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Z. Kolarik
Institut für Heiße Chemie

Kernforschungszentrum Karlsruhe

KERNFORSCHUNGSZENTRUM KARLSRUHE

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SEPARATION OF ACTINIDES AND LONG-LIVED FISSION PRODUCTS FROM HIGH-LEVEL RADIOACTIVE WASTES (A REVIEW)

Zdenek Kolarik

Kernforschungszentrum Karlsruhe GmbH, Karlsruhe

Kernforschungszentrum Karlsruhe GmbH
Postfach 3640, 7500 Karlsruhe 1

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ABTRENNUNG VON ACTINIDEN UND LANGLEBIGEN SPALTPRODUKTEN AUS HOCHRADIOAKTIVEN ABFÄLLEN

Zusammenfassung

Die Entsorgung von hochradioaktiven Abfällen wird vereinfacht, wenn toxische, langlebige Actiniden und Spaltprodukte aus den Abfällen noch vor der Endlagerng abgetrennt werden. Besonders wichtig ist dabei die Abtrennung von Americium, Curium, Plutonium, Neptunium, Strontium, Cesium und Technetium. Die abgetrennten Nuklide könnten getrennt von der Hauptmenge der hochradioaktiven Abfälle endgelagert oder, anstrebenswerter, zu kurzlebigeren Nukliden transmutiert werden. Dieser Bericht bietet eine Übersicht der chemischen Eigenschaften von Actiniden und langlebigen Spaltprodukten, die für ihre Abtrennung aus Abfällen von Bedeutung sind. Außerden werden chemische und physikalische Eigenschaften der Abfälle sowie ihre Konditionierung beschrieben und allgemeine Aspekte der Partitionierung kurz diskutiert. Die größte Aufmerksamkeit wird der Extraktionschemie der abzutrennenden Elemente und der Anwendung der Extraktion in Einzeloperationen von Partitionierungsverfahren gewidmet. Weiter wird das Verhalten der Elemente bei der Ionenaustauschchromatographie, Fällung, Elektrolyse aus wässrigen Lösungen und Schmelzen sowie der Verteilung zwischen geschmolzenen Salzen und Metallen erörtert. Fließschemata ausgewählter Partitionierungsverfahren werden als Beispiele gezeigt.

Abstract

The management of high-level radioactive wastes is facilitated, if long-lived and radiotoxic actinides and fission products are separated before the final disposal. Especially important is the separation of americium, curium, plutonium, neptunium, strontium, cesium and technetium. The separated nuclides can be deposited separately from the bulk of the high-level waste, but their transmutation to short-lived nuclides is a much more favourable option. This report reviews the chemistry of the separation of actinides and fission products from radioactive wastes. The composition, nature and conditioning of the wastes are described. The main attention is paid to the solvent extraction chemistry of the elements and to the application of solvent extraction in unit operations of potential partitioning processes. Also reviewed is the behaviour of the elements in the ion exchange chromatography, precipitation, electrolysis from aqueous solutions and melts, and the distribution between molten salts and metals. Flowsheets of selected partitioning processes are shown and general aspects of the waste partitioning are shortly discussed.

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1.0 GENERAL CONSIDERATIONS

1.1 INTRODUCTION

There may be two reasons for the separation of actinides and long-lived fission products from high-level radioactive wastes: recovery of radionuclides as useful, marketable products, and reduction of risks and costs of the treatment and final disposal of the wastes. As useful products the isolated radionuclides can be used as radiation or heat sources, or they can serve as starting materials for the production of another radionuclides. Let me give some examples: The isotopes ^{241}Am and ^{137}Cs are potential γ-radiation sources, and ^{99}Tc und ^{147}Pm may be sources of a soft β-radiation. The isotopes ^{90}Sr and ^{238}Pu are potential sources of heat which can subsequently be converted to electric energy. ^{238}Pu is little abundant in radioactive wastes. However, more abundant is there the isotope ^{237}Np, which is the starting material for the production of ^{238}Pu. Long-term neutron irradiation of americium and curium isotopes yields the nuclide ^{252}Cf, which can find numerous applications as a neutron source. More detailed information about present and potential applications of radionuclides can be found e.g. in [1].

Concerning problems of the final disposal of radioactive wastes, long-lived actinides and some long-lived fission products are those components which increase the over-all waste radiotoxicity (see e.g. [2]) and, consequently, the disposal costs. The radiotoxicity of Pu, Am and Cm isotopes has ever been estimated as high. On the other hand, it has been established only in the recent decade that the isotope ^{237}Np has also to be considered strongly radiotoxic (see e.g. [3]). It is a favourable circumstance that the mass and volume of highly radiotoxic nuclides represents only a small fraction of the total mass and volume of high-level wastes. Recovered from the entire amount of the wastes, the highly radiotoxic isotopes can be separately deposited at a reduced risk and costs or, much better, trasmuted to short-lived and less radiotoxic nuclides (see e.g. [4]).

The aim of the separation of long-lived radioisotopes from wastes determines the concept of the respective separation procedure. If the isotopes are to be separated as useful products, they must be gained in a chemically, or at least radiochemically pure state. The yield plays a secondary role, and the interest is concentrated on Am, Cm and Np among the actinides and on Sr and Cs among the fission products. If long-lived radioisotopes are separated for facilitating the waste management, they must be separated with a considerably high yield. In this case the purity of the separated products is of secondary importance only. The necessity of removing also Pu from the waste is obvious and Tc has most probably also to be separated.

Looking back to the history of the nuclear technology, the recovery of radioisotopes as useful products can be perceived as the first incentive for the separation of actinides and fission products. Separation processes were developed, with considerable optimism, as early as in the 1950s. Later the optimism had to give way to some disenchantment, as it turned out that the marketability of radioactive isotopes was less eminent than expected.

It was a consequence of the fading nuclear enthusiasm in the 1970s and 1980s that facilitation of the waste disposal became the only reason, if any, for the potential partitioning of radioactive wastes. Recently we have experienced some renaissance of the partitioning idea, mainly due to progress in the examination of possible nuclear transformation reactions. A Japanese intiative, namely the proclamation of the Omega project played a prompting role. Still more stimulating could be the most recent proposal (Los Alamos concept) based on the use of a high current accelerator for the transmutation. At present, the partitioning and transmutation (P+T) are nothing more and nothing less than a potential new way in the radioactive waste strategy. It is not yet possible to predict its feasibility, impact and profit. It is evident that a positive impact cannot be expected in near future. It also is evident that on industrial scale the partitioning would be coupled with considerable costs and with some risk. Nevertheless, it appears that the P+T idea is worthy of further discussions, plannings and even experimental research programmes.

This report is a contribution to the assessment of those possibilities, which the basic chemistry of actinides and fission products gives for the development of separation processes. It is the aim of this report to compile information about the distribution behaviour of the respective elements in different heterogenous systems, utilization of the results in the design of separation processes for the partitioning of high-level wastes, and experiences in process tests performed with simulated or real waste solutions. Moreover, a critical evaluation of the collected data is attempted. Emphasis is laid on information on unit operations, rather than on complete process flowsheets. It is an important piece of development work to utilize basic data for the elaboration of efficient unit operations. Once optimized, the unit operations can be sequenced as construction kit elements for assembling any flowsheet. It must be pointed out that this report deals exclusively with the chemistry and, to a much lesser extent, the engineering of the actinide and fission product separation. Topics like the analysis of the possible impact of the waste partitioning and transmutation, physical aspects of the transmutation of nuclides, problems and strategy of the waste management, general considerations about future developments of the nuclear technology etc. are beyond the scope of the report.

1.2 NOMENCLATURE, ABBREVIATIONS AND SYMBOLS

The term solvent is used for the barren organic phase of a liquid-liquid system. If the organic phase contains components to be separated, it is called loaded solvent. Typically, the solvent is a solution of an extractant in a diluent. Solvents consisting of an undiluted extractant or pure diluent are less common.

Distribution ratio is designed D, with the distributed element given as subscript, e.g. D_{Am}, D_{Cm} and D_{Eu}. If the valency of the distributed element is to be pointed out, it also is given in the subscript, e.g. $D_{U(VI)}$. A separation factor is defined as a quotient of two distribution ratios, e.g. the Am/Eu separation factor is $\alpha_{Am/Eu} = D_{Am}/D_{Eu}$. A decontamination factor (DF) is defined as a ratio of the radioactivity of a component before and after the separation, whereat the radioactivity can be related to the volume or the mass of the original material. Species and their concentrations in the organic phase are denoted with a bar over the formula.

Abbreviations will be used only for a limited number of more or less common extractants and complexants. They are

BAMBP.................4-sec-butyl-2-(α-methylbenzyl)phenol
OΦD(iB)CMPO ....n-octyl(phenyl)-N,N-di*iso*butylcarbamoylmethylphosphine oxide
DNNS....................dinonylnaphthalene sulfonic acid
DTPA.....................diethylenetriamine-N,N,N′,N′,N″-pentaacetic acid
HDEHP..................di(2-ethylhexyl) phosphoric acid
TBP.......................tri-*n*-butyl phosphate
TOA.......................tri-*n*-octylamine
TPTZ......................2,4,6-tris(2-pyridyl)-1,3,5-triazine
TTA........................thenoyltrifluoroacetone
DC18C6.................dicyclohexano-18-crown-6

Other abbreviations are

HAW......................high-level radioactive waste
FBR.......................fast breeder reactor
LWR......................light water cooled reactor
MOX......................mixed oxide

1.3 SCOPE, PARTICULAR ASPECTS AND AIMS OF THE WASTE PARTITIONING

1.3.1 Composition of High-Level Liquid Radioactive Waste

High-level liquid radioactive waste is typically originated in the reprocessing of irradiated nuclear fuel in the Purex process (see e.g. [5] for the description of its conventional form). Aqueous raffinate from the simultaneous extraction of U(VI) and Pu(IV) in the first extraction cycle represents the major part of the waste. Most fission products and minor actinides are left in the raffinate and, thus, follow the shortest way to the waste. Essential fractions of problem elements like neptunium and technetium can follow uranium and plutonium and must be removed in purification cycles [6]. Raffinates or raffinate concentrates from the purification cycles must then be added to the high-level waste, if escape of Np and Tc into medium-level waste is to be prevented. A small fraction of the Pu inventory is kept in the used solvent, recovered in the solvent wash with sodium carbonate, and directed to the medium-level waste.

The splitting of actinide and fission product paths, and escape of actinides and fission products into the medium-level waste is largely avoided in an advanced modification of the Purex process. The modification (Impurex process) was developed in author's institute (see [7-9] and references therein), and includes only one solvent extraction cycle. U(VI) and Pu(IV) are extracted to a high solvent loading at a high concentration of nitric acid and at elevated temperature. Then Tc can be directed into the raffinate, if the loaded solvent is scrubbed at an optimized nitric acid concentration and an optimized flow ratio [10]. Np is predominantly left in the raffinate even without any precautions, and its separation is improved if the loaded solvent is scrubbed in an electroreduction contactor. The used solvent is washed with hydrazine carbonate, which can be destroyed in the wash product. The volume of the product can be minimized and the concentrate is added to the high-level waste.

The concept of a partitioning process must be compatible with the fact that minute amounts of actinides and rather small amounts of fission products are to be separated from macro components of a very complex system. The high-level liquid waste contains a considerable number of components. The concentration of them ranges from micrograms to hundreds of grams per litre, and they can be nonradioactive or posses a minute to high specific radioactivity. Moreover, the liquid waste is seldom a clear solution. A precipitate is deposited from the solution during its concentration by evaporation or even during mere storage in a tank. The liquid phase of the waste, i.e. the HAW solution, contains nitric acid from the fuel dissolution and from the U(VI) and Pu(IV) extraction in the Purex process. It further contains fission and corrosion products, and sometimes also Gd(III) which is used in the Purex process as a neutron poison. Finally, the HAW solution contains residues of the Purex process extractant, tributyl phosphate, which is predominantly destroyed to dibutyl and monobutyl phosphates and even to phosphoric acid. Concentrations of components of the HAW solution are dependent on numerous factors and may vary in broad limits. Let us mention factors like the material used in the fabrication of fuel elements, physical parameters of the nuclear reactor, the burn-up of the fuel, material used for the construction of a reprocessing plant, particular details of the Purex process flowsheet, the degree of concentration of the rafinate from the first Purex process cycle, the storage time of the concentrate etc. Some examples of the composition of HAW solutions are given in Table 1. The solutions were originated in the reprocessing of oxidic, stainless steel cladded fuels. Such solutions were considered typical which resulted from a fuel treatment initiated by the chop-and-leach procedure. Table 1 involves no example of a solution from a treatment including total dissolution of a zircalloy cladded fuel. Such solutions contain up to 50 g Zr/l and represent a particular case. Also atypical are alkaline HAW solutions resulting from early processes for the production of weapon plutonium.

Table 1. Composition of HAW Solutions from the Purex process: All examples refer to uranium oxide, stainless steel cladded fuels initially containing 3 - 5% ^{235}U. The cladding remained undissolved in the fuel dissolution and no aluminium nitrate was used as a salting-out agent in the Purex process. The volume of the HAW solution before concentration by evaporation was ~5000 l/t fuel.

Specification, Component	*Specific values and concentrations*			
	[11]	*[12,13,14]*	*[15]*	*[16]*
burn-up of the fuel, MWd/t	35000	33000	28000	25000
cooling time of the fuel, d	150	150	1830	-
volume of HAW, l/t fuel	570	5000	500	380
HNO_3 , Mol/l	~1	4	2.0	2.0
Am, g/l	0.92	0.031	0.29	2.2
Cm, g/l	0.05	0.007	0.06	0.73
Pu, g/l	0.17	0.009	0.23	0.48
Np, g/l	0.85	0.015 - 0.15	-	0.71
U, g/l	18	0.95	1.8	13
Ag, g/l	0.14	0.012	0.09	0.16
Rb, g/l	0.61	0.066	0.63	0.81
Cs, g/l	4.6	0.54	5.1	5.2
Sr, g/l	1.5	0.18	1.5	1.5
Ba, g/l	3.0	0.28	2.8	3.2
Cd, g/l	0.24	0.017	0.095	0.18
La, g/l	2.3	0.25	2.0	2.5
Ce, g/l	4.5	0.58	4.6	4.8
Pr, g/l	2.3	0.24	1.9	2.3
Nd, g/l	7.3	0.78	6.3	7.9
Pm, g/l	0.06	-	0.17	0.07
Sm, g/l	1.8	0.16	1.3	1.8
Eu, g/l	0.30	0.036	0.29	0.30
Y, g/l	0.73	0.094	0.75	0.85
Zr, g/l	6.6	0.73	6.3	6.7

Table 1 (continued)

Specification, Component	*Specific values and concentrations*			
	[*11*]	[*12,13,14*]	[*15*]	[*16*]
Sn, g/l	0.045	0.011	-	0.11
Sb, g/l	0.020	0.0035	-	0.024
Mo, g/l	6.2	0.69	6.6	7.0
Se, g/l	0.024	0.01	-	-
Te, g/l	0.95	0.11	0.87	1.0
Tc, g/l	1.6	-	1.5	1.7
I, g/l	-	0.054	-	-
Br, g/l	0.024	0.003	-	-
Ru, g/l	4.1	0.45	3.4	4.4
Rh, g/l	0.89	0.08	0.82	1.1
Pd, g/l	2.7	0.26	1.9	3.2
Na, g/l	0.18	1.6	1.75	0.23
Cu, g/l	-	0.02	-	-
Ni, g/l	0.14	0.047	0.35	0.20
Zn, g/l	-	0.024	-	-
Fe, g/l	3.5	1.9	2.1	3.0
Al, g/l	-	0.002	0.02	-
Cr, g/l	0.35	0.096	0.47	0.50
Gd, g/l	16	0.021	0.16	24
H_3PO_4 , g/l	3.6	-	0.22	4.0

1.3.2 Precipitates and Undissolved Residues

When released as a rafinate from the Purex process, the HAW solution contains no coarse solids and may only be polluted with colloids. However, a precipitate separates from a HAW solution ($\sim$5000 l/t fuel and $\sim$4 M HNO_3) when it is stored even without concentration by evaporation [17,18]. The formation of a precipitate is not avoided, if dissolved or dispersed remainders of TBP are almost fully removed from the HAW solution [19]. Nevertheless, remainders of TBP support the precipitation because they are decomposed predominantly to phosphoric acid. Then zirconium phosphate represents the major part of the precipitate, which further contains hydoxides, nitrates and phosphomolybdates (see references in [18]). When a simulated HAW solution (36000 MWd/t, ~4000 l/t fuel, ~4.5 M HNO_3) was stored for 9 monts, a precipitate was formed containing 24% Pd, 18.4% Pu and 18% Zr [17].

The precipitate formation is intensified, if the HAW solution is concentrated. To study the phenomenon, a simulated HAW solution was concentrated by evaporation in vacuum. During concentration by a factor of 40, a precipitate formed in which the mixed nitrate compound $Ba_{0.5}Sr_{0.5}(NO_3)_2$, the heteropoly acid $P_2O_5.24MoO_3.7H_2O$ and the zirconium molybdate compound $Zr(OH)_2.Mo_2O_7.(H_2O)_2$ could be identified. When the HAW solution was concentrated by a factor of 20 and subsequently stored, the zirconium molybdate compound precipitated slowly. The precipitation was accelerated by a temperature increase and by lowering the concentration of nitric acid [20].

The precipitate formation is particularly intensive, if a HAW solution is simultaneously concentrated by evaporation and denitrated. A concentration of a simulated HAW solution by a factor of 3 - 6 and denitration by formic acid caused the formation of < 1 g solid per kg fuel, if the HNO_3 concentration did not decrease below 2.5 M. The amount of solids increased to ~15 g per kg fuel, if the acid concentration was suppressed to ~1 M. The precipitation can be seen as a reason for limiting the denitiration during the evaporation so that the concentrate contains e.g. > 1 M HNO_3. The precipitate retains a fraction of actinides (and also fission products), and the fractions retained are strongly increased with decreasing resulting concentration of HNO_3 in the concentrate. When a HAW solution was concentrated by a factor of 6 and simultaneously denitrated to 1 M HNO_3, a precipitate was formed which retained ~80% Zr, ~50% Pu and ~1.5% Am. The retained fractions were as low as ~1% Zr, ~0.05% Pu and ~0.005% Am, when the solution was evaporated without denitration and the resulting HNO_3 concentration was 6 M [19].

An alpha contaminated solid is also produced in the very beginning of the Purex process. A solid residue remains undissolved in the dissolution of the irradiated fuel in hot nitric acid. The residue retains a variable fraction of the Pu inventory. At a high burn-up (> 20000 MWD/t), the Pu fraction retained is very small in the dissolution of uranium oxide LWR fuels, namely 0.01 - 0.08% of the Pu inventory [21,22]. A larger fraction of plutonium is retained in the insoluble residues in the dissolution of mixed oxide fuels. The fraction is dependent on the burn-up and the fabrication method of the fuel. Mechanically mixed LWR and FBR fuels (> 25000 MWd/t) leave in the residue a Pu fraction ranging from 1.3 - 4.5% [21,23] to 12.4% [24]. Coprecipitated MOX fuels are dissolved more easily and leave mere 0.005 - 0.08% of the Pu inventory in the solid residue [23,24]. The fraction of americium and curium retained by the residue may neither be negligible [22]. Thus, separation of actinides from solid dissolver residues might appear necessary, if the removal of actinides from reprocessing wastes is to be complete. Some problems may then arise in the conversion of the residues to a manageable solution.

1.3.3 Thermal Output of High-Level Radioactive Wastes

At a waste age of 10 - 100 y, the total thermal output is predominantly made up of the decay heat of the isotope pairs ^{90}Sr-^{90}Y and ^{137}Cs-^{137m}Ba [25]. A numerical example can be given for a fuel which was burned-up to 30000 MWd/t and reprocessed after a cooling period of 180 d. After 5 years the thermal output of the waste (related to 1 t fuel) consisted of 94 W yielded by transuranium elements, 1500 W yielded by the pairs ^{90}Sr-^{90}Y and ^{137}Cs-^{137m}Ba, and 158 W yielded by other fission products [26]. After a ~160 y ageing, the contribution of the pairs ^{90}Sr-^{90}Y and ^{137}Cs-^{137m}Ba to the heat output is approximately equal to the contribution of the isotopes ^{241}Am and ^{243}Am. The Am isotopes are predominating heat sources in waste aged for $\geq$400 y [25].

A more detailed illustration of the contribution of particular fission product to the total thermal output of little aged wastes is given in Table 2. Unfortunately, the original source [27] provides no information about the partial heat output of actinides.

Table 2. Thermal output of fission product elements in high-level radioactive waste: Values calculated for waste produced in the reprocessing of LWR uranium oxide fuels [27].

Fission product element	*Thermal output in W/(t fuel) after different cooling periods*			
	1 y	*2 y*	*5 y*	*10 y*
Sr	124	96.8	89.7	79.3
Y	506	435	403	356
Cs	2170	1590	675	236
Ba	391	382	356	317
Ru	27.4	9.46	1.19	0.038
Rh	3340	1670	211	6.71
Tc	0.0097	0.0097	0.0097	0.0097
Ce	449	183	12.6	0.146
Pr	4230	1740	120	1.39
Pm	46.1	34.4	15.5	4.14
Sm	2.21	2.19	2.14	2.06
Eu	61.3	57.5	48.8	38.6
Total waste	12000	6270	1960	1060

1.3.4 Effectiveness of the Actinide Separation

It is the principle aim of a separation process to attain those decontamination factors, which are desirable for a particularly defined reduction of the radiotoxicity of wastes. The attainment of target DF values is especially important in the removal of alpha emitters, which not only are more radiotoxic than beta and gamma emitters, but also have longer half-times. Table 3 shows DF values, which are proclaimed to be desirable in the removal of actinides from radioactive wastes. The values are based on different criteria and, correspondingly, differ considerably from source to source.

Table 3. **Requested effectiveness of the actinide removal from radioactive wastes:** Decontamination factors (DF) to be reached in the partitioning of HAW solutions derived from different fuel types. It is supposed that 99.5% Pu is recovered in the Purex process. *Criteria*: a) The toxicity index of vitirified waste will after 1000 y decrease to a value of 3×10^6 m^3 H_2O/m^3 glass [19]; b) the content of actinides in the waste is so far reduced that their radiotoxicity is equal to that of ^{99}Tc [28]; c) the toxicity index of the waste is after 1000 y equal to 5% of the toxicity index of pitchblende containing 70% U [29]; d) a dimensionless toxicity index will after 2000 y decrease to 10^6 [18].

