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SAVANNAH RIVER PLANT
200 AREA TECHNICAL MANUAL - PART SP

PROCESSING OF Np^{237} AND Pu^{238}

Compiled by
A. J. Hill
Separations and Services Section

January 1961

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DPSTM--200-SP

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Revised: 1/3/63

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ABSTRACT

This manual covers the technology involved in the 200 Area process for the recovery of Np^{237} from certain aqueous waste streams in the separations plants, for the recovery of Np^{237} and Pu^{238} from irradiated NpO_2-Al slugs and for the fabrication of NpO_2-Al slugs. The manual contains sections on the fundamental chemistry, the primary recovery of Np by ion exchange, the decontamination of Np by ion exchange, the processing of NpO_2-Al targets, the separation and purification of Np^{237} and Pu^{238}, the finishing of Np, the preparation of NpO_2, the disposal of spent resin, and the safety aspects of the handling of hydrazine. The section on the fabrication of NpO_2-Al slugs will be added later.

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1.0 FUNDAMENTAL CHEMISTRY

1.1 Process Description

Plutonium-238 is of interest as a source of alpha particles for α,n nuclear reactions because of its relatively short half life (90 yr) and intense alpha activity, which is approximately 270 times that of Pu^{239}. It is also a heat source, generating approximately 0.5 watt/gram. Pu^{238} can be produced by the irradiation of Np^{237} (half life 2.2×10^6 yr), which is a by-product from the irradiation of uranium. Np^{237} is recovered from aqueous waste streams that are generated during the processing of irradiated uranium. The Np is purified, converted to neptunium oxide, NpO_2, mixed with aluminum, compacted, and canned by hot-press bonding into target slugs for irradiation. The irradiated target elements are dissolved in nitric acid. The Pu^{238} and unreacted Np^{237} are separated from aluminum and fission products. Subsequently, the Np^{237} is separated from Pu^{238} and essentially all of the remaining fission products. The Np^{237} is concentrated and reconverted to the oxide for fabrication of targets. The Pu^{238} is purified and then shipped directly to the customer as a nitric acid solution containing a minimum of 1 gm/l of Pu^{238} and no more than 1 gm of Np^{237} per 100 gm of Pu. The conversion of Np^{237} to Pu^{238} in a single irradiation must be limited to about 16% to keep the quantity of higher Pu isotopes below 20 atom %.

Under normal operating conditions for the Purex process, the Np^{237} is diverted primarily to the high activity aqueous waste stream (1AW) and is concentrated in the high activity waste concentrate (HAWC). Np^{237} is present in irradiated natural uranium at levels of 2-4 ppm, depending upon reactor exposure. The HAWC is a strong nitric acid solution containing the bulk of the fission products plus K, Mn, Al and some undissolved solids. The separation of the small quantity of Np^{237} from this heterogeneous mixture, which contains approximately 5×10^4 curies of fission products per gram of Np, can be accomplished by taking advantage of the ability of the actinide elements to form anionic nitrate complexes and of the selectivity of anion exchange resins for these actinide complexes. In addition to the separation of Np from fission products, it is necessary to remove UX_1 or Th^{234} from Np to decrease the activity, and to remove Pu and Th^{232} to produce a chemically pure product. The purification of Np from residual Pu and fission products is accomplished by additional anion exchange and Th can be removed by cation exchange. Similarly, after the irradiated NpO_2 targets

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are dissolved in nitric acid, the Np and Pu can be separated from the other cations and then from each other by ion exchange of their anionic complexes.

Anion exchange was selected in preference to solvent extraction both for the recovery of Pu^{238} and Np^{237} from irradiated targets and for the recovery of Np^{237} from Purex wastes because of the following advantages: (1) minimum interference with the natural or enriched uranium separations processes currently in operation in the Plant, (2) minimum canyon space requirements, (3) greater concentration of Np, and (4) lower cost.

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1.2 Nuclear Transitions

Np^{237} is produced from U^{236} and U^{238} in irradiated natural uranium by the following reactions:

$$U^{238}\ (n,2n)\ U^{237}$$

$$U^{236}\ (n,\gamma)\ U^{237}$$

$$U^{237} \longrightarrow Np^{237} + \beta$$

The quantity of Np^{237} formed is a function of exposure to neutrons in a reactor and has been calculated to vary with exposure.(1.14)

Exposure, MWD/T	Np^{237} Produced, gm/T
600	2.12
800	2.87
1000	3.65
1200	4.46

At 1200 MWD/T, the quantity of Np produced from irradiated natural uranium is approximately 2.7 kg/reactor year; at 35% burnup, 2.4 kg/reactor year would be produced in enriched uranium fuel(1.15). This quantity can be increased by recycling the uranium product, thereby increasing the quantity of U^{236}; the increase is essentially linear and by the fifth cycle, with 35% burnup per cycle, would be equivalent to approximately 10.5 kg/reactor year.(1.16)

Pu^{238} is produced by irradiation of Np^{237} according to the reactions

$$Np^{237}\ (n,\gamma)\ Np^{238}$$

$$Np^{238} \longrightarrow Pu^{238} + \beta$$

By successive n,γ reactions, Pu^{239}, Pu^{240}, Pu^{241}, and Pu^{242} are also formed but in lesser amounts. The quantity of Pu^{238} that is formed is a function of reactor exposure and the initial concentration of Np^{237} in the targets; both can be varied. The production of Pu^{238} for a series of Np^{237} concentrations and reactor exposures has been calculated(1.17-1.20) for SRP reactors. According to calculations, the established upper limit of 20 atom % of higher plutonium isotopes is reached at an exposure of approximately 200,000 megawatt days. Other variables, such as the target location in the reactor, will affect the production of Pu^{238}.(1.18-1.20)

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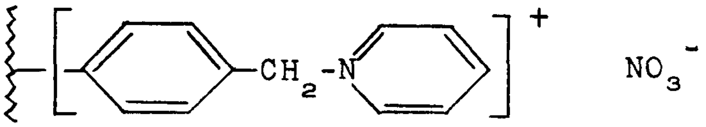
1.3 Anion Exchange

Neptunium and plutonium in the (IV) valence state form anionic complexes that are strongly absorbed on appropriate anion exchange resins. The formation and stability of the complexes is a function of the nitrate ion concentration and can be represented by the equation

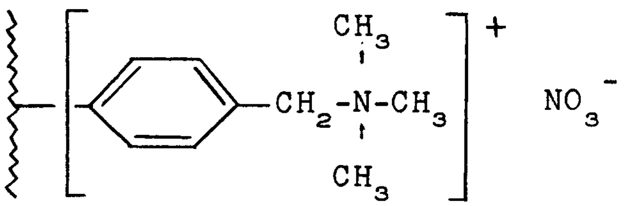
$$M(IV) + 6NO_3^- \rightleftharpoons M(NO_3)_6^=$$

where M is Np or Pu. Np(V) and (VI) and Pu(III) and (VI) form only weak complexes that are not strongly absorbed(1.21); Pu(V) does not form an anionic complex.

Anion exchange resins based on polystyrene incorporating various functional groups are suitable and are in the general form of $R^+(NO_3)^-$ where R represents the resin matrix. Typical resins are "Permutit" SK, which contains pyridinium groups furnishing ion exchange sites shown schematically by



and "Dowex" 1-X4, which contains quaternary ammonium groups



In the absorption of anion complexes, the nitrate ion is replaced by the anionic complex.

$$2RNO_3 + M(NO_3)_6^= \rightleftharpoons R_2M(NO_3)_6 + 2NO_3^-$$

where R represents the resin matrix and M is either Np or Pu in the (IV) valence state.

The resins are in the form of small spheres or beads, and the actual absorption of the anionic complex involves subsequent diffusion of the complex from the resin surface into the resin. Normally such resins are chlorides rather than nitrates. The nitrate form is required to prevent excessive corrosion of stainless steel process

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equipment and to assure adequate decontamination of Np from zirconium.

The exchange capacity of the resins is 1.2-1.3 mole equivalents of anionic complex per liter of packed resin(1.22), but the capacity that is attained in practical use is dependent upon the time of contact and the ions being exchanged. At flow rates that are practical for the absorption of the anionic nitrate complexes of Np(IV) and Pu(IV), only about 20% of the capacity of the resin is utilized. The sizes of commercial resins vary widely. Resin size affects the rate of exchange and the physical behavior of a resin bed. A decrease in particle size increases the rate of ion exchange but also increases the pressure drop of solution flow through a resin bed. A compromise is necessary. "Permutit" SK and "Dowex" 1-X4 in 40-60 mesh size have been found to be acceptable.

Resins tend to expand and contract in aqueous solutions of different ionic composition; these volume changes affect the rate of exchange. The maximum volume occurs during elution of the resin with dilute acid. The volume change is reduced by cross-linking the polymer through copolymerization of styrene with divinyl benzene (DVB). A maximum cross-linked resin (10-12% DVB) has low expansion, but is slow in the rate of exchange. Again, a compromise is necessary; a 4% cross-linked resin with less than 10% volume change is acceptable. Resins with less than 4% cross-linking tend to agglomerate and are not suitable for process use. A rapid change from dilute to concentrated nitric acid, or the reverse, can cause cracking of the resin beads which decreases the size of the resin and increases the pressure drop across the bed. However, resin cracking is not a problem with the changes in the range of 0.35M (dilute) to 8M (strong) nitric acid that are required in the absorption and elution of Np and Pu.

The rate of ion exchange is affected by the process solutions as well as by the physical and chemical properties of the resin.

The formation of the anionic complex of Np(IV) or Pu(IV) is an equilibrium reaction and depends on the concentration of nitrate ion. Since the anionic complex is the absorbed specie, the absorption likewise is a function of nitrate ion concentration. Absorption of Np(IV) or Pu(IV) is quite effective over the range of 7-10M nitrate ion (Figure 1.1).

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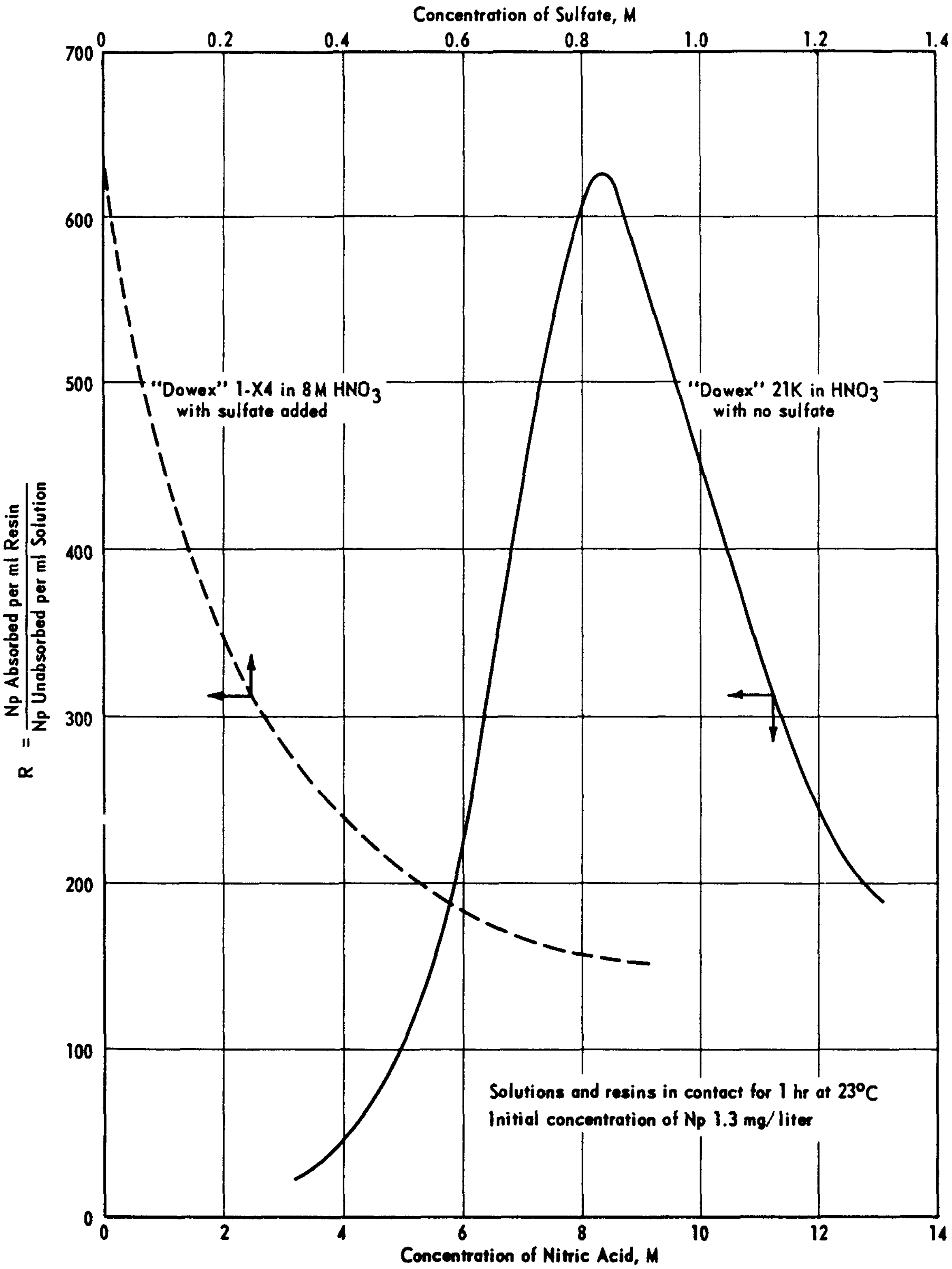

Solutions and resins in contact for 1 hr at 23°C
Initial concentration of Np 1.3 mg/liter

FIG. 1.1 EFFECT OF CONCENTRATIONS OF NITRIC ACID AND SULFATE ON DISTRIBUTION RATIO FOR NEPTUNIUM

[redacted]

Low nitrate concentration causes ionization of the absorbable anionic nitrate complex and results in desorption of the complex from the resin. The desorption is essentially complete when the nitrate concentration is less than 2M. It is necessary to maintain an acid concentration of greater than 0.25M nitric acid to prevent hydrolysis or polymerization reactions and to obtain good desorption rates. The rate of desorption is most rapid at a solution concentration of about 0.35M nitric acid.(1.1) The exchange equilibria depend more strongly on nitrate ion concentration than on nitric acid. Provided more than 1M nitric acid is present, the exchange equilibria are essentially the same with acid - nitrate salt mixtures, such as HNO_3-$NaNO_3$, as with acid alone, but the reaction rates are slower in the acid - salt system.

Other anions, such as sulfate and phosphate, which are present in the aqueous streams from the processing of irradiated uranium, also affect ion exchange. The effects of such ions have been studied primarily within the concentrations and under the conditions anticipated in the process range. Thus, sulfate ion that is present in Purex high activity waste decreases the absorption of neptunium ion by anion exchange resin, probably by preventing the formation of the nitrate complex. The effect of sulfate ion concentration on the absorption of Np on "Dowex" 1-X4 is shown in Figure 1.1, and the results of experiments with synthetic HAWC are shown in the following table.

Effect of Sulfate Concentration on Absorption of Neptunium

Sulfate Conc. of Aqueous Phase, M	$R = \frac{\text{Np/ml Resin}}{\text{Np/ml Solution}}$	Predicted Loss(a) Over 50 Bed Volumes(b), %
0.0	800	3.5
0.1	470	5
0.2	350	6.5
0.3	320	7.5
0.5	225	9
0.7	170	100

Aqueous Phase: Synthetic HAWC, 8M NO_3^-, plus indicated conc. of H_2SO_4
Resin: "Permutit" SK, 40-80 mesh
R determined after equilibration for 100 minutes

(a) On the basis of limited work with process solutions, actual losses may be 2-3 times the predicted losses.

(b) Bed volumes $= \frac{\text{Volume of solution}}{\text{Bulk volume of settled resin}}$

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Similarly, the recovery of Np from Purex HAWC is adversely affected by the phosphate-containing degradation products of tributyl phosphate. Studies with synthetic HAWC have shown that phosphoric acid, monobutyl phosphate (MBP), and dibutyl phosphate (DBP) are harmful to the absorption of Np from HAWC by anion exchange resins. The degree of interference of these compounds depends largely upon the composition of the HAWC. Iron probably is beneficial since it forms strong complexes with phosphoric acid and MBP and effectively removes DBP by precipitation. Aluminum has similar but less pronounced effects. The removal of DBP by precipitation with iron and aluminum which are normally present may be an important factor in keeping the phosphate content of HAWC within workable concentrations. Unless the concentration of aluminum or iron is about 0.2M, the tolerable limit of phosphate as phosphoric acid or MBP is probably less than 0.01M. The phosphate in HAWC hinders the absorption of Np, but the phosphate does not accumulate to any significant degree on the resin. Analyses of anion resin after exposure to cold HAWC containing phosphoric acid and MBP have shown on the order of 0.01M phosphate in the resin directly after absorption and less than 0.001M after conventional washing with 8M HNO_3. The effect of phosphate, as phosphoric acid, on the recovery of Np from HAWC is shown in the table below.

Effect of Phosphate on Recovery of Neptunium from HAWC by Anion Exchange

Resin	Solution Composition, M				Predicted Loss Over 50 Bed Volumes$^{(b)}$, %
	$PO_4^{\equiv}$	NO_3^-	$Fe^{+++(a)}$	Al^{+++}	
"Permutit" SK	None	8.0	0.02	0.20	3.2
	0.003	8.0	0.02	0.20	3.5
	0.01	8.0	0.02	0.20	13
	0.03	8.0	0.02	0.20	29
	0.10	8.0	0.02	0.20	63
	0.05	8.0	0.22	0.20	19
"Dowex" 1-X4	None	7.5	0.02	0.20	4
	0.03	7.5	None	None	30
	0.03	7.5	0.2	None	14
	0.03	7.5	None	0.2	18
	0.03	7.5	None	0.4	14

(a) Does not include 0.05M iron added as $Fe(NH_2SO_3)_2$

(b) Bed volumes= $\dfrac{\text{Volume of solution}}{\text{Bulk volume of settled resin}}$

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Laboratory experiments with HAWC have also indicated that the useful life of either "Dowex" 1-X4 or "Permutit" SK is limited by the absorption of an unknown specie or species which is not removed from the resin during product elution with dilute nitric acid or during fission product removal with strong nitric acid. The loss of Np is shown in the following table.

Neptunium Absorption by an Agitated Resin Bed

No. of Anion Cycles	Cumulative Bed Volumes of HAWC Processed	Neptunium Loss, % "Dowex" 1-X4, 20-50 Mesh	Neptunium Loss, % "Permutit" SK, 20-50 Mesh
1	50	7	8
2	95	9	9
3	140	21	34
4	190	51	45
5	240	79	--

Although analyses of "poisoned" "Dowex" 1-X4 resin have indicated phosphate, ruthenium, and molybdate to be possible suspects, laboratory tests with inactive simulated waste solutions have not proved any of these ions to be the poison. However, it is believed that the useful life of the resin is limited by some chemical effect rather than by radiation damage. When the resin is exposed to HAWC, the loss in efficiency is evident in less time than that required for significant radiation damage.

Effects of Radiation

The process solutions contain beta- and gamma-emitting fission products and alpha emitters such as Pu^{238} and Np^{237}. In the recovery of Np^{237} from Purex waste concentrates, the gamma radiation is a problem; in target processing, the alpha radiation from Pu^{238} is of more concern.

Gamma radiation affects both the valence of Np^{237} and the stability of the anion exchange resin. Laboratory studies with simulated HAWC containing nitric acid, sodium nitrate, and manganous nitrate show that nitrite ion (NO_2^-) is generated radiolytically from nitrate ions and that an equilibrium concentration of 0.02-0.06M nitrous acid (HNO_2) is reached after 12-24 hours. In the strong acid solution the nitrous acid acts as a mild reducing agent which tends to stabilize Np in the (IV) valence state and limit the amount of oxidation to the (V) state which does not form a nitrate complex and therefore

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is not absorbed. Hydrazine and ferrous sulfamate are added to increase the stability of Np(IV) and thus increase the amount absorbed. The effect of solution adjustment on Np absorption from HAWC on an anion exchange resin is shown in Figure 1.2.

In the presence of hydrazine and ferrous sulfamate, the absorption of Np is only slightly less from HAWC than from synthetic solutions where there is no radiation indicating that gamma radiation does not have a serious effect on the total capacity of the resin. However, the effect of gamma radiation on the rate of absorption is significant. Gamma radiation causes deterioration of anionic resins such as "Dowex" 1-X4 and "Permutit" SK. Radiation degrades "Dowex" 1-X4 at a somewhat greater rate than it does "Permutit" SK. The cross-linking in the "Dowex" resin matrix is broken, and the strongly basic tertiary amine functional groups are replaced with weak base primary and secondary amine groups. The rate of absorption is affected to a greater extent than the total capacity. In an experiment with "Dowex" 1-X4, an 8% decrease in the total capacity of the resin was accompanied by a tenfold decrease in the rate of absorption.

In the recovery of Np^{237} and Pu^{238} from irradiated Np^{237}, the radiation of primary concern is the alpha emission from Pu^{238} which affects the valence of both Np and Pu and also degrades the anion exchange resin. In solutions that contain low concentrations of nitric acid and total nitrate, the alpha radiation from Pu^{238} forms radiolysis products, particularly nitrous acid which rapidly oxidizes Np(IV) to higher oxidation states. Under these conditions, Pu(IV) is not oxidized by nitrous acid. In solutions which are in the range of 6-9M in total nitrate, the tetravalent states of both Np and Pu are stabilized by formation of the anionic nitrate complex and other valence states are not produced as readily.

The intense alpha radiation from Pu^{238} absorbed on "Permutit" SK resin degrades the resin by breaking the cross-linking of the resin matrix, and the strongly basic pyridinium groups are replaced by weak base groups. The result is a decrease in the absorption capacity of the resin. Since long exposure results in severe degradation of the resin beads, Pu^{238} should not be left absorbed on a resin longer than absolutely necessary for the process purpose. When Pu^{238} is loaded on resin and washed to remove fission products, a 1 to 2% loss of Pu occurs which is attributed to valence changes produced by radiolysis; the loss does not occur when Pu^{239} is processed under the same conditions.(1.2)

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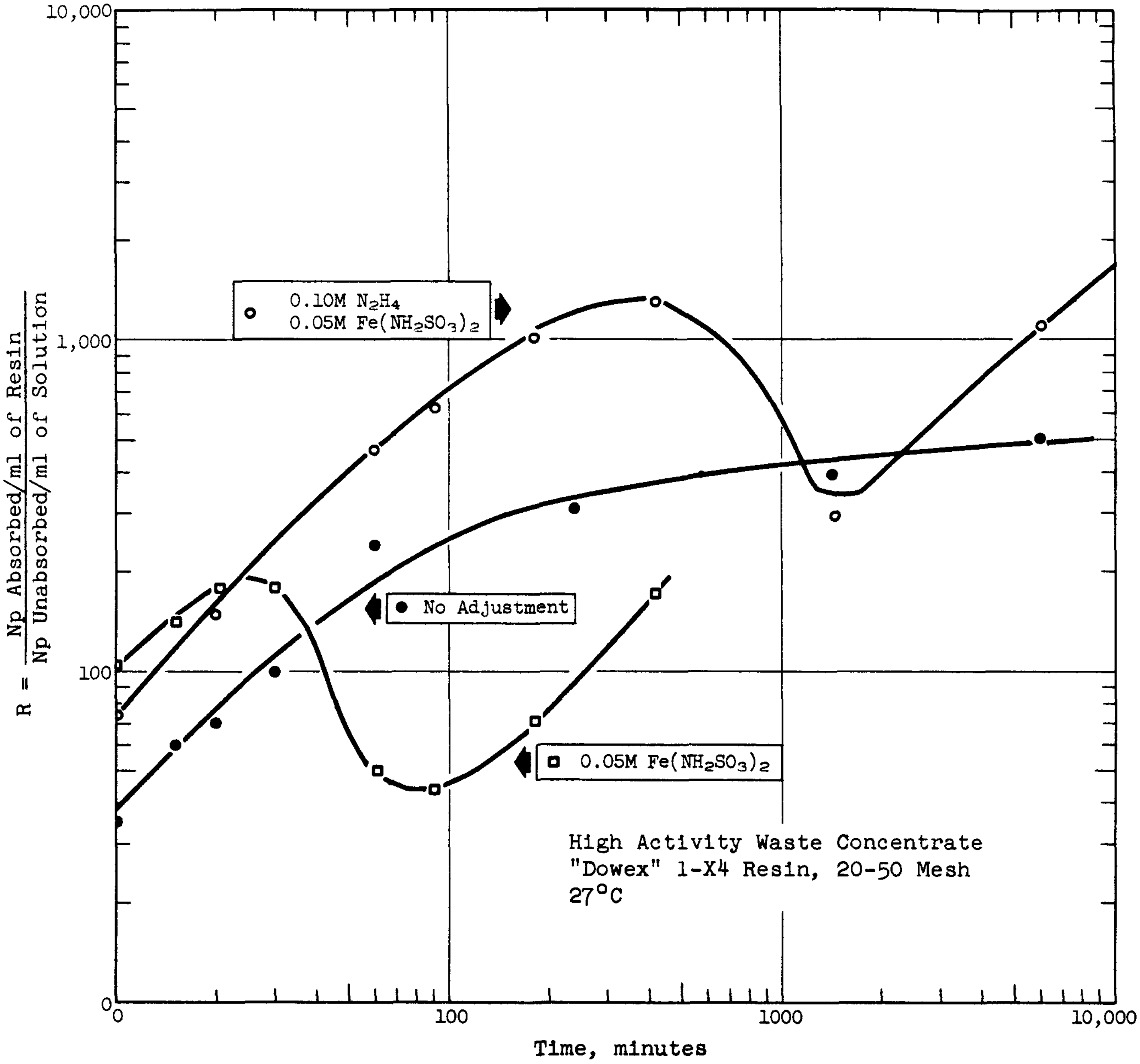

FIG. 1.2 Np DISTRIBUTION AS A FUNCTION OF SOLUTION ADJUSTMENT

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Other Absorbable Ions

Since Pu(IV) and Np(IV) are two of the few metal cations capable of forming stable anionic nitrate complexes which are strongly absorbed on anion resins, excellent separation from most contaminants is attained. After absorption of the complexes, a strong nitric acid wash makes it possible to attain decontamination factors (DF) from fission products of 50-1000 per cycle of anion exchange. The DF is increased by the addition of a trace of fluoride ion (0.005M) to the wash and possibly by washing at 60°C. Other cations that originate from the dissolution of targets or the corrosion of stainless steel tanks are separated from Np^{237} and Pu^{238} by a factor of at least 10^3. Protactinium-233, the alpha decay product of Np^{237}, is separated from Np^{237} and Pu^{238} by a factor of 10^2 in a single exchange cycle.

