AQUEOUS REPROCESSING OF REACTOR FUEL

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I. INTRODUCTION

Periodic reprocessing of reactor fuel is necessary for the purpose of removing fission products in order to maintain satisfactory neutron economy and to recover fissionable and fertile nuclides for fuel element refabrication. Reprocessing is also frequently necessitated by structural damage which occurs at high fuel burn up.

The fission products which are important in reprocessing may, for convenience, be divided into two groups: (a) radioactive or stable fission products which have high thermal neutron capture cross section, notably krypton, xenon, and some of the rare earths and (b) radioactive isotopes of relatively long half-life and significant yield.

In the case of the first group, high fission product decontamination factors are essential if the recovered material is to be refabricated as a nuclear fuel, and in the second group, a high degree of decontamination is desirable if expensive remote handling fuel refabrication procedures are to be avoided. In general, a high degree of fission product decontamination is achieved by aqueous reprocessing rather than by alternative high-temperature processes (16, 49, 66, 109, 121, 123, 145, 191). Besides offering greater fission product decontamination, aqueous methods also provide greater operational flexibilities. This paper will review the various aqueous processing methods which have been developed and used for reprocessing reactor fuels.

The present review covers the literature up to August 15, 1965, giving particular emphasis on the work published in open journals. Several reviews (40, 51, 55, 57, 58, 107, 119, 219) appeared which do not deal with the basic chemistry of all the aqueous processes.

The following abbreviations will be adopted.

K	Equilibrium constant
$K_{o/a}$	Partition coefficient
M	Actinide metal ion
X	Acid anion
B	Free base amine
TBP	Tri-*n*-butyl phosphate
DBP	Di-*n*-butyl phosphate
Butex	β,β'-Dibutoxyldiethyl ether
TTA	Thenoyltrifluoroacetone
DNOA	Di-*n*-octylamine
TNOA	Tri-*n*-octylamine
TIOA	Triisooctylamine
DTDA	Di(tridecyl)amine
MNDDA	Methyl-*n*-didecylamine

II. URANIUM–PLUTONIUM FISSION PRODUCT PROCESSES

Naturally occurring uranium contains 0.7% of the fissionable isotope uranium-235. The remainder, uranium-238, after neutron absorption gives rise to fissionable plutonium-239.

$$\underset{\substack{n\downarrow \\ \text{fission} \\ \text{products}}}{\text{U-235}} \quad \text{U-238} \xrightarrow{n} \underset{\substack{23.5 \\ \text{min}}}{\text{U-239}} \xrightarrow{\beta^-} \underset{\substack{2.33 \\ \text{days}}}{\text{Np-239}} \xrightarrow{\beta^-} \text{Pu-239} \qquad \text{(Eq 1)}$$

After short cooling times the neptunium-239 will have decayed, spent fuel elements will contain uranium and plutonium which will require recovery and purification, and fission products must be isolated for disposal. Some idea of the quantities involved can be gauged from the formulations: from 1 kg of natural uranium irradiated for 300 days at a flux of 10^{13} neutrons/cm^2 sec (*i.e.*, an irradiation of $1000MWD/T$), approximately 1 g of uranium-235 will have undergone fission to produce a similar mass of fission products, and just under 1 g of plutonium-239 will have been produced from irradiation of the uranium-238. The

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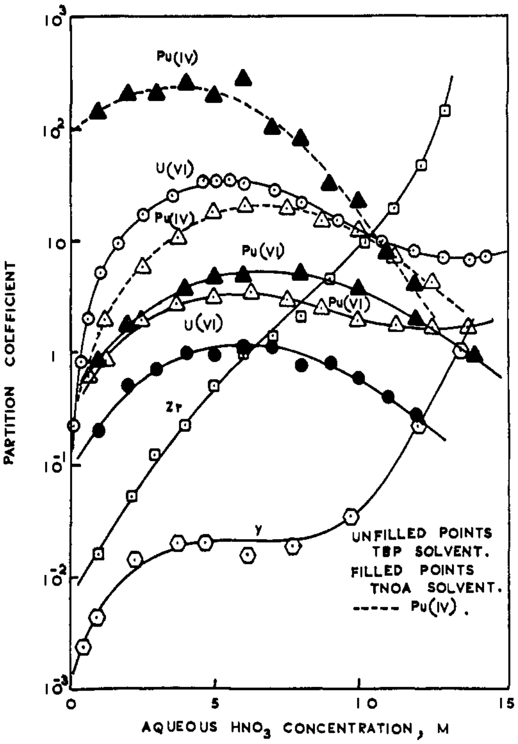

Figure 1.—The partition coefficients of tetra- and hexavalent uranium, plutonium, and fission products with TBP and TNOA from varying nitric acid concentrations: U and Pu, 19% TBP in kerosine (4); Zr, 19% TBP in kerosine (5); Y, 19% TBP in kerosine (173); U and Pu, 10% TNOA in xylene (112).

total fission product activity immediately after irradiation will be approximately 2 kcuries and will decay about a quarter of the value after 100 days.

Enriched uranium-235 fuels will necessarily produce less plutonium, but the necessity for efficient recovery of the unburnt uranium will be even more important. Enriched fuels are frequently alloyed with other metals—particularly aluminum from which separation must also be effected in reprocessing; much higher fission product activities per unit mass of fuel will also be present.

A. ALKYL PHOSPHATE SOLVENTS

1. *Extraction from Nitrate Media*

The mechanism for the extraction of inorganic nitrates with TBP has been extensively and systematically investigated by many workers (3–5, 42, 72–74, 76, 91–94, 99–102, 131, 132, 137, 139, 167). The nitrates are extracted as neutral molecular species with a definite number of attached TBP molecules in the case of the most commonly and widely studied alkyl phosphate solvent, TBP.

The complexes for the different actinides have been established (4, 22, 98–100, 137) as: trivalent, $M(NO_3)_3 \cdot 3TBP$; tetravalent, $M(NO_3)_4 \cdot 2TBP$; hexavalent, $MO_2(NO_3)_2 \cdot 2TBP$.

In the extraction of metals from nitrate media by a solution of TBP in a suitable diluent, *e.g.*, kerosine, the important species present are: (i) aqueous phase: H^+, M^{x+}, NO_3^-, and complexes $M(NO_3)^{(n-1)+}$, $M(NO_3)_2^{(x-2)+}$, . . ., etc., of which mostly the neutral complex $M(NO_3)_x$ and to a slightly lesser extent $HM(NO_3)_{x+1}$ and $H_2M(NO_3)_{x+2}$ are extractable by TBP; (ii) organic phase: TBP, diluent molecules, $HNO_3 \cdot TBP$, $M(NO_3)_x \cdot y TBP$, $HM(NO_3)_{x+1} \cdot y TBP$, and $H_2M(NO_3)_{x+2} \cdot y TBP$.

To a first approximation the extraction system may be represented as

$$M^{x+}_{aq} + xNO_{3aq} + yTBP_{org} \rightleftharpoons M(NO_3)_x \cdot yTBP_{org} \quad \text{(Eq 2)}$$

equilibrium constant

$$K = \frac{[M(NO_3)_x \cdot yTBP]_{org}}{[M^{x+}]_{aq}[NO_3^-]^x_{aq}[TBP]^y_{org}} \quad \text{(Eq 3)}$$

and partition coefficient

$$K_{o/a} = \frac{[M(NO_3)_x \cdot yTBP]_{org}}{[M^{x+}]_{aq}} \quad \text{(Eq 4)}$$

$$= K[NO_3^-]^x_{aq} \cdot [TBP]^y_{org} \quad \text{(Eq 5)}$$

The above treatment is only approximate and true only for dilute solution. The nitric acid employed can seldom be described as dilute, although frequently the TBP concentration may be considered so (5% TBP solutions) and

$$K_{o/a} \propto [TBP]^y_{org} \quad \text{(Eq 6)}$$

i.e., the partition coefficient is proportional to the power of the TBP concentration corresponding to the number of TBP molecules attached to the extracted complex. This feature represents one method whereby the composition of the extracted complex may be determined. In actual practice difficulties arise in interpretation of the slopes of logarithmic partition coefficient *vs.* TBP concentration plots owing to different solvates formation and nonideality of the system (146, 152, 153, 162, 173). In higher acid concentration—greater than 4 *M* HNO_3—the extraction mechanism changes and more complicated species of the actinides such as $yTBP \cdot HM(NO_3)_6$ and $yTBP \cdot H_2M(NO_3)_6$ are formed (63, 186). The extractibility of the complex acid $H_2M(NO_3)_6$ is favored in the lower acid concentration in the sequence $Th^{4+} > U^{4+} > Pu^{4+}$ according to the stability of the complex $[M(NO_3)_6]^{2-}$ for this series of elements. The formation of third phase with uranyl nitrate–TBP extraction is attributed due to the formation of $H \cdot [UO_2(NO_3)_3] \cdot 2TBP$ (188).