Actinide	*DF value to be reached at a given origin of the waste*								
	LWR U oxide				*LWR MOX*		*FBR MOX*		
	[19]	*[28]*	*[29]*	*[18]*	*[19]*	*[29]*	*[19]*	*[29]*	*[18]*
Np	20	20	20	10	2	20	1	3	10
Pu	50	50	10	150	100	50	100	50	500
Am, Cm	200	1000	1000	1000	600	1000	400	1000	1000

1.3.5 Chioce of Unit Operations

Numerous viewpoints of safety, engineering feasibility and economy must be respected in the choice of process steps. Let us give some examples:

- All chemical reactions and separation operation must be controllable. A reaction with a burst after an induction period must be avoided, as well as any impetuous reactions producing off gases contaminated with radioactive aerosols. To prevent fluid-dynamic perturbations caused by the formation of stable emulsions, solids and fines must largely be removed from all solutions to be fed into extractors or ion exchanger columns. Also posterior deposition of precipitates after the solid removal must be avoided.

- Production of additional liquid or solid waste in the course of the HAW partitioning must strictly be limited to a minimum extent. Entire process streams or single chemicals must be recycled as far as possible.

- Actinides and fission products to be separated must not be distributed beween different streams leaving a partitioning process. It could at most be acceptable that e.g. an actinide is distributed between a liquid process stream and an extremely insoluble solid, which can be disposed as a low volume, alpha contamined waste.

- Product streams of a partitioning process should not contain large amounts of substances which could interfere with the subsequent treatment, e.g. concentration and vitrification of the partitioned waste. To be avoided are salting-out substances like aluminium or sodium nitrates, complexants decomposing to precipitate forming products etc.

1.4 CONDITIONING OF HAW SOLUTIONS FOR THE PARTITIONING

Suppression of the HNO_3 concentration in the HAW solution may be desirable or even necessary before e.g. extraction operations. If actinides or fission products are to be extracted with an acidic extractant like HDEHP, the acid concentration must be in the range pH 1 - 3. Even in the exctraction of actinide or fission product nitrates with solvating exctractants it can be advantageous to reduce the acid concentration to 1 - 2 M. Reductive decomposition of nitric acid to gaseous products is much more profitable than e.g. neutralization. Common reductants like saccharose, formaldehyde and formic acid can be used, and formic acid is the preferred substance. The reaction starts, sometimes violently, after an induction period and a reaction time of several hours is necessary to reduce the HNO_3 concentration from initially ≥ 3 M to pH 1 - 3. Average 1.65 mol formic acid are consumed per mol HNO_3 destroyed [30]. Addition of nitrite to the reaction mixture shortens the induction period and prevents a violent start of the reaction [15]. Prolonged reaction with excess formic acid results in the reduction of nitrate ion to ammonia, and a pH value as high as 9 can be reached.

The outline of some partitioning processes supposes the HAW solution to be denitrated to pH 2 - 3. As mentioned above, a precipitate is formed at ≤ 2 M HNO_3. The amount of the precipitate increases with decreasing acid concentration, and is considerable at pH 2. The precipitate consists mainly of hydroxides, elemental platinum metals, and phosphates. Strongly hydrolyzing elements like Zr(IV) are fully retained in the solid phase. Also retained is neptunium, which in later denitration stages is reduced to Np(IV). Lanthanides(III) and actinides(III) are retained to a much lesser extent. The distribution of actinides and fission products between the unwashed precipitate and the liquid phase is illustrated by data in Table 4.

Table 4. Losses of actinides and fission products to the solid phase in the denitration of HAW solutions: Fractions retained in the unwashed solid phase in the denitration of true [30] and simulated (other sources) HAW solutions with formic acid to different resulting HNO_3 concentrations.

Ele-ment	*Fraction in the Precipitate (%) at*								
	2 M HNO_3 [15]	*pH 0.5 [15]*	*pH 0.9 [15]*	*pH 1.0 [15]*	*pH 2.0 [15]*	*pH 4.8 [15]*	*pH 2 [31]*	*pH 2.2 [30]*	*pH 2 [17]*
Am,Cm	-	-	-	-	-	-	5-10	<1	5
Pu	-	-	-	-	-	-	20-30	6.6	5
Np	0.5	0.8	-	2.1	-	-	80-90	-	90
Zr	35	87	100	-	98	100	100	-	-
Mo	69	87	100	-	93	100	100	-	-
Ru	1	10	31	-	48	85	42	-	-
Rh	-	-	-	-	-	-	30	-	-
Pd	-	-	-	-	-	-	90	-	-
La	0.004	0.01	0.23	-	0.74	18	-	-	-
Y	-	-	-	-	-	-	20	-	-
Sr	0.4	0.4	-	0.8	-	-	-	-	-
Cs	0.1	0.28	2.8	-	1.1	1.8	-	-	-

Data in Table 4 do not give proper information about the behaviour of plutonium during the denitration. Before the HNO_3 concentration is lowered to 1 M, plutonium remains predominantly in the liquid phase as Pu(IV). When the acid concentration is further decreased, plutonium is increasingly transferred to the solid phase, still as Pu(IV). The retained fraction of Pu reaches a maximum (~95%) at pH 1.3, i.e. after a reaction time of 2 h. At continued denitration to lower acid concentrations, Pu(IV) is reduced to Pu(III) and simulatenously desorbed. When a pH value of 2.3 is reached, Pu(IV) is predominantly reduced to Pu(III) and present in the liquid phase. The fraction of Pu adsorbed at pH 0 - 2 is strongly bonded in the solid phase. If the denitration is interrupted in this acidity region, the adsorbed Pu fraction cannot be desorbed with solutions of nitric acid [17,32].

Retained fractions of Am(III) and Cm(III) can easily be desorbed with diluted formic acid (see Table 5). Warm 4 M HNO_3 is needed for the desorption of neptunium [12,31]. The desorption of residually retained Pu is still more difficult and hydrofluroic acid must be added to the desorption solution (see Table 5). It need not be pointed out that the necessity of the desorption with $\geq$8 M solutions of HNO_3 is troublesome. A considerable part of the precipitate is dissolved and the used desorption solution must be directed back to the denitration step.

Table 5. **Distribution of actinides during and after the denitration:** A true HAW solution was denitrated with formic acid and the precipitate formed was successively washed with 3 desorption solutions [30].

Process stream	*Volume (l)*	*Fraction in the Precipitate (%)*		
		Pu	*Am*	*Cm*
HAW solution, not conditioned, 4.35 M HNO_3	42	100	100	100
denitrated HAW solution, 1 M HCOOH, pH 2.2	48	~93.4	>99	>99
1st desorption solution, 0.5 M HCOOH	4.2	~4.1	~0.33	~0.3
2nd desorption solution, 0.5 M HCOOH	4.2	~0.8	~0.05	~0.05
3rd desorption solution, 8 M HNO_3 + 0.1 M HF	2.0	~1.6	~0.11	~0.09
washed denitration precipitate		<0.2	<0.2	<0.2

2.0 SEPARATION OF ACTINIDES

2.1 SOLVENT EXTRACTION

2.1.1 Common Extraction of Lanthanides(III) and Transplutonides(III)

2.1.1.1 Solvating Extractants

Monofunctional Phosphoryl Extractants: Solvating extractants, at least those studied up to date, do not separate the group of transplutonides(III) from the group of the fission product lanthanides(III). Data given below in tables and figures show that, in the absence of particular complexants, transplutonides(III) and light lanthanides(III) exhibit a very similar extractability. Common extraction of both groups may be a useful unit operation, if no transplutonide/lanthanide separation is aimed in a partitioning proces, or if it is attained in a subsequent process step. The problem is to find an extractant which extracts the weakly extractable elements of the two groups with a satisfactory efficiency. TBP, which is a very common extractant in the nuclear chemistry extracts transplutonides(III) from HNO_3 solutions too weakly. Figure 1 shows that low distribution ratios are reached even with undiluted extractant. The distribution ratio of Am(III) is as low as < 0.001, if a simulated HAW solution (5 M HNO_3) is contacted with a 30 vol.% solution of TBP in dodecane [13]. Salting-out agents are needed for a higher extraction efficiency. $D_{Am} > 1$ is reached, if a simulated HAW solution (500 l HAW/t fuel, 0.1 - 0.2 M free HNO_3) contains 0.65 M aluminium nitrate and 1.3 M sodium nitrate. Then a 30% solution of TBP in dodecane extracts in three contacts 99.4% Am(III) and 99.1% Ce(III). The phase ratio is indeed unfavourable, namely org/aq = 3. The extraction is little selective, because 68% Ru is coextracted [12,13]. If a simulated HAW solution contains 0.5 M Al(III) and 5 M $NaNO_3$, D_{Am} = 50 in the extraction with 50% TBP in an unspecified diluent [19].

Thus, application of TBP to the extraction of transplutonides(III) from HAW solutions is hardly possible without producing waste streams with a high salt content. It would seem reasonable to refrain from the use of TBP in a partitioning process. Nevertheless, flowsheets have been elaborated in which 50% TBP in kerosene or undiluted TBP are used as solvents and aluminium nitrate [33] or both aluminium and sodium nitrates [34] are added to the HAW solution. A still less promising flowsheets supposes that a HNO_3 concentration as extremely high as 15.6 M is adjusted in the HAW solution and undiluted TBP is taken as solvent [35].

A dialkyl alkyphosphonate extracts Am(III) more effectively than TBP, but has also to be used undiluted (Figure 1). Trialkyl phosphine oxides extract Am(III) quite well, but the concentration of HNO_3 in the aqueous phase must low. At high concentrations HNO_3 competes too strongly for the extractant and the extraction of Am(III) is suppressed. A 0.5 M solution of an unspecified trialkyl phosphine oxide in an unspecified diluent

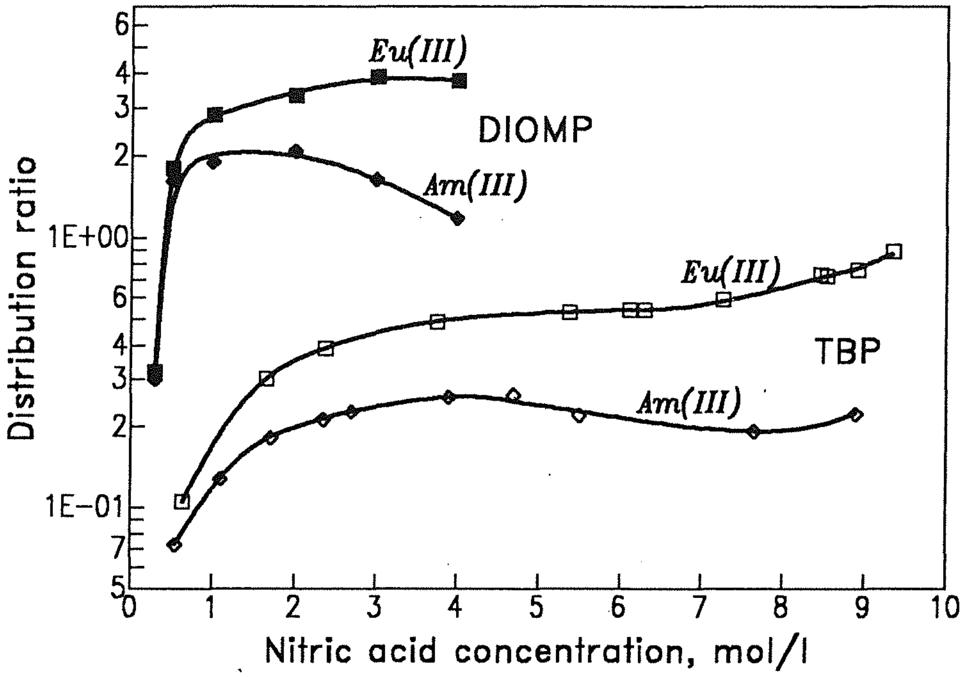

Figure 1. **Extraction of Am(III) und Eu(III) with solvating extractants:** Extraction with undiluted tributyl phosphate (TBP) [36,37] and di*iso*octyl methylphosphonate (DIOMP) [38] from HNO_3 solutions

extracts Am(III) with $D_{Am} = 20$, if the aqueous phase contains 0.5 M HNO_3. At 5 M HNO_3 the distribution ratio of Am(III) is suppressed to ≤ 0.1 [19].

Bifunctional Diphosphoryl or Phosphoryl-Carbonyl Extractants: Bifunctional extractants promise a good extraction efficiency for transplutonides(III). Extractants with two phosphoryl groups in the molecule were tested as early as in the 1960s, but they found little resonance as extractants for transplutonides(III). For example, D_{Am} values of >1 are reached in the extraction with >20% tetrapentyl methylenediphosphonate in diethylbenzene from 4 M HNO_3 [39]. Much more attention is paid to compounds bearing a phosphoryl and a carbonyl group in the molecule, namely N,N-disubstituted carbamoyl phosphonates, phosphinates and phosphine oxides. Solvent extraction studies with dihexyl and dibutyl N,N-diethylcarbamoyl methylphosphonates were started as early as in the late 1960s. Flowsheets of processes were developed, in which the dihexyl [40] and the dibutyl [41] compounds were applied to the extraction of transplutonides(III) from particular HAW solutions with high contents of aluminium and zirconium. Also elaborated was a flowsheet for the partitioning of conventional HAW solutions with the dihexyl compound [42].

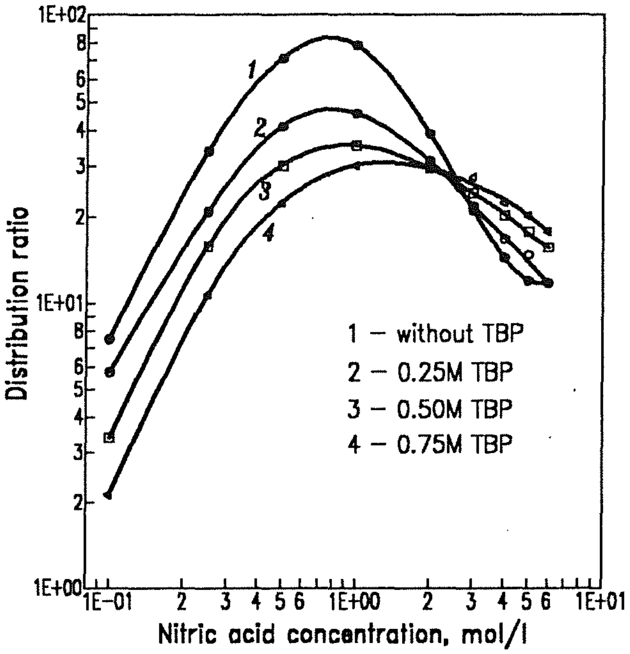

Figure 2. **Influence of TBP on the extraction of Am(III) with OΦD(iB)CMPO:** Extraction with 0.25 M OΦD(iB)CMPO in decalin from HNO_3 solutions at different concentrations of TBP in the solvent; 25°C [43].

More recently the extractant properties of phosphoryl carbamoyl compounds for Am(III) were studied more extensively and systematically. The effectiveness and the selectivity of the Am(III) extraction were investigated as functions of the extractant structure. The type of the extractant (phosphonate, phosphinate and phosphine oxide), the size of the link between the carbonyl and phosphoryl groups, and the N-bound or P-bound substitutents were varied. As it can be expected, with the same or comparable substituents the extraction efficiency increases in the order phosphonate < phosphinate < phosphine oxide type. With a methylene link the extraction is more effective than with an ethylene link. A good extraction effectiveness is reached, if P-bound aryl substitutents are introduced into the extractant molecule [44,45]. n-Octyl phenyl N,N-diisobutylcarbamoylmethyl phosphine oxide (OΦD(iB)CMPO) has been selected as the compound with optimum extractant properties. It also has been taken into consideration that OΦD(iB)CMPO can be synthesized and purified more easily and less expensively than compounds with comparably good extractant properties. OΦD(iB)CMPO has also been suggested to be applied as an extractant for the separation of transplutonides(III) and other actinides from aged HAW solutions [46].

A solution of OΦD(iB)CMPO alone in an aliphatic diluent cannot be used as a solvent in a partitioning process. The solubility of actinide nitrate OΦD(iB)CMPO solvates in such a solvent is very low. An appropriate solubility of the solvates is needed, because in the

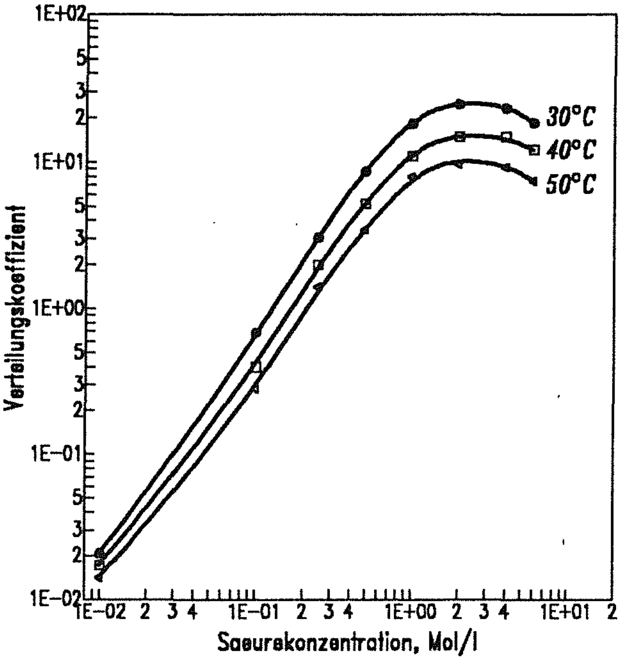

Figure 3. Extraction of Am(III) with a typical TRUEX solvent from HNO_3 solutions: The solvent is 0.20 M OΦD(iB)CMPO + 1.4 M TBP in Conoco (a mixture of C_{12} - C_{14} n-paraffins) [46].

extraction from a HAW solution the solvent would be loaded with lanthanides(III) to a considerable extent. Thus, the solubility of the extracted OΦD(iB)CMPO solvates must be increased by the addition of a polar modifier. TBP has been chosen as a cheap, stable and efficient substance. Its concentration must be > 1 M, if the OΦD(iB)CMPO solvates are to be prevented to separate as second, heavy organic phase [46,47]. A 0.2 M OΦD(iB)CMPO + 1.2 M TBP solution in dodecane can at ≥25°C be satisfactorily loaded with e.g. Nd(III). The tendency to the formation of the second organic phase can further be suppressed, if the dodecane diluent is substituted by a branched paraffin diluent [47].

The distribution ratio of Am(III) is favourably influenced by TBP (see Figure 2). The D_{Am} value is increased at HNO_3 concentrations of > 2.5 M, which are suitable for the forward extraction of Am(III). On the other hand, the D_{Am} value is suppressed by TBP at low acid concentrations and this facilitates the back extraction of Am(III) with diluted HNO_3 solutions [43,48].

As mentioned above, OΦD(iB)CMPO is intended to be applied to a large scale recovery of actinides from HAW solutions. A solvent extraction process (TRUEX) has been developed, in which the solvent is a 0.2 M OΦD(iB)CMPO + 1.2 - 1.4 M TBP solution in an aliphatic diluent. A mixture of C_{12} - C_{14} n-alkanes has been selected as the diluent, because of its sufficiently high flash point [46]. Figure 3 shows that the Am(III) extraction with this solvent is appropriately effective also at moderately elevated temperature.

The selectivity of the actinide recovery with bifunctional extractants from a HAW solution can be improved by oxalate complexing. The distribution ratios of Am(III) and Cm(III) are little influenced, while those of Zr(IV), Mo(VI) und Al(III) are substantially suppressed. Unfortunately, the complexing does not improve enough the separation of actinides from platinum metals. The effect of the oxalate complexing on the separation of transplutonides(III) is illustrated by data in Table 6. In a procedure like the TRUEX process, oxalic acid can be added to the HAW feed solution or the loaded solvent can be scrubbed with a solution containing oxalic acid. It is recommended [46] to denitrate the HAW solution to 1 - 2 M HNO_3 before the actinide extraction with OΦD(iB)CMPO. Transplutonides(III) are still well extractable in this acidity region, and Tc is then also extractable from the waste (see Table 6).

Table 6. **Extraction of HAW components in the presence and absence of $H_2C_2O_4$:** (1) 0.20 M OΦD(iB)CMPO + 1.4 M TBP in Conoco (a mixture of C_{12} - C_{14} n-paraffins), extraction from a simulated HAW solution (1 M HNO_3) with variable additions of $H_2C_2O_4$, phase volume ratio org/aq = 0.5; 40°C [46].
(2) 30% dihexyl N,N-diethylcarbamoyl methylphosphonate (DHDECMP) in di*iso*propylbenzene, extraction from a simulated HAW solution (2.9 M HNO_3) with an addition of $NaNO_2$ (0.1 M), phase volume ratio org/aq = 1; 23°C [42].
(3) Solvent loaded in (2) was contacted with 3.0 M HNO_3 + 0.05 M $H_2C_2O_4$, phase volume ratio org/aq = 5; 23°C [42].

Element	*Distribution ratio*				
	with OΦD(iB)CMPO			*with DHDECMP*	
	(1) *0.05 M* $H_2C_2O_4$	*(1)* *0.10 M* $H_2C_2O_4$	*(1)* *0.20 M* $H_2C_2O_4$	*(2)* *without* $H_2C_2O_4$	*(3)* *0.05 M* $H_2C_2O_4$
Am	10.0	10.0	7.1	4.3	4.1
Cm	-	-	-	3.0	2.9
La	5.2	5.0	3.4	6.5	6.1
Ce	8.2	8.2	5.4	5.8	5.2
Pr	9.1	8.0	5.7	5.3	-
Nd	9.0	8.6	5.6	4.3	-
Sm	7.9	7.8	5.1	3.4	-
Eu	6.8	6.8	4.4	2.9	3.2
Y	1.5	1.5	1.1	0.60	0.66
Sr	< 0.01	< 0.01	< 0.01	0.017	0.019
Ba	< 0.01	< 0.01	< 0.01	0.013	0.012
Cd	< 0.04	< 0.04	< 0.05	0.0067	-

Table 6 (continued)

Element	*Distribution ratio*				
	with OΦD(iB)CMPO			*with DHDECMP*	
	(1) *0.05 M* $H_2C_2O_4$	*(1)* *0.10 M* $H_2C_2O_4$	*(1)* *0.20 M* $H_2C_2O_4$	*(2)* *without* $H_2C_2O_4$	*(3)* *0.05 M* $H_2C_2O_4$
Zr	0.58	0.13	0.013	1.8	0.022
Mo	0.80	0.31	0.11	0.39	0.10
Tc	-	-	3.0	2.3	1.4
Ru	0.39	0.38	0.30	0.27	0.96
Rh	0.078	0.080	0.11	0.018	-
Pd	0.71	0.65	0.44	0.53	0.47
Al	0.012	0.0097	<0.006	-	-
Fe	0.057	0.057	0.041	-	-
Cu	0.014	0.014	<0.007	-	-
Mn	0.0085	0.0095	0.01	-	-

The flowsheet of the TRUEX process is shown in Figure 7 on page 33 as an example of the common removal of transplutonides(III) and lanthanides(III) from radioactive waste. A decontamination factor of 4×10^4 was found for Am(III) in a batch counter-current test [49]. Another example can be found in [42], where the flowsheet of an extraction process with dihexyl N,N-diethylcarbamoyl methylphosphonate is described. The phosphonate extractant is less effective than OΦD(iB)CMPO and must be used at a higher concentration, namely as a 30% solution in diisopropylbenzene. The HAW feed solution contains 3.5 M HNO_3, 0.1 M sodium nitrite and 0.044 M oxalic acid. It is fed into the 6th stage of an 8-stages mixer-settler at a relative flow of 1.0. The solvent is introduced in the 1st stage (relative flow 1.67). A scrub solution is fed into the 8th stage (relative flow 1.0) and contains 3.5 M HNO_3 and 0.05 M oxalic acid. As litlle as 0.013% Am is left in the raffinate.