In the recovery of Np from Purex HAWC there are several ions that are absorbed on the anion resin bed and affect the purity or the radioactivity of the recovered Np. The most important species in this respect are the nitrate complexes of Th(IV), Pu(IV), and RuNO(III).

Thorium in the HAWC is due to a Th^{232} impurity present in the uranium fuel before irradiation, and also to the radioisotope Th^{234} (UX_1, half life of 24.1 days) produced by the alpha decay of U^{238}. Thorium is extracted poorly in the Purex process and is removed in the 1AW, which is subsequently evaporated to produce the HAWC. Less than 8 ppm of Th^{232} is present in the uranium metal; the quantity of Th^{232} in the HAWC is estimated to be about equal to the quantity of Np. The activity of the Th^{234} in the HAWC is 1/6 curie for each ton of uranium processed through solvent extraction. The separation of Th from Np is necessary both for decontamination and product purity.

Th(IV) absorbs on an anion exchange resin as the $Th(NO_3)_6^{=}$ ion, with a distribution coefficient about one-fifth of the Np distribution coefficient. On the initial recovery bed, about 30% of the Th in the feed is lost during the absorption, and an additional loss of 20% occurs during the fission product elution.(1.3) This is only a decontamination factor of 2; under the more efficient absorption conditions used in subsequent anion exchange cycles, there is little, if any, separation from Th. The separation from Th is accomplished by ion exchange on a cationic resin (Section 2.2).

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Plutonium occurs in the Purex HAWC from the loss of Pu in the first solvent extraction cycle. In normal Purex operation the quantity of Pu in the HAWC is equal to 40 to 80% of the quantity of the Np. Plutonium absorbs on the anion resin as the Pu(IV) nitrate complex, similar to the absorption of Np(IV) and Th(IV). The conditions for the adjustment of the HAWC to reduce Np to Np(IV) might normally be expected to reduce Pu to the nonabsorbing Pu(III), but nitrate complexing in this solution stabilizes Pu(IV) so that the majority of the plutonium is present as Pu(IV). The distribution coefficient of Pu(IV) toward the anion resin is about a factor of two less than Np(IV), and the loss of Pu on the initial recovery bed is about the same as the Np loss. As with Th, there is essentially no loss of Np under the more efficient absorption conditions of a fixed bed; separation of Np from Pu is achieved by reduction of Pu to the nonabsorbing Pu(III) with nitric acid - ferrous sulfamate - hydrazine solution.

The major fission product contamination in the recovered Np is ruthenium (Ru), which accounts for about 75% of the gamma activity in all the process streams except the initial HAWC. Six isotopes of ruthenium are formed as a result of the fission process, the 1-yr Ru^{106}, the 40-day Ru^{103}, and the stable isotopes Ru^{99}, Ru^{101}, Ru^{102}, and Ru^{104}. The quantity of ruthenium present in HAWC is about 0.4 gm/l. During evaporation of the 1AW to form HAWC, nearly all the Ru is converted to nitrato and nitro complexes of nitrosyl ruthenium, RuNO(III). The nitrato complexes are absorbed slightly by anion resin; the distribution coefficient is about 3 in 8M HNO_3 and about 1 in 10M HNO_3. This absorption is greater than that for other gamma-emitting fission products such as Zr-Nb; as a consequence, the decontamination from Ru determines the decontamination from fission products through most of the process.

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1.4 Chemistry of Neptunium and Plutonium in Nitric Acid Solution

To understand differences in the kinetics of the oxidation-reduction reactions of Np and Pu an appreciation of the differences in the degree of stability of their oxidation states is necessary. Neptunium can have either a (IV), (V), or (VI) valence in nitric acid solution depending upon the concentration of acid, the concentration of nitrate ion, and the presence of reducing or oxidizing agents. All three valences can exist together in solution, but in most solutions an oxidizing or reducing agent is necessary to fix the Np in a single oxidation state. Np(III) oxidizes rapidly and is unstable in nitric acid solution. The most stable state is Np(V). In aqueous solution, Np(IV) exists as Np^{+4} ion or as a complex ion depending on the anions present. On the bases of spectroscopic data and the structural studies of Sjoblom and Hindman(1.4), Np(V) and (VI) are in the form NpO_2^{+} and NpO_2^{++}, respectively. Very little is known of the hydrolytic behavior of Np, particularly Np(IV). There is no evidence of oxidation states higher than (VI).

Plutonium has four oxidation states, (III), (IV), (V), and (VI), which can exist in equilibrium with each other in finite concentrations. In aqueous solution, Pu(III) is present as the ion Pu^{+3}. In aqueous solutions of 0.1M H^{+} or more, Pu(IV) exists as the unhydrolyzed ion Pu^{+4} or as a complex ion of Pu^{+4} depending on the anions present. On the basis of infrared absorption studies by Jones and Penneman(1.4), Pu(V) and (VI)in solution are considered to be the ions PuO_2^{+} and PuO_2^{++}, respectively. There is no evidence of the existence of oxidation states higher than (VI).

The oxidation-reduction reactions of Np and Pu are important since they are the basis for the separation of Np and Pu from fission products. The differences in the stability of the various oxidation states are the bases for the separation of Np and Pu from each other. The (VI) state of Np is more stable than Pu(VI). Neptunium(V) is relatively stable, while Pu(V) is unstable in acid solution and tends to disproportionate to (IV) and (VI). Conversely, Pu(III) is quite stable, whereas Np(III) is unstable and does not exist in aqueous solution. Thus, it is possible to prepare solutions of Np and Pu, each in a different oxidation state, and since the chemical properties of the different oxidation states differ, to effect separation.

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The half-cell reactions of importance are as follows(1.5):

Reaction	E_o
Neptunium	
$NpO_2^{+2} + 4H^+ \longrightarrow Np^{+4} + 2H_2O - 2e$	+1.89v
$NpO_2^{+} + 4H^+ \longrightarrow Np^{+4} + 2H_2O - 1e$	+0.74v
$NpO_2^{+2} \longrightarrow NpO_2^{+} - 1e$	+1.15v
Plutonium	
$Pu^{+4} \longrightarrow Pu^{+3} - 1e$	+0.97v
$PuO_2^{+2} + 4H^+ \longrightarrow Pu^{+4} + 2H_2O - 2e$	+1.04v
Iron	
$Fe^{+3} \longrightarrow Fe^{+2} - 1e$	+0.77v

Since Pu has a charge of +3 or more in all of the ions stable in aqueous acid solution, it has a marked tendency for interaction with the medium and for the formation of complex ions with various anions. The equilibria involved and the kinetics and mechanisms of the oxidation-reduction reactions have been studied extensively(1.4, 1.6) and will not be reviewed in detail here.

Plutonium in any of its oxidation states can be absorbed readily from dilute aqueous solutions by cation exchange. The absorption strength of the more important cations in order of decreasing strength are (IV), (III), and (VI). Plutonium in the (IV) and (VI) states forms strong anionic complexes which can be absorbed on anion exchange resins. Several anions in order of decreasing effectiveness in forming such complexes are $SO_4^{=}$, NO_3^{-}, and Cl^{-}. Pu(IV) is the most highly charged of the Pu ions and therefore more prone to complex formation. Pu(IV) is much stronger than Pu(III) in complexing strength. The association constant for Pu(IV) and nitrate ion is 2.9 ±0.6 in 2M total acid and is described by the equilibrium equation,

$$Pu^{+4} + NO_3^{-} \rightleftharpoons Pu(NO_3)^{+3}$$

Pu(III) is not very stable even in dilute nitric acid (1M) solution without a reductant and is oxidized readily to the more stable Pu(IV).

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1.5 Oxidation-Reduction Reactions

The effects of some oxidizing and reducing agents on the valence of Np in nitric acid are shown in the table below.(1.2,1.7-1.13,1.23-1.25)

Oxidation-Reduction Reactions of Neptunium Ions

Reaction	Reagent	Solution	Rate[a] (at 25°C)	Reference
Np(V) → Np(IV)	Fe^{++}	0.3-9M HNO_3	Rapid	1.2,1.7,1.8,1.9
	H_2O_2	0.5M HNO_3	Slow	1.7
	H_2O_2	0.3M HNO_3	Rapid	1.23
	NH_2OH	0.5M HNO_3	Slow	1.7,1.24,1.25
	N_2H_4	0.5M HNO_3	Slow	1.7,1.24,1.25
	HNO_2	6-8M HNO_3	Slow	1.8,1.12
	--	3-8M HNO_3	Very Slow	1.8,1.9,1.12
Np(VI) → Np(IV)	Fe^{++}	0.3-9M HNO_3	Very Rapid	1.2,1.8,1.24
Np(VI) → Np(V)	H_2O_2	0.5-1.5M HNO_3	Very Rapid	1.7,1.23
	HNO_2	0.5-1.5M HNO_3	Very Rapid	1.7
	NH_2OH	0.5-1.5M HNO_3	Very Rapid	1.7,1.24,1.25
	N_2H_4	0.5-8M HNO_3	Very Rapid	1.7,1.8,1.24,1.25
	$H_2NNHCONH_2$	0.5-8M HNO_3	Very Rapid	1.8,1.11
Np(IV) → Np(V)	HNO_3	0.35M HNO_3	Slow	1.8
	Fe^{+++}	0.35M HNO_3	Rapid	1.2
	HNO_2	0.5-1M HNO_3	Very slow	1.12
Np(IV) → Np(VI)	--	5-8M HNO_3	Rapid	1.12
Np(V) → Np(VI)	HNO_2	3M HNO_3	Moderate	1.10
	VO_2^{+}	3M HNO_3	Moderate	1.13
	Ce^{+4}	0.5-8M HNO_3	Rapid	1.7,1.10
	$KMnO_4$	0.5-8M HNO_3	Rapid	1.7
	$K_2Cr_2O_7$	0.5-8M HNO_3	Rapid	1.11

(a) Very Rapid - t 1/2 less than time of mixing
Rapid - t 1/2 less than 10 minutes
Moderate - t 1/2 of the order of 1 hour
Slow - t 1/2 of the order of 3 hours
Very Slow - t 1/2 of the order of 12 hours

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Since the recovery of Np from Purex waste, the separation of Np and Pu from fission products, and the separation of Np from Pu depend on differences in the oxidation-reduction chemistry of Np and Pu, a comparison of the effect of specific agents is necessary. The oxidation-reduction reaction of Np with ferric and ferrous ion is of particular importance and may be expressed as follows:

$$\mathrm{Np(IV)} + \mathrm{Fe(III)} \rightleftharpoons \mathrm{Np(V)} + \mathrm{Fe(II)}$$

The rate constant in the forward direction is diminished in the presence of NO_3^- because of NO_3^- complexing with Np(IV). In 1M nitric acid, Np(IV) is unstable and slowly oxidizes to Np(V) at room temperature (25°C). Oxidation with nitric acid at elevated temperature produces a mixture of (V) and (VI). Np(IV) can also be oxidized to either (V) or (VI). In the presence of Pu(IV) or Fe(III), the (V) state of Np is predominant because any Np(IV) which is formed tends to be reduced by Pu(IV) or by the Fe(II) resulting from the reduction of Fe(III). Similarly, when strong oxidizing agents are employed in stoichiometric amounts equivalent to the Np(IV), Np(V) is the predominant state since any Np(VI) produced tends to be reduced to the more stable (V) state by unoxidized Np(IV). In strong acid (8M) the oxidation of Np(V) to (VI) will occur at room temperature; in more dilute acid Np(IV) also can be oxidized to Np(VI) by refluxing. Thus, in the dissolution of target material in strong nitric acid (8-9M) at the boiling point, Np is essentially completely oxidized to Np(VI) as the NpO_2^{++} ion. The oxidation of Pu(III) to (IV) in concentrated nitric acid is very fast. In contrast to Np(IV), the oxidation of Pu(IV) to (VI) normally does not take place in strong acid solution. When the dissolution of target material is completed, only about 40% of the Pu is in the (VI) oxidation state.

Np(IV) can be stabilized in strong nitric acid (8M) solution by the addition of ferrous sulfamate so that oxidation to Np(V) is slow even at 55°C. The stability is due to the combined effects of sulfamate stabilization by rapid reaction with NO_2^-, and formation of the Np(IV) nitrate complex. The oxidation of Pu(III) to Pu(IV) is autocatalytic in nitric acid but it is probably fastest in low acid concentration (0.5M); the formation of the Pu(IV) complex with nitrate ion increases as the nitrate ion concentration is increased. With the addition of sulfamate ion the rate of oxidation of Pu(III) to (IV) is decreased but it is still quite rapid in strong acid (8M)

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at 55°C. Thus, when a strong nitric acid (8M) solution of Np(IV) and Pu(III) containing ferrous sulfamate is heated to 55°C, Pu(III) is oxidized to Pu(IV) and Fe(II) to Fe(III) as shown in the following equations.

$$\mathrm{Pu(III)} + 2\mathrm{HNO_3} \xrightarrow{55^\circ\mathrm{C}} \mathrm{Pu(IV)} + \mathrm{NO_3^-} + \mathrm{NO_2} + \mathrm{H_2O}$$

$$\mathrm{Fe(II)} + 2\mathrm{HNO_3} \xrightarrow{55^\circ\mathrm{C}} \mathrm{Fe(III)} + \mathrm{NO_3^-} + \mathrm{NO_2} + \mathrm{H_2O}$$

There is very little oxidation of Np(IV) to (V). This difference in oxidation behavior is important in the separation of Np and Pu from fission products.

As indicated by the standard potentials, the reduction by Fe(II) of Pu(VI) to (IV), Pu(IV) to (III), and Np(VI) to (V) can occur at 1M H^+ concentration. The reduction of Np(V) to (IV) by ferrous sulfamate in nitric acid solution is rapid, because it is a fourth power function of the H^+ concentration and it is promoted by the shift in equilibrium potential due to the complexing of Pu(IV) with nitrate ion.

The reduction of Np(V) to (IV) and Pu(VI) or (IV) to (III) by ferrous ion, Fe(II), in strong nitric acid (6-8M) is rapid and complete if sulfamate ion or hydrazine is present to decrease the rate of oxidation of Fe(II) to Fe(III) by nitrous acid. A similar reaction is important in the isolation of Np from Purex waste. Neptunium must be in the (IV) state for nitrate complexing and subsequent absorption. Nitrous acid, HNO_2, which is a product of the radiolysis of nitric acid, is a mild reducing agent which tends to stabilize Np(IV) and limit the amount oxidized to Np(V); it is not a strong enough reducing agent to hold all of the Np in the (IV) state or to reduce Np(V) to (IV). If ferrous sulfamate is added to the system, it will prevent oxidation and appears to stabilize the Np(IV) for several hours, but then, it has a detrimental reaction since it reacts preferentially with nitrite ions (NO_2^-) destroying both itself and the nitrite according to the equation

$$\mathrm{NH_2SO_3^-} + \mathrm{NO_2^-} \longrightarrow \mathrm{N_2} + \mathrm{SO_4^{=}} + \mathrm{H_2O}$$

In the absence of the stabilizing effect of Fe^{++} and NO_2^-, more Np(IV) is oxidized to Np(V). Although hydrazine cannot reduce Np(V) to (IV) in strong acid solution, if it is added to the nitrate-nitrite solution with ferrous sulfamate, the hydrazine will react

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preferentially with nitrous acid according to the equation

$$N_2H_5^+ + 2HNO_2 \longrightarrow N_2O + N_2 + 3H_2O + H^+$$

thus leaving the ferrous sulfamate available to reduce Np(V) to (IV). In the presence of both ferrous sulfamate and hydrazine the Np(IV) is stable for more than 8 hours in strong nitric acid.

Semicarbazide and hydrazine in strong nitric acid (6-8M) are capable of reducing Pu(IV) to (III) but the rate is too slow for process use. Hydrazine is used to maintain Pu in the (III) state.

Neptunium(VI) is rapidly reduced to (V) in nitric acid solutions of at least 0.5M concentration by hydrogen peroxide, hydroxylamine, hydrazine, or semicarbazide, but the reduction of Np(V) to (IV) is very slow if the acid concentration is less than 1M. Hydrogen peroxide rapidly and effectively reduces Np(VI) or (V) to (IV) in 8M nitric acid. In laboratory tests, the reduction was essentially quantitative. However, the presence of fission products or other ions in the process solutions interfere with the reaction so that it does not appear to be satisfactory for general process application.

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In aqueous acid solutions Pu(IV) can exist as the ion Pu^{+4} in the absence of complexing anions but it has a marked tendency to disproportionate to an equilibrium condition expressed by

$$3\mathrm{Pu(IV)} \rightleftharpoons 2\mathrm{Pu(III)} + \mathrm{Pu(VI)}$$

The equilibrium is affected by acid concentration and anions present. Pu(V), which exists in solution as the ion PuO_2^+, is quite unstable under most conditions with respect to oxidation and reduction systems and tends to go to either the (IV) or (VI) state. In dilute acid solution at low concentrations, Pu(V) can be the predominant state at equilibrium and the disproportionation is relatively slow.

Np, like Pu, in any of the three oxidation states that are stable in aqueous solution, can be absorbed on cation exchange resins such as the sulfonated polystyrenes. The oxidation states in order of decreasing absorption bond strength are (IV), (VI), and (V). In the (IV) valence state, Np forms quite stable complex ions with a number of anions including F^-, NO_3^-, $SO_4^=$, PO_4^{-3}, and $C_2O_4^=$ (oxalate). In acid solutions containing no complexing ions, Np(IV) shows little tendency to disproportionate. As indicated by the half-cell reactions, high acidity favors Np(IV), and the Np(IV) - Np(V) couple is dependent upon the 4th power of the H^+ concentration whereas the Np(V) - Np(VI) couple is essentially independent of acid concentration. Although the disproportionation of Np(V) to Np(IV) and Np(VI) is slight in dilute acid medium (1M), at higher acid concentration disproportionation does occur because of the strong H^+ dependence.

$$2NpO_2^+ + 4H^+ \rightleftharpoons Np^{+4} + NpO_2^{++} + 2H_2O$$

In sulfuric or nitric acid solution the equilibrium is shifted strongly to Np^{+4} formation because of the formation of the Np^{+4} anionic complexes with $SO_4^=$ and NO_3^-. Since Np(V) as NpO_2^+ in solution is a large ion with only a single charge, it complexes only weakly, if at all. It is reported to form a complex with oxalate. Complexes are formed by NpO_2^{++} when Np is in the (VI) valence state, but they are weaker than those of Np^{+4}.

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2.0 PRIMARY RECOVERY OF NEPTUNIUM

2.1 Recovery Process

Neptunium can be recovered from Purex waste solutions such as the HAWC by absorption on an anion exchange resin. The Np from the primary exchange is subsequently processed through two additional cycles of anion exchange to remove residual Pu and fission products. Thorium which is absorbed with the Np in the anionic absorption cycles is separated from the Np by absorption on a cationic resin. A schematic diagram for the recovery of Np from Purex HAWC is shown in Figure 2.1.

2.1.1 Recovery from Irradiated Natural Uranium

2.1.1.1 Agitated Resin Bed

The primary recovery of Np from Purex HAWC by anion exchange is complicated by the presence of solids which will plug a normal fixed resin bed. Although filtration appeared to be feasible in early laboratory development work, the method failed in subsequent plant tests. A new approach was necessary to adapt ion exchange to the limited space available in existing plant facilities and to conform to the operational limitations. The successful use of an agitated ion exchange resin to recover streptomycin from a yeast broth containing solids was reported by C. R. Bartels(2.1) of the Squibb Institute for Medical Research. Since no data were available on the performance of such beds, an investigation of ion exchange beds was made. A single-stage agitated bed (Figure 2.2) was selected after laboratory and plant-scale tests. Pulsed single-stage beds and multistage agitated columns showed promise but require further study and development.(2.3)

The resin is supported by a metal plate perforated with tapered holes. The narrow ends of the holes face the resin and are sized to retain the resin. The perforated plate is equivalent to a 100 mesh screen. Solid particles which are smaller than the holes pass through unimpeded while larger particles are swept away from the holes by movement of the aqueous media stirred by a motor-driven agitator. The agitator has two paddles, one about 1/4 inch above the screen and the other near the top of the vessel. The pressure drop across perforated plates with more than 7% open area is small over the range of flows required. Woven wire screens normally used to support ion exchange resins tend to plug and are not satisfactory.

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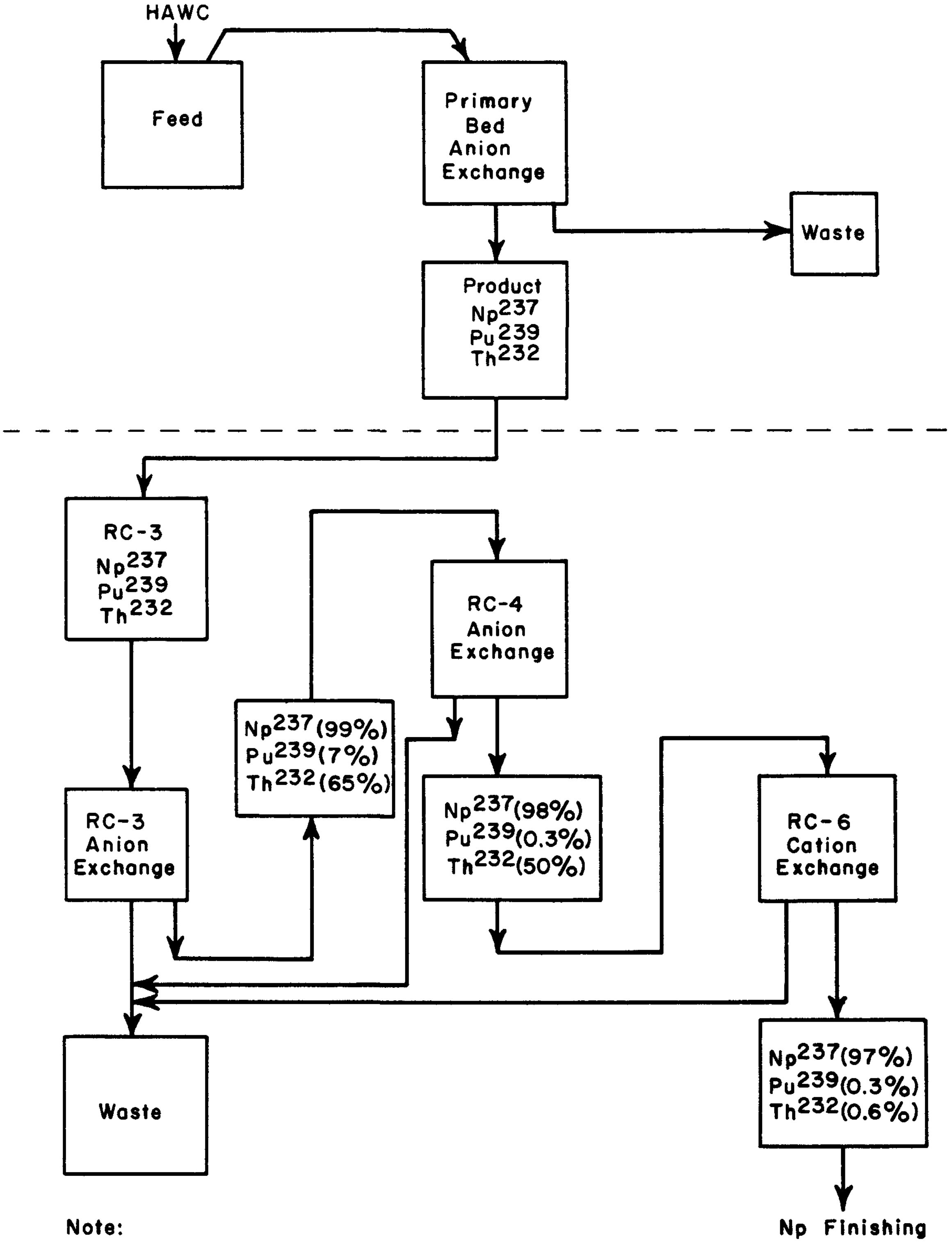

Note:
Per cents indicate quantity of the isotope relative to the product from the primary bed.