The fission products, zirconium, niobium, ruthenium, and rare earths, show a similar extraction mechanism to that of actinides with TBP in nitric acid solutions (35, 62, 72, 74–76, 91, 99, 149, 162, 173). Two solvates

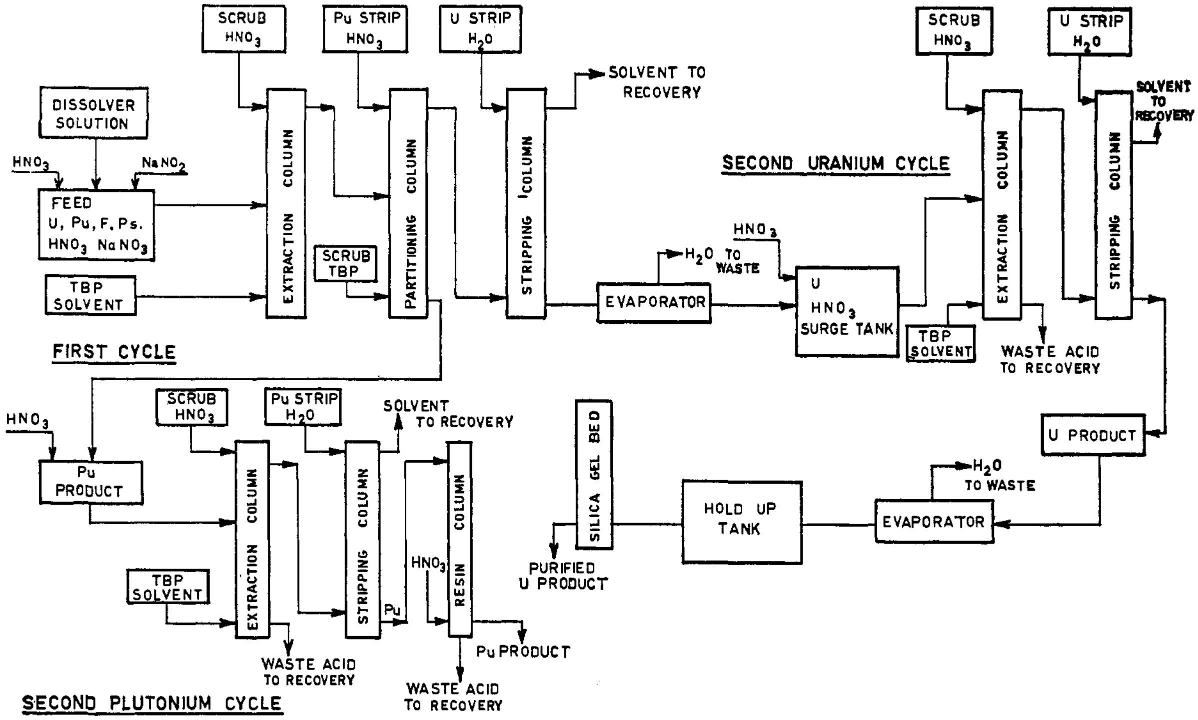

Figure 2.—Purex flow sheet of extraction of U and Pu (70).

of zirconium having the composition, $Zr(NO_3)_4 \cdot TBP$ and $Zr(NO_3)_4 \cdot 2TBP$ are formed with varying TBP concentrations from nitric acid solutions (62).

Of the different series of nitrato and nitro complexes of ruthenium only the nonionic trinitrato complex and the tetranitrato acid of nitrosyl ruthenium are fairly extractable by TBP (72, 74–76, 149). The species formed in the organic phase are confirmed to be $RuNO(NO_3)_3(TBP)_2$ and $H[RuNO(NO_3)_4](TBP)_3$ (3, 35, 74, 76).

The partition coefficients of different actinides and fission products with TBP as a function of aqueous nitric acid concentration are plotted in Figure 1 from the data of several workers (4, 5, 35, 112, 173). In the case of tetravalent and hexavalent actinides the partition coefficient increases with increasing nitric acid concentration. At higher acid concentrations the partition coefficient passes through a maximum and then falls. In the case of zirconium and yttrium the partition coefficient increases with higher nitric acid concentration. The partition coefficient of cerium(III) at first increases with increased acid concentration and then falls at approximately 3 *M* HNO_3 but again rises at higher acid concentration.

McKay (137) reported that by replacement of nitric acid with an inorganic nitrate such as $Al(NO_3)_3$, the partition coefficient increased sometimes by a factor of as high as 10^3. Differences in the extractability between the different valence states are frequently high, and frequent use is made of this feature in separation processes as, for example, the reduction of plutonium as a means of stripping this element from the solvent phase (70).

Several processes (55, 57, 70, 80, 81, 84, 106, 107, 158, 159, 174, 178, 194, 198, 213, 214) for the separation of uranium, plutonium, and fission products have been developed and placed in operation in various countries. They usually involve the following basic steps: (i) dissolution of the fuel elements in excess nitric acid; (ii) extraction of uranium(VI) and plutonium(IV) by the solvent leaving the fission products in the aqueous raffinate; (iii) stripping of the plutonium(III) with such reagents as ferrous sulfamate, hydroxylamine, or better still uranous ion; (iv) stripping of uranium by back-washing with very dilute acid.

Typical of many such uranium–plutonium recovery processes using TBP is the Purex process described by Flanary (70). In this process in Figure 2 sodium nitrate was added to the solution from the dissolver to act as a salting-out agent. The uranium and plutonium were extracted by 30% TBP in the first extraction column leaving the fission products and sodium nitrate in aqueous raffinate. The plutonium was stripped by reduction to plutonium(III) from the solvent in the second column of the primary process and passed to a second plutonium cycle for additional purification and concentration by solvent extraction and anion exchange. In the third column of the primary process the uranium was stripped with water and passed to a second uranium solvent extraction cycle for further purification and concentration. This process was followed by the earlier Redox process (57, 120) which

TABLE I

SUMMARY OF THE PUREX AND MODIFIED PUREX PROCESSES FOR REPROCESSING URANIUM FUELS

Process	Fuel type	Organic solvent	Aqueous solvent	Country	Ref
Purex	Natural uranium	30% TBP	1.0 M HNO_3	U. S. A. Japan	57, 70
Purex (Dounreay)	Enriched uranium–aluminum alloy	5 and 20% TBP	1.2 M nitrate, acid-deficient	U. K.	40
Purex (Fontenay aux-roses)	Natural uranium	40%	1.4–1.7 M HNO_3	France	84, 158
Purex (JENER)	Natural uranium	20% TBP	3.0 M HNO_3	Norway	17
Modified Purex	Enriched uranium	5–12% TBP	HNO_3 deficient, 1.33 M $Al(NO_3)_3$	U. S. A.	159
Modified Purex process	Natural uranium	20% TBP	5.0 M HNO_3, $Fe(NO_3)_3$	U. S. S. R.	178
Modified Purex	Natural uranium	29.3% TBP in CCl_4	HNO_3	U. S. S. R.	156
Modified Purex	Natural uranium	30% TBP	1.0 N HNO_3, $NaNO_2$	India	174
Modified Purex	Natural uranium	30% TBP	HNO_3	Sweden	80, 81
Modified Purex	Enriched uranium	10% TBP	2.24 M HNO_3	U. S. A.	159

employed extraction from an acid-deficient medium by methyl isobutyl ketone.

Solvent extraction from a nitric acid medium by Butex (107) was the basis of the first processing plant at Windscale in the United Kingdom, but in subsequent plants this solvent has been replaced by TBP (40). Some of the features of TBP extraction systems used for reprocessing uranium fuels are summarized in Table I. Extensive work on the modification and improvement of the Purex process, due to which the development of the above processes have been possible, has been studied by a number of workers (17, 65, 67, 71, 97, 110, 132, 135, 154, 183, 193, 198).

The complication in TBP–nitrate solvent extraction systems which are encountered are: (i) interference in the extraction process by dibutyl phosphate and monobutyl phosphate which is formed in the solvent by radiation decomposition of TBP. Uranium, for example, forms a hexacoordinated polymeric complex with dibutyl phosphate of the composition $[UO_2(DBP)_2]_n \cdot 2HDBP$ (35) which has high partition coefficient at low acidity and is responsible for the retention of uranium in the stripping stage. Plutonium also forms complexes which are difficult to strip.