A comparative evaluation has been made of the two most studied extractants for actinides from HAW solutions, namely dihexyl N,N-diethylcarbamoyl methylphosphonate and OΦD(iB)CMPO. The phosphonate compound is concluded to be the preferred extractant. One of several reasons is that the difference between the extractant power of the compounds is rather small at higher HNO_3 concentrations, but is much larger at low HNO_3 concentrations. Thus OΦD(iB)CMPO yields only a moderate advantage in the extraction of Am(III), but the back extraction with a very diluted HNO_3 solution is much easier with the phosphonate extractant [50].

Bifunctional Diamide Extractants: N,N,N′,N′-tetrasubstituted diamides of dicarboxylic acids represent another class of promising extractants for transplutonides(III). Figure 4 shows the extraction of Am(III) with alkyl substituted diamides of oxalic and malonic

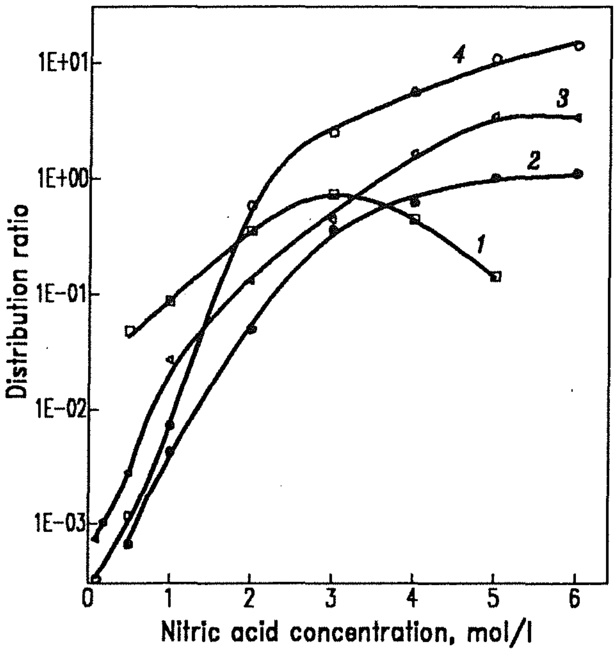

Figure 4. Extraction of Am(III) with substituted diamides: The solvent is a 0.5 M solution of the extractant in *tert*-butylbenzene, the aqueous phase is a HNO_3 solution. *1* - malonic acid *sym*-dioctyldimethyldiamide, *2* - oxalic acid *sym*-dibutyldimethyldiamide, *3* - (3-oxapentyl)malonic acid *sym*-dibutyldimethyldiamide, *4* - (3,6-dioxadodecyl)malonic acid *sym*-dibutyldimethyldiamide [51].

acids. The diamides are less effective extractants than carbamoylmethyl phosphine oxides. This desires a rather high diamide concentration in the solvent but, on the other hand, makes the back extraction of transplutonides(III) with a dilute HNO_3 solution easier. Compared with carbamoylmethyl phosphine oxides, the diamide extractants have some unambiguous advantages: they can be incinerated to exclusively gaseous products, they are cheaper, and their degradation products do not impede the reextraction of transplutonides(III) with dilute acid solutions [52].

Among different compounds tested, (3-oxanonyl)malonic acid *sym*-dibutyldimethyldiamide has been chosen as an extractant for the separation of transplutonides(III) and other alpha nuclides from HAW solutions. The structure is a compromise between an acceptable price and good extractant properties. A flowsheet test was performed with a simulated HAW concentrate containing ~50 mCi alpha activity/l. The solvent was a 0.5 M solution of the extractant in *tert*-butylbenzene and the HAW feed contained 5 M HNO_3. Am(III) and Eu(III) were extracted in 12 stages of a mixer-settler at a flow ratio of 1.0. The loaded solvent was washed in few stages with 2 M HNO_3 The decontamination factors for Am(III) and Eu(III) were 12600 and 6700 respectively. Both elements were reextracted with 0.1 M HNO_3, again at a flow ratio of 1.0, but at 45°C. The effectiveness of the back extraction was lower than that of the forward extraction: 0.125% Am(III) and 0.4% Eu(III) remained in the solvent [53].

The aromatic diluent has probably been chosen for warranting a sufficient solubility of extracted complexes in the solvent. Since aliphatic diluents are preferred in nuclear separation processes, it would be desirable to test their applicability with eventually added solvent modifiers.

2.1.1.2 *Acidic Extractants, Alone or Combined with Neutral Synergists*

General Comparison: Acidic extractants possess a limited ability to separate transplutonides(III) from lanthanides(III) in the absence of particular complexing agents. The separation and extraction efficiency is illustrated by data in Table 7 and Figure 5. It is seen there that only acidic organophosphates, derivatives of 3-acyl-5-pyrazolone and perhaps TTA are to some extent able to distinguish between Am(III) and Eu(III). However, weakly acidic extractants like TTA are not suitable for a partitioning process. They must be used at a rather high pH value, which cannot be kept without a buffer substance. In fact, only acidic organophosphorus extractants are compatible enough with requirements of a nuclear separation process: They are effective, cheap and chemically stable.

Table 7. Extraction and separation efficiency of acidic extractants for the pair Am(III) - Eu(III): Separation factors in the extraction of Eu(III) und Am(III) from 0.1 M (Na,H)ClO$_4$, and pH ranges in which the distribution ratios of Am(III) and Eu(III) are ~0.01 to ~100. The solvent is a 0.05 M solution of 5,7-dichlorooxine or a 0.1 M solution of any other extractant in chloroform or methyl *iso*butyl ketone. Room temperature [54].

Extractant	*Separation factor* $\alpha = D_{Eu}/D_{Am}$	*pH range of* $0.01 < D_{Am} < 100$ *and* $0.01 < D_{Eu} < 100$
dibutyl phosphoric acid	23	0.7 - 1.6
di(2-ethylhexyl) phosphoric acid (HDEHP)	14	1.3 - 2.3
1-phenyl-3-methyl-4-acetyl-5-pyrazolone	3.5	1.6 - 2.8
thenoyltrifluoroacetone (TTA)	3.0	3.4 - 4.6
neocupferron	1.74	2.4 - 3.6
N-benzoylphenylhydroxylamine	1.66	4.2 - 5.5
N-2,4-dichlorobenzoylphenylhydroxylamine	1.32	4.0 - 5.3
β-isopropyltropolone	0.98	2.6 - 4.0
1-hydroxy-2-naphthoic acid	1.07	3.8 - 5.1
2-hydroxy-1-naphthoic acid	1.02	3.4 - 4.7
3-hydroxy-2-naphthoic acid	0.95	3.4 - 4.7
5,7-dichloro-8-hydroxyquinoline	0.102	3.9 - 4.9

Monoacidic Organophosphorus Extractants: Di(2-ethylhexyl) phosphoric acid (HDEHP) is a very common, commerciably available acidic organophosphorus extractant. It is extremely slightly soluble in aqueous solutions and unlimitedly miscible with organic diluents. The solubility of the sodium salt and of extracted complexes of HDEHP in the solvent phase is either high without precautions, or can satisfactorily be enhanced in the presence of a modifier. These properties make HDEHP especially adequate to large scale applications, irrespective of the fact that many other acidic organophosphorus compounds are much more effective extractants. Let us mention e.g. 2-ethylhexyl phenylphosphonic acid (see Figure 5), bis(hexoxyethyl) phosphoric acid [15] or dibutyl phosphoric acid (see Table 7 on page 20). The two former extractants are too expensive for large scale applications. Dibutyl phosphoric acid exhibits too a high aqueous solubility, and its extracted complexes may be little soluble in the solvent phase.

Di*iso*decyl phosphoric acid seems to be another potential organophosphorus extractant for large scale processes. It probably can be cheaply synthesized and has been chosen by Japanese investigators as an extractant for the partitioning of HAW solutions. It is more effective than HDEHP, but forms less soluble extracted complexes. Even if a 0.5 M solution of di*iso*decyl phosphoric acid in an alkane diluent is modified with 0.1 M TBP, a gelatinous precipitate is formed in the contact with a HAW concentrate. To prevent the precipitation, a HAW concentrate must be diluted to the concentration level of an unconcentrated HAW solution [15].

As a unit operation, the common extraction of tranplutonides(III) and lanthanides(III) with an organophosphorus acid can easily be performed in any counter-current extractor. A conventional flowsheet is fully satisfactory, i.e. the solvent and an aqueous scrub solutions are introduced into the first and last stages, and the feed solution is directed into the middle region of the extractor. The feed is obtained by the denitration of a HAW solution, in most cases with formic acid. A complexing agent is in some flowsheets added to the feed, in order to direct into the raffinate those residual fission and corrosion product which have not been retained in the denitration precipitate. A polar modifier must be added to the solvent, if it contains HDEHP and an aliphatic diluent. This is because the solvent wash includes the conversion of HDEHP to its sodium salt which is little soluble in liquid paraffins. The solubility of the sodium salt is augmented in the presence of a polar substance. Almost exclusively, TBP is used as a modifier. No modifier is necessary in the application of aromatic diluents, which dissolve well the sodium salt of HDEHP.

A detailed description of the flowsheet of some unit operations gives an idea of the effectiveness, with which transplutonides(III) can be removed from wastes if they are extracted together with lanthanides(III). In all examples the extractor is a mixer-settler and the relative flow of the feed solution is 1.0:

- The feed solution is adjusted to pH 2.0±0.5 and introduced into the 9th stage (total 16 stages). The solvent is 0.3 M HDEHP + 0.2 M TBP in an alkane mixture (relative flow 2.5) and the scrub solution is 0.02 M HNO_3 (relative flow 0.67). 99.97% Am(III) is extracted from a simulated HAW solution [55].

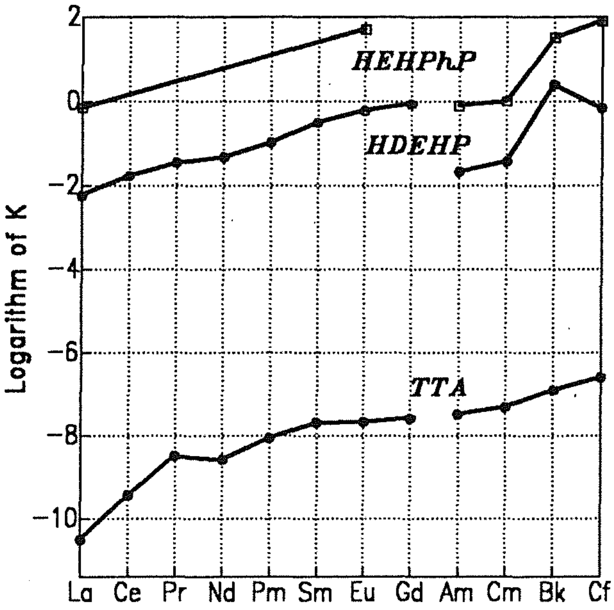

Figure 5. Extraction of transplutonides(III) and lanthanides(III) with acidic extractants: The solvents are solutions of thenoyltrifluoroacetone (TTA) in benzene, of HDEHP in toluene and of 2-ethylhexyl phenylphosphonic acid (HEHPhP) in diethylbenzene. The aqueous phase is a dilute solution of a mineral acid. K is the equilibrium extraction constant, defined as $K = D[H^+]^3[\overline{H_2A_2}]^{-3}$ for HEHPhP and HDEHP, and as $K = D[H^+]^3[\overline{HA}]^{-3}$ for TTA. Data on HDEHP and TTA were gathered in [56], see therein for references to original sources. Data on HEHPhP were taken from [57].

- The feed solution is the raffinate from an operation, in which the initial HAW solution has been diluted by a factor of three, contacted with a TBP solvent and deacidified. The feed contains 0.1 M HNO_3 and is introduced into the 6th stage (total 8 stages). The solvent is 1.0 M HDEHP in an alkane mixture (relative flow 0.50) and the scrub solution is 0.1 M HNO_3 (relative flow 0.10) [58]. >99.98% Am(III) has been extracted in a hot test from a real HAW solution [59].

- The feed solution is adjusted to pH 0.5 - 0.8 and introduced into the 7th stage (total 11 stages). The solvent is 0.5 M di*iso*decyl phosphoric acid + 0.1 M TBP in a mixure of n-alkanes (relative flow 4.0). The scrub solution is 0.1 M HNO_3 (relative flow 1.0). >99.99% Am and Cm has been extracted in a hot test from a real HAW solution [26].

- The feed solution is adjusted to pH 2.5 and introduced into the 6th stage (total 8 stages). The solvent is 0.3 M HDEHP + 0.2 M TBP in n-dodecane (relative flow 1.0). The scrub solution is 0.5 M formic acid (relative flow 0.2). >99.9% of the total alpha radioactivity is extracted from a simulated HAW solution [30]. A good extraction yield appears to be also attainable, if the relative flows of the solvent and the scrub solution are 0.58 and 0.1 respectively [17].

- The feed solution is adjusted to 0.25 M sodium citrate and pH 2.5. It is introduced into the 9th stage (total 16 stages). The solvent is 0.3 M HDEHP + 0.15 M TBP in Shell Sol T (relative flow 1.0). The scrub solution is 0.25 or 0.35 M sodium citrate (pH 2.5, relative flow 0.22). >99.98% Am(III) is extracted from a simulated HAW solution [60].
- The feed solution is adjusted to 1.0 M lactic acid and introduced into one of the middle stages (total ≥6 stages). The solvent is 1 M HDEHP in di*iso*propylbenzene (relative flow 2.0) and the scrub solution is 1 M lactic acid (relative flow 0.4). The extraction of Am(III) in three stages has been characterized as complete [39].

Substituted 4-Acyl-5-pyrazolones: A synergistic combination of a substituted 4-acyl-5-pyrazolone and a crown ether can extract transplutonides(III) and lanthanides(III) rather effectively from moderately acidic solutions. Let us mention the extraction with e.g. 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone, which is synergistically enhanced by dicyclohexano-18-crown-6 or benzo-15-crown-5. Trace Am(III), Cm(III) and Cf(III) are extracted by solutions of the reagents in chloroform at pH>2.5. Eu(III) is extracted somewhat more effectively than the transplutonides(III) [61]. In the presented form the system might be of interest in laboratory separations. Application potential in a partitioning process is difficult to be assesed. It would not be high if the chloroform diluent cannot be substituted by an alkane diluent, and if the pyrazolone derivative is expensive or chemically instable.

2.1.1.3 Extraction of Ion-Pairs

A solution of trioctyl amine in cyclohexanone or methyl isobutyl ketone extracts Am(III) and Eu(III) almost identically from a solution containing aluminium nitrate alone, or together with nitric acid. Transplutonides(III) and lanthanides(III) can be extracted simultaneously with ~0.8 M amine from ≤0.5 M HNO_3 and >2 M aluminium nitrate [62].

Am(III) and lanthanides(III) are extractable into polar diluents as dissociated ion-pairs in which the counter-ion is a sandwich type, polyhedral dicarbolide anion, $[\pi\text{-(3)-1,2-}B_9C_2H_{11}]_2Co^-$. The distribution ratio of Am(III) is increased by a factor of ~1000, if the HNO_3 concentration in the aqueous phase is supressed from 1 to 0.1 M. The extraction efficiency is synergistically increased by polyethylene glycols. The separation factors of the couples Am(III)/Ce(III) und Am(III)/Eu(III) range from 1 to 1.7, and alkaline elements are strongly extracted. The extraction of Zr(IV) can be suppressed by an addition of citric acid. The diluent must contain ≥80% nitrobenzene, which is not a favorite diluent in nuclear separation processes. The reextraction of transplutonides(III) and lanthanides(III) may be slow [63].

2.1.2 Selective Extraction of Transplutonides(III) or Lanthanides(III)

2.1.2.1 Solvating extractants

Phosphoryl compounds extract transplutonide(III) thiocyanates with a moderate selectivity over lanthanide(III) nitrates. Am/Eu separation factors of 3.1 and 4.2 are reached, if trace Am(III) and Eu(III) are extracted with 0.003 - 0.006 M tributyl phosphine oxide and 0.0015 - 0.007 M trioctyl phosphine oxide in xylene respectively from 1 M NH_4SCN at pH 2.0 - 2.7 [64]. Somewhat better separation can be achieved with dibutyl butylphosphonate in di*iso*propylbenzene ($\alpha_{Am/Eu}$ = 5.8). Carbamoylmethyl and carbamoylethyl phosphonates in the same diluent gave fairly good to promising results. The $\alpha_{Am/Eu}$ value ranged from 6.8 with dihexyl N,N-diethylcarbamoylmethylphosphonate to 10.8 with dihexyl N,N-di*iso*butylcarbamoylmethylphosphonate (0.244 M extractrant, 0.06 M NH_4SCN, 0.001 M HCl) [65].

2.1.2.2 Acidic Extractants, Alone or Combined with Neutral Synergists

Monoacidic Organophosphates with Selective Complexing in the Aqueous Phase: Transplutonide(III) complexes of some complexons are much more stable than analogous lanthanide(III) complexes. The difference is especially pronounced with diethylenetriaminepentaacetic acid (DTPA), which essentially changes the relative extractability of the two element groups with acidic organophosphates. Comparison of Figure 5 and Figure 6 gives an illustration of the change of the extractability with HDEHP. A similar shift of the extractabilities in the presence of DTPA was observed in the extraction with 2-ethylhexyl phenylphosphonic acid [39] and di*iso*decyl phosphoric acid [66]. Thus it is possible to extract lanthanides(III) and to leave transplutonides(III) in the aqueous phase. Reversely, it is possible to reextract transplutonides(III) selectively from a solvent which is loaded with both element groups. A hydroxycarboxylic acid must be added in both cases to the aqueous phase. The acid acts as a buffer substance and as an accelerator in the attainment of the distribution equilibrium. Glycine as well as glycolic, tartaric, citric and diglycolic acids have been tested, but lactic acid is most frequently used [67,68].

The optimum concentrations of DTPA and lactic acid are 0.05 - 0.1 M and 1 M respectively, and the optimum acidity region is pH 2 - 3. In this range the effectiveness of the group separation is little dependent on the extractant, DTPA and hydrogen ion concentrations. This has been observed in the extraction with HDEHP (see e.g. [67-70]) or di*iso*decyl phosphoric acid [66]. The extraction of Am(III) [67] from solutions of DTPA and lactic acid as well as the reextraction of lanthanides(III) with such solutions [71] are rather slow. 5 - 20 min can be needed for reaching a distribution equilibrium at 1 M lactic acid, and the attainment of the equilibrium can take hours at lower lactic acid concentrations [71].

The effect of radiation on the separation of transplutonides(III) from lanthanides(III) has been studied in the presence of glycine or glycolic acid. The solvent has been 0.3 M

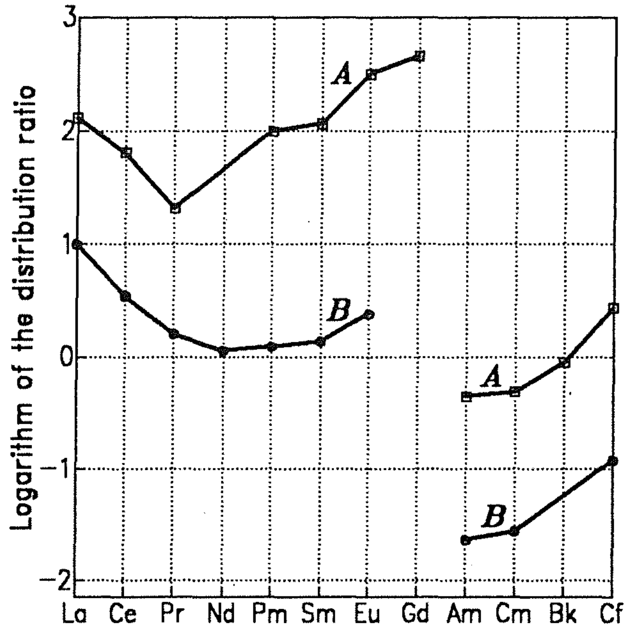

Figure 6. Extraction of transplutonides(III) und lanthanides(III) with HDEHP from DTPA solutions: (A) Extraction with 0.5 M HDEHP in decane from 0.07 M DTPA + 1.0 M lactic acid at pH 3.1 [72,69]. (B) Extraction with 0.3 M HDEHP in di*iso*propylbenzene from 0.05 M DTPA + 1.0 M lactic acid at pH 3.0 [67]. Room temperature.

HDEHP in di*iso*propylbenzene. The radiation destroys DTPA, the extraction of transplutonides(III) is then less suppressed, and the effectiveness of the separation is deteriorated. For example, at 0.025 M DTPA and 1 M glycolic acid a gamma radiation dose of 95 Wh/l suppresses the Ce/Am separation factor from 100 to 33. At 0.1 M DTPA, an alpha radiation dose of 330 Wh/l suppresses the La/Cm separation factor from 50 to 40 with 1 M glycolic acid present, and from 120 to 18 with 1 M glycine present. Low absorbed doses of gamma and alpha radiation, namely < 10 Wh/l and < 100 Wh/l respectively, cause a slight improvement of the separation efficiency [67].

To illustrate the transplutonide(III)/lanthanide(III) separation as a unit operation, some flowsheets are described below. First the selective extraction of lanthanides(III) in a mixer-settler (TALSPEAK process) will be shown. In experiments with simulated HAW solutions, the solvent and a scrub solution were introduced into the first and last stages respectively. The feed solution (relative flow 1.0) was directed into a middle stage:

- The feed solution contains 1 M lactic acid and is fed into the 3rd stage (total 6 stages). The solvent is 1.0 M HDEHP in di*iso*propylbenzene (relative flow 3.0) and the scrub solution is 0.1 M DTPA + 1.0 M lactic acid (pH 3.0, relative flow 2.0). The results promise a reasonable group separation at a higher number of stages [39].

