tank	373.67-6	W163978	W162064	W144292	IH	-	I	IH	-	-	-	X	X	-	CW	-	-	2	X

SYMBOLS:

I - Indicator
R - Recorder
C - Controller
S - Steam
H - High Alarm
L - Low Alarm
I_f- Interface
CW - Cooling Water
W_h - Hot Water
X - Present

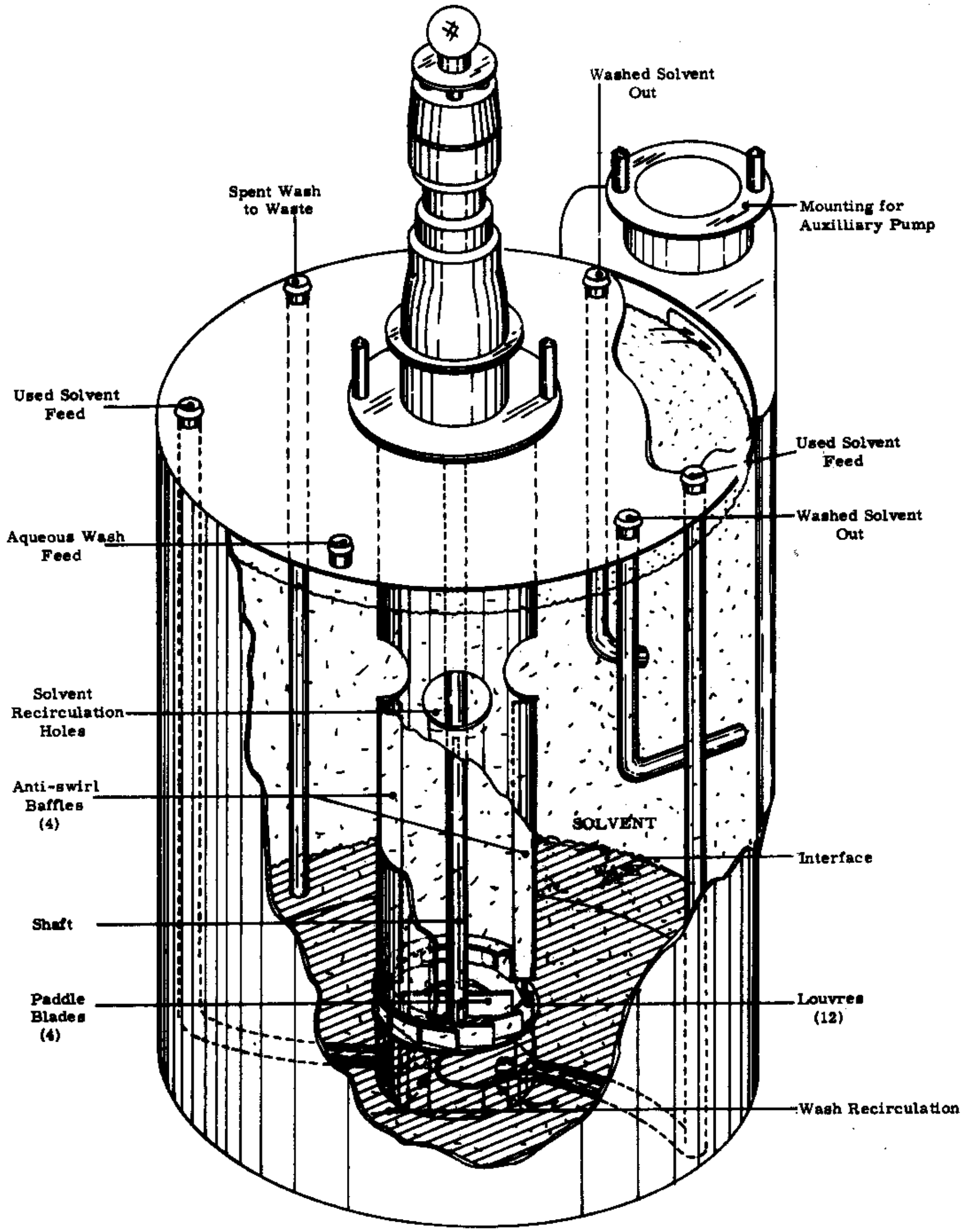

FIGURE 9.3 Continuous Solvent Washer

The warm solvent recovery systems include continuous washers for alkaline washing in the canyon and acid washing in Building 211. The unit for alkaline washing is basically of the same design as the hot solvent continuous washers, except the washers are 8x11-ft tanks. These washers were designed to allow reuse of 8 to 10% carbonate solution for about 100-volume contacts and to produce washed solvent containing less than 0.04 wt % entrained aqueous phase. Figure 9.4 shows typical entrainment values at various mixing ratios of solvent and carbonate wash. Plant experience has indicated that the actual useful life of 2.5% carbonate wash solution is about 100-volume throughputs of solvent. The units for washing the 1EW and 2EW with acid are identical to the 1CW acid washer.

9.4.2 Batch Washing

Each of the two systems for batch washing consists of a wash tank for alkaline washing of the solvent, a decanter, a common hold tank for spent wash solutions, and a washer outside in Building 211 for acid or process water washing (described previously in Section 9.4.1). Continuous washing of the spent solvent is performed on a routine basis; batch washing is available as an alternate.

Each wash tank is provided with a decanter which serves only that tank. A decanter is a rectangular box (7 ft long x 18 in. wide x 18 in. deep) that contains three sections arranged to permit organic and aqueous phases to be automatically separated by density difference. The decanters rest on elevated frames to allow gravity discharge to the hold tanks. Figure 9.5 illustrates the flow of aqueous and organic solutions through the unit.

9.4.3 Pumps

Short-shaft centrifugal pumps (shown in Chapter II) are used to transfer the solvent from the 1CW run tank to the first 1CW continuous washer, from the first 1CW continuous washer to the second washer, from the second 1CW washer to the 1CW acid washer, from the 1EW continuous washer to the 1EW acid washer, from the 2BW run tank to the 2BW continuous washer, and from the 2BW continuous washer to the 2BW acid washer. These pumps maintain adequate capacity for continuous operation. Installation and operation specfications for the pumps used in the solvent recovery system are shown in Table 9.2. No extensive maintenance problems have been encountered with continuous pump operation.