FIG. 2.1 RECOVERY OF NEPTUNIUM FROM IRRADIATED NATURAL URANIUM

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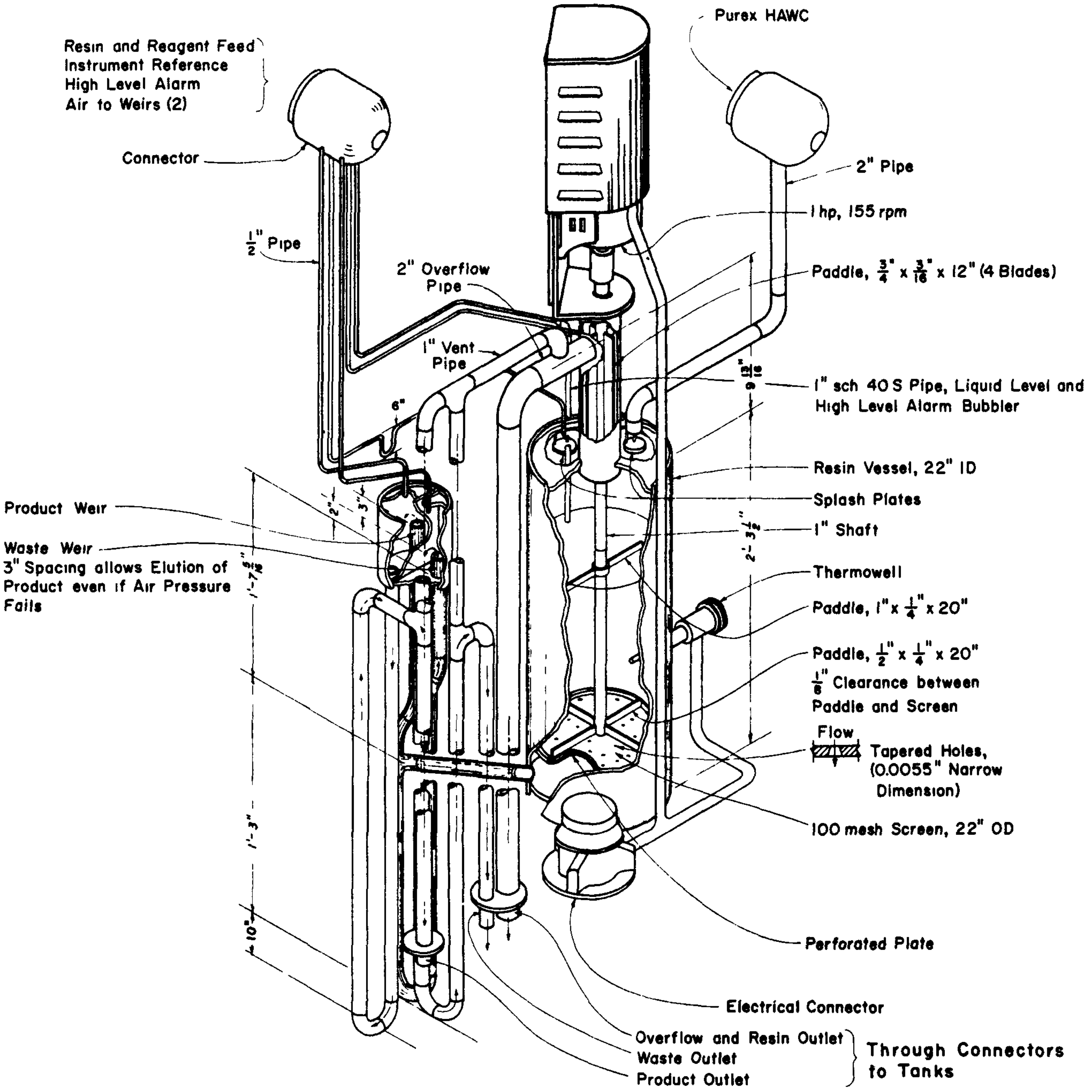

FIG. 2.2 AGITATED ION EXCHANGE BED FOR PRIMARY RECOVERY

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The agitated bed has other unique features. The resin is not restrained, and since the densities of solutions (1.30-1.33) to be processed are nearly the same as that of the resin (1.25), all solutions are passed downflow through the bed to avoid carrying resin out with the solutions. The resin is easily discharged by overflowing the vessel with a solution having a specific gravity approaching that of the resin. Solutions containing 26 wt % sodium nitrate or 22 wt % aluminum nitrate, which have specific gravities of about 1.2, are satisfactory with "Dowex" 1-X4 and "Permutit" SK. Similarly, fresh resin can be charged to the vessel in a slurry with either of the above solutions. Water has been tested as a medium for introducing resin into the vessel because of the potential economy in material cost and reduced waste; thus far, water has not proved to be acceptable because the lower density allows resin to settle in the cold feed lines to the vessel.

In order to attain simple, reliable operation and to reduce remote handling and maintenance problems, all effluent streams are controlled by air weirs rather than valves.

The agitated bed has an additional advantage. It can be used as a fixed bed, for optimum processing, simply by stopping the agitation; when the resin has settled it is, in effect, a fixed bed. There is one disadvantage in an agitated bed; the resin is in motion and is mixed with the feed solution, which passes through the vessel, so that the resin acts as a single-stage contactor and the actinides are absorbed uniformly on all of the resin. In contrast, a fixed bed acts as a multistage contactor so that there is a concentration gradient on the resin and the ion concentration decreases in the direction of the fluid flow. Thus, the efficiency of absorption on an agitated bed is lower than that on a fixed bed, and the potential for loss of product in the absorption step and in subsequent washes is greater in an agitated bed.

The resin must be selected on the basis of its physical properties relative to satisfactory performance in an agitated bed contactor as well as on its chemical properties such as stability and absorption.

Satisfactory chemical and hydraulic performance was obtained in semiworks tests of a plant bed with simulated HAWC containing 400 ppm

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silica(2,4). With Th as a stand-in for Np, the absorption obtained on the plant bed was essentially equivalent to that obtained in developmental beds (Figure 2.3). Performance during the wash and elution steps also agreed with prior experiments (Figure 2.4). Pressure drops for the bed for both fixed and agitated operation and for the empty vessel are shown in Figure 2.5.

2.1.1.2 Solution Adjustment

Before Np is recovered from concentrated waste, the Np must be reduced to the (IV) state in order to form the absorbable anionic nitrate complex. It has been estimated that only about 70% of the available Np can be absorbed directly from the strong nitrate - nitric acid solution, which also contains nitrite ions as nitrous acid from radiolysis of nitric acid. To increase the recovery of Np, first hydrazine and then ferrous sulfamate is added. The hydrazine reacts preferentially with the nitrite ions present and protects the ferrous sulfamate which reduces Np(V) and (VI) to (IV).

If ferrous sulfamate alone is added, only about 60% of the neptunium can be absorbed. The ferrous ions are oxidized within approximately one-half hour by radiation and other agents. In the absence of ferrous or nitrite ions some of the neptunium is oxidized to the (V) state which is not absorbed, and the sulfate ions produced in the oxidation of ferrous sulfamate may further increase the loss of Np. By addition of both hydrazine and ferrous sulfamate, the amount of Np absorbed can be increased to approximately the theoretical amount, which is about 92% of the Np available. The reactions of ferrous sulfamate and hydrazine with nitrite ions are discussed in detail in Section 1.4. After the addition of each reagent, it is necessary to agitate the waste concentrate thoroughly to assure adequate mixing. It is also important to maintain the temperature of the waste below 40°C during the valence adjustment to avoid loss of ferrous sulfamate through oxidation by nitric acid.

2.1.1.3 Absorption and Elution

The first ion exchange cycle is comprised of three steps: (1) absorption of Np from the adjusted waste solution, (2) flushing the absorbed Np on the resin bed to remove contaminants and traces of residual solids, and (3) elution or desorption of the absorbed Np from the resin.

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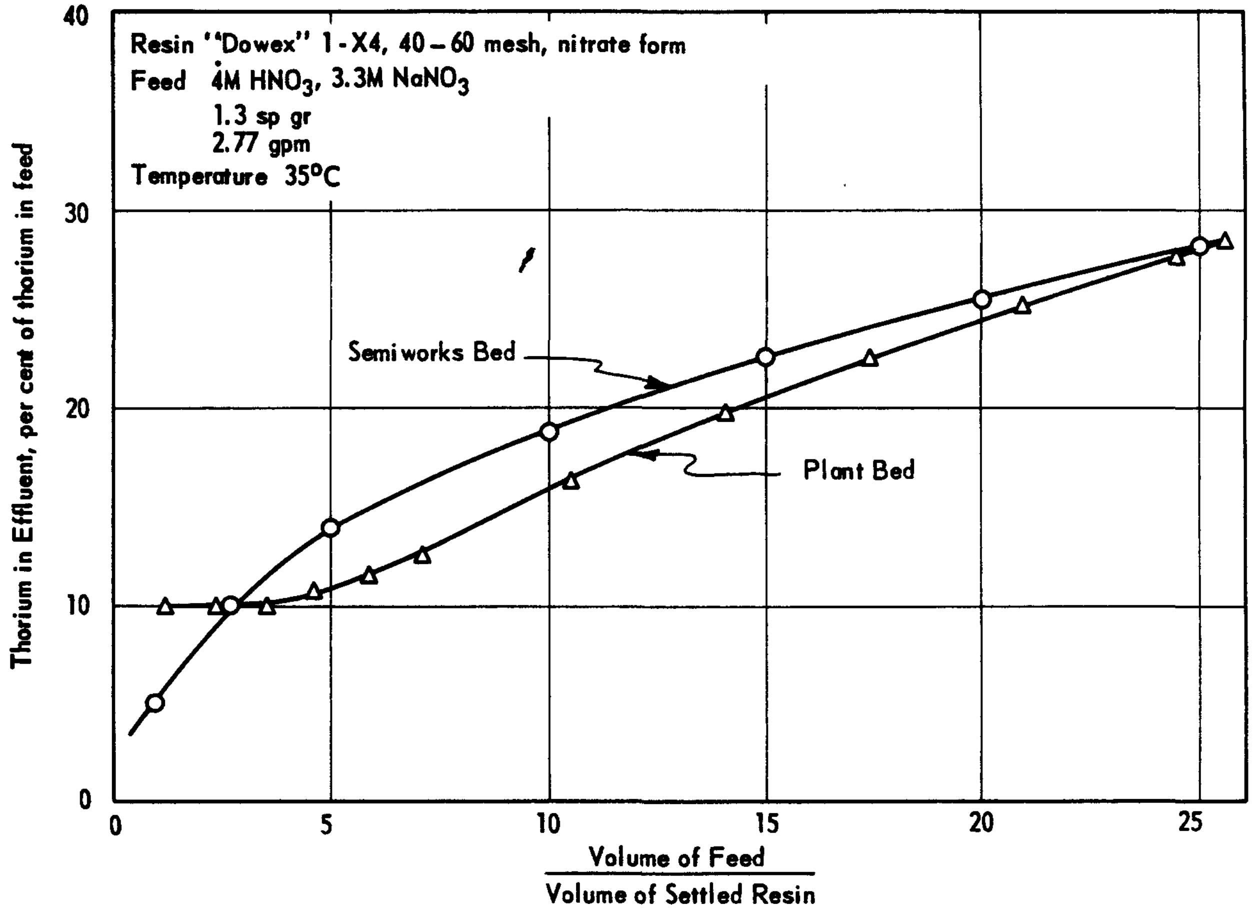

FIG. 2.3 ABSORPTION OF THORIUM ON AGITATED BED

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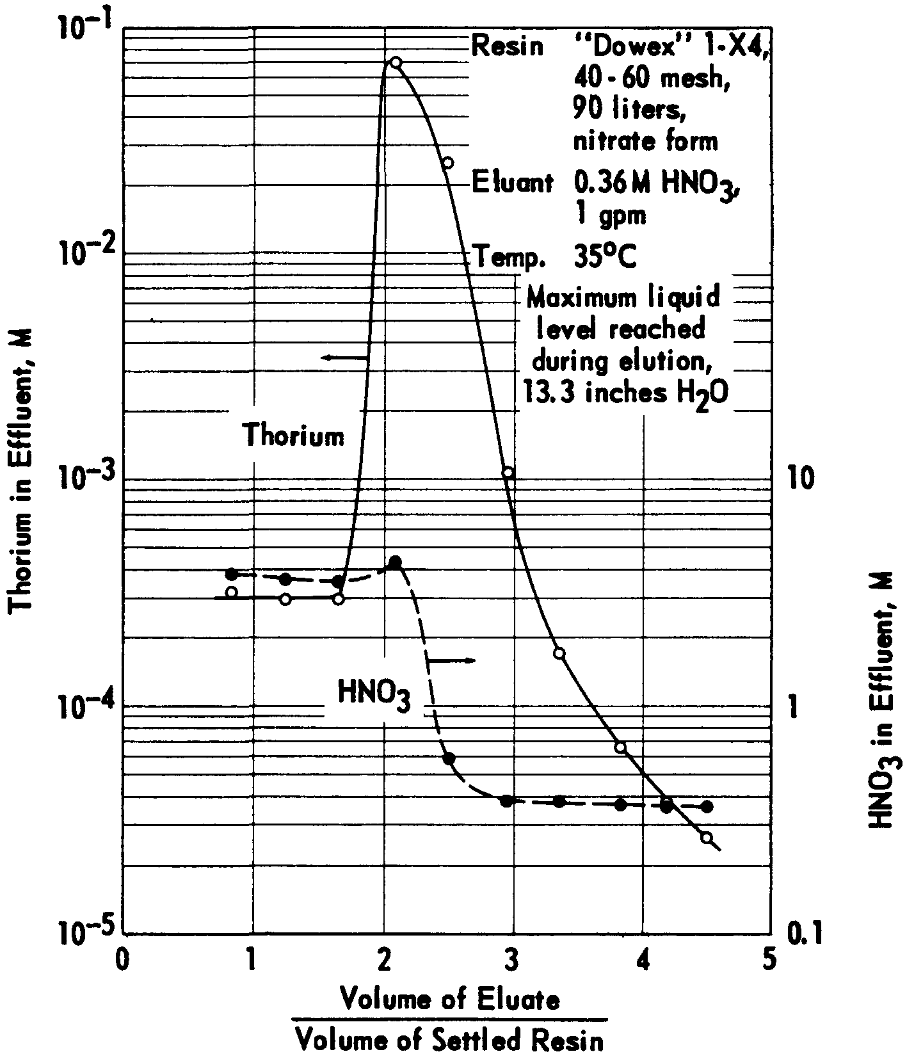

FIG. 2.4 ELUTION OF THORIUM FROM SETTLED RESIN

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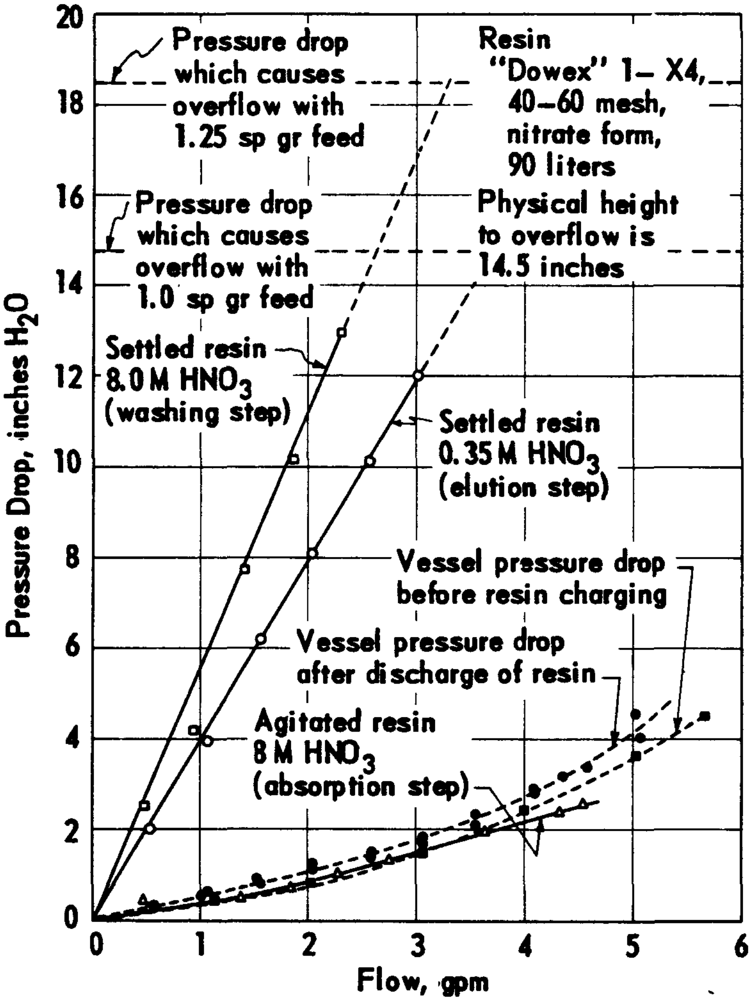

FIG. 2.5 HYDRAULIC CHARACTERISTICS OF PLANT PRIMARY BED

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Assuming a favorable chemical system for the absorption of Np(IV) and the use of only a small fraction of the resin capacity, the absorption of Np(IV) from solution depends upon the properties of the particular resin and on the time the solution is in contact with the resin. For a particular size and volume of resin, the contact time is a function of the liquid residence time or the ratio of the total volume of solution in the contactor to the volume rate of solution flow. The amount of absorption expressed as the ratio of Np absorbed per unit volume of resin to unabsorbed Np per unit volume of solution increases with increased contact or liquid residence time as shown in Figure 2.6. The initial absorption is rapid and is attributed to saturation of the resin surface. As the surface approaches saturation, the rate of absorption decreases and absorption is believed to be limited primarily by the rate of diffusion of Np from the surface into the resin. The desorption of Np also increases as more Np is absorbed. Although the desorption contributes to the observed decrease in the rate of absorption, the effect is believed to be slight. Thus, the loss of Np during absorption decreases as the contact time or liquid residence time is increased and increases as the volume of feed or amount of Np absorbed increases. The loss of Np as a function of liquid residence time and volume of feed has been calculated from distribution ratios for Np between synthetic HAWC and "Dowex" 1-X4 resin. The results are shown in Figure 2.7.(2.2) Good agreement has been obtained between the predicted losses and losses determined in experiments with synthetic HAWC as shown in Figure 2.8. Since the losses of Np accumulate, a compromise is necessary in determining the liquid residence time and the volume of feed. Calculations of the cumulative loss of Np for various periods of liquid residence time at a constant volume of feed have indicated 7-10 minutes to be a reasonable range. The data are summarized in Figure 2.9. With liquid residence times less than 5-6 minutes the Np loss increases rapidly; the decrease in loss after 12 minutes is slight.

Within the range of 25-60°C considered for the process, increasing the temperature of the feed does not significantly increase the efficiency of the absorption.

After the Np is absorbed on the agitated resin bed, agitation is no longer required since the suspended solids in the feed solution have passed through to the waste stream. To remove fission products retained on the resin with the Np, the resin bed is washed with strong nitric acid, which may contain a small amount of fluoride.

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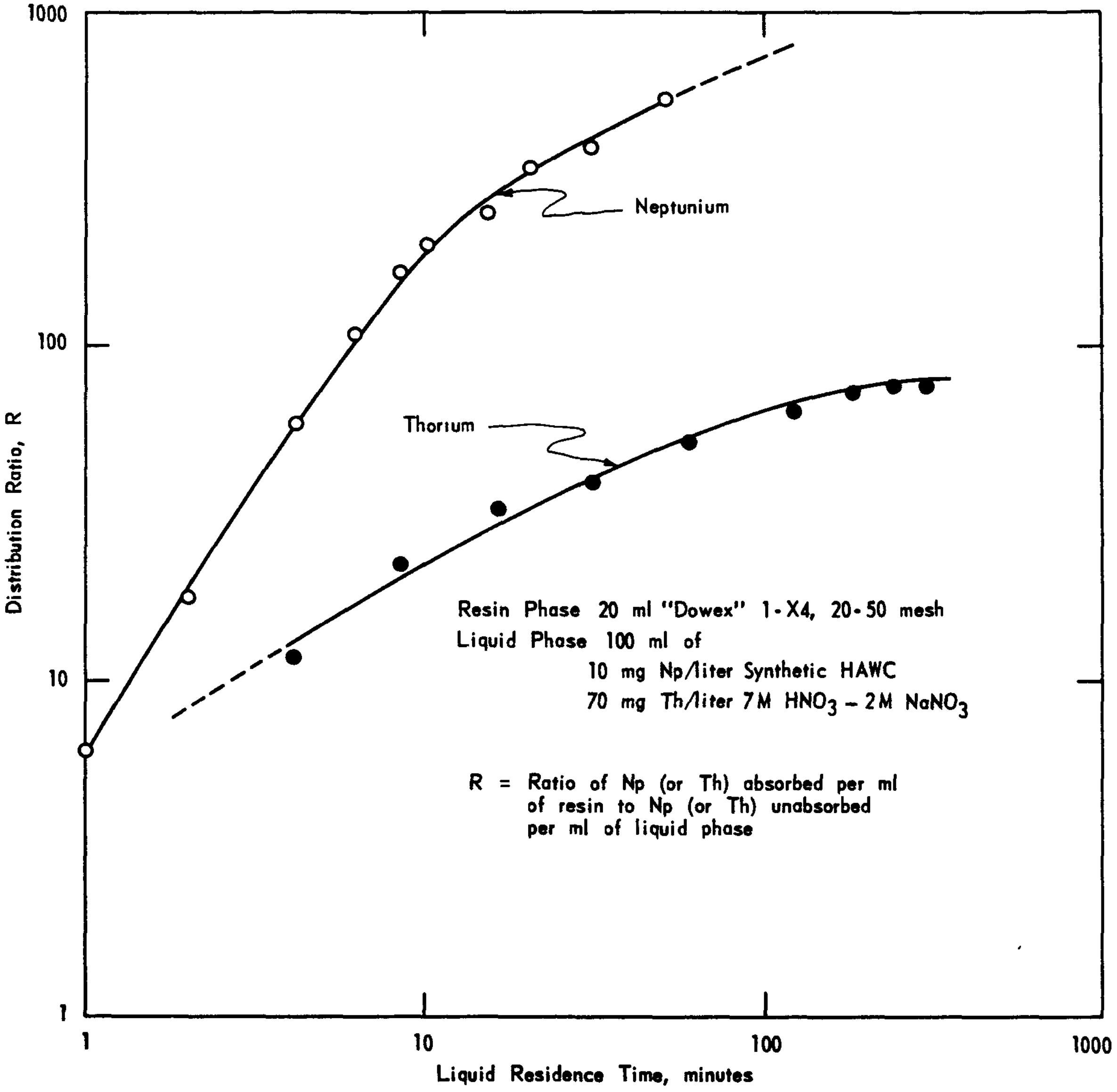

FIG. 2.6 EFFECT OF LIQUID RESIDENCE TIME ON DISTRIBUTION RATIO (R)

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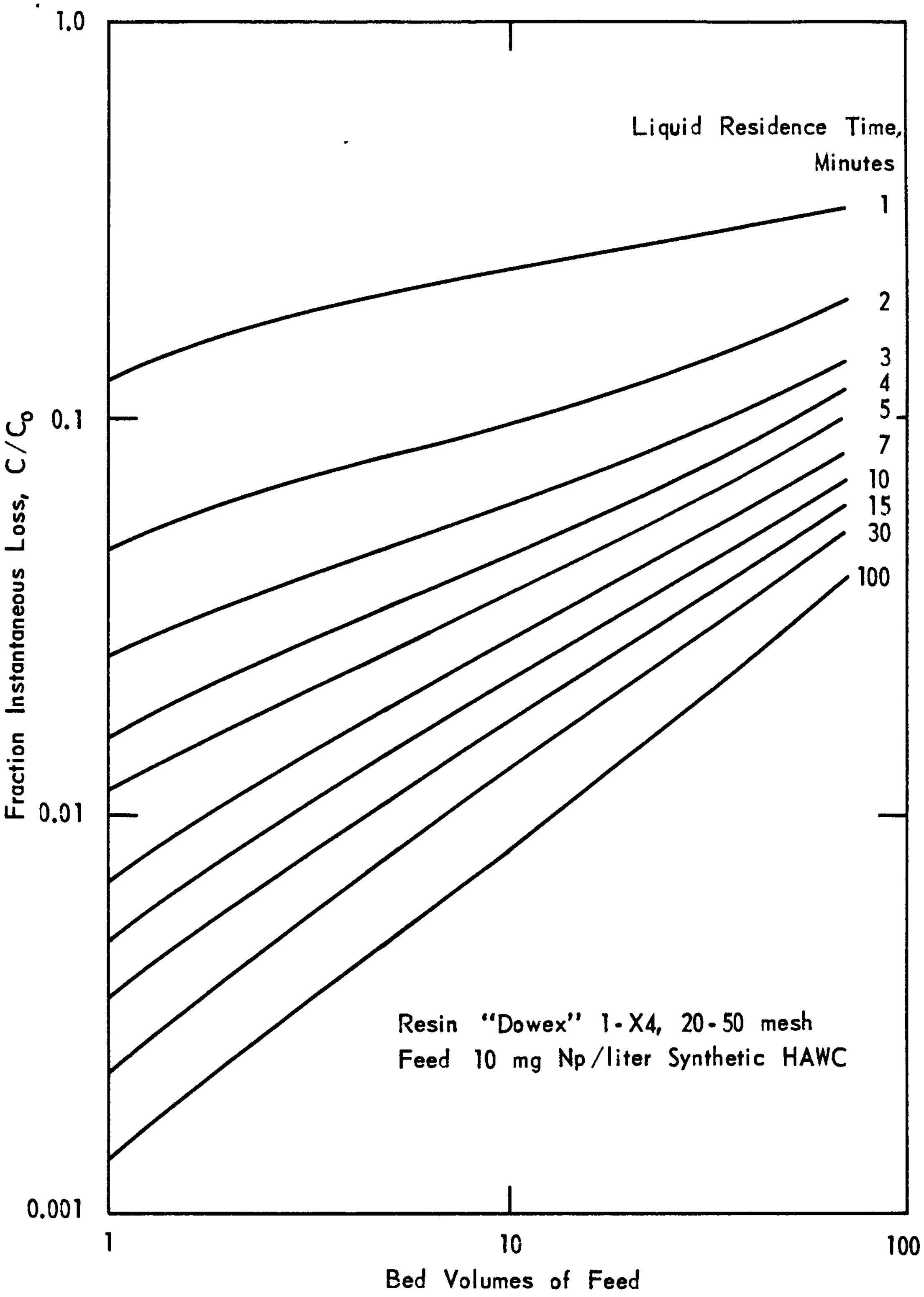