- The feed solution contains 1 M lactic acid and is fed into a middle stage (the total number of stages is not given). The solvent is 0.1 M 2-ethylhexyl phenylphosphonic acid in diethylbenzene (relative flow 2.0) and the scrub solution is 0.22 M DTPA + 1.0 M lactic acid (the pH value is not given, relative flow 1.0). The extracted fractions are 99% lanthanides(III) and 0.1% Cm(III) [73].

As a more frequent option, it has been suggested to extract transplutonides(III) simultaneously with lanthanides(III) and to accomplish the group separation by a selective reextraction of the transplutonides(III) (reversed TALSPEAK process). In this mode an organic scrub solution and an aqueous strip solution are fed into the first and last stages of a mixer settler. The organic feed solution (relative flow 1.0) is introduced into a middle stage. If not given otherwise in the examples below, the organic feed has been obtained by extracting transplutonides(III) and lanthanides(III) from a simulated HAW solution:

- The feed and the scrub (relative flow 0.20) solutions contain 1 M HDEHP in di*iso*propylbenzene. The feed solution is introduced into the 3rd stage (total 6 stages). The strip solution is 0.05 M DTPA + 1.0 M lactic acid (the pH value is not given, relative flow 0.75). 99.4% Am(III) and ≤0.1% lanthanides(III) are reextracted [39].

- The feed and the scrub (relative flow 0.20) solutions contain 0.3 M HDEHP + 0.2 M TBP in dodecane. The feed is introduced into the 7th stage (total 12 stages). The strip solution is 0.05 M DTPA + 1.0 M glycolic acid (pH 3, relative flow 0.17). 99.98% Am(III) and Cm(III) are reextracted, together with ≤0.02% Ce(III) and 0.12% Eu(III) [17].

- The feed and the scrub (relative flow 0.36) solutions contain 0.3 M HDEHP + 0.2 M TBP in Shell Sol T. The feed is introduced into the 10th stage (total 16 stages). The strip solution is 0.05 M DTPA + 1.0 M lactic acid (pH 3.0, relative flow 0.40). ~99% Am(III) and Cm(III) are reextracted, together with ~0.06% Ce(III) and ~0.22% Eu(III) [60].

- The feed and the scrub (relative flow 0.33) solutions contain 0.3 M HDEHP + 0.2 M TBP in an alkane mixture. The feed is introduced into the 10th stage (total 16 stages). The strip solution is 0.05 M DTPA + 1.0 M lactic acid (pH 3.0, relative flow 0.33). ~99% Am(III) and Cm(III) are reextracted, together with <0.1% lanthanides(III) [55].

- The feed and the scrub (relative flow 0.10) solutions contain 1.0 M HDEHP in an alkane mixture. The feed is introduced into the 8th stage (total 16 stages). The strip solution is 0.05 M DTPA + 1.5 M lactic acid (pH 3.6, relative flow 0.83) [58]. In a hot test, 0.14% Am(III) has remained with the lanthanide(III) fraction in the solvent, and 0.74% Eu(III) has been reextracted together with the transplutonides(III) [59,74].

Heterocyclic Thione Derivatives: It would be advantageous to extract the actinide micro components and to leave the unwanted lanthanide(III) bulk in the raffinate. This should be possible with ligands comprising soft donor atoms like sulfur, which may preferentially complex transplutonides(III). Thus, acidic compounds with a sulfur donor atom in a bulky, lyophilic molecule could extract transplutonides(III) selectively over lanthanides(III). 4-Benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione is one of such compounds. Alone it does not extract Am(III) and Eu(III) at pH 2 - 3, but a good extraction efficiency is reached in the presence of trioctyl phosphine oxide [75,76]. Anions of common mineral acids can participate in the formation of the extracted complexes, in which they can substitute a pyrazolthione anion. Thus the Am/Eu separation factor depends on the ionic medium in the aqueous phase and on the pyrazolthione concentration in the organic phase. It also depends on the concentration ratio of the thione extractant to the phosphine oxide synergist. The extraction from a perchlorate solution gives better separation factors than the extraction from nitrate and chloride solutions [76]. Typical values found at pH 3.0 and 0.1 M $LiClO_4$, and with benzene diluent are $\alpha_{Am/Eu}$ = 30 - 70 at 0.1 - 0.3 M pyrazolthione and 0.01 - 0.05 M phosphine oxide [75]. Elsewhere an optimized value of $\alpha_{Am/Eu}$ = 125 is reported with the same aqueous phase for 0.2 M pyrazolthione and 0.05 M phosphine oxide in toluene [76].

The phosphine oxide synergist can be replaced by 4,7-diphenyl-1,10-phenanthroline. With toluene diluent and at 0.2 M $NaClO_4$ in the aqueous phase (pH 3.75), the separation factor is almost 200 at 0.03 M pyrazolthione and 0.0014 - 0.0027 M phenanthroline [77]. A variation of the structure of the soft acidic complexant has also been studied. 4-Thiobenzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one has been tested as an alternative and no higher separation factor than $\alpha_{Am/Eu}$ = 15 could be found (0.09 M thiobenzoyl pyrazolone and 0.01 M trioctyl phosphine oxide in toluene, 0.1 M $LiClO_4$, pH 3.0) [76]. The benzoyl pyrazolthione derivative is rather stable and its oxidation to a disulfide dimer is as slow as < 1%/d [75]. The thiobenzoyl pyrazolone derivative is essentially less stable and its hydrolysis to the benzoyl analogon is even accelerated by the phosphine oxide synergist [76].

Di(2-ethylhexyl) Dithiophosphoric Acid: A 1 M solution of the soft-ligand extractant in dodecane extracts Am(III) at pH > 1 somewhat better than Eu(III). The separation factor is little pronounced, but an addition of TBP can improve it to a value of > 50. At the same time TBP acts as a synergist and essentially improves the extraction efficiency [78,79]. The separation potential of the extractant was examined in a counter-current experiment. The feed solution (relative flow 1.0) contained Am(III), Eu(III) and 0.05 M HNO_3, and was fed into the 6th stage of a nine-stages mixer-settler. The solvent was 0.75 M di(2-ethylhexyl) dithiophosphoric acid + 0.25 M TBP in dodecane, and was introduced into the 1st stage (relative flow 0.5). The scrub solution was 0.05 M HNO_3 (relative flow 1.0). 99.5% Am(III) and ~0.4% Eu(III) were extracted [80]. Information about the radiation and hydrolytic stability of the extractant would be of interest.

5-Nitro-8-hydroxyquinoline: An Am/Eu separation factor as high as 54 is reached, if trace amounts of the elements are extracted with a 0.05 M solution of the extractant in chloroform at pH 4.3 [81]. In a partitioning process it would be very desirable to substitute chloroform by a more appropriate diluent, and to extract at a lower pH value, i.e. at a higher extractant concentration.

Mono(2-ethylhexyl) Phosphoric Acid: Lanthanides(III) are extracted more effectively than transplutonides(III) with 0.5 M extractant in xylene from 10 M LiCl + 0.5 M HCl. A raffinate can be produced, which is transplutonide(III) enriched and lanthanide(III) depleted. The lanthanide(III) depletion is less pronounced in the absence of lithium chloride [82]. The option is hardly of interest.

Carboxylic or Sulfo Acids with N-Heterocyclic Synergists: Some combinations of a heterocyclic N-base and a carboxylic or sulfo acid are able to extract transplutonides(III) more effectively than lanthanides(III). An Am/Eu separation factor of 12 - 18 is reached in the extraction with 0.25 M 1,10-phenanthroline + 0.25 M pelargonic acid at pH 4.5 - 5.1 [78,79]. The rather high pH value needed for the extraction and, still more, a considerable solubility of phenanthroline in the aqueous phase are indeed disadvantageous. More promising is 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ) as a heterocyclic N-base. Combined with α-bromocapric acid in decanol, it yields at pH 2.2 transplutonide/lanthanide separation factors of 8 - 10 (see Table 8). With similar separation factors reached, the extraction is effective at still higher H^+ ion concentrations if dinonylnaphtalenesulfonic acid (DNNS) is the acid component and *tert*-butylbenzene (see Table 8 and [79]) or CCl_4 [83] is taken as the diluent.

Table 8. Extraction of transplutonides(III) and lanthanides(III) with TPTZ and organic acids: Distribution data illustrating the potential of a transplutonide/lanthanide group separation [78].

Extracted element	*Distribution ratio in the extraction with*		
	0.1 M TPTZ + 1 M α-bromocapric acid in decanol from 1 M (K,H)NO_3 at pH 2.2	*0.01 M TPTZ + 0.01 M DNNS in tert-butylbenzene from 0.12 M HNO_3*	*0.01 M TPTZ + 0.01 M DNNS in tert-butylbenzene from 0.08 M HNO_3*
Am(III)	0.85	1.35	6.30
Cm(III)	0.80	1.40	-
Ce(III)	-	0.16	0.40
Nd(III)	0.08	-	-
Eu(III)	0.10	0.20	0.50
Gd(III)	-	0.18	0.45

The feasibility of a transplutonide/lanthanide group separation was demonstrated in a series of counter-current runs with the TPTZ/DNNS extractant pair. Flowsheet variations and results of counter-current runs are gathered in Table 9.

Table 9. **Group separation of transplutonides(III) from lanthanides(III) with TPTZ:** Flowsheets and results of counter-current runs in a mixer-settler (total 16 stages). Feed solution: Trace Am(III) und Eu(III) + variable Ce(III) + 0.125 M HNO_3 + 0.003 M TPTZ. Solvent: 0.03 M TPTZ + 0.05 M DNNS in CCl_4. Scrub solution: 0.125 M HNO_3 + 0.003 M TPTZ [83,84].

[Ce(III)] in feed Mol/l	*Feed stage*	*Relative flow*			*Fraction extracted (%)*		
		Feed	*Solvent*	*Scrub solution*	*Am(III)*	*Eu(III)*	*Ce(III)*
trace	8	1.0	1.0	2.0	99.9	2	2
0.025	6	1.0	1.0	0.67	99.8	10	11
0.025	6	1.0	1.0	1.0	99.5	4.5	5

2.1.2.3 Extraction of Ion-Pairs

Amines with Complexing in the Aqueous Phase: Selective complexing of transplutonides(III) in the aquoues phase can make it possible to separate transplutonides(III) from lanthanides(III) also in the extraction with long chain amines. Also in this case DTPA is the preferred complexant. The aqueous phase must contain an alkali nitrate as a salting-out agent. Optimum results are obtained at high concentrations of lithium nitrate, but even then the Eu/Am separation factor is mere 8.1 [85,86].

Dicarbolide Extractants: A partitioning process has been developed, which is based on the use of a chloroderivative of Co(III) dicarbolide in probably nitrobenzene as a solvent [87]. It is postulated in the original source that transplutonides(III) and lanthanides(III) are obtained in two separate fractions. Unfortunately, not even a vague insinuation is made about the mode of separating the groups.

Amines in Chloride and Thiocyanate Systems: Alamine 336 (a commercial mixture of C_{24} - C_{30} trialkyl amines) in an aromatic diluent extracts transplutonides(III) from LiCl solutions with a considerable selectivity over lanthanides(III). Distribution ratios of Am(III) and Cm(III) are by two orders of magnitude higher than those of lanthanides(III). However, the LiCl concentration in the aqueous solution must be as extremely high as 11 M [57]. Small additions of nitrates ($\leq$0.1 M) improve the extraction efficiency, but deteriorate the effectiveness of the separation [73].

The method was developed in Oak Ridge National Laboratory and has been used there for the production of actinides from special targtes. It certainly has appropriate applicability in that particular field but, with respect to the high LiCl concentration needed, can hardly be useful in a waste partitioning process. Nevertheless, let us shortly describe a flowsheet based on the method. The feed solution contains 11 M LiCl and 0.1 - 0.17 M $AlCl_3$. The HCl concentration is as low as 0.02 - 0.05 M HCl, because at higher acidity the extraction efficiency is suppressed. The feed solution (relative flow 1.0) is directed into the middle region of an extractor. The solvent is 0.6 M Alamine 336 (chloride form) in diethylbenzene (relative flow 1.5 - 3.0). The loaded solvent is scrubbed with 11 M LiCl + 0.02 M HCl (relative flow 0.75 - 1.0) [57,73].

Aliquat 336-S in thiocyanate form (tricapryl methyl ammonium thiocyanate) also extracts transplutonides(III) over lanthanides(III) from thiocyanate media. Suitable composition of the solvent and the aqueous phase is 0.6 M Aliquat 336-S in xylene and 0.6 M NH_4CNS + 0.1 - 0.2 M H_2SO_4 respectively [88]. The separation efficiency is good, even if somewhat lower than in the extraction with Alamine 336 from 11 M LiCl.

2.1.2.4 Extraction of Higher Oxidation States of Transplutonides

Am(III) is oxidized by sodium, potassium and ammonium persulfate. If no particular complexants are added and Ag(II) catalyst is present, Am(VI) is the resulting valence state in moderately acid solutions. Am(VI) is essentially more extractable with acidic organophosphorus extractants than transplutonides(III) and lanthanides(III). This makes it possible to separate Am from Cm, La, Pr, Nd etc. but not from Ce, which is oxidized to its highly extractable tetravalent state. HDEHP is applicable as extractant, but organophosphates with deeply branched alkyl chains like bis(2,6-dimethyl-4-heptyl) phosphoric acid discriminate much more between the hexavalent and trivalent metals [89]. Extracted Am(VI) is not quite stable in the solvent phase. It is reduced to Am(III) even if the diluent is a reductant as weak as individual or mixed paraffins. The reduction is rather slow at higher Am concentrations. On the other hand, trace Am(VI) is reduced so quickly that the extractability of Am(VI) can hardly be utilized in a separation procedure.

The oxidation of Am(III) to Am(VI) has been utilized in an extraction process for the separation of americium from curium. Cm(III) is not oxidized and Am(VI) is selectively extracted. The solvent is a solution of bis(2,6-dimethyl-4-heptyl) phosphoric acid, HDEHP alone, or HDEHP and trioctyl phosphine oxide in an alkane mixture. Difficulties resulting from the instability of Am(VI) in the solvent are alleviated by the application of centrifugal extractors [90].

If the Ag(II) catalyst is not present, potassium persulfate oxidizes Am(III) even at elevated temperature to Am(V) (90°C, 0.05 M HNO_3, reaction time 10 - 15 min). Am(V) is weakly extractable and remains in the aqueous phase, while Cm(III) and lanthanides(III) can be extracted at room temperature with a synergistic mixture of TTA and trioctyl phosphine oxide [91].

Some ligands, especially anions of unsaturated heteropoly acids stabilize americium in the tetravalent state. The persulfate oxidant combined with the Ag(II) catalyst oxidizes Am(III) in acid solutions only to Am(IV), if the salt $K_{10}P_2W_{17}O_{61}$ is added before the oxidation. Am(IV) exists in the solution as an anionic complex formed with anions of the heteropoly salt. The anionic complex is well extractable with long-chain dialkyl amines in chloroalkane diluents like CCl_4 or dichloroethane. The extraction is ineffective if the diluent is chloroform, heptane, xylene, diethyl ether or methyl *iso*butyl ketone. The oxidation of Am(III) and the extraction of Am(IV) can effectively be performed in nitrate and sulfate systems [92]. Increase of the HNO_3 concentration above 2 M suppresses both the extraction efficiency and the oxidation kinetics [93]. Also Cm(III) is reported to be oxidized to Cm(IV) in the presence of the heteropoly salt. The oxidation is observed in non-acidified aqueous solutions and Cm(IV) is rather instable. At initially 0.1 M $K_2S_2O_8$ and 0.0043 - 0.011 M $K_{10}P_2W_{17}O_{61}$, it is reduced back to Cm(III) during ~2 h [94]. The separation potential of the oxidation of Am(III) to Am(IV) is difficult to be assessed. The stabilization of the tetravalent state is a phenomenon common to many *f*-elements. Thus, not only Am(IV), Ce(IV) and Tb(IV) are stabilized in the presence of the heteropoly anion, but also Pr(IV) [95].

2.1.3 Extraction of Plutonium and Neptunium

Removal of these actinides from HAW solutions is discussed shortly in this report, because it is not expected to cause serious problems. Both Pu and Np can exist in different valence states, and at least in one of them the elements are well extractable with common extractants. TBP extracts Pu(IV) nitrate quite effectively (see e.g. [96]). Np(VI) nitrate is well extractable with TBP, while the extractability of Np(IV) nitrate is moderate (see e.g. [97]). The extractability of Pu(IV), Np(IV) and Np(VI) nitrates with the bifunctional OΦD(iB)CMPO extractant is extremely high [98]. Pu(IV) nitrate is well extractable also with diamides of dicarboxylic acids, e.g. with (3,6-dioxadodecyl)malonic acid *sym*-dibutyldimethyldiamide [51].

Np(VI), Np(IV) and Pu(IV) can simply be rextracted from TBP solutions with ≤0.1 M HNO_3 (see data in [96,97]). On the other hand, even very diluted HNO_3 solutions are little effective in the reextraction from solvents involving bifunctional extractants, and the element to be reextracted must be complexed or converted to a little extractable valence state. Pu(IV) can be reextracted from a OΦD(iB)CMPO solution by complexing with fluoride ions [49,46,99], and reduction to Pu(III) promotes the reextraction from a solution of (3-oxanonyl)malonic acid *sym*-dibutyldimethyl diamide [53]. The reextraction of Np(IV) from the same diamide solution is achieved by oxalate complexing [53].

A fraction of Pu(IV) can remain unextracted, if it exists in a HAW solution as an inextractable hydrolytic polymer. Such a fraction can be small, but not negligible: An extraction yield of >98% Pu was reached in a mixer-settler in a hot experiment with a real HAW solution. The feed solution contained 2 M HNO_3 and was contacted in 7 stages with a 30 vol.% solution of TBP. The loaded solvent was scrubbed with 2 M HNO_3 in 5 stages [26].

HDEHP extracts tetravalent actinides even at rather high acid concentrations. Pu(IV) is effectively extracted with 0.25 M HDEHP in mesitylene from a simulated HAW solution, which contains 4 M HNO_3 + 0.1 M $NaNO_2$ [12,13,31]. A 4 M solution of HNO_3 reextracts Pu(IV) negligigbly from 0.3 M HDEHP + 0.2 M TBP in dodecane [12,31]. As much as

>99.99% Pu was extracted in a mixer-settler from a real HAW solution (total 7 stages, 1 M HDEHP in an alkane mixture, 6 M HNO_3 in the feed solution) [59]. Either the inextractable polymeric Pu(IV) fraction was very small in the HAW solution, or HDEHP converts the inextractable Pu(IV) form to extractable species. Np(IV) is well extracted from a simulated HAW solution even at low HDEHP concentrations: Distribution ratios of 250 - 1100 are reached with 0.04 M HDEHP + 0.02 M TBP in Shell Spray Base at 0.5 - 5 M HNO_3 [100].

Nitrate complexes of Pu(IV) and Np(IV) are very effectively extracted with nitrates of long-chain tertiary amines [101,102] and quaternary bases [103]. Distribution ratios of Pu(IV) and Np(IV) are very high at 1 - 7 M HNO_3. The extraction is very selective, because nitrates of fission product elements and of actinides(III,VI) are extracted much less effectively. The only problem might arise in the back extraction, where even very diluted HNO_3 solution need not necessarily be effective.

Denitration of a HAW solution with formic acid destroys inextractable Pu(IV) polymers. The reason is that Pu(IV) is reduced to Pu(III) in an advanced stage of the operation. Oxidation of Pu(III) back to Pu(IV) after the denitration yields extractable Pu species [17,32].

2.2 EXAMPLES OF FLOWSHEETS OF SOLVENT EXTRACTION PROCESSES

Numerous unit operations are at disposal for the planning of partitioning processes. Some operations, like the common or selective extraction of transplutonides(III) and lanthanides(III) are described above. Further unit operations are common or selective extraction of Np and Pu, strip of transplutonides(III) and lanthanides(III) with diluted or concentrated acid solutions, strip with complexing solutions etc. To elaborate a process flowsheet, the unit operations can as single process steps be ordered subsequently or parallelly in a suitable sequence or combination. Numerous flowsheets in rich variations can be devised in this way and, consequently, numerous flowsheets have also been published. Few of them have been tested in hot experiments with real HAW solutions, many of them have been tested in cold runs with simulated HAW solutions, and some of them have not been tested at all. It is not the aim of this paper to list all partitioning flowsheets published. Potentialities of waste partitioning are to be discussed generally in this paper, and it suffices to give some illustrative flowsheet examples.

The flowsheet is quite simple, if actinides are to be recovered together with lathanides and no transplutonide/lanthanide separation is intended. The flowsheet of the TRUEX process is given in Figure 7 as an example. The process must probably be started with a denitration step, which is not included in the chart. Notice in Figure 7 that all liquid-liquid distribution operations are done in mere 19 extractor stages. The loss of Np to the raffinate was rather high (14%) at the time of the publication of the original source, but this certainly has not been the last word in the development of the process.