(ii) Some fission products, notably ruthenium, zirconium, and niobium, show measurable extraction with TBP (35, 62, 72, 74–76, 91, 99, 162, 173). Zirconium and niobium are more strongly extracted (93) by DBP than uranium. Karraker (111) has reported increased fission product decontamination factors by operation at elevated temperature due to higher scrubbing efficiency for these elements. Decontamination factors of 3×10^6 obtained by operation of a two-cycle TBP process at 20° were increased to 2×10^8 by operation at 70°.

2. Extraction from Sulfate Media

Less work has been done using sulfuric acid as a medium for reprocessing irradiated uranium fuels than has been done using nitrate, although in the case of uranium extraction from ores the reverse is the case.

The recovery of uranium (148) from stainless steel fuel elements was shown to be possible by dissolution in sulfuric acid followed by the addition of nitric acid to make the solution 3 M HNO_3 and extracting with 10% TBP. In the modified Purex process for zirflex and sulfex processes (85), the stainless steel clad uranium fuels were dissolved in 8 N H_2SO_4 and the uranium and plutonium are extracted with 30% TBP in Amsco. The gross γ-decontamination factors of 1.5×10^4 for uranium and 5×10^3 for plutonium products were obtained.

B. AMINE SOLVENTS

While extensive studies have been made on the potential use of amines in uranium ore processing (34, 54, 56, 161), much less work has been done on the possibility of employing amine as extractants for irradiated fuel reprocessing. Amines offer certain advantages as solvents by comparison with alkyl phosphates in processing irradiated fuels due to the greater radiation susceptibility of the latter. The radiation induced decomposition products of amines are relatively innocuous in sharp contrast to alkyl phosphates, and in addition are soluble in aqueous media so that decomposition products do not accumulate in the organic phase.

The mechanism for the extraction of metal ions by amine solvents can be and frequently is considered (15, 43, 53, 208, 217) as a process analogous to anion exchange; hence the term liquid exchangers (52) is applied to amines.

The anion-exchange mechanism of extraction can be represented as

hexavalent actinides

$$MO_2X^{-m}{}_{(m+n)\mathrm{aq}} + mBHX_{\mathrm{org}} \rightleftharpoons (BH)_m \cdot MO_2X_{(m+n)\mathrm{aq}} + mX^-{}_{\mathrm{aq}} \quad \text{(Eq 7)}$$

tetravalent actinides

$$\mathrm{MX^{-m}}_{(m+n)\mathrm{aq}} + m\mathrm{BHX_{org}} \rightleftharpoons \mathrm{(BH)}_m\mathrm{MX}_{(m+n)\mathrm{org}} + m\mathrm{X^-}_{\mathrm{aq}} \quad \text{(Eq 8)}$$

Metal cations forming anionic complexes with acid ligands are favorably extracted (50, 52, 114) by amine solvents. The formation of the anionic species in the aqueous phase is not an essential prerequisite for the extraction of the cations by amines—rather these species may be formed in the organic phase (124, 125). Besides the anion-exchange mechanism the hydrogen bonding of the anionic complexes of the metal with the proton of the alkylamine salts plays significant contribution to the bonding according to the views of Keder and Wilson (114) and Ryan (165, 166).

Some authors (50, 51, 53), notably Verstegen (211), oppose this treatment and favor the mechanism of adduct formation, more properly described by

hexavalent actinides

$$\mathrm{MO_2X}_{n\mathrm{aq}} + m\mathrm{BHX_{org}} \rightleftharpoons \mathrm{(BH)}_m\cdot\mathrm{MO_2X}_{(m+n)\mathrm{org}} \quad \text{(Eq 9)}$$

tetravalent actinides

$$\mathrm{MX}_{n\mathrm{aq}} + m\mathrm{BHX_{org}} \rightleftharpoons \mathrm{(BH)}_m\cdot\mathrm{MX}_{(m+n)\mathrm{org}} \quad \text{(Eq 10)}$$

However, as Coleman (50, 51) so rightly points out, the two systems are thermodynamically equivalent, are only different methods of arriving at the same end, and lead to the identical predictions concerning the equilibrium condition. Accepting the view that anion-exchange mechanism plays major role in extraction by amines, the equilibrium constant, from Eq 7, of hexavalent actinides can be represented as

$$K = \frac{[\mathrm{(BH)}_m\mathrm{MO_2X}_{(m+n)}]_{\mathrm{org}}[m\mathrm{X^-}]_{\mathrm{aq}}}{[\mathrm{MO_2X^{-m}}_{(m+n)}]_{\mathrm{aq}}[\mathrm{BHX}]^m{}_{\mathrm{org}}} \quad \text{(Eq 11)}$$

and the partition coefficient

$$K_{\mathrm{o/a}} = \frac{[\mathrm{(BH)}_m\mathrm{MO_2X}_{(m+n)}]_{\mathrm{org}}}{[\mathrm{MO_2X^{-m}}_{(m+n)}]_{\mathrm{aq}}} \quad \text{(Eq 12)}$$

$$= K\,\frac{[\mathrm{BHX}]^m{}_{\mathrm{org}}}{[m\mathrm{X^-}]_{\mathrm{aq}}} \quad \text{(Eq 13)}$$

At constant aqueous ligand concentration

$$K_{\mathrm{o/a}} \propto [\mathrm{BHX}]^m{}_{\mathrm{org}} \quad \text{(Eq 14)}$$

This treatment is only approximate and true only for dilute solutions. According to the law of mass action the log–log plot of the partition coefficient *vs.* free amine salt concentration at a constant aqueous ligand concentration should be equal to m, the amine association number. Deviations from this situation are, however, frequently found (8, 12, 15, 200), particularly in the case of secondary amines (15). Allen (6) who first observed these discrepancies attributed them to the aggregation of amine salts, but subsequent physical measurements did not substantiate these early conclusions (8), and the apparent constant amine sulfate activity in the extraction of inorganic sulfates by amines is still open to some doubt.

1. *Extraction from Nitrate Media*

The extraction of mineral acids (6, 7, 21, 23, 43, 78, 79, 103, 114, 115, 129, 147, 179, 180, 182, 185, 203, 204, 208–210, 221) by various amines is being studied in order to understand the fundamental chemistry of extraction equilibria connected with the separation processes. An amount of acid considerably in excess of the stoichiometric amine concentration has been reported to extract with some acids (21, 43, 114, 115, 179). The extraction of excess nitric acid has been attributed to simple distribution without formation of a particular amine–acid complex of definite stoichiometric ratio (21, 43). On the other hand, Kertes and Platzner (115) have suggested that the formation of a single adduct $\mathrm{B\cdot HNO_3\cdot HNO_3}$ is followed by simple distribution of molecular $\mathrm{HNO_3}$. Recently it has been shown that the amount of excess acid extracted and the dependence of this extraction on aqueous acid concentration are markedly dependent on types of diluent and acid (114).

A considerable amount of work has been done on the extraction of tetra- and hexavalent actinides from nitric acid media with various amines (21, 31, 43, 47, 48, 60, 112–115, 126, 177, 207, 215, 218). The extraction mechanism of the actinides with amines from nitric acid solutions is explained based on an anion-exchange process, similar to an anion-exchange resin. The tetravalent actinides are extracted as $\mathrm{(BH)_2M(NO_3)_6}$ whereas the hexavalent actinides are extracted as $\mathrm{BH\cdot MO_2(NO_3)_3}$ or $\mathrm{(BH)_2MO_2(NO_3)_4}$ from nitric acid solutions (18, 63, 64, 112–114, 126, 171, 195, 203, 205, 208). Unlike the TBP extraction, the complex acid $\mathrm{HUO_2(NO_3)_3}$ is inextractable (18) by amines above 6 M $\mathrm{HNO_3}$.

The partition coefficient of tetra- and hexavalent uranium and plutonium with TNOA as a function of varying nitric acid concentration is shown in Figure 1. The partition coefficient of both the tetra- and hexavalent plutonium increases with increased nitric acid concentration and then falls off at very high acid concentration. The decreased extraction of the actinides with tertiary amines from higher nitric acid concentrations is attributed to the competition of the nitric acid for the alkylamine cation and the formation of inextractable species (18, 43). The hexavalent uranium shows similar extraction characteristics to those of hexavalent plutonium, but it has a lower partition coefficient than that of plutonium. The partition coefficient of both the tetra- and hexavalent plutonium is higher with amine extractant than that with TBP solvent whereas uranium(VI) has a lower partition coefficient with amine than with TBP.

