

SOME MILESTONE SOLVENT EXTRACTION PROCESSES AT THE OAK RIDGE NATIONAL LABORATORY

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ABSTRACT

After ether extraction was scaled up to plant status, solvent extraction grew rapidly, intensively, and extensively. This paper recounts developments at the Oak Ridge National Laboratory (ORNL) in three fields: Fuel Reprocessing, Uranium Production, and Transplutonium Element Recovery.

Fuel Reprocessing: In the late 1940's, soon after tributyl phosphate (TBP) was discovered to be an extractant, the Purex process was developed to recover, decontaminate, and separate plutonium and uranium (from nitric acid solutions of spent reactor fuels) without the need of added salting agents. World-wide, Purex is the basis for most fuel reprocessing, active and planned; derivative processes recover thorium, ^{233}U , and ^{235}U in special applications.

Uranium Production: Around 1950, the ORNL Raw Materials Section launched an intensive search for reagents that could (in contrast to ether and TBP) extract uranium from sulfuric acid leach liquors. This was accomplished with the liquid ion exchangers: di(2-ethylhexyl)phosphoric acid (HDEHP) and a suite of high-molecular-weight alkylamines. The resulting Dapex and Amex processes eventually dominated domestic uranium production, spread world-wide, and provided bases for innovative processes in other fields.

Transplutonium Element Recovery: Tramex and Talspeak processes accomplish separation of the trivalent actinides from the very similar lanthanides. Tramex (1961; amine extraction from concentrated lithium chloride) has been used in the ORNL Transuranium processing Plant (TRU) since 1966. Talspeak (1964; HDEHP extraction from carboxylic acid + amino-polyacetate complexer) has wider potential because it is less corrosive, and it is being extensively studied for separating americium and curium from fuel reprocessing wastes.

INTRODUCTION

Solvent extraction is now a familiar tool in metallurgy and heavy chemicals, as well as in smaller-scale uses. It is now one of the processes that is considered in attacking any new separations problem, but it was not so familiar in 1940. Modern solvent extraction grew up with the nuclear industry, and essentially developed from the ether extraction of uranyl nitrate. Under other circumstances, an equally vigorous extraction technology might have started from the ether

extraction of ferric chloride, from two-phase distribution in petroleum refining, or even from the Parkes process for extracting silver from lead with zinc, but the circumstances that did occur led through uranium.

The solvent extraction processes considered here had their beginning in the discovery that uranyl nitrate is freely soluble in diethyl ether (Bucholz, 1805) and in the use of ether extraction as a means for purifying laboratory samples of uranyl nitrate (Péligot, 1842). In 1942, in order to supply the high-purity uranium required by the Manhattan Project, analytical ether extraction was studied for purification potential by J. I. Hoffman (Smythe, 1945) and was rapidly scaled up to a heavy-chemical plant operation at the Mallinckrodt Chemical Works, already expert in making and handling ether. During and after that Project, many other extractants were examined, and a few were used. These included dibutyl carbitol or "triether," used for uranium recycle in the Y-12 electromagnetic separation plant and later in the Butex process of the British fuel reprocessing plant at Windscale (operational in 1952); methyl isobutyl ketone, "MIBK" or "hexone," used in the Redox process at the Hanford Works (operational in 1951); and tri-*n*-butyl phosphate or "TBP."