Resin "Dowex" 1-X4, 20-50 mesh
Feed 10 mg Np/liter Synthetic HAWC

FIG. 2.7 PREDICTED LOSSES OF NEPTUNIUM – EFFECT OF LIQUID RESIDENCE TIME

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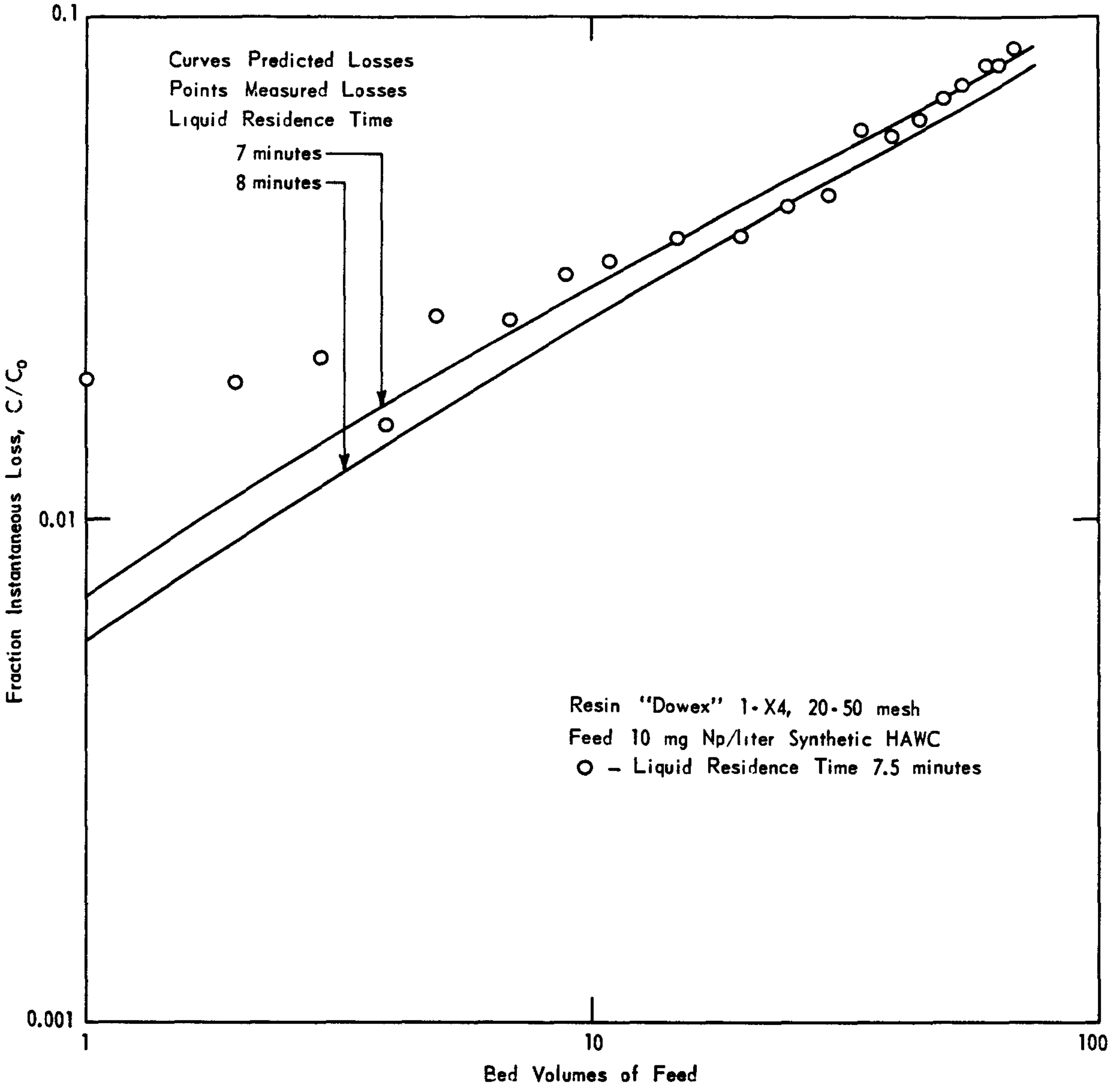

FIG. 2.8 PREDICTED AND MEASURED LOSSES OF NEPTUNIUM

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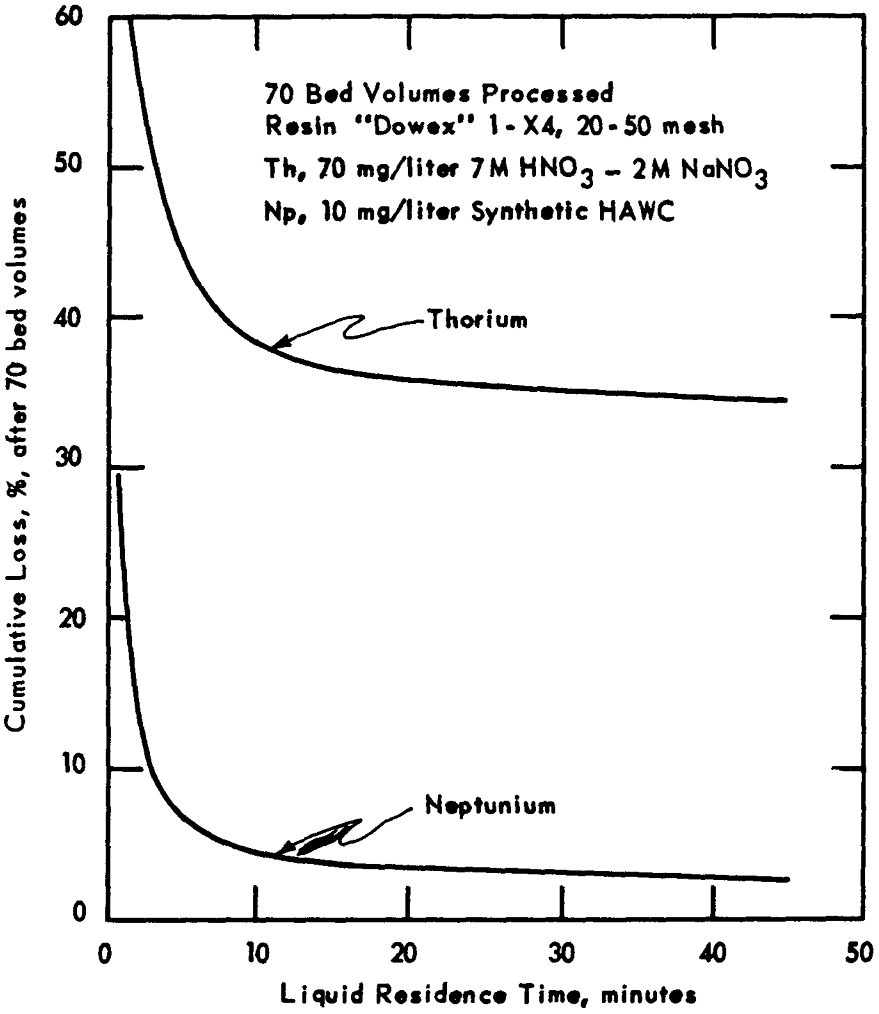

FIG. 2.9 EFFECT OF LIQUID RESIDENCE TIME ON CUMULATIVE LOSS OF THORIUM AND NEPTUNIUM

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The concentrations of HNO_3 and fluoride, the volume of the wash, and the temperature are important. Some Np is removed with the wash, and a compromise is necessary between loss of Np and decontamination from fission products. About 8M HNO_3 is satisfactory. An increase in the acid concentration decreases the removal of fission products and increases the volume of wash required. At lower acid concentrations, the wash is less effective in removing fission products and the loss of Np increases. With 8M HNO_3 at 25°C, the loss of Np is about 0.06% per bed volume of wash solution. The effect of the volume of 8M nitric acid wash on the removal of fission products is shown in Figure 2.10. Within the range of 25-60°C considered for the process, increasing the temperature increases the removal of fission products but also increases the loss of Np. At 40°C, the ambient temperature in the plant, the loss of Np increases to approximately 0.1% per bed volume of 8M HNO_3 wash. The removal of fission products can be improved by the addition of a small amount of fluoride, but the loss of Np also increases. The fluoride concentration should not exceed 0.006M.

After the wash step, Np is eluted from the resin with dilute nitric acid. Agitation of the resin is not required and, on the basis of limited work, appears to be detrimental. As in the wash step, temperature has a marked effect; increasing the temperature aids the elution of Np. The effects of temperature and agitation, as determined experimentally in the elution of Np from "Dowex" 1-X4, are shown in Figure 2.11.

The rate of flow of the elutriant solution is limited by the rate of desorption of Np to less than 0.8 ml/(min)(cm^2) of resin; more rapid flow dilutes the Np concentration in the product solution. The acidity of the elutriant solution is important and must be maintained in the range of 0.3-1.0M HNO_3; lower acid concentration may allow Np(IV) to polymerize and higher acidity results in poor elution.

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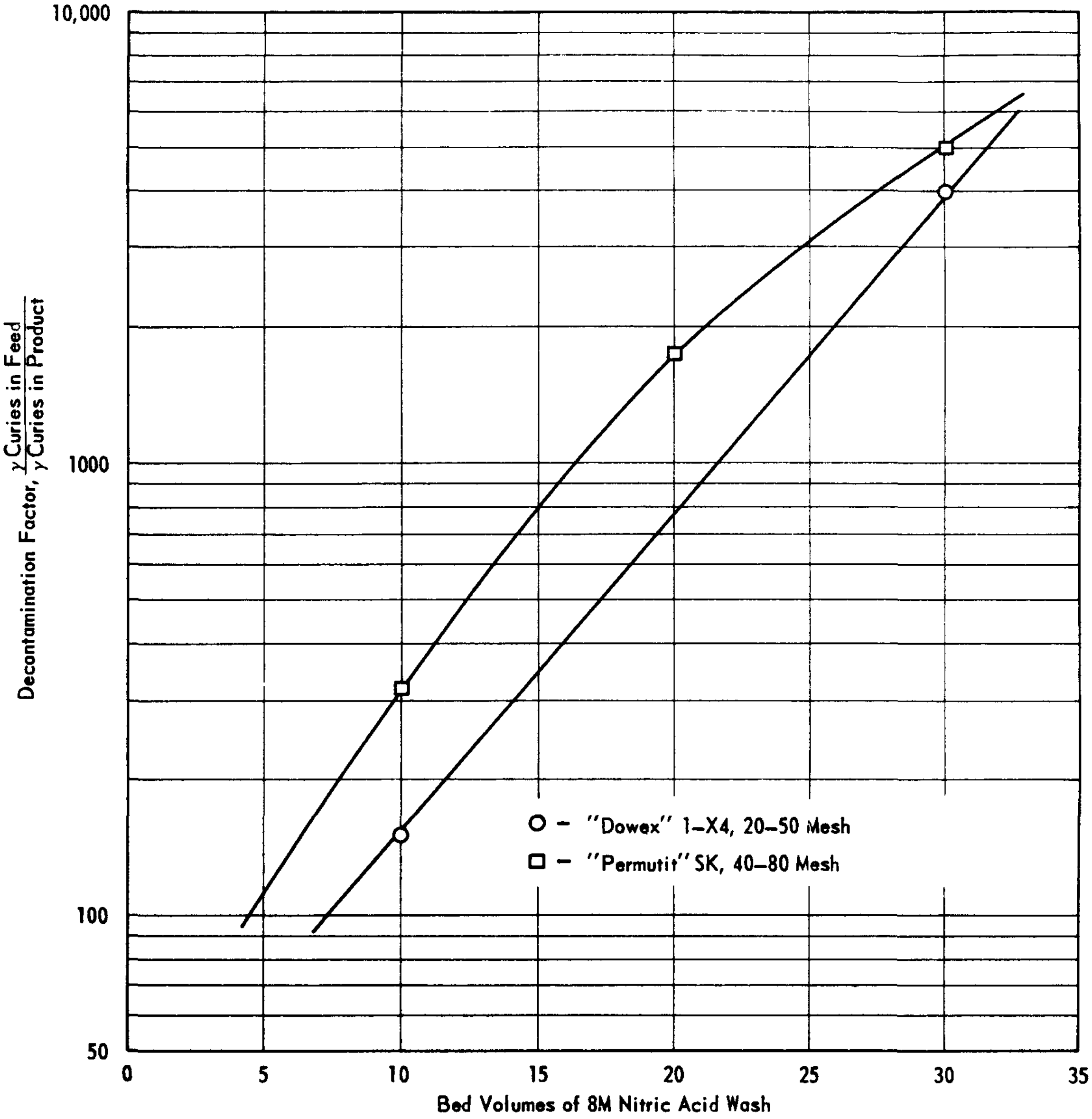

FIG. 2.10 DECONTAMINATION FROM GAMMA EMITTING FISSION PRODUCTS – EFFECT OF WASHING WITH NITRIC ACID

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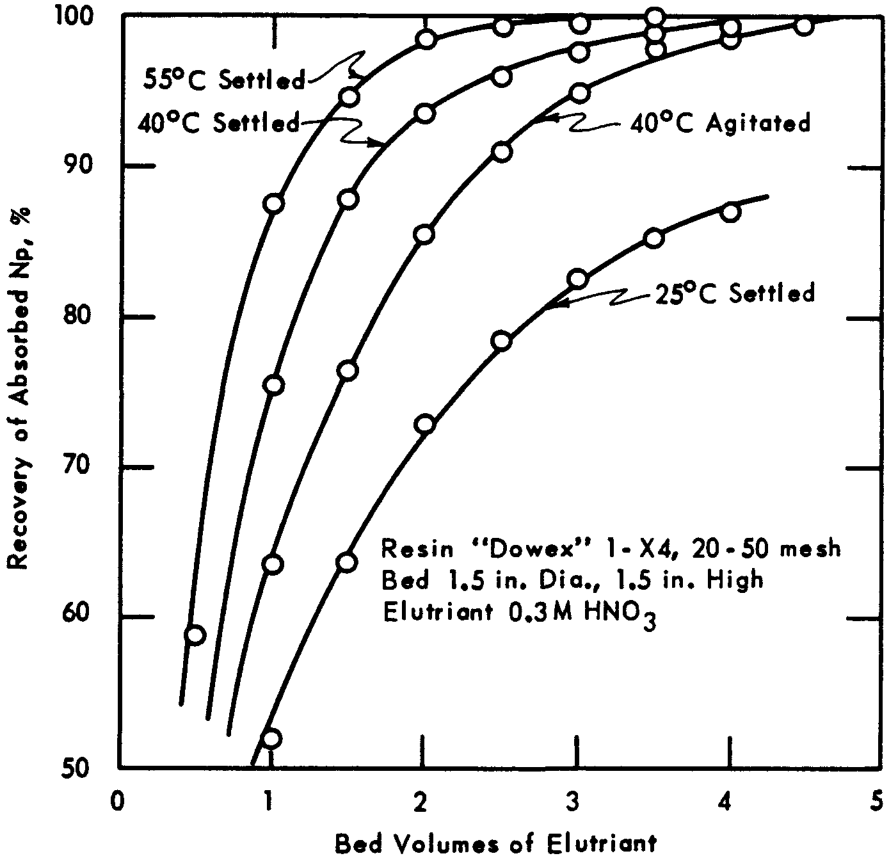

Resin "Dowex" 1-X4, 20-50 mesh
Bed 1.5 in. Dia., 1.5 in. High
Elutriant 0.3M HNO_3

FIG. 2.11 ELUTION OF NEPTUNIUM – EFFECT OF TEMPERATURE AND AGITATION

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2.2 . Decontamination of Neptunium

The primary anion exchange recovery of Np from HAWC achieves a decontamination factor (DF) of approximately 10^3 from fission products and a separation from most stable elements of about 10^4. Decontamination from UX_1, or thorium (Th), is of the order of 2 because of the chemical similarity of Th(IV) to Np(IV). Additional decontamination from fission products and separation of Th from Np is necessary. Any Pu^{239} present in the HAWC is also absorbed with the Np. The required decontamination can be accomplished by additional ion exchange. Thorium can be separated by absorption on a cation exchange resin providing Np(IV) is first oxidized to Np(V) to prevent Np(IV) from being absorbed with Th(IV). Neptunium can be separated from fission products and Th by solvent extraction but the process requires subsequent concentration of Np by cation exchange prior to finishing operations. Precipitation processes could also be used to purify recovered Np but several cycles of precipitation and dissolution would be required.

2.2.1 Anion Exchange

The removal of fission products can be accomplished in two cycles of anion exchange, conducted chemically in the same manner as in the recovery of Np from HAWC except that a fixed bed is used since no solids are present. The product Np solution from primary recovery is adjusted to about 8M nitric acid and nitrate by addition of nitric acid. Ferrous sulfamate is added to reduce any oxidized Np to the (IV) state. Hydrazine is not required since radiolytic degradation of HNO_3 to HNO_2 is negligible. The solution is agitated and time is allowed for the reduction to be completed. The solution is heated to destroy residual ferrous sulfamate which would cause severe gassing on the resin. The solution is cooled and fed through a fixed anion exchange bed. Fission products are removed from the bed by strong (8M) nitric acid wash, which may contain not more than 0.005M fluoride ion to increase the degree of decontamination from fission products, as in primary recovery. About 20% of the Th is also removed from the bed in the decontamination wash. If an excess of Pu^{239} is present, the fission product decontamination wash may be followed by a partition wash of nitric acid (6M) containing ferrous sulfamate and hydrazine to remove the Pu. The partition wash reduces the Pu(IV) to the (III) state which is only weakly absorbed. The nitrate concentration in 6M HNO_3 is sufficient to hold the Np(IV) anionic complex absorbed on the resin while Pu(III) is desorbed and eluted in the wash. The partition wash

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is discussed in more detail in Section 3.3. The absorbed Np is subsequently eluted from the bed with dilute (0.3-0.5M) nitric acid. After the Np is eluted, the resin bed is reconditioned with strong nitric acid (8M) so that the absorption efficiency of the resin is not reduced by residual dilute nitric acid from the preceding elution step. The reconditioning wash also contains a small amount of fluoride (0.1M) to remove residual fission products from the resin. Experimental work has shown that if the fission products are not removed from the resin, they accumulate and reduce the efficiency of decontamination in successive runs. Finally, the resin bed is flushed with strong nitric acid which may contain not more than 0.006M fluoride. The resin is reconditioned just before it is reused rather than after the preceding cycle, in order to avoid the oxidation of the resin which takes place under static conditions in the presence of strong nitric acid.

The third anion exchange cycle is identical with the second unless there is still an excess of Pu^{239}. To remove the Pu, a partition wash may be used. However, in contrast to the second cycle, in the third cycle the order of washes is reversed. Thus, the Pu partition wash of nitric acid, ferrous sulfamate, and hydrazine precedes the fission product decontamination wash of strong nitric acid containing a little fluoride. This order is necessary to keep hydrazine out of the Np eluate. Hydrazine stabilizes Np(IV) and would interfere with the feed adjustment for the cation exchange cycle where Np is oxidized to the (V) state.

2.2.2 Cation Exchange

The Np product solution from the third anion exchange cycle is heated to 80°C in the presence of Fe(III) to oxidize Np(IV) to (V). When the oxidation is complete, the solution is cooled to about 30°C. Sodium nitrite is added to maintain Np(V) in solution when in contact with the resin. The cooled solution is fed through a fixed cation exchange bed to absorb Th. The purified Np remains in solution and is ready for concentration and precipitation to convert it to the oxide form for the fabrication of target material (Section 4.0).

When analyses of the product Np solution show too much Th remaining after cation exchange, the cation exchange bed is saturated with Th and must be regenerated. The Th is removed from the resin by

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elution with sodium acid sulfate solution ($NaHSO_4$) after which the resin must be reconverted to the hydrogen form by treatment with dilute nitric acid. It may be desirable to remove Th from the resin after a specific number of absorption cycles according to operating experience.

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2.R References

2.1 Bartels, C. R., et al. "A Novel Ion-Exchange Method for the Isolation of Streptomycin". Chem. Eng. Progr. 54, No. 8, pp. 49-51 (1954).

2.2 Prout, W. E. and L. P. Fernandez. Recovery of Neptunium and Plutonium from Purex Waste by an Agitated Bed of Anion Exchange Resin. E. I. du Pont de Nemours and Co., Aiken, S. C. AEC Research and Development Report DP-453, February 1960 (Secret).

2.3 DPST-59-595, Technical Data Summary - Recovery of Neptunium from Irradiated Natural Uranium, W. J. Mottel, Coordinator, October 5, 1959 (Secret).

2.4 DPST-60-1-8, Technical Division - Monthly Progress Report, August 1960 (Secret).

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3.0 RECOVERY OF Pu^{238} AND Np^{237}

3.1 Target Process

The target process comprises dissolving irradiated Np-Al target elements in nitric acid and separation of the products (Figure 3.1). Unirradiated targets that are rejected during fabrication, after the hot pressing step (Section 7.1.3), may be dissolved with irradiated targets. The target elements are a mixture of neptunium dioxide and aluminum powder compacted and contained in a small cylindrical aluminum can.(3.4) The cans or "slugs" are approximately 1 inch in diameter by 6 inches long and are sealed by an aluminum cap welded to the can. A typical core contains nominally 24.5 wt % NpO_2 or about 42 gm before irradiation. For a reactor exposure of 200,000 megawatt days and a cooling time of 100 days, the predicted average compositions of irradiated targets for two concentrations of NpO_2 in the slugs(3.5) are shown in the table.

Composition of Irradiated Neptunium Targets
(200,000 MWD, Mark VIIA Sparger Jets)

Irradiated Target Composition (Cooled 100 Days)	Initial Concentration of NpO_2 in Target 21.2 gm	42.5 gm
Aluminum, gm	177	172
Np^{237}, gm	14.2	30
Pu^{238}, gm	3.2	5.6
Pu^{239}, gm	0.6	1.0
Pu^{240}, gm	0.1	0.1
Fission Products, gm	0.6	0.8
Gamma Curies	240	320
Beta Curies	360	480

For normal periods of irradiation, the fission product activity is a function of the cooling time, as shown below.

Cooling Time, days	Curies/gm of Fission Products Gamma	Beta
50	1000	1150
100	400	600
150	240	420

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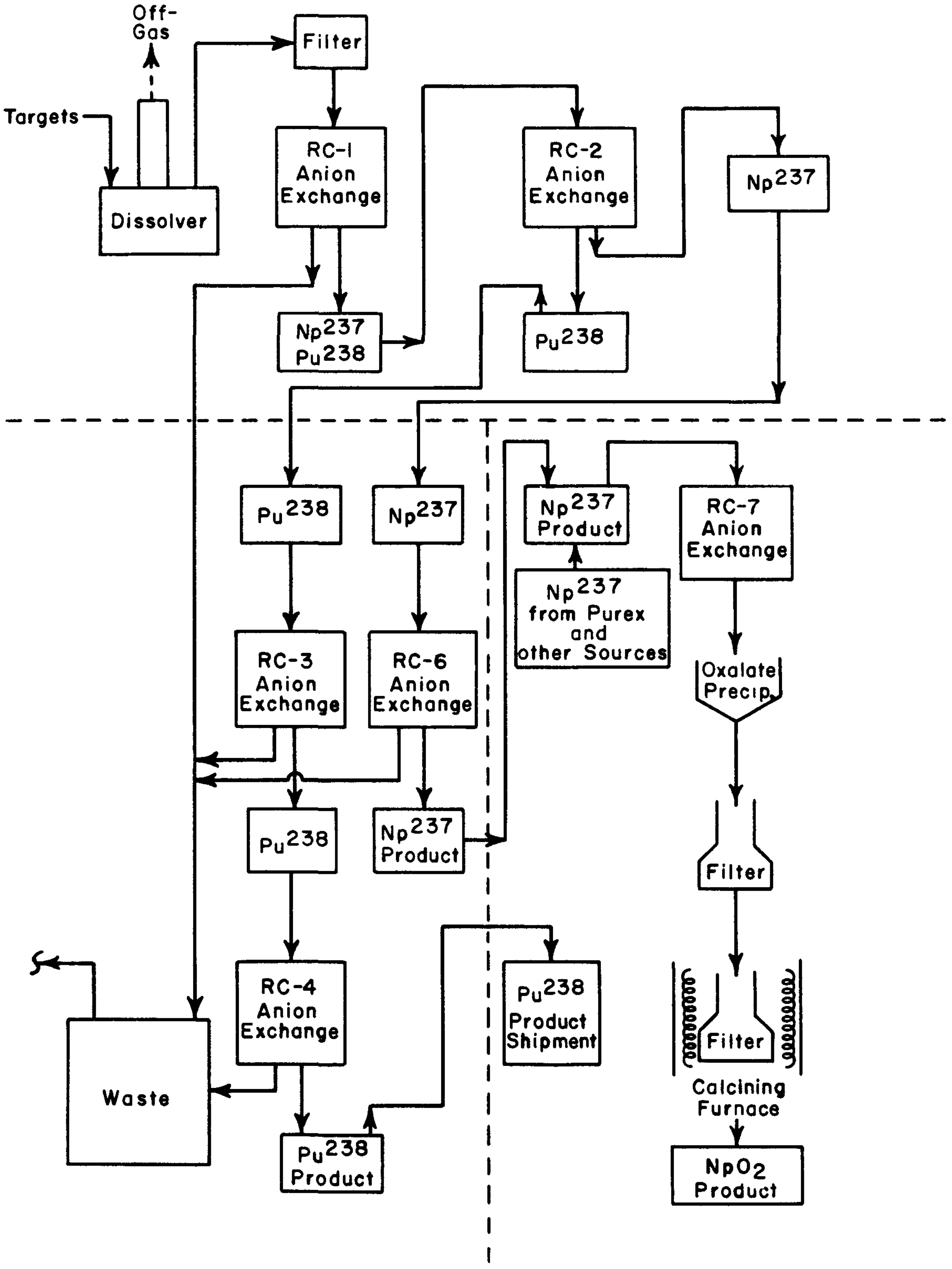

FIG. 3.1 TARGET PROCESS – SCHEMATIC FLOWSHEET

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3.2 Dissolving of Targets

The irradiated slugs are dissolved in boiling nitric acid. Two catalysts are required: mercuric nitrate to catalyze the dissolving of aluminum, and fluoride ion to catalyze the dissolving of the heavy metal oxides.