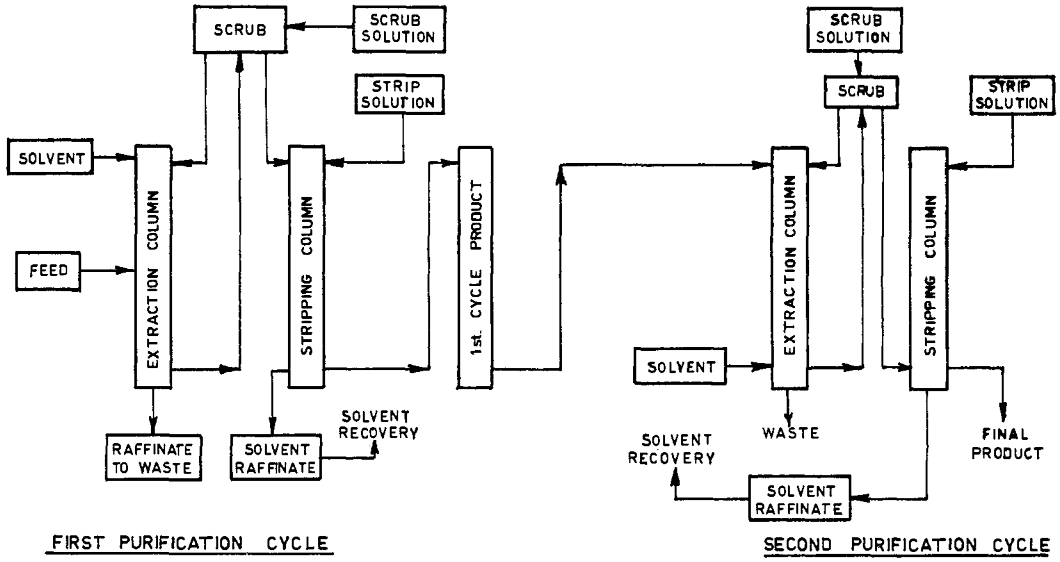

Figure 3.—Eurex process flow sheet for recovery of uranium from uranium-aluminum alloy (18).

The extraction of fission product elements, ruthenium, niobium, zirconium, and rare earths, has been investigated with different amines (63, 64, 181, 182, 206) from nitric acid solutions. The partition coefficient of cerium(III), ruthenium, and zirconium is shown in Figure 5 as a function of aqueous nitric acid concentration. Cerium(III) shows a higher partition coefficient from higher aqueous nitric acid concentration whereas the partition coefficient of zirconium decreases with increased acid concentration. In the case of ruthenium the partition coefficient is higher in lower acidity which reaches a maximum value at 0.3 *M* HNO_3, and with further increased nitric acid concentration the partition coefficient sharply falls off.

Extensive data for the extraction of uranium and selected fission products from nitrate solution using several amines (primary, secondary, and tertiary) have been given by Vaughen and Mason (199). The extraction of uranium and fission products increases in the order primary > secondary > tertiary > quaternary salts. Nitrosylruthenium gave the highest extraction coefficients of the fission products studied. The partition coefficients of molybdenum, zirconium, cerium, and samarium were found to be less than 0.01 in nitric acid concentration greater than 2 *M* although molybdenum extracted quantitatively at low acidity. Salting-out effects produced by the addition of sodium nitrate increased the distribution coefficient of uranium, cerium, ruthenium, and samarium. Tertiary amines gave the greatest separation factors between the actinides and fission products, the separation for uranium and ruthenium being similar to that obtainable with TBP and the separation factor for the other fission products being somewhat better than with TBP. Further detailed studies concerning the extraction of plutonium by tertiary amines has been investigated by Wilson (215) and by others (112–114).

Plutonium recovery from waste streams using amine solvent from nitrate media has been suggested by Winchester and Maraman (219) and Sheppard (177). The former authors described a small-scale plutonium recovery and fission product decontamination process developed for the treatment of residues from a pyrometallurgical process. Extraction was by a secondary amine from an 8 *M* nitric acid solution and stripping by reduction of the plutonium in the solvent phase using 0.1 *N* hydroxylamine nitrate. Sheppard, on the other hand, had investigated the use of tertiary amine TNOA for the recovery of plutonium and separation of neptunium from Purex process waste streams. The extractability of both of these elements in the tetravalent state was shown to be high, and the amine was not adversely affected by high levels of radiation. The Eurex process for reprocessing enriched uranium spent fuels by tertiary amine–Alamine 336 has been recently reported (18). The partition coefficient of uranium is high and it is further enhanced by the salting-out effect of aluminum nitrate. The chemical and radiation stabilities are satisfactory. High radiation doses result in a decreased zirconium decontamination without causing retention of uranium in the organic phase. The chemical flow sheet of the Eurex process shown in Figure 3 is based on two separate solvent extraction cycles with 4% v/v Alamine 336 in aromatic hydrocarbon diluent. The salting-out action in the second cycle is provided by adding additional aluminum nitrate to the scrub solution. Most recently some work (118) on the separation of uranium, plutonium, and fission products using Alamine 336 in diluent Dibutyl Cellosolve has been reported. Recovery and purification of uranium and plutonium from spent fuel using amine solvent in pulse extraction column is suggested (61). Initial separation in this process is achieved by a TBP extraction cycle.

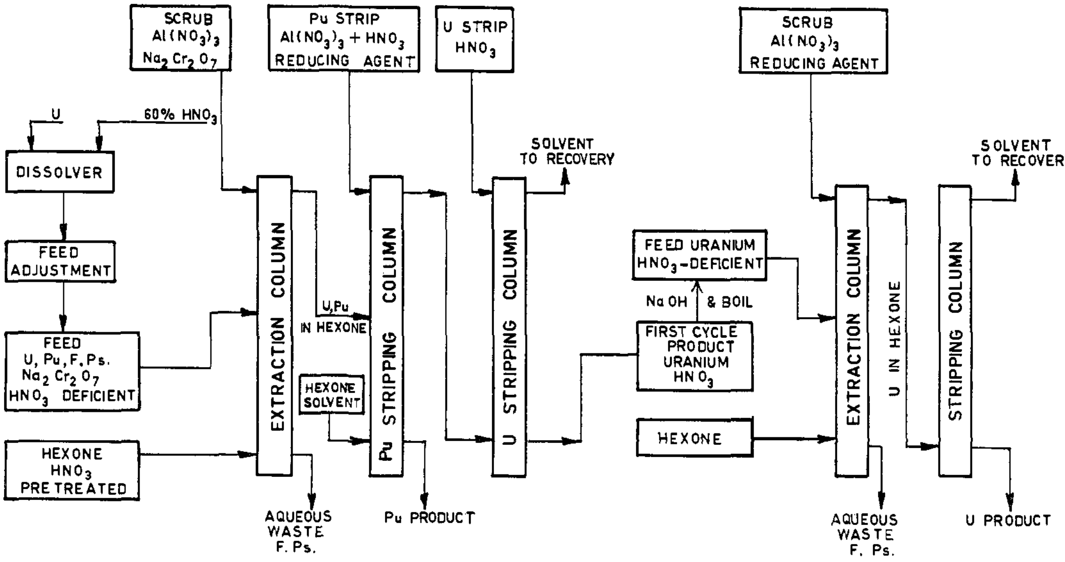

Figure 4.—Flow sheet of Redox process for separation of U and Pu (57).

The final purification is done with trilaurylamine followed by precipitation of plutonium as oxalate directly from the organic phase without using any reducing agent. The possibility of separation and purification of uranium and plutonium from uranium–zirconium fuel by amine–tributyl phosphate solvent has been investigated (96). In this process the initial separation is carried out by an amine solvent, and the isolated uranium is finally purified by a TBP extraction cycle.

2. Extraction from Sulfate Media

The fundamental extraction studies of uranium and plutonium with various amines from sulfuric acid solutions have been investigated by many workers (8–12, 28, 29, 33, 34, 53, 64, 133, 168–171). The extraction mechanism of uranium and plutonium by amine from sulfuric acid is similar to that from nitric acid solutions. The extracted species of uranyl sulfate in the organic phase is established to be $(BH)_m \cdot UO_2(SO_4)_n$ (9, 11, 53, 133, 168), where m and n vary with various amines and varying sulfuric acid concentration. In contrast to the nitrate system, the partition coefficient of uranium(VI) from sulfate media is very high from a lower sulfuric acid concentration, less than 0.1 N H_2SO_4, and decreases sharply with increased acid concentration due to bisulfate formation (53, 133, 170).