FUEL REPROCESSING: PUREX

That TBP could extract the nitrates of uranium and other actinides was recognized at least as early as 1944. It was included in lists of candidate extractants screened for plutonium [1], thorium [2], and cerium(IV) [3]. (Bracketed numbers refer to the reports listed in Table 1.) TBP was a readily available chemical (a plasticizer), and in retrospect it seems a mistake that it was passed over in each of those early surveys. One reason, not well founded but reasonable at the time, was the fear that the ester would be excessively degraded by acid hydrolysis. More pressing reasons were its high viscosity and density; even its attractive high extraction power was two-edged, in that stripping of the extracted metals by the methods then familiar was difficult. Those difficulties are, of course, ameliorated by dilution. However, the idea of diluting an extractant was quite foreign to the concepts and experience of solvent extraction reached by that time, and it was a new departure when Spedding and his co-workers at Iowa State College made TBP usable for thorium extraction by mixing it with the lighter extractant, dibutyl ether (Warf, 1949). It was another real innovation when Barse and his co-workers at Battelle Memorial Institute replaced that ether with a nonextracting hydrocarbon, hexane [4]. In fact, it was with surprise that the Battelle group noted that the shift from ether to hexane improved the extraction power for thorium, in addition to improving the physical properties.

The foregoing thorium extractions were the direct ancestors of the ORNL Purex process. In 1948 and 1949, one of the

active problems in the ORNL Technical Division was recovery of the uranium contained in the stored wastes from the plutonium pilot plant. The Metal Recovery Group, under the supervision of F. R. Bruce, quickly recognized the applicability of the Battelle TBP/hexane extraction to the (uranium) metal recovery problem and the major advantage of extracting without addition of anything besides nitric acid to the waste solution [5, 6]. (Dibutyl carbitol, in contrast, could not extract uranium from those wastes without added nitrate salts, although nitric acid "salting" is sufficient for it in Butex fuel processing.) Development proceeded rapidly, reaching semi-works design by July 1949 [7]. The development included the testing of heavier hydrocarbon diluents [7, 8] to decrease the flammability hazard (and also carbon tetrachloride for an alternative heavier-than-water solvent [7]). It also included establishment of the conditions to prevent contamination of the recovered uranium with the plutonium that had been lost to the waste, and hence, conversely, the conditions to obtain co-recovery of plutonium with the uranium.

By September 1949, major attention had shifted from waste metal recovery to the concept of TBP extraction of uranium and plutonium from dissolved spent fuel, and this concept had been christened "Purex" for "Plutonium Uranium Reduction Extraction" [9]. The initial concept used 15% TBP in Varsol (a varnish-maker's refined kerosene) to co-extract plutonium(IV) and uranium(VI) from 1 M $\text{UO}_2(\text{NO}_3)_2$, 6 M HNO_3 solution. "Purex Flowsheet No. 1" [10] used 30% TBP for the co-extraction (Fig. 1). Then the plutonium was stripped by reduction, concentrated, and re-extracted in a second cycle with 10% TBP. The uranium was "water-stripped" (with 0.001 M sulfuric acid solution) and re-extracted with 30% TBP. "Purex Flowsheet No. 2" [11], incorporating suggestions from the Hanford Engineering works, used only the 30% TBP; plutonium and uranium were co-extracted and co-stripped, then co-extracted in a second cycle and stripped separately. "Purex Flowsheet No. 3" [12] continued to use 30% TBP throughout, but returned to separate stripping in the first cycle and to separate second cycles for plutonium (without a concentration step) and uranium, and eliminated the sulfuric acid from the water used to strip the uranium.

Purex reached plant operation at Savannah River in 1954 and at Hanford in 1956, and soon thereafter was used in many plants throughout the world. Plant flowsheets continued to evolve, and have been published in the UN (Geneva) Conferences on the Peaceful Uses of Atomic Energy and the Pergamon Press Series on Progress in Nuclear Energy/Process Chemistry.