Although the mechanism of the dissolving of aluminum by nitric acid is complex the reaction can be represented by the general equation

$$\mathrm{Al} + 3.75\mathrm{HNO_3} \xrightarrow[\text{catalyst}]{\mathrm{Hg(NO_3)_2}} \mathrm{Al(NO_3)_3} + 0.25\mathrm{NO} + 0.15\mathrm{N_2O}$$
$$+ 0.11\mathrm{N_2} + 1.87\mathrm{H_2O}$$

The dissolving of neptunium dioxide, NpO_2, also involves oxidation of Np from the (IV) state to the (VI) state and formation of the cation NpO_2^{++}. It can be represented by the equation

$$3\mathrm{NpO_2} + 8\mathrm{HNO_3} \xrightarrow[\text{catalyst}]{\mathrm{F^-}} 3\mathrm{(NpO_2)(NO_3)_2} + 2\mathrm{NO} + 4\mathrm{H_2O}$$

If it is assumed that Pu exists as an oxide in the irradiated slugs, the dissolving can be represented by the equation

$$3\mathrm{PuO_2} + 8\mathrm{HNO_3} \xrightarrow[\text{catalyst}]{\mathrm{F^-}} 3\mathrm{(PuO_2)(NO_3)_2} + 2\mathrm{NO} + 4\mathrm{H_2O}$$

Although the equation shows Pu to be in the (VI) valence state, only about 40% of the Pu is oxidized from the (IV) to the (VI) state. A minimum concentration of about 0.02M fluoride ion is required for complete dissolving of the heavy metal oxides.(3.1)

Approximately 0.8 mole of off-gas is produced per mole of metal. The exact composition varies considerably depending on the temperature, concentration of reactants, and the efficiency of the off-gas condenser(3.2, 3.3). Nitric oxide, NO, is formed in the dissolver and reacts both with nitric acid and air to form nitrogen dioxide. The latter may react in part with water in the condenser to re-form

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nitric acid. These reactions may be summarized by the equations

$$NO + 2HNO_3 \longrightarrow 3NO_2 + H_2O$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

The maximum evolution of gaseous products may reach five times the average rate for the complete dissolving. During the peak, approximately 10% hydrogen may be present and air must be supplied to keep the hydrogen concentration below 3%. The lower explosive limit for hydrogen in air is about 4%.

The conditions for dissolving target material are difficult to define because the reactions which occur are complex. For example, the rate of dissolving of aluminum is dependent upon a number of variables such as: temperature, the surface area of the metal, the concentrations of mercuric and fluoride ions, the concentrations of aluminum nitrate and nitric acid, and the metallurgical history of the aluminum. The effects of many of these variables have been studied in connection with other projects and the data obtained can be used as a guide.(3.2,3.6) In small-scale dissolving it has been demonstrated that more uniform gas evolution is obtained by charging target slugs to the appropriate quantity of strong nitric acid then adding about half of the fluoride catalyst. After the reactants are heated to boiling, mercuric nitrate is added in small increments to maintain the controlled rate of dissolving. The remaining fluoride may be added after all of the mercuric nitrate has been added and the rate of reaction has decreased. The addition of fluoride before the mercury may etch the surface of the aluminum and allow a smoother initiation of the mercury catalyzed reaction. When all of the mercury has been added, the dissolver solution is refluxed until the dissolving of the core material is complete.

By delaying the final addition of fluoride until the aluminum concentration in solution is high, the rate of corrosion of the dissolver can be reduced substantially. Care must be taken to avoid carrying the dissolving to acid deficiency which would result in excessive hydrogen evolution, precipitation of the mercury catalyst, and polymerization of Np and Pu. The solubility of aluminum nitrate in nitric acid must also be considered. Data on the solubility of aluminum nitrate in aqueous nitric acid is shown in Figure 3.2.

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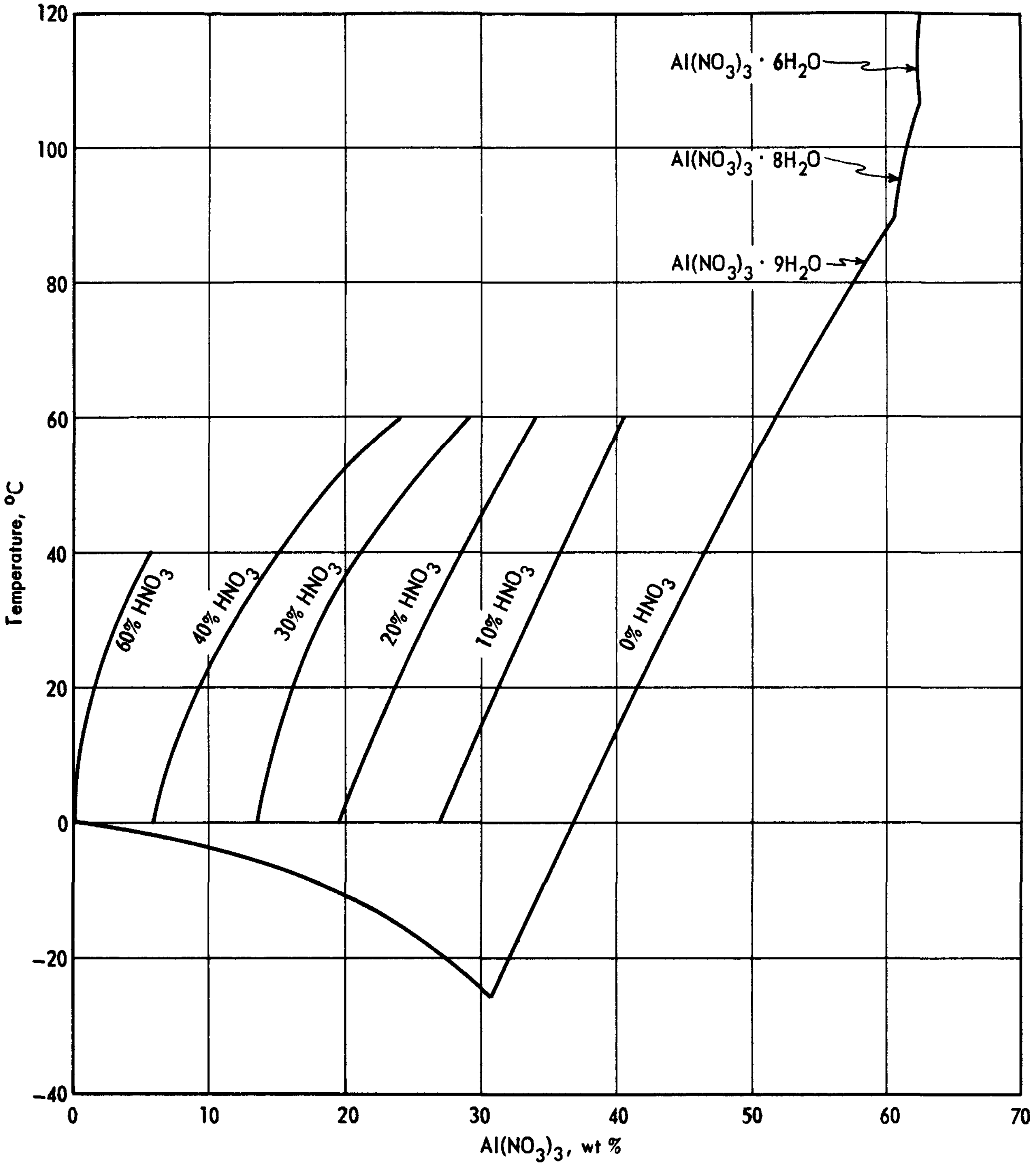

FIG 3.2 PHASE DIAGRAM – $Al(NO_3)_3$ – HNO_3 – H_2O

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It is desirable to avoid carrying the dissolving to completion, since the reaction rate decreases rapidly and becomes very slow. Leaving a heel of undissolved targets will also aid in the initiation of the dissolving of a fresh batch of target slugs.

The dissolver solution contains small quantities of undissolved solids, primarily silica, which can plug a fixed ion exchange bed if they are not removed. The solids arise mainly from impurities in the target metals. The solids can be removed by filtering the raw metal solution through a sintered stainless steel filter having approximately a 5-micron pore size. Small-scale tests indicate that the quantity of product retained on the filter is not significant. The filter can be backflushed periodically to avoid plugging. Laboratory experience has indicated that the filter selected for plant processing should effectively filter the solution associated with 250 targets before backflushing is required. After filtration the solution is ready for acid adjustment and subsequent absorption of Np and Pu on a fixed bed of anion exchange resin.

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3.3 Separations

Anion exchange is suitable for the separation of Pu^{238} and Np^{237} as well as for the recovery of Np^{237} from Purex wastes. Six cycles are required. The first cycle separates the Np^{237} and Pu^{238} from aluminum and fission products. The second cycle separates, or partitions, the Np^{237} from Pu^{238} and provides additional decontamination from fission products. The Pu^{238} then undergoes two successive anion exchange cycles to accomplish the necessary purification or decontamination and concentration. The Np^{237} receives an additional anion exchange decontamination; it is then ready for final decontamination, concentration, and conversion back to the oxide and may be combined for these steps with Np^{237} recovered from Purex waste or other sources.

3.3.1 Co-absorption of Neptunium and Plutonium

In order to co-absorb Np and Pu they must be in the (IV) valence state. Since the dissolving of target elements is accomplished in boiling nitric acid, Np is oxidized to the (VI) state whereas Pu is only partially oxidized and is present in both the (IV) and (VI) states in the nitric acid - aluminum nitrate mixture. The solution is adjusted to about 8M nitrate and acid concentration by the addition of strong nitric acid. Ferrous sulfamate is added to reduce Np to the (IV) state and Pu(IV) and (VI) to Pu(III). The oxidation of excess Fe(II) to Fe(III) and of Pu(III) to (IV) is accomplished by heating the solution to 55°C. When the oxidation reactions are essentially complete, the solution contains the anionic complexes of Np(IV) and Pu(IV) in suitable nitrate concentration for absorption. The absorption may begin immediately at the elevated temperature, but it is necessary to start cooling the feed solution promptly to prevent oxidation of Np(IV) to (V). The solution must be cooled to 35°C within one hour to avoid excessive loss of Np.

The adjusted feed solution is passed downflow through a fixed bed of anion exchange resin and the complex anions of Pu^{238} and Np^{237} are selectively absorbed. The rate of flow of the feed and the total quantity of actinides absorbed must be limited to avoid excessive loss of Np and Pu. In experimental work with "Dowex" 1-X4 resin, a 1.4% loss of Np occurred when the resin was loaded with an average of 15 gm of total actinides per liter of resin. The loss of Np increased approximately twofold when the average actinide loading was increased to about 20 gm/l.(3.7) The Pu loss was

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less than 1% in both cases. Most of the fission products and other cations are not appreciably absorbed and pass through with the effluent. The rate of flow of the feed solution should not exceed about 3 ml/(min)(cm^2) of resin if the total actinide concentration in the solution is greater than 1.6 gm/l or exceed 6 ml/(min)(cm^2) of resin if the concentration is less than 1.6 gm/l. The flow of solutions through the bed is by the gravity head. Since the pressure drop across the bed increases with increase in the depth of the bed, the depth is limited so as not to exceed the available head. Laboratory work has also indicated that it is necessary to have the ratio of the depth of the bed to the diameter greater than 1 in order to have good performance.

More complete decontamination from fission products, particularly Zr^{95}-Nb^{95}, is attained by washing the resin bed with nitric acid (8M) containing a little fluoride. Although the addition of fluoride to the wash improves the decontamination from fission products, it also causes the band of absorbed Np and Pu to spread down the resin bed. If the fluoride concentration is not carefully controlled, the loss of Np and Pu will increase substantially. A compromise is necessary, and a decontamination factor of approximately 500 may be attained with less than 2% loss Np and Pu if the fluoride concentration is less than 0.006M. The normal product loss to the wash depends upon the concentration of fluoride, the rate of flow, and the total volume of wash.

Np and Pu are eluted downflow from the resin bed with dilute nitric acid. It is necessary to maintain the acidity of the elutriant in the range of 0.2-0.5M HNO_3; lower acidity may allow polymerization of Np(IV) and Pu(IV) and higher acidity requires an undesirable increase in the volume of elutriant. Before the resin bed is used again to absorb Np and Pu, the resin is reconditioned with strong nitric acid (8M) so that the absorption efficiency of the resin is not reduced by residual dilute nitric acid from the preceding elution. The reconditioning wash also contains a small amount of fluoride (0.1M) to remove residual fission products from the resin. Experimental work has shown that if the fission products are not removed, they tend to accumulate and reduce the efficiency of decontamination in successive runs. Finally, the resin bed is flushed with strong nitric acid which may contain not more than 0.006M fluoride. The resin is regenerated just before use rather than after the preceding cycle since, under static conditions, the rate of oxidation of the resin is greater in strong nitric acid than in the dilute acid remaining after the elution step.

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3.3.2 Partition of Plutonium from Neptunium

In the partition or separation of Pu from Np it is important to keep the losses of both elements as low as possible and to keep cross-contamination of the two product solutions at a minimum. It is also desirable to attain a high degree of decontamination from any residual fission products. The efficiency of the partition step is a function of the Np/Pu ratio. With a normal ratio of about 4/1 the partition of Pu from Np is feasible in one cycle. If a lower ratio occurs, under unusual circumstances, too much Pu remains with the Np and more than one cycle may be required to effect separation. The partition can be accomplished by co-absorbing Np and Pu and subsequently eluting first the Pu and then Np or by absorbing Np alone and allowing the Pu to flow through the resin bed with the Np-depleted feed solution. A compromise is necessary between the quality of the Np and Pu product solutions and the losses. Experimental work has demonstrated that co-absorption of Np and Pu and subsequent separation of Np and Pu result in better decontamination and less cross-contamination than absorption of only Np. The losses of Np and Pu are somewhat higher.

The eluate from the first cycle co-absorption of Np and Pu contains Np(IV) and (V) and Pu(IV) and (VI) in about 3M nitric acid solution. Nitric acid is added to increase the acid concentration to approximately 8M for reduction of Np to the (IV) state and of Pu to Pu(III) with ferrous sulfamate. As in the first cycle, the excess Fe(II) is oxidized to Fe(III) and Pu(III) to Pu(IV) by heating the solution to about 55°C. The adjusted solution, containing the Pu(IV) and Np(IV) anionic nitrate complexes in a nitrate concentration favorable for absorption, is fed downflow through a fixed anion exchange resin bed. The Np and Pu can be absorbed in a relatively small and sharply defined volume or "band" at the top of the bed. The flow is critical and, for a given acid concentration, it is directly related to the concentration of Np and Pu in the feed. As the concentration increases, the flow must be decreased to avoid spreading the narrow absorption band down the bed which adversely affects the subsequent partition of Pu from Np. Thus, if the concentration of total actinides in the feed solution is greater than 1.6 gm/l, the flow should not exceed about 3 ml/(min)(cm^2) of resin. If the concentration of actinides is less than 1.6 gm/l, the flow may be increased but should not exceed about 6 ml/(min)(cm^2) of resin.

After the absorption is complete, the resin bed is washed with strong nitric acid (8M) containing not more than 0.006M fluoride to remove

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more of the residual fission product contaminants from the absorbed. Np and Pu. Although the addition of fluoride increases the loss of Np and Pu, normally it is not excessive. An excess of Np in the wash may require the decontamination wash to be segregated rather than blended with the Pu partition wash to prevent excessive contamination of the Pu product.(3.8) The Pu can be selectively eluted from the resin bed by reduction to Pu(III), which is only weakly absorbed; a high nitrate concentration must be maintained to stabilize the Np in the (IV) state so that the latter is retained on the resin. It is not practical to partition Pu from Np in 8M acid because of the large volume of solution that would be required. The partition is accomplished by washing the bed with 5.4M nitric acid containing small amounts of hydrazine (0.05M) and ferrous sulfamate (0.05M). The Fe(II) reduces Pu(IV) to Pu(III). The hydrazine protects the ferrous sulfamate from nitrous acid oxidation and stabilizes Pu(III). Hydrazine also eliminates the gassing on the resin bed which occurs if Pu is reduced on the resin without hydrazine present. The stability of the partition wash solution is quite limited and is a function of time and temperature. To be most effective, the reductants must be added to the acid below 25°C, and unless the reducing solution is to be used promptly it must be stored below 25°C. It is also important to add the hydrazine to the acid before adding ferrous sulfamate to minimize the oxidation of Fe(II) to Fe(III) by nitrite.

The nitrate ion concentration in the partition wash is critical. In 5.4M nitric acid the stabilizing effect of the nitrate ion on the Pu(IV) and Np(IV) anionic complex is not as great as in higher nitrate concentrations. Thus, Pu is quite readily reduced to the (III) state and is eluted without using a large volume of reducing wash solution. However, the Np(IV) complex also is not as strongly absorbed so that the Np tends to migrate down the resin bed and will contaminate the Pu product solution. If the Pu on the resin is not completely reduced and eluted by the partition wash, it will be eluted with the Np and contaminate the Np product solution. In order to avoid cross-contamination of Np and Pu, approximately 95% of the Pu is removed in a product cut of approximately 60% of the volume needed to remove all of the Pu. The final 40% of the partition wash, which contains the remaining 5% of the Pu and about 1% of the Np, is diverted and recycled through the co-absorption step. After the Pu is removed from the resin by the partition wash, the Np is eluted in dilute nitric acid (0.35M). Less than 1% of the total initial Pu remains with the Np and the quantity is less than 0.2 wt % of the Np product. Before reuse the resin bed is reconditioned

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and flushed as previously described.

Pu can be partitioned from Np at a higher nitrate concentration. With approximately 6M nitric acid and no change in the amounts of hydrazine and ferrous sulfamate, the higher nitrate concentration stabilizes the Np(IV) anionic complex absorbed on the resin so that it does not migrate and does not contaminate the Pu. However, the Pu(IV) complex is also stabilized and a larger volume of reducing wash is required to reduce and elute the Pu from the resin. The higher acid partition gives approximately the same decontamination from fission products as the lower acid processing but the cross-contamination in the Np and Pu product solutions is increased. The Np losses in either method are about the same and are attributed primarily to the co-absorption of Np and Pu on the resin in a rather narrow band of high saturation. The concentration of Pu causes radiolysis and oxidation of some of the Np(IV) absorbed on the resin; the oxidized Np is desorbed and eluted with the fission product decontamination wash.

To decrease the loss of Np, it is feasible to absorb Np under reducing conditions in approximately 6M acid solution containing ferrous sulfamate and hydrazine. The solution is not heated, so most of the Pu is in the (III) state. The solution is fed directly to the anion resin bed and the Np(IV) nitrate complex is absorbed in a relatively concentrated band. Although most of the Pu in the feed solution is in the (III) state, there is an equilibrium between the (III) and (IV) state which is shifted toward the (IV) state as the Pu(IV) nitrate anion complex is absorbed on the resin. Thus, about one third of the Pu is absorbed but not in a concentrated band. The Pu is distributed broadly down the resin bed. The Pu which remains in the (III) state is not absorbed and passes through the resin bed with the feed solution. The Pu on the resin is partitioned from the Np with the same solution as the feed; that is, nitric acid (6M), ferrous sulfamate (0.05M), and hydrazine (0.05M). The Np absorbed on the column is washed with strong acid containing not more than 0.006M fluoride to remove fission products. Since the absorption of Np and the partition of Pu are carried out in a reducing medium and without a high concentration of Pu on the resin bed, the loss of Np through oxidation by radiolysis products is negligible. The decontamination from fission products is decreased. Furthermore, it is necessary to maintain close control over the acid concentration to avoid loss of Np, and the temperature must be kept at a minimum, preferably at or below 25°C to hold Pu in the (III) state and minimize the oxidation to Pu(IV).

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3.3.3 Decontamination of Neptunium

The Np eluate from the separation of Pu from Np contains Np(IV) and (V) in about 3M acid solution. As in previous anion exchange cycles, it is necessary to adjust the acid concentration by addition of nitric acid and then to reduce Np(V) to (IV) with ferrous sulfamate. When the reduction of Np(V) to (IV) is complete, the excess Fe(II) is oxidized to Fe(III) by heating the nitric acid solution to 55°C. The adjusted feed solution then contains the Np(IV) anionic nitrate complex in a nitrate solution in concentration favorable for absorption by anion exchange. The feed is passed downflow through a fixed resin bed and the Np(IV) nitrate complex is absorbed. After the absorption is complete, the bed is washed with nitric acid containing no more than 0.006M fluoride to decontaminate the Np from fission products. Any Pu carried over in the (IV) state as a contaminant in the Np eluate from the Np-Pu partition will also be absorbed with Np. If the amount of Pu is higher than about 1 wt % of the Np, a partition wash of nitric acid containing hydrazine and ferrous sulfamate may be utilized to reduce the Pu(IV) to (III) and desorb it from the resin as previously described. It is necessary to consider this step carefully since a compromise must be made between the undesired contamination of the Np with residual Pu^{238} and the loss of Np which occurs in the partition wash; it is impractical to remove all of the Pu^{238} from the Np. It is possible to remove Pu with a partition wash prior to the fission product decontamination wash, but since the partition wash is carried out with a slightly lower concentration of acid, the area or band of distribution of Np on the resin bed is increased. As a result, in the subsequent wash to remove fission products, there is a further loss of Np.

Neptunium is eluted downflow from the resin bed in dilute (0.35M) nitric acid. The mixture of Np(IV) and (V) in nitric acid solution is ready for the final purification and finishing processes described in detail in Section 4.2. It is desirable to have the fission product activity level in the Np eluate less than $3x10^{-5}$ curie/gm. Since the initial feed in the recovery process contains about 15 curies/gm, the over-all decontamination factor is approximately $5x10^{5}$. Before reuse the resin bed is reconditioned with nitric acid (8M) containing a little fluoride, as previously described, and should be flushed to remove residual fission products.

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3.3.4 Decontamination of Plutonium

To meet product specifications, the Pu partitioned from Np requires further processing to remove fission products and to concentrate the solution for shipment. The partition solution contains Pu(III), Fe(II), and hydrazine. The acid concentration is increased to about 8M by adding nitric acid; Pu(III) and Fe(II) are oxidized to Pu(IV) and Fe(III), respectively, by heating the strong nitric acid solution to about 55°C. If the solution is held for more than about 2 weeks prior to heat kill, it is necessary to add fresh ferrous sulfamate to reduce Pu to (III), then heat to about 55°C to oxidize the Pu(III) to Pu(IV). This prevents the loss of any Pu which may have been oxidized to the (VI) state.

The nitrate ion concentration is favorable for formation of the Pu(IV) anionic nitrate complex. The adjusted solution is fed downflow through an anion exchange resin in a fixed bed and the Pu complex is absorbed. The resin bed is washed downflow with strong nitric acid containing a little fluoride to remove residual fission products. Adequate decontamination can be attained with a Pu loss not exceeding 1.5%.

The Pu is eluted from the resin downflow with dilute (0.3M) nitric acid. After desorption of the Pu, the resin must be reconditioned with nitric acid (8M) and should be decontaminated with nitric acid - fluoride solution as previously described. Because of the high alpha activity, some radiolysis occurs and some Pu is oxidized to Pu(VI) in the dilute acid solution. The nitric acid solution is adjusted to about 8M with nitric acid and any Pu(VI) is reduced to Pu(III) by ferrous sulfamate. The oxidation of Fe(II) to (III) and of Pu(III) to (IV) is again accomplished by heating the acid solution to about 55°C. The resin is washed with nitric acid containing a little fluoride as in the preceding step. An additional decontamination factor of about 10 may be attained with a further loss of approximately 1% of the Pu^{238}. Elution of Pu^{238} and reconditioning of the resin is carried out by the same procedure used in the preceding purification cycle.

The decontaminated Pu^{238} solution is ready for transfer to the customer. It must contain a minimum of 1 gm/l of Pu^{238} and no more than 1 gm of Np^{237}/100 gm Pu^{238}. The Pu^{238} must be at least 80% of the Pu isotope content of the solution and the quantity of other metals must be less than 1%. It is desirable to have the fission product activity level less than 10^{-4} γ curie/gm. Since the initial feed solution contains about 60 curies/gm, a total decontamination factor of about 10^5 is required in the process.

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3.R References

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3.2 Caracciolo, V. P. Dissolver for Uranium - Aluminum Alloy Tubes. E. I. du Pont de Nemours and Co., Aiken, S. C. AEC Research and Development Report DP-398, September 1959 (Confidential).