The earlier trend of research in this field was to study amine extraction for reprocessing from sulfate media, but less attention has been given to this system recently. A comprehensive study by amines of uranium, plutonium, and fission products from sulfate media has been reported by Chesné (44). A preliminary process scheme for the solvent extraction of uranium and plutonium from sulfuric acid stainless steel decladding solutions with primary amines was proposed (33). The extraction of tetravalent uranium and plutonium is carried out with successive streams of 0.10–0.30 M primary amine and stripping the combined extracts with dilute nitric acid. The uranyl ion in the feed solutions is reduced with iron or chromous sulfate. The partition coefficient is high, to 10^4, and varies with the cube of the uncomplexed amine concentration. The recovery of uranium and plutonium with amine extractants from spent reactor fuels was investigated by Bruce, Blanco, and Bresee (37). Primary amine is suggested for the recovery of uranium and plutonium from sulfex decladding wastes. Isolation and purification of uranium and plutonium are suggested (105) by the extraction of hexavalent uranium and plutonium from stainless steel decladding solution with an N-benzyl secondary alkylamine from sulfuric acid solutions.

3. Extraction from Chloride Media

Very little work is done on reprocessing reactor fuels from chloride media with amines. The chloride media is possibly unpopular due to the corrosion problems which are encountered with hydrochloric acid than any inherent feeling of the solvent system as a suitable separation process. However, Chesné (44) first reported amine extraction of uranium, plutonium, and fission products from chloride media. Another author having investigated amine extraction from chloride media was Moore (141–143). The extraction of uranium and plutonium from hydrochloric acid solution by TIOA in xylene, in general, gave superior decontamination for fission products than could be obtained with TBP, although ruthenium separation appears to be poor. Recently the isolation of transplutonium elements by tertiary amines from concentrated chloride solution (19) was shown to be feasible. The extraction of zirconium and niobium with quaternary ammonium salts from chloride media has also been studied (216).

C. MISCELLANEOUS METHODS

1. Solvent Extraction Methods

A variety of other solvents with varying chemical and physical properties and stable toward radiation can also be used in fuel processing. Ethers, ketones, esters, and higher alcohols were used to a considerable extent in developing early solvent extraction processes (57, 59, 107, 201). The fundamental studies of uranium and plutonium with some selective solvent like ethers and ketones have been investigated by Fletcher (72) and McKay (136) from nitric acid solutions. A series of hydrated nitrate complexes such as

$$[UO_2NO_3]^+,\ [UO_2(NO_3)_2],\ [UO_2(NO_3)_3]^-$$

are present in a solution of uranyl nitrate. There exists an equilibrium mixture of these nitrate complexes, the relative proportion of which depends on the nitrate ion concentration. The uncharged dinitrate complex and the anionic trinitrato complexes are significantly soluble in many organic solvents. Even though only a small fraction of the uranyl ions may exists as a particular extractable complex in solution, its removal by extraction will result in a relatively large amount being extracted by the solvent, as the equilibrium concentration is continuously re-established in the aqueous phase.

Butex (β,β'-dibutoxyldiethyl ether) was the basis of early processing (107) at Windscale in the United Kingdom while hexone (methyl isobutyl ketone) was the basis of many of the earlier U. S. solvent extraction systems (57, 59, 120). The selective separation and purification of uranium and plutonium from enriched uranium–aluminum reactor fuel using hexone is known as the so-called Redox process (57); the chemical flow sheet is shown in Figure 4. This is a two-cycle solvent extraction process for the separation of uranium and plutonium from each other and from most of the fission products. An acid-deficient uranyl nitrate containing sodium dichromate is used as a feed solution. The uranium and plutonium are extracted with hexone which is pre-equilibrated with acid. The organic extract is scrubbed in the same column with acid-deficient aluminum nitrate. The plutonium is stripped from the organic phase in a second column by being reduced to the inextractable trivalent state without affecting the uranium. The uranium is then stripped from the organic phase in a third column by dilute nitric acid. A survey of the more important processes which have been developed with hexone, Butex, and other solvents in this category is shown in Table II. Haeffner, Nelson, and Hultgren reported (95) the possibility of the extraction of uranium and plutonium by new complexing agents such as tetrabutylammonium nitrate, cupferron, and neocupferron. Neocupferron appeared to be a little better solvent than the other two for the separation of uranium and plutonium, but it is not promising for reprocessing reactor fuel due to its decomposition in nitric acid.

TABLE II

SUMMARY OF THE REPROCESSING OF URANIUM–PLUTONIUM BY HEXONE, BUTEX, ETHER, AND OTHER SOLVENTS

Process	Fuel type	Organic solvent	Aqueous solvent	Ref
Early Redox	Enriched uranium–aluminum alloy	Hexone	HNO_3, $Hg(NO_3)_2$, catalyst, $Al(NO_3)_3$	57
Modified Redox	Natural uranium	Hexone	2.0 M HNO_3, 0.3 M $Na_2Cr_2O_7$, 0.1 M $NaNO_3$	120
Modified Redox	Natural uranium	Hexone	HNO_3, $Al(NO_3)_3$	57
Butex	Natural uranium	β,β'-Dibutoxyl-diethyl ether	3 M HNO_3	107
Ether	Natural uranium	Dibutyl ether	0.63 M HNO_3, $Ca(NO_3)_2$	201
Chelation	Natural uranium	TTA	HNO_3	57

The extraction of irradiated uranium by methylcyclohexanone has been investigated by Vesely, Beranova, and Maly (212). The experimental results showed that satisfactory extraction of irradiated uranium with a high decontamination from fission products could be obtained. However, this solvent is comparatively unstable toward radiation and inferior to TBP. The solvent extraction of uranium and plutonium with various solvents such as diisopropylcarbinol, diisopropyl ether, monobutyl ether, dioctylphosphoric acid, and other solvents has been mentioned in the literature (57).

2. Ion-Exchange Methods

A convenient and versatile method of radiochemical separation on the laboratory scale is that of ion exchange. Problems associated with the high radiation levels associated with nuclear fuel feed solutions have, however, rendered the use of ion exchange impracticable on a plant scale for primary separation processes. They have, of course, been extensively employed in uranium extraction processes (14, 89, 104, 127, 151, 160, 176, 197) from ores.

The ability of certain naturally occurring inorganic material (82, 83) to adsorb and desorb ions under suitable conditions has been known for a long time, but the further use of ion exchanges as a chemical separation process only really developed after the advent of the synthetic ion-exchange resin (1, 116, 117). These are generally 8 to 12% cross-linked polystyrene resins (88, 189) into the molecular structure of which has been introduced appropriate active groups. The so-called cation-exchange resins which adsorb and desorb cations generally contain sulfonic acid groups while the anion-exchange resins contain quaternary ammonium groups. These synthetic exchangers, which are manufactured by a number of companies under different trade names, normally have an exchange capacity of some 1 to 2 equiv/l. of wet resin.

As mentioned above, ion-exchange processes for the laboratory-scale separations of small quantities of irradiated material are frequently employed. In plant-scale operations the gassing of the columns and radiation decomposition and degradation of the resin make ion-exchange processes unattractive by comparison with solvent extraction. Ion-exchange resins do, however, find extensive use in the final product concentration and purification stages of many solvent extraction processes. Typical of the early adoption of resins to fulfill this function is the use of a cation resin Dowex-50 to concentrate and purify the plutonium separated in the primary solvent extraction stage of the Purex system (36). The plutonium as a cation and in the trivalent state is adsorbed. It is then

$$\mathrm{Pu^{3+}{}_{aq} + 3H^{+}\,(resin) \rightleftharpoons Pu^{3+}\,(resin) + 3H^{+}{}_{aq}} \quad \text{(Eq 15)}$$

washed with 0.25 M H_2SO_4–0.05 M hydroxylamine sulfate and eluted with 6 M HNO_3–0.3 M NH_2SO_3H solution. Decontamination factors of 20 and 40 for niobium and zirconium which frequently carry over with the plutonium to a limited extent and a product concentration factor of some 250 are obtained. Prevot and Regnaut described (155) the purification and concentration of plutonium with cation- and anion-exchange resins. The plutonium from the Purex solvent extraction cycle is adsorbed on a cation resin as plutonium(III) from 0.7 M HNO_3 solution and eluted with 4 M HNO_3. The final purification of plutonium from uranium and iron is obtained by the separation on two anion-exchange columns from hydrochloric acid media. The trivalent plutonium is oxidized with sodium nitrite to tetravalent plutonium and then adsorbed on resin from 7 M HCl. The plutonium is eluted with 0.7 M HCl and precipitated as plutonium oxalate. The over-all decontaminations obtained from γ activities and uranium are 10^2 and 2×10^3, respectively. Concentration and purification of uranium, plutonium, and neptunium by ion exchange has been reported by Tober (196). The plutonium(III) is adsorbed on a cation-exchange resin from 0.25 M HNO_3 in the presence of 0.025 M $(NH_3OH)_2SO_4$ solutions. The elution of plutonium product is achieved with 5.7 M nitric acid stabilized with 0.3 M sulfamic acid. More than 99.99% of plutonium is recovered in this process.