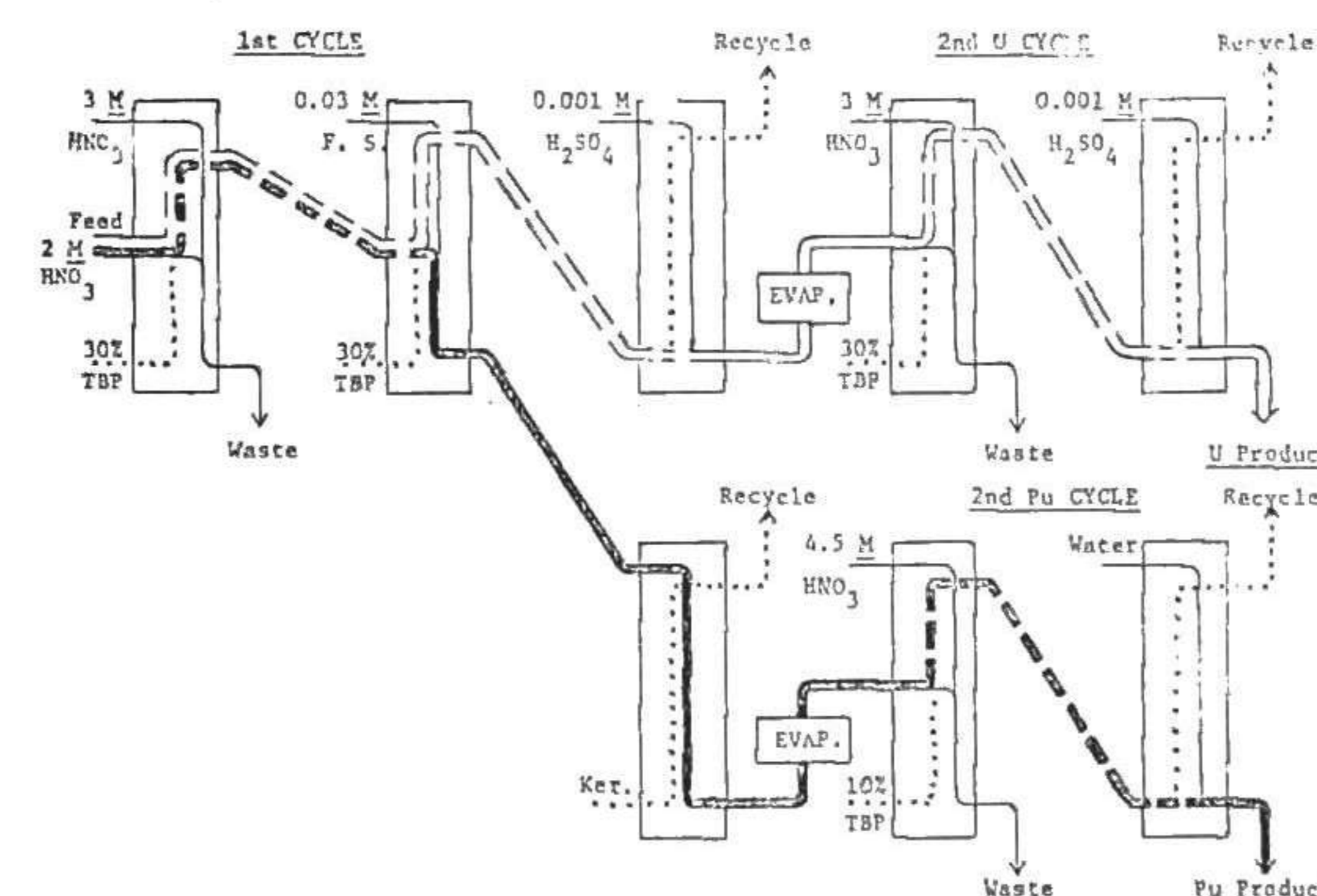


FIG. 1. "Purex Flowsheet No. 1" (Plutonium Uranium Reduction Extraction), according to the description in a progress report, August, 1950 [10].

Derivative Processes

By the shifts of extraction-rejection and selectivity obtainable through variation in TBP concentration, aqueous concentrations and acidity, and loading ratios, the Purex process or

some part of it has been adapted to a number of other uses.

The *Metal Recovery* process uses 12.5% TBP for uranium only (Culler, 1956a). (As indicated above, the *Metal Recovery* process was more an antecedent than a derivative of Purex—both developed by the same group, at nearly the same time.) One variant used a modified Purex process in order to recover plutonium in addition to uranium: "Application of the Purex Process to ORNL Metal Waste Recovery" [13].