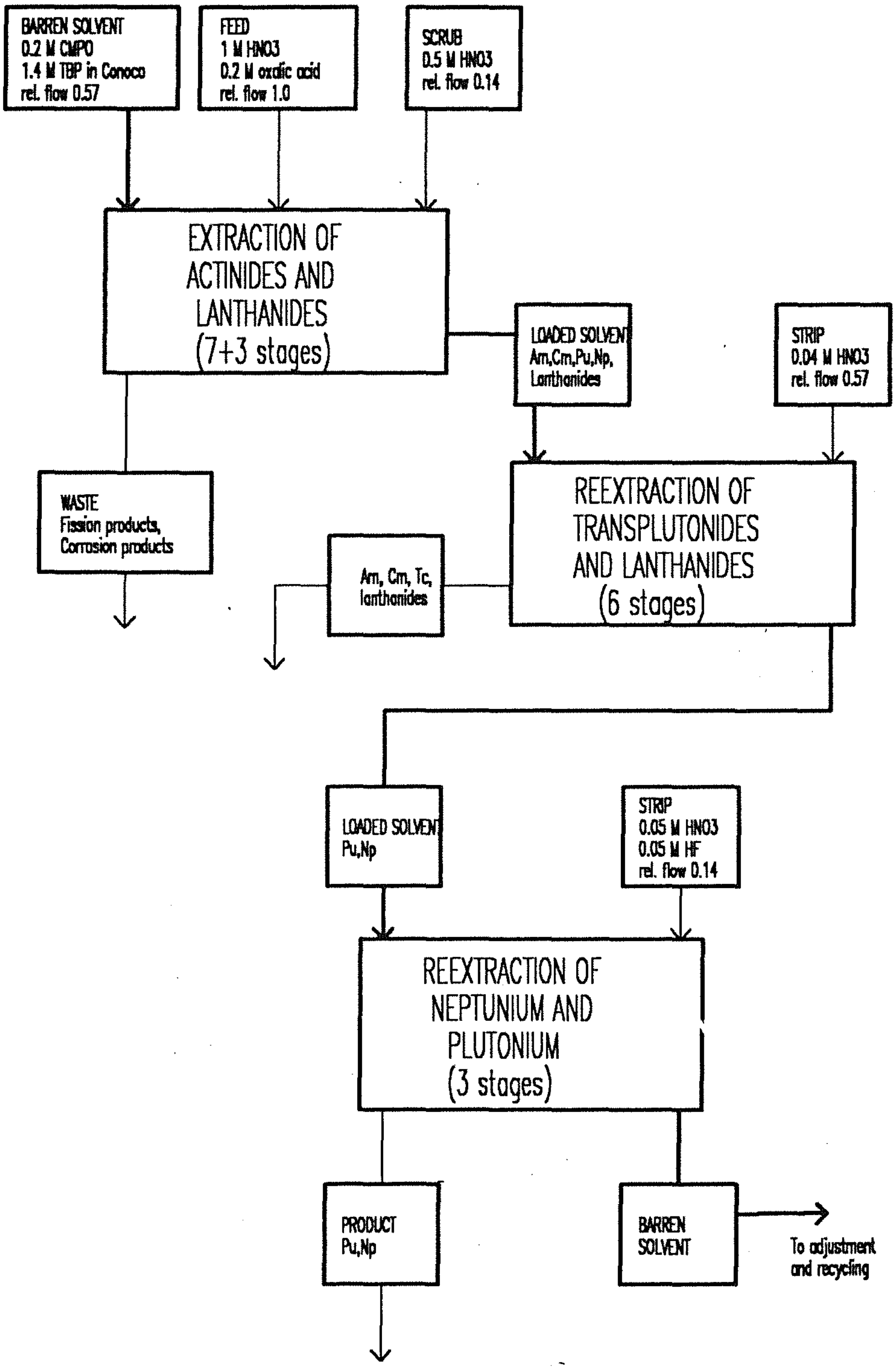

Figure 7. HAW partitioning without transplutonide(III)/lanthanide(III) separation: Flowsheet of the TRUEX process (ANL, Argonne and Rockwell, Hanford, USA) [49]. CMPO is OΦD(iB)CMPO, Conoco is a mixture of C_{12} - C_{14} n-paraffins, and the feed is a HAW solution with oxalic acid added.

The flowsheet becomes more complicated, if a transplutonide(III)/lanthanide(III) separation is to be included in the process. A still moderately complex flowsheet is shown in Figure 8. As reported in the original source [17], the losses of Pu, Am and Cm to the denitration precipitate are $\leq 2\%$. However, an Np fraction as considerable as 90% is retained in the precipitate, and this would desire additional unit operations if the process is to be operated. The dissolved Np fraction splits in the distribution operations: It is predominantly extracted with Pu, transplutonides(III) and lanthanides(III) and 3% of total Np is then stripped together with Pu. The rest is stripped with a carbonate solution during the solvent regeneration.

A more complex alternative to the flowsheet shown in Figure 8 is given in the same original source [17]. The HAW solution is denitrated to a HNO_3 concentration of 1 M and the precipitate formed is washed with 1 M HNO_3. Pu is extracted as Pu(IV) with 30% TBP in dodecane and reductively stripped with 0.15 M hydroxylamine nitrate at pH 2. The raffinate is adjusted to a low acid concentration, 1.1 M Na(I) and 0.54 M Al(III) by adding sodium nitrate and acid deficient aluminium nitrate solutions. Then transplutonides(III) and lanthanides(III) are extracted with 30% TBP in dodecane and stripped with very diluted HNO_3 (pH 1.5). Hereinafter, to achieve the separation of transplutonides(III) from lanthanides(III), HDEHP must still come into play. The strip is adjusted to 1 M glycolic acid, 0.05 M DTPA and pH 3, and lanthanides(III) are selectively extracted with 0.3 M HDEHP + 0.2 M TBP in dodecane. They are rextracted with 5 M HNO_3. Only a small fraction of Np (7%) is retained in the denitration precipitate. 70% of total Np is directed to the Pu product and the pathway of the rest is not described in the paper [17]. Presumedly, less complex flowsheets will be sought in the future partitioning research.

An example of a very sofisticated and extremely complex flowsheet is given in Figure 9. The flowsheet comprises not fewer than 16 extractors in not fewer than 3 cycles, and supposes the use of two extractants. The HAW solution is not denitrated, but adjusted to an acidity of 6 M HNO_3 and to a fission product concentration of 10 g/l. Water or recycled nitric acid are used for the adjustment. The solution is fed into the 1st HDEHP cycle (extractors 1A to 1H). U, Pu and Np are extracted in the 1A extractor, together with Zr, Nb, Mo and Pa. Traces of coextracted trivalent metals are removed from the solvent in the 1B scrub extractor, and Zr, Nb and Pa are stripped in the 1C extractor. Small HF amounts are transferred into the solvent in this step, and must be washed out in the 1D extractor. U, Pu, Np and Mo are stripped with an ammonium carbonate solution in the 1G extractor. This operation also removes mono(2-ethylhexyl) phosphoric acid from the solvent. To prevent the evolution of CO_2 in the 1G extractor, the loaded solvent is first directed to the 1E contactor where HDEHP is converted to its ammonium salt. The salt is converted back to the acidic form of HDEHP in the 1H extractor.

The raffinate from the 1A extractor is transferred into the TBP cycle (extractors 2A to 2D). HNO_3, Ru, Tc and Pd are extracted in the 2A extractor. The three fission products are stripped in the 2B extractor and adsorbed on an ion-exchanger column. Nitric acid is stripped in the 2C extractor and the solvent is carbonate washed in the 2D extractor.

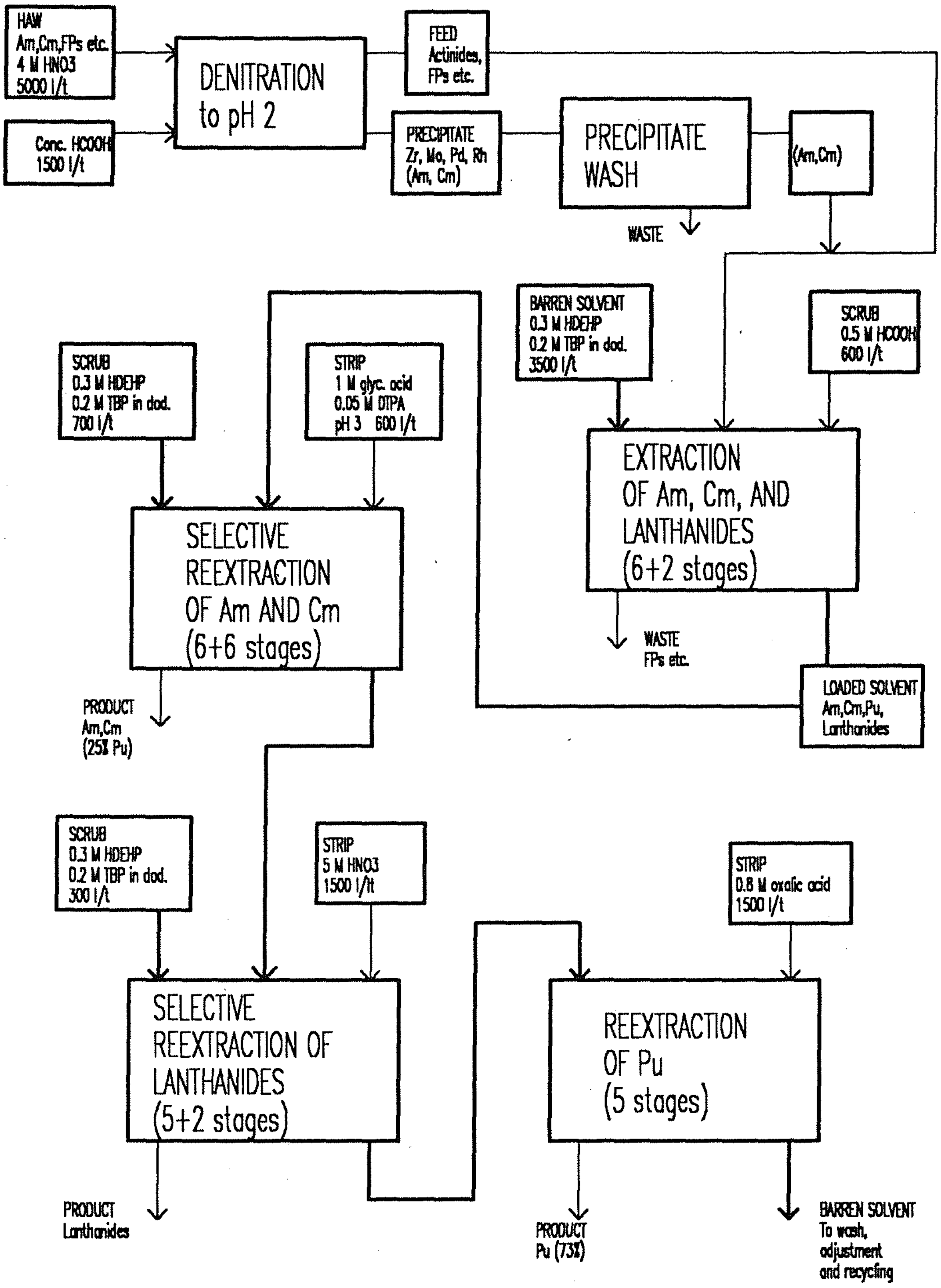

Figure 8. HAW partitioning with transplutonide(III)/lanthanide(III) separation: Flowsheet of a process for the removal of actinides from HAW solutions (Euratom in Ispra, Italy) [17]. Dod. is dodecane and glyc. acid is glycolic acid

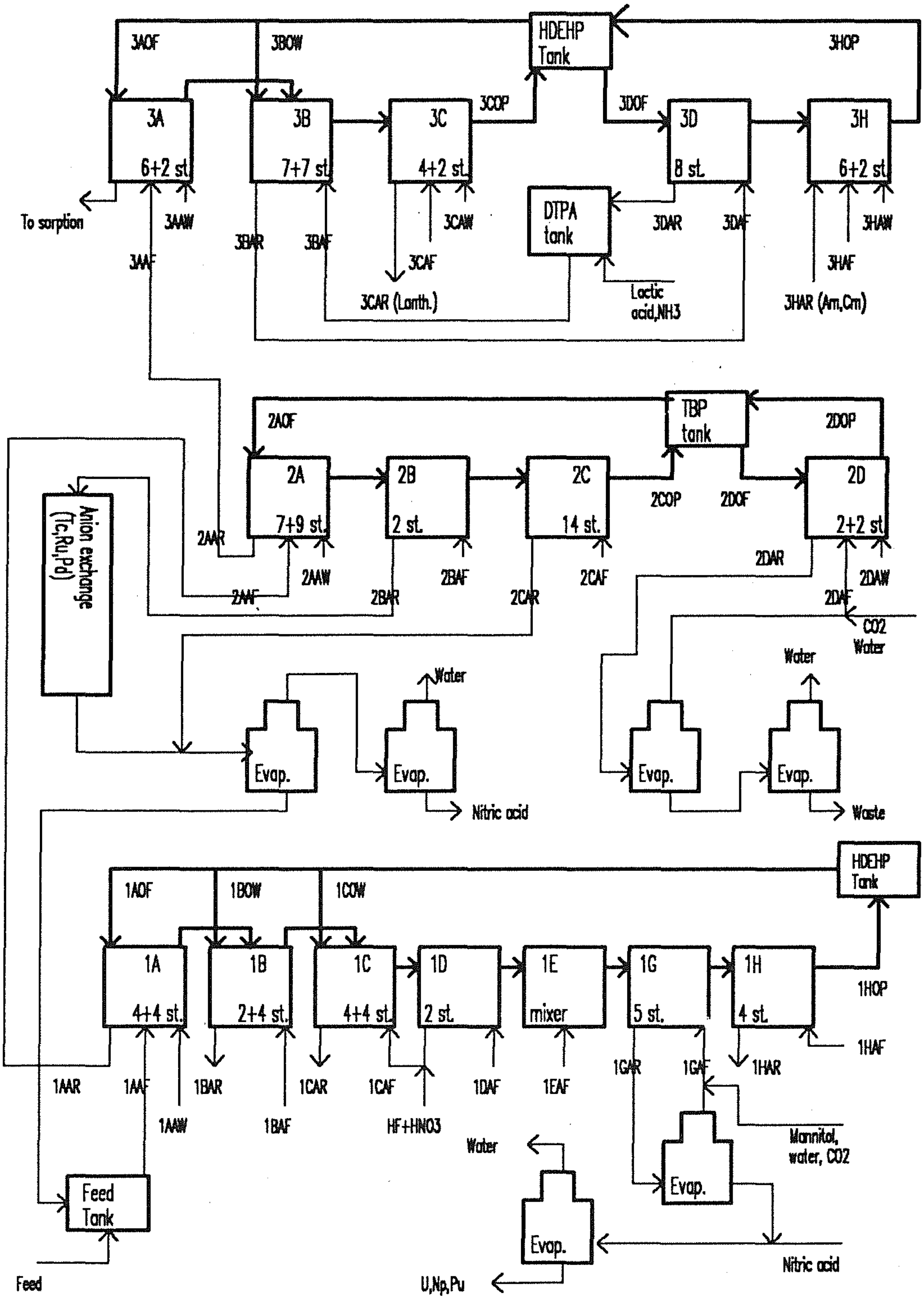

Figure 9. HAW partitioning with transplutonide(III)/lanthanide(III) separation: Flowsheet of a complex process for the partitioning of HAW solutions (Chalmers University, Göteborg, Sweden). Evap. denotes an evaporator. The composition of process streams is given in Table 10 on page 37 [58].

Finally, the raffinate from the 2A extractor is directed to the 2nd HDEHP cycle (extractors 3A to 3H). Transplutonides(III) and lanthanides(III) are extracted in the 3A extractor. The group separation is achieved in the 3B extractor, where transplutonides(III) are selectively stripped under careful pH adjustment. Lanthanides(III) are stripped in the 3C extractor. In the 3D extractor, the transplutonides(III) are extracted from the product stream of the 3B extractor. Strip in the 3H extractor yields a complexant free transplutonide(III) product.

Table 10. Specifications to Figure 9: Composition and flows of process streams [58].

Stream	*Composition*	*Relative flow*
1AAF	HAW solution, 6 M HNO_3	1.0
1AAW	6 M HNO_3	0.1
1AOF	1 M HDEHP in Nysolvin 75 A (alkane mixt.)	1.0
1BAF	6 M HNO_3	1.0
1BOW	1 M HDEHP in Nysolvin 75 A	0.1
1CAF	0.4 M HF + 0.4 M HNO_3	0.605
1COW	1 M HDEHP in Nysolvin 75 A	0.061
1DAF	0.01 M HNO_3	0.24
1EAF	25% NH_3 + 0.1 M mannitol	0.106
1GAF	0.5 M $(NH_4)_2CO_3$ + 0.1 M mannitol	1.0
1HAF	6 M HNO_3	0.6
2AAF	HAW solution, 6 M HNO_3	1.1
2AAW	H_2O	2.2
2AOF	50% TBP in Nysolvin 75 A	16.5
2BAF	9 M HNO_3	3.15
2CAF	H_2O	8.25
2DOF	50% TBP in Nysolvin 75 A	3.3
2DAF	0.5 M $(NH_4)_2CO_3$	0.15
2DAW	H_2O	0.15
3AAF	HAW solution, 0.1 M HNO_3	3.13
3AAW	0.1 M HNO_3	0.313
3AOF	1 M HDEHP in Nysolvin 75 A	1.56
3BAF	0.05 M DTPA + 1.5 M lactic acid, pH 3.63	1.30
3BOF	1 M HDEHP in Nysolvin 75 A	0.159
3CAF	6 M HNO_3	0.215
3CAW	H_2O	0.086
3DOF	1 M HDEHP in Nysolvin 75 A	2.68
3DAW	NH_3 , DTPA, lactic acid	0.079
3HAF	6 M HNO_3	0.268
3HAW	H_2O	0.107

2.3 *METHODS OTHER THAN SOLVENT EXTRACTION*

2.3.1 Ion-Exchange

Data in [104] indicate that transplutonides(III) could be separated from lanthanides(III) on a column of sodium titanate. The lanthanides(III) are sorbed at an unspecified acid concentration somewhat less effectively than transplutonides(III). Hydrated titanium, zirconium and niobium oxides do not distinguish between transplutonides(III) and lanthanides(III). Both groups are strongly sorbed at $pH > 2$ [105]. Np(IV) is strongly adsorbed on anion exchangers from ≥ 8 M HNO_3 [106,107]. The sorption is selective with respect to fission products, and other tetravalent actinides are the only species sorbed together with Np(IV). The phenomenon was utilized in Savannah River, USA, for a large scale separation of Np from a HAW concentrate. A separation line was operated as an extension of the Savannah River Purex plant [108]. To direct Np predominantly (95%) to the HAW stream in the Purex process, nitrite was introduced into the common extraction of U and Pu in the 1st extraction cycle. The remaining 5% of the total Np passed into the raffinate of the U extraction in the 2nd extraction cycle. The HAW solution and the raffinate were combined, concentrated by evaporation, and cooled to 35°C. The Np valency was adjusted to Np(IV) by adding hydrazinium nitrate and Fe(II) sulfamate, each to 0.15 M. The total nitrate concentration was adjusted with 13 M HNO_3 to a value of ~ 8 M. The solution carried some vol.% of suspended solids, but they were not removed. The suspension was consecutively passed through 3 beds of an anion exchanger, which retained $> 90\%$ Np. Pu was prevailably trivalent in the feed, but was also sorbed. This was due to the very strong affinity of the exchanger to Pu(IV), which evoked progressive reattainment of the Pu(III)/Pu(IV) equilibrium in the liquid phase, up to almost complete reoxidation of Pu(III). The loaded exchanger bed was eventually washed with 8 M HNO_3, and Np and Pu were desorbed with 0.035 M HNO_3. The same sorption and desorption operations were utilized for the purification of the Np product. In addition, Pu was eluted before Np using 0.05 M Fe(II) sulfamate and 0.05 M hydrazinium nitrate in 4 - 6 M HNO_3

2.3.2 Pyrochemical Methods

In the context of this paper, the comprehensive term pyrochemical methods particularly denotes hight temperature liquid-liquid extraction. Components to be separated are distributed between immiscible molten metal and salt phases, which at room temperature are solid. Reactions and equilibria in such systems were extensively studied in the 1960s, but the work was obviously suspended in early 1970s. The work was indeed not performed in the scope of an actinide separation programme. It was a part of the development of a salt melt based breader reactor. Nevertheless, distribution data gained in the work (see e.g. [109-111]) might well be useful for a waste partitioning procedure. For example, molten Bi extracts transplutonides from fluoride melts with a good selectivity

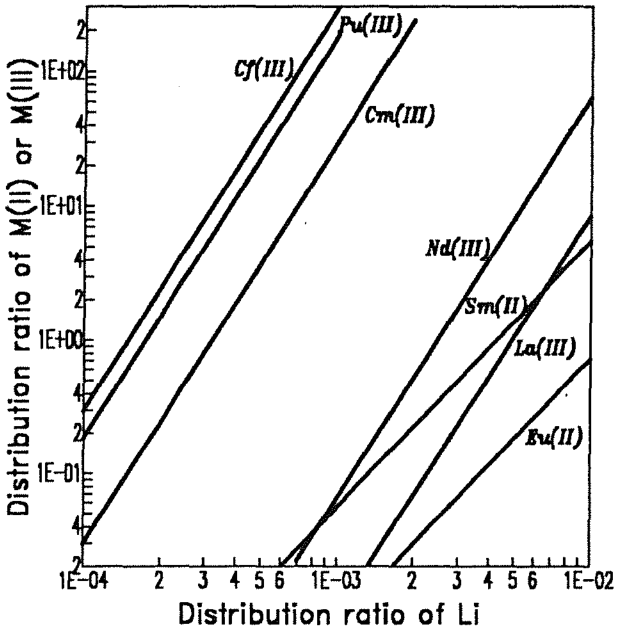

Figure 10. Extraction of actinides und lanthanides with bismuth from a fluoride melt: Effect of the Li concentration in the bismuth phase on the distribution ratio. 66.7 mol% LiF and 33.3 mol% BeF_2, 600°C [110].

over lanthanides (Figure 10 and Figure 11). The separation efficiency increases moderately with decreasing temperature (Figure 12). The extraction form chloride melts is much less selective for transplutonides (Figure 13).

All lines in Figure 10 to Figure 13 are calculated from parameters given in the original sources. Distribution ratios are defined as quotients of mol fractions (N_{Metal}/N_{Salz}). Distribution ratio of Li is given in two figures as the independent variable. Since the Li concentration in the salt phase is constant, the ratio is proportional to the concentration of Li in the metal phase. The significance of the latter variable is made clear by the equation of the extraction reaction, namely $MF_{n(Salt)} + nLi_{(Bi)} = M_{(Bi)} + nLiF_{(Salt)}$. It is worth noticing that Am, Cf, Sm and Eu can be partially or predominantly reduced to a bivalent state in the salt phase.