Anion exchange offers a greater advantage over cation exchange for uranium and plutonium processing because of the ease of decontaminating the plutonium from normally encountered impurities. Fundamental studies on the anion-exchange separation of the actinides have been made by several workers (108, 163–166). Besides the adsorption of anionic species by an anion-exchange mechanism such as

$$\mathrm{MX}_n{}^{-ny+m}{}_{\mathrm{aq}} + \left(\frac{ny - m}{y}\right)\mathrm{X\,(resin)} \rightleftharpoons \mathrm{MX}_n{}^{-ny+m}\,\mathrm{(resin)} + \left(\frac{ny - m}{y}\right)\mathrm{X}^{-y}{}_{\mathrm{aq}} \quad \text{(Eq 16)}$$

the free acid of the complex anion such as

$$\mathrm{MX}_n{}^{-ny+m}{}_{\mathrm{aq}} + (ny - m)\mathrm{H}^{+}{}_{\mathrm{aq}} \rightleftharpoons \mathrm{H}_{ny-m}\mathrm{MX}_{n\mathrm{aq}} \quad \text{(Eq 17)}$$

plays a predominant part in the anion-exchange separation (77, 130, 164). Most recently Ryan (165, 166) showed that hydrogen bonding contributes a significant role on the mechanism of anion-exchange separation of anionic complexes of tetra- and hexavalent actinides.

The separation and recovery of plutonium from nitrate solution in the presence of some metal nitrates such as aluminum, magnesium, and calcium by an anion resin is described by Tober (196). Plutonium is adsorbed from a solution of 5.5 M HNO_3 and 9 M total nitrate and eluted with 0.3 M nitric acid.

Anion-exchange resins have been applied to the recovery of plutonium (163) from irradiated reactor fuel. A comprehensive study of plutonium(IV) adsorbed on a variety of anion resins from both nitric acid and $CaNO_3$ media showed that a maximum distribution coefficient of the order of 2×10^4 is obtained from 7 to 7.5 M HNO_3 solution. Elution of the plutonium was effected from 0.3 to 0.6 M HNO_3 solution. These studies showed good separation from uranium and decontamination from fission products—with zirconium–niobium decontamination factors of the order of 10^6. The process is suited mainly to secondary separation and purification of plutonium recovered from a primary TBP–HNO_3 process.

An interesting modification of ion-exchange plutonium concentration is the direct adsorption of plutonium on silica gel from the solvent stream as suggested by Hultgren and Haeffner (106). The silica gel column is pretreated by passing an aqueous solution of a reducing agent—0.04 M sulfamic acid—through the column and then displacing the mobile water phase with 30% TBP containing extracted uranium and plutonium. Plutonium(III) is absorbed on the column while most of the uranium passes through with only a small holdup. The plutonium is eluted with aqueous nitric acid solution.

Aiken (2) and Campbell (41) have suggested ion exchange, although not generally suited to primary processing, for the separation of plutonium from irradiated uranium. The plutonium which is adsorbed from high nitrate media as plutonium(IV) on an anion resin is subsequently eluted with reducing agent as plutonium(III). The processing rates and the concentration under these conditions were, however, low. Investigation for the separation of the actinides from each other in hydrochloric acid solution with anion-exchange resin has been reported by Hyde (108). The hexavalent uranium and plutonium are readily absorbed from a solution in greater than 6 M HCl

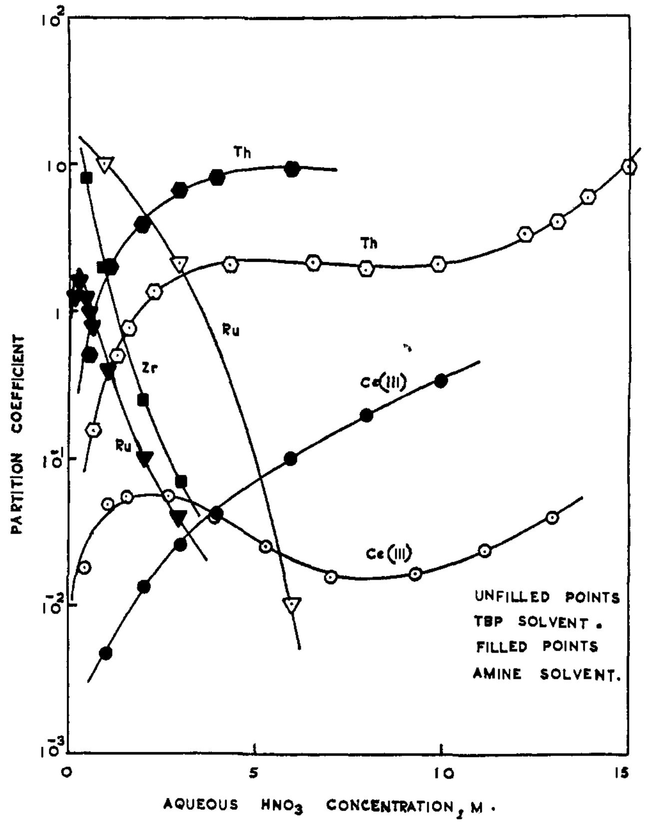

Figure 5.—The partition coefficients of thorium and fission products with TBP, TNOA and TIOA from varying nitric acid concentrations: Th, 19% TBP in kerosine (99); Ru, 19% TBP in kerosine (35, 73); Ce(III) 48% TBP in kerosine (173); Th, 14.1% TNOA in xylene (43); Ru, 10% TNOA in xylene (181); Ce(III), 17.5% TIOA in xylene (64); Zr, 10.5% TNOA in chloroform (206).

concentration and desorbed in dilute acid solution. The tetravalent thorium is not adsorbed at any HCl concentration whereas the tetravalent uranium and plutonium are adsorbed in concentrated solution.

The possibility of reprocessing uranium, plutonium, and fission products has been suggested by Bobleter (27) using exclusively cation exchangers on wood basis. The separation of uranium and cerium was obtained from a diluted NH_4NO_3-HNO_3 solution with a cation exchanger on wood basis. Isolation of individual fission products by this process was shown to be possible.

Some of the objections to ion-exchange primary separation processes can be overcome by using the less radiation-sensitive inorganic exchangers such as a synthetic zeolite. The uses of such inorganic material for the processing of uranium–plutonium have been reported (90) recently. Besides difficulties in remote plant operation these exchangers have a characteristic disadvantage in that they are unstable in a solution of pH lower than 5.

3. Precipitation Methods

In the early days of the war, Manhattan project methods based on the volatility, adsorption, solvent extraction, and precipitation were all investigated. Although solvent extraction has become the most used and important method, the first Hanford plant was set up for a precipitation process (187). This followed from the fact that conventional chemical studies on the small amounts of plutonium available at that time had provided more information on the solubility products of various plutonium compounds than on other aspects. These processes (187, 194) were based on the carrier precipitation of plutonium in both the tetravalent and hexavalent states. The process was capable of repetition until suitable decontamination was achieved. The greater decontamination and convenience in the remote operation of solvent extraction have replaced precipitation methods, but it is still nevertheless interesting that the first plant constructed for the processing of irradiated uranium fuel was based on a precipitation process.

III. THORIUM–URANIUM FISSION PRODUCT PROCESSES

Thorium is not itself a fissile reactor fuel material, but upon neutron absorption and β decay it leads to uranium-233 which is fissile and has suitable nuclear properties which make it desirable for use in thermal breeder reactors. The thorium which may be incorporated in the fuel elements or used as a blanket around the reactor core gives rise to uranium-233 by the reaction

$$\text{Th-232} \xrightarrow{\text{n}} \text{Th-233} \xrightarrow[\text{23.3 min}]{\beta^-} \text{Pa-233} \xrightarrow[\text{27.4 days}]{\beta^-} \text{U-233} \qquad \text{(Eq 18)}$$

An important feature of the thorium–uranium-233 system is the fact that the intermediate nuclide protactinium-233 has a moderately long half-life—unlike the intermediate neptunium-239 of the uranium–plutonium-239 system. This in turn implies that either extremely long cooling times must be allowed so that the protactinium-233 can decay to uranium-233 or else the chemical extraction process must be such that the protactinium-233 can also be isolated and stored as potential uranium-233. The first alternative involves a large fuel inventory while the second alternative implies that besides the extraction of thorium and uranium-233, a third nuclide protactinium-233 must be quantitatively isolated in a pure state.

At first glance it would seem that there would be no fission products. This is not so for two reasons. (i) Thorium though not thermally fissile does undergo fission as a result of fast neutron bombardment. (ii) Some fission of the uranium-233 will occur as it is formed.