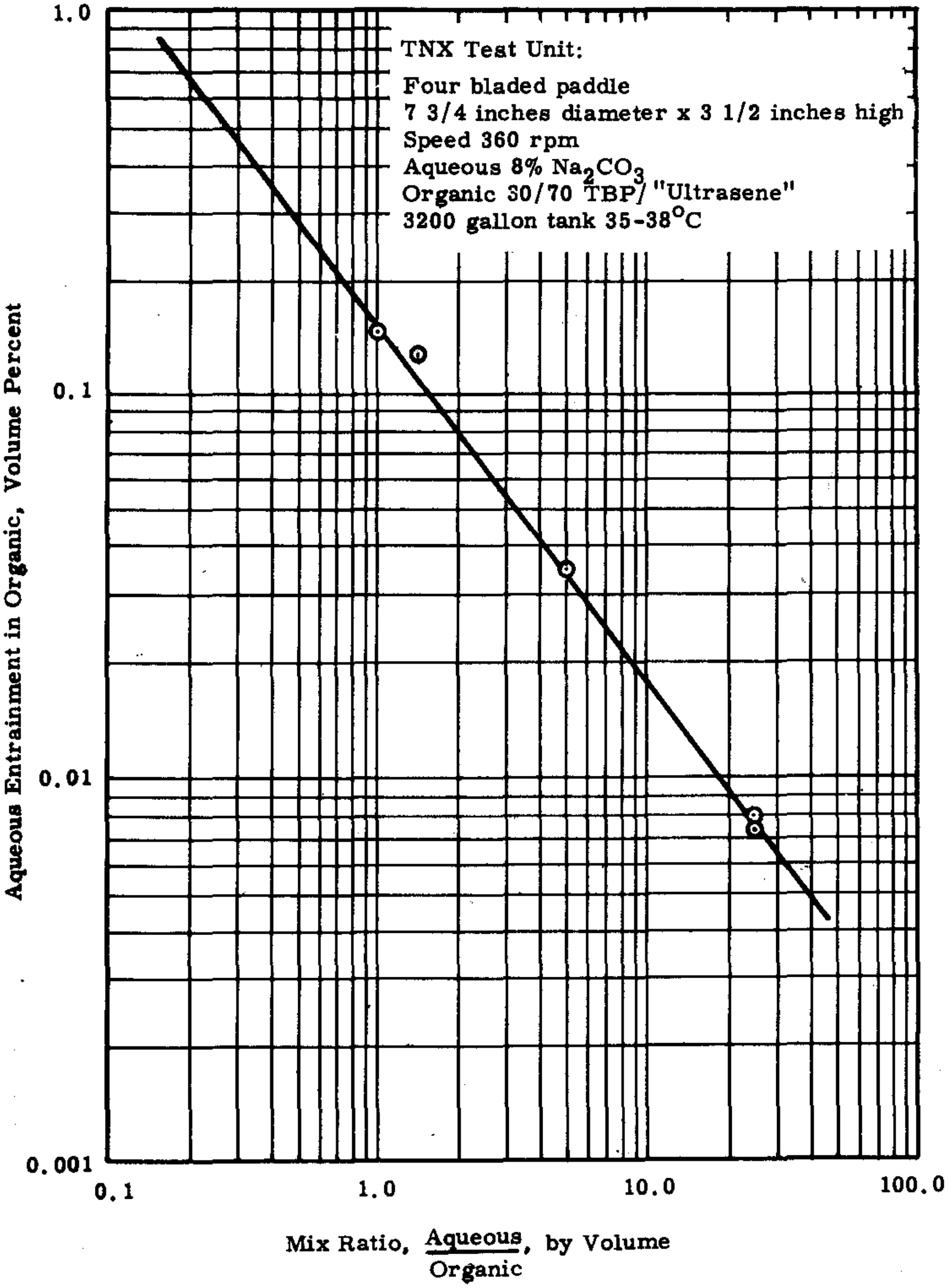

FIGURE 9.4 Entrainment in Continuous Solvent Washer

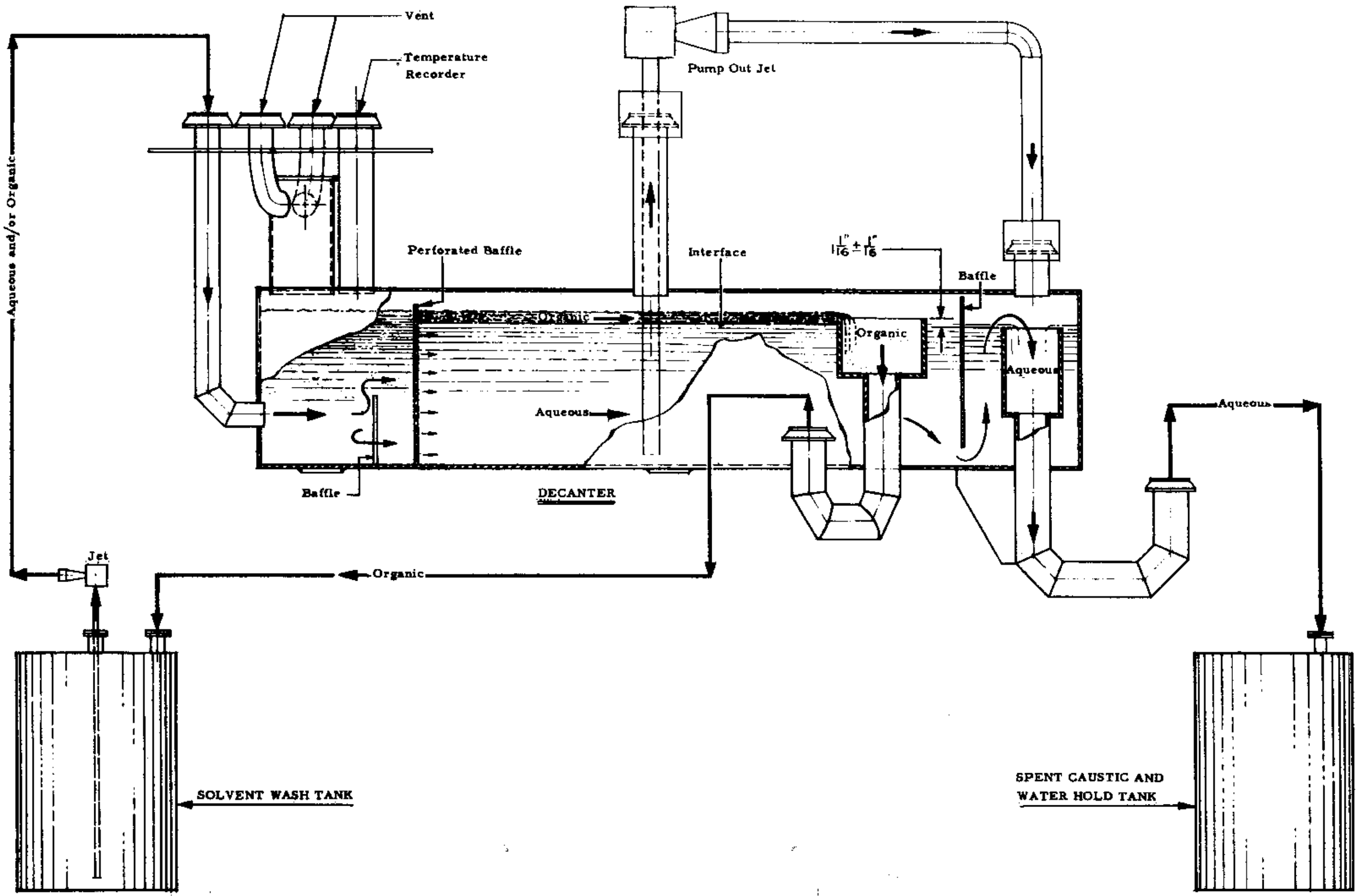

FIGURE 9.5 Solvent Recovery Decanter for Batch Washing

TABLE 9.2

Installation and Operational Specifications for the Solvent Pumps

Location	*Orifice Diameter, inches*	*Required flow, gpm*	*Tested Flow,[a] gpm*
1CW Run Tank to 1st 1CW Washer	0.494	20	19.3 - 21.5
1st 1CW Washer to 2nd 1CW Washer	0.520	22	21.4 - 22.2
2nd 1CW Washer to 1CW Acid Washer	0.591	24	24.4 - 26.1
1EW Washer to 1EW Water Washer	0.502	18	18.2 - 19.3
2BW Washer to 2BW Acid Washer	0.301	2.8	5.8 - 6.5
2BW Run Tank to 2BW Washer	0.253	2.5	4.8 - 5.3

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[a] Range of flow rates is caused by change in liquid level in tank.

9.4.4 Solvent Storage

The alkaline washed "hot" and "warm" solvents flow by gravity from the acid washers to 10x13-ft storage tanks in Building 211. From these tanks, solvent is pumped through removable filters to third-level head tanks for return to the mixer-settlers. The filters and hot solvent tanks are provided with shielded enclosures, but the radiation level of the warm solvent tanks do not require such protection. A sketch of a shielded solvent filter is shown in Figure 9.6.

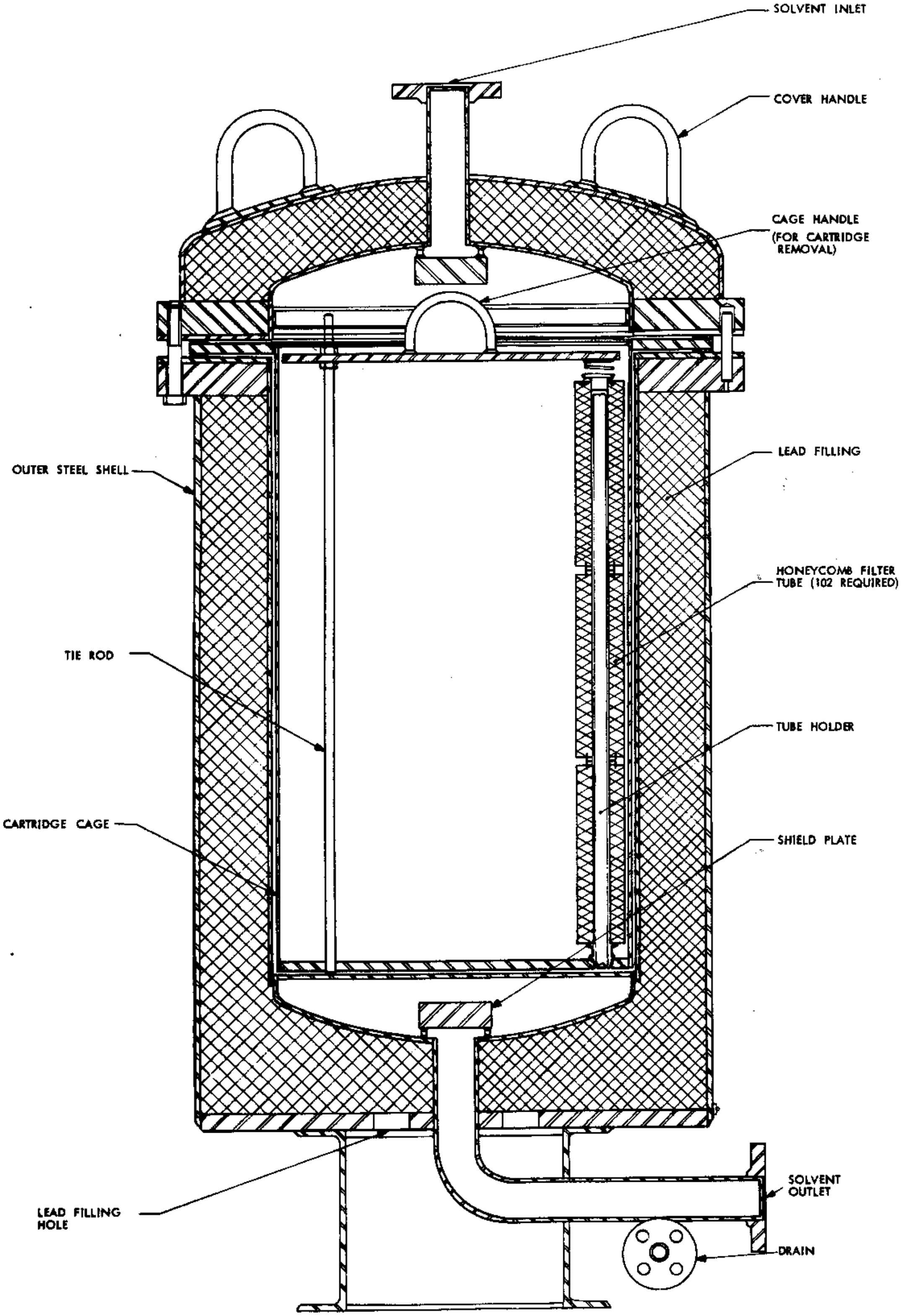

FIGURE 9.6 Shielded Solvent Filter

9.5 REFERENCES

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10. ACID RECOVERY

10.1 GENERAL

Recovery and reuse of acid reduces the waste storage cost that would be associated with disposal. The acid recovery unit concentrates to 50% nitric acid the condensate from acidic evaporation of canyon waste streams.[1]