Application of the high temperature extraction to the waste partitioning was suggested a decade ago. A chloride system is supposed to be used, with a mixture of 50 mol% $MgCl_2$, 30 mol% NaCl und 20 mol% KCl as the salt phase. The metal phase is pure magnesium or its alloys with ≤70% zinc or copper. The phases are contacted at 827°C. Distribution ratios of actinides and fission products are varied within one or two orders of magnitude, if the zinc or copper content in the metal phase is changed. A potential flowsheet has been proposed for partitioning radioactive waste into several fractions. Fission products would be obtained in a mixture with copper after the evaporation of

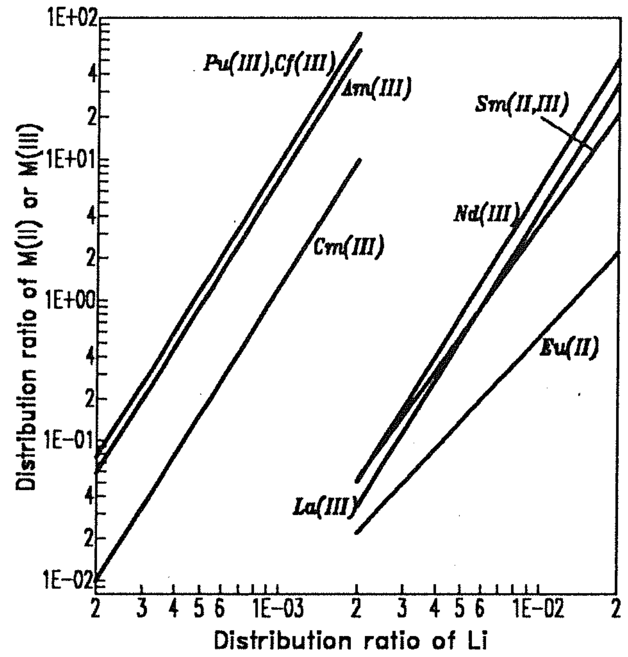

Figure 11. Extraction of actinides und lanthanides with bismuth from a fluoride melt: Effect of the Li concentration in the bismuth phase on the distribution ratio. 76 mol% LiF, 16 mol% BeF_2 und 12 mol% ThF_4, 600°C [109].

magnesium. Actinides would be split between two fractions. One of them would contain intermediately trivalent U, Np, Pu and Cm, finally obtained as metals after the evaporation of Zn and Mg. Bivalent Am and Cf would be left in a chloride melt in the extraction of lanthanides into Bi metal and, subsequently, extracted into a Zn/Mg alloy. The final form would be a metal remainder after evaporating Zn and Mg [112].

The flowsheet involves five extraction or reextraction operations. They would have to be performed in counter-current contactors and it is difficult to assess their feasibility and risks. The authors of [112] are optimistic, but extensive research and development of the equipment would be needed. Several potential advantages of the process are foreseen in the original paper [112]. First, process streams would have high densities and the process could be operated in a compact plant. Second, molten phases are little damaged by ionizing radiation. Finally, radioactive products would be obtained in a solid, compact form. It should be noticed here that the bivalency of e.g. Am and Cf in the melts could offer separation potential which is unconceivable in aqueous systems.

Electrolytical deposition from molten salts extends the separation potential of pyrochemical methods (see “Electrolysis” on page 42).

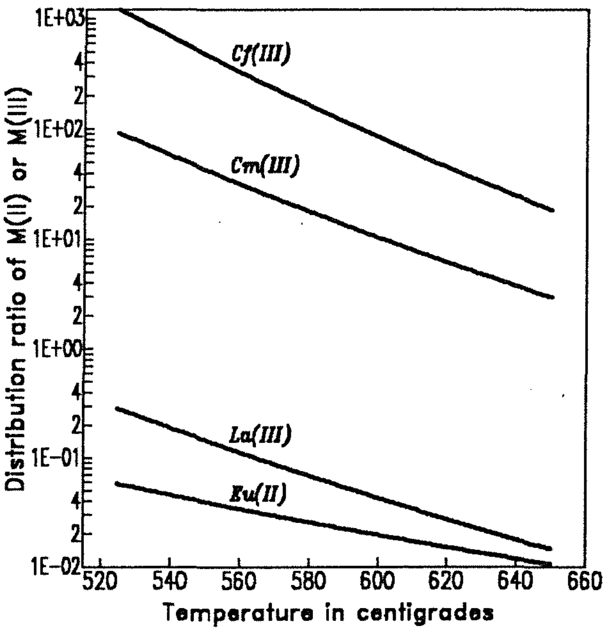

Figure 12. Extraction of actinides und lanthanides with bismuth from a fluoride melt: Effect of temperature on the distribution ratio. 76 mol% LiF, 16 mol% BeF_2 und 12 mol% ThF_4, the distribution ratio of Li is 0.002 [109].

2.3.3 Precipitation of Actinides and Lanthanides

2.3.3.1 Precipitation of Oxalates

A process has been developed, in which the precipitation is accomplished by the denitration of an HAW solution with formic acid in the presence of oxalic acid. In this way a pH value is reached which is needed for a complete precipitation of transplutonides(III). Moreover, plutonium is also converted to oxalate and is not irreversibly adsorbed on the precipitate. Lanthanides(III) are of course also precipitated and, besides, 15 - 40% fractions of other fission products like Cs, Sr and Ru are coprecipitated. 99.2 - 99.8% Am and Cm, ~99.4% Pu, >99% Np and >99.5% lanthanides(III) are transferred into the precipitate at a total mole ratio of $HCOOH/HNO_3$ = 1.8 and after a reaction time of 1 - 2 h. The precipitate is washed with a solution of oxalic acid and dissolved in diluted nitric acid. The process must then be continued with more selective methods than the precipitation. Np and Pu are removed by solvent extraction, transplutonides(III) are separated from lanthanides(III) by the TALSPEAK method and small rests of actinides are removed by cation exchange from the mother liquor of the oxalate precipitation [32,113,114].

It is seen that the potential contribution of the oxalate precipitation to the partitioning is limited. As described above, the precipitation does not represent more than an extension

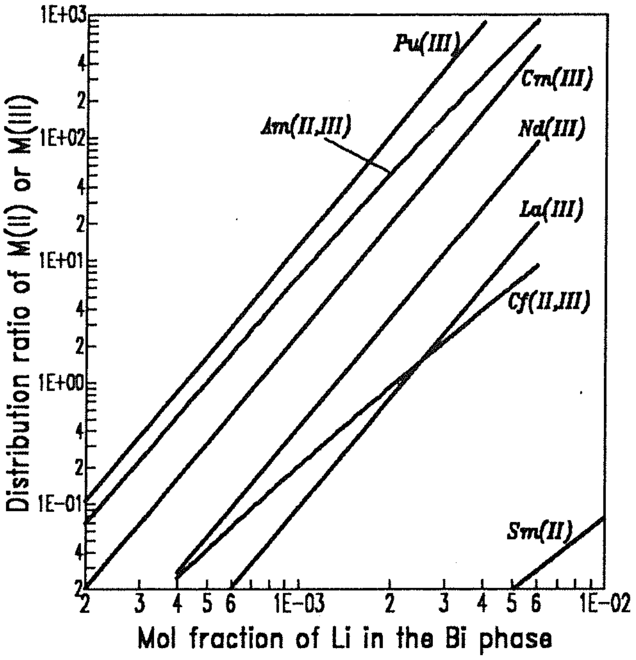

Figure 13. Extraction of actinides und lanthanides with bismuth from an LiCl melt: Effect of the Li concentration in the bismuth phase on the distribution ratio. 640°C [111].

of an extraction process. None the less, the method has further been examined in Japan and it has been recommended to add oxalic acid only after the denitration. Then zirconium and molybdenum are removed in the denitration solid, are not present in the oxalate precipitation, and the coprecipitated fraction of Sr is suppressed to $<10\%$. Neptunium is precipitated, if it is reduced with ascorbic acid before the addition of oxalic acid [115].

2.3.3.2 Precipitation of Fluorides

Fluorosilicic acid precipitates lanthanides(III) from 5 M HNO_3 and leaves a major part of transplutonides(III) in the solution. So 70 - 85% Am and $\sim$10% lanthanides(III) remain in the solution at 35 - 40°C and 1 M H_2SiF_6 [116]. The ancient method is mentioned here just for the sake of completeness.

2.3.4 Electrolysis

Partial transplutonide/lanthanide separation is reached in the electrolysis from solutions, in which initially concentrated HCl has been neutralized with ammonia. At a current density of 0.9 A/cm^2, 100% Am and only 45% Eu are deposited after 8 min on a platinum or gold cathode [117].

Pyrometallurgical electrorefinig could also have separation potential for waste partitioning. A method has been developed in the last decade, in which uranium and plutonium are recovered from a metallic, fast breeder reactor fuel. The fuel is dissolved in molten cadmium, which serves as an anode and is kept in contact with molten alkali or alkaline earth chlorides. Pu and U are deposited on a cathode immersed in the salt layer. Lanthanide and alkaline earth fission products remain in the salt phase [118,119]. Yet unpublished results of assessment work made in the USA show that the method promises a possibbilty of separating transplutonides from lanthanides. According to preliminary computations, Am could be separated form radioactive waste with a 99.9% efficiency together with Pu, Np, Cm and U. The cathode deposit would contain mere 9% lanthanides.

3.0 SEPARATION OF LONG-LIVED FISSION PRODUCTS

3.1 *SOLVENT EXTRACTION*

3.1.1 Extraction of Strontium

3.1.1.1 Solvating Extractants

Phosphoryl extractants extract Sr(II) very weakly from HNO_3 solutions. Even an extractant as powerful as OΦD(iB)CMPO yields for Sr(II) hardly a distribution ratio higher than 0.01 (s. Table 6 on page 17). Extraction with other oxygenated electron donors (amine and sulfide oxides, carboxylic acid amides, ketones etc.) is correspondingly less efficient. Crown ethers represent one of the very seldom classes of solvating extractants which are able to extract Sr(II) efficiently from nitrate solutions. Generally, crown ethers exhibit a considerable extraction power also for alkali metals. A search of such crown ethers has thus been made which exhibit a good selectivity for Sr(II) over Na(I). Three selective crown ether extractants have been recommended in [120], namely 18-crown-6, bis(4-phenyl- butyl)-18-crown-6 and dicyclohexano-18-crown-6 (DC18C6). Not only DC18C6, but also its 4,4′(5′)-dimethyl and dibutyl derivatives have been shown to possess good extractant properties for Sr(II) [121]. 18-crown-6 is not well applicable, because it is too soluble in the aqueous phase. Most attention has been paid to DC18C6 as a promising extractant for Sr(II).

Figure 14 shows the range of the HNO_3 concentration, in which Sr(II) can effectively be extracted with DC18C6 in chloroethanes. Chloroethane diluents have been used, because crown ethers yields adequate distribution ratios of Sr(II) in polar diluents only. The highest extraction efficiency is reached with DC18C6 in di- and trichloromethane as well as di- and tetrachloroethane. Dissolved in unpolar aliphatic or aromatic diluents, the extractant gives only low distribution ratios [120]. Since HCl can be released in the radiolytic degradation of chlorinated hydrocarbons, alternative diluents have been sought for crown ethers. Oxygen containing polar liquids have been shown to be applicable. Among them, pentanol and pentanoic acid give a better extraction efficiency than ketones and esters. Selected data are given as an illustration in Figure 15. In each diluent class, i.e. alcohols, ketones, carboxylic acids and esters, the efficiency of the extraction with DC18C6 decreases with increasing molecular weight of the diluent. Moreover, there is a correlation between the water solubility in the diluents and the equilibrium constants of the Sr(II) extraction [122].

The rather high price of crown ethers and the aqueous solubility of a low-molecular-weight diluent like pentanol are unfavourable circumstances. It is difficult to assess their impact on the application of crown ethers in a large scale partitioning process. Anyway, encouraged by good results of laboratory work, investigators from ANL, Argonne, USA suggest to operate a ^{90}Sr extraction process (SREX) in tandem with the TRUEX process.

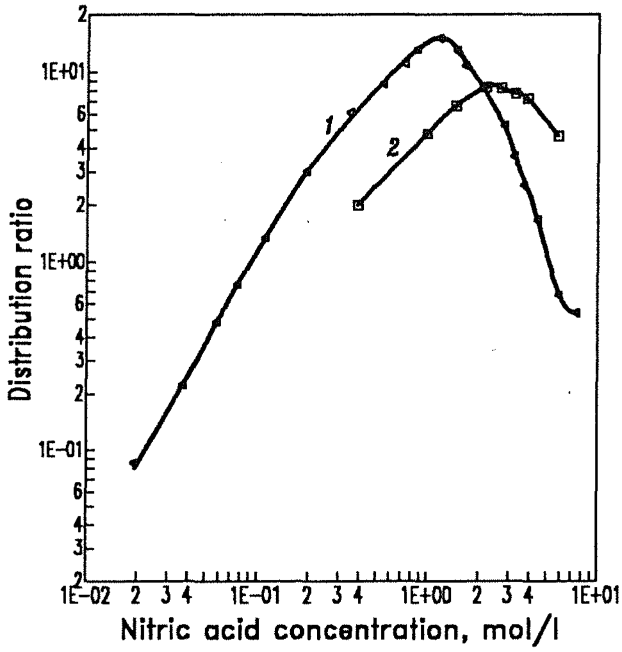

Figure 14. Extraction of strontium with dicyclohexano-18-crown-6: Influence of the diluent and the HNO_3 concentration on the distribution ratio. Curve *1*: 0.0137 M DC18C6 in 1,1,2,2-tetrachloroethane, 2 × 10^{-5} M Sr(II), room temperature [120]. Curve *2*: 0.1 M DC18C6 in dichloroethane, 0.03 M Sr(II), 25°C [123].

The SREX process is based on the use of a 0.2 M solution of di-*tert*-butylcyclohexano-18-crown-6 in 1-octanol. Sr(II) can be extracted from a HAW solution at $\geq$1.0 M HNO_3 and can then be reextracted with $<$0.05 M HNO_3. Only Ba(II) and Tc(VII) are extracted together with Sr(II). The solvent exhibits a good radiation stability and the Sr yield is as high as 99.7% in mere three extraction stages [124].

Numerous Sr(II) salts are much more effectively extracted by crown ethers than nitrate. Especially extractable are salts of voluminous, lyophilic anions. The extraction effectiveness is in such systems good enough even if a nonpolar diluent like benzene, toluene or an alkane is taken. A trialkylphenol and phenyltetrazolin-5-thione are donors of suitable lyophilic anions. They make it possible to extract Sr(II) with a crown ether at pH 2 - 6 [125]. Rather much attention has been paid to the extraction of Sr(II) picrate. High distribution ratios of Sr(II) have been shown to be reached even at low free picrate concentrations (see e.g. [125-127] and references therein). However, the data have been obtained in systems with very small amounts of foreign ions in the aqueous phase. The extraction of Sr(II) picrate from a HAW solution would be highly disadvantageous, because HAW solutions obtain rather large amounts of sodium ions (see Table 1 on page 5) which also form extractable picrates. Large amounts of picrate anions would have to be added for reaching an appraciable concentration of free picrate ions.

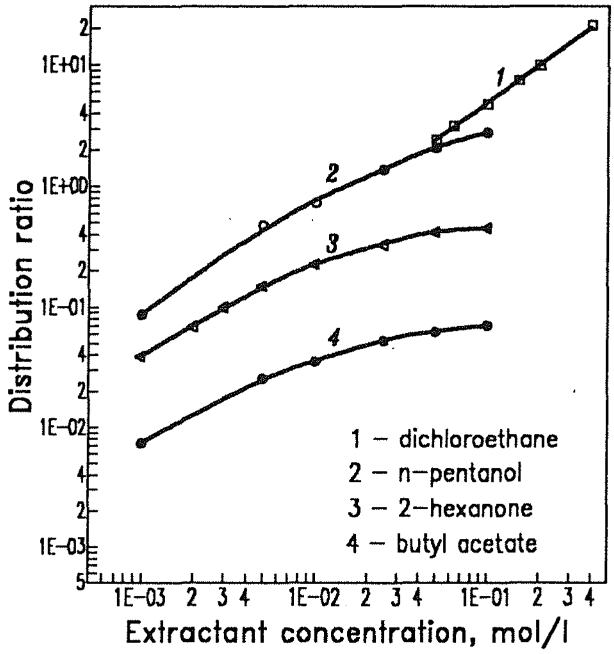

Figure 15. **Extraction of strontium with dicyclohexano-18-crown:** Influence of the diluent and the extractant concentration on the distribution ratio. 1 M HNO_3, 25°C. Taken from [123] (curve *1*) and [122] (other curves).

A considerably higher application potential can be assigned to the extraction of a HDEHP salt of Sr(II) with crown ethers. The salt is well extracted at pH 2 - 3 with different 24-crown-8 compounds in CCl_4 or kerosene [128]. Nitric acid lowers the extraction efficiency, because it suppresses the dissociation of the moderately strong HDEHP acid. More promising results are obtained with dialkylnaphthalene sulfonic acids as anion donors. An Sr(II) salt of didodecylnaphthalene sulfonic acid is acceptably extractable with a number of 18-crown-6 and 24-crown-8 compounds in a TBP/kerosene mixture (3/7). The distribution ratio of Sr(II) at pH 2.5 ranges from 4 to 6 [129]. In spite of the high acid strength of didodecylnaphthalene sulfonic acid, the extraction of its Sr(II) salt can be suppressed at high HNO_3 concentrations. The extent of the suppression is considerably dependent on the molecular structure of the crown ether extractant, and is large with many of them. Bis-4,4′(5′)-(1-hydroxyheptyl)cyclohexano-18-crown-6 is one of few compounds, which are able to extract Sr(II) also at 3 M HNO_3. Moreover, didodecylnaphthalene sulfonic acid can as an anion donor be substituted by its commercially common dinonyl analogon (DNNS) [130]. The extractability of Sr(II) has in [128-130] been studied in the presence of TBP, in order to make the solvent compatible with the Purex process solvent (usually 30 vol.% TBP in kerosene).

The extraction with bis-4,4′(5′)-(1-hydroxyheptyl)cyclohexano-18-crown-6 has been suggested to be utilized for the separation of ^{90}Sr from HAW solutions. The recommended solvent contains ≥0.02 M crown ether, 0.1 M DNNS, 27 vol.% TBP and 68 vol.% kerosene. Only Ba(II) and Zr(IV) are extracted together with Sr(II), and all extracted metal species can be stripped with 0.5 - 1.0 M HNO_3 [130]. It appears that the reextraction is not very effective and would desire many extractor stages.

3.1.1.2 Acidic Extractants

Strontium(II) is well extractable with HDEHP at pH > 3 [131]. Nonpolar aliphatic or aromatic liquids are favourable diluents [131], and the extraction is synergistically increased by TBP or dibutyl butylphosphonate [132,133]. The effectiveness of the extraction is illustrated in Figure 16. Polar degradation products of HDEHP like 2-ethylhexanol and mono(2-ethylhexyl) phosphoric acid suppress the Sr(II) extraction [133]. If the HDEHP and TBP concentrations are appropriately high, Sr(II) is well extractable also in the presence of citrate or tatrtate (Figure 16). The complexants keep fission and corrosion products like ^{106}Ru, ^{95}Zr, ^{95}Nb and Fe(III) in the aqueous raffinate, and make the extraction of Sr(II) selective. ^{90}Sr is then accompanied only by lanthanides(III), if it is extracted from a denitrated and, eventually, neutralized HAW solution [134].

The good extractability of Sr(II) with HDEHP encouraged the development of processes for the recovery of ^{90}Sr from HAW solutions. Let us mention processes which were developed at Oak Ridge [135] und Hanford [134,136], USA. A solution of HDEHP and TBP in kerosene is used as the solvent in both processes. TBP acts not only as a synergist, but also as a solvent modifier. It increases the solubility of HDEHP complexes in the organic phase. It is especially important to increases the solubility of the sodium salt of HDEHP, which is formed in the solvent wash. The extraction of fission and corrosion products is supressed by tartrate in the Oak Ridge process and by citrate in the Hanford process. Flowsheets of the processes are shown in "EXAMPLES OF PROCESS FLOWSHEETS" on page 54.

3.1.1.3 Extraction of Ion-Pairs

Bulky lyophilic anions form with Sr(II) ion-pairs, which are extractable with strongly polar solvents like nitrobenzene. For example, Sr(II) dipicrylaminate or tetraphenylborate [137] and tripyrocatechinoarsenate [138] are such extractable ion-pairs. Extraction of these ion-pairs, however, is of interest in laboratory procedures rather than in the HAW partitioning. Much more promising for an HAW treatment are anions of polyhedral cobalt(III) dicarbolide, $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Co^-$, and of polyiodide. Both form with Sr(II) ion-pairs, which are extractable with nitrobenzene in the presence of polyethylene glycol synergists [139]. Figure 17 illustrates the effect of a commercially available polyethylene glycol on the extractability of Sr(II).

The extraction of a ion-pair formed by Sr(II) with the Co(III) dicarbolide anion in the presence of a polyethylene glycol has been incorporated into an extensive partitioning process. A mixture of nitrobenzene and CCl_4 has been used as diluent, and a yield of 99.8% ^{90}Sr has been attained in a hot test [140]. Later the unsubstituted dicarbolide

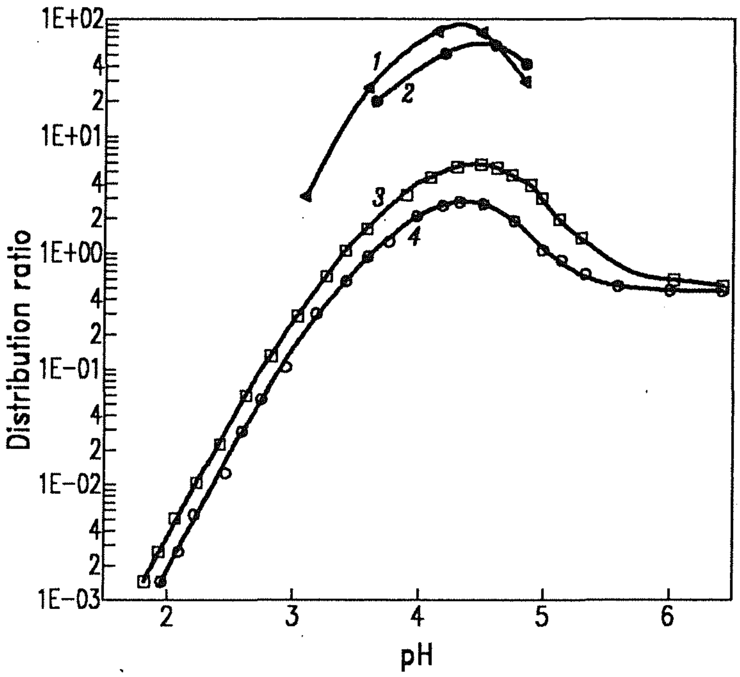

Figure 16. **Extraction of strontium with HDEHP at 25°C:** Extraction from simulated HAW solutions with 0.37 M HDEHP + 0.2 M TBP in kerosene, in the presence of 0.12 M citrate + 0.35 M acetate (curve 1) and 0.12 M tartrate + 0.35 M acetate (curve 2) [134]. Extraction from 4 M $NaNO_3$ with 0.1 M HDEHP + 0.05 M TBP in nonane (curve 3) and with 0.1 M HDEHP in nonane (curve 4) [132].

extractant has been replaced by a chlorinated derivative, which exhibits a higher chemical stability and a good radiation resistency. The ^{90}Sr yield in a hot operation with the chlorinated dicarbolide extractant is given as 98% [140]. Unfortunately, the paper gives no information about the composition and flow rates of process streams in particular extraction operations.