3.3 Buckman, J. A. and M. D. Martin. The Composition of Off Gas from Batch Uranium - Aluminum Dissolution. Phillips Petroleum Co., Idaho Falls, Idaho. AEC Research and Development Report IDO-14361, December 1955 (Declassified July 15, 1960).

3.4 DPST-59-585, H. G. Marsh to V. R. Thayer, Hot Pressing of Al-NpO_2 Slugs, October 12, 1959 (Secret).

3.5 DPST-60-204, F. E. Driggers to C. W. J. Wende, Irradiation of Np-237, March 3, 1960 (Secret).

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4.0 NEPTUNIUM FINISHING

4.1 Finishing Process

Purified Np recovered from Purex HAWC or other sources can be combined with recycle material from the processing of irradiated slugs. The dilute Np solutions contain low level fission products plus residual Pu^{238} and Pu^{239}. The finishing process comprises concentration of the dilute Np solution by anion exchange, precipitation of Np as the dioxalate from the concentrated solution, and finally calcination of the dried oxalate to yield neptunium dioxide, NpO_2. The oxide is of suitable quality for use in neptunium target elements and it is packaged for transfer to a target manufacturing facility. The fabrication of target slugs from NpO_2 is described in Section 6.0.(4.1)

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Neptunium (IV) in nitric acid solution is sensitive to oxidation due to the nitrite ion; ferric ion or warm nitric acid will readily oxidize Np(IV) to (V). To destroy nitrite ions and thus maintain Np in the (IV) state, hydrazine is added to the nitric acid elutriant in the ion exchange concentration of Np (Section 4.2). Even in the presence of hydrazine some oxidation occurs but the rate is low.

Since Np(V) does not form an insoluble oxalate, any Np(V) present is lost to the filtrate when the Np(IV) dioxalate is filtered. Ferrous sulfamate is not a satisfactory reductant since iron would contaminate the product. The reduction can be accomplished with ascorbic acid.(4.6) The rate of reduction is a function of the temperature and H^+ concentration. The reduction will take place at room temperature in about 4M nitric acid and it is rapid in about 1M nitric acid at 50°C. Since the precipitation of oxalate is not a fast reaction, it is feasible to perform the ascorbic acid reduction simultaneously with the oxalate precipitation.(4.7) The quality of the Np(IV) oxalate precipitate with respect to filtration and subsequent air drying is better when the reduction is performed at elevated temperature in the milder acid solution. The reduction can be accomplished at room temperature if the H^+ concentration is greater than 3.5M. The filtration requires more time, and the losses are slightly higher but acceptable. With ascorbic acid reduction of Np(V) to Np(IV), the quantity of Np lost in the filtration of Np(IV) dioxalate is essentially no greater than the equilibrium solubility of the oxalate. The use of ascorbic acid to reduce the relatively small amount of Np(V) formed in the Np eluate from the anion exchange concentration does not eliminate the necessity of hydrazine to inhibit the oxidation prior to precipitation.

A decontamination from residual fission products, primarily Zr-Nb activity, is obtained in the oxalate precipitation but there is no separation from any residual Pu or Pa.

The precipitated neptunium oxalate is cooled and filtered. The filter cake is washed with additional nitric acid - oxalic acid solution to remove retained impurities and then it is air dried at ambient temperature.

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4.2 Concentration of Neptunium Solution

Neptunium in the product solution from the previous decontamination is in the (IV) and (V) valence states at a concentration of about 4 gm/l in approximately 3M nitric acid. Nitric acid is added to increase the acid concentration to about 8M and ferrous sulfamate is added to reduce Np(V) to (IV). The solution is heated to about 55°C in order to oxidize the excess reductant, Fe(II), to Fe(III) and to prevent severe gassing in the resin column. If the adjusted solution is cooled to 25°C it is quite stable for 24 hours.(4.2) At 33°C, the loss of Np is approximately 0.3% in 24 hours, which is a factor of 2 greater than the loss at 25°C. To minimize losses, the concentration of Np or total actinides in the feed solution should not exceed 3 gm/l. The feed solution is passed through an anion exchange resin bed and the Np(IV) anionic nitrate complex is absorbed. The absorbed material can be retained on the resin up to 24 hours if necessary. Any residual Pu is in the (IV) state and will be absorbed on the resin with the Np(IV). Approximately 33 gm of Np can be absorbed per liter of resin; the total quantity of Np which can be concentrated in one cycle is limited primarily by the volume of resin.

The Np is washed on the column with strong (8M) nitric acid containing a small amount of fluoride to remove residual iron, fission products, and protactinium. If an excessive amount of Pu(IV) is absorbed with the Np, the decontamination wash may be preceded by a partition wash of nitric acid (6.2M) containing a little ferrous sulfamate and hydrazine. The Pu(IV) is reduced to Pu(III) which is desorbed and eluted in the wash. The order is important, and the partition wash is done first followed by the decontamination wash in order to eliminate iron as a contaminant in the Np product. Some additional loss of Np occurs since the partition wash is slightly lower in acidity and nitrate concentration than the decontamination wash and the Np is not as strongly absorbed on the resin. The Np tends to migrate down the resin bed spreading the absorption band so that further loss of Np also occurs in the subsequent decontamination wash.

Neptunium is eluted from the resin with dilute (0.35M) nitric acid containing not more than 0.05M hydrazine to retard the oxidation of Np(IV) to Np(V) in the concentrated product solution. Neptunium must be in the (IV) state for the next step which is precipitation of neptunium oxalate. In the presence of hydrazine, the rate of oxidation is very slow. If Np is precipitated within a week, the

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losses to the filtrate are less than 0.1% of the Np; if Np is precipitated from fresh eluate, the loss is 0.03%. After a forerun or displacement fraction is taken, approximately 90% of the absorbed Np is eluted in the product fraction. The residual Np is removed in a tail fraction which is combined with the forerun fraction for recycle.

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4.3 Precipitation of Neptunium Oxalate

Both Np(IV) and Np(V) will form oxalate complexes but only Np(IV) forms a complex which is insoluble enough to remove Np quantitatively from dilute aqueous solution. The solubilities of the complexes of Np(IV) with oxalate ions are dependent on the concentration of hydrogen ions and oxalate ions.(4.3) Figure 4.1 shows the solubility of Np(IV) oxalate as a function of hydrogen ion concentration with nitric acid.(4.4) The solubility of Np(IV) oxalate as a function of oxalate ion concentration from oxalic acid is shown in Figure 4.2.

At high concentrations of hydrogen ion, the solubility decreases with increasing concentration of oxalic acid. However, with low concentrations of hydrogen ion, the solubility of Np(IV) oxalate increases with increasing concentration of oxalate. This behavior is attributed to the formation of a soluble oxalate anion in the presence of excess oxalate. Thus, Np(IV) reacts with oxalate to form first a soluble cationic complex or mono-oxalate, and as the oxalate ion concentration is increased, the dioxalate forms and precipitates.

$$H_2C_2O_4 \rightleftharpoons 2H^+ + C_2O_4^= \qquad (1)$$

$$Np^{+4} + C_2O_4^= \rightleftharpoons Np(C_2O_4)^{++} \quad \text{(Soluble)} \qquad (2)$$

$$Np(C_2O_4)^{++} + C_2O_4^= \rightleftharpoons Np(C_2O_4)_2 \quad \text{(Insoluble)} \qquad (3)$$

With a high concentration of H^+, the ionization of oxalic acid is suppressed, limiting the amount of oxalate available, and the reaction of Np(IV) with oxalate ion does not proceed beyond formation of the dioxalate. With low H^+ concentration, the ionization of oxalic acid is not suppressed. Thus, the concentration of available oxalate ion increases as the concentration of oxalic acid increases and the reaction of Np^{+4} with a third oxalate ion occurs to give a soluble anionic complex.

$$Np(C_2O_4) + C_2O_4^= \rightleftharpoons Np(C_2O_4)_3^= \quad \text{(Soluble)} \qquad (4)$$

With about 0.1M excess oxalic acid in 1.4M nitric acid, the equilibrium solubility of Np(IV) oxalate is approximately 0.01 gm Np/l.(4.5)

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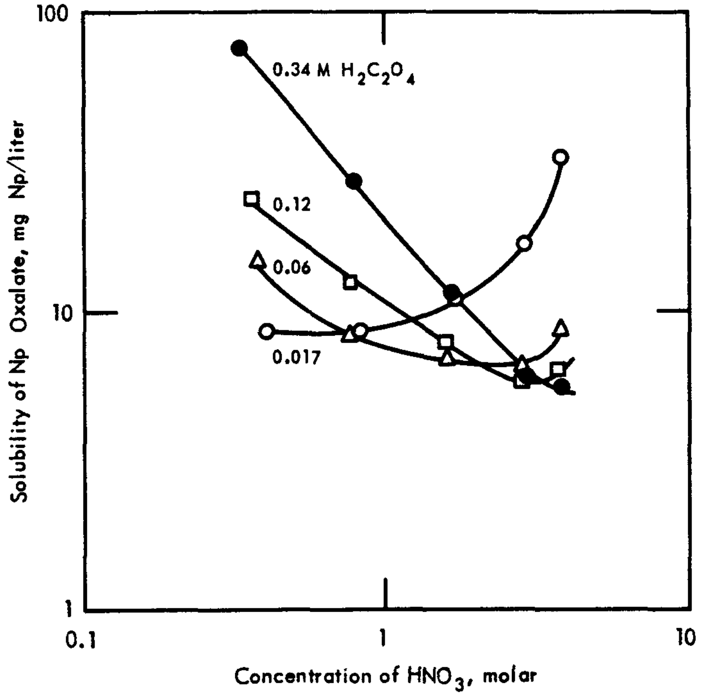

FIG. 4.1 EFFECT OF HNO_3 ON SOLUBILITY OF Np OXALATE

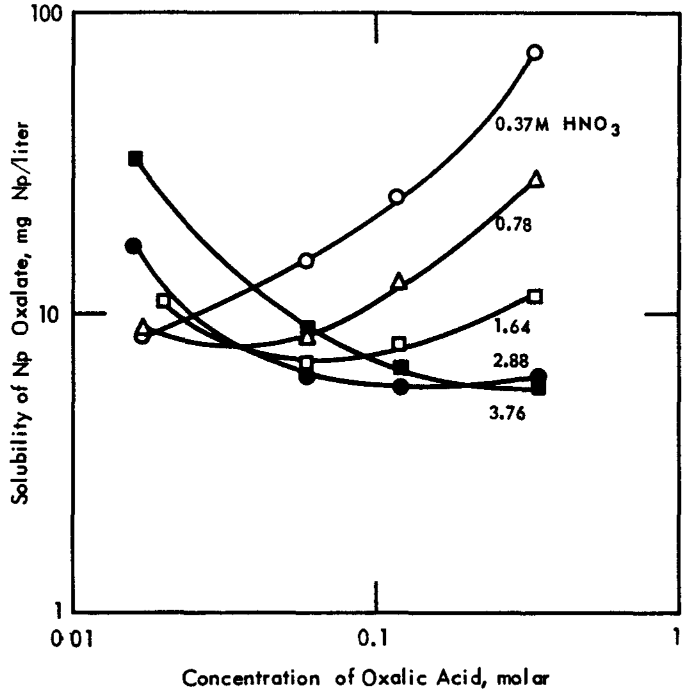

FIG. 4.2 EFFECT OF OXALIC ACID ON SOLUBILITY OF Np OXALATE

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4.4 Conversion of Neptunium Oxalate to Neptunium Oxide

Air-dried neptunium oxalate contains approximately 4 moles of water per mole of neptunium oxalate.(4.4) This hydrate is heated to about 150°C to remove the water of hydration.

$$Np(C_2O_4)_2 \cdot 4H_2O \xrightarrow[\Delta]{150^\circ C} Np(C_2O_4)_2 + 4H_2O\uparrow$$

Neptunium oxalate decomposes between 330 and 350°C

$$Np(C_2O_4)_2 \xrightarrow[\Delta]{>350^\circ C} NpO_2 + 2CO\uparrow + 2CO_2\uparrow$$

Either air or nitrogen may be used to sweep water vapor and then the gaseous products from the furnace during the calcination. In experimental work there was no detectable difference in the mode of decomposition or the quality of the product obtained with air and with nitrogen. The neptunium dioxide is a finely divided gray-green powder with a bulk density of approximately 2.5 gm/cc and a packed density of about 3.5 gm/cc. X-ray diffraction patterns of NpO_2 prepared in the laboratory were found to be in excellent agreement with patterns presented in the literature and showed no detectable quantities of other oxides as impurities. When product prepared at 550°C was reheated to 600°C, the weight loss did not exceed 0.1 wt %. After the neptunium dioxide is removed from the calcination furnace and cooled, it is packaged for transfer to the facilities for the fabrication of NpO_2-Al targets.

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4.R References

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5.0 DISPOSAL OF SPENT RESIN

After varying periods of use, anion exchange resins used in the recovery of Np and in the processing of Np targets lose their efficiency and they must be replaced. The failure appears to be due to a combination of radiation damage and the absorption of some anions which are not eluted by the normal process media.

In the vessels designed for remote operation in the canyons, the resin is not restrained at the top of the bed. If the vessel is flooded with an aqueous solution of sodium nitrate or aluminum nitrate, spent resin is readily removed by flotation through the vessel overflow. Solutions containing about 25 wt % sodium nitrate or 22 wt % aluminum nitrate with specific gravities of approximately 1.2 improve the flotation of the solid resin and thus reduce the volume needed to remove the resin.

One method of disposal of the resin is to discharge it directly to the waste tanks with sufficient caustic to neutralize any residual acid plus the theoretical quantity of carbon dioxide, which would eventually be formed by radiolytic decomposition of the resin in the waste tank. Although an excess of caustic can be added, direct disposal of the resin is questionable because local accumulations may occur and the liberation of carbon dioxide then could cause local areas of caustic deficiency by the reaction

$$NaOH + CO_2 \longrightarrow NaHCO_3$$

Excess carbon dioxide would react with water to form carbonic acid, which will cause corrosion of the mild steel waste tanks.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

The disposal of spent resin can also be accomplished by digesting the resin in aqueous solutions of alkaline permanganate ($KMnO_4$). The reaction of $KMnO_4$ solution with resin is slightly exothermic and is easily controlled. The rate of reaction increases with increased temperature; solubilization of resin is virtually complete in 6 hours at 70°C or in 1 hour at 100°C. The amount of permanganate required is independent of the permanganate concentration, sodium nitrate concentration, or of temperature within the range of 70-100°C. The pH of the medium is important. In acid solution, ruthenium is volatilized by permanganate; in basic solution permanganate (Mn^{+7}) is reduced to manganate (Mn^{+6}), increasing the amount of permanganate required for dissolving. The optimum pH for the reaction is in the range of 7 to 10. The method is applicable both to resins with

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quaternary ammonium functional groups such as "Dowex" 1-X4 and those with pyridinium groups such as "Permutit" SK, but the chemical behavior is different.

The estimated carbon content of "Permutit" SK resin is approximately 50 wt % and that of "Dowex" 1-X4 is 55 wt %. The dry weight of resin contained in one liter of settled resin slurry is about 380 gm. The decomposition of the resins is complex and involves breaking the carbon bonds to form soluble organic fragments and subsequent oxidation of the fragments to CO_2. The over-all reaction may be summarized by the equation.(5.1)

$$5KMnO_4 + 3[-CH-] + H_2O \longrightarrow 5KOH + 5MnO_2 + 3CO_2$$

$$KOH + CO_2 \longrightarrow KHCO_3$$

Thus, the theoretical quantity of $KMnO_4$ required for complete oxidation of the resin is approximately 22 gm/gm of carbon or an average of approximately 4.5 kg/l of resin (380 gm).

"Permutit" SK resin can be solubilized and partially oxidized by reaction with about 3.6 kg of $KMnO_4$ in a 6-12% solution in 6 hours at 70°C. With a slight excess of $KMnO_4$, the oxidation is 90% complete in 15 hours at 70°C and approximately 4.3 kg of $KMnO_4$ is consumed. If the digestion is carried out at 100°C, the time is decreased to about 1 hour for dissolving and partial oxidation, but carbon dioxide is evolved, possibly by the reaction

$$KHCO_3 \longrightarrow KOH + CO_2\uparrow$$

and an estimated 1-5% of the $KMnO_4$ is decomposed, presumably by the reaction

$$4KMnO_4 + 2H_2O \longrightarrow 4KOH + 4MnO_2 + 3O_2\uparrow$$

Since no nitrogen compounds have been found in the off-gases, the nitrogen in the pyridinium groups may be oxidized to nitrate.

There are two disadvantages in the use of permanganate for the disposal of resin. Because of the low solubility of $KMnO_4$, up to 75 volumes of solution are required per volume of resin, and about 5 volumes of MnO_2 are produced per volume of resin destroyed.

In contrast to the "Permutit" SK resin, "Dowex" 1-X4 resin is readily solubilized in about 1 hour at 70°C in a small amount of 6-12% $KMnO_4$ in mild alkaline solution. The quantity of $KMnO_4$

consumed is approximately 0.6 kg/l of resin which is equivalent to 12% oxidation of the resin. However, further oxidation of the soluble organic fragments is very slow even at 100°C. With a moderate excess of alkaline permanganate, about 35% of the carbon in the resin is destroyed in 15 hours at 70°C, and about 60% is consumed in 6 hours at 100°C(5.2) or in 50 hours at 70°C. On the basis of laboratory experiments it is estimated that digesting "Dowex" 1-X4 for one week at 70°C would oxidize 60 to 80% of the dissolved resin to CO_2.(5.3) At 100°C, the off-gas is primarily carbon dioxide with a small quantity of oxygen corresponding to the reaction of 1-5% of the permanganate with water. The quantity of gas liberated at 70°C is not significant.

The experimental work on the dissolving and oxidation of "Dowex" 1-X4 and "Permutit" SK resins has been confirmed on a semiworks scale.(5.3,5.4) The rates of dissolving of the two resins determined in the semiworks are shown in Figure 5.1.

Alternate anion exchange resins, which have been considered, such as "Duolite" A-42 dissolve in alkaline permanganate without difficulty. A few resins which have resisted the alkaline permanganate treatment have also shown poor anion exchange properties.

Typical cationic resins such as "Dowex" 50W with sulfamic acid functional groups are readily solubilized with approximately 1.5 kg permanganate/l of resin digested for 8 hours at 70°C or 2 hours at 100°C. If these resins are assumed to have a carbon content of approximately 50%, the consumption of permanganate represents about 30% degradation of the resin. The behavior of the cationic resins tested is quite similar to that of the "Permutit" SK anionic resins rather than "Dowex" 1-X4.

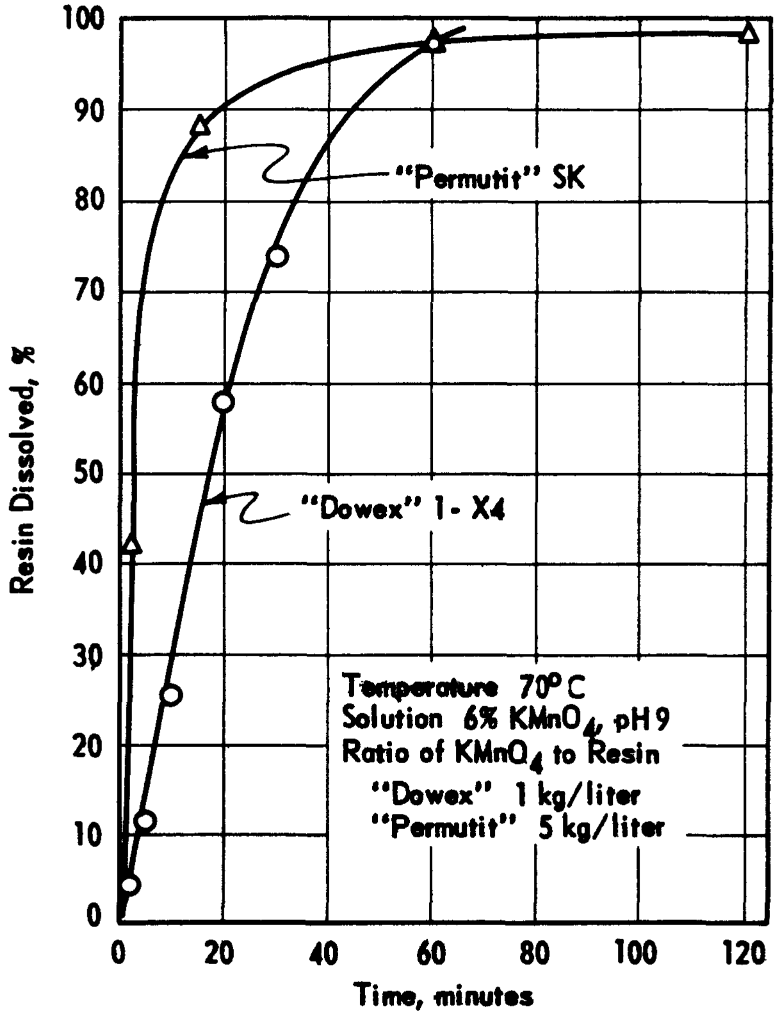

FIG. 5.1 DISSOLVING ANION EXCHANGE RESIN

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5.R References

5.1 DPST-60-19-3, Separations Chemistry - Monthly Progress Report, March 1960 (Secret).

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6.0 FABRICATION OF NEPTUNIUM OXIDE - ALUMINUM TARGETS

6.1 Fabrication Process - General Description

Target slugs for the irradiation of neptunium are made by a powder metallurgy process(6.1) which was selected to obtain the maximum utilization of neptunium and the maximum uniformity of composition. Conventional casting techniques were believed to be unsatisfactory because of the large amounts of scrap generated and because of the excessive segregation that is characteristic of aluminum-actinide alloy systems.

All of the experimental development leading to the selection of the powder metallurgy process was done using either uranium oxide (UO_2) or thorium oxide (ThO_2) as a stand-in for neptunium oxide (NpO_2). Thus, data on the Al-NpO_2 system are available on only a few aspects of the process in which questions arose during the operation of the production facility.

Neptunium oxide, as received from the neptunium finishing process, is blended with aluminum powder into a uniform dispersion. The powder is cold compacted on a double-acting press into cylinders nominally 0.859 inch in diameter and 2 inches long*. Three of the cold compacts are loaded into an impact-extruded aluminum can, an end cap is inserted, and the assembly is hot pressed in vacuum, using a floating die; this process forms a metallurgically bonded slug. The slug is trimmed to remove flash from hot pressing and the end cap-can interface is "Heliarc" welded. The slug is then "smeared" to test for freedom from radioactive contaminants on the surface, and inspected before shipment to the 100 Areas for irradiation. Details of the finished slug are shown in Figure 6.1.

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*Note: The compact length of 2 inches described here was originally used during start-up and early operation of the fabrication facility in Building 235-F. Two compacts 3 inches long are now used in each slug to obtain a higher productivity in the compacting operation. Other combinations could be used equally well depending upon the needs of the production operation and the length of core required.

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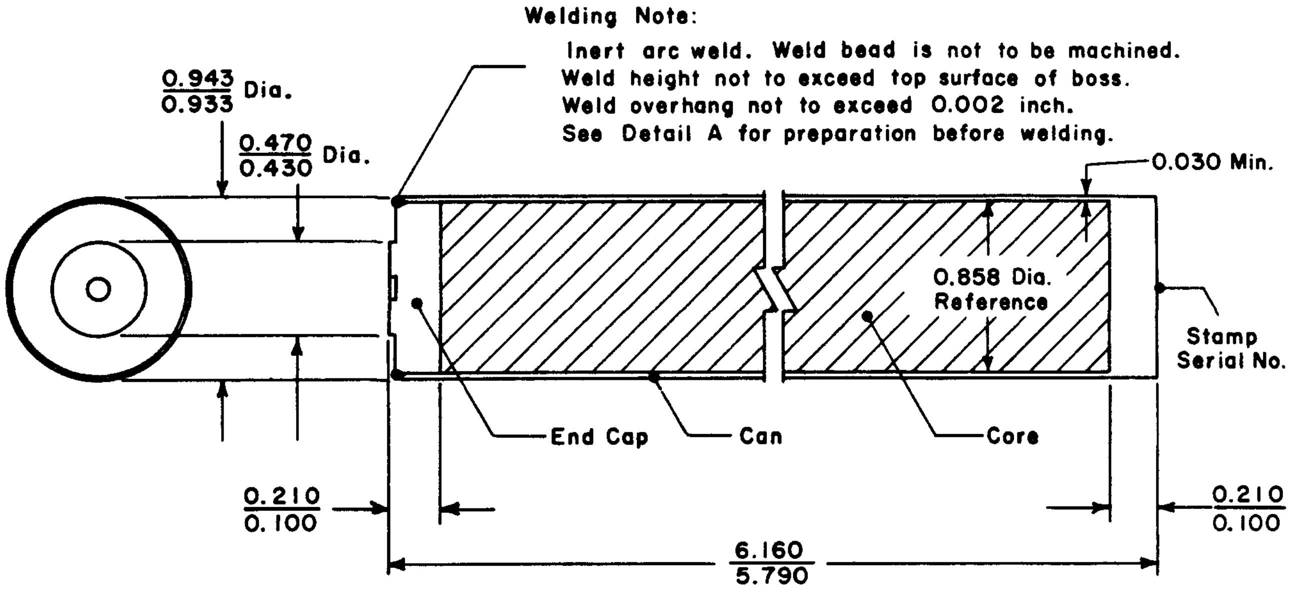
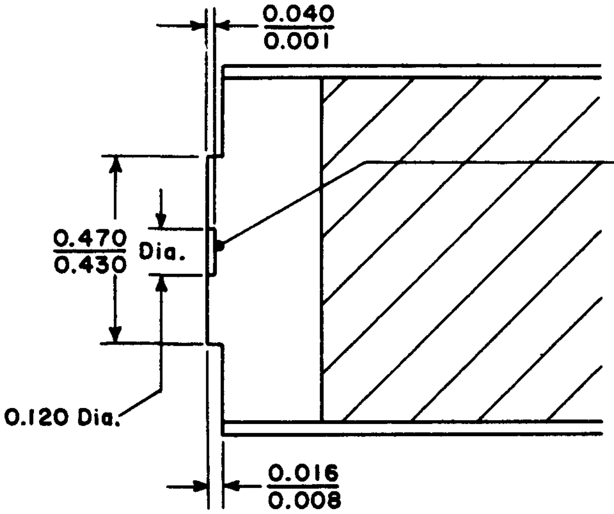
Welding Note:

Inert arc weld. Weld bead is not to be machined.
Weld height not to exceed top surface of boss.
Weld overhang not to exceed 0.002 inch.
See Detail A for preparation before welding.