Although small, in comparison with uranium–plutonium-239 fuel cycle, there will be considerable amounts of fission products by the above processes

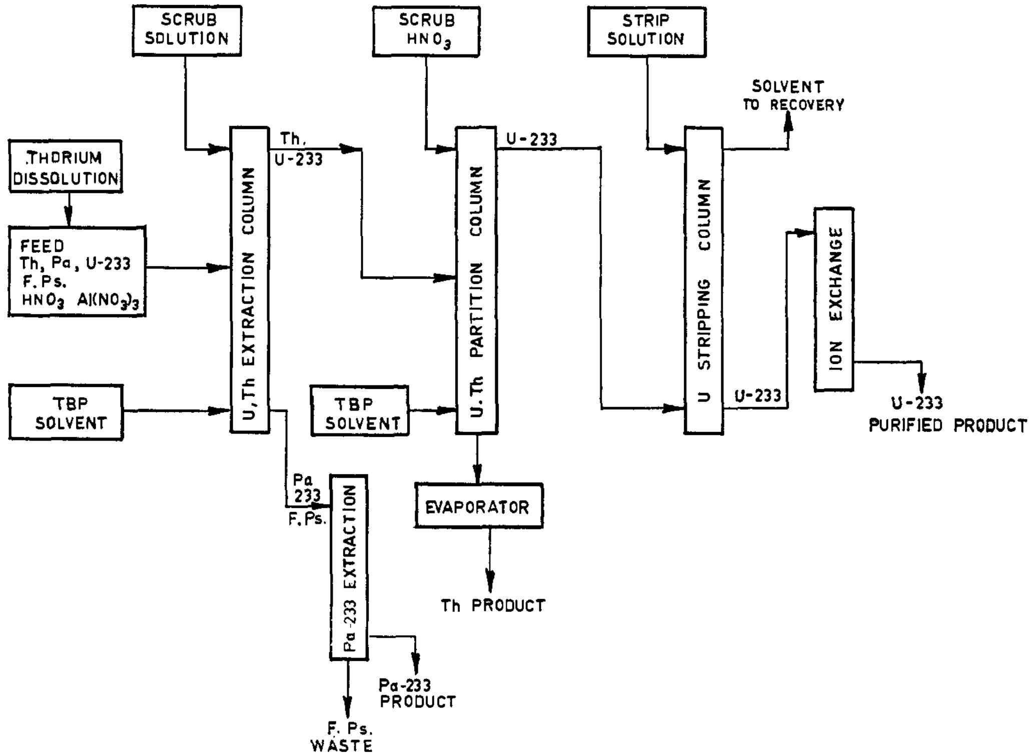

Figure 6.—Thorex flow sheet for extraction of U-233 and Th (86).

which have to be isolated. In the case when thorium is contained in the fuel element itself, there will be, of course, a fission product problem comparable to the uranium–plutonium-239 system. If short-cooled irradiated thorium is to be processed, the order of separation steps are chosen as: (i) separation of highly radioactive protactinium and fission products from the uranium and thorium products; (ii) separation of the thorium from the uranium-233; (iii) isolation and purification of uranium-233. In the case of long-cooled thorium the first step is unnecessary.

A. ALKYL PHOSPHATE SOLVENTS

The basic studies of the extraction of thorium by TBP from nitric acid solutions has been investigated by McKay (137, 138) and by others (99, 100, 152). The extraction mechanism of thorium by TBP is similar to that of uranium and plutonium. The partition coefficients of thorium, cerium(III), and ruthenium are shown in Figure 5. The thorium partition coefficient is low at low nitric acid concentration and rises sharply at approximately 4 M HNO_3 and remains constant up to 10 M HNO_3. There is a sharp rise in the partition coefficient with further increased acid concentration greater than 13 M HNO_3. The partition coefficient of cerium(III) shows a similar trend to that of thorium, but it is lower by an order of magnitude. In low acid concentration the partition coefficient of ruthenium is higher than that at high acid concentration. It falls off very sharply with the increased concentration of the acid.

Extraction Processes with Tri-n-butyl Phosphate

Typical of the many processes (20, 24–26, 30, 39, 86, 87, 139, 140, 192, 214) for the treatment of irradiated thorium are the U. S. Thorex process first outlined by Gresky (86) and the process developed in the United Kingdom, the preliminary work for which was described by McKay and Fletcher (139) and subsequently developed by Wells and Nichols (214). Both of these systems showed one thing in common—that they were intended for long-cooled irradiated thorium, and protactinium isolation was not integral part of the process. In Gresky's earlier work the removal of protactinium, if present, from the fission product stream is suggested by supplementary treatment. The chemical flow sheet of the U. S. Thorex process (86) is shown in Figure 6. In this process both thorium and uranium-233 are co-extracted in the first extraction column and then separated subsequently in the second column by selective stripping. In the process outlined by Wells and Nichols (214) only the uranium-233 is selectively extracted with 5% TBP and the thorium is allowed to go along with the fission product wastes. In both systems the recovered uranium was subsequently purified by ion exchange.

As the decontamination from the fission product in the single-cycle Thorex process is not satisfactory, a two-cycle Thorex process (39) was developed. The chemical flow sheet of the process is shown in Figure 7. The thorium and uranium-233 are extracted with 42.5% TBP in Amsco 125-82 from an acid-deficient aluminum

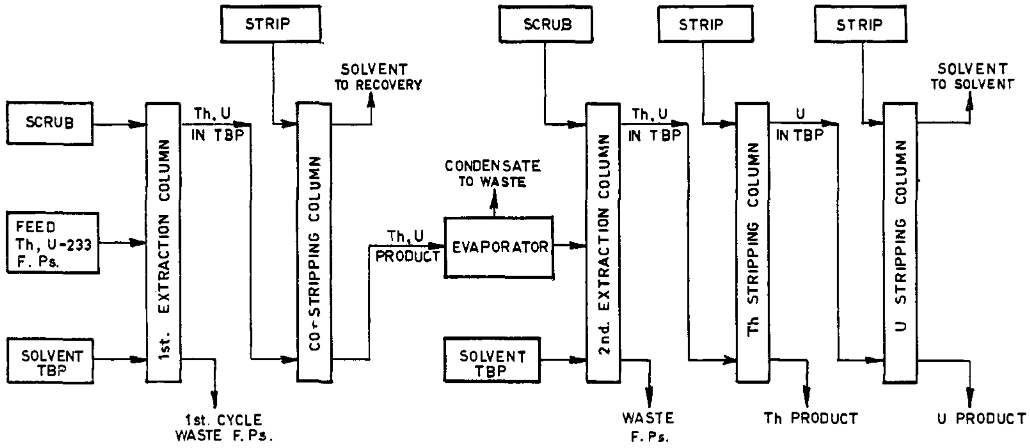

Figure 7.—Two-cycle Thorex process flow sheet (39).

Table III
Summary of the Thorex and Modified Thorex Processes

Process	Organic solvent	Aqueous solvent	Notes	Ref
Earlier Thorex	30% TBP	1 M HNO_3	Extraction of Th and U; Pa is not isolated	184
Thorex	50% TBP	4–5 M HNO_3, $Al(NO_3)_3$	Extraction of Th and U; selective stripping	140
Thorex	42.5% TBP	HNO_3, $Al(NO_3)_3$, $FeSO_4$, PO_4^{3-}	Co-extraction of Th and U; Pa is not isolated	220
Thorex	30% TBP	0.115 M HNO_3, $Al(NO_3)_3$, $NaHSO_3$	Co-extraction and co-stripping of Th and U	25
Interim 23 TBP	1.5% TBP	HNO_3Hg^{2+}, catalyst, F^-	Selective extraction of U; Pa and Th are not isolated	68
Acid interim 23 TBP	5% TBP	Acid-deficient $Al(NO_3)_3$, F^-	Extraction of U only	24
Thorex	42.5% TBP	Acid-deficient $Al(NO_3)_3$	Extraction of Th and U; selective stripping	39
Acid Thorex	30% TBP	1.0 M HNO_3, $Al(NO_3)_3$, F^-	Th and U extraction; selective stripping	192
Thorex	10% TBP	0.5 M HNO_3, $Al(NO_3)_3$	Extraction of U only; Pa and Th are not isolated	39
Modified Thorex	42.5% TBP	Acid-deficient $Al(NO_3)_3$, F^-	Th and U extraction; selective stripping; Pa is not isolated	55
Modified Thorex	30% TBP	HNO_3, $Al(NO_3)_3$, high acidic feed	Co-extraction of Th and U; Pa is also isolated; selective stripping	26
Modified Thorex	42.5% TBP	0.3 M HNO_3, $Al(NO_3)_3$, $NaNO_3$, F^-, PO_4^{3-}	Co-extraction and co-stripping of Th and U; Pa is not isolated	175

nitrate feed in the first extraction cycle. Sodium bisulfite is added in the feed for complexing ruthenium to an inextractable species by TBP. The first-cycle product of thorium and uranium-233 is stripped with 0.01 M $Al(NO_3)_3$. In the second cycle, the extraction is made from 0.24 M nitric acid solution. The extracted thorium–uranium is selectively stripped with water and dilute nitric acid and subsequently purified by ion exchange. The improvement and subsequent development of various Thorex processes for the separation and purification of thorium and uranium-233 are summarized in the Table III. Most recently Brown (32) reported that higher decontamination of zirconium–niobium and ruthenium was obtained by extraction of uranium with TBP in the presence of diacetyl monoxime both from acidic and acid-deficient feed solution.