The *TBP 25* process ["25" = ^{235}U] uses 5% TBP for uranium-only recovery from fuels containing highly enriched uranium, which therefore produce very little plutonium (Culler, 1956a). The *TBP Interim-23* process ["23" = ^{233}U] uses 1.5% TBP for uranium-only recovery from irradiated thorium, leaving the thorium and (if short-decayed) the ^{233}Pa (Culler, 1956b).

The *Thorex* process uses 42.5% TBP to recover and separate ^{233}U and ^{232}Th from irradiated thorium, leaving undecayed ^{233}Pa for auxiliary separation (Gresky, 1956), or after precipitation of the protactinium (Ferguson, 1956). A related process, designed to produce an experimental supply of ^{233}U after essentially complete decay of ^{233}Pa , used 5% TBP for the uranium and 40% TBP for the thorium (McKay, 1956; Wells, 1956).

Derived Reagents

The success of TBP, and also its observed limitations, induced a continuing search for alternative reagents that might be still better, at least in particular circumstances. A homolog of TBP, tri-*n*-hexyl phosphate, shows a potential advantage in that it has lower aqueous solubility and, hence, should produce less of troublesome chemical and radiolytic degradation products in the high-activity aqueous process streams [14].

Two analogs of TBP, di-*n*-butyl phenylphosphonate (DNBPP) and di-*sec*-butyl phenylphosphonate (DSBPP), show markedly better radiation stability, along with higher extraction power for uranium and plutonium, and better selectivity [15]. The selectivity is especially useful in separations of uranium from thorium, so that DSBPP (in diethylbenzene) has been instrumental in the success of several processes requiring highly efficient purification of ^{233}U : (1) the "Kilorod Project"—the preparation of a thousand ThO_2 - $^{233}\text{UO}_2$ fuel rods [16]; (2) the storage, purification, and distribution of ^{233}U by the ORNL Central Dispensing Facility (Parrott, 1967); and (3) the preparation of $^{233}\text{UO}_2$ powder for the Light Water Breeder Reactor Program [17, 18].

HYDROMETALLURGY: DAPEX AND AMEX

Most of the uranium produced from ores is obtained by sulfuric acid leaching. TBP and the other uranium processing extractants mentioned above require high nitrate concentrations, and they have very little tolerance for sulfate. Around 1950, the ORNL Raw Materials Section, under the supervision of K. B. Brown, began a search for reagents that could extract uranium effectively and economically from the sulfate leach liquors [19]. Several hundreds of organic compounds were begged, bought, or synthesized, and screened for potential utility. Many new compounds had to be synthesized, especially as the surveys progressed, in order to obtain the high molecular weights necessary for sufficient suppression of aqueous solubility.

Dapex

Most of the acid reagents studied were organophosphorus acids—orthophosphoric acid esters, phosphonic acids, and phosphinic acids. It was already known that the mono- and dibutyl phosphoric acids (MBP and DBP) contaminating TBP solutions can extract a range of otherwise-rejected ions [20, 21], and that organic solutions of DBP can be used for extracting metal ions [22, 23]. DBP, however, is far too water-soluble for hydrometallurgical use. Its homolog di-*n*-octyl phosphoric acid has low aqueous solubility, and in hydrocarbon solution is a strong extractant for uranyl ion [24], even from the sulfate leach liquors. However, it forms troublesome precipitates with some of the other metal ions typically present [25]. Di(2-ethylhexyl)phosphoric acid (D2EHPA or HDEHP) is free of significant precipitation problems and has somewhat lower but still usefully high extraction power. This is a function of the steric hindrance and/or strain due to the degree of

alkyl branching [25] (Blake, 1958): as the branch-point is moved farther away from the ester linkage, in branched dialkylphosphoric acids of similar molecular weight, both the extraction power and the susceptibility to precipitations increase. HDEHP has a close-to-optimum compromise of properties, works well in various diluents, including kerosene, and has become the preeminent cation-exchange extractant for a wide range of uses. For the early work, HDEHP was obtained from a commercial mixture through separation by two-phase distribution [26] (Stewart, 1951). Later, as its process potential was shown, it became available from several commercial sources (Coleman, 1961).