NpO_2 -Al Target Slug



Gaging dimple in cap of as-pressed slug must not be removed during machining for welding; first weld only. May be removed if slug re-machined to reclaim for weld rejection; provided overall length tolerances are maintained.

Preparation for Welding
Detail A

FIG. 6.1 DETAILS OF NpO_2-Al TARGET SLUG

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6.2 Powder Preparation

The neptunium oxide and aluminum powders are weighed into a jar mill and enough porcelain balls are added to provide an internal stirring action. There is a tendency for the combined powders to form clumps of like particles. The kneading action obtained in the ball mill not only mixes the oxide with the aluminum uniformly and prevents the formation of clumps, but produces a blend that does not segregate on standing.

The NpO_2 powder particles range from 6 to 20μ in diameter, as determined by metallographic examinations of a production slug. This range in particle size is satisfactory for uniform blending and bonding of the slugs. Routine particle size determinations are not made on the as-received NpO_2, since close control is required for optimum yield in the preceding chemical steps of precipitation and calcining which fix the particle size distribution. A wide latitude in particle size is acceptable for slug fabrication, so minor variations due to limitations in the Np finishing are not objectionable.

The aluminum powder used is ALCOA Type 101, an atomized powder made by spraying molten 1100 aluminum through a nozzle. The particle size distribution is 100% (-80) mesh, and 80% (-325) mesh (U. S. Standard Sieve Size). Composition limits of the Type 101 powder are identical to those for wrought 1100 aluminum. Aluminum oxide (Al_2O_3) content will be slightly higher due to the high surface area of the powder, but oxygen pickup in the powder after manufacture is slight as long as the powder is stored in its shipping container.

Some fine particles (-325) mesh were found to be necessary in maintaining a stable blend. A series of experiments using (-325) mesh ThO_2 and aluminum powder with a particle size distribution of 100% (-80) mesh, and 95% (+170) mesh showed that the (-325) mesh ThO_2 sifted through the coarse aluminum particles and segregated to the bottom of the container. The minimum amount of fine aluminum particles required to prevent segregation was not determined.

Control of the homogeneity of the blended powders is maintained by statistical analysis of the γ activity of five random samples withdrawn from each blender batch after blending is completed. The γ radiation is due to the Pa^{233} daughter of the Np^{237} α decay, and for

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any single batch, the γ activity is proportional to the Np content. The mean and standard deviation in count rate for the five samples are calculated, and the blender batch is accepted if the standard deviation is less than 6.5% of the mean. This level of control provides 99% confidence that the standard deviation of concentration in 1-cc volumes does not exceed 24% of the mean concentration. The standard deviation in count rate for 36 blends averaged 2.0% of the mean with a range of 0.3% to 4.2%, indicating that variations in blend composition are small. The count rate technique is not applicable for an absolute determination of NpO_2 content of the blend, because the γ activity level of the sample increases with time. However, with the uniformity of the blend established, an assay for neptunium is not required and the quantity of NpO_2 in any batch can be controlled by a material balance with the gross weight of NpO_2 and aluminum that are charged into the blending mill.

The reliability of the count rate procedure as a control method was established by a special series of experiments using blends of ThO_2 and Al powders. Random samples of the blended powders and crushed samples 1 cc in volume taken from various locations in random compacts made from these blends were compared. The count rates made on the compact samples did not differ significantly from those made on samples removed from the blender. This work demonstrated that the variation of composition within a finished compact was no greater than the variation within the blend from which it was made, and that no detectable segregation of the dispersed phase occurred during the weighing, pouring, or cold compacting of the powder blend.

The use of too many balls in the blender or excessive blending time causes some work hardening of the aluminum powder particles, and lower compact densities result, but the blend uniformity is not affected.

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6.3 Cold Compacting

One-third of the blender powder required for a slug is weighed out, loaded into a steel die and cold pressed into a "green" compact on a double-acting hydraulic press. Cold compacting reduces the volume of the blended powder so that the ram travel in hot pressing is not excessive. Pressing conditions are selected to give a reproducible green compact density without requiring an excessively high compacting pressure.

The effect of compacting pressure on the density of the cold compact for pure aluminum powder and ThO_2 and UO_2 mixtures with aluminum powder is shown in Figure 6.2.(6.2) Note that these data will apply exactly only for the materials and compact sizes given. For aluminum-NpO_2 compacts containing 25 weight per cent NpO_2 a density of about 91% is obtained by pressing at 19.8 tsi.

6.3.1 Tools

A double-acting press is used so that compacting force is transmitted through punches equally to both ends of the compact. The identical result can be achieved by use of a single-acting press and floating die, but additional die handling is necessary for compact ejection. The use of a single-acting press with a fixed die for a compact having a length-to-diameter ratio of greater than about one will result in a low density at the end next to the stationary punch, and the green compact does not have sufficient strength to be handled without crumbling unless excessively high compacting pressures are used. The die-and-punch arrangement is shown schematically in Figure 6.3.

6.3.2 Lubrication

The die lubricant is n-dodecyl alcohol (also called n-dodecanol or lauryl alcohol), which is removed by distillation during the heating and out-gassing cycle prior to hot pressing. Technical n-dodecyl alcohol is manufactured by high pressure hydrogenation of lauric acid derived from palm oil or coconut oil, and has a sufficiently high viscosity at room temperature to provide good lubricating properties. Pure n-dodecanol has a melting point of 23°C and a boiling point of

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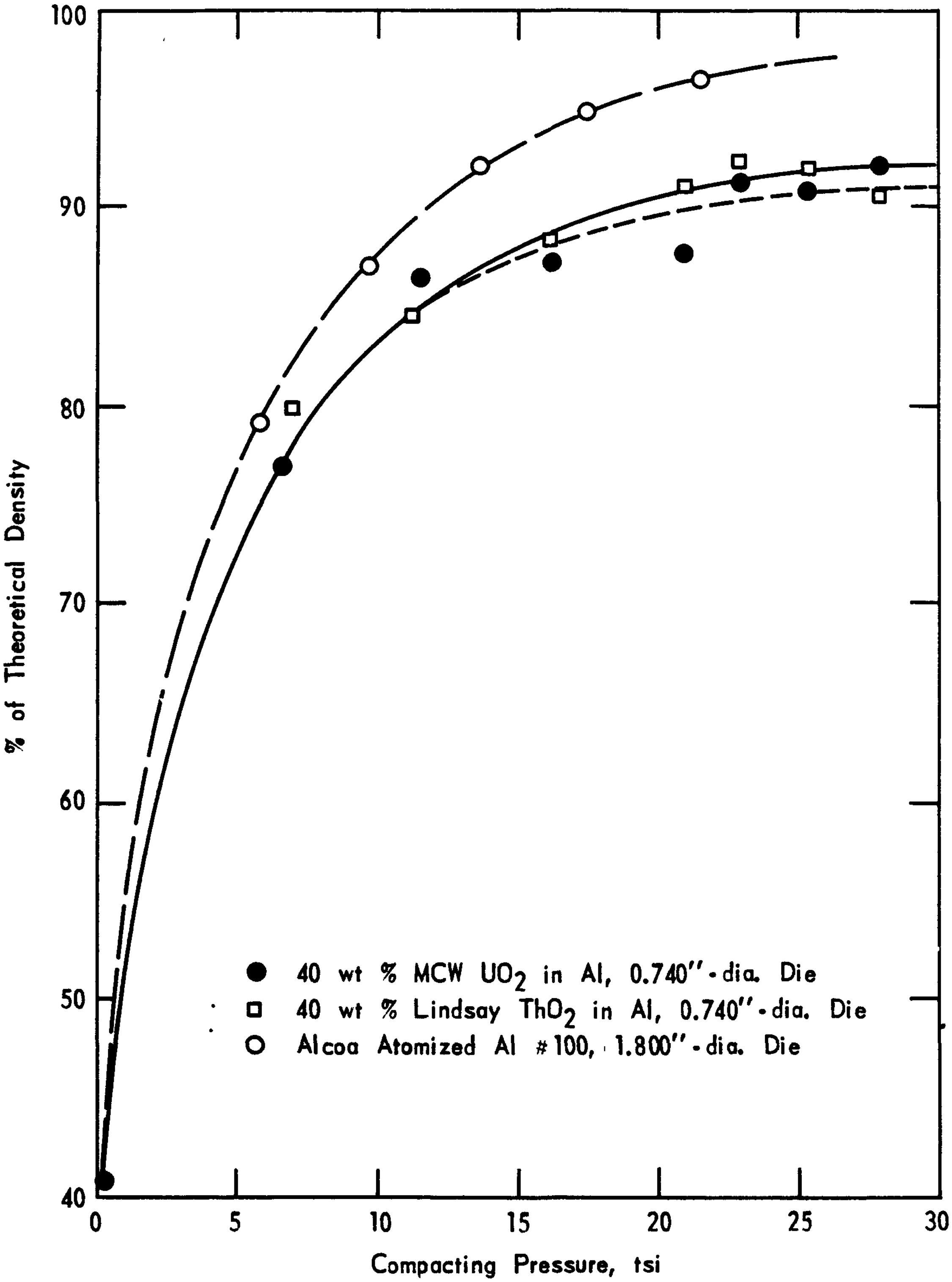

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FIG. 6.2 DENSITY OF COLD COMPACTS

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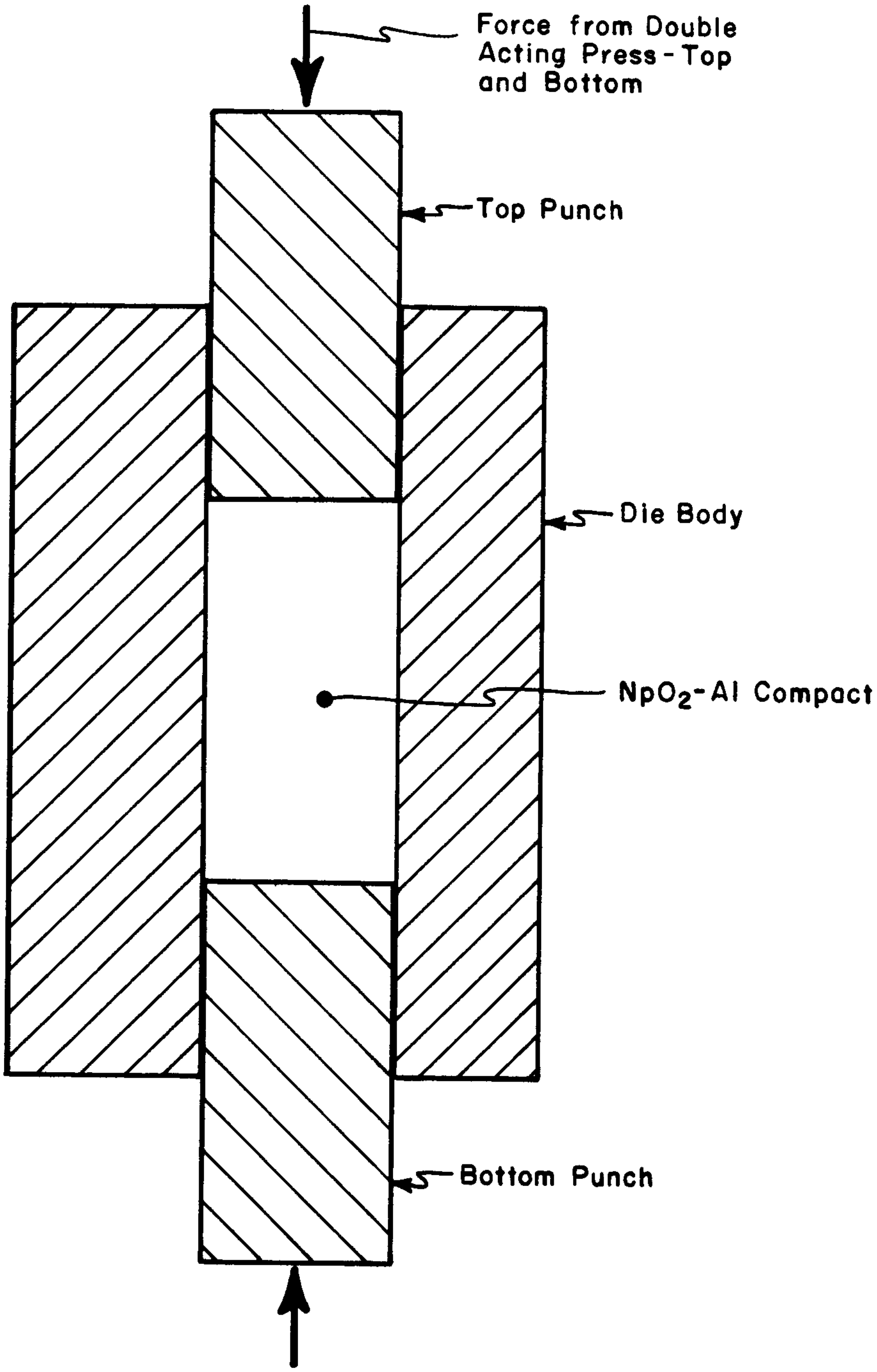

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FIG. 6.3 SCHEMATIC ARRANGEMENT OF COLD COMPACTING DIE about 255°C. The technical grade melts at between 16°C and 18°C, and boils over the range 240-260°C. Evaporation of technical dodecanol leaves a white residue of about 0.1% of the original sample, due to the presence of small quantities of higher alcohols. About 500 milligrams of dodecanol remain in each green compact after cold pressing. Residue after evaporation amounts to about 0.5 milligrams, or less than 10 ppm in the compact. The consistent high-strength bonds achieved in dummy runs show that the dodecanol residue is not objectionable.(6.3)

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6.4 Hot Pressing

In the hot-pressing operation, three compacts are loaded into an impact-extruded aluminum can, an end cap is inserted, and the entire assembly is hot pressed to create a bonded unit.

6.4.1 Tooling

The furnace is heated by resistance elements wrapped around a steel housing which encases an "Inconel X" backup die. The backup die is supported within the furnace on a spring so that a double-action pressing effect is obtained. The furnace can be evacuated to a pressure of 50 microns, and a bellows seal is used at the top so that the slug may be pressed under vacuum. The slug to be pressed is loaded into an "Inconel X" die liner outside the furnace. Top and bottom punches are inserted into the die liner and the assembled slug, liner, and punches are lowered into the backup die inside the furnace. The furnace assembly is shown in Figure 6.4.

6.4.2 Die Lubricants

The die liner must be lubricated on the outside so that it may be easily removed from the backup die. For this purpose, a mixture of colloidal graphite and water has been found to be adequate. The inside surface of the die liner is lubricated with a suspension of molybdenum sulfide (MoS_2) in water. A continuous and adherent coating of MoS_2 is essential, or the aluminum from the slug will diffuse into the die liner during hot pressing and make removal of the slug very difficult with possible damage to the slug. The die liner is heated to about 160°F before the lubricant is applied to speed drying of the lubricants and to give a more adherent lubricant film. The addition of a small amount of sugar to the MoS_2-water suspension sometimes improves the adherence of the lubricant film.

6.4.3 Assembly

Three NpO_2-Al green compacts are selected that meet the total length requirements. These are loaded into an impact-extruded aluminum can, which has been previously cleaned and inspected, through an airlock between the powder-processing and hot-pressing sections of the fabrication line. Before the end cap is loaded, the end cap-can interface is wiped clean with a cotton swab that has been moistened with isopropyl alcohol to remove contamination that may have been spread during the loading operation. The slug is then loaded into the lubricated die; care is taken not to allow any MoS_2 particles to fall into the cap-can interface. The slug and die-liner assembly is loaded into the preheated furnace.

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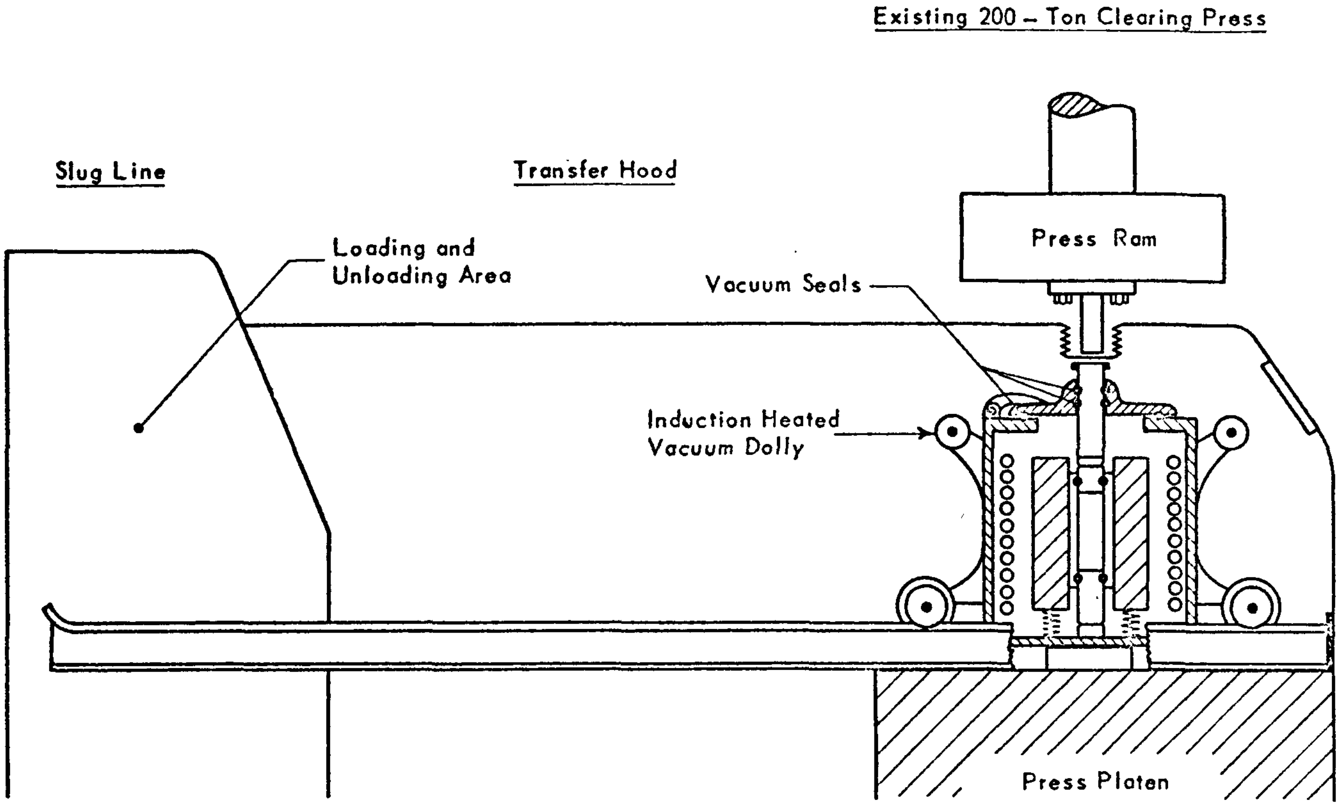

FIG. 6.4 SCHEMATIC DIAGRAM OF HOT PRESS ARRANGEMENT

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6.4.4 Pressing

As soon as the slug and die-liner assembly is loaded into the furnace, the vacuum pumpdown must begin. There are three reasons for the pumpdown: (1) The dodecanol that remains in the compacts may begin to burn rather than to distill, and leave a residue of carbon inside the slug that will interfere with a metallurgical bond. (2) The MoS_2 lubricant inside the die liner will oxidize, making disassembly after hot pressing very difficult. (3) The interior surfaces of the slug will oxidize, making bonding more difficult.

The furnace heat load is balanced at the pressing temperature when the slug is loaded, but a temperature drop of 20-30°C occurs when the cold die liner and slug are loaded. A period of 10 to 20 minutes is required for the slug to heat to the pressing temperature. The temperature is indicated by a thermocouple within the backup die, which must be calibrated by periodic comparisons with a probe that has thermocouples placed within a dummy slug. Satisfactory bonding may be achieved at temperatures as low as 540°C, if the dispersed oxide has a particle size distribution large enough that the aluminum powder particles do not become coated by the oxide. Preliminary runs, with ThO_2 as a stand-in for NpO_2, indicated that a temperature above 600°C was necessary for uniform bonding.(6.4) Subsequent metallographic examination of the ThO_2-Al slugs showed that the ThO_2 formed a powder layer between the core compact and the can wall, and high strength bonds could not be achieved until the slug temperature was made high enough that the ThO_2 was reduced by Al to form a bonding layer of $ThAl_3$. One slug containing NpO_2 was subsequently examined(6.5) and it was found that the particles were coarser than the ThO_2, and that bonding occurred by contact of the aluminum can to aluminum powder.

NpO_2 reacts rapidly with Al to form $NpAl_4$ and Al_2O_3 at temperatures above 615°C.(6.5) This reduction is accompanied by a 4.4% decrease in volume of reactants as calculated from the theoretical densities of reactants and products. This reduction is exothermic and hence is accompanied by an increase in slug temperature. The actual temperature rise encountered experimentally averaged 25°C during the reaction. The temperature rise that occurs in hot pressing is undoubtedly less than was observed experimentally, since the hot-pressing dies will conduct the heat from the slug. Above 649°C, the $NpAl_4$ and aluminum melt by a eutectic reaction. This molten eutectic follows the grain boundaries of the can to the outer slug surface, thereby penetrating the can wall. For this reason, the slug temperature must not be permitted to exceed 640°C during hot pressing.

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The force used in pressing the slug is not critical, but should be above 10 tons so that enough flash is extruded past the top plug to break up the oxide on the surfaces and produce good bonding at the interface between the end-cap and can at the top of the slug. Increasing the pressure beyond that required for good bonding serves no useful purpose, but tends to aggravate disassembly problems since more flash is formed between the plugs and die liner. The life of the die liners is also decreased by additional force since the stress-rupture life of the liner is exceeded.

Pressing time is fixed to allow time for densification of the core and bonding of the core to the can. The pressing time has a greater influence on the ease of disassembly than on the quality of the slug. Limits on the pressing time are selected on the basis of operating experience.

The disassembly clearance between the slug and "Inconel X" die liner is provided by the difference in coefficient of thermal expansion between the two materials. Aluminum has an average coefficient of thermal expansion of 26×10^{-6} per $^{\circ}$C. "Inconel X" has a coefficient of 16×10^{-6} per $^{\circ}$C. over the temperature range 25 to 600°C. In cooling from 600 to 25°C, the ID of the die liner shrinks from 0.954 to 0.946 inch. The slug OD shrinks from 0.954 to 0.940 inch, leaving sufficient clearance between the slug and die liner for disassembly.

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6.5 Cleaning of Hot-Pressed Slugs

After hot pressing, the slug, with flash intact, is cleaned in a hot caustic solution to remove residual surface lubricant. When the lubricant has been etched off, the slug is rinsed in cold water, then dipped in HNO_3 to neutralize the caustic and to remove the surface smut left by the caustic etch, and given a final rinse in cold water. The entire procedure is repeated in a second set of baths to remove residual surface contamination. The slug is then dried before the flash is trimmed.

The concentration and temperature limits on the "Oakite" No. 160 caustic etch were established to give a uniform rate of surface attack of about 0.001 inch per minute. A temperature above the limit causes a more rapid attack that may pit the slug surface. Too low a temperature will not clean the slug surface in the time allowed. Time and temperature of the HNO_3 dip are not critical, but need be only long enough to de-smut the slug to give a bright, clean surface. The use of deionized water in the rinse tanks is not necessary, since the slugs will receive a final cleaning just prior to shipment.

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6.6 Welding

The slug is trimmed to remove the flash and to prepare the top end for the weld. A gauging dimple is pressed into the top end cap during hot pressing so that the slug may be trimmed and rewelded several times, if necessary, to get a sound weld, before measurement of the cap thickness by radiography is required. If a slug is trimmed beyond the gauging dimple, it must be radiographed to determine the actual cap thickness before it can be trimmed further.

The slug is welded by a direct-current, straight-polarity, helium-shielded, tungsten arc. A sound weld is clean and bright with no evidence of cracks or porosity. The weld serves two purposes. It is an inspection step for the soundness of the top end cap because any volatile material trapped in the cap-can interface will result in a blowout or discoloration of the weld surface. Inclusions in the interface must be trimmed off before a sound weld can be made. The weld also serves as a final closure on the slug.

In-process weld control is maintained by destructively evaluating dummy weld samples. Dummy samples may be of solid aluminum bar stock, since the heat-affected zone on a NpO_2-Al slug does not extend below the top end cap.

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6.7 Inspection

The final inspection of the finished slugs provides maximum assurance that the slugs will withstand irradiation. Slugs that contain NpO_2 are not destructively examined for process control purposes because of the need to minimize the loss of NpO_2 and to minimize the delay in irradiating this material. Instead, slugs containing a substitute for NpO_2, are made periodically and examined destructively to provide the required process control data.