3.1.2 Extraction of Cesium

3.1.2.1 Solvating Extractants

Crown ethers are among the rare solvating extractants, which are able to extract Cs(I). Cs(I) is little extractable as nitrate, and is much better extractable as e.g. perchlorate [141]. Like Sr(II), also Cs(I) is well extractable with crown ethers as picrate (see e.g. [127]). The extraction of Cs(I) picrate is synergistically enhanced by TBP and trioctyl phosphine oxide [142]. As in the case of Sr(II), the picrate extraction can hardly be utilized in a HAW partitioning process.

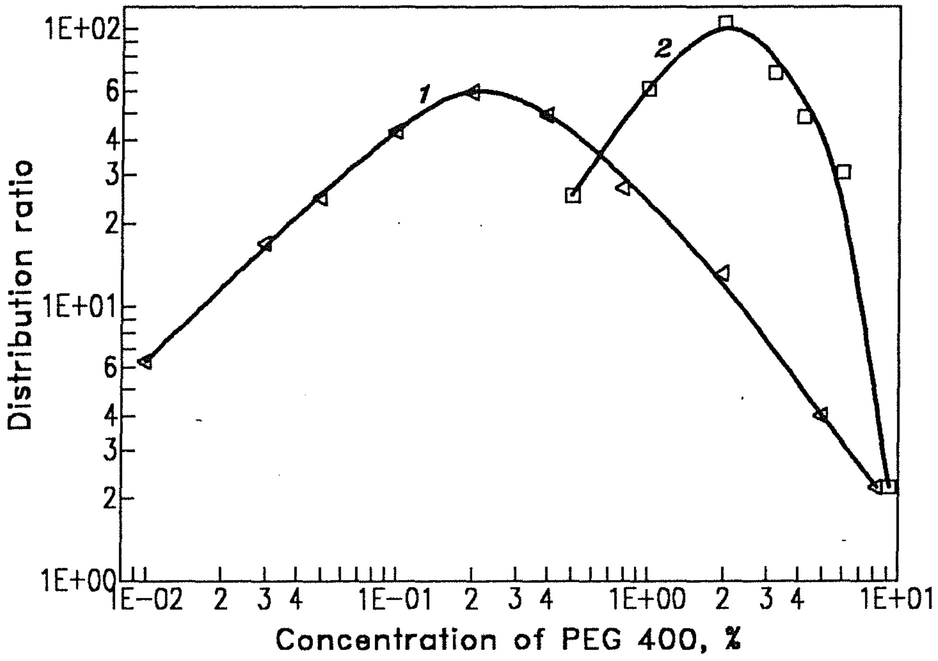

Figure 17. Extraction of ion pairs of strontium: Influence of polyethylene glycol PEG 400 on the extraction with nitrobenzene from 0.5 M HNO_3 at 24°C. The anion donor in the organic phase is 0.01 M cobalt(III) dicarbolide (curve 1) and 0.1 M I_2 + 0.04 M HI (curve 2) [139].

A Cs(I) salt of HDEHP is effectively extracted with 0.125 M dicyclohexano-18-crown-6 + 0.125 M HDEHP in benzene. The distribution ratio of Cs(I) is >10 at pH>2.5 and reaches a maximum of ~50 at pH 4.5 [143]. A satisfactory extraction efficiency is attained also with 0.02 M bis-4,4′(5′)-di-*tert*-butylbenzo-24-crown-8 + 50 vo.% HDEHP + 25 vol.% TBP in kerosene. The distribution ratio decreases with increasing hydrogen ion concentration. It is 1.45, 1.0 and <0.1 at pH 5.5, 3.5 - 4.5 and <2 respectively [128].

If HDEHP is as an anion donor replaced by a dialkylnaphthalene sulfonic acid, the distribution ratio of Cs(I) is less sensitive to the nitric acid concentration. 0.02 M bis-4,4′(5′)-(1-hydroxyheptyl)cyclohexano-18-crown-6 + 5 vol.5 didodecylnaphthalene sulfonic acid + 27 vol.% TBP in kerosene extracts Cs(I) from 3 M HNO_3 with a distribution ratio of 2. Sr(II) is little extracted [129]. Also 0.05 M bis-4,4′(5′)-(1-hydroxy-2-ethylhexyl)cyclohexano-18-crown-6 + 5 vol.% DNNS + 27 vol.% TBP in kerosene extracts Cs(I) effectively and selectively. The solvent has been recommended for the recovery of ^{137}Cs from HAW solutions [130].

Crown ethers also extract Cs(I) salts of inorganic complex acids. Some illustrative data are given in Table 11. The data compare the extractability of cesium nitrate with that of complex salts, and indicate the optimum size of the crown ring and the optimum form of the anion donor. The diluent must be a polar liquid.

Table 11. **Extractability of Cs(I) salts with crown ethers:** Extraction of initially $\leq 3 \times 10^{-5}$ Cs(I) from 1 M HNO_3 without or with an additional anion donor added. Room temperature [144].

Crown ether	*Additional anion donor*	*Diluent*	D_{Cs}
0.012 M dibenzo-21-crown-7	none	nitrobenzene	1.7
0.012 M dibenzo-15-crown-5	0.004 M $H_3[PMo_{12}O_{40}]$	nitrobenzene	8.2
0.003 M dibenzo-18-crown-6	0.001 M $H_3[PMo_{12}O_{40}]$	nitrobenzene	5.4
0.012 M dibenzo-21-crown-7	0.004 M $H_3[PMo_{12}O_{40}]$	nitrobenzene	483
0.012 M dibenzo-24-crown-8	0.004 M $H_3[PMo_{12}O_{40}]$	nitrobenzene	5.5
0.018 M dibenzo-21-crown-7	0.018 M $Na[SbCl_6]$	1,1,2,2-tetrachloroethane	245
0.018 M dibenzo-24-crown-8	0.018 M $Na[SbCl_6]$	1,2-dichloroethane	9.2
0.012 M dibenzo-18-crown-6	0.012 M $Na[BiI_4]$	nitrobenzene	0.11
0.018 M dibenzo-21-crown-7	0.018 M $Na[BiI_4]$	nitrobenzene	23.5
0.012 M dibenzo-24-crown-8	0.012 M $Na[BiI_4]$	nitrobenzene	3.8
0.018 M dibenzo-21-crown-7	0.012 M $H[SbCl_6]$	1,1,2,2-tetrachloroethane	226
0.018 M dibenzo-21-crown-7	0.012 M $Na[SbCl_6]$	1,1,2,2-tetrachloroethane	253
0.018 M dibenzo-21-crown-7	0.012 M $NH_4[SbCl_6]$	1,1,2,2-tetrachloroethane	81.2
0.018 M dibenzo-21-crown-7	0.012 M $K[SbCl_6]$	1,1,2,2-tetrachloroethane	67.3
0.018 M dibenzo-21-crown-7	0.012 M $Tl[SbCl_6]$	1,1,2,2-tetrachloroethane	1.7

3.1.2.2 *Acidic Extractants*

Few acidic extractants are able to extract Cs(I) with a good extraction yield. Substituted phenols like *o*-phenylphenol, 4-chloro-2-phenylphenol, 4-chloro-2-benzylphenol and 4-*sec*-butyl-2-(α-methylbenzyl)phenol do it as 1 M solutions in di*iso*propylbenzene at pH > 12. The last compound (BAMBP) has been recommended for the extraction of ^{137}Cs from alkalized HAW solutions. It is not the most effective extractant among the compounds named, but it exhibits a very low aqueous solubility and extracts Cs(I) with a good selectivity with respect to Na(I) [135]. Still more effective are compounds, the molecule of which consists of several substituted phenol molecules linked with methylene bridges. They extract Cs(I) as 1 M solutions in benzene at pH > 8 [145].

The applicability of BAMBP to the extraction of ^{137}Cs from liquid radioactive wastes was tested with a simulated HAW solution. Fission and corrosion products were masked with tartrate, and Sr(II) had been removed from the solution by solvent extraction. The solution was adjusted with NaOH to pH 12.6 and directed (relative flow 1.0) into a mixer-settler. There it was contacted in 5 - 6 stages with 1 M BAMBP in di*iso*propylbenzene (relative flow 1.0). The loaded solvent was washed in 2 stages with 0.3 M NaOH (relative flow 0.2). To reduce losses of BAMBP to the aqueous raffinate, the aqueous stream was acidified with 3 M HNO_3 (relative flow 0.075) to pH 10 - 11 just before leaving the extractor. An extraction yield of > 99.8% Cs was reached with this flowsheet. The strip of Cs(I) with 0.05 M HNO_3 (relative flow 0.05) was accomplished in one single contactor stage. The aqueous product stream contained 2.4 g Cs/l, 0.2 g Na/l and 0.04 g Fe/l [135].

More recently it has been found out that the pH range of the extractability of Cs(I) with BAMBP can essentially be extended by a synergistic action of HDEHP [146,147]. A 0.5 M BAMBP + 0.3 M HDEHP solution in kerosene extracts Cs(I) at pH 4 - 10 with a distribution ratio of 5 - 10. Sr(II) is simultaneously extracted with a distribution ratio of 7 - 40. This offers a possibility of common recovery of ^{137}Cs and ^{90}Sr from radioactive waste solutions [146]. It should be noticed that the introduction of crown ether extractants strongly diminished the interest in phenolic extractants for Cs(I).

3.1.2.3 *Extraction of Ion-Pairs*

Numerous Cs(I) salts are extractable as ion-pairs, in which the anion need not necessarily be voluminous and lyophilic. So Cs(I) is extractable as cobalt(III) dicarbolidate [148], dipicrylaminate [149], picrate [150], 2,4-dinitro-N-picryl-1-naphthylaminate [151], nitrophenolate [152], tetraphenylborate [153], tripyrocatechinoarsenate [138], molybdophosphate [154], polyiodate [155], iodobismutate [156,157], hexabromothallate(III) [158], tetrachloroaurate or -ferrate(III) [159] and dianilinetetrathiocyanatochromate(III) [160]. The extracted ion-pair is dissociated in both phases and, thus, the diluent must be polar. The highest extraction efficiency is reached with nitrobenzene, nitromethane, nitropropane and other nitro derivatives. Addition of other oxygen containing liquids, even if it is as small as 15%, suppresses the distribution ratio of Cs(I) by one to three orders of magnitude [148]. Ions of other alkali metals as well as hydrogen ions are also extractable and interfere with the extraction of Cs(I). The selectivity of the Cs(I) extraction toward Na(I) depends on the nature of the anion and the diluent, as well as on the ionic strength in the aqueous phase. For example, the selectivity is improved, if the nitrobenzene diluent is substituted by 1-chloro-2,4-dinitrobenzene or its 1-fluoro analogon [149].

Only few of the above anions are applicable as counter-ions in the extraction of Cs(I) from HAW solutions. Some of them are unstable or little effective in HNO_3 solutions, desire addition of foreign substances like HCl to the HAW solution, or are too expensive. It is a general inconvenience that a polar diluent like a nitro compound has to be used as a diluent. On the other hand, the ion-pair extraction offers a good selectivity for Cs(I) with respect to other fission products. In most systems Sr(II) is the only element which is extracted together with Cs(II).

Cs(I) polyiodide is one of ion-pairs which can be extracted from solutions of nitric acid. The extraction of this pair was successfully tested as a method for the separation of Cs from a simulated HAW solution. An efficient separation of Cs from other fission products was achieved in a mixer-settler with 16 stages. The Cs content in the HAW solution was reduced by a factor of 10^6 [161]. Also dipicrylamine has been suggested as a reagent for the extraction of Cs from HAW. Counter-current tests were performed with a simulated HAW solution, which indeed had to be denitrated and adjusted to pH 7 - 8. Hydrolyzable elements were complexed with citrate anions [162].

Another, more extensively developed process is based on the use of dicarbolide compounds as anion donors for the Cs(I) ion-pair extracted. Using Co(III) dicarbolide and a chlorinated derivative of it, 99.8 and 98% ^{137}Cs respectively was removed from a true HAW solution in a hot counter-current test [140]. Problems might arise in the reextraction of Cs(I) from a solution of the chlorinated derivative, because a rather concentrated HNO_3 solution is needed. It has recently been suggested to strip Cs(I) with 0.3 - 0.5 M HNO_3 in the presence of a complexon. The complexon forms a molecular complex with the dicarbolide extractant and lowers in this way the distribution coefficient of Cs(I). DTPA, ethylenediamine diacetic acid, oxyethylidene diphosphonic acid and nitrilotrimethylene phosphonic acid are satisfactorily efficient [87]. The chlorinated dicarbolide derivative is not specified in the paper, and almost nothing is said there about the flowsheet of the process. A 0.05 M aqueous DTPA solution and a 0.06 M solution of a chlorinated Co(III) dicarbolide in nitrobenzene have been used in batch distribution experiments, but it is not obvious whether the same solutions have been used in counter-current runs.

3.1.3 Extraction of Technetium

3.1.3.1 Solvating Extractants

Technetium is present in HAW solutions as pertechnetic acid. The stable Tc(VII) oxidation state is at 0.2 - 1.5 M HNO_3 extractable with TBP in dodecane. A maximum distribution ratio of $\sim$1.3 is reached at 0.7 M HNO_3 in the extraction with 30 vol.% TBP in dodecane, i.e. with the typical Purex process solvent. The maximum attainable distribution ratio increases steeply with the TBP concentration, and is ~6 at 50 vol.% TBP in dodecane [163]. This phenomenon was utilized in the flowsheet shown in Figure 9, where Tc(VII) is extracted in the 2A extractor with 50% TBP. The distribution of the soft beta nuclide ^{99}Tc could not be followed in a hot test. However, calculations predicted that 99% Tc would be extracted. An unfavourable splitting of Tc is expected in the further course of the process. 61% and 9% Tc is to be stripped with 9 M HNO_3 in the 2B extractor and with water in the 2C extractor respectively. The rest of Tc is to pass through the solvent wash in the 2D extractor, the 2DAR stream and two evaporators into the waste [59].

As it can be expected, trioctyl phosphine oxide [164] as well as OΦD(iB)CMPO and dihexyl-N,N-diethyl carbamoylmethylphosphonate (see Table 6 on page 17) extract Tc(VII) more effectively than TBP. It might be of interest that Tc(VII) is coextracted in the extraction of metal nitrates with TBP. The reason is that mixed complexes of the type $M(NO_3)_{(n-1)}(TcO_4).xTBP$, are formed, with n being the charge of the extracted metal ion M^{n+} . Tc(VII) is especially strongly coextracted with Zr(IV). If for example the solvent is 30% TBP in dodecane and contains 0.01 M Zr(IV), the distribution ratio of Tc(VII) is at 5 M HNO_3 as high as ~2.5. In the absence of-Zr(IV) the distribution ratio of Tc(VII) is ~0.01 [165]. Tc(VII) is less effectively coextracted with Pu(IV) [10] and still less effectively with U(VI) [165].

Ketones extract Tc(VII) from alkaline solutions. The use of undiluted cyclohexanone for the removal of ^{99}Tc from alkaline radioactive waste solutions has been suggested. A salting-out agent must be present in the aqueous phase. Sodium carbonate and sulfate are more effective than sodium chloride, nitrate or hydroxide. The distribution ratio of Tc(VII) is suppressed by two orders of magnitude, if the starting Tc(VI) concentration in the aqueous phase is increased from 10^{-5} M to 0.01 M. The ^{99}Tc removal was tested with a feed solution containing 1 M NaOH and 5 M $NaNO_3$. The extraction yield was 99.2 - 99.7% ^{99}Tc in 12 stages of a mixer-settler. Tc(VII) can be recovered from cyclohexanone by reextraction with water, or by sorption on macroreticular ion exchanger [166].

Pyridine and its derivatives, quinoline and quaternary ammonium bases also extract Tc(VII) from alkaline solutions (see references in [166]).

3.1.3.2 Extraction of Ion-Pairs

Pertechnetic acid is extracted by trioctyl amine, and the extraction can be quite effective even at rather high concentrations of nitric acid. If 0.5 M TOA in CCl_4 is the solvent and the aqueous HNO_3 concentration is increased from 1 to 4 M, the distribution ratio of Tc(VII) is suppressed from ~300 auf ~10. Tc(VII) can be rextracted from the TOA solution with 1 M NaOH or NH_4OH . The stripping from fresh TOA solutions is fast, but the stripping rate decreases after the solution has been reused several times. To overcome this drawback, it is recommended to strip Tc(VII) with a solution of ammonia and ammonium thiocyanate [167]. The extraction of Tc(VII) is very selective among fission and corrosion products. Pd is the only element extracted together with Tc(VII). Mere 4 stages of a mixer settler suffice for extracting >99% Tc from a simulated HAW solution containing 3.2 M HNO_3 [168]. The stability of TOA solutions in CCl_4 toward chemical and radiolytical decomposition is high enough for the application to the ^{99}Tc separation from true HAW solutions [169]. Quaternary ammonium extractants also appear to be suitable for the extraction of Tc(VII) from HAW solutions [170,171].

3.2 *EXAMPLES OF PROCESS FLOWSHEETS*

Two illustrative examples are given, namely processes which were developed in the USA for the separation of ^{90}Sr. The general chemistry of the processes is described in "Acidic Extractants" on page 47. Figure 18 shows the flowsheet of a simple process developed and operated at the Hanford site. The simplicity of the flowsheet can be considered an advantage, but ^{90}Sr is not more concentrated in the course of the process than by a factor of 5. It is worth noticing that the separated ^{90}Sr is practically sodium free and contains little calcium. This is due to favourable properties of the HDEHP extractant, which extracts Ca(II) with a considerable selectivity over Sr(II). The final product is a Sr carbonate solid, which contains largely isotopically pure ^{90}Sr (97%).

The process was applied at Hanford on a plant scale. It can be supposed that the process proved effective and well feasible, because it was or has been operated for many years. A visit to the plant (1981) gave to understand that the costs of the process were reasonably low. The chemistry of the process made it possible to keep the process control little expensive. For example, important information was gained as the easily and cheaply measurable pH value in the raffinate.

A more complex process was developed at Oak Ridge National Laboratory (see Figure 19). The process has not been applied on industrial scale. The flowsheet involves considerably more extractors than the Hanford process. However, this disadvantage is to some extent compensated by the fact that ^{90}Sr is concentrated by a factor of 300 during the process. Both the Hanford and the Oak Ridge processes have a common drawback: they contaminate the HAW solution strongly with organic components like tartrate or citrate.

3.3 *OTHER METHODS*

3.3.1 Ion-Exchange of Strontium

Organic cation exchangers of the sulfonic or phenolsulfonic acid type are not very selective and effective sorbents for Sr(II). A process should be mentioned here, in which a Dowex 50W resin was used for the separation and purification of large amounts of ^{90}Sr needed as a heat source. The ^{90}Sr was separated not directly from a HAW solution, but from a crude pre-concentrate. The pre-concentrate was obtained by coprecipitation of

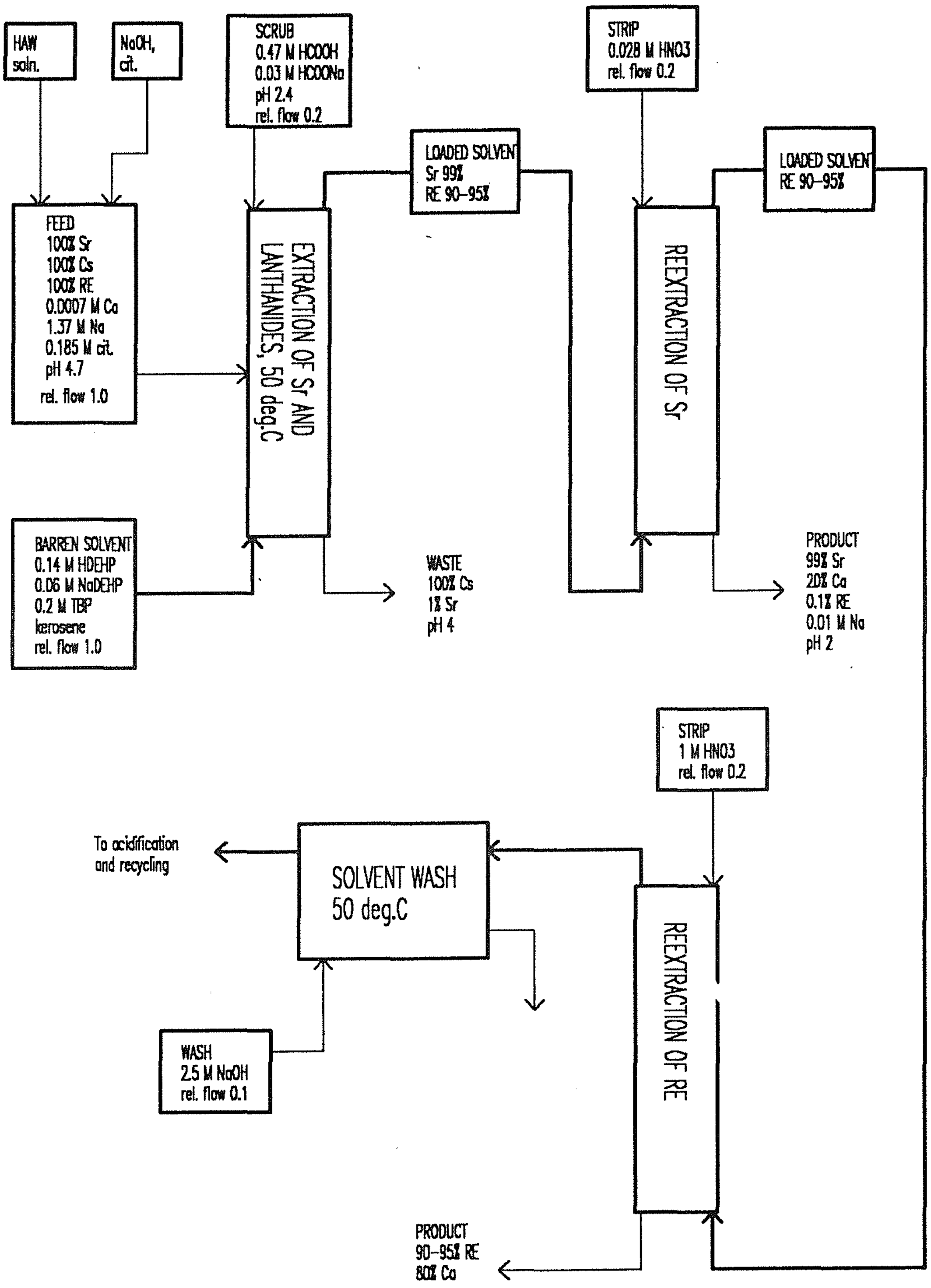

Figure 18. **Separation of ^{90}Sr from a HAW concentrate or solution:** Flowsheet of a simple separation process (Hanford, USA) [136]. RE denotes total lanthanides and cit. is total citrate.