A major part of the development of HDEHP extraction into the Dapex process was the establishment of an acceptable means for stripping the extracted uranium (or other extracted value) back into an aqueous solution (Brown, 1958). Stripping can be accomplished by contact with sufficiently concentrated acid (sufficiently high hydrogen ion concentration to reverse the cation-exchange extraction) and/or by contact with a sufficiently competitive complexing agent. More desirable in hydrometallurgy is stripping by cation exchange with a basic aqueous solution. For uranium, sodium or ammonium carbonate solution yields uranyl tricarbonate in the aqueous phase and converts the extractant to NaDEHP or NH₄DEHP. These salts, although soluble in water, are virtually insoluble in the salt-containing strip solutions. However, they may also be insufficiently soluble in the organic phase: alkali salts of dialkylphosphoric acids tend either to precipitate from a kerosene diluent or to form a third liquid phase containing the salt, some diluent, and some water. NaDEHP and NH₄DEHP do the latter, and one key step in the process development was learning how to keep them in a homogeneous organic phase by modifying the hydrocarbon diluent with a polar compound—a high-molecular-weight alcohol, TBP, or one of several other neutral organophosphorus compounds. The critical additive concentration at a given temperature can be related to the extractant concentration by a linear equation [27].

When the added modifier is an alcohol, the extraction power for uranium is impaired, although it remains high enough for many process applications. On the other hand, when the modifier is one of the neutral organophosphorus compounds, the extraction power for uranium is synergistically enhanced. This effect increases in the order phosphates < phosphonates < phosphinates < phosphine oxides. Although poor extractants from sulfate leach liquors if used alone, these reagents increase the extraction coefficients of HDEHP for uranyl ion 4- to 50-fold [28] (Schmitt, 1958; Blake, 1958; Baes, 1963).

The Dapex process (TBP-synergized) was first used in uranium production by Kerr-McGee Company (Hazen, 1957). It was also used in several other plants but, subsequently, has been mainly replaced in domestic uranium production by the more selective Amex process. A recent modification, phosphine-oxide synergized, is now used for uranium recovery from wet-process phosphoric acid (Hurst, 1972). Modifications have also been developed for vanadium recovery [29] (Blake, 1958; Quinn, 1957), thorium recovery (Brown, 1958), uranium recovery from sulfuric acid anion-exchange eluates [30] and from fluoride solution of spent reactor fuel (Coleman, 1966), rare earth separations, and curium recovery [31]. Dapex was the basis for the Talspeak process (below). Other wide-spread uses for HDEHP—processing, analytical, and physicochemical—are beyond the scope of this paper to enumerate.

Amex

The first reported use of amine extraction was in the separation of strong and weak acids (Smith, 1948), using several amines, of which the most satisfactory (because the largest then available) was methyl-di-*n*-octylamine (MDOA). This information was applied to analytical metal-ion extraction by F. L. Moore (1960) [32], and soon thereafter to the survey search for uranium process extractants [33, 34] (J. G. Moore, 1957).