B. AMINE SOLVENTS

1. *Extraction from Nitrate Media*

The extraction of thorium by amines has been studied by several workers (43, 113, 114, 202, 211) from nitric acid solution. The mechanism of extraction is similar to that of other actinides. It is established that thorium is extracted as $(BH)Th(NO_3)_5$ and $(BH)_2Th(NO_3)_6$ species (43) by TIOA and TNOA from nitric acid solution. The extraction of cerium(III) (64), ruthenium (181), and zirconium (206) has been studied with tertiary amine. The partition coefficients of thorium, cerium(III), ruthenium, and zirconium are shown in Figure 5 as a function of aqueous nitric acid concentration. The partition coefficients of thorium and cerium(III) increase with increasing nitric acid concentration, but cerium(III) has a much lower partition coefficient than thorium. Both cerium(III) and thorium have higher partition coefficients with amine from higher nitric acid concentration in comparison with TBP extraction. Thorium shows higher partition coefficients in the whole range of acid concentration whereas cerium(III) shows lower values at low acid concentration. Apparently no work has been done on the reprocessing of thorium–uranium-233 fuel by amine extraction from nitrate media.

2. *Extraction from Sulfate Media*

Thorium extraction by amines from sulfuric acid solutions has been studied by a few investigators (13, 15, 34, 56, 134). The extraction mechanism of thorium sulfate by amine salt is explained as an anion-exchange process (15, 134) analogous to anion-exchange resin. The composition of the extracted species in the organic phase has been formulated as

$(BH)_{2n-4}Th(SO_4)_n$ (13, 15)

where n may be equal to 3 or 4. The use of amines for the separation of thorium from ores (33, 56) has been employed for some time. Much work has been done on the processing of uranium and plutonium by amines, but until recently no extensive work has been carried out for reprocessing irradiated thorium.

The possibility of using amine extractants for the processing of irradiated thorium in the thorium–uranium-233 fuel cycle was recently reported by Awwal (15). Secondary and tertiary amines are shown to be promising. Two secondary amines, DNOA (di-*n*-octylamine) and DTDA (di(tridecyl)amine), as well as two tertiary amines, TNOA (tri-*n*-octylamine) and MNDDA (methyl-*n*-didecylamine), were studied in detail. Extraction as a function of aqueous phase sulfuric acid concentration, sodium sulfate concentration, and thorium loading were presented. Both the secondary and tertiary amines have shown suitable extraction properties for both uranium and thorium in sulfuric acid concentration in the range 10^{-2}–10^{-1} N H_2SO_4. The secondary amines show a preferential extraction of thorium while the tertiary amines preferentially extract uranium. The secondary amine sulfate at a concentration of 0.10 N shows a partition coefficient for the extraction of thorium which decreases from a value in excess of 10^3 for acid concentration of 10^{-2} N H_2SO_4 to approximately unity at an aqueous acid concentration of 0.5 N. Under similar conditions uranium shows similar extraction characteristics but reduced in magnitude by a factor of 4. With 0.10 N tertiary amines the partition coefficient for the extraction of thorium decreases from a value of approximately 5 at 10^{-2} N H_2SO_4 to a value of approximately 0.5 at 0.5 N H_2SO_4. Under the same conditions uranium shows similar extraction properties with partition coefficients increased by a factor of 10^2.

Subsequently the secondary amines provide the higher partition coefficients for the extraction of thorium and uranium while the tertiary amines provide the greatest difference between the values for the extraction of uranium and thorium under similar conditions. It was suggested that the secondary amines would appear attractive, especially DTDA, to extract both the uranium and thorium from a feed solution, while the tertiary amine solvents offer better subsequent thorium and uranium separation by selective stripping of the solvent.

Of the amines studied MNDDA was selected for the process studies, because of its higher extraction for thorium in the presence of higher sulfate ion concentrations. The preliminary extraction studies of thorium with 0.25 N MNDDAS from a feed solution containing 6 g/l. of thorium and 0.005 N with respect to H_2SO_4 showed 99.9% recovery. The uranium is quantitatively extracted under the proposed process conditions. An outline of the proposed separation method is given in Figure 8 in which the thorium is stripped off the organic phase with 1 N H_2SO_4 and uranium with 5 N H_2SO_4. The final purification of both thorium and uranium is suggested by ion-exchange separation.

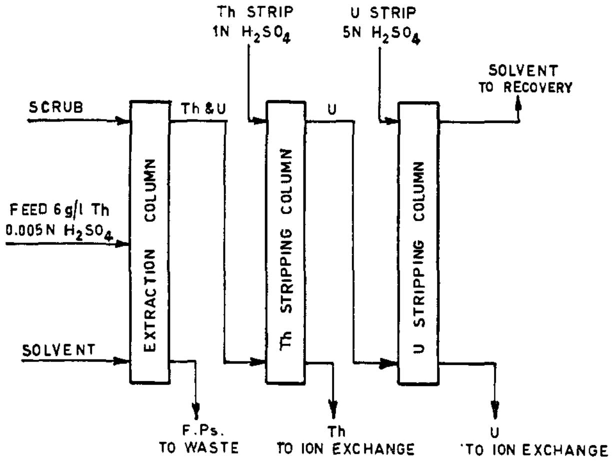

Figure 8. Outline of Th-U amine extraction process (15).

C. MISCELLANEOUS METHODS

1. *Solvent Extraction Method*

Besides alkyl phosphates and amines, other solvents such as ethers and ketones have been used less extensively for the separation of uranium-233 from irradiated thorium. Preliminary studies on the extraction of uranium-233 with hexone has been reported by Steahly (190). A comparison of four continuous solvent extraction processes for the recovery of uranium-233 from thorium and fission products using hexone, diisobutyl ether, and Dibutyl Cellosolve is described by Ferguson and Leuze (69). Both diisopropyl ether and hexone processes were shown to provide adequate uranium-233 separation from thorium and fission products. The interim-23 hexone process (57) was designed to investigate the reprocessing of uranium-233 from irradiated thorium. The uranium-233 is selectively extracted with hexone from acid-deficient aqueous feed containing aluminum nitrate. Thorium is sufficiently inextractable in hexone. Decontamination factors for most fission products were greater than 10^5. A selective extraction of uranium from irradiated fuel employing 2.5% di-*sec*-butyl phenylphosphate in diethylbenzene is reported (128) from an acidic feed solution.

2. *Ion-Exchange Methods*

Since the fission product activities are an order of magnitude lower for thorium blanket processing compared to uranium fuel reprocessing, ion-exchange processes (122, 150) for the separation of uranium-233 from irradiated thorium appear to be feasible. The separation of U-233 from the Thorex process solvent stream by silica gel and cation resin is described by Bruce (38). The formation of anionic complexes of uranium and protactinium in strong hydrochloric acid solution has been utilized by Chesné and Regnaut (46) for their separation from thorium and fission products by adsorption on anion resin. The uranium-233 and protactinium-233 are absorbed from 8 M HCl solution. More than 99% of uranium-233 is eluted with 0.5 M HCl. A method of separation of uranium and thorium by cation resin followed by anion resin is described by Chesné and Mannone (45). The final product uranium-233 was purified by a multistage solvent extraction method with trilaurylamine sulfate in hydrocarbon diluent. Raaen and Thomason (157) have successfully separated uranium-233 and protactinium-233 by paper chromatographic techniques. A practical application of the method was demonstrated with a solution similar to the Thorex process. A good separation was obtained. Recently a process for recovering protactinium-233 by adsorption on unfired Vycor glass was reported (144) from short-cooled irradiated thorium–uranium fuel element. In this process the protactinium is adsorbed from 10.1 M HNO_3 solution on a Vycor glass bed (60–80 mesh), and 92% of the product is recovered with a decontamination factor of 10^3 from fission products.

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