10.2 PROCESS DESCRIPTION AND CHEMISTRY

Acid is recovered from the HAW evaporator condensate, LAW evaporator condensate, the 1DW evaporator condensate, and the 2BP evaporator condensate. The condensates are transferred to collection tanks and then to the acid recovery feed tank, from which they are fed to the acid recovery unit. The boiling point in the acid reboiler is about 87°C at the reduced pressure.[2] The feed acid is pumped through a preheater, which raises the temperature to the boiling point. Nitric acid, the less volatile component in the system, concentrates at the bottom of the recovery column; the bottoms are passed continuously through the natural recirculating-type reboiler. Nitric acid concentrated to 50% is continuously withdrawn from the bottom of the column. The acid product is cooled to about 35°C and pumped to the recovered acid run tanks.

The recovered acid may be: 1) transferred to the storage tank ready for use, 2) adjusted to 50% acid with fresh 60% nitric acid or with process water and sent to storage, or 3) returned to the feed tank for reprocessing. Fresh 50% acid is added to the acid storage tank to maintain an inventory to meet the demands of the canyon process.

The concentration of chloride ion on the lower trays of the column presents a potential corrosion and stress cracking problem. Chloride in the feed to the column is minimized by rigorously excluding it from evaporator feed solutions because it would also be highly corrosive to the evaporators. The chloride ion concentration in the feed and column has been a small fraction of the tolerable amounts.[3-5]

10.3 SAFETY

The principal problems associated with operation of the acid recovery process are: 1) exposure of operating personnel to radiation, 2) potential energetic decomposition of organic compounds, and 3) those industrial hazards common to chemical process equipment.

Control procedures based on routine monitoring are sufficient to avoid excessive personnel exposure, but particular vigilance is required during periods when upset of the canyon process results in abnormally high levels of radiation in Building 211-H.

Careful control of operations to prevent contact with hot acid fumes is maintained. All operations are performed remotely.

10.4 REFERENCES

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The concentration of chloride ion on the lower trays of the column presents a potential corrosion and stress cracking problem. Chloride in the feed to the column is minimized by rigorously excluding it from evaporator feed solutions because it would also be highly corrosive to the evaporators. The chloride ion concentration in the feed and column has been a small fraction of the tolerable amounts.[3-5]

11. WASTE HANDLING

11.1 GENERAL

Liquid wastes from separations processes are divided into three principal categories: high-activity, low-activity, and miscellaneous very-low-activity wastes. Most high-activity and low-activity wastes are concentrated by evaporation before storage in tanks. All of these wastes are made alkaline before storage. Very low activity or essentially cold aqueous waste is released to seepage basins. Recovery of nitric acid during concentration reduces the amount of sodium hydroxide that must be added and consequently reduces the volume of the waste to be stored.

Other process wastes include solid materials and gases. Most solids are buried; gases are treated to reduce fission product activity before release to the environment.

11.2 PROCESS DESCRIPTION AND CHEMISTRY

Evaporator performance and chemical effects in H-Area waste evaporations are similar to those process solution evaporations discussed in Sections 5.3.9, 6.3.5, and 7.3.4. Acid recovery from waste solutions is described in Chapter 10. Two other topics that apply generally to waste handling, regardless of category, are evaporator corrosion and waste neutralization.

The rate of corrosion of a stainless steel evaporator is a function of temperature, acid concentration, and the concentrations of materials, such as aluminum, chromium, iron, fluoride, or sulfate. Operating experience indicates an average corrosion rate of about 2 mils/month in evaporating "normal" HM wastes. Plant practice has been to control the acid concentration in evaporators to about 8M because the effects of various impurities on corrosion rates at higher HNO_3 concentrations are unpredictable. Operation at 8M HNO_3 concentrations should be only as long as required to accomplish the desired volume reduction and acid stripping.

Some process wastes contain fluoride. Hydrofluoric acid or fluoride ion in nitric acid corrodes stainless steel. Aluminum complexes fluoride, thereby reducing its effectiveness in solution and decreasing the corrosion rate. The aluminum concentration must be equal to or greater than the fluoride to reduce the corrosion rate of type 304L stainless steel to 2 mils/year or less.[1] The corrosion rate is further reduced by addition of extra aluminum. Addition of aluminum to increase the Al/F molar ratio to 4 has given favorable results.

After evaporation, wastes that do not contain aluminum must be neutralized with NaOH to a minimum pH of 8 to avoid damage to carbon steel waste storage tanks. Wastes containing aluminum must be adjusted to pH >10.5 to avoid forming aluminum hydroxide precipitates that may plug the waste headers. At the higher pH values aluminum forms soluble sodium aluminate. The maximum dissolved salts content of such waste solutions is about 45 wt %.

11.2.1 High-Activity Waste

High-activity waste (HAW) has the composition given in Table 11.1; Mark 16 fuel is used as the example.* This material is evaporated to form a high-activity waste concentrate (HAWC) which is neutralized before transfer to waste storage (Building 241). However, if process 1AW contains chromium from fuels containing stainless steel, evaporation is omitted due to the potential for corroding the evaporator (see Section 5.3.9). Such waste is neutralized directly and sent to waste storage. The head end cake slurry is not evaporated, but transferred to underground waste storage following neutralization.

Operation of the high activity waste evaporation system is as follows:

- The 1AW and miscellaneous wastes are combined in the HAW hold tank.
- The composite waste in the feed tank is pumped to the first stage evaporator at the desired rate until a batch of concentrate is accumulated.
- Following completion of evaporation, the concentrate is cooled, transferred to the HAW neutralization tank, and neutralized for storage in underground waste tanks. Table 11.1 lists the composition before and after neutralization.
- Evaporator condensate from the first stage is re-evaporated in the condensate evaporator (second-stage) for further decontamination.

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*The data shown are for an older flowsheet that used a 1AS stream of 1.6M $Al(NO_3)_3$ and therefore introduces about 25% more aluminum nitrate into the 1AW than the current flowsheet. There are also other small differences between the waste composition now produced and that shown in the table.

TABLE 11.1

HM Process Wastes[a]

Vessel or Stream	*kg*	*Liters*	*Density*	*Water, kg*	HNO_3		$Fe(NH_2SO_3)_2$		$Al(NO_3)_3$		$Hg(NO_3)_2$		$NaNO_3$		Na_2CO_3		*Dissolved TBP*		*Solids*
					M	*kg*	*M*	*kg*	*M*	*kg*	*M*	*kg*	*M*	*kg*	*M*	*kg*	*M*	*kg*	*wt %*
HAW Evap.																			
1AW	1685	1343	1.255	1183	1.20	101	0.020	6.7	1.36	388	0.0146	6.4					0.000414	0.148	
9.4	1736																		
8.1	1788																		
Evap. feed	1841																		
Evap. overheads	649	649		646	∿0.07	3													
Evap. bottoms	1192	851	1.400	693	1.88	98	0.032	6.7	2.14	388	0.023	6.4					0.00066	0.148	
8.4	1228	887	1.384	729	1.76	98	0.030	6.7	2.05	388	0.022	6.4					0.00063	0.148	
Unneutralized[b] HAWC	1265	924	1.369	766	1.69	98	0.029	6.7	1.97	388	0.021	6.4					0.00060	0.148	39.5
LAW Evap.																			
2AW	2756	2459	1.121	2162	3.73	578	0.026	15.6									0.00068	0.445	
Solvent washes[c]	628	612	1.026	612											0.24	15.7	0.001	0.163	
8.7	3740	3436	1.089	3140	2.58	559	0.018	15.6					0.09	25			0.00084	0.61	
Dilution water	4321			4321															
8.7	8061	7751	1.040	7461	1.15	559	0.01	15.6					0.04	25			0.00037	0.61	
Evap. feed	8302																		
Strip water	3321																		
Evap. overheads	11369	11113	1.023	10866	∿0.7	503													
Stripped bottoms	254	200	1.267	157	4.47	56	0.32	15.6					1.48	25			0.014	0.61	
8.6	262	209	1.258	165	4.28	56	0.30	15.6					1.42	25			0.014	0.61	
Unneutralized HAWC	270	217	1.244	173	4.12	56	0.29	15.6					1.36	25			0.013	0.61	35.9