Examination and comparison of an increasingly wide range of amines (including quaternary ammoniums with amines, by a convenient misuse of nomenclature) eventually gave a working picture of the different yet interdependent effects of amine class, symmetry, size and shape of alkyl (or aryl) groups, and choice of diluent (Coleman, 1958). Conversely, as understanding

of amine extraction developed, and especially as the Amex process for uranium recovery reached commercial acceptance, the interest of manufacturers grew in supplying the secondary and tertiary amines needed, and at the higher molecular weights needed, for process extraction (Coleman, 1963). In turn, the spread of amine extraction into many diverse fields was markedly accelerated by the commercial availability of suitable amines such as Amberlite LA-3 (a primary (trialkylmethyl)-amine), Amberlite LA-1 (secondary dodecyl(trialkylmethyl)-amine), Amberlite LA-2 (secondary *n*-dodecyl(trialkylmethyl)-amine), TLA (tertiary tri-*n*-dodecylamine), Alamine 336 and Adogen 363 (tertiary tri-*n*-octyl, *n*-decyl)amines, and Aliquat 336 and Adogen 364 (quaternary methyltri-*n*-octyl, *n*-decyl)-ammoniums).

The study of the various amines showed that the expected analogy with anion-exchange resins is indeed valid and useful, but only as a starting point since the amine solutions have so many more variables. As in resinous anion exchange, uranyl sulfate is extracted by amine sulfate as a sulfate complex, and the extraction is strongest at moderately low sulfate concentration, e.g., 0.5-1 *M*, and pH not too far from 1 or 2. But while primary, secondary, and tertiary amines are roughly alike in extracting uranyl sulfate, they vary extremely in extracting uranous sulfate (and sulfates of many other three- and four-valent metal ions): primary >> secondary >> tertiary. Again in analogy with resins, extracted uranium can be stripped by displacement with chloride or nitrate ions; but further, they (excluding the quaternary ammoniums) can also be stripped by neutral and basic solutions that hydrolyze the amine salt to free-base amine. The wide choices for extraction control and the options in stripping permit considerable versatility in process design [35].

The Amex process for uranium uses typically 0.1 *M* tertiary or branched secondary amine in kerosene (sometimes modified with an alcohol) for extraction at pH ≈ 1; and for stripping it uses a solution of carbonate, chloride, or nitrate or a slurry of magnesium oxide, with an overall increase in the uranium concentration by a factor of 20 to 40 (Brown, 1958). The Amex process for vanadium uses a similar amine solution for extraction of oxidized vanadium at pH ≈ 2, and sodium carbonate solution for stripping (Brown, 1958). The Amex process for thorium uses a primary amine or a straight (or slightly branched) secondary amine in alcohol-modified kerosene for extraction, and chloride, nitrate, or carbonate for stripping [36] (Crouse, 1959); this can be modified to separate thorium from uranium, or to separate thorium, uranium, and rare earths [37]. Amex is the basis for the Tramex process (below). As noted above for HDEHP, it is beyond the scope of this paper to list the current processing, analytical, and physicochemical uses of amine extraction.

TRANSPUTONIUM ACTINIDES:

TRAMEX AND TALSPEAK

Neutron irradiation of plutonium involves a series of neutron captures and beta decays to produce higher atomic weights and atomic numbers. Although ²³⁹Pu and several other nuclides on the main growth path may fission when capturing neutrons, causing large losses, long-term irradiation of plutonium in nuclear reactors has been the principal method used to produce the transplutonium elements up through fermium. Fermi recognized the value of this method and initiated a program for irradiating plutonium in the Hanford Reactors in 1944 (Bentley, 1955). Information from these irradiations stimulated considerable interest and led to further work at several installations [38, 39]. Much larger scale irradiations were started in the Savannah River reactors (Groh, 1965) and continued in the Oak Ridge High Flux Isotope Reactor (HFIR), designed specifically for producing large quantities of the transplutonium elements through californium and experimental quantities of einsteinium and fermium (Leuze, 1970).