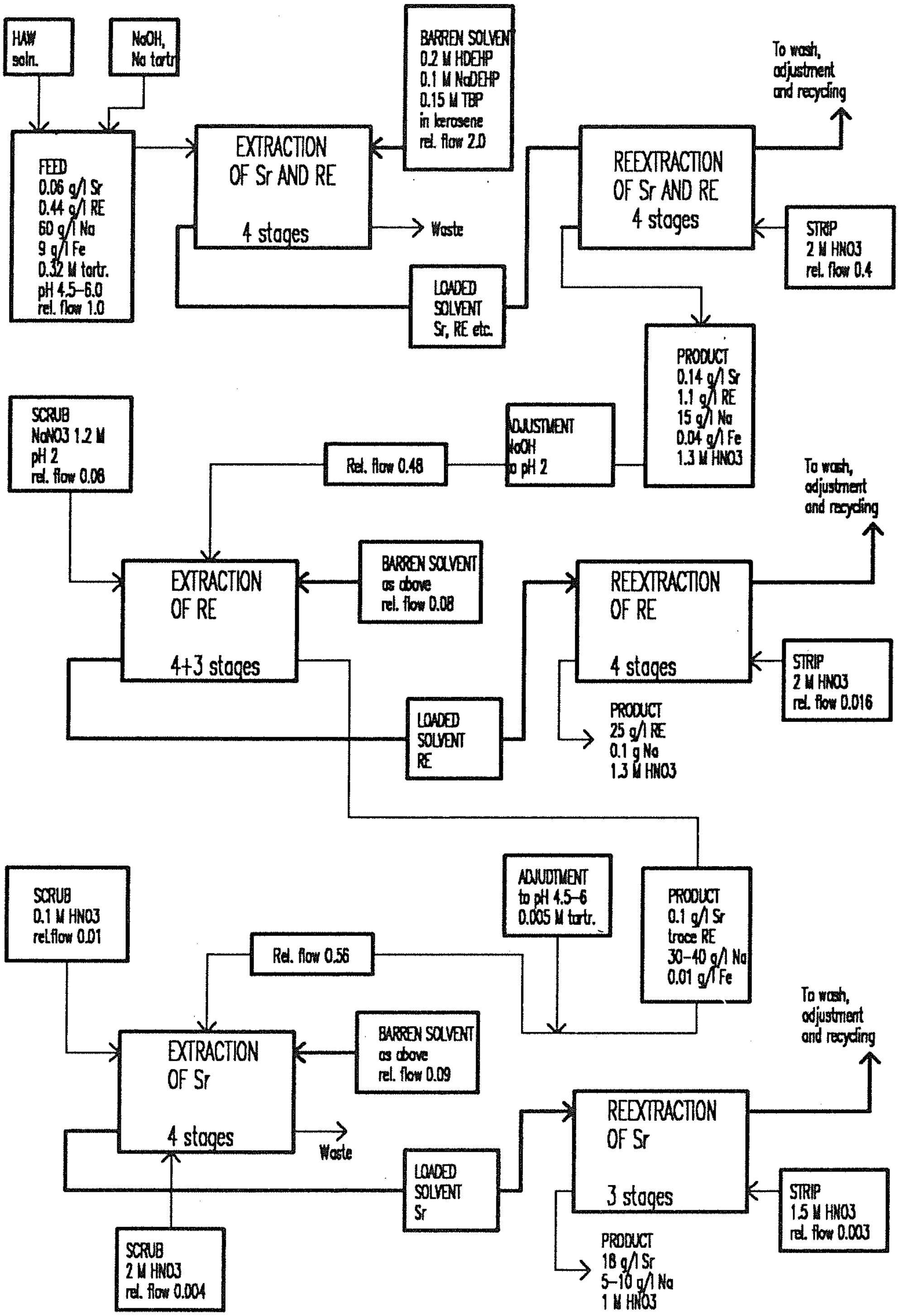

Figure 19. Separation of ^{90}Sr from a HAW concentrate or solution: Flowsheets of a rather complex separation process (Oak Ridge, USA) [135]. RE denotes total lanthanides and tartr. is tartrate.

sulfates with Pb sulfate as a carrier, conversion to carbonates, and oxalate precipitation. The cation-exchange procedure itself involved adsorption from a solution of ethylenediamine N-hydroxyethyl N,N',N'-triacetic acid at pH 4 and elution with 0.03 M ethylenediamine N,N,N',N'-tetraacetic acid at pH 8.6 [172].

There are inorganic ion-exchangers which adsorb Sr(II) from weakly or moderately acid solutions. Among them, sodium titanate is a widely regarded sorbent [104,173-175]. It sorbs Sr(II) at pH 2 with a distribution coefficient of $\geq$1000 and exhibits at pH > 5 an ion-exchange capacity of ~4 mequiv./g [175]. Nevertheless, it is too optimistic to characterize Na(I) titanate as a highly selective adsorbent for Sr(II), as it is done in [173]. It has a high affinity also to U(VI), Mo(VI), Zr(IV), lanthanides(III), Y(III), Am(III) and Ba(II). Only Cs(I), Na(I) und Ru are sorbed less effectively than Sr(II) [104,174,175]. In fact, sorption on Na(I) titanate has been investigated as a mode of the compacting of radioactive waste, rather than a mode of waste partitioning. Actinides and fission products can be retained on a column of the sorbent from a neutralized HAW solution. The loaded sorbent can then be pressed at > 1000°C to a compact material, from which the sorbed components cannot be lixiviated. The compact product is suitable for final disposal [104,174].

Polyantimonic acid is also considered a promising sorbent for Sr(II), and its application to the ^{90}Sr removal from HAW solutions has been suggested [175,176-178]. Sr(II) is sorbed from acid solutions (up to 5 M HNO_3 [175]), but the sorption capacity does not exceed 1 mequiv. Sr(II)/g. It also is disadvantageous that the uptake of Sr(II) is irreversible. Elution of Sr(II) becomes possible only if the sorption ability of polyantimonic acid is destroyed. For example, Sr(II) can be desorbed with a large volume of 2 M $Pb(NO_3)_2$ + 0.1 M HNO_3 at 60°C [176] or 1 M $AgNO_3$ + 8 M HNO_3 at 80°C [175]. Alternatively to the desorption of Sr(II), the sorbent matrix can be volatilized by dry HCl at 250°C. The sorbent is converted to Sb chloride, water and chlorine, and Sr(II) chloride is preserved as a solid residue [176].

Zeolites sorb Sr(II) from moderately acid solutions (pH > 2), but the sorption is little selective. Cs(I), lanthanides(III), Zr(IV) and other elements are also retained [175].

3.3.2 Ion-Exchange of Cesium

3.3.2.1 *Organic Ion-Exchangers*

Cs(I) is weakly adsorbed from acid solutions on organic cation exchangers bearing sulfonic acid and, eventually, phenolic functional groups. Sorption from alkaline or alkalized waste solutions is quite effective. A satisfactory selectivity toward Na(I) is reached e.g. in the sorption on the sulfonic-phenolic exchanger Duolite ARC-359. Based on the sorption on the exchanger, processes for the recovery of ^{137}Cs from high level alkaline waste solutions have been developed in Hanford [179] and in Savannah River [180]. The processes include the elution of Cs(I) with solutions containing 1.65 - 2.8 M $(NH_4)_2CO_3$ and 0.75 - 2 M ammonia. The Hanford process was operated for years. It took the advantage of the stability of the ARC-359 echanger, which was attacked by the alkaline feed solution less than e.g. zeolites [181]. More recently, investigators in Savannah River suggested to replace the ARC-359 resin by a weakly acidic, phenolic or carboxy-phenolic exchanger. Then it is possible to elute Cs(I) with a formic acid solution, which can be recycled or decomposed [182].

3.3.2.2 Inorganic Ion-Exchangers

Cs(I) is sorbed by numerous inorganic cation exchangers, and the sorption is in some cases considerably effective. Ammonium phosphomolybdate is one of promising sorbents. It can be loaded up to ~0.5 mequiv. Cs/g without suppressing the sorption effectiveness. The acid concentration plays between 8 M HNO_3 and pH 9.5 an insignificant role. The Cs(I) sorption is at 1 - 8 M HNO_3 not influenced by the presence of 3.6 M sodium nitrate [183]. Cs(I) is effectively sorbed also in the presence of Al(III) nitrate [177] and, generally, the Cs(I) sorption is very selective with regard to fission and corrosion products [175]. The very weak effect of the acid concentration on the Cs(I) sorption is in fact a disadvantage, because it excludes the use of HNO_3 solutions for the elution. Even concentrated nitric acid fails to elute Cs(I) from the sorbent. A concentrated solution of ammonium nitrate has to be taken, or the sorbent must be destroyed by NaOH.

Ammonium phosphotungstate sorbs Cs(I) as selectively as ammonium phosphomolybdate [175], and its mixture with zirconium phosphate is also a good sorbent for Cs(I) [177]. A complex sorbent has been synthesized, which is presented as an improved form of ammonium phosphomolybdate. It consists of the latter salt and titanium phosphate. The elution of Cs(I) from the complex sorbent is easier than from simple ammonium phosphomolybdate, and grains of the complex sorbent have better mechanical properties. The price of these achievements is that the complex sorbent sorbs Cs(I) less effectively and less selectively than simple phosphomolybdate. A mixture of fission products can be partitioned with the sorbent into several fractions, and one of them contains only ^{137}Cs [184].

Hexacyanoferrates(II,III) of bivalent or polyvalent metals represent a large group of potential sorbents for Cs(I). Only some of them are indeed able to sorb Cs(I) from acid solutions. Hexacyanoferrate(II)-molybdate sorbs Cs(I) even from 2 M HNO_3 [176,185] and, at least at pH 0.4 - 4, the sorption is very selective toward fission and corrosion products [175]. Unfortunately, the sorption ability of the material for Cs(I) deteriorates gradually in repeated contacting with HNO_3 solutions. This has been observed not only in basic research work [186], but also in the development of a process for the separation of ^{137}Cs from high-level wastes [176]. The elution of Cs(I) with 4 M NH_4NO_3 + 0.1 M HNO_3 is little effective: 20 - 40% Cs(I) is eluted with 26 - 29 bed volumes [176]. 1.5 or 3 M HNO_3 elutes 90 - 100% Cs(I) sorbed. However, 3 M HCl is preferred elutriant, because it elutes 95.6 - 99.7% Cs(I) without deteriorating the sorption ability of the sorbent [186].

Other hexacyanoferrates sorb Cs(I) less effectively from acid solutions, but this does not exclude their applicability. Examples are titanium(IV) hexacyanoferrate(II) [175], nickel, sodium nickel or potassium nickel hexacyanoferrates(II) [178,183], potassium or ammonium cobalt(II) hexacyanoferrates(II) [175,183], sodium zinc hexacyanoferrate(II) [178], potassium copper hexacyanoferrate(II) [187], chromium(III) hexacyanoferrate(II) [188] and chromium(III) hexacyanoferrate(III) [189].

Many other inorganic substances are able to sorb Cs(I) more or less effectively and selectively. Let us mention Zr phosphate [175,177,183, 190,191], Ti phosphate [175,176, 183], and titanium(IV) and antimonium(V) oxides [175]. Aluminosilicates like zeolite or mordenite can be used unmodified [175,192,193] or modified with hexacyanoferrates(II) [194,195]. Application of clinoptilolite to the ^{137}Cs separation from Purex waste has been suggested. Cs(I) is sorbed from a moderately acid HAW solution (0.45 M HNO_3), while Na(I), Sr(II), Ce(III) and Ru are left in the effluent. Solutions of ammonium salts elute Cs(I) quite well, and a 2 M $(NH_4)_2CO_3$ solution is also an effective eluant [196].

3.3.3 Ion-Exchange of Technetium

Tc(VII) is sorbed on those ion-exchangers which contain basic nitrogen atoms in their structure. These include not only strongly and weakly basic anion exchangers, but also chelating cation exchangers with aminodiacetic acid type groupings. The sorption of Tc(VII) on 20 exchangers of various types and provenances has been compared. If the HNO_3 concentration is raised from 0.1 to 10 M, the distribution coefficient of Tc(VII) is suppressed from 500 - 4000 to 5 - 20. This gives a possibility of eluting sorbed Tc(VII) with 3 M and 9 M HNO_3 from weakly and strongly basic anion exchangers respectively [197].

The sorption of Tc(VII) on anion exchangers is rather selective with respect to fission products. Pd and Rh are the only elements sorbed together with Tc. Data in [197] indicate that the sorption of Pd on many anion exchangers from <0.5 M HNO_3 is much weaker than the sorption of Tc(VII). Based on this fact is the separation on the anion exchangers Wofatit SBW and Wofatit SBK. It is suggested to sorb Pd and Tc(VII) simultaneously from a HAW solution at 3 M HNO_3, and to elute them successively with 0.1 - 1 M and 8 - 9 M HNO_3 respectively [198].

Other separation procedures are based on the use of two columns in a series. The strongly basic anion exchanger Amberlite IRA-401 sorbs Pd predominantly on the first column, while Tc(VII) and Rh distribute beween both columns. The elution yields three product fractions. A 1 - 6 M HNO_3 solution elutes a major part of Tc(VII) together with small parts of Pd and Rh. 10 M NH_4OH elutes a part of Pd, and 4 M NH_4SCN elutes the major portion of Rh with small parts of Pd and Tc [199]. Alternatively, Tc(VII), Ru, Rh and Pd are sorbed on the Amberlite IRA-938 anion exchanger, and are successively eluted with 3 M HNO_3, 6 M HNO_3, 8 M HNO_3 and water respectively [200].

Tc(VII) is at pH 2 sorbed on a sorbent, which is marketed under the name Vitrokele 592 [201]. The original paper does not describe the chemical nature of the sorbent but, obviously, it is an inorganic ion exchanger. Active carbon sorbs Tc(VII) in a broad acidity range, namely between 2 M HNO_3 and pH 10, and the sorption mechanism is postulated as anion exchange. The sorption ability of active carbon for Tc(VII) deteriorates after contact with acidic nitrate solutions [202].

3.3.4 Precipitation of Strontium and Cesium

A proces has been developed at the Hanford site, USA, which is based on the coprecipitation of Sr(II) with lead sulfate. Megacurie amounts of ^{90}Sr have been separated in this way [181]. More recently it has been reported that the coprecipitation from a HAW solution is complete only after a denitration and at 60 - 80°C. The acidity must be adjusted to a pH value of >4, which is not further specified in the paper. A considerable fraction of lanthanides(III) and, of course, entire Ba(II) are also coprecipitated. Only a part of the coprecipitated Sr(II) is converted to carbonate, if the bulk precipitate is treated with 5 M NaOH + 1 M Na_2CO_3 at 60°C [175].

Cs(I) can be precipitated as phosphotungstate from HAW solutions at 0.5 - 2 M HNO_3. The reaction was utilized in a large scale operation at the Hanford site, USA [181]. Ni hexacyanoferrate(II) or other hexacyanoferrates(II,III) can be used for the precipitation of Cs(I) from alkaline waste solutions [181]. A process was developed in the 1980s, in which ^{137}Cs is separated from alkaline wastes by the precipitation of tetraphenylborate [181,177].

3.3.5 Electrolytic Deposition of Technetium

Tc metal can be electrolytically deposited from acid solutions and, eventually, separated in this way from Pt elements. It was intended to recover Tc in this manner from eluates after an ion exchange separation. Nitric acid must be removed from the eluate by evaporation, and replaced by sulfuric and perchloric acids. Before Tc is recovered, Pd and Rh can be deposited on a Pt cathode at -0.04 V and on a Cu plated Pt cathode at -0.31 V respectively. Tc is then deposited at -0.4 V on a Ti cathode (all voltages are related to an Ag/AgCl reference electrode) [200].

More important is a possibility of depositing Tc directly from acid HAW solutions. To achieve it, the HNO_3 concentration in a HAW concentrate is reduced from 8 M to 0.2 - 1 M by neutralization with 50% NH_4OH. Then 99% Tc is deposited in ~48 h at -0.40 V (with respect to Ag/AgCl). The separation is little selective, because 99% of each Pd and Rh as well as ~60% Ru are deposited together with Tc. The current density decreases during the deposition from 70 to 0.3 mA/cm^2. The Tc, Pd and Ru deposits are dissolved in concentrated HNO_3, while Rh is loosened from the cathode in the form of solid flakes [203].

4.0 WASTE MANAGEMENT, PROCESS ENGINEERING AND ECONOMICAL CONSIDERATIONS

The storage time of an HAW solutions may influence the performance and results of a partitioning process. It has been suggested to extend the storage period to several years. Fission products like ^{95}Zr, ^{144}Ce and ^{106}Ru are then largely decayed and the radiation damage of process chemicals and streams would essentially be reduced. Moreover, ^{242}Cm is partially decayed and this would reduce the additional formation of ^{238}Pu in the separated transplutonide(III) fraction [204]. However, the advantages could be partially or prevailably compensated by the risks and costs of the storage of a high-level radioactive liquid. It also is of importance that a considerable amount of solids could deposit from the waste during a prolonged storage. To reduce or avoid problems with solids, the partitioning a fresh HAW solution just released from the Purex process is worth considering.

Whatever the principal partitioning method is (solvent extraction, ion exchange etc.), the process will most probably have to include a treatment of solids. It has to be checked how much plutonium is retained in the precipitate formed during the waste storage. If the amount is considerable, the Pu must be extracted from the solids or the solids must be solubilized. Eventual necessity of removing Pu from dissolver residues must also be kept in mind. The residues are acid resistent and their solubilization, or extraction of Pu from them might be a costly and difficult operation. Alternatively, the dissolver residues can separately be deposited as an alpha contaminated, but little voluminous solid waste. A small amount of plutonium would escape the recovery and transmutation in this way, but this possibly would be the lesser evil in comparison with e.g. a high temperature solubilization of the residues.

Treatment of solids cannot be avoided, if the HAW solution is denitrated in an early stage of the partitioning process. In this case the solid could be too bulky for being deposited as an alpha contaminanted, low volume waste. Thus, alpha nuclides would have to be effectively washed out from the denitration precipitate. The precipitate is amorphous and contains large amount of occluded water, and the washing of the precipitate would considerably augment the volume of liquid to be treated in the partitioning process. Moreover, transplutonides(III) are the only actinides which can be washed out rather easily. Pu can be desorbed with aggressive solutions only and Np is very uneasy to be washed out (see "CONDITIONING OF HAW SOLUTIONS FOR THE PARTITIONING" on page 10). It is supposed [204] that the denitration precipitate must be washed with an acid solution as concentrated as ~5 M. The wash would of course dissolve a fraction of the precipitate and the loaded wash solution would have to be denitrated. The dissolved components would again be precipitated in the denitration and, as a consequence, would be accumulated in the process. Thus, it is higly desirable to avoid denitration to low acid concentrations. It could be acceptable to denitrate to a limited extent, e.g. to 2 M HNO_3. Such a small suppression of the acid concentration is quite sufficient if solvating extractants like OΦD(iB)CMPO are used.

When methods are to be chosen for a partitioning process, solvent extraction is unambiguously preferred. Operation of Purex plants has clearly demonstrated that the method is suitable for a large scale treatment of highly radioactive solutions. The chemical literature presents detailed information about the basic chemistry of solvent extraction, and there exist extented distribution data on numerous liquid-liquid systems. Many extractants and diluents are commercially available or, if desired, could be produced in large amounts and at a reasonable price. There is no lack of knowledge and experience considering the construction and operation of counter-current extractors like mixer-settlers and pulsed columns. These two types of contactors are well established in nuclear processes and it is not uneasy to find an experienced producer of them. It can be expected that centrifugal extractors will also be developed to a routine operation readiness. Their application can reduce radiation damage of chemicals and would facilitate a partitioning process.

The radiation damage of the solvent will in a partitioning process be more serious than in the Purex process. A higly radioactive aqueous solution passes in the Purex process only one extractor, or even only a part of an extractor. The highly radioactive fission products are very weakly extracted and the solvent undergoes only an external irradiation. In a partitioning process the fission products would be extracted, and the solvent would be irradiated internally. In this case it would absorb a higher radiation dose than in the external irradiation in the Purex process [205]. Moreover, the residence time of the fission products in the solvent could in a partitioning process be rather long. At least some fission products could be kept in the solvent during several consecutive operations like the simultaneous extraction of transplutonides(III) and lanthanides(III), the selective strip of Pu and Np, and the selective strip of transplutonides(III).

The radiolysis would most probably play a less important role in a pyrochemical extraction process. Difficulties can be expected in the accomplishment of counter-current contacting. The molten phases must be contacted at 500 - 900°C and, to prevent corrosion, in an inert atmosphere. It is asserted in [112] that, generally, such operations are not a new ground in the chemical engineering, and have already been tested in the USA. Nevertheless, can be supposed that routine performance would not be feasible without intensive and costly R&D activities.

Conversion of the high-level waste to a suitable chemical form would be another difficult part of a pyrochemical partitioning process. In remote future the waste will perhaps be produced in a high-temperature reprocessing process and will have a metallic or salt form. Nowaday, the waste typically has the form of an acid nitrate solution. For a pyrochemical process the waste would have to be evaporated to dryness, thermally decomposed to oxides, and reduced to metals or directly coverted to salts. The reduction, if it is not avoided and is made e.g. with elemental Ca or Mg would hardly be an easy process step. To extend the list of energy consuming manipulations in a pyrochemical partitioning process, let us mention that evaporation of Zn, Mg and Bi metals is in [112] suggested to be inserted between counter-current operations.

Ion exchange can also have essential importance for the waste partitioning. Processes were operated in the USA, at least temporarily, in which commercial ion exchangers were applied in an intense radiation field. Examples of such processes are mentioned above (e.g. separation of ^{237}Np or ^{90}Sr). A still higher radiation resistance is ascribed to inorganic ion exchangers. It is an advantage of inorganic ion exchangers that their effectiveness and selectivity can largely be controlled by variations of their chemical composition. On the other hand, the sorbents may have some general disadvantages. Let us mention a low sorption capacity, slow sorption or desorption rate, partially or prevailably irreversible sorption, low chemical or mechanical resistance in contact with nitric acid solutions, badly reproducible sorbent properties and a high price.

The costs of the partitioning have been estimated as 15% of the reprocessing costs [206,207]. The estimate includes only the separation of actinides, while other operations like the conversion of the products in a suitable final form have not been taken into account. Even so the estimate seems to be more than optimistic. Investment costs have been estimated elsewhere for a partitioning facility which could treat waste released in the reprocessing 2000 t fuel per year. Related to 1979, the costs were $\sim 10^6$ US$ [208].

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