Vessel or Stream	*kg*	*Liters*	*Density*	*Water, kg*	$NaNO_3$		$Fe(OH)_3$		Na_2SO_4		$NaAlO_2$		$Hg(OH)_2$		$NaOH$		$PO_4^{\equiv}$	*Solids*
					mol	*kg*	*mol*	*kg*	*mol*	*kg*	*mol*	*kg*	*mol*	*kg*	*mol*	*kg*	*mol*	*wt %*
HAWC[d]																		
8.4	1228	887	1.384	729														
Dilution water	115			115														
8.4	1343	1002	1.340	844														
50% NaOH	786			393											9827	393		
8.4	2127	∿1564	∿1.36	1331	7006	596	27	2.9	54	7.7	1820	149	19.6	4.6	893	36	0.557	
Neutralized HAWC	2191	∿1628	∿1.35	1395	7006	596	27	2.9	54	7.7	1820	149	19.6	4.6	893	36	0.557	36.3
LAWC																		
8.6	262	209	1.258	165														
50% NaOH	90			45											1122	45		
8.6	347	∿271	∿1.28	228	1064	90	63	6.7	126	17.9					102	4.1	2.28	
Neutralized LAWC	357	∿281	∿1.27	238	1064	90	63	6.7	126	17.9					102	4.1	2.28	33.3

---

a. Basis: 1000 liters of 1AF Vessel or Stream. This table includes aluminum nitrate added to 1AS, as formerly practiced.
b. This information is provided in the event stainless steel tanks are provided for waste storage.
c. Solvent wash basis: 16,000 lb/wash, 4 washes/week, 3850 lb Al in 1AF processed/week.
d. Does not include HAWC which has been processed through low-grade ^{238}Pu recovery.

- Condensate from the second stage evaporation is sent to the acid recovery unit.

- Bottoms from the second stage evaporation are returned to the first stage evaporator at predetermined intervals or when the condensate shows excessive activity.

11.2.2 Low-Activity Waste

Composition of low-activity waste (LAW) is given in Table 11.1; Mark 16 fuel is used as the example. LAW is evaporated, neutralized, and transferred to underground waste storage. Condensate is transferred to the acid recovery unit. Figure 11.1 outlines the process.

The LAW evaporation is operated as follows:

- Acidic 2AW is mixed with sodium carbonate solvent wash at a prescribed rate and with adequate venting for the carbon dioxide produced.

- The acidic mixed waste is transferred to the LAW decanter to remove solvent.

- LAW is moved to the LAW feed tank where it is combined with any available dehumidification condensate. Process water is added to dilute the feed to about 7% nitric acid to minimize corrosion.

- Diluted waste is transferred to any or all of the three low-activity evaporators which are in parallel. Operating conditions are similar to those of the HAW evaporators. After the nonvolatile solids content of the concentrate reaches 12%, about three volumes of stripping water per volume of concentrate are added gradually to evaporate at a constant specific gravity. About one-third of the residual nitric acid is boiled off and collected as condensate. The dilute feed is concentrated 40 to 80 times, yielding 15% solids and 27% nitric acid.

- At the completion of evaporation, the concentrate is cooled to 60°C and transferred to the concentrate neutralizer tank. Neutralization is made with sodium hydroxide. Compositions before and after neutralization are given in Table 11.1. Following neutralization, the LAWC is sent to underground waste storage.

- Condensate from the evaporators flows to the low-activity condensate tank and is pumped via the basin transfer tank to the acid recovery unit.

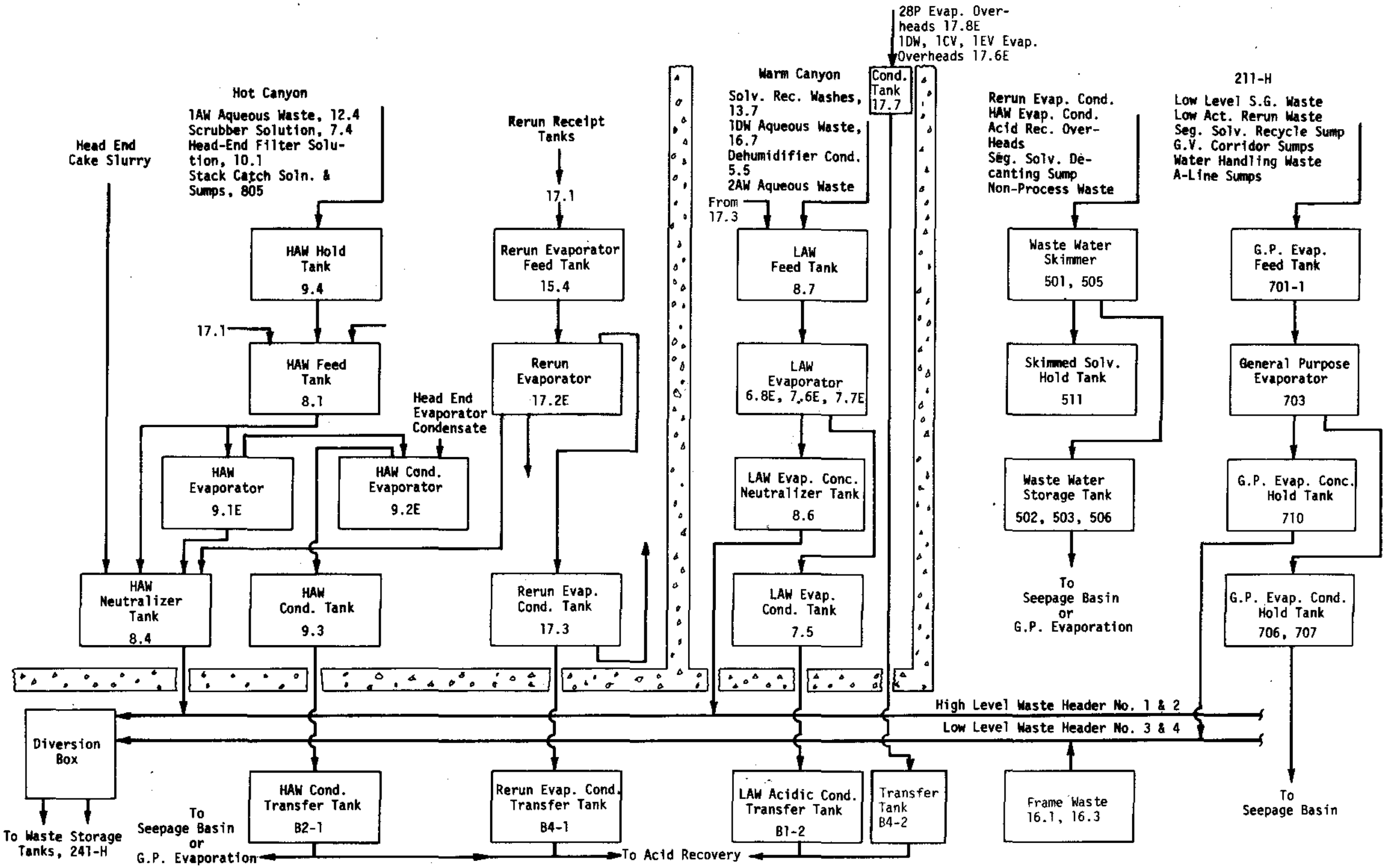

FIGURE 11.1 Outline of 200-H Area Waste Disposal

A special waste disposal condition arises when oxalic acid is used to wash solvent prior to disposal (see Section 9.2.2). Sodium oxalate is formed when the oxalic acid wash wastes are neutralized with NaOH. The solubility of sodium oxalate in water is 3.3% by weight at 20°C (Sp. Gr. = 1.0255) and is higher at temperatures.[2] If excess NaOH or other sodium salts are added, the solubility of the sodium oxalate is depressed below 3.3 wt % by the added sodium ion. Since oxalic acid is more soluble than sodium oxalate (8.3 wt % vs 3.3 wt % at 20°C),[3] oxalic-acid-containing waste solutions may have to be diluted before neutralization to avoid precipitating sodium oxalate solids that can plug the waste transfer jets and headers.

Alternatively, oxalic acid may be neutralized with KOH. The solubility of potassium oxalate in water at 20°C is 26.0 wt % (Sp. Gr. = 1.215) and is higher at higher temperatures.[4] Consequently, 8% oxalic acid solution can be neutralized with a large excess of KOH without exceeding the solubility of potassium oxalate.

The following equations[3] may be used to avoid oxalate precipitates:

$$[Na^+]^2\ [C_2O_4^=] \leqq 0.064 \text{ (molar)}$$

$$[K^+]^2\ [C_2O_4^=] \leqq 27.4 \text{ (molar)}$$

The quantities in brackets represent the total molar concentrations present, that is, the solubility product constant is used in the above expressions, but the ion concentrations are calculated from the charge composition on the basis that no precipitate forms.

11.2.3 Miscellaneous Waste Facilities (Seepage Basins and General-Purpose Evaporator)

Large volume waste streams with little or no activity are processed in Building 211. Figure 11.2 shows the schematic flow diagram for this system. Contaminated wastes contain negligible amounts of fission products and are discharged to seepage basins. The general-purpose evaporator may be used as a neutralizing station for treating low-level wastes or as an evaporating station to concentrate wastes before discharge. Low-level waste streams are classified as follows:

- Streams discharged directly to seepage basin drain without analysis such as sump and drain wastes from Buildings 211 and 221.

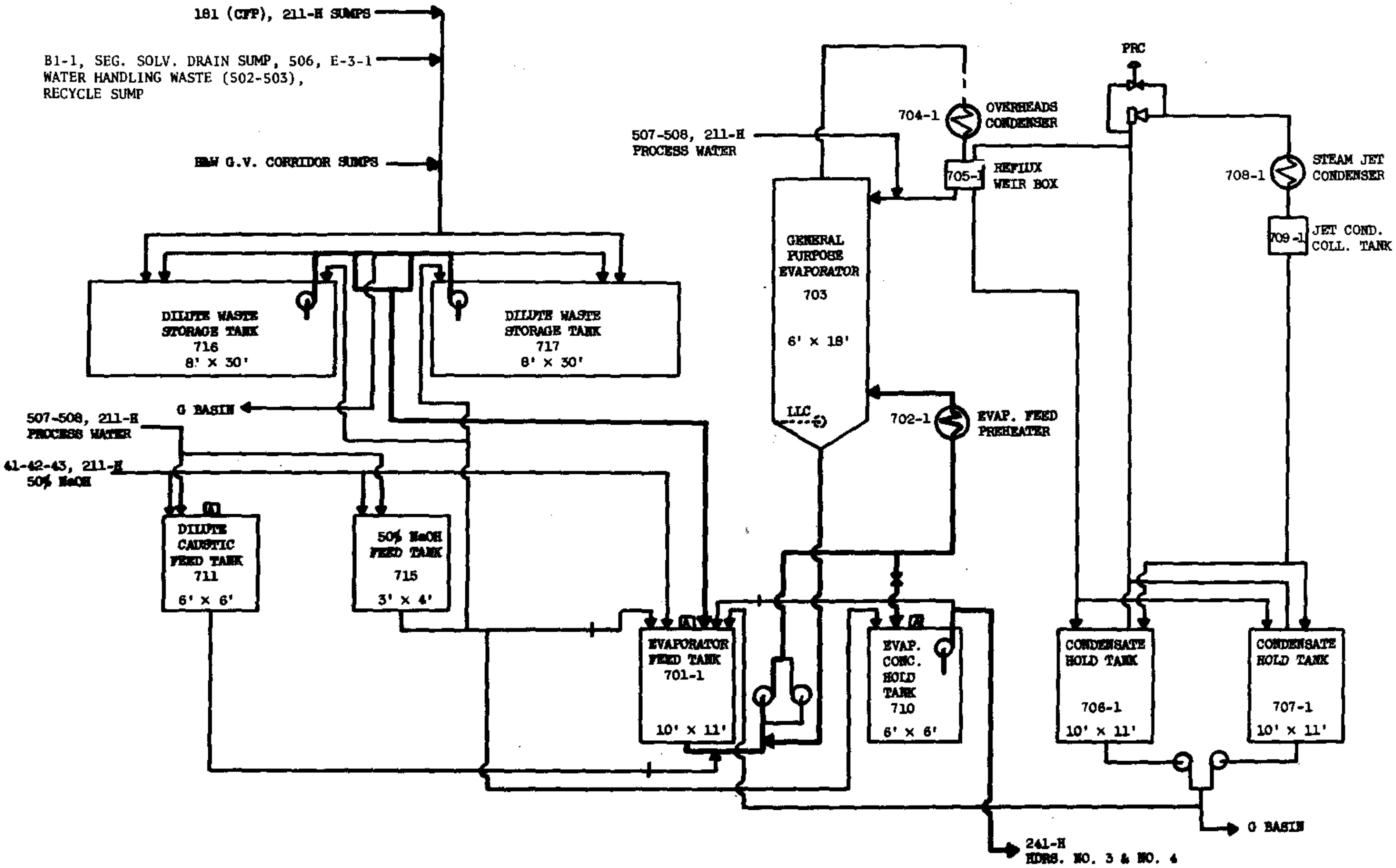

FIGURE 11.2 General-Purpose Evaporator Flow Diagram

- Streams that are sent to the waste water skimmer and held for analyses before transfer to the general-purpose evaporator or before discharge to the seepage basin.
- Streams that are held for analysis before sending to the general-purpose evaporator or to the seepage basin.

The general-purpose evaporation system is operated as follows (Sections 6.3.5 and 7.3.4 also apply):

- Wastes containing activity in excess of the basin discharge specifications are transferred to one of the general-purpose evaporator feed tanks.
- The waste is neutralized batchwise with 50% sodium hydroxide in the neutralizer tank.
- The neutralized feed is pumped continuously through a superheater and into the evaporator where it flashes into bottoms and vapor. The bottoms are continuously recirculated by the pump through the heater and into the evaporator at a rate of about 750 gpm. The vapor passes through four trays of bubble caps and a condenser. About 1 gpm of the condensate is returned as reflux, and the remainder flows by gravity into hold tanks. The evaporator and the condensate hold tanks are maintained at an absolute pressure of 200 millimeters of mercury by a steam ejector. The boilup rate in the evaporator is 7000 to 8000 lb/hr or about 270 lb/(hr-ft^2) which corresponds to a superficial vapor velocity in the bubble cap de-entrainment section of 7 to 8 ft/sec. The instantaneous decontamination factor (DF_I) averages about 10^5 and overall decontamination is about 10^4.
- The evaporator is operated until the bottoms contain 40 to 43% total solids or until the radiation intensity reaches the maximum allowable limit. The concentrate is pumped to the concentrate hold tank and subsequently transferred as low level waste to underground storage.
- The overhead from the evaporator is collected in the hold tanks, analyzed, and discharged to the seepage basins.

Each seepage basin facility consists of a group of three excavated shallow pits connected in series and arranged for gravity flow. The first two pits allow settling of the bulk of the solids in the waste stream, and will provide considerable seepage capacity until the settled solids restrict the percolation. The outlets of these settling sections have baffled weirs which prevent any floating solvent or oils from reaching the third pit.

The third pit has no overflow and the liquid can escape only by seepage into the soil; a minor amount of water evaporates. The soil in the vicinity of the seepage basins consists principally of sandy clay, which is expected to absorb the fission products as the liquid waste percolates through it in the manner of ground water. The first two sections have capacities of 1,000,000 and 3,000,000 gallons, respectively. The third section, where nearly all seepage will eventually occur, has a capacity of 30,000,000 gallons.

11.3 SAFETY

Safety problems associated with the waste disposal operation are the possible accumulation of a critical amount of enriched uranium, pressurization of evaporators, exposure of personnel to radiation, contamination of the environment, and possible temperature excursion during neutralization of acidic waste.

11.3.1 Criticality

A serious hazard in the waste evaporation system is the potential accumulation of a critical amount of enriched uranium. Nuclear safety aspects of and limits for the vessels concerned (evaporators and feed tanks) are specified from general nuclear safety limits.

11.3.2 Evaporator Pressurization

This hazard can occur from excessively rapid chemical reactions of the following: entrained organic material in the evaporator feed (see Section 6.3.5), ammonium- and hydroxylamine-containing compounds (see Section 7.3.4), hydrazine nitrate and hydrazoic acid. These latter two compounds are not normally used in the HM process, but are sometimes present in other process wastes that are blended with HM process wastes.

Hydrazoic acid is hazardous in both the aqueous solution and the vapor phase, but hazardous concentrations cannot be reached by evaporating solutions containing less than 0.05 molar hydrazine. Concentrated hydrazine nitrate solutions are sensitive to impact; therefore, evaporation of solution containing hydrazine and nitrate ion must be avoided. Hazardous conditions are avoided by oxidizing the hydrazine and hydrazoic acid to N_2O and N_2 by adding at least two moles of sodium nitrite per mole of hydrazine to the evaporator feed.[5]

11.3.3 Radiation Exposure

Although the exposure of personnel to excessive amounts of radiation has been largely eliminated by building design, precautions must be taken to avoid excessive amounts of fission product activity in the condensate and other wastes sent to the 211 Building. The handling of discarded equipment during burial, and the transportation of hot lab wastes are carefully monitored to prevent excessive exposure.

11.3.4 Area Contamination

The possibility of contamination of the plant environment arises from the storage of large amounts of radioactive waste in underground tanks, the discharge of activity to the seepage basins, and the discharge of activity from the stacks.

The spread of contamination from the storage tanks due to leakage is highly improbable due to the many safety features incorporated in their design. A possible occurrence which has a low probability of materializing but a high potential for spreading activity to the environment is the explosion of accumulated hydrogen in the underground waste storage tanks. Due to the extreme levels of activity in these tanks, hydrogen and oxygen are generated at significant rates. To prevent the accumulation of an explosive mixture, the air spaces of the tanks are analyzed routinely and purged with air when necessary. Uptake of CO_2 by the stored solution may permit a change in pH and an increase in the rate of hydrogen generation by corrosive attack on the mild steel tank. Care must be exercised to assure that an adequate amount of excess caustic is maintained in the stored waste.

Activity would spread from seepage basins almost entirely by migration through the soil, but the degree of absorption in the clay constituent of the soil is expected to prevent the development of a hazardous condition. The rate of migration of activity through the soil is being observed by monitoring wells placed at varying distances from the basins. Under current limitations on the rate of discharge of activity to the seepage basins and the normal loss of activity by decay and seepage, the activity level of the water in the basins is not more than 100 times the limits permissible for drinking water. Under any rates of discharge of activity now contemplated and considering the effects of ion exchange and dilution with ground water, the possibility of the spread of dangerous amounts of activity from the seepage basins to the environment seems remote.

The spread of activity from the stacks is minimized and controlled largely by containment through plant design and process conditions as described more completely elsewhere. The activity that is released is due almost entirely to volatile materials, which are effectively dispersed in the atmosphere. The rate of release of this activity is monitored at the top of each stack; and special provision is made for determining the rate of release to the atmosphere of radioiodine which is specifically limited to 1.25 Ci/yr for the separations areas. The chief hazard is the discharge and subsequent fallout of flakes of contaminated ammonium nitrate; these flakes form from ammonia and nitric acid fumes and accumulate activity. To reduce this hazard, the inner chamber of each stack is flushed periodically with water.

11.3.5 Heat of Neutralization

Neutralization of acidic waste solutions with sodium hydroxide presents a potential hazard in the heat of reaction generated by this exothermic reaction. Boilover of the neutralizer tank with evolution of large amounts of radioactive aerosols to the vent system is possible if the reaction is not controlled. However, the neutralization reaction is controlled by limiting the temperature of the reaction to a maximum of 80°C in a well-agitated vessel supplied with cooling coils. The addition of caustic to the waste is discontinued at this temperature. No serious hazard results from the neutralization of waste under these conditions.

11.3.6 Hydrogen Evolution

The lower explosive limit of hydrogen in air is 4.1%.[6] Hydrogen is generated slowly by radiolysis in waste solutions containing nitrate (as HNO_3 and/or metal nitrates). During evaporation the evolved hydrogen is diluted below its explosive limit with steam. After evaporation explosive mixtures may be attained if the solution in the evaporator is not boiled periodically or otherwise purged with air or an inert gas. The purge rate required or maximum time that solutions may be stored in unpurged evaporators before the solutions must be boiled or transferred out must be calculated from the volumes of solution and vapor space in the evaporator and the hydrogen generation rates of 0.090, 0.008 and 0.003 cc/min for each watt, respectively, of alpha, beta and gamma radiation energy generated in this solution. These values are based on "G" values of 0.66, 0.06 and 0.02 molecules per 100 electron volts, respectively, for alpha, beta and gamma energies and on the assumption that all alpha, beta, and gamma energy is absorbed.[7]

11.3.7 Ammonium Nitrate Accumulation

Neutralization of waste solutions with caustic volatilizes some of the ammonia that may be present in these solutions. Small amounts of ammonia are present in some solutions as a result of hydrolysis of reagents such as sulfamic acid or hydrazine, or from minor impurities present in nitric acid or other reagents. Ammonia thus volatilized has been found to accumulate as ammonium nitrate in process vessel vent filters in both the warm and hot canyons. Ammonium nitrate in large (several hundred kg) quantities would represent an explosion hazard should initiation be possible; the only possible source of initiation identified at this time would be ignition by a major canyon fire. The accumulation of ammonium nitrate is presently being limited by procedures that require periodic flushing or removal of accumulated material to the maximum extent practical with installed filters, and by control of operations in the canyon that may hydrolyze reagents to produce ammonia.

Solutions of ammonium nitrate from filter flushes are presently returned to the waste neutralization tank and sent to the waste tanks following addition of caustic. This operation must be controlled carefully to avoid generating flammable concentrations of ammonia gas in the canyon or waste tank farm.

11.4 TRANSFER OF WASTE TO STORAGE

The wastes to be stored are transferred from the process vessels in the hot and warm canyons into 10-inch-diameter waste headers located below grade outside the hot canyon. Two pairs of separate headers are used for the high level and low level wastes. The wastes flow from the hot canyon pipe rack through pipe imbedded in the concrete wall of the building. Because sections of the waste transfer lines between the pipe rack and the imbedded waste headers lie outside of the building concrete, it is necessary to shield these short lengths of exposed pipe with concrete casements. Between Building 221 and the storage tanks, the waste headers are encased in an underground concrete trough to ensure against spread of active material to the environment. These waste headers lead to a diversion box, an underground concrete vault equipped with interchangeable pipe jumpers and remote connectors such as used in the canyons. Lines from the diversion box lead to the underground waste storage tanks.

11.5 EQUIPMENT

Items for waste handling include the evaporators (continuous, batch, and general purpose), waste transfer lines, and the underground storage tanks. The use and purpose of such equipment has been described.[8]

11.6 REFERENCES

1. P. M. Kranzlein. *Corrosion of Stainless Steel in HNO_3-HF Solutions.* USAEC Report DP-486, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1960).

2. A. Seidell and W. F. Linke, *Solubilities of Inorganic and Metal-Organic Compounds,* 4th Ed., Vol. II, p 951, American Chemical Society, Washington, DC (1965).

3. A. Seidell, *Solubilities or Organic Compounds,* 3rd Ed., Vol. II, p 79, D Van Nostrand Co. (1941).

4. Reference 2, p 106.

5. E. K. Dukes and R. M. Wallace. *Formation of Hydrazoic Acid from Hydrazine in Nitric Acid Solution.* USAEC Report DP-728, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1962).

6. N. Irving Sax. *Dangerous Properties of Industrial Materials, 2nd Edition,* p. 885. Reinhold Publishing Co., New York (1963).

7. G Values were calculated by N. E. Bibler from data in:

   a. A. R. Kazanjian, F. J. Miner, A. K. Brown, P. G. Hagan, and J. W. Barry. *Trans. Faraday Society.* 66, 2192 (1970)

   b. J. W. Boyle and H. A. Mahlman. *Nucl. Sci. Eng.* 2, 492 (1957)

8. *Integrated Radioactive Defense Waste Management Plan.* USERDA Report SRO-TWM-77-1, Savannah River Operations Office, Aiken, SC (1977).

12. RERUN

12.1 GENERAL

The rerun station is a facility for special processing of waste streams, off-standard materials, etc., located in Sections 15-18 of the hot canyon. It contains a standard canyon evaporator, a rectangular decanter (similar to that used in solvent recovery (Figure 9.5), and numerous standard canyon tanks (Figure 12.1). Batch extraction, evaporation, solvent washing, and similar operations can be performed in this equipment; considerable flexibility is obtained by changing the connections between vessels as required for each particular process. Among the operations performed are concentration of waste streams prior to disposal, recovery of enriched uranium from off-standard process streams or sump solutions, washing spent solvent prior to disposal, and recovery of plutonium from high-activity waste.

12.2 PROCESS DESCRIPTION

12.2.1 Aqueous Uranium and Waste Streams

Recoverable ^{235}U from off-standard streams or canyon sump is stored until a quantity sufficient to justify treatment has been accumulated. The uranium solution is normally washed with diluent to remove organic contaminants. The solution is recycled to head end in an amount limited by the aluminum and nitric acid concentrations of the recycle and raw metal solutions. The blend of these two streams must be within specifications for feed to first cycle solvent extraction.

Solutions that do not contain recoverable amounts of ^{235}U are treated as waste. These solutions are accumulated in an aqueous hold tank and evaporated. The waste concentrate is transferred to the frame waste recovery resin digestion tank or HAW neutralizer tank 8.4 for neutralization before transfer to the 221-H waste storage tanks.

Figure 12.2 shows piping of rerun equipment for evaporation of frame waste raffinate while simultaneously recovering uranium and other products from miscellaneous wastes by batch extraction.

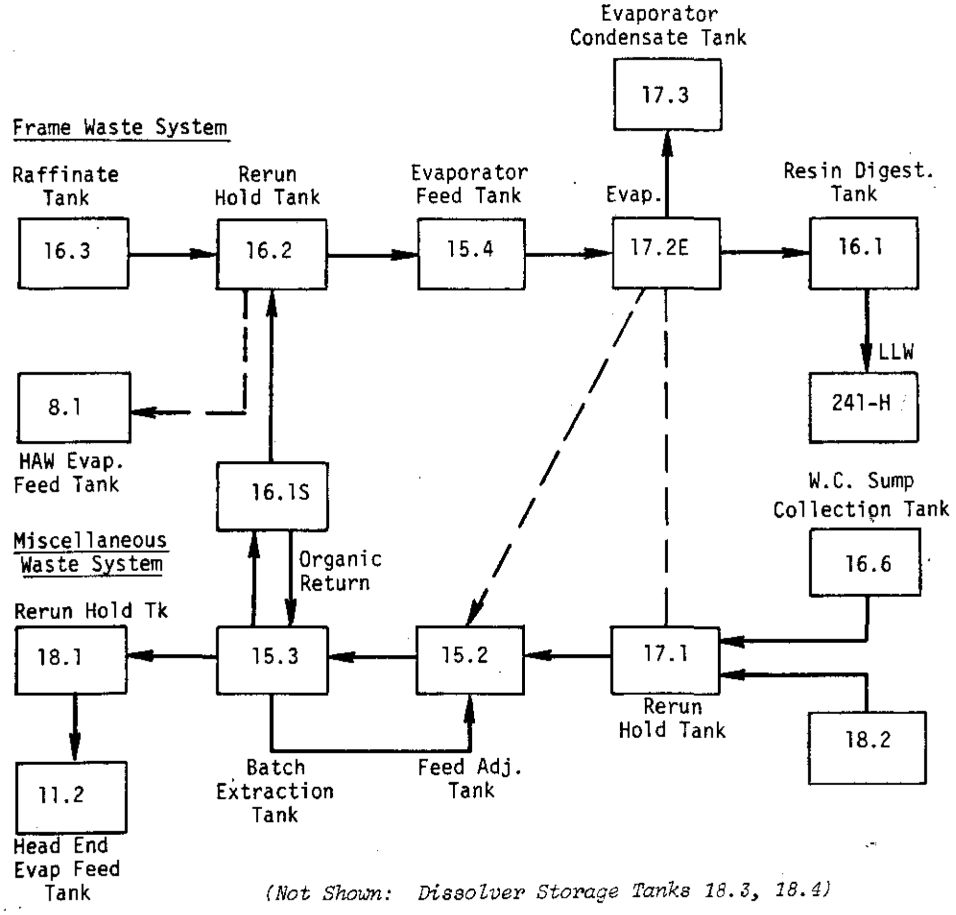

FIGURE 12.1 Rerun Equipment Showing Connections for Simultaneous concentration of Frame Waste Raffinate and Recovery of Uranium from Waste

Frame waste raffinate from tank 16.3 is transferred via Tank 16.2 to the evaporator feed tank (15.4) where it is diluted with water and fed to evaporator 17.2E. Concentrated bottoms are neutralized in resin digestion Tank 16.1 and discarded to low-level waste in Building 241-H.

Miscellaneous wastes accumulated in Tanks 16.6, 18.2, and 17.1 are adjusted with acid in Tank 15.2 and batch extracted with 5% TBP in the extraction tank (15.3). Raffinate is decanted (16.1S) to Tank 16.2 and either combined and discarded with frame waste or combined and discarded with HAW via the HAW evaporator feed tank (8.1). Strip solutions from the extraction tank (15.3) are decanted to Tank 18.1, transferred to the head-end tank (11.2), and blended with feed for first cycle.

A batch may be extracted twice by returning (from 15.3) and holding it in Tank 15.2 while products from the first extraction are stripped from the solvent. Whenever rerun evaporator 17.2E is not in use, miscellaneous waste from Tank 17.1 may be evaporated and returned to Tank 15.2 before extraction. Extraction is more efficient and can be done more quickly if the volume of feed is reduced by evaporation. Accountability for losses to waste and returns to the process is made by analyzing raffinate in Tank 16.2 and strip solution in Tank 18.1. Transfers of strip solution from 15.3 to 18.1 and raffinate from 15.3 to 15.2 must be made from settled solutions without benefit of a decanter. To prevent transfer of solvent when strips are decanted, large heels are left behind, and Tank 18.1 is analyzed for solvent before transferring any solution to head end.

About 75% recovery of product from waste is expected, using one extraction followed by three strips. About 95% recovery is expected with two extractions and five strips (two after the first extraction and three after the second).

12.2.2 Solvent

Solvent which does not contain recoverable amounts of ^{235}U is accumulated and decontaminated in rerun and is subsequently sent to the burial ground. Solvent containing significant amounts of ^{235}U is received in rerun and washed to recover the uranium.

The major source of solvent in return is the diluent added for washing enriched uranium-bearing solutions in return. Spent process solvent is also received from canyon vessels. The TBP concentration of the solvent in return is limited. The maximum has been set at 6% to prevent excess extraction of uranium. Solvent received from either second cycle must be diluted to 6% TBP with diluent before further processing. Spent solvent is washed and neutralized with 2.5% sodium carbonate to reduce the fission product content before transfer to the burial ground.

12.2.3 Plutonium Recovery

Plutonium formed in enriched uranium fuels is normally rejected in the 1AW stream (Chapter 7) and accumulates in the high-activity waste. The low-assay plutonium, typically 20% to 40% ^{238}Pu, can be recovered in rerun by extraction. The principal process steps are:

- Concentration of the HAW solution to give a solution >1.8M in $Al(NO_3)_3$ and <1M in HNO_3. Addition of caustic or steam stripping may be required to reduce the HNO_3 concentration (Figure 12.2). As an example of steam stripping, 1000 lb of typical waste evaporated to 525 lb, then steam stripped with 125 lb of H_2O yields a product containing 2.8M ($Al(NO_3)_3$ and <1.4M HNO_3 that may be diluted to 1.8 to 2.0M $Al(NO_3)_3$ and <1M HNO_3. Precipitates may form during this process but are readily redissolved.

- Valence adjustment to form Pu(IV). This is accomplished by sequential addition of 0.02M ferrous sulfamate and 0.1M $NaNO_2$. Any mercuric sulfamate precipitate will be destroyed by the nitrite.

- Batch solvent extraction with 5% TBP. Extraction of uranium and plutonium under these conditions may be predicted from the curves in Figure 12.3. Separation of the phases is conducted using the decanter 16.1S. Layout of the connections for this process is shown in Figure 12.4.

- Stripping of the plutonium and uranium from the organic phase into a solution of 0.1M HNO_3 and ferrous sulfamate (Figure 12.5). The solution of uranium and plutonium so obtained can be concentrated and partitioned and purified by solvent extraction. Recovery of plutonium by this process will depend on the composition of the 1AW stream and especially on the sulfate concentration, but will normally exceed 90%; uranium recoveries are higher.

Use of rerun equipment for simultaneous recovery of plutonium and ^{147}Pm was described in Reference 1.

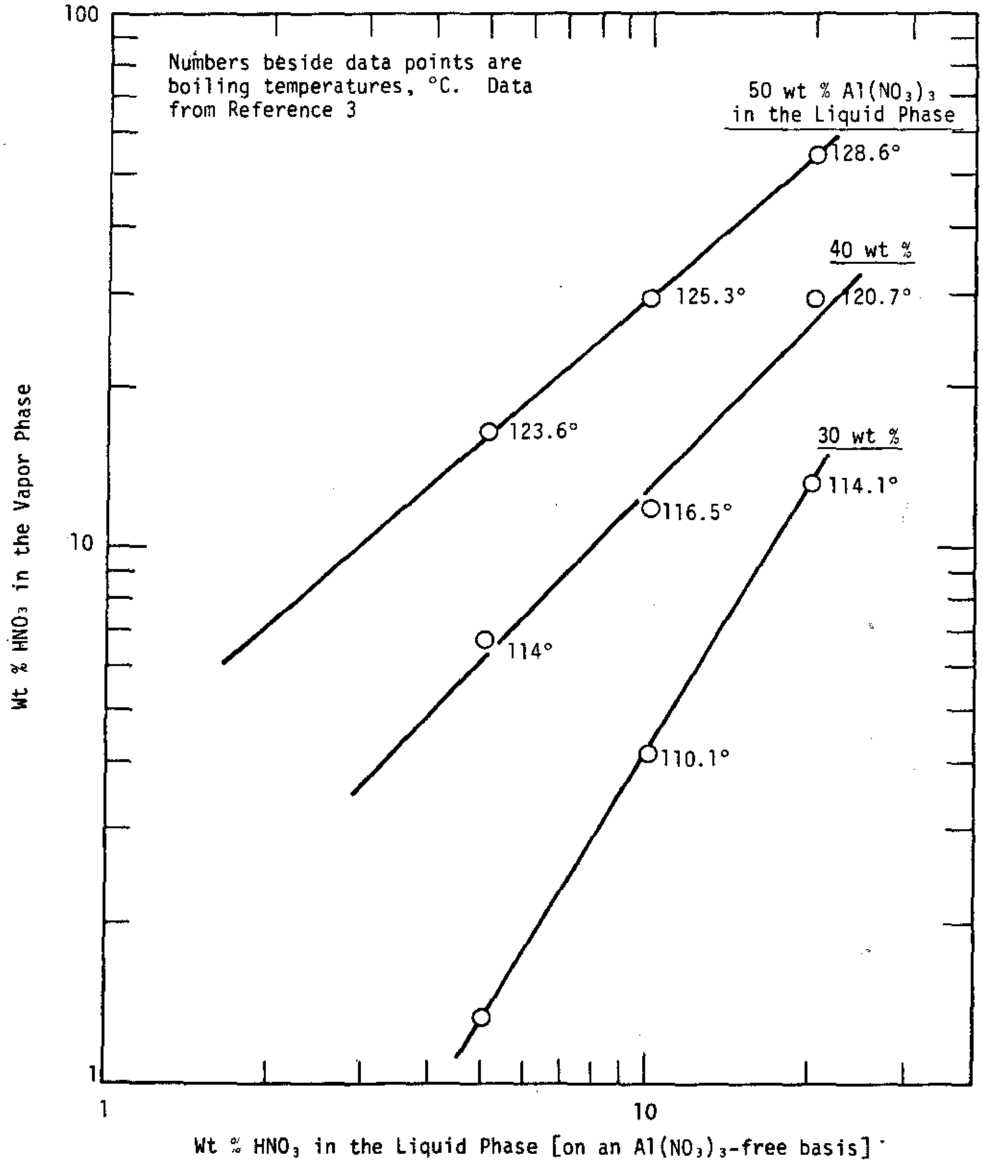

FIGURE 12.2 Vapor-Liquid Equilibria of HNO_3 from $Al(NO_3)_3$ Solutions

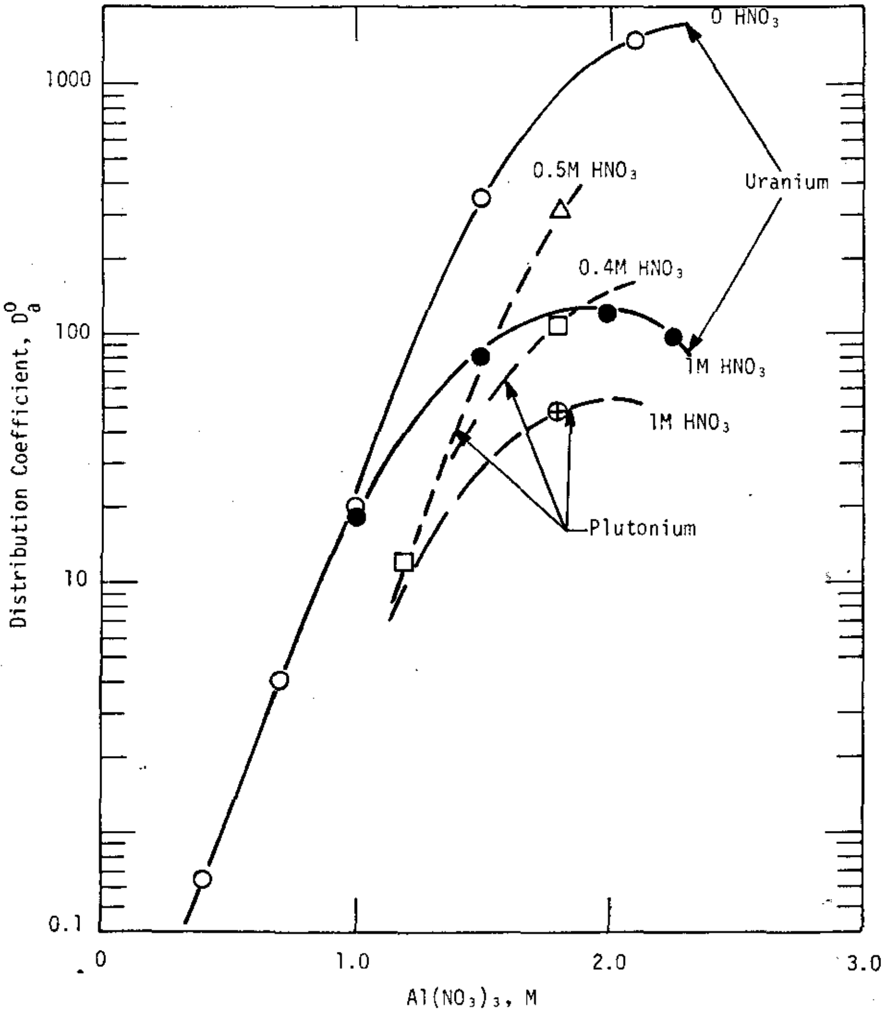

FIGURE 12.3 Extraction of Uranium and Plutonium from $Al(NO_3)_3$-HNO_3 Solutions by 5% TBP

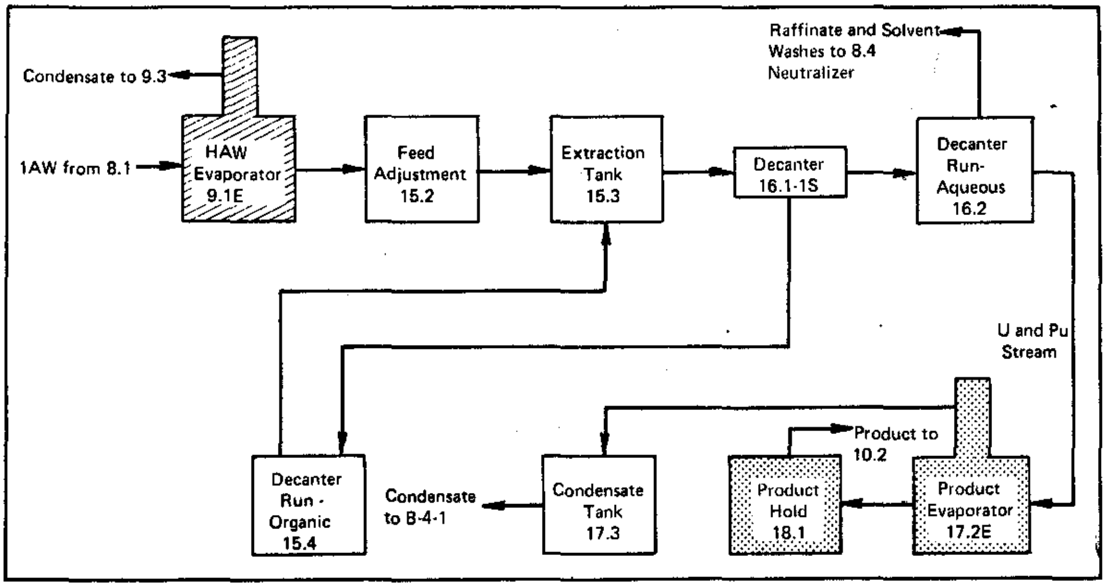

FIGURE 12.4 Recovery of Low-Assay Plutonium and Uranium in Rerun Equipment

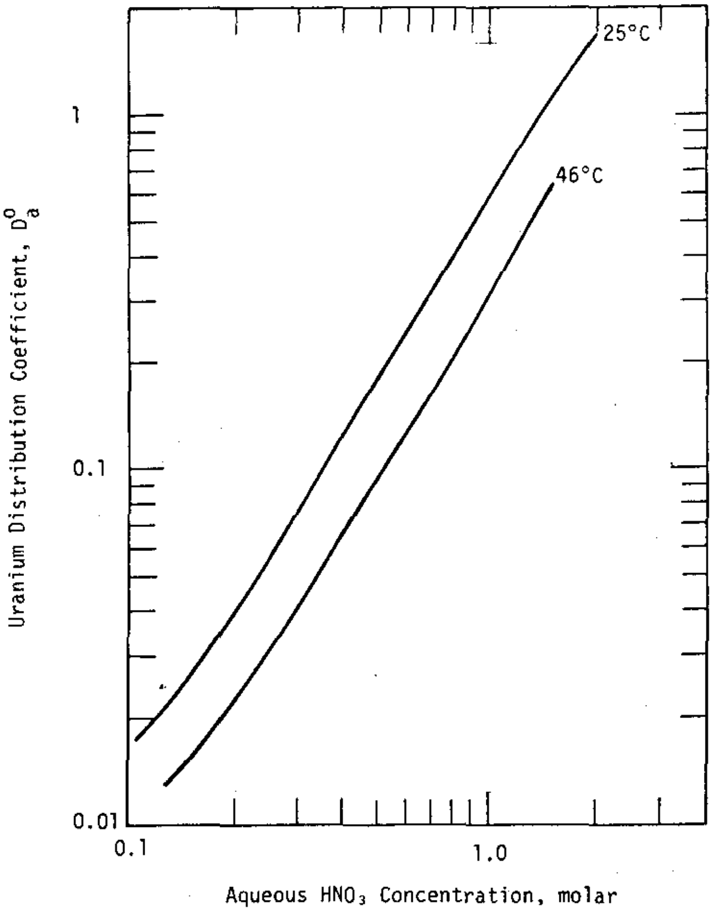

FIGURE 12.5 Stripping of Uranium from 5% TBP with Dilute Nitric Acid

12.3 SAFETY

Safety considerations in rerun are identical to those for similar equipment elsewhere in the canyon. The precautions applied are generally identical for such operations as evaporation, solvent handling, etc. Special requirements are noted here.

12.3.1 Criticality

The flexibility and quantities of uranium processed demand that stringent controls be maintained to prevent a nuclear excursion. Most processing is performed with acidic solutions to ensure that the uranium will remain in solution. Upon completion of solvent washing, the remaining basic heels are acidified before further use of the tankage.

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