As mentioned above, most of the starting material is lost by fission—99.7% fission products in obtaining a 0.3% yield of ²⁵²Cf. About a third of the fission products are trivalent lanthanides. Since the trivalent transplutonium actinides are chemically very similar to the lanthanides, this presented extreme difficulty in separation and purification. For the small scale

preparations, this was accomplished by ion exchange (IX) chromatography, the most successful process using elution from anion exchange resin with hot, concentrated (>10 *M*) lithium chloride solution (Katz, 1957; Hulet, 1961). But chromatography was not suitable for the larger scale and remote operation required for the Savannah River and HFIR irradiations—a solvent extraction process was desired for the TRU facility, the chemical separation and refabrication plant that complements the HFIR. Various extractions using TBP or organophosphorus acids were tried without complete success. Then F. L. Moore (1961) reported successful group separation at tracer levels by tertiary amine extraction from 12 *M* lithium chloride solution, chemically analogous to the lithium chloride chromatographic method. B. Weaver and R. D. Baybarz developed the extraction system into a full-scale process, "Tramex" (Leuze, 1963; Baybarz, 1963). The tertiary amine extractant, e.g., Alamine 336 chloride in diethylbenzene, is used at 0.6 *M*, which is about the highest concentration permitted by the effects of viscosity and density on phase separation. The irradiated targets are dissolved in hydrochloric acid and adjusted to 10 *M* LiCl, 0.1 *M* (0.3 *N*) AlCl₃, 0.02 ± 0.005 *M* HCl. The pregnant extract is scrubbed with 11 *M* LiCl (no aluminum) at the same acidity, then stripped with 8 *M* HCl. The lanthanides and most other contaminant ions are rejected in the raffinate. Of the extracted contaminants, only nickel(II) is stripped with the actinides, and the actinides are now in a suitable condition for separation and purification by small-scale IX chromatography. Details of process design for the remote operation of Tramex, including specialized equipment, corrosion tests, safety tests, etc., are given by Peishel (1966) and Bottenfield (1966).

While highly successful for its purpose, Tramex has drawbacks, particularly the corrosive nature of the chloride solution. Concurrently with the Tramex development, B. Weaver and F. A. Kappelmann found a different group separation that uses organophosphorus acid extraction from an aqueous carboxylic acid solution containing a strong complexer, and developed it into an alternative process, "Talspeak" [40] (Kappelmann, 1966; Weaver, 1968). Of various possible extractants and aqueous complexers, HDEHP and diethylenetriaminepentaacetic acid (DTPA) are probably the best. The process can accept the actinide-fission product feed in, for example, 1 *M* lactic acid solution, in countercurrent contact with 0.5 *M* HDEHP in diisopropylbenzene, and add 0.1 *M* Na₂DTPA as a component of a 1 *M* lactate (pH 3) scrub solution. Without the DTPA, the actinide and lanthanide groups would overlap, as usual. The DTPA interferes somewhat with extraction of the fission product lanthanides, but considerably more with extraction of the actinides, enough more to give complete separation of the two groups.

Although Talspeak did not supplant Tramex in its immediate target—the HFIR-TRU operations at ORNL—it has a considerably wider range of applicability, and it has been widely examined and adapted both here (Ritter, 1969; Filer, 1974) and abroad (Koch, 1970; Kolarik, 1974a, 1974b; Berger, 1970; Ali, 1971; Fardy, 1973; Lunichkhina, 1973). These studies include fundamental investigations, analytical applications, and process development; one particularly important field of current interest is that of improving nuclear waste management by separating the actinides from the fission products in fuel-reprocessing wastes.

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NOTE: The availability of these reports varies greatly. They range from formal reports given wide standard distribution, and fully covered by the appropriate abstracting journals, down to exceedingly informal intragroup ad hoc memoranda. In contrast to the usual situation, where an inaccessible reference approaches worthlessness, the identifying and listing of these inaccessible reports may be a chief value of this review.

CONCLUSION

At ORNL, which is one of the institutions in the forefront of solvent extraction science and technology, three development milestones have been particularly significant:

(1) *Purex*, because it focused the virtues of one extractant into a process that dominates its specialized field.

(2) *Dapex and Amex*, because they solved the immediate needs of a specialized field, and more because they opened up far wider general fields to solvent extraction technology.

(3) *Tramex and Talspeak*, because they typify successful adaptation of those processes to an extremely difficult problem, and are reaching still farther.

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