The first step in final inspection is the smear for surface contamination before the slug is removed from the cabinet line. This smear ensures that there is no danger of spreading contamination outside the line during subsequent handling. Those slugs having smearable surface contamination in excess of prescribed limits must be cleaned by recycling through the second decontamination baths, or by scrubbing, or both. Fixed, or nonsmearable alpha contamination of less than $5x10^6$ d/m on the slug surfaces will not affect either handling or inpile operation of the slugs.

The slugs are gauged for length, diameter, and bow to be certain that they can be satisfactorily assembled into housing tubes for irradiation.

Satisfactory bonding is demonstrated by a transmission-type ultrasonic nonbond test in which any discontinuities in the bond between the core-cladding interface can be detected. Any slug that fails the nonbond test may be re-pressed for recovery with no detrimental effect on slug quality. The nonbond tester is calibrated before each run by the use of standard slugs containing ThO_2 dispersed in aluminum. These slugs have mica inserts representing the maximum size of nonbond area that is acceptable and the minimum size of nonbond that is cause for rejection. The nonbond tester does not measure the physical strength of the bond zone; bond strength is determined by periodic destructive evaluation of dummy slugs.

The slug is radiographed at 90° intervals; the radiographs are examined a) to measure the cladding and end-cap thickness, b) to observe evidence of core run-out (smearing of core material along the cap-can interface during hot pressing), c) weld porosity, and d) inclusions in the can wall or end cap. Inclusions are cause for rejection if they are exposed on the outer cladding surface. Inclusions within the cladding are not cause for rejection of a slug

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unless the total thickness of the cladding on both sides of the inclusion is less than the limit on the minimum cladding thickness.

The slug is inspected visually to ensure that the surface is clean and free of pressing lubricants and has no excessive nicks, scratches or gouges that would reduce cladding thickness below the 0.020-inch minimum. The weld is visually inspected to assure that it is clean and free from shrinkage cracks and porosity visible from the outside surface.

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6.8 Re-pressing of Reject Slugs

Chemical reprocessing of reject slugs to recover the NpO_2 reduces the capacity of the target process described in Chapter 3.0 and several weeks are required to return the NpO_2 to the slug fabrication process. For these reasons it is desirable to recover rejected slugs within the fabrication process wherever possible. Tests with dummy slugs containing either ThO_2 or UO_2(6.6,6.7) showed that slugs rejected for the following defects could be recovered by re-pressing:

a) poor bonding
b) small diameters
c) marred surfaces
d) thin caps.

Slugs containing any of the defects except thin caps are recovered by simply re-pressing in the same manner as for the original slugs. These defects are repaired during re-pressing, and are accompanied by slight reductions in the minimum cladding thickness and the minimum cap thickness. These reductions are generally quite small, less than 0.007 inch for the cladding and less than 0.050 inch for the cap, and the slugs will pass all of the required quality standards.

Slugs with thin caps require the addition of a second cap to produce acceptable results; in this case re-pressing is carried out in two steps. The slug is first pressed to extrude the existing cap and can-wall into the flash recess at the bottom of the top punch. This flash forms a cup-like depression in the top of the slug into which the second cap is placed. The slug is then re-pressed a second time to bond the new cap to the slug. This method of recovery is effective only if the original cap is at least 0.100 inch thick; in this case the residual cladding thickness after recovery will be at least 0.020 inch. On a slug whose original cap is less than 0.100 inch, the residual cladding thickness at the cap-can interface may be as low as 0.005 inch after re-pressing, which is unacceptable.

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6.9 Final Cleaning

Metals that are cathodic to aluminum will plate out on aluminum surfaces. Such deposits will result in local galvanic corrosion between the deposit and the aluminum and cause pitting of the aluminum surfaces. This phenomenon is insidious and, for example, the copper that is dissolved from tubing carrying process water may be sufficient to cause damage by corrosion. Aluminum is also susceptible to attack by heavy metallic salts of mercury, cobalt, lead or nickel; when present, these salts promote pitting attack.(6.8) For this reason, the slugs are cleaned in nitric acid to remove any metallic contamination that may have occurred during processing. Contact between the slug and materials that cause pitting corrosion, whether in the form of pure metals, alloys, or solutions, should be avoided at all stages in the fabrication process.

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6.R References

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7.0 SAFETY ASPECTS

7.1 Resin Decomposition

Standard explosive tests applied to "Permutit" SK and "Dowex" 1-X4 resins have demonstrated that the nitrate forms are explosive if the resin is dry.(7.5) "Permutit" SK detonated in the falling hammer test. Closed bomb tests showed that the explosive force developed by "Permutit" SK was twice that of "Dowex" 1-X4. A wet sample of "Dowex" 1-X4 did not react in a closed bomb test at temperatures up to 200°C; similar results have been obtained with wet "Permutit" SK.

Since the resins are safer wet than dry, the resin beds should be kept wet at all times. The reaction rate is temperature dependent, but the latent heat consumed in the evaporation of interstitial water limits the temperature and thus limits the reaction rate to low values where the decomposition is not hazardous.

The rates of reaction and the gaseous products formed have been measured at SRL by isothermal pyrolysis of the dried nitrates of both "Dowex" 1-X4 and "Permutit" SK. The heats of reaction calculated from a study of the gas analyses were 250 cal/gm for "Dowex" 1-X4 and 310 cal/gm for "Permutit" SK. For comparison, the value for tributyl phosphate (TBP), the solvent used in the Purex process, is 180 cal/gm. The energy release of all three materials is sufficient to generate hazardous chemical degradation. Two slow and identical reaction rates have been observed for both resins. "Permutit" SK contained a third faster specie which was a significant fraction of the total. No significant fast specie was observed with "Dowex" 1-X4. The faster rate observed for "Permutit" SK confirms the results of the explosive tests.

Resin such as "Dowex" 1-X4 exposed to HAWC in the recovery of neptunium may receive a total dose estimated about 1.5×10^7 R before it is removed from the resin bed for disposal. Radiolysis of the resin decreases the thermal stability. Dried samples of the nitrate form of "Dowex" 1-X4 irradiated to 10^8 and 10^9 R were exploded at furnace temperatures of 128 and 88°C, respectively. Unirradiated resin did not explode at 140°C. "Dowex" 1-X4 resin irradiated to 10^9 R and wet with 8M nitric acid reacted violently at 100°C. The reaction products foamed out of the sample container and solidified. Solids generated in this manner could plug process pipes. When the acid resin slurry was made alkaline, foaming did not occur.

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Safety considerations indicate that the total radiation dose received by anion exchange resins should be limited to 10^9 R. However, the loss of exchange capacity limits the resin irradiation level to about 10^8 R. Since there is no process requirement which necessitates heating the acid form of the resin above 55°C, limitation of maximum temperature to 60°C covers both process considerations and safety aspects.

The neutralization of resin prior to discharge to the waste tanks or the digestion of resin in alkaline permanganate eliminates the hazard of resin-induced explosion in the waste tank.

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7.2 Hydrazine - Hydrazoic Acid

Hydrazine is important in the recovery of neptunium and in the target process primarily because it is capable of reacting rapdily with nitrous acid and consuming it without the excessive evolution of gas that occurs in the reaction of ferrous sulfamate with nitrous acid. The rate of reaction of hydrazine with nitrous acid is much faster than that of sulfamic acid with nitrous acid. Although hydrazine will not reduce Np(V) to (IV), the reducing action stabilizes Np in the (IV) state.

Because hydrazine is unstable under certain conditions, an understanding of the physical properties and pertinent reactions is necessary. Reactions by which hydrazoic acid, HN_3, is formed are particularly important because hydrazoic acid is potentially of more concern than hydrazine.

7.2.1 Hydrazine

Hydrazine is completely miscible with water and forms a weak base(7.1) as follows:

$$N_2H_4 + HOH \rightleftharpoons N_2H_5OH \rightleftharpoons N_2H_5^+ + OH^-$$

In dilute aqueous solution hydrazine slowly decomposes to ammonia, nitrogen, and hydrogen according to the reaction,

$$3N_2H_4 \longrightarrow 2NH_3 + 2N_2 + 3H_2$$

At high pH, the decomposition products are nitrogen and hydrogen. Concentrated nitric acid oxidizes hydrazine to nitrogen, ammonia, and water(7.1) as expressed by the equation.

$$4N_2H_4 + O_2 \longrightarrow 2N_2 + 4NH_3 + 2H_2O$$

Some hydrazoic acid is also formed. In alkaline solution, hydrazine is quite unstable and is readily oxidized.

Hydrazine is both a reducing and an oxidizing agent. The potentials of some of the half-cell reactions have been reported.(7.2) In general the oxidation of hydrazine to nitrogen is quantitative, but many oxidizing agents which gain one electron per molecule react with hydrazine to form both nitrogen and the ammonium ion, NH_4^+, in the ratio of one to two. Thus, in the presence of ferric ions,(7.2)

$$N_2H_5^+ + Fe^{+++} \longrightarrow Fe^{++} + 1/2N_2 + NH_4^+ + H^+$$

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Reduction to ammonia is observed with Zn, Sn, Sn^{++}, and Ti^{+++}. With some oxidizing agents ammonia and hydrazoic acid are formed. Although hydrazine is relatively stable in mild acid solution, the decomposition is catalyzed by Cr^{+++}, Fe^{+++}, Cu^{++}, Al^{+++}, Ni^{++}(7.1).

Hydrazine solutions are nonexplosive and pure liquid hydrazine cannot be ignited by a hot wire.(7.3) Aqueous solutions of hydrazine are not sensitive to impact, friction, or detonation but some materials of construction are to be avoided. Hydrazine nitrate solutions above 50% nitrate are sensitive to impact; therefore, evaporation of solutions containing hydrazine and nitrate ion must be avoided. Alkaline evaporation is not considered hazardous because the hydrazine ion is unstable and decomposes to N_2 and H_2.

Solutions of hydrazine - hydrazine nitrate that contain 30% water show no decomposition when heated to 121°C.(7.3) Slow decomposition of 0.1M hydrazine occurs in strong nitric acid at 60°C. On a large scale this reaction may present troublesome off-gas rates and foaming.

Thirty per cent hydrazine nitrate, pH 6, is proposed for use at SRP because of its stability, ease of handling, and the potential hazards involved in adding concentrated hydrazine solutions to strong nitric acid. After two months of normal exposure to light and air at 23°C, no decomposition of a sample of 30% hydrazine nitrate could be detected. Little or no decomposition is anticipated in plant storage at 30-40°C.

Hydrazine vapor has caused serious discomfort to the eyes and temporary blindness, but no permanent injury resulted. Although inhalation of the vapors may cause dizziness and nausea, the sharp irritating odor is so intolerable that it becomes impossible to breathe quantities sufficient to cause permanent damage. Some persons react to hydrazine vapors with a form of dermatitis. Evidence that long, repeated exposure to hydrazine caused attack of the liver cytoplasm has been observed. Dr. Stephen Krop of the Army Chemical Center(7.3) reports that the toxicity of hydrazine is in a class with phosgene and cyanides.

Aqueous solutions of hydrazine are no more hazardous to handle than any strong acid or base and similar precautions should be used.(7.6) Any contact of liquid hydrazine with the skin should be immediately washed with soap and water. If the eyes are exposed to the liquid or vapor they should be flushed with copious quantities of water. If hydrazine is accidentally taken into the mouth and swallowed, for immediate first aid, the mouth should be flushed with water and an emollient, followed by a mild emetic. The patient should be kept quiet and a physician called at once.

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If clothing should come in contact with hydrazine, the clothing should be immediately removed and washed with water to reduce fire hazard. The clothing should be thoroughly washed before being reused.

If sufficient ventilation is provided in the work area so that no odor of hydrazine is noticed, no exposure effects will be encountered. If it is necessary to enter an area where a high concentration of vapor exists, an ammonia gas mask will provide adequate protection. Protective clothing such as rubber apron, rubber gloves, and face shield should serve to reduce the hazard arising from accidental spills.

The materials of construction for use with hydrazine solutions are selected primarily to avoid the problem of decomposition of the hydrazine. Metals that form oxides which can flake off and accumulate in the bottom of the vessel are to be avoided. Aluminum is satisfactory, but where acids are likely to be present, Type 304 stainless steel is recommended. Reference is made to the catalytic effect of molybdenum on the decomposition of 100% hydrazine, but this is small and may not be of importance with a 30% solution. Mathieson(7.4) recommends the use of Type 304 stainless steel.

7.2.2 Hydrazoic Acid(7.7,7.8)

Nitrous acid can react with hydrazine to form hydrazoic acid. Hydrazoic acid is easily detected in solutions of nitric acid that contain Fe(III) because of the formation of the ferric azide complex, FeN_3^{++}, which gives a reddish-brown color to the solution. Since the characteristic color was observed in solutions in laboratory experiments, it was necessary to study the hazards of hydrazoic acid, the conditions relating to the formation of hydrazoic acid, and finally to determine whether or not hazardous quantities of hydrazoic acid could be formed in the process. Under the conditions proposed for the process, competing reactions limit the quantity of hydrazoic acid formed to concentrations which are not considered hazardous.

The lower explosive limit for aqueous solutions of hydrazoic acid is 17%. This concentration can be attained only through condensation of vapors that are formed by the distillation of solutions that contain at least 0.05M HN_3 at 20°C. At normal process temperatures (40°C) more water is equilibrated so that solutions containing 0.05M HN_3 deposit condensate that is within safe concentration range.

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A lower limit of hazardous concentration of HN_3 in air was estimated by calculating the pressure increase for adiabatic constant volume decomposition. Vapor-liquid equilibrium data were also calculated. These data show that solutions containing less than 0.05M HN_3 cannot evolve sufficient HN_3 into the vapor phase at any temperature to damage a run tank, even if a spontaneous chemical reaction should occur.

Process solutions may contain mixtures of HN_3 and mercuric nitrate, and under certain conditions mercuric azide is explosive. Laboratory tests show that spontaneous detonation can occur when the solvent is water and the concentration of mercuric azide is about 0.023M. Spontaneous detonation does not occur at concentrations less than 0.02M mercuric azide even with water as the solvent. Precipitates form less readily in acidic solutions; concentrations of 0.16M HN_3 and 0.08M Hg were necessary to form a precipitate in 5M HNO_3. The precipitates formed in acidic solutions could not be detonated if they remained covered with solution. Removed and dried, the precipitates spontaneously detonated.

An analytical method was developed which permitted the simultaneous analysis of hydrazoic acid and ferric ion or the analysis of each component separately.(7.9) The method employs spectrophotometric measurement of the ferric azide complex and determination of the concentration of acid. The method was applied to simulated and to actual process solutions to determine the extent of conversion of hydrazine to hydrazoic acid.

No hydrazoic acid was formed after 3 days at 23°C in 4-7M HNO_3 containing 0.05-0.2M N_2H_4. Measurable amounts of hydrazoic acid were formed in solutions of nitric acid that contained hydrazine and ferrous sulfamate. The rate of formation of hydrazoic acid in synthetic process solutions depends on the concentration of HNO_3 and ferrous sulfamate, and the temperature. The final concentration of hydrazoic acid depends on the concentration of hydrazine and ferrous ion. A direct relation exists between the oxidation of ferrous ion to ferric ion and the formation of HN_3 from N_2H_4, since no increase in the concentration of HN_3 occurs after all of the ferrous ion has been oxidized.

The slow reaction between nitric acid and ferrous ion to form nitrous acid is well known. It is also known that nitrous acid reacts with hydrazine to form hydrazoic acid. Undoubtedly the formation of hydrazoic acid in solutions of nitric acid that contain low concentrations of ferrous sulfamate and hydrazine occurs, according to the general equations

[redacted]

[redacted]

$$2Fe^{++} + HNO_3 + 2H^{+} \longrightarrow HNO_2 + 2Fe^{+++} + H_2O \quad \text{(Slow)} \qquad (1)$$

$$HNO_2 + N_2H_4 \longrightarrow HN_3 + 2H_2O \quad \text{(Rapid)} \qquad (2)$$

However, hydrazoic acid also reacts with nitrous acid according to the equation

$$HNO_2 + HN_3 \longrightarrow N_2O + N_2 + H_2O \quad \text{(Rapid)} \qquad (3)$$

Reactions (1-3) have been verified in the laboratory. In Reaction (2) if the ratio of N_2H_4 to HNO_2 is large, one mole of HN_3 is produced for each mole of HNO_2. Thus in a system initially containing equimolar quantities of Fe^{++} and N_2H_4, theoretically 50% of the N_2H_4 could be converted to HN_3. However, in practical process solutions the concentration of N_2H_4 is low, and during the reaction the concentration of HN_3 increases sufficiently so that Reaction (3) becomes important in competing for the nitrous acid. Since the rates of Reactions (2) and (3) are comparable, the actual yield of HN_3 is considerably less than 50% conversion of the N_2H_4. Actually a maximum yield of 25% HN_3 was found in synthetic solutions containing initially 0.05M N_2H_4 and 0.05M $Fe(NH_2SO_3)_2$ in nitric acid. In process solutions, additional nitrous acid is produced because of radiation, but laboratory tests showed that with an excess of HNO_2 the concentration of HN_3 goes through a maximum of 0.012M for solutions that contained 0.05M N_2H_4.

The safety of the target and virgin Np recovery processes, with respect to hydrazoic acid, was determined by analyzing actual process solutions that were most likely to contain the maximum concentration of HN_3.

In the target process, the most susceptible point occurs when the partitioning solution, containing Pu^{238} from the second anion exchange cycle, is heat-killed to prepare feed for the subsequent anion exchange purification of Pu^{238}. Actual process samples from the interim facility has been analyzed at this step. The results are shown in Figure 7.1. In addition, Figure 7.2 shows these results and compares them with concentrations calculated from the reaction mechanism, with concentrations measured in synthetic solutions, and with the maximum safe concentrations. It can be seen that all of the values are well below the conservative safe limits.

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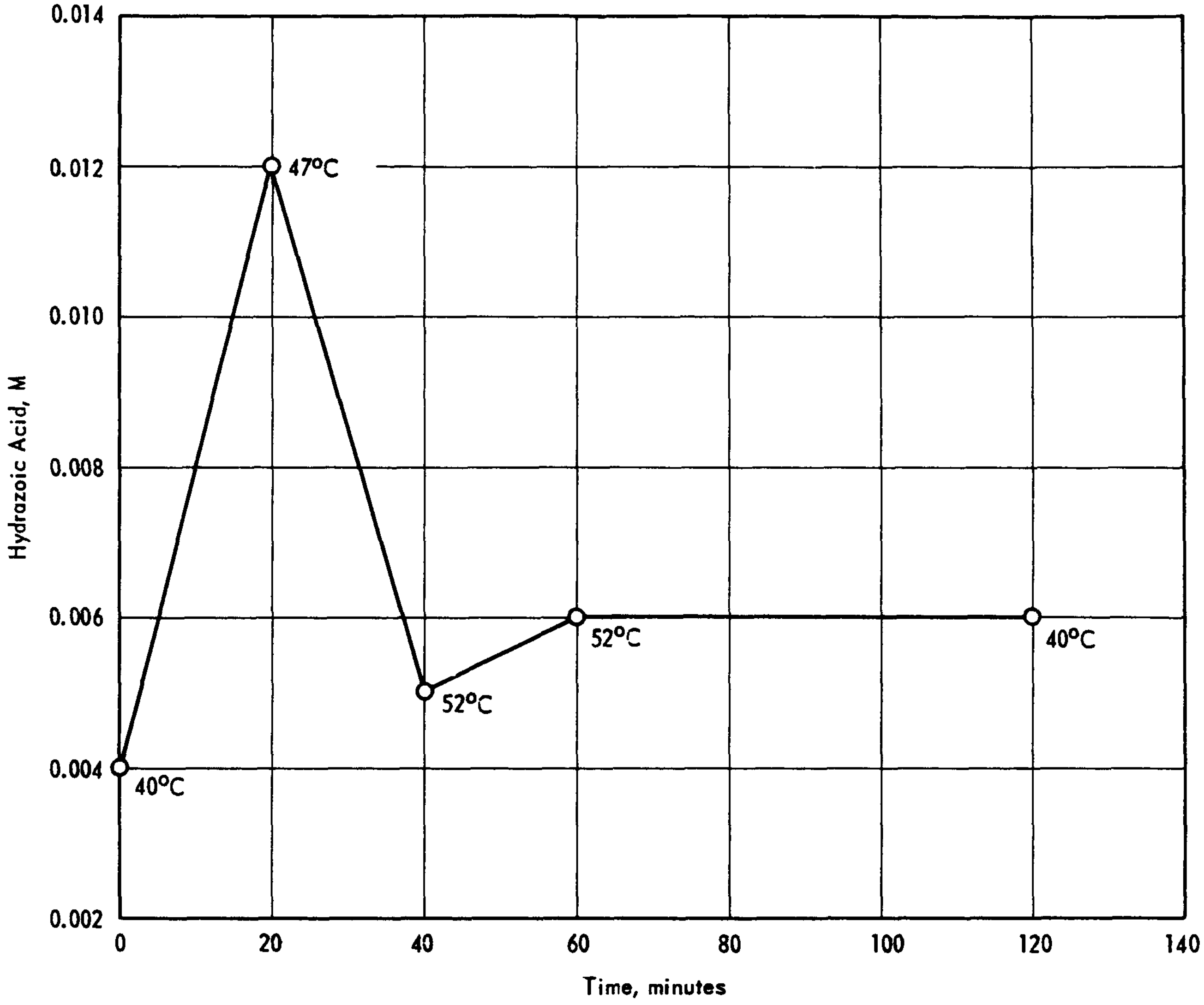

FIG. 7.1 HYDRAZOIC ACID IN FEED SOLUTION FOR Pu^{238} PURIFICATION

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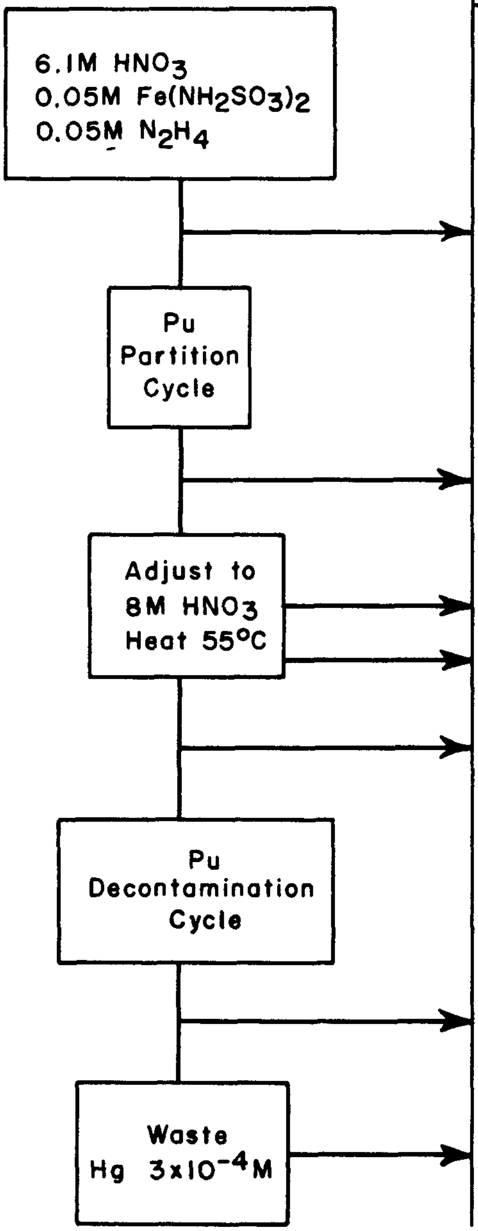

Hydrazoic Acid, M			
Synthetic Solution		Process Solution	Safe Concentration
Calculated	Found		
0.012	0.007	—	0.05
0.012	0.004	—	0.05
0.009	0.003	0.006	0.05
0.012	0.0016	0.012	0.05
0.012	0.0016	0.006	0.05
0.012	0.0016	—	0.05
0.01	—	—	0.02 (Hg ppt)

FIG. 7.2 HYDRAZOIC ACID IN TARGET PROCESS

[redacted]

[redacted]

In the recovery of Np from Purex HAWC, the maximum concentration of HN_3 occurs after the addition of N_2H_4 and $Fe(NH_2SO_3)_2$ if the solution is allowed to stand for se~~v~~veral hours. An actual sample of Purex HAWC was adjusted for Np absorption and the HN_3 concentrations were measured. Six hours after hydrazine was added the concentration of HN_3 reached a maximum of 0.01M; the concentration decreased to 0.001M after 20 hours.

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7.3 Aluminum Powder

Type 101 aluminum powder is combustible at airborne concentrations greater than 1.1 grams per cubic foot.(7.10) The rate of propagation is not sufficient to generate a high blast pressure, but more nearly approximates a rapid burning. Once ignited, bulk quantities of the powder will continue to burn. The powder is not subject to spontaneous ignition in air, but sufficient heat for ignition may be generated by reaction with water if bulk quantities are stored in a moist condition.

Several precautions are necessary in handling the powder. Stored powder is to be left in the shipping container with the lid fixed in place. Storage must be in an area where there is no danger of flooding with water. Transfer and weighing of the powder is to be done in an area where there is no sparking equipment or open flame. Working areas outside the containment line must be kept clean of dust accumulations. Within the part of the containment line in which the bulk powder is handled, all electrical equipment must be of the explosion-proof type and must be grounded. All hand tools used should be of a nonsparking material. Cleanliness in the working areas is essential and accumulations of fines from dusting must not be permitted.

In the event of an aluminum powder fire, water must be avoided, since contact can result in a severe explosion due to the release of hydrogen. CO_2 will not extinguish an aluminum fire but will support the combustion. The best procedure is to use a "Metal-X" type fire extinguisher. A suitable alternative is to bank the fire with sand and permit it to burn itself out.

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7.